PHYSICO-CHEMICAL INVESTIGATION OF TRANSPORT AND THERMODYNAMIC PROPERTIES OF SOME ELECTROLYTES IN VARIOUS SOLVENT SYSTEMS

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I have the pleasure to certify the thesis of Mrs. **Mousumi Das**, M.Sc. (Senior lecturer, Department of Chemistry, B.N. College, Dhubri, ASSAM) entitled "**Physico-Chemical Invesigationt of Transport and Thermodynamic Properties of Some Electrolytes in Various Solvent Systems**" to be submitted for the degree of Doctor of Philosophy at the University of North Bengal.

She completed the research work under my supervision and guidance by taking a teacher fellowship under UGC, Govt. of India [F.5-*7/2003 (NER/TF/2177*)]. To the best of my knowledge the thesis is based on her original work and is completed as per the guidelines of the University. Her thesis may be accepted for submission and placed before the experts for evaluation. In my opinion, she is fit and proper person for awarding the degree of Doctor of Philosophy (Ph. D.) in Chemistry at the University of North Bengal.

I wish her every success in life.

Mahendra Nath Roy

Dated: March, 2007.

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CHAPTER I

Scope and Object of the Research

1.1. *Object and application of the work*

The physico-chemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts have been directed at an understanding of such properties at microscopic and macroscopic levels. In order to gain insight into the mechanism of such interactions thermodynamic, transport and acoustic studies on binary and ternary solvent systems are highly useful. Young[1] made the first systematic attempt in these directions by collecting a number of data on the thermodynamic and mechanical properties of liquid mixtures. The proper understanding of the molecular interactions form the basis of explaining the influence of the solvent and the extent of interactions of ions in solvents and paves the way for real understanding of the different phenomena associated with Solution Chemistry.

In recent years, there has been an increasing interest in the behavior of electrolytes in non-aqueous and mixed solvents with a view to investigate solute-solute and solute-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for physical chemists and interest in organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry [2].The importance and uses of the chemistry of electrolytes in non- aqueous and mixed solvents are well organized. The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Franks [3], Meck [4], Popovych [5], Bates [6,7], Parker [8,9], Criss and Salomon [10], Mercus[11] and others[12-14] . The solute-solute and solute - solvent interactions has been subject of wide interest as apparent from recent Faraday Trans. of the chemical society [15].

Fundamental research on non-aqueous electrolyte solutions has catalyzed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ionic conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and super capacitors, electro-deposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions had brought the biggest successes.[16-18] Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photoelectrochemical cells, electromachining, etching, polishing and electro-synthesis. In spite of wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes along with thermodynamic and acoustic studies, give very valuable information about molecular interactions in solutions.[19,20] The influence of these solute-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in diverse areas such as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction.[21]

Excess thermodynamic properties are important parameters for understanding molecular interactions in the solution phase. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus these properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Also physico-chemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the process industries and in the design of industrial separation processes. Information of these excess thermodynamic functions can also be used for the development of empirical correlations and improvement of new theoretical models.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become evident that the solvents significantly influence the majority of the solutes. Conversely, the nature of strongly structured solvents like water, is substantially modified by the presence of solutes.[22]

A knowledge of ion-solvent interactions in non-aqueous solutions[23] is very important in many practical problems concerning energy transport, heat transport, mass transport and fluid flow. Besides finding applications in engineering branch, the study is important from practical and theoretical point of view in understanding liquid theory. The non-aqueous systems have been of immense importance to the technologist and theoretician as many chemical processes occur in these systems.

It is thus, apparent that the real understanding of the molecular interactions is a difficult task. The aspect embraces a wide range of topics but we have embarked on a series of investigations based on the volumetric, viscometric, interferometric and conductometric behavior to study the chemical nature of the structure of solutes and solvents and their mutual and specific interactions.

1.2. *Importance of solvents used:*

Acetonitrile, 1,4-Dioxane, 1,3-Dioxolane, Tetrahydrofuran, 2-ethoxyethanol, Alchohols (Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1- octanol, t-butyl alchohol), Hydrocarbons- (n-pentane, n-hexane, n-heptane), Dimethylsulfoxide, butyl acetate, 2-butanone, butylamine, 2-Methoxyethanol, Carbon Tetrachloride, along with water which is a universal solvent have been chosen as solvents in this research work. The study of these solvents, in general, is of great interest because of their wide use as solvents and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole-dipole forces predominate. It has a wide range of technological applications, namely, in battery systems and plating techniques.[24,25]

1,4-dioxane, 1,3-dioxolane and tetrahydrofuran are all cyclic ethers and they figure prominently in the high-energy battery technology[24] and have also found application in organic synthesis as manifested from the physico-chemical studies in these media. 1,4-dioxane and 1,3-dioxolane are cyclic diethers differing in one methylene group and thus they differ in quadrupolar and dipolar order.[26]

The increasing use of 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran and their aqueous or binary liquid mixtures in many industrial processes have greatly stimulated the need for extensive information on their various properties. Viscosity and density of these liquid mixtures are used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications.[27,28]

The alkoxyethanols (2-ethoxyethanol and 2-Methoxyethanol) occupiers an important place in many industrial processes such as pharmaceutical and cosmetics industry and have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures.

Alcohols and its aqueous and non-aqueous mixtures are widely used in pharmaceutical industry as excipients in different formulations or as solvents. Alcohols have varied applications in chemical and cosmetic industries. These are useful in enology and as an alternative energy source.[29,30] Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc. A knowledge of their physico-chemical characteristics helps to understand their behavior in concrete manner.

Carbon tetrachloride is used to make compounds such as Chlorofluoromethanes, used as refrigerants and aerosol-spray propellants, in fire extinguishers and for dry cleaning of fabrics.

The hydrocarbons, both aromatic and aliphatic have varied applications. n-hexane, which is familiar in the laboratory as the principle component of petroleum ether, is used as solvent, dry-cleaner and motor fuel.

Dimethyl sulfoxide (DMSO), a typical aprotic solvent having both polar and nonpolar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells.[31] This solvent has wide range of applicability as a solvent in chemical and biological processes.

Water is the most widely used solvent in the chemical industries, since it is the most physiological and best tolerated excipient. However, in some cases, water cannot be used as a solvent because the active substance or solute is insoluble or slightly soluble in it. The non-aqueous solvents with common characteristics of being soluble or miscible in water are thus used. Such solvents can be used to prepare binary or ternary mixtures and they can serve different purposes such as increasing water solubility, modifying the viscosity, absorption of the dissolved substance.

The knowledge of the type and structure of the complex species in solution is essential for the optimal choice of solvents. Even though these solvents have drawn much focus in recent years as solvents for physico-chemical investigations, still a lot remains to be explored.

1.3. *Methods of Investigation*

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occur in these systems. The structures and existence of free ions, solvated ions, and ion pairs depend on concentration regions [32].

Various techniques [33,34] have been employed to study the solvation structure, ion-solvent interactions and dynamics of ions in aqueous and non-aqueous media.

The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometric, viscometric, densitometry and ultrasonic interferometer to probe the problem of solvation phenomena.

Thermodynamic properties of solutions are not only useful for estimation of feasibility of chemical reactions in solution, but they also offer one of the better methods of investigating the theoretical aspects of solution structure. Thermodynamic properties, like apparent molar volumes, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution.

The change in solvent viscosity by the addition of electrolytes is attributed to inter-ionic and ion-solvent effects. The B-coefficients gives a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, preferential solvation and structure-breaking or structure-making capacity of the solutes.

The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and provides useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions. Various acoustical parameters have been derived in carrying out the investigation.

The excess properties such as excess molar volume, viscosity deviations, excess isentropic compressibility along with the correlating equations explains molecular interactions in a more effective way.

The transport properties are studied using the conductance data, specially the conductance at infinite dilution. Conductance data obtained as a function of concentration are used to study the ion-association with the help of appropriate equations.

1.4. *Summary of the works done*

The volume of work covered under this dissertation has been divided into twelve chapters. Brief summaries of each of the chapters are given below.

Chapter I

This chapter involves the object and scope of the research work. This mainly comprised the choice of the main solvent used and its applications in different fields, methods of investigation and summary of the work done.

Chapter II

This chapter contains the general introduction of the thesis and the background of the present work. A brief review of notable works in the field of ion-solvent interaction has been given. The discussion includes solute-solvent, solute-solute and solvent-solvent interactions of mixed solvent systems and of electrolytes in pure, aqueous, non-aqueous solvent systems at various temperatures in terms of various derived parameters of density, viscosity, ultrasonic speed and conductance. Critical evaluations on the relative merits and demerits of the different methods used on the basis of various assumptions employed from time to time of obtaining the single ion values and their implications have been made. The molecular interactions are interpreted based on various equations. The trends in solvation models stress the importance of the work.

Chapter III

This chapter contains the experimental section that mainly involves the source and purification of the solvents and solutes used and the details of the experimental methods employed for measurement of the thermodynamic, transport and acoustic properties.

Chapter IV

This fourth chapter deals with the study of excess properties of binary mixtures of acetonitrile with some cyclic ethers (1,4-dioxane, 1,3-dioxolane, tetrahydrofuran) at 298.15 K, 308.15 K and 318.15 K. Densities and viscosities of the binary mixtures of acetonitrile with tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane were measured over the entire range of composition atall the experimental temperatures. Ultrasonic speeds of these binary mixtures have also been measured at 298.15 K. From the experimental data, values of excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and deviations in isentropic compressibility (ΔK_S) have been calculated. These results were fitted to Redlich-Kister polynomial equation. The density and viscosity data were analyzed by some semi empirical viscosity models, and the results have been discussed in terms of molecular interactions and structural effects. To explore the nature of the interactions, various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) have also been derived from the density and ultrasonic speed data.

Chapter V

In this chapter the densities, viscosities, and ultrasonic speeds of binary mixtures of 2-ethoxyethanol with 1-alkanols (methanol to 1-octanol) have been measured at 298.15 K. The excess molar volume (V^E), viscosity deviations ($\Delta\eta$) and Gibbs excess free energy of activation for viscous flow (G^{*E}) have been investigated from the experimentally measured density (ρ) and viscosity (η) values. The viscosity data have been correlated by Grunberg and Nissan, Tamura-Kurata and Hind correlation equation. The deviations in isentropic compressibility (ΔK_S) were also calculated using the measured speeds of sound. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding. The sound speeds were predicted by using Free length and Collision factor theoretical formulations, by Nomotto equation, by Vandeal Vangael ideal mixing relation and the impedance dependence relation. The deviations have been fitted to a Redlich-Kister equation and the results are discussed in terms of molecular interactions and structural effects.

Chapter VI

The measured densities and viscosities of binary mixtures of tetrahydrofuran + n-pentane, tetrahydrofuran +n-hexane and tetrahydrofuran +n-heptane at 288.15, 293.15 and 298.15 K. have been used to calculate the excess molar volume, excess free energy, deviation in viscosity of the composition and the interaction parameter of Grünberg and Nissan over the entire composition range. The results have been interpreted in terms of molecular interactions existing between the components of these mixtures.

Chapter VII

This chapter involves the studies on the solute-solvent interactions and ultrasonic speed of resorcinol in 2-methoxyethanol and tetrahydrofuran at different temperatures. In this chapter, the densities, viscosities and ultrasonic speeds of resorcinol in pure 2-methoxyethanol and pure tetrahydrofuran are determined experimentally at 303.15 K, 313.15 K and 323.15 K. Apparent molar volumes (V_ϕ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_v^*) derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data have been analyzed using Jones-Dole equation and the derived parameters B and A have also been interpreted in terms of solute-solvent and solute-solute interaction respectively. The structure making/breaking capacity of this solute investigated here has been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the solute particles.

Chapter VIII

In this chapter, Conductance measurements for selected alkali chlorides, MCl (M^+ = Li, Na, K) are performed in the binary mixtures of methanol with carbon tetrachloride and 1,4-dioxane at 298.15 K. The limiting equivalent conductance (Λ_0), the association constant (K_A), and the Walden products ($\Lambda_0\eta_0$) for the three salts are evaluated at all the mole fractions of the solvent mixtures using the 1978 Fuoss conductance equation. Based on the composition dependence of walden product ($\Lambda_0\eta_0$) the influence of the mixed solvent composition on the solvation of ions has also been discussed. The results have been discussed in terms of ion-solvent and ion-ion interactions and the structural changes in the mixed solvent systems.

Chapter IX

The densities, viscosities and ultrasonic speeds of some monobasic acetate salts, viz. ammonium acetate (CH_3COONH_4), lithium acetate (CH_3COOLi), sodium acetate (CH_3COONa) and potassium acetate (CH_3COOK) in methanol water mixtures (10%, 20%, 30%) have been measured at (298.15, 308.15, 318.15) K. The limiting apparent molar volumes (V_ϕ^0), the experimental slope (S_v^*), supplemented with the measured density data have been interpreted in terms of solute-solvent and solute- solute interactions respectively. The parameters B and A obtained from viscosity data analyzed using Jones-Dole equation have also been interpreted in terms of solute-solute and solute-solvent interactions respectively. The structure making or structure breaking nature of the acetates in the solvent-mixtures studied here has been discussed. The compressibility data supplemented with the ultrasonic speeds explain the electrostriction of the solvent molecules around the positive ions.

Chapter X

Apparent molar volumes, Viscosity B-Coefficients, and apparent molar Isentropic compressibilities of Glycine, L-Alanine, L-Valine and L-Leucine in aqueous tetra butyl ammonium bromide (TBAB) Solution of three different concentrations (0.062, 0.125and 0.256 mol·kg $^{-1}$) have been determined at 298.15 K from the experimental density, flow time and sound speed measurements respectively. The standard partial molar volumes and compressibilities are used to calculate the corresponding volume of transfer at infinite dilution, from water to aqueous TBAB solutions. The linear correlation of partial molar volumes for a homologous series of amino acids has been utilized to calculate the contribution of charged end groups and other alkyl chains of the amino acids to partial molar volumes. The hydration numbers of amino acids have also been determined. Viscosity B coefficients have been calculated using the Jones-Dole equation. The values of the charged end-groups contribution to the viscosity B-coefficients of the amino acids are also calculated.

Chapter XI

Densities and viscosities of binary mixtures of Dimethyl sulfoxide (DMSO) with tert-butyl alcohol, butyl acetate, 2-butanone and butyl amine were determined over the entire range of mole fractions at the temperatures of 298.15 K, 308.15 K and 318.15 K. At each temperature, the excess molar volume (V^E), viscosity deviations ($\Delta\eta$)' Gibbs excess free energy of activation for viscous flow (G^{*E}) have been investigated from these measured density and viscosity values. The experimental viscosity data were correlated by means of the equations of Grunberg-Nissan, Tamura and Kurata and Hind. The deviations have been fitted to a Redlich-Kister equation and the results are discussed in terms of molecular interactions and structural effects.

Chapter XII

The dissertation ends with some concluding remarks in this chapter.

References:

1. S. T. Young, *Phil. Mag.*, **1882**, *33,* 153.
2. C. M. Criss, M. Salomon, *J. Chem. Edu*, **1976**, *53,* 763.
3. F. Franks, *Physico-Chemical Processes in Mixed Aqueous Solvents*, Ed. F. Franks, Heinemann Educational Books Ltd., pp. 141-151 **1967**.
4. D. K. Meck, *The Chemistry of Non- Aqueous solvents*, Ed., J.J. Logowski, Academic Press, New York, London, Part 1 Chapter 1, **1996**.
5. O. Popovych, *Crit. Rev. Anal. Chem.*, **1970**, *1,* 73
6. R. G. Bates, *Determination of pH Theory and Practice*, Second Ed., John Wiley and sons. N.Y., Chapter 8, **1973**.
7. (a) R. G. Bates, *Solute-solvent Interactions*, Ed., J.J. Coetzee and C.D. Ritchie, Marcel Dekker, New York and London, **1969**
   (b) R.G. Bates and A.J. Parker, *Chemical Physics of Ionic solutions*, Ed., B.E. Conway and R.G. Barrades, John Wiley and Sons. Inc., New York, pp.211, **1966**.
8. A.J. Parker and J.H. Sharp, *Proceeding of the Royal Australian Chemical Institute*, pp. 89, **1972**.
9. A.J. Parker, *Electrochim. Acta.*, **1976**, *21,* 671.
10. C. M. Criss and M. Salomon, *J. Chem. Educ.*, **1976**, *53,* 763.
11. Y. Mercus, *Ion Solvation*, Wiley, Chinchester, **1986**.
12. E.J. King, *Acid- Base Equilibria*, Pergamon Press, Oxford, **1965**.
13. O. Popovych and R.T.P. Tomkins, *Non-Aqueous solution Chemistry*, John Wiley and Sons, New York, **1981**.
14. R.R. Dogonadze, E. Kalman, A.A. Kornyshev, and J. Ulstrup, *The Chemical Physics of Salvation*, Part C, Elsevier, Amsterdam, **1988**.
15. *Faraday Discussion of the Chemical Society*, **1977**, No.67 .
16. Y. Marcus, *Ion Properties*, Dekker, New York, **1997**.
17. A. Masquez, A Vargas, P. B. Balbuena, *J. Electron. Soc.*, **1998**, 45, 3328.
18. A. F. D. Namor, M. A. L. Tanco, M. Solomon, *J. Phys. Chem.*, **1994**, 98, 11796.

19. A. Chandra, B. Bagchi, *J. Phys. Chem. B.*, **2000**, *104*, 9067.
20. G. Atkinson, R. Garney, M. J. Taft, *Hydrogen Bonded Solvent Systems*, Eds. A. K. Covington, P. Jones, Taylor and Francis, London, **1968**.
21. W.E. Waghorne, *Chem. Soc. Rev.* **1993**, 285.
22. K. Gunaseelau, S. Dev, K. Ismail, *Ind. J. Chem.*, **2000**, *39A*, 761.
23. O. Popovych, R. P. T. Tomkins, *Non-Aqueous Solution Chemistry*, John Wiley and Sons, New York, **1981**.
24. C. G. Janz, R. P. T. Tomkins, *Non-Aqueous Electrolytes Handbook*, Academic, New York, 2, **1973**.
25. R. Jasinski, *High Energy Batteries*. Plenum Press. New York. **1967**.
26. P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo, *J. Chem. Eng. Data.* **1999**, *48*, 1341.
27. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, Int. J. Thermophys., **2004**, 55 1735.
28. P. S. Nikam, L. N. Shirsat, M. Hasan, J. Ind. Chem. *Soc.* **2000**, *77*, 244.
29. J. V. Herraez, R. Belda, O. Diez, *Phys. Chem. Liq.*, **2004**, *42*, 467.
30. B. Sinha, A. Sinha, A. Jha and M. N. Roy, *J. Ind. Chem. Soc.* **2005**, *82*, 814.
31. T. Kamiyama, M. Morita, and T. Kimura, *J. Chem. Eng. Data*, **2004**, *49*, 1350.
32. Y. Mercus, *Ion Solvation*, Wiley, Chinchester, **1986**.
33. R. G. Bates, *Solute-solvent Interactions*, Ed., J.J. Coetzee and C.D. Ritchie, Marcel Dekker, New York and London, **1969**.
34. H. Ohtaki and T. Radnai, *Structure and Dynamics of Hydrated Ions*, *Chem. Rev.*, **1993** *93*, 1157.

CHAPTER-II

General Introduction

2.1 The *Importance of Solution Chemistry*

The mixing of different solute or solvent with another solvent gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed by many thermodynamic variables, by excess properties in case of solvent-solvent mixtures and by apparent molar properties in case of solute-solvent mixtures. These thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally, and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute-solute, solute-solvent, and solvent-solvent species.[1]

The branch of physical chemistry that studies the change in properties that arise when one substance is dissolved in another is recognized as solution chemistry. In particular, it investigates the solubility of substances and how is it affected by the chemical nature of both the solute and the solvent.

One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometry, viscometry, densitometry, spectroscopy, ultrasonic interferometry and other suitable methods and to interpret the experimental data collected.[2-8]

In the last few decades, considerable emphasis has been placed on research in the behavior of electrolytes in non-aqueous and mixed solvents to investigate the ion-ion (solute-solute) and ion-solvent (solute-solvent) interactions under varied conditions.

Different sequences of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry [9].

2.2. *Investigation on Ion-Solvent Interaction*

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolyte solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

The organic solvents have been classified based on dielectric constants, organic group type, acid-base properties or association through hydrogen bonding [10], donor - acceptor properties [11], hard and soft acid-base principles [12] etc. As a result, the different solvent systems show a wide divergence of properties, which would naturally be reflected on the thermodynamic and transport properties of electrolytes and non-electrolytes dissolved in these solvents. The determination of thermodynamic and transport properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions, which are the "controlling forcers" in infinitely dilute solutions where ion-ion interactions are absent. It is possible by separating these functions into ionic contributions to determine the contributions due to cations and anions in the ion -solvent interactions. Thus ion-solvent interactions play a very important role to understand the physico-chemical properties of solutions.

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of density, viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation [13,14], the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated [15,16] and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature [17].

Ion-solvent interactions can be studied spectroscopically, the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes of free energy, enthalpy and entropy etc. associated with a particular reaction can be qualitatively and quantitatively evaluated using various physico-chemical techniques from which conclusions regarding the factors associated with the ion-solvent interactions can be worked out.

Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of different properties such as density, viscosity, ultrasonic speed and conductance of electrolytes and the various factors associated with ionic solvation can be derived from the obtained data.

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosity, conductance, ultrasonic speed and isentropic compressibility of alkali metal halides, some acetate salts and resorcinol in the pure as well as in the mixed organic solvent and also in binary aqueous solvent systems.

2.3. *Density*

One of the well-recognized approaches to the study of molecular interactions in fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions.

Various concepts regarding molecular processes in solutions, such as electrostriction[18], hydrophobic hydration[19], micellization[20] and cosphere overlap which occur during solute-solvent interactions[21] have been derived and interpreted from the partial molar volume data of many compounds.

2.3.1. *Apparent and Partial Molar Volumes*

The molar volume of a pure substance can be determined from density measurements. However, the volume contributed to a solvent by the addition of 1 mole of an ion is difficult to determine. This is so because, upon entry into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the influence of the ion's electric field i.e., Electrostriction. Electrostriction[22] is a general phenomenon and whenever there are electric fields of the order of 10^9-10^{10} V m^{-1}, the compression of ions and molecules is likely to be significant.

The effective volume of an ion in solution, the partial molar volume, can be determined from a directly obtainable quantity- apparent molar volume (V_ϕ). The apparent molar volumes, V_ϕ of the solutes can be calculated by using the following relation [23]:.

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/(c\rho_0) \tag{1}$$

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of solvent and solution respectively and c is the molarity of the solution.

The partial molar volumes, $\overline{V_2}$ can be obtained from the equation [24]:

$$\overline{V_2} = V_\phi + (1000 - cV_\phi)/(2000 + c^{3/2}.\partial V_\phi/\partial\sqrt{c})\sqrt{c}.\partial V_\phi/\partial\sqrt{c} \tag{2}$$

The extrapolation of the apparent molar volume of electrolyte to infinite dilution and the expression of the concentration dependence of the apparent molar volume have been made by four major equations over the period of years - the Masson equation [25], the Redlich-Meyer equation [26], the Owen-Brinkley equation [27] and the Pitzer equation [28]. Masson found that the apparent molar volume of electrolyte, V_ϕ, vary with the square root of the molar concentration by the linear equation:

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \tag{3}$$

where V_ϕ^0 is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution, $\overline{V}_2^0$) and S_V^* is the experimental slope. The majority of

V_ϕ data in water and nearly all V_ϕ data in non-aqueous [30-34] solvents have been extrapolated to infinite dilution through the use of equation (3).

The temperature dependence of V_ϕ^0 for various investigated electrolytes in various solvents can be expressed by the general equation as follows:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{4}$$

where a_0, a_1 and a_2 are the coefficients of a particular electrolyte and T is the temperature in Kelvin.

The limiting apparent molar expansibilities (ϕ_E^0) can be calculated from the general equation (4). Thus,

$$\phi_E^0 = (\partial V_\phi^0 / \partial T)_P = a_1 + 2a_2 T^2 \tag{5}$$

The limiting apparent molar expansibilities (ϕ_E^0) change in magnitude with the change of temperature.

During the past few years it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler [35] developed a technique of examining the sign of $(\partial^2 V_\phi^0 / \partial T^2)_P$ for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$(\partial C_P / \partial P)_T = -(\partial^2 V_\phi^0 / \partial T^2)_P \tag{6}$$

On the basis of this expression, it has been deduced that structure-making solutes should have positive value, whereas structure-breaking solutes should have negative value.

However, Redlich and Meyer[26] have shown that an equation of the form of (3) cannot be more than a limiting law, where for a given solvent and temperature the slope, S_V^* should depend only upon the valence type. They suggested following equation for representing by V_ϕ:

$$V_\phi = V_\phi^0 + S_V \sqrt{c} + b_V c \tag{7}$$

$$\text{where, } S_V = K w^{3/2} \tag{8}$$

S_V is the theoretical slope, based on molar concentration, including the valence factor:

$$w = 0.5\sum_{i}^{j}\gamma_i Z_i^2 \qquad (9)$$

and, $$K = N^2 e^2 (8\pi/1000\varepsilon^3 RT)^{1/2}[(\partial \ln\varepsilon/\partial P)_T - \beta/3] \qquad (10)$$

where β is the compressibility of the solvent. But the variation of dielectric constant with pressure was not known accurately enough, even in water, to calculate accurate values of the theoretical limiting slope.

The Redlich-Meyer[26] extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However, studies [36-38] on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation.

Thus for polyvalent electrolytes, the more complete Owen-Brinkley equation [27] can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of V_ϕ. The Owen-Brinkley equation derived by including the ion-size parameter is given by:

$$V_\phi = V_\phi^0 + S_V\tau(Ka)\sqrt{c} + 0.5w_V\theta(Ka) + 0.5K_V c \qquad (11)$$

where the symbols have their usual significance. However, equation (12) has not be widely employed for the treatment of results for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue[39] and Atkinson to fit the apparent molar volume data. The Pitzer equation for the apparent molar volume of a single salt $M_{\gamma\mathrm{M}}M_{\gamma\mathrm{X}}$ is:

$$\begin{aligned} V_\phi = V_\phi^0 + V|Z_\mathrm{M}Z_\mathrm{X}|A_V|2bIn(I + bI^{0.5}) + \\ 2\gamma_\mathrm{M}\gamma_\mathrm{X}RT[mB_\mathrm{MX}^2 + m^2(\gamma_\mathrm{M}\gamma_\mathrm{X})^{0.5}C_\mathrm{MX}^V] \end{aligned} \qquad (12)$$

where the symbols have their usual significance.

2.3.2. *Ionic Limiting Partial Molar Volumes*

The individual partial ionic volumes provide information relevant to the general question of the structure near the ion i.e., its solvation. The calculation of the ionic limiting partial molar volumes in organic solvents is a very difficult task. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions[40] to non-aqueous electrolyte solutions.

In the last few years, the method suggested by Conway et al.[40] has been used more frequently. These authors used the method to determine the limiting partial molar volumes of the anion for a series of homologous tetraalkylammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume, $\overline{V}^0_{\mathrm{R_4NX}}$ for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{\mathrm{R_4N^+}}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\overline{V}^0_{\mathrm{R_4NX}} = \overline{V}^0_{\mathrm{X^-}} + bM_{\mathrm{R_4N^+}} \tag{13}$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, $\overline{V}^0_{\mathrm{X^-}}$.

Uosaki et al.[41] have used this method for the separation of some literature values and of their own $\overline{V}^0_{\mathrm{R_4NX}}$ values into ionic contributions in organic electrolyte solutions. Krumgalz[42] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.3.3. *Excess Molar Volumes*

The study has been carried out with the binary and ternary aqueous and non-aqueous solvent mixtures. The excess molar volumes, V^E, are calculated from density of these solvent mixtures according to the following equation: [43,44]

$$V^E = \sum_{i=1}^{j} x_i M_i (1/\rho - 1/\rho_i) \tag{14}$$

where ρ is the density of the mixture and M_i, x_i and ρ_i are the molecular weight, mole fraction and density of ith component in the mixture, respectively.

2.4. *Viscosity*

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively. [45, 46] Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, $\overline{V_2}$ i.e., the partial molar volume, gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solutions.

The viscosity relationships of electrolytic solutions are highly complicated. There are strong electrical forces between the ions and between the ions and solvent and separation of the forces are not really possible. But from careful analysis, valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system.

The viscosity is a measure of the friction between adjacent, relatively moving parallel planes of the liquid. Anything that increases or decreases the interaction between the planes will raise or lower the friction and therefore, increase or decrease the viscosity.

If large spheres are placed in the liquid, the planes will be keyed together in increasing the viscosity. Similarly, increase in the average degree of hydrogen-bonding between the planes will increase the friction between the planes, thereby viscosity. An ion with a large rigid co-sphere for a structure promoting ion will behave as a rigid sphere placed in the liquid and increase the inter planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity.

The first systematic measurements of viscosities of a number of electrolyte solutions over a wide concentration range were performed by Grüneisen [47] in 1905. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole[48] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations, *c*:

$$\eta/\eta_0 = \eta_r = 1 + A\sqrt{c} + Bc \tag{15}$$

The above equation can be rearranged as:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \tag{16}$$

Here, A and B are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non-aqueous solvent systems where there is no ionic association and has been used extensively. The term $A\sqrt{c}$ originally ascribed to Grüneisen effect, arose from the long range coulombic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory [49] of inter-ionic attractions in 1923.

Falkenhagen's [50-52] did the theoretical calculations of the constant, *A* using the equilibrium theory and the theory of irreversible processes in electrolytes developed by Onsager and Fuoss [53]. The *A*-coefficient depends on the ion-ion interactions and can be calculated from the physical properties of solvent and solution using the Falkenhagen Vernon [52] equation:

$$A_{Theo}=\frac{0.2577\Lambda_0}{\eta_0(\varepsilon T)^{0.5}\lambda_+^0\lambda_-^0}[1-0.6863\left(\frac{\lambda_+^0-\lambda_-^0}{\Lambda_0}\right)^2] \qquad (17)$$

where Λ_0, λ_+^0, λ_-^0 are the limiting conductances of the electrolyte and the ions respectively at temperature T, ε and η_0 are the dielectric constant and viscosity of the solvent. In very accurate work on aqueous solutions,[54] A-coefficient has been obtained by fitting η_r to equation (16) and compared with the values calculated from equation (17), the agreement was normally excellent. The accuracy achieved with partially aqueous solutions was however poorer,[55] A-coefficient suggesting that should be calculated from conductivity measurements. Crudden et al.[56] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

$$\frac{\eta_r-1-A\sqrt{\alpha c}}{\alpha c}=B_i+B_P(\frac{1-\alpha}{\alpha}) \qquad (18)$$

where A, B_i and B_P are characteristic constants and α is the degree of dissociation of ion pair. Thus a plot of $(\eta_r-1-A\sqrt{\alpha c})/\alpha c$ against $(1-\alpha)/\alpha$, when extrapolated to $(1-\alpha)/\alpha=0$ gave the intercept B_i. However for the most of the electrolytic solutions both aqueous and non-aqueous, the equation (16) is valid up to 0.1 (M) [23, 45, 57] within experimental errors.

At higher concentrations, the extended Jones-Dole equation (19) involving an additional constant D, originally used by Kaminsky [58] has been used by several workers [59,60]. The constant D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (16) is used by the most of the workers.

$$\eta/\eta_0=1+A\sqrt{c}+Bc+Dc^2 \qquad (19)$$

The plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ against $\sqrt{c}$ for the electrolytes should give the value of A. But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur[58,61,62]. Thus, instead of determining A-values from the plots or by the least square method, the A-values are generally calculated using Falkenhagen-Vernon equation (17).

A-coefficient should be zero for non-electrolytes. According to Jones and Dole, the A-coefficient probably represents the stiffening effect on the solution of the electric forces between the ions which tend to maintain a space-lattice structure [48].

The B-coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ion-size and the solvent and cannot be calculated a priori. The B-coefficients are obtained as slopes of the straight lines using the least square method and intercepts equal to the A values.

The factors which influence B-values are [59,63]:

(1) The effect of ionic solvation and the action of the field of the ion in producing long range order in solvent molecules, increase η or B-value.

(2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or de-polymerisation effect) decrease η values.

(3) High molal volume and low dielectric constant, which yield high B-values for similar solvents.

(4) Reduced B-values are obtained when the primary solution of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

2.4.1. *Viscosities at Higher Concentration*

It had been found that the viscosity values at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade [64]:

$$\eta = A\exp^{b/T} \qquad (20)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [65-69] and the equation suggested by Angell [71,72] based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly noteworthy. The equation is:

$$1/\eta = A\exp[-K_1/(N_0 - N)] \qquad (21)$$

where N represents the concentration of the salt in eqv. litre^{-1}, A and K_1 are constants supposed to be independent of the salt composition and N_0 is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumder et al.[70-72] introducing the limiting condition, that as $N \rightarrow 0, \eta \rightarrow \eta_0$ which is the viscosity of the pure solvent. Thus, we have:

$$\ln\eta/\eta_0 = \ln\eta_{\mathrm{Rel}} = K_1\, N/N_0(N_0 - N) \qquad (22)$$

The equation (22) predicts a straight line passing through the origin for the plot of $\ln\eta_{Rel}$ vs. $N/(N_0 - N)$ if a suitable choice for N_0 is made. The equation (22) has been tested by Majumder et al. using the data from the literature and from their own experimental results. The best choice for N_0 and K_1 was selected by a trial and error methods. The set of K_1 and N_0 which produce minimum deviation between $\eta_{\mathrm{Re}l}^{Exp}$ and $\eta_{\mathrm{Re}l}^{Theo}$ was accepted.

In dilute solutions, $N \ll N_0$ and we have:

$$\eta_{\mathrm{Rel}} = \exp(K_1 N/N_0^2) \cong 1 + K_1\, N/N_0^2 \qquad (23)$$

which is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K_1/N_0^2$. The arrangement between B-values determined in this way and using Jones-Dole equation has been found to be good for several electrolytes.

Further, the equation (22) written in the form:

$$N/\ln\eta_{\mathrm{Rel}} = N_0^2/K_1 - (N_0/K_1)N \qquad (24)$$

It closely resembles the Vand's equation[65] for fluidity (reciprocal for viscosity):

$$2.5c/2.3 \log \eta_{\mathrm{Rel}} = 1/V - Qc \qquad (25)$$

where c is the molar concentration of the solute and V is the effective rigid molar volume of the salt and Q is the interaction constant.

2.4.2. *Division of B-coefficient into Ionic Values*

The viscosity B-coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents. [63, 76-106] However, the B-coefficients as determined experimentally using the Jones-Dole equation, does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total solute-solvent interaction. The division of B-values into ionic components is quite arbitrary and based on some assumptions, the validity of which may be questioned.

The following methods have been used for the division of B-values in the ionic components -

(1) Cox and Wolfenden[107] carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in $LiIO_3$ are proportional to the ionic volumes which are proportional to the third power of the ionic mobilities. The method of Gurney[108] and also of Kaminsky[54] is based on:

$$B_{K^+} = B_{Cl^-} \text{ (in water)} \tag{26}$$

The argument in favour of this assignment is based on the fact that the B-coefficients for KCl is very small and that the mobilities of K^+ and Cl^- are very similar over the temperature range of 288-318K. The assignment is supported from other thermodynamic properties. Nightingle,[109] however preferred RbCl or CsCl rather than KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron[59] is based on the assumption that the Et_4N^- ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation,[110]

$$B = 0.0025\overline{V}_0 \tag{27}$$

and by having an accurate value of the partial molar volume of the ion, $\overline{V}_0$, it is possible to calculate the value of 0.359 for $B_{Et_4N^+}$ in water at 298K.

Recently Sacco *et al.* proposed the "reference electrolytic" method for the division of B-values.

Thus, for tetraphenyl phosphonium tetraphenyl borate in water, we have:

$$B_{BPh_4^-} = B_{PPh_4^+} = B_{BPh_4PPh_4}/2 \tag{28}$$

$B_{BPh_4PPh_4}$ (scarcely soluble in water) has been obtained by the following method:

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \tag{29}$$

The values obtained are in good agreement with those obtained by other methods.

The criteria adopted for the separation of B-coefficients in non-aqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilutions.

(a) Criss and Mastroianni assumed $B_{K^+} = B_{Cl^-}$ in ethanol based on equal mobilities of ions.[127] They also adopted $B^{25}_{Me_4N^+} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss[111] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer et al.,[112] $\lambda^0_{25}(Bu_4N^+) = 61.4$ and $\lambda^0_{25}(Ph_4B^-) = 58.3$ in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \tag{30}$$

(c) Gopal and Rastogi[77] resolved the B-coefficient in N-methyl propionamide solutions assuming that $B_{Et_4N^+} = B_{I^-}$ at all temperatures.

(d) In dimethyl sulphoxide, the division of B-coefficients were carried out by Yao and Beunion[62] assuming:

$$B_{[(i-pe)_3BuN^+]} = B_{Ph_4B^-} = 1/2B_{[(i-pe)_3BuNPh_4B]} \tag{31}$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate[113] solutions.

The methods, however, have been strongly criticized by Krumgalz.[114] According to him, any method of resolution based on the equality of equivalent Conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which $\lambda^0_+ = \lambda^0_-$ in all solvents at all temperatures. Thus, though $\lambda^0_{K^+} = \lambda^0_{Cl^-}$ at 298K in methanol, but is not so in ethanol or in any other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the B-coefficient values are calculated. Further, according to him, equality of dimensions of $(i-pe)_3BuN^+$ or $(i-Am)_3BuN^+$ and Ph_4B^- does not necessarily imply the equality of B-coefficients of these ions and they are likely to be solvent and ion-structure dependent.

Krumgalz[114, 116] has recently proposed a method for the resolution of B-coefficients. The method is based on the fact that the large tetraalkylammonium cations are not solvated [117,118] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B-values for large tetraalkylammonium ions, R_4N^+ (where R > Bu) in organic solvents are proportional to their ionic dimensions. So, we have:

$$B_{R_4NX} = a + br^3 R_4N^+ \tag{32}$$

where $a = B_{X^-}$ and b is a constant dependent on temperature and solvent nature.

The extrapolation of the plot of B_{R_4NX} (R > Pr or Bu) against $r^3 R_4N$ to zero cation dimension gives directly B_{X^-} in the proper solvent from which B-ion values can be calculated.

The B-ion values can also be calculated from the equations:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \tag{33}$$

$$B_{R_4N^+} / B_{R'_4N^+} = r^3_{R_4N^+} / r^3_{R'_4N^+} \tag{34}$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data. [119]

Gill and Sharma[97] used Bu_4NBPh_4 as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that Bu_4N^+ and Ph_4B^- ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of (5.00Å) Bu_4N^+ and Ph_4B^- (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

$$B_{Ph_4B^-} / B_{Bu_4N^+} = r^3_{Ph_4B^-} / r^3_{Bu_4N^+} = (5.35/5.00)^3 \tag{35}$$

and,
$$B_{Bu\ NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \tag{36}$$

The method requires only the B-values of Bu_4NBPh_4 and is equally applicable to mixed non-aqueous solvents. The B-ion values obtained by this method agree well with those reported by Sacco et al. in different organic solvents using the assumption as given below:

$$B_{[(i-Am)_3BuN^+]} = B_{Ph_4B^-} = 1/2\, B_{[(i-Am)_3BuNPh_4B]} \tag{37}$$

Recently, Lawrence and Sacco[100] used tetrabutylammonium tetra-butylborate (Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal van der Waals volume. Thus, we have:

$$B_{\mathrm{Bu_4N^+}} / B_{\mathrm{Bu_4B^-}} = V_{W(\mathrm{Bu_4N^+})} / V_{W(\mathrm{Bu_4B^-})} \tag{38}$$

$$\text{or, } B_{\mathrm{Bu_4N^+}} = B_{\mathrm{Bu_4NBBu_4}} / 1 + V_{W(\mathrm{Bu_4B^-})} / V_{W(\mathrm{Bu_4N^+})} \tag{39}$$

A similar division can be made for Ph_4PBPh_4 system.

Recently, Lawrence et al. made the viscosity measurements of tetraalkyl (from Pr to Hept.) ammonium bromides in DMSO and HMPT. The B-coefficients $B_{\mathrm{R_4NBr}} = B_{\mathrm{Br^-}} + a[f_x R_4 N^+]$ were plotted as functions of the van der Waals volumes. The $B_{\mathrm{Br^-}}$ values thus obtained were compared with the accurately determined $B_{\mathrm{Br^-}}$ value using Bu_4NBBu_4 and Ph_4PBPh_4 as reference salts.. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritcheit[120] suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali metal halide salts by employing Fajans' competition principle[121] and 'volcano plots' of Morris.[122] The principle was extended to derive absolute single ion B-coefficients for alkali metals and halides in water. They also observed that $B_{\mathrm{Cs^+}} = B_{\mathrm{I^-}}$ suggested by Krumgalz[114] to be more reliable than $B_{\mathrm{K^+}} = B_{\mathrm{Cl^-}}$ in aqueous solutions. However, we require more data to test the validity of this method.

It is apparent that almost all these methods are based on certain approximations and anomalous results may arise unless proper mathematical theory is developed to calculate B-values.

2.4.3. *Temperature dependence of B - ion Values*

A regularity in the behaviour of $B_\pm$ and $dB_\pm/dT$ has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminski. He observed that (i) within a group of the periodic table the B-ion values decrease as the crystal ionic radii increase, (ii) within a group of periodic system, the temperature co-efficient of B_{Ion} values increase as the ionic radius increases. The results can be summarized as follows:

$$\text{(i) } A \text{ and } dA/dT > 0 \tag{40}$$

$$\text{(ii) } B_{Ion} < 0 \text{ and } dB_{Ion}/dT > 0 \tag{41}$$

Characteristic of the structure breaking ions.

$$\text{(iii) } B_{Ion} > 0 \text{ and } dB_{Ion}/dT < 0 \tag{42}$$

Characteristic of the structure making ions.

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvational layer may be different from those present in the bulk structure. This is well reflected in the 'Co-sphere' model of Gurney,[123] A, B, C Zones of Frank and Wen[121] and hydrated radius of Nightingle.[109]

Stokes and Mills gave an analysis of the viscosity data incorporating the basic ideas presented before. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent (η_0) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighbourhood. Thus, the Jones-Dole equation:

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta(A\sqrt{c} + Bc) \tag{43}$$

η^* is the positive increment in viscosity caused by coulombic interaction. Thus:

$$\eta^E + \eta^A + \eta^D = \eta_0 BC \tag{44}$$

B-coefficient can thus be interpreted in terms of the competitive viscosity effects.

Following Stokes, Mills and Krumgalz [111] we can write for B_{Ion} as:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{\mathrm{Reinf}} \tag{45}$$

whereas according to Lawrence and Sacco:

$$B_{Ion} = B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \tag{46}$$

B_{Ion}^{Einst} is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^E or B_{Shape}). B_{Ion}^{Orient} is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to η^A or B_{Ord}). B_{Ion}^{Str} is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymetrically and solvent to keep its own structure (this corresponds to η^D or B_{Disord}). B_{Ion}^{Reinf} is the positive increment conditioned by the effect of 'reinforcement of the water structure' by large tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents. B_W and B_{Solv} account for viscosity increases and attributed to the van der Waals volume and the volume of the solvation of ions.

Thus, small and highly charged cations like Li^+ and Mg^{++} form a firmly attached primary solvation sheath around these ions (B_{Ion}^{Einst} or η^E positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in $B_{Ion}^{Orient}(\eta^A)$, $B_{Ion}^{Str}(\eta^D)$ is small for these ions. Thus, B_{Ion} will be large and positive as $B_{Ion}^{Einst} + B_{Ion}^{Orient} > B_{Ion}^{Str}$. However, B_{Ion}^{Einst} and B_{Ion}^{Orient} would be small for ions of greatest crystal radii (within a group) like Cs^+ or I^+ due to small surface charge densities resulting in weak orienting and structure forming effect. B_{Ion}^{Str} would be large due to structural disorder in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure. Thus $B_{Ion}^{Einst} + B_{Ion}^{Orient} < B_{Ion}^{Str}$ and B_{Ion} is negative.

Ions of intermediate size (e.g. K^+ and Cl^-) have a close balance of viscous forces in their vicinity, *i.e.*, $B_{Ion}^{Einst} + B_{Ion}^{Orient} = B_{Ion}^{Str}$, so that B is close to zero.

Large molecular ions like tetraalkylammonium ions have large B_{Ion}^{Einst} because of large size but B_{Ion}^{Orient} and B_{Ion}^{Str} would be small, *i.e.*, $B_{Ion}^{Einst} + B_{Ion}^{Orient} >> B_{Ion}^{Str}$ and B would be positive and large. The value would be further reinforced in water arising from B_{Ion}^{Reinf} due to hydrophobic hydrations.

The increase in temperature will have no effect on B_{Ion}^{Einst}. But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in B_{Ion}^{Str}. B_{Ion}^{Orient} will decrease slowly with temperature as there will be less competition between the ionic field and reduced solvent structure. The positive or negative temperature co-efficient will thus depend on the change of the relative magnitudes of B_{Ion}^{Orient} and B_{Ion}^{Str}.

In case of structure-making ions, the ions are firmly surrounded by a primary solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in B_{Ion} and concomitant decrease in entropy of solvation and the mobility of ions. Structure breaking ions, on the other hand, are not solvated to a great extent and the secondary solvation zone will be disordered leading to a decrease in B_{Ion} values and increases in entropy of solvation and the mobility of ions. Moreover, the temperature induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So there is a correlation between the viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic B-coefficient and the entropy of solvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication of structure making and structure breaking character of ions.

The linear plot of ionic B-coefficients against the ratios of mobility viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney[123] clearly demonstrates a close relation between ionic B-coefficients and ionic mobilities.

Gurney also demonstrated a clear correlation between the molar entropy of solution values with B-coefficient of salts. The ionic B-values show a linear relationship with the partial molar ionic entropies or partial molar entropies of hydration ($\overline{S}_h^0$) as:

$$\overline{S}_h^0 = \overline{S}_{aq}^0 - \overline{S}_g^0 \tag{47}$$

where, $\overline{S}_{aq}^0 = \overline{S}_{ref}^0 + \Delta S^0$, $\overline{S}_g^0$ is the calculated sum of the translational and rotational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic B-coefficients for all monoatomic ions by equating the entropy of the hydrogen ion ($\overline{S}_{H^+}^0$) to -5.5 cal. $\mathrm{Mol^{-1}deg^{-1}}$. Asmus[125] used the entropy of hydration to correlate ionic B-values and Nightingale[109] showed that a single linear relationship can be obtained with it for both monoatomic and polyatomic ions.

The correlation was utilized by Abraham et al.[126] to assign single ion B-coefficients so that a plot of ΔS_e^0,[128,129] the electrostatic entropy of solvation or $\Delta S_{I,II}^0$,[128,129] the entropic contributions of the first and second solvation layers of ions against B points (taken from the works of Nightingale) for both cations and anions lie on the same curve. There are excellent linear correlations between ΔS_e^0 and ΔS_I^0 and the single ion B-coefficients. Both entropy criteria (ΔS_e^0 and $\Delta S_{I,II}^0$) and B-ion values indicate that in water the ions Li^+, Na^+, Ag^+ and F^- are not structure makers, and the ions Rb^+, Cs^+, Cl^-, Br^-, I^- and ClO_4^- structure breakers and K^+ is a border line case.

2.4.4. *Thermodynamics of Viscous Flow*

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [130] approach as:

$$\eta = Ae^{E_{Vis}/RT} = (hN/V)e^{\Delta G^{*}/RT} = (hN/V)e^{(\Delta H^{*}/RT - \Delta S^{*}/R)} \tag{48}$$

where E_{Vis}= the experimental entropy of activation determined from a plot of $\ln\eta$ against $1/T$. ΔG^{*}, ΔH^{*} and ΔS^{*} are the free energy, enthalpy and entropy of activation respectively.

Nightingale and Benck[131] dealt in the problem in a different way and calculated the thermodynamics of viscous flow of salts in aqueous solution with the help of the Jones-Dole equation (neglecting the $A\sqrt{c}$ term).

Thus, we have:

$$R[d\ln\eta/d(1/T)] = r[d\ln\eta_0/d(1/T)] + R/(1+Bc).d(1+Bc)/d(1/T) \tag{49}$$

$$\Delta E^{\neq}_{\eta(Soln)} = \Delta E^{\neq}_{\eta_0(Solv)} + \Delta E^{\neq}_{V} \tag{50}$$

$\Delta E^{\neq}_{V}$ can be interpreted as the increase or decrease of the activation energies for viscous flow of the pure solvents due to the presence of ions, i.e., the effective influence of the ions upon the viscous flow of the solvent molecules.

Feakins et al.[131] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = (\overline{V}_1^0 - \overline{V}_2^0)/1000 + \overline{V}_1^0(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/1000RT \tag{51}$$

where $\overline{V}_1^0$ and $\overline{V}_2^0$ are the partial molar volumes of the solvent and solute respectively and $\Delta\mu_2^{0\neq}$ is the contribution per mole of solute to the free energy of activation for viscous flow of solution. $\Delta\mu_1^{0\neq}$ is the free energy of activation for viscous flow per mole of the solvent which is given by:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln\eta_1\overline{V}_1^0/hN \tag{52}$$

Further, if B is known at various temperatures, we can calculate the entropy and enthalpy of activation of viscous flow respectively from the following equations as given below:

$$d(\Delta\mu_2^{0\neq})/dT = -\Delta S_2^{0\neq} \tag{53}$$

$$\Delta H_2^{0\neq}=\Delta\mu_2^{0\neq}+T\Delta S_2^{0\neq} \qquad (54)$$

2.4.5. Effects *of Shape and Size*

Stokes and Mills have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein[110] leads to the equation:

$$\eta/\eta_0 = 1+2.5\phi \qquad (55)$$

where ϕ is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by (i) Simha[132] on the basis of departures from spherical shape and (ii) Vand on the basis of dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monoatomic cations).

Thus we have from equation (55):

$$2.5\phi = A\sqrt{c}+Bc \qquad (56)$$

Since $A\sqrt{c}$ term can be neglected in comparison with Bc and $\phi = c\overline{V}_1$, where $\overline{V}_1$ is the partial molar volume of the ion, we get:

$$2.5\overline{V}_1 = B \qquad (57)$$

In the ideal case, the B-coefficient is a linear function of partial molar volume of the solute, $\overline{V}_1$ with slope to 2.5. Thus, $B_\pm$ can be equated to:

$$B_\pm = 2.5\overline{V}_\pm = 2.5\times 4/3(\pi R_\pm^3 N/1000) \qquad (58)$$

assuming that the ions behave like rigid spheres with a effective radii, $R_\pm$ moving in a continuum. $R_\pm$ calculated using the equation (58) should be close to crystallographic radii or corrected Stoke's radii if the ions are scarcely solvated and behave as spherical entities. But, in general, $R_\pm$ values of the ions are higher than the crystallographic radii indicating appreciable solvation.

The number n_b of solvent molecules bound to the ion in the primary solvation shell can be easily calculated by comparing the Jones-Dole equation with the Einstein's equation:[131]

$$B_{\pm} = 2.5/1000(V_i + n_b V_S) \tag{59}$$

where V_i is the molar volume of the base ion and V_S, the molar volume of the solvent. The equation (59) has been used by a number of workers to study the nature of solvation and solvation number.

2.4.6. *Viscosity Deviations*

Quantitatively, as per the absolute reaction rates theory,[133] the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i \eta_i) \tag{60}$$

where η is the dynamic viscosities of the mixture and x_i, η_i are the mole fraction and viscosity of i^{th} component in the mixture, respectively.

2.4.7. *Gibbs Excess Energy of Activation for Viscous Flow*

Quantitatively, the Gibbs excess energy of activation for viscous flow, G^{*E} can be calculated as: [134]

$$G^{*E} = RT[\ln\eta V - \sum_{i=1}^{j} x_i \ln\eta_i V_i] \tag{61}$$

where, η and V are the viscosity and molar volume of the mixture, η_i and V_i are the viscosity and molar volume of i^{th} pure component, respectively.

2.5. *Ultrasonic Speed*

The acoustic property, ultrasonic speed is a sensitive indicator of molecular interactions and can provide useful information about these phenomena, particularly in cases where partial molar volume data alone fail to provide an unequivocal interpretation of the interactions.

2.5.1. Apparent *Molal Isentropic Compressibility*

Although for a long time attention has been paid to the apparent molal isentropic compressibility for electrolytes and other compounds in aqueous solutions,[135-139] measurements in non-aqueous[21,25] solvents are still scarce. It has been emphasized by many authors that the apparent molal isentropic compressibility data can be used as a useful parameter in elucidating the solute-solvent and solute-solute interactions.

The isentropic compressibility (K_S) of the solution was calculated from the Laplace's equation: [140]

$$K_S = 1/(u^2\rho) \tag{62}$$

where ρ is the solution density and u is the ultrasonic speed in the solution.

The apparent molal isentropic compressibility (ϕ_K) of the solutions was determined from the relation:

$$\phi_K = MK_S/\rho_0 + 1000(K_S\rho_0 - K_S^0\rho)/m\rho\rho_0 \tag{63}$$

K_S^0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute, *m* is the molality of the solution.

The limiting apparent molal isentropic compressibility (ϕ_K^0) was obtained by extrapolating the plots of ϕ_K versus the square root of molal concentration of the solute, $\sqrt{m}$ to zero concentration by a least-squares method:[135,138]

$$\phi_K = \phi_K^0 + S_K^*\sqrt{m} \tag{64}$$

where S_K^* is the experimental slope.

The limiting apparent molal isentropic compressibility (ϕ_K^0) and the experimental slope (S_K^*) can be interpreted in terms of solute-solvent and solute-solute interactions respectively. It is well established that the solutes causing electrostriction leads to the decrease in the compressibility of the solution. [141,142] This is reflected by the negative values of ϕ_K^0 of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering that is induced by them in the water structure. [20, 141]

The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved. [141] However, the poor fit of the solute molecules [143,144] as well as the possibility of flexible hydrogen bond formation appear to be responsible for causing a more compressible environment (and hence positive ϕ_K^0 values have been reported in aqueous non-electrolyte [145] and non-aqueous non-electrolyte [146] solutions.

2.5.2 *Acoustical Parameters*

To investigate the nature of the interactions, various acoustical parameters[147-152] such as specific acoustic impedance Z, intermolecular free length L_f, Vander Wall's constant b, molecular radius r, geometrical volume B, molar surface area Y, available volume V_a, molar speed of sound R, collision factor S and molecular association M_A, has been calculated using the sound speed and density of the mixtures and pure solvents which are sensitive to interaction between solute and solvent.

$$L_f = K\sqrt{K_S} \tag{65}$$

$$Z = u\rho \tag{66}$$

$$b = \left(M/\rho\right) - \left(RT/\rho^2u^2\right)\left\{\left[1 + \left(Mu^2/3RT\right)\right]^{\frac{1}{2}} - 1\right\} \tag{67}$$

$$r = \left(3b/16\pi N\right)^{\frac{1}{3}} \tag{68}$$

$$B = \frac{4}{3}\pi r^3 N \tag{69}$$

$$Y = \left(36\pi NB^2\right)^{\frac{1}{3}} \tag{70}$$

$$V_a = V - \left(1 - \frac{u}{u_\infty}\right) \tag{71}$$

$$V_0 = V - V_a \tag{72}$$

$$R = Mu^{\frac{1}{3}}/\rho \tag{73}$$

$$R_A = \left(\rho_{mix}/\rho\right)\left(u/u_{mix}\right)^{\frac{1}{3}} \tag{74}$$

$$M_A = \left(u_{mix}/\sum_{i=1}^{2} x_i u_i\right)^2 - 1 \tag{75}$$

where K is a temperature dependent Jacobson's constant (= (93.875 + 0.375 T) x 10^{-8}), V_0 is volume at absolute zero, V is the molecular volume, u_∞ is taken as 1600 m. s^{-1}.

2.5.3 *Deviation in Isentropic Compressibility, Intermolecular free Length and Acoustic Impedance*

The deviation in isentropic compressibility, intermolecular free length and specific acoustic impedance of the mixture ΔK_S, ΔL_f, ΔZ can be calculated using the following equations: [153-155]

$$\Delta K_S = K_S - \sum_{i=1}^{j}(x_i K_{s,i}) \tag{76}$$

$$\Delta L_f = L_f - \sum_{i=1}^{2} x_i L_{fi} \tag{77}$$

$$\Delta Z = Z - \sum_{i=1}^{2} x_i Z_i \tag{78}$$

Where K_S, L_f and Z are the isentropic compressibility, intermolecular free length and specific acoustic impedance of the mixture and x_i, K_{S_i}, L_{f_i} and Z_i are the mole fraction, isentropic compressibility, intermolecular free length and specific acoustic impedance of *i*th component in the mixture, respectively.

2.5.4. *Theoretical Approaches to Sound Speed*

The sound speed 'u' may be calculated by several empirical equations. Among which the free length theory, collision factor theory, Nomoto Equation, the Vandeal Vangael ideal mixing relation, the impedance dependence relation etc. are notable. For comparison, the theoretical values of the sound speed u has been calculated by using the above five theories and empirical equations. The following equations are used for calculation sound speeds:

(*a*) According to free length theory[148], the speed of sound is given by,

$$u_{FLT} = K_s / L_f \rho^{\frac{1}{2}} \tag{79}$$

The free length L_f is obtained by:

$$L_f = \left(V - \sum_i x_i V_{0i}\right) \Big/ \sum_i x_i y_i \tag{80}$$

where, V_{0i} is the molar volume of the pure component i at absolute zero and is given by Sugden's formula,

$$V_{0i} = V_i\left(\left(1 - T\right) \big/ T_{ci}\right)^{0.3} \tag{81}$$

where T_{ci} is the critical temperature for the pure components.

Y_i is the surface area per mole for the pure component i and is given by,

$$Y_i = \left(36\pi N V_{0i}^2\right)^{1/3} \tag{82}$$

(*b*) Collision Factor Theory[149,151]:

$$u_{CFT} = u_{\infty}[x_1S_1] + \left[{(x_1B_1 + x_2B_2)} / {V_{12}} \right] \tag{83}$$

(*c*) Nomoto equation, [152,157]

$$u_N = \left[{(x_1R_1 + x_2R_2)} / {(x_1V_1 + x_2V_2)} \right] \tag{84}$$

(*d*) Vandeal Vangael [158] ideal mixing relation

$$\frac{1}{x_1M_1 + x_2M_2} \frac{1}{u_{mix}^2} = \frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2} \tag{85}$$

(*e*) Impedance dependence relation [159,160]

$$u = \sum x_iZ_i / x_i\rho_i \tag{86}$$

where, K_S, S, B, R, Z, ρ are the isentropic compressibility, collision factor, geometrical volume, molar speed of sound, specific acoustic impedance and density respectively for pure solvents (1) and (2), and the mixtures (12) respectively.

2.6. *Correlating Equations*

Several semi-empirical models have been proposed to estimate the dynamic viscosity of the binary liquid mixtures in terms of pure-component data.[161, 162] Some of them we examined are as follows:

a) The viscosity values can be further used to determine the Grunberg-Nissan parameter, d_{12} as: [162]

$$\eta = \exp[\sum_{i=1}^{j} (x_i \ln \eta_i) + d_{12} \prod_{i=1}^{j} x_i] \tag{87}$$

and d_{12} is proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The negative values of d_{12} indicate the presence of dispersion forces[163] between the mixing components in the mixtures while its positive values indicate the presence of specific interactions[164,165,166] between them.

b) Tamura-Kurata[167] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i\phi_i\eta_i + 2T_{12}\prod_{i=1}^{j}[x_i\phi_i]^{1/2} \tag{88}$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of ith pure component in the mixture.

c) Molecular interactions may also be interpreted by the following viscosity model of Hind et al: [168]

$$\eta = \sum_{i=1}^{j} x_i^2\eta_i + 2H_{12}\prod_{i=1}^{j} x_i \tag{89}$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[169]It has been observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other, this is in agreement with the view put forward by Fort and Moore[170] in regard to the nature of parameter T_{12} and H_{12}.

d) McAllister multibody interaction model[171] is widely used to correlate the kinematic viscosities $\left(\upsilon = \eta/\rho\right)$ of the binary mixtures with mole fraction.

McAllister assumed that

i) the interaction in liquid mixtures are mostly three body type

ii) the probability for their occurance is concentration dependent only

iii) the free energy of activation of terms are additive.

With these assumptions, the McAllister equation involving three body intractions for multicomponent mixtures is as follows,

$$\ln \upsilon_m = \sum_{i=1}^{n} x_i^3 \ln \upsilon_i M_i - \ln M_{av} + 3\sum_{i=1}^{n}\sum_{j=1}^{n} x_i^2 x_j \ln \upsilon_{ij} M_{ij} +$$
$$6\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{\substack{k=1 \\ i\neq j\neq k}}^{n} x_i x_j x_k \ln \upsilon_{ijk} M_{ijk} \tag{90}$$

Where, $M_{av} = \sum_{i=1}^{n} x_i M_i$

$$M_{ij} = \left(\frac{2M_i + M_j}{3}\right)$$

$$M_{ijk} = \left(\frac{M_i + M_j + M_k}{3}\right)$$

For binary mixtures the equation reduces to

$$\ln\upsilon = x_1^3\ln\upsilon_1 + x_2^3\ln\upsilon_2 + 3x_1^2x_2\ln\upsilon_{12} + 3x_2^3x_1\ln\upsilon_{21}$$
$$-\ln\left[x_1+\frac{x_2M_2}{M_1}\right] + 3x_1^2x_2\ln\left[\frac{2}{3}+\frac{M_2}{3M_1}\right] + 3x_2^2x_1\ln\left[\frac{1}{3}+\frac{2M_2}{3M_1}\right] + x_2^3\ln\left[\frac{M_2}{M_1}\right] \tag{91}$$

The viscosities of liquid mixtures are also correlated by using the Mcallister equation based on four body interactions[171], when hydrogen bonding are included in the system and the behaviour of the systems become complex. Mcallister equation for n-component mixture containing four body interactions are given below,

$$\ln\upsilon_m = \sum_{i=1}^{n} x_i^4\ln(\upsilon_i M_i) + 4\sum_{i=1}^{n}\sum_{j=1}^{n} x_i^3x_j\ln\left[\upsilon_{iiij}\left(\frac{3M_i+M_j}{4}\right)\right] + 6\sum_{i}^{n}\sum_{j}^{n} x_i^2x_j\ln\left[\upsilon_{iijj}\left(\frac{M_i+M_j}{2}\right)\right]$$
$$+12\sum_{\substack{i\\ i\neq j}}^{n}\sum_{\substack{j\\ j\neq k}}^{n}\sum_{\substack{k\\ j<k}}^{n}\left[\upsilon_{iijk}\left(\frac{2M_i+M_j+M_k}{4}\right)\right] - \ln\left(\sum_{i}^{n} x_iM_i\right) \tag{92}$$

For binary mixture, the equation reduces to,

$$\ln\upsilon = x_1^4\ln\upsilon_1 + 4x_1^3x_2\ln\upsilon_{1112} + 6x_1^2x_2^2\upsilon_{1122} + 4x_1x_2^3\ln\upsilon_{2221} + x_2^4\ln\upsilon_2$$
$$-\ln\left[x_1+x_2\left(\frac{M_2}{M_1}\right)\right] + 4x_1^3x_2\ln\left[\frac{3}{4}+\frac{M_2}{4M_1}\right] + 6x_1^2x_2^2\ln\left[\frac{1}{2}+\frac{M_2}{2M_1}\right]$$
$$+4x_1x_2^3\ln\left[\frac{1}{3}+\frac{3M_2}{4M_1}\right] + x_2^4\ln\left[\frac{M_2}{M_1}\right] \tag{93}$$

Where υ , υ_1 and υ_2 are kinematic viscosities of the mixture, the pure component 1 an2 respectively, υ_{12} , υ_{21} , υ_{1112} , υ_{1122} , υ_{2221} are model parameters and M_i is the mole fraction and molecular weight of the *i*th pure component in the mixture, respectively.

The Mcallister equation of viscosity was modified byDizechi.[172]

e) Heric and Brewer[173] have proposed an equation for the kinematic viscosity of the binary liquid mixtures

$$\upsilon = x_1\upsilon_1 + x_2\upsilon_2 + x_1x_2\{a + b(x_1-x_2) + c(x_1-x_2)^2\} \tag{94}$$

Where, *a* , *b* and *c* are model parameters and M_i, x_i are the molecular weight and mole fraction of the *i*th pure component in the mixture, respectively.

The percentage standard deviation[174] was calculated by using equation (95).

$$\sigma\% = \left[\frac{\sum \left(100\left(\upsilon_{exptl} - \upsilon_{calcd}\right) \Big/ \upsilon_{exptl} \right)^2}{(n-m)} \right]^{\frac{1}{2}} \tag{95}$$

where n represents the number of experimental points and m the number of coefficients.

In non ideal liquid mixture the difference in structure and force fields of individual components are so numerous that number of possibilities of molecular interactions can not be accounted for by considering the molecular pairs alone. The equations obtained as a effort of Mcallister,[171] Kalidas and Ladha[175], Katti and Chaudhuri[176], Herric[175] and Herric and Brewer[173] have been tested for completely miscible liquid mixtures and they accounted for the non-ideality to different extents depending on the number of adjustable parameters involved.

Moreover, The excess properties (V^E, $\Delta\eta$, G^{*E} and K_S^E) have been fitted to Redlich-Kister [178] polynomial equation using the method of least squares involving the Marquardt algorithm [179] to derive the binary coefficient, a_i :

$$Y^E = x_1 x_2 \sum_{i=1}^{j} a_i (x_1 - x_2)^i \tag{96}$$

where Y^E refers to an excess property and x_1 and x_2 are the mole fraction of the solvent 1 and solvent 2, respectively. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The standard deviation (σ) was calculated using,

$$\sigma = [(Y^E_{\exp} - Y^E_{cal})^2 / (n-m)]^{1/2} \tag{97}$$

where n is the number of data points and m is the number of coefficients.

2.7. *Conductance*

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte of solutions.[180,181] The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic theories are not applicable. Fortunately, accurate theories of electrolytic conductances are available to explain the results even up to a concentration limit of κd (κ = Debye-Huckel length, d = distance of closest approach of free ions). Recently developed experimental techniques provide an accuracy of ±0.01% or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitation, however, is the colligative-like nature of the information obtained.

Since the conductometric method primarily depends on the mobility of ions, it can be suitably utilized to determine the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents. The conductometric method in conjunction with viscosity measurements gives us much information regarding the ion-ion and ion-solvent interactions. However, the choice and application of theoretical equations as well as equipment and experimental techniques are of great importance for precise measurements. These aspects have been described in details in a number of authoritative books and reviews.[180-193]

The study of conductance measurements were pursued vigorously both theoretically and experimentally during the last five decades and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents.

The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager[194] to derive the Kohlrausch's equation representing the molar conductance of an electrolyte. For solutions of a single symmetrical electrolyte the equation is given by:

$$\Lambda = \Lambda_0 - S\sqrt{c} \tag{98}$$

$$\text{where, } S = \alpha \Lambda_0 + \beta \tag{99}$$

$$\alpha = (ze)^2 \kappa \big/ 3(2+\sqrt{2})\varepsilon_r kT\sqrt{c} = 82.406\times10^4\, z^3 \big/ (\varepsilon_r T)^{3/2} \tag{100a}$$

$$\beta = z^2 e F\kappa \big/ 3\pi\eta\sqrt{c} = 82.487\, z^3 \big/ \eta\sqrt{\varepsilon_r T} \tag{100b}$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent.[195] *In the subsequent years,* Pitts (1953) [196] and Fuoss and Onsager (1957)[185, 197] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably[195] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned.[181, 198, 199] The original Fuoss-Onsager equation was further modified by Fuoss and Hsia[200] who recalculated the relaxation field, retaining the terms which had previously been neglected.

The results of conductance theories can be expressed in a general form by:

$$\Lambda = \Lambda_0 - \alpha\Lambda_0\sqrt{c}/(1+\kappa a)(1+\kappa a/\sqrt{2}) - \beta\sqrt{c}/(1+\kappa a) + G(\kappa a) \qquad (101)$$

where $G(\kappa a)$ is a complicated function of the variable. The simplified form:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2\sqrt[3]{c} \qquad (102)$$

is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini.[181, 201, 202] Further correction of the equation (102) was made by Fuoss and Accascina.[185]

They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2\sqrt[3]{c} - \mathrm{F}\Lambda c \qquad (103)$$

where, $\mathrm{F}c = 4\pi R^3 N_A/3$

In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions.[203]

2.7.1. *Ionic Association*

The equation (103) successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against $\sqrt{c}$ (limiting Onsager equation) is used to assign the dissociation or association of electrolytes. Thus, if Λ^0_{expt} is greater than Λ^0_{theo}, i.e., if positive deviation occurs (ascribed to short range hard core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviation ($\Lambda^0_{expt} < \Lambda^0_{theo}$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_0 + \beta$) occurs, the electrolyte may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in Λ^{0}_{expt} and Λ^{0}_{theo} would be considerable with increasing association.[205]

Conductance measurements help us to determine the values of the ion-pair association constant, K_A for the process:

$$\mathrm{M}^{Z+} + \mathrm{A}^{Z-} = \mathrm{MA} \tag{104}$$

$$K_A = (1-\alpha)/\alpha^2 c\gamma_{\pm}^2 \tag{105}$$

$$\alpha = 1 - \alpha^2 K_A c\gamma_{\pm}^2 \tag{106}$$

where $\gamma_{\pm}$ is the mean activity coefficient of the free ions at concentration αc. For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation[205] or Shedlovsky's equation:[204]

$$T(z)/\Lambda = 1/\Lambda_0 + K_A/\Lambda_0^2 . c\gamma_{\pm}^2 \Lambda/T(z) \tag{107}$$

where $T(z) = F(z)$ (Fuoss-Kraus method) and $1/T(z) = S(z)$ (Shedlovsky's method):

$$F(z) = 1 - z(1 - z(1 - ....)^{-1/2})^{-1/2} \tag{108a}$$

and $$1/T(z) \equiv S(z) = 1 + z + z^2/2 + z^3/8 + ... \tag{108b}$$

A plot of $T(z)/\Lambda$ against $c\gamma_{\pm}^2 \Lambda/T(z)$ should be a straight line having $1/\Lambda_0$ for its intercept and K_A/Λ_0^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (107).

The Fuoss-Hsia[200] conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \tag{109}$$

The equation was modified by Justice.[207] The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c}) + E(\alpha c)\ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \tag{110}$$

$$(1-\alpha)/\alpha^2 c\gamma_{\pm}^2 = K_A \tag{111}$$

$$\ln\gamma_{\pm} = -k\sqrt{q}/(1 + kR\sqrt{\alpha c}) \tag{112}$$

The conductance parameters are obtained from a least square treatment after setting, $R = q = e^2/2\varepsilon kT$ (Bjerrum's critical distance).

According to Justice the method of fixing the J-coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. Since the equation (110) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as must as possible by J_2 rather than by K_A, whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction.

From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach, a, of two free ions to form an ion-pair. The following equation has been proposed by Fuoss:[208]

$$K_A = (4\pi N_A a^3/3000)\exp(e^2/a\varepsilon kT) \qquad (113)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a. The distance parameter was finally determined from the more general equation due to Bjerrum:[209]

$$K_A = 4\pi N_A a/1000\int_{r=a}^{r=q} r^2\exp(z^2e^2/r\varepsilon kT)\,dr \qquad (114)$$

The equations neglect specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilized by Douheret.[210]

2.7.2. *Ion size Parameter and Ionic Association*

For plotting, equation (81) can be rearranged to the 'Λ' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec\ln c = \Lambda_0 + J_1c + J_2\sqrt[3]{c} = \Lambda_0 + J_1c \qquad (115)$$

with J_2 term omitted.

Thus, a plot of Λ_0 vs c gives a straight line with Λ_0 as intercept and J_1 as slope and a values can be calculated from J_1 values. The a values obtained by this method for DMSO were much smaller[204] than would be expected from sums of crystallographic radii. One of the reasons attributed to it is that ion-solvent interactions are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in a values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction leads to a larger value of a[211] but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J.[212]

Fuoss[213] in 1975 proposed a new conductance equation. Latter he subsequently put forward another conductance equation in 1978 replacing the old one as suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

(i) Ions finding an ion of opposite charge in the first shell of nearest neighbours (contact pairs) with $r_{ij} = a$. The nearest neighbors to a contact pair are the solvent molecules forming a cage around the pairs.

(ii) Ions with overlapping Gurney's co-spheres (solvent separated pairs). For them $r_{ij} = (a + ns)$, where n is generally 1 but may be 2, 3 etc.; 's' is the diameter of sphere corresponding to the average volume (actual plus free) per solvent molecule.

(iii) Ions finding no other unpaired ion in a surrounding sphere of radius R, the diameter of the co-sphere (unpaired ions).

Thermal motions and interionic forces establish a steady state, represented by the following equilibria:

$$\mathrm{A^+ + B^+} = \underset{\text{Solvent separated pair}}{(\mathrm{A^+......B^+})} = \underset{\text{Contact pair}}{\mathrm{A^+B^-}} = \underset{\text{Neutral molecule}}{\mathrm{AB}} \qquad (116)$$

Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- = AB$ e.g., H_3O^+ and CH_3COO^-. Let γ be the fraction of solute present as unpaired ($r > R$) ions. If $c\gamma$ is the concentration of unpaired ion and α is the fraction of paired ions ($r \leq R$), then the concentration of the solvent separated pair is $c\,(1-\alpha)(1-\gamma)$ and that of contact pair is $\alpha\, c(1-\gamma)$.

The equation constants for (94) are:

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 f^2 \qquad (117)$$

$$K_S = \alpha/(1-\alpha) = \exp(-E_S/kT) = e^{-\varepsilon} \qquad (118)$$

where K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter R around cations and can be calculated by continuum theory; K_S is the constant describing the specific short-range ion-solvent and ion-ion interactions by which contact pairs form and dissociate. E_S is the difference in energy between a pair in the states ($r = R$) and ($r = a$); ε is E_S measured in units of kT.

Now, $(1-\alpha) = 1/(1+K_S)$ (119)

And the conductometric pairing constant is given by:

$$K_\Lambda = (1-\alpha)/c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \tag{120}$$

The equation determines the concentration, $c\gamma$ of active ions that produce long-range interionic effects. The contact pairs react as dipoles to an external field, X and contribute only to changing current. Both contact pairs and solvent separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is, therefore, neglected in calculating long-range effects (activity coefficients, relaxation field ΔX and electrophoresis $\Delta\Lambda_e$). The various patterns can be reproduced by theoretical fractions in the form:

$$\Lambda = p[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e] = p[\Lambda_0(1+R_X) + E_L] \tag{121}$$

which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_0, R, E_S)$ and $\Delta X/X$ (the relaxation field) and $\Delta\Lambda_e$ (the electrophoretic counter current) are long-range effects due to electrostatic interionic forces and p is the fraction of solute which contributes to conductance current. R is the diameter of the Gurney co-sphere.

The parameter K_R (or E_S) is a catch-all for all short-range effects:

$$p = 1 - \alpha(1-\gamma) \tag{122}$$

In case of ionogens or for ionophores in solvents of low dielectric constant, α is very near to unity $(-E_S/kT)$ » 1 and the equation becomes:

$$\Lambda = \gamma[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e \tag{123}$$

The equilibrium constant for the effective reaction, $A^+B^- = AB$, is then:

$$K_\Lambda = (1-\gamma)/c\gamma^2 f^2 \approx K_R K_S \tag{124}$$

as K_S »1. The parameters and the variables are related by the set of equations:

$$\gamma = 1 - K_R c\gamma^2 f^2/(1-\alpha) \tag{125}$$

$$K_R = (4\pi N_A R^3/3000)\exp(\beta/R) \tag{126}$$

$$-\ln f = \beta_\kappa/2(1+\kappa R), \quad \beta = e^2/\varepsilon kT \tag{127}$$

$$\kappa^2 = 8\pi\beta\gamma n = \pi\beta N_A \gamma c/125 \tag{128}$$

$$-\varepsilon = \ln[\alpha/(1-\alpha)] \tag{129}$$

The details of the calculations are presented in the 1978 paper.[213]The shortcomings of the previous equations have been rectified in the present equation that is also more general than the previous equations and can be used for higher concentrations (0.1 N in aqueous solutions).

2.7.3. *Limiting Equivalent Conductance*

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surroundings solvent molecules, as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \tag{130}$$

At present, limiting equivalent conductance is the only function that can be divided into ionic components using experimentally determined transport number of ions,

$$\text{i.e.,}\ \lambda_+^0 = t_+\Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_-\Lambda_0 \tag{131}$$

Thus, from accurate value of $\lambda^0$of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions.[212]However, accurate transference number determinations are limited to few solvents only. Spiro[213] and Krumgalz[214] have made extensive reviews on the subject.

In absence of experimentally measured transference numbers, it would be useful to develop indirect methods to obtain the limiting equivalent conductance in organic solvents for which experimental transference numbers are not yet available.

The method has been summarized by Krumgalz[214] and some important points are mentioned below:

(i) Walden equation,[216] $$(\lambda_{\pm}^0)_{\text{water}}^{25} \cdot \eta_{0,\,\text{water}} = (\lambda_{\pm}^0)_{\text{acetone}}^{25} \cdot \eta_{0,\,\text{acetone}} \tag{132}$$

(ii) $$\left.\begin{aligned} \lambda_{\text{pic}}^0 . \eta_0 &= 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^0 . \eta_0 &= 0.296 \end{aligned}\right|^{216,217} \text{based on } \Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^0 = 0.563 \tag{133}$$

Walden considered the products to be independent of temperature and solvent. However the $\Lambda^0_{\mathrm{Et_4N_{pic}}}$ values used by Walden was found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

(iii) $\lambda^0_{25}(\mathrm{Bu_4N^+}) = \lambda^0_{25}(\mathrm{Ph_4B^-})^{217}$ (134)

The equality holds good in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

(iv) $\lambda^0_{25}(\mathrm{Bu_4N^+}) = \lambda^0_{25}(\mathrm{Bu_4B^-})^{218}$ (135)

The method appears to be sound as the negative charge on boron in the Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^-.

(v) The equation suggested by Gill[219] is:

$$\lambda^0_{25}(\mathrm{R_4N^+}) = zF^2/6\pi N_A\eta_0[r_i - (0.0103\varepsilon_0 + r_y)] \qquad (136)$$

where Z and r_i are charge and crystallographic radius of proper ion, respectively; η_0 and ε_0 are solvent viscosity and dielectric constant of the medium, respectively; r_y = adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents respectively.

However, large discrepancies were observed between the experimental and calculated values.[215(a)] In a paper,[215(b)] Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents e.g. butan-1-ol, acetonitrile and nitromethane.

(vi) $\lambda^0_{25}[(\mathrm{i-Am})_3\mathrm{BuN^+}] = \lambda^0_{25}(\mathrm{Ph_4B^-})^{221}$ (137)

It has been found from transference number measurements that the $\lambda^0_{25}[(\mathrm{i-Am})_3\mathrm{BuN^+}]$ and $\lambda^0_{25}(\mathrm{Ph_4B^-})$ values differ from one another by 1%.

(vii) $\lambda^0_{25}(\mathrm{Ph_4B^-}) = 1.01\lambda^0_{25}(\mathrm{i-Am_4B^-})^{222}$ (138)

The value is found to be true for various organic solvents.

Krumgalz[215] suggested a method for determining the limiting ion conductance in organic solvents. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_0 values into ionic components for non-aqueous electrolytic solutions.

Considering the motion of solvated ion in an electrostatic field as a whole, it is possible to calculate the radius of the moving particle by the Stokes equation:

$$r_S = |z|F^2 / A\pi\eta_0\lambda^0_\pm \tag{139}$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in case of perfect slipping). Since the r_S values, the real dimension of the non-solvated tetraalkyl (aryl) onium ions must be constant, we have:

$$\lambda^0_\pm\eta_0 = \text{constant} \tag{140}$$

This relation has been verified using $\lambda^0_\pm$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the i - Am_4B^-, Ph_4As^+ and Ph_4B^- ions and for tetraalkylammonium cations starting with Et_4N^+. The relationship can be well utilized to determine $\lambda^0_\pm$ of ions in other organic solvents from the determined Λ_0 values.

2.7.4. *Solvation Number*

If the limiting conductance of the ion *i* of charge z_i is known, the effective radius of the solvated ion can easily be determined from the Stokes' law. The volume of the solvation shell V_S, can be written as:

$$V_S = (4\pi/3)(r_S^3 - r_C^3) \tag{141}$$

where r_C is the crystal radius of the ion; the solvation number, n_S would then be obtained from:

$$n_S = V_S / V_0 \tag{142}$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects[222] from:

$$V_S^0 = 4.35 r_S^3 \tag{143}$$

where V_S^0 is expressed in mol/litre and r_S in angstroms. However, the method of determination of solvation number is not applicable to ions of medium size though a number of empirical equations[186] and theoretical corrections [223-226] have been suggested to make the general method.

2.7.5. *Stokes' Law and Walden's Rule*

The limiting conductance, λ_i^0 of a spherical ion of radius, R_i moving in a solvent of dielectric continuum can be written according to Stokes' hydrodynamics, as:

$$\lambda_i^0 = |z_i e| \hat{e} F / 6\pi\eta_0 R_i = 0.819|z_i| / \eta_0 R_i \qquad (144)$$

where η_0 = macroscopic viscosity by the solvent in poise, R_i is in angstroms. If the radius R_i is assumed to be the same in every organic solvent, as would be the case in case of bulky organic ions, we get:

$$\lambda_i^0 \eta_0 = 0.819|z_i| / R_i = \text{constant} \qquad (145)$$

This is known as Walden's rule.[227] The effective radii obtained using the equation can be used to obtain solvation number. The failure of Stokes' radii to give the effective size of the solvated ion for small ions is generally ascribed to the inapplicability of Stokes' law to molecular motions.

Robinson and Stokes,[186] Nightingale[130] and others[228-230] have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of those large ions, a calibration curve was obtained for each solvent. However, the experimental results indicate that the method is incorrect as the method is based on the wrong assumption of the invariance of Walden's product with temperature. The idea of microscopic viscosity[231] was invoked without much success[232, 233] but it has been found that:

$$\lambda_i^0 \eta^p = \text{constant} \qquad (146)$$

where p is usually 0.7 for alkali metal or halide ions and p = 1 for the large ions.[234, 235]

Attempts to explain the change in the Stokes' radius R_i have been made. The apparent increase in the real radius, r has been attributed to ion-dipole polarization and the effect of dielectric saturation on R .

The dependence of Walden product on the dielectric constant led Fuoss[236] to consider the effect of the electrostatic forces on the hydrodynamics of the system. Considering the excess frictional resistance caused by the dielectric relaxation in the solvent caused by ionic motion, Fuoss proposed the relation:

$$\lambda_{i,0}^0 = Fe|z_i| / 6\pi R_\propto (1 + A/\varepsilon R_\propto^2) \qquad (147)$$

or, $R_i = R_\propto + A/\varepsilon$ (148)

where $R_\propto$ is the hydrodynamic radius of the ion in a hypothetical medium of dielectric constant where all electrostatic forces vanish and A is an empirical constant.

Boyd[224] gave the expression:

$$\lambda_i^0 = Fe|z_i|/6\pi\eta_0 r_i[1+(2/27\pi\eta_0 . Z_i^2 e^2 \tau/r_i^4 \varepsilon_0)] \quad (149)$$

by considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles.

Zwanzig[225] treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda_i^0 = z_i^2 eF/\{A_V \pi\eta_0 r_i + A_D[z_i^2 e^2(\varepsilon_r^0 - \varepsilon_r^\propto)\tau/\varepsilon_r^0(2\varepsilon_r^0+1)r_i^3]\} \quad (150)$$

where $\varepsilon_r^0, \varepsilon_r^\alpha$ *are the static and limiting high frequency (optical) dielectric constants.* A_V = 6 and A_D = 3/8 for perfect sticking and A_V = 4 and A_D = 3/4 for perfect slipping. It has been found that Born's[223] and Zwanzig's[225] equations are very similar and both may be written in the form:

$$\lambda_i^0 = Ar_i^3/(r_i^4 + B) \quad (151)$$

The theory predicts[237] that λ_i^0 passes through a maximum of $27^{1/4}A/4B^{1/4}$ at $r_i = (3B)^{1/4}$. The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius.

For comparison with results in different solvents, the equation (150) can be rearranged as:[236]

$$z_i^2 eF/\lambda_i^0 \eta_0 = A_V \pi r_i + A_D z_i^2/r_i^3 . e^2(\varepsilon_r^0 - \varepsilon_i^\propto)/\varepsilon_r^0(2\varepsilon_r^0+1).\tau/\eta_0 \quad (152)$$

or, $L^* = A_V \pi r_i + A_D z_i^2/r_0^3 P^*$ (153)

In order to test Zwanzig's theory, the equation (151) was applied for Me_4N^+ and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol.[237-242] Plots of L^* against the solvent function P^* were found to be straight line. But the radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that relaxation effect is not the predominant factor affecting ionic mobility and these mobility differences could be explained quantitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from the Stokes' law.[243]

It is found that the Zwanzig's theory is successful for large organic cations in aprotic media where solvation is likely to be minimum and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large, i.e., for solvents of high P^* and for ions of small r_i. Like any continuum theory Zwanzig has the inherent weakness of its inability to account for the structural features,[238] e.g.,

(i) It does not allow for any correlation in the orientation of the solvent molecules as the ion passes by and this may be the reason why the equation is not applicable to the hydrogen-bonded solvents.[239]

(ii) The theory does not distinguish between positively and negatively charged ions and therefore, cannot explain why certain anions in dipolar aprotic media possess considerably higher molar concentrations than the fastest cations.[238]

The Walden product in case of mixed solvents does not show any constancy but it shows a maximum in case of DMF + water and DMA + water[237-247] mixtures and other aqueous binary mixtures.[248-251] To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts[224,225,252] have been made with different models for ion-solvent interactions but no satisfactory expression has been derived taking into account all types of ion-solvent interactions because (i) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression and (ii) it is not possible to account for some specific properties of different kinds of ions and solvent molecules.

Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Though Zwanzig's expression accounts for a change in Walden product with solvent composition but does not account for the maxima. According to Hemmes,[253] the major deviations in the Walden products are due to the variation in the electrochemical equilibrium between ions and solvent molecules of mixed polar solvent composition.

In cases where more than one types of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Hubbard and Onsager[254] have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the concept of kinetic polarization deficiency has been introduced.

However, quantitative expression is still awaited. Further, improvements[255,256] naturally must be in terms of (i) sophisticated treatment of dielectric saturation, (ii) specific structural effects involving ion-solvent interactions.

From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to explore this problem using different experimental techniques. We have, therefore, utilized four important methods, viz., volumetric, viscometric, interferometric and conductometric for the physico-chemical studies in different solvent media.

2.8. *Solvation Models- Some Recent Trends*

The interactions between particles in chemistry have been based upon empirical laws-principally on Coulomb's law. This is also the basis of the attractive part of the potential energy used in the SchÖdinger equation. Quantum mechanical approach for ion-water interactions was begun by Clementi in 1970s.[22] A quantum mechanical approach to salvation can provide information on the energy of the individual ion-water interactions provided it is relevant to solution chemistry, because it concerns potential energy rather than the entropic aspect of salvation. Another problem in quantum approach is the mobility of ions in solution affecting salvation number and coordination number. However, the Clementi calculations concerned stationary models and can not have much to do with the dynamic salvation numbers. Covalent bond formation enters little into the aqueous calculations,[22] however, with organic solvents the quantum mechanical approaches to bonding may be essential. The trend pointing to the future is thus the molecular dynamics technique. In molecular dynamic approach, a limited number of ions and molecules and Newtonian mechanics of movement of all particles in solution is concerned. The foundation of such a approach is the knowledge of the intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last decade (1990-2000) witnessed some interesting trends in the development of solvation models and computer softwares. Based on a collection of experimental free energy of solvation data, C.J. Cramer, D.G. Truhlar and co-workers from the University of Minnesota, U.S.A. constructed a series of solvation models (SM1-SM5 series) to predict and calculate the free energy of solvation of a chemical compound.[257-261] These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are, molecular formula, geometry, refractive index, surface tension, Abraham's α (acidity parameter) and β (basicity parameter) values, and, in the latest models, the dielectric constants.

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 KCl/mole. These are especially useful when other methods are not available. One can also analyze factors like electrostatics, dispersion, hydrogen bonding, etc. using these tools. They are also relatively inexpensive and available in easy to use computer codes.

A. Galindo et al.[262,263] have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibrium of electrolytic aqueous solutions. The water molecules are modeled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions.

Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity becomes very close to unity, especially when the mean spherical approximation is used, indicating a good description of the solvent. E. Bosch et al.[264] of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

2.9. *Conductance- Some Recent Trends*

Recently Blum, Turq and coworkers[265,266] have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from the same continuity and hydrodynamic equations used in the more classical treatment; however, an important difference exists in the use of MSA expressions for the equilibrium and structural properties of the electrolytic solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem to be relatively small, it has been claimed that the performance of MSA equation is better with a much wider concentration range than that covered by the classical equations. However, no through study of the performance of the new equation at the experimental uncertainty level of conductivity measurement is yet available in the literature, except the study by Bianchi et al.[267] They compared the results obtained using the old and new equations in order to evaluate their capacity to describe the conductivity of different electrolytic solutions. In 2000, Chandra and Bagchi[268] developed a new microscopic approach to ionic conductance and viscosity based on the mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structural factors of charge and number density of the electrolytic solutions. They claim that their new equation is applicable at low as well as at high concentrations and it describes the cross over from low to high concentration smoothly. Debye-Huckel, Onsager and Falkenhagen expressions can be derived from this self-consistent theory at very low concentrations. For conductance, the agreement seems to be satisfactory up to 1 M.

References:

1. Kim, E. S.; Marsh, K. N.; *J. Chem. Eng. Data* **1988**, 33, 288.
2. Y. Marcus, *Introduction to Liquid State Chemistry,* Wiley-Interscience, New York, **1997**.
3. G.A.Krestov, *Thermodynamics of Solvation,* Ellis Horwood, Chichester, 1991.
4. J. Padova, in *Water and Aqueous Solutions,* Ed. R.A.Horne, Wiley-Interscience, New York, **1972**, chapter 4.
5. R. Fernandez-Prini, H. Corti and M. Japas, *High Temperatures Aqueous Solutions: Thermodynamic Properties,* C.R.C. Press, Boca Raton, Florida, **1992**.
6. V.N. Afanasyev and I.E.Korolev, *Thermodynamics of Electrolyte Solutions,* Institute of Non-Aqueous Solution Chemistry, Ivarovo, Russia, **1992**.
7. J.Barthel, H-J. Gores, G. Schmeer and R. Water, in *Non-aqueous Electrolyte Solutions in Chemistry and Modern Technology,* Topics in Current Chemistry, Vol.3, Springer Verlag, Berlin-Heidelberg, New York, **1983**.
8. O. Popovych and R.P.T. Tomkins, *Non-aqueous Solution Chemistry,* Wiley-Interscience, New York, **1981**.
9. E.S. Amis and J.F. Hinton, *Solvent Effects on Chemical Phenomena,* Academic Press, New York, **1973**.
10. *The Organic Chemistry of Electrolyte solutions*, Ed., J.E. Gordon, Wiley-Interscience, **1975**.
11. V. Gutmann, *Elecrtrochim. Acta.*, **1976**, *21*, 66.
12. R.G. Pearson, *Hard and Soft Acids and Bases*, Dowdon, Hutchinson and Ross, Strondsburgh, **1973**.
13. J.D. Pandey and A. Yasmin, *Proc. Ind. Acad. Sci.*, **1997**, *109*, 289.
14. J.D. Pandey, Y. Akhtar and A.K. Sharma, *Ind. J. Chem.* **1998**, *37A*, 1094.
15. J. I. Kim, *J. Phys. Chem.*, **1978**, *82*, 191.
16. N. Saha and B. Das, *J. Chem. Eng. Data*, **1997**, *42*, 117.

17. W. Kemp, *Organic Spectroscopy*, 3rd (ELBS) Ed., Macmillan Press, Hampshire, U.K., **1993**.
18. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold, New York, **1943**, Chapter 8.
19. C. Tanford, *Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley-Interscience, New York, **1980**, *2nd ed.*
20. E. Vikingstad, *Aggregation Process in Solutions*, Eds. E. Wyn-Jones and J. Gormally, Elsevier, Amsterdam, **1983**, 100.
21. J.E. Desnoyers, M. Arel, H. Perron, C. Jolicoenn, *J. Phys. Chem.* **1969**, *73*, 3347.
22. J. O'M. Bockris, A. K. N. Reddy, Modern Electrochemistry, 2nd ed., Plenum Press, New York, **1923**.
23. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, **1973**, Chapter 2.
24. D.K. Hazra, B. Das, *J. Chem. Eng. Data*, **1991**, *36*, 403.
25. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.
26. O. Redlich, D.M. Meyer, *Chem. Rev.* **1964**, *64*, 221.
27. B.B. Owen, S.R. Brinkley, *Jr. Ann. N. Y. Acad. Sci.* **1949**, *51*, 753.
28. K.S. Pitzer, G. Mayorga, *J. Phys. Chem.* **1973**, *77*, 2300.
29. F.J. Millero, *In Water and Aqueous Solutions: Structure, Thermo-dynamics and Transport Processes*, Ed. R.A. Horne, Wiley-Interscience, New York, **1972**.
30. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* **1969**, *73*, 3390.
31. J. Padova, I. Abrahmen, *J. Phys. Chem.* **1967**, *71*, 2112.
32. R. Gopal, D.K. Agarwal, R. Kumar, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1973.
33. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)*, **1970**, *69*, 1.
34. B. Das, D.K. Hazra, *J. Chem. Eng. Data.* **1991**, *36*, 403.
35. L.G. Hepler, *Can. J. Chem.* **1969**, *47*, 4617.
36. L.G. Hepler, J.M. Stokes, R.H. Stokes. *Trans. Faraday Soc.* **1965**, *61*, 20.
37. F.H. Spedding, M.J. Pikal, B.O. Ayres. *J. Phys. Chem.* **1966**, *70*, 2440.

38. L.A. Dunn, *Trans. Faraday Soc.* **1968**, *64*, 2951.

39. R. Pogne, G. Atkinson, *J. Chem. Eng. Data.* **1988**, *33*, 370.

40. B.E. Conway, R.E. Verral, J.E. Desnoyers. *Trans. Faraday Soc.* **1966**, *62*, 2738.

41. K. Uosaki, Y. Koudo, N. Tokura, *Bull. Chem. Soc. Jpn.*, **1972**, *45*, 871.

42. B.S. Krumgalz, *J. Chem. Soc. Faraday Trans. I.* **1980**, *76*, 1887.

43. A.W. Quin, D.F. Hoffmann, P. Munk, *J. Chem. Eng. Data,* **1992**, *37*, 55.

44. Z. Atik, *J. Solution Chem.* **2004**, *33*, 1447.

45. R.H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Great Britain, **1965**.

46. F. Vaslow, *Water and Aqueous Solutions*, Ed. R.A. Horne, Wiley-Interscience, **1972**, Chapter 12.

47. Gruneisen, Wiss, Abhaudl, *Physik-tech. Reich-austatt*, **1905**, *4*, 239.

48. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950.

49. P. Debye, E. Hückel, *Z. Phys. Chem.* **1923**, *24*, 185.

50. H. Falkenhagen, M. Dole, *Z. Phys. Chem.* **1929**, *30*, 611.

51. H. Falkenhagen, *Z. Phys. Chem.* **1931**, *32*, 745.

52. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* **1932**, *P4*, 537.

53. L. Onsager, R.N. Fuoss, *J. Phys. Chem.* **1932**, *36*, 2689.

54. M. Kaminsky, *Discussions Faraday Soc.* **1957**, *24*, 171.

55. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday I.* **1974**, *70*, 795.

56. J. Crudden, G. M. Delancy, D. Feakins, P. J. O'Relly, W. E. Waghorne, K. G. Lawrence, J. Chem. Soc. Faraday Trans 1., 82 (1986) 2195.

57. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, **1958**, *3rd ed*, 240.

58. M. Kaminsky, *Z. Phys. Chem.* (Frankfurt), **1957**, *12*, 206.

59. J. Desnoyers, G. Perron, *J. Soln. Chem.*, **1972**, *1*, 199.

60. R.J.M. Bicknell, K.G. Lawrence, D. Feakins, *J. Chem. Soc. Faraday I*, **1980**, *76*, 637.

61. R.L. Kay, T. Vituccio, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* **1966**, *70*, 2336.

62. N.P. Yao, D.N. Bennion, *J. Phys. Chem.* **1971**, *75*, 1727.

63. Andrade, *Phil. Mag.* **1934**, *17*, 698.

64. J. Vaud, *J. Phys. Chem.* **1948**, *52*, 277.

65. D.G. Thomas, *J. Colloid Sci.* **1965**, *20*, 267.

66. S.P. Moulik, *J. Indian Chem. Soc.* **1972**, *49*, 483.

67. D. England, G. Pilling, *J. Phys. Chem.* **1972**, *76*, 1902.

68. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* **1977**, *55*, 1062.

69. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* **1978**, *56*, 1442.

70. C.A. Angell, *J. Phys. Chem.* **1966**, *70*, 2793.

71. C.A. Angell, *J. Chem. Phys.* **1967**, *46*, 4673.

72. K. Roy Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1983**, *28*, 23.

73. K. Roy Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1983**, *28*, 597.

74. K. Roy Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1984**, *29*, 1371.

75. P.P. Rastogi, *Bull. Chem. Soc. Japan.* **1970**, *43*, 2442.

76. R. Gopal, P.P. Rostogi, *Z. Phys. Chem. (N.F.).* **1970**, *69*, 1

77. C.M. Criss, M.J. Mostroianni, *J. Phys. Chem.* **1971**, *75*, 2532.

78. K. Tamaski, Y. Ohara, Y. Isomura, *Bull. Chem. Soc. Japan.* **1973**, *46*, 1951.

79. P.P. Deluca, T.V. Rabagay, *J. Phys. Chem.* **1975**, *79*, 2493.

80. B.N. Prasad, N.P. Singh, M.M. Singh, *Ind. J. Chem.* **1976**, *14A*, 322.

81. B.N. Prasad, M.M. Agarwal, *Ind. J. Chem.* **1976**, *14A*, 343.

82. R.T.M. Bicknell, K.G. Lawrence, M.A. Scelay, D. Feakins, L. Werblan, *J. Chem. Soc. Faraday I.* **1976**, *72*, 307.

83. J.M. Mcdowall, N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* **1976**, *72*, 654.

84. A. Sacco, G. Petrella, M. Castagnola, *J. Phys. Chem.* **1976**, *80*, 749.

85. R.L. Blokhra, Y.P. Segal, *Ind. J. Chem.* **1977**, *15A*, 36.

86. N.C. Das, P.B. Das, *Ind. J. Chem.* **1977**, *15A*, 826.

87. A. Sacco, G. Petrella, M. Della Monica, M. Castagnola, *J. Chem. Soc. Faraday I*, **1977**, *73*, 1936.
88. P.K. Mandal, B.K. Seal, A.S. Basu, *Z. Phys. Chem.* (Leipzig). **1977**, *258*, 809.
89. J.I. Kim, *J. Phys. Chem.* **1978**, *82*, 191.
90. S.K. Vijaylakshamna, *Ind. J. Chem.* **1979**, *17A*, 511.
91. A. Sacco, G. Petrella, M.D. Monica, *J. Chem. Soc. Faraday I.* **1979**, *75*, 2325.
92. P.T. Thomson, M. Durbana, J.L. Turner, R.H. Wood, *J. Soln. Chem.* **1980**, *9*, 955.
93. K. Kurotaki, S. Kawamura, *J. Chem. Soc. Faraday I.* **1981**, *77*, 217.
94. N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday Trans I.* **1981**, *77*, 141.
95. A. Sacco, A.D. Giglio, A.D. Atti, *J. Chem. Soc. Faraday I.* **1981**, *77*, 2693.
96. D.S. Gill, A.N. Sharma, *J. Chem. Soc. Faraday I.* **1982**, *78*, 475.
97. A. Sacco, G. Petrella, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* **1982**, *78*, 1507.
98. A. Sacco, A.D. Giglio, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* **1983**, *79*, 431.
99. K.G. Lawrence, A. Sacco, *J. Chem. Soc. Faraday I.* **1983**, *79*, 615.
100. K. Miyajima, M. Sawada, M. Nakagaki, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 827.
101. J. Domenech, S. Rivera, *J. Chem. Soc. Faraday I.* **1984**, *80*, 1249.
102. D. Dasgupta, S. Das, D.K. Hazra, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1246.
103. S. Taniewska-Osinska, M. Jozwaik, *J. Chem. Soc. Faraday Trans I*, **1989**, *85*, 2147.
104. D. Nandi, D.K. Hazra, *J. Chem. Soc. Faraday Trans I.* **1989**, *85*, 4227.
105. I. Ibulci, M. Nakahara, *J. Phys. Chem.* **1990**, *94*, 8370.
106. W.M. Cox, J.H. Wolfenden, *Proc. Roy. Soc. London.* **1934**, *145A*, 475.
107. R.W. Gurney, *Ionic Processes in Solution*, McGraw Hill, New York, **1953**.
108. E.R. Nightingale, *J. Phys. Chem.* **1959**, *63*, 1381.
109. A. Einstein, *Ann. Phys.* **1906**, *19*, 289.
110. D.F.T. Tuan, R.M. Fuoss, *J. Phys. Chem.* **1963**, *67*, 1343.
111. C.H. Springer, J.F. Coetzee, R.L. Key, *J. Phys. Chem.* **1969**, *78*, 471.
112. G. Petrella, A. Sacco, *J. Chem. Soc. Faraday I.* **1978**, *74*, 2070.

113. B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1980**, *76*, 1275.
114. Andrade, *Phil. Mag.* **1934**, *17*, 698.
115. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1972**, *46*, 858.
116. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1973**, *47*, 956.
117. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1974**, *48*, 1163.
118. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1971**, *45*, 1448.
119. H.D.B. Jenkins, M.S.F. Pritcheit, *J. Chem. Soc. Faraday I.* **1984**, *80*, 721.
120. K. Fajan, *Naturwissenschaften.* **1921**, *9*, 729.
121. D.F.C. Morris, *Struct. Bonding*, **1969**, *6*, 157.
122. R.W. Gurney, *Ionic Processes in Solutions*, Doves, New York, **1962**.
123. H.S. Frank, W.Y. Wen, *Disc. Farad. Soc.* **1957**, *24*, 133.
124. Asmus, *Z. Naturforsch.* **1949**, *4A*, 589.
125. M.H. Abraham, J. Liszi, E. Papp, *J. Chem. Soc. Faraday I.* **1982**, *78*, 197.
126. G.S. Benson, A.R. Gordon, *J. Chem. Phys.* **1945**, *13*, 473.
127. M.H. Abraham, J. Liszi, L. Meszaros, *J. Chem. Phys.* **1979**, *70*, 249.
128. M.H. Abraham, J. Liszi, *J. Chem. Soc. Faraday I.* **1980**, *76*, 1219.
129. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, **1941**, 477.
130. E.R. Nightingale, R.F. Benck, *J. Phys. Chem.* **1959**, *63*, 1777.
131. Simha, *J. Phys. Chem.* **1940**, *44*, 25.
132. D. Feakins, K.G. Lawrence, *J. Chem. Soc.* **1966**, *A*, 212.
133. S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, **1941**, 514.
134. D.S. Gill, T.S. Kaur, H. Kaur, I.M. Joshi, J. Singh, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1737.
135. J.G. Mathieson, B.E. Conway, *J. Soln. Chem.* **1974**, *3*, 455.
136. S. Bhowmik, R.K. Mohanty, *Ind. J. Chem.* **1986**, *25A*, 416.
137. M.V. Kaulgud, K.S. Mohan Rao, *Ind. J. Chem.* **1988**, *27A*, 12.
138. K.J. Patil, A.B. Wazalwar, G.R. Mehta, *Ind. J. Chem.* **1988**, *27A*, 799.
139. M. Iqbal, R.E. Verral, *Can. J. Chem.* **1989**, *67*, 727.
140. M. Kikuchi, M. Sakurai, K. Nitta, *J. Chem. Eng. Data.* **1996**, *41*, 1439.

141. B.E. Conway, R.E. Verral, *J. Phys. Chem.* **1966**, *70*, 3952.
142. K. Gekko, H. Noguchi, *J. Phys. Chem.* **1979**, *83*, 2706.
143. W.L. Masterson, *J. Chem. Phys.* **1954**, *22*, 1830.
144. L.G. Hepler, *Can. J. Chem.* **1969**, *47*, 4613.
145. M.V. Kaulgud, K.J. Patil, *J. Phys. Chem.* **1976**, *80*, 138.
146. K.J. Patil, G.R. Mehta, R.K. Chandewar, *Ind. J. Chem.* **1986**, *25A*, 1147.
147. R. K. Dewan, C. M. Gupta, and S. K. Mehta, *Acoustica.* **1998**, *65*, 245.
148. B. Jacobson *J. Chem. Phys.* **1952**, *20*, 927.
149. W. Schaaffs, *Acoustica.* **1975**, *33*, 272 .
150. M. R. Rao *Indian J. Chem.*, **1940**, *14*, 109.
151. W. Schaaffs, *Z. Phys.* **1974**, *114*, 110.
152. O.Nomoto, *J. Phss: Soc. Jpn.* **1958**, *13*, 1528.
153. S. K. Mehta, R. K. Chauhan ,and R. K. Dewan, *J. Chem. Soc. Faraday Trans.* 1. **1966**, *92*, 1167.
154. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, *Int. J. of Thermophy.* **2004**, *25*, 1735.
155. G. Douheret, A. Pal, M.I. Davis, *J. Chem. Therm.* **1990**, *22*, 99.
156. I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, *J. Soln. Chem.* **2002**, *31*, 905.
157. V. Tiwari. And L. R. Mishra. *Acoustica*, **1981**, *48*, 257.
158. M. Kalidoss., R. Srinavasamorthy.,*J. Pure Appl. Ultrason.* **1997**, *9*, 4.
159. J. D. Pandey and K. Shukla., *J. Pure Appl, Phys.* **1993**, *15*, 37.
160. Tasi, F. N *J. Chem. Eng. Data*, **1994**, *39*, 441.
161. R. C. Reid, J. M. Prausnitz, B. E. Poling, *The properties of Gases and Liquids*, 4th ed., McGraw-Hill International, **1987**.
162. L. Grunberg, A.H. Nissan, *Nature*, **1949**, *164*, 799.
163. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.* **1966**, *62*, 1112.
164. K. Ramamoorthy. *J of Pure and Appl. Phys.* **1973**, *11*, 556.
165. J.B. Irving,Viscosity of liquid mixtures NEL Report No. 630 and 631,National Engineering Laboratory,East Kilbride,Glassgow,**1977**.
166. T. M. Reed and T. E. Taylor, *J. Phys. Chem*, **1959**, *63*, 58.
167. M. Tamura, M. Kurata, *Bull. Chem. Soc. Jpn.* **1952**, *25*, 32.

168. R. K. Hind, E. McLaughlin, A. R. Ubbelohde *Trans. Faraday. Soc,* **1960**, *56,* 328.
169. R. Meyer, M. Meyer and J. Metzer, A. Peneloux. *Chem. Phys,* **1971**, *62,* 406.
170. R. J. Fort and W. R. Moore, *Trans. Faraday. Soc.* **1965**, *61,* 2102.
171. R. A. McAllister, *AIChE J.* **1960**, *6,* 427.
172. M. Dizechi, F. Marshl, *J. Chem. Engg. Data.* **1982**, *27, 358.*
173. E. L. Heric, J. G. Brewer, *J. Chem. Eng. Data,* **1967**, *12*, 574.
174. S. K. Mehta, R. K. Chauhan, R. K. Dewan, *J. Chem. Soc. Faraday Trans.* **1996**, *92,* 1167.
175. R. Kalidas, G.S. Ladha, *J. Chem. Eng. Data,* **1969**, *14,* 58.
176. P.K.Katti, M.M. Chaudhari, *J. Chem. Eng. Data,* **1964**, *9,* 442.
177. E. L. Heric, *J. Chem. Eng. Data,* **1966**, *11*, 66.
178. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* **1948**, *40,* 345.
179. D. W. Marquardt, J. Soc. *Ind. Appl. Math.,* **1963**, 11, 431.
180. D.F. Evans, Sister Marry, A. Matesich, *Electro Chemistry,* Ed. E. Yeager, A.J. Salkind, John-Wiley and Sons, **1973**, *2,* Chapter 1.
181. R. Fernandez-Prini, *Physical Chemistry of Organic Solvent Systems,* Ed.A.K. Covington, T. Dickinson, Plenum Press, New York, **1973**, Chapter 5.
182. D.A. McInnes, *The Principles of Electro Chemistry,* Reinhold, New York, **1961**.
183. S. Glasstone, *An Introduction to Electrochemistry,* Van Nostrand, New York, **1942**.
184. T. Shedlovsky, *In Techniques of Organic Chemistry,* Vol. *1,* part 4, Ed. A, Weissberger, Wiley, New York, **1959**, *3rd ed.,* 3011.
185. R.M. Fuoss, F. Accascina, *Electrolyte Conductance,* Wiley, New York, **1959**.
186. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions,* Butterworths, London, **1959**, *2nd ed.*
187. J. Banthel, Angew, *Chem. Internat. Edit.* **1968**, *7,* 260.
188. J. Banthel, G.D. Robbins, *J. Chem. Ed.* **1971**, *48,* 53.
189. E.J. King, *Acid-base Equilibria,* Pergamon, Great Britain, **1965**.
190. G. Jones, R.C. Joseph, *J. Am. Chem. Soc.* **1928**, *50,* 1049.

191. G. Jones, Bradshaw, *J. Am. Chem. Soc.* **1933**, *55*, 1780.

192. C.W. Davies, *Ion-Association*, Butterworths, London, **1962**.

193. R.M. Fuoss, *J. Chem. Educ.* **1955**, *32*, 527.

194. L. Onsager, *Z. Phys. Chem.* **1927**, *28*, 277.

195. R.M. Fuoss, *Rev. Pure Appl. Chem.* **1968**, *18*, 125.

196. E. Pitts, *Proc. Roy. Soc.* **1953**, *217A*, 43.

197. R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1957**, *61*, 668.

198. R.M. Fuoss, *Chemical Physics of Ionic Solutions*, Eds. B.E. Conway, R.G. Barradas, Wiley, New York, **1966**, 462.

199. E. Pitts, R.E. Tabor, J. Daly, *Trans. Faraday Soc.* **1969**, *65*, 849.

200. (a) R.M. Fuoss, K.L. Hsia, *Proc. Natl. Acad. Sci.* **1967**, *57*, 1550.
(b) R.M. Fuoss, K.L. Hsia, *J. Am. Chem. Soc.* **1968**, *90*, 3055.

201. R. Fernandez-Prini, J.E. Prue. *Z. Phys. Chem.* (Leipzig), **1965**, *228*, 373.

202. R. Fernandez-Prini, J.E. Prue. *Z. Phys. Chem.* (Leipzig), **1965**, *228*, 473.

203. D.F. Evans, R.L. Kay, *J. Phys. Chem.* **1966**, *70*, 366.

204. D.F. Arrington, E. Griswold, *J. Phys. Chem.* **1970**, *74*, 123.

205. R.M. Fuoss, C.A. Kraus. *J. Am. Chem. Soc.* **1933**, *55*, 476.

206. T. Shedlovsky, J. Franklin, *Instt.* **1938**, *225*, 739.

207. (a) J.C. Justice, *J. Chem. Phys.* **1968**, *65*, 353.
(b) J.C. Justice, R. Bury, C. Treiner, *J. Chem. Phys.* **1968**, *65*, 1708.

208. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Wiley, New York, **1959**, 207.

209. N. Bjerrum, *K. Dan. Vidensk. Selek.* **1926**, *7*, 9.

210. M. Tissier, G. Douheret, *J. Soln. Chem.* **1978**, *7*, 87.

211. R. Fernandez-Prini, J. Prue, *Trans. Faraday Soc.* **1966**, *62*, 1257.

212. (a) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1962**, *66*, 1722.
(b) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1963**, *67*, 621.

213. (a) R.M. Fuoss, *J. Phys. Chem.* **1975**, *49*, 525.
(b) R.M. Fuoss, *J. Phys. Chem.* **1978**, *82*, 2427.

214. M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Ed. A.K. Covington, T. Dickinson, Plenum, New York, **1973**, *2*, Chapter 5.

215. (a) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1983**, *79*, 571.
(b) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1985**, *81*, 241.

216. P. Walden, H. Ulich, D. Bush, *Z. Phys. Chem.* **1926**, *123*, 429.

217. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* **1960**, *82*, 1018.

218. S. Takezawa, Y. Kondo, N. Tokura, *J. Phys. Chem.* **1973**, *77*, 2133.

219. (a) D.S. Gill, *J. Chem. Soc. Faraday I.* **1981**, *77*, 751
(b) D.S. Gill, N. Kumari, M.S. Chauhan; *J. Chem. Soc. Faraday Trans I.* **1985**, *81*, 687.

220. M.A. Coplan, R.M. Fuoss, *J. Phys. Chem.* **1964**, *68*, 1177.

221. J.F. Coetzee, G.P. Cunningham, *J. Am. Chem. Soc.* **1965**, *87*, 2529.

222. R.H. Stokes, R.A. Robinson, *Trans. Faraday Soc.* **1957**, *53*, 301.

223. M. Born, *Z. Phys. Chem.* **1920**, *1*, 221.

224. R.H. Boyd, *J. Chem. Phys.* **1961**, *35*, 1281.

225. R. Zwanzig, *J. Chem. Phys.* **1963**, *38*, 1603, 1605.

226. E.J. Passeron, *J. Phys. Chem.* **1964**, *68*, 2728.

227. (a) P. Walden, *Z. Phys. Chem.* **1906**, *55*, 207.
(b) P. Walden, *Z. Phys. Chem.* **1912**, *78*, 257.

228. R. Gopal, M.M. Hussain, *J. Ind. Chem. Soc.* **1963**, *40*, 981.

229. L.G. Longsworth, *J. Phys. Chem.* **1963**, *67*, 689.

230. M. Della Monica, U. Lamauna, L. Seutatore, *J. Phys. Chem.* **1968**, *72*, 2124.

231. S. Brocus, *J. Chem. Phys.* **1958**, *28*, 1158.

232. D.G. Miller, *J. Phys. Chem.* **1960**, *64*, 1598.

233. G.J. Hills, *Chemical Physics of Ionic Solutions*, Ed. B.E. Conway, R.G. Barradas, Wiley, New York, **1966**, 571.

234. R.H. Stokes, I.A. Weeks, *Aust. J. Chem.* **1964**, *17*, 304.

235. R.H. Stokes, *The Structure of Electrolytic Solutions*, Ed. W.J. Hamer, Wiley, New York, **1959**.

236. R.M. Fuoss, *Proc. Nati. Acad. Sci.* (U.S.A.), **1959**, *45*, 807.

237. H.S. Franks, *Chemical Physics of Ionic Solutions*, Ed. B.E. Conway, R.G. Barradas, Wiley, New York, **1966**, Chapter 4.

238. G. Atkinson, S.K. Koz, *J. Phys. Chem.* **1965**, *69*, 128.

239. R.L. Kay, G.P. Cunningham, D.F. Evans, *Hydrogen bonded Solvent Systems*, Ed. A.K. Covington, P. Jones, Taylor and Francis, London, **1968**, 249.
240. R.L. Kay, B.J. Hales, G.P. Cunningham, *J. Phys. Chem.* **1967**, *71*, 3925.
241. R.L. Kay, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* **1965**, *69*, 4208.
242. D.F. Evans, J.L. Broadwater, *J. Phys. Chem.* **1968**, *72*, 1037.
243. J. Padova, *Water and Aqueous Solutions*, Ed. R. A. Horne, Wiley Interscience, Chapter 4 (1972).
244. R. Fernandez-Prini, G. Atkinson, *J. Phys. Chem.* **1971**, *75*, 239.
245. L. Bahadur, M.V. Ramanamurti, *J. Chem. Soc. Faraday I.* **1980**, *76*, 1409.
246. L. Bahadur, M.V. Ramanamurti, *J. Electrochem. Soc.* **1981**, *128*, 339.
247. L. Bahadur, M.V. Ramanamurti, *Can. J. Chem.* **1984**, *62*, 1051.
248. J.L. Broadwater, R.L. Kay, *J. Phys. Chem.* **1970**, *74*, 3803.
249. S. Das, D.K. Hazra, *Ind. J. Chem.* **1988**, *274*, 1073.
250. S. Das, D.K. Hazra, *J. Ind. Chem. Soc.* **1988**, *LXV*, 100.
251. (a) R.L. Kay, J.L. Broadwater, *Electrochim. Acta.* **1971**, *16*, 667.
     (b) R.L. Kay, J.L. Broadwater, *J. Solution Chem.* **1976**, *5*, 57.
252. A.D. Aprano, R.M. Fuoss, *J. Phys. Chem.* **1963**, *67*, 1704, 1722.
253. P. Hemmes, *J. Phys. Chem.* **1974**, *78*, 907.
254. J. Hubbard, L. Onsager, *J. Chem. Phys.* **1977**, *53*, 4850.
255. N. Islam, M.R. Islam, M. Ahmed, *Z. Phys. Chem.* (Leipzig) **1981**, *262*, 129.
256. D.S. Gill, A.N. Sharma, H. Schneider, *J. Chem. Soc. Faraday. I.* **1982**, *78*, 465.
257. C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* **1991**, *113*, 8305.
258. D.J. Giesen, J.W. Stores, C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* **1995**, *117*, 1057.
259. (a) C.J. Cramer, D.G. Truhlar, *J. Org. Chem.* **1996**, *61*, 8720.
     (b) C.J. Cramer, D.G. Truhlar, *Erratum.* **1999**, *101*, 309.
260. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B.* **1997**, *101*, 7147.
261. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B.* **1998**, *102*, 3257.
262. A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, *J. Chem. Phys.* **1997**, *106*, 4168.
263. A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, *Mol. Phys.* **1998**,*93*, 241.

264. M. Roses, C. Rafols, J. Ortega, E. Bosch, *J. Chem. Soc. Perkin Trans* 2, **1995**, 1607.

265. O. Bernard, W. Kunz, P. Turq, L. Blum, *J. Phys. Chem.*, **1992**, *96* 3833.

266. S. Durand-Vidal, P. Turq, O. Bernard, J. Phys. Chem., **1996**, *100*, 17345.

267. H. L. Bianchi, I. Dujovne, R. Fernandez-Prini, *J. Soln. Chem.*, **2000**, *29*, 237.

268. A. Chandra, B. Bagchi, *J. Phys. Chem. B.*, **2000**, *104*, 9067.

CHAPTER III

Experimental Section

3.1. Source and Purification of the Reagents used

3.1.1. *Pure Solvents*

Acetonitrile (ACN, CH_3CN), M.W. 41.05, Merck, India, GR, was distilled from P_2O_5 and then from CaH_2 in an all glass distillation apparatus.[1] The middle fraction was collected. The purified solvent had a density of 776.8 kg. m^{-3} and a coefficient of viscosity 0.3443 mPa.s at 298.15 K which agrees with the literature values.[1]

1,4-Dioxane (DO, $C_4H_8O_2$), M.W. 88.11, Merck, India, extrapure, was kept several days over potassium hydroxide (KOH). This was followed by refluxing over excess of sodium for 12 hours. Finally, it was distilled from sodium.[2] The pure compound had a density of 1028.7 kg. m^{-3} and a coefficient of viscosity of 1.1779 mPa.s at 298.15 K, in excellent agreement with literature values .[3]

1,3-Dioxolane ($C_3H_6O_2$), M.W. 74.08, S.D.Fine chemicals, India, LR, was heated under reflux with PbO_2 for 2 hrs., then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled[4]. The solvent obtained after purification had a density of 1057.7 g. cm^{-3} and a coefficient of viscosity of 0.5878 mPa.s at 298.15 K, compared well with literature values [5].

Tetrahydrofuran (THF, C_4H_8O), M.W. 72.11, Merck, India, for synthesis, was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over $LiAlH_4$.[6] The purified solvent had boiling point of 339 K / 760 mm, a density of 880.8 kg. m^{-3} and a coefficient of viscosity 0.4631 mPa.s at 298.15 K[7].

2-Ethoxyethanol (Cellosolve, $C_4H_{10}O_2$), M.W. 90.12, Merck, India, for synthesis, was kept several days over anhydrous $CaSO_4$. Then it was refluxed for 4 h over CaO. Finally, it was distilled at low pressure. Details have been described elsewhere[8]. The pure compound had a density of 925.4 kg. m^{-3} and a coefficient of viscosity of 1.85061 mPa.s at 298.15 K, which agrees with the literature values.[9,10]

Experimental Section

2-Methoxyethanol (ME, $C_3H_8O_2$), M.W. 79.07, Merck, India, for synthesis, was allowed to stand overnight with $CaSO_4$ and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenyhydrazine [8]. The purity of liquid was checked by gas chromatography and purified liquid had a density of 957.7 kg. m^{-3} at 30^0C, viscosity 1.39329 mPa.s at 30^0C which is compared well with literature values [11].

Dimethylsulphoxide[12] (DMSO, C_2H_6SO), M.W. 78.13, Merck, India, was kept several days over anhydrous $CaSO_4$, refluxed for 4 hours over CaO. Finally, it was distilled at low pressure. The pure compound had a density of 1095.1 kg. m^{-3} and a co-efficient of viscosity of 1.9923 mPa.s at 298.15 K, in well agreement with the literature values.[13]

Monoalcohols (methanol to 1-Octanol), (E. Merck, India, uvasol grade, 99.5% pure) were dried over 3A° molecular sieves and distilled fractionally. The middle fraction were collected and redistilled. The purities of the solvents were checked by gas chromatography and the water content were found to be 0.023-0.022-weight %. The density and viscosity of the purified solvent had compared well with the literature values [14-20].

Normal pentane (C_5H_{12}), M.W. 72.15 , hexane(C_6H_{14}), M.W. 86.20, heptane (C_7H_{116}), M.W. 100.20, Merck, India, LR, were purified according to the standard procedures.[21,22] The purities were checked by density determination dilafometrically. The densities and viscosities of pure liquids are compared well with the literature values[21,22,23] .

Carbon tetrachloride (CCl_4), M.W. 153.82, Merck, India was shaken vigorously with potassium hydroxide for several hours and was washed with water. This step was repeated for several times and then shaking was done with concentrated sulphuric acid until there was no further coloration, washed again with water, dried with $CaCl_2$, and distilled over P_2O_5.The density and viscosity values are in excellent agreement with literature values .[8,22]

tert-butanol, $[(CH_3)_3COH]$, M.W. 74.12, n-butyl acetate, $[CH_3COO(CH_2)_3 CH_3]$, M.W. 116.16, 2-butanone, (C_5H_{12}), M.W. 72.15, n-butylamine, $[(CH_3)_3CNH_2]$, M.W. 73.14, (S. D. Fine Chemicals, India, Analytical Reagent, Purity > 99%) were used after drying. The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature [24-28]

Water was first deionized and then distilled from an all glass distilling set using alkaline $KmnO_4$ solution. The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled water had specific conductance less than 1×10^{-6} $ohm^{-1}cm^{-1}$.

3.1.2. *Solutes*

Resorcinol ($C_6H_6O_2$, M.W. 110.10), S.D.Fine chemicals, India, extrapure, was crystallized from benzene/ethyl ether. The compound was dried and stored in a vacuum desiccator[29].

The mineral salts viz., ammonium acetate (CH_3COONH_4, M.W. 77.08), and sodium acetate ($CH_3COONa.3H_2O$, M.W. 136.08), Loba Chemie, India, A.R. grade, Lithium acetate ($CH_3COOLi.2H_2O$, M.W. 102.02)and potassium acetate (CH_3COOK, M.W. 98.14), S.D.Fine chemicals, India, LR, were used after drying over P_2O_5 in a desiccator for more than 48 hours. [8]

Lithium chloride ($LiCl_3$, M.W.42.39), Merck, India, AR, was recrystallized from conductivity water, dried for several hours at 403 K and stored in a vacuum desiccator. [8] Sodium chloride ($NaCl$, M.W. 58.44), BDH, ANALAR, was dried for 48 hours under reduced pressure in presence of P_2O_5 at 473 K without preceding purification and stored under dry nitrogen. [8] Potassium chloride (KCl, M.W.74.55), Merck, India; LR, crystals were dissolved in conductivity water, filtered, saturated with chlorine and precipitated by HCl after boiling off Excess chlorine. The precipitate was washed, dissolved in conductivity water, recrystallized by cooling to 268 K, dried at room temperature in a vacuum desiccator, fused under dry nitrogen, cooled and stored in a desiccator.[8]

Glycine ($C_2H_5NO_2$, M.W. 75.07), Merck, India; ANALAR, L-alanine ($C_3H_7NO_2$, M.W. 89.06), S.D. Fine Chemicals, India, L-Valine, ($C_5H_{11}NO_2$, M.W. 117.15), Loba Chemie, India, and L-leucine, ($C_6H_{13}NO_2$, M.W. 131.18), Loba Chemie, India, Tetra butyl ammonium bromide [$(C_4H_9)_4NBr$], M.W. 322.37 ,Thomas Baker, India, were used for the present study. These were used without further purification and dried over anhydrous P_2O_5 in a vacuum desiccator before use.

3.1.3. *mixed Solvents:*

The research work has been carried out with single solvents like 1,4-dioxane, along with binary solvent mixtures such as 2-Ethoxyethanol + monoalcohols (Methanol to 1-Octanol), Acetonitrile1 + (1,4-dioxane; 1,3-Dioxolane; tetrahydrofuran), H_2O + 1,4-dioxane, H_2O+ Carbon tetrachloride, DMSO + (tert-butanol; n-butyl acetate; 2-butanone; n-butylamine), H_2O + Methanol etc.

The mixed solvents were prepared accurately by mixing the requisite volume of 1,4-dioxane and H_2O with earlier conversion of required mass of the respective solvents to volume by using experimental densities of the solvents at experimental temperature. The mixtures were prepared by mixing pure liquids in airtight-stoppered bottles. The density, viscosity and the sound speeds of the mixtures were determined immediately after mixing. The reproducibility in mole fraction was within ± 0.0002. The physical properties of solvent mixtures at different temperatures are recorded along with literature values (wherever available).

3.2. Experimental Method

3.2.1. *Measurement of Density*

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 303.15, 308.15, 313.15 and 318.15 K with doubly distilled water and benzene using density and viscosity values from the literature.[30,31] The pycnometer filled with air bubble free experimental liquid was kept vertically in a thermostatic water bath maintained at ± 0.01K of the desired temperatures for few minutes to attain thermal equilibrium. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. Adequate precautions were taken to avoid evaporation losses during the time of actual measurements. An average of triplicate measurements was taken into account. Mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The precision of the density measurement was $\pm 3 \times 10^{-4}$ $g.cm^{-3}$.

The temperature of the thermostatic water bath was preset at the desired temperature by using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.[32] The solutions were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of the determining possible dispersion of the results obtained. Details of methods and techniques of density measurement is given in the literature.[33, 34-37]

3.2.2. *Measurement of Viscosity*

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[38] viscometer. The time of efflux of a constant volume of the experimental liquid through the capillary was measured with the aid of a Racer stop watch capable of measuring times accurate to ± 0.1s. The viscometer was always kept in a vertical position in the thermostatic bath with an accuracy of ± 0.01 K of the desired temperature. The efflux time for water at 298.15 K was measured to be 428.9 s. The flow times of pure liquids and liquid mixtures ware measured a number of times and the average of the readings was taken into account.

The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations.

$$\nu = Kt - L/t \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

where t is the average time of flow, ρ is the density and K and L are the characteristic constants of the particular viscometer. The values of the constants K and L, determined by using water and methanol as the calibrating liquids, were found to be 2.1040×10^{-3} and 11.5477 respectively. The kinetic energy corrections were done from these values and they were found to be negligible.

Relative viscosities (η_r) were obtained using the equation:

$$\eta_r = \eta/\eta_0 = \rho t/\rho_0 t_0 \tag{3}$$

where η, η_0, ρ, ρ_0 and t, t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively. The uncertainty in the viscosity measurements, based on our work on several pure liquids, was ± 2 × 10^{-4} mPa.s. Figure 1 shows a suspended-level Ubbelohde viscometer used in our works.

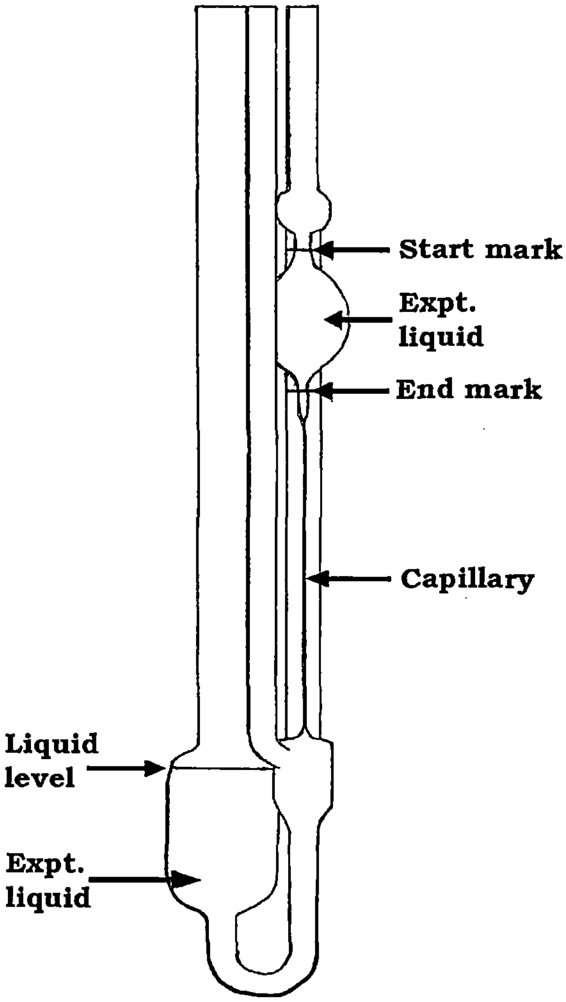

Figure 1. A suspended-level Ubbelohde viscometer.

3.2.3. *Measurement of Ultrasonic Speed*

Ultrasonic speeds were measured, with an accuracy of 0.2 %, using a single-crystal variable-path ultrasonic interferometer[39] (Model M-81, Mittal Enterprise, New Delhi) operating at 4 MHz, which was calibrated with water, methanol and benzene at the experimental temperature. The temperature stability was maintained within ± 0.01 K by circulating thermostatic water around the cell with the aid of a circulating pump.

The principle used in the measurement of the ultrasonic speed (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance originates an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum.

If the distance is increased or decreased maintaining the variation of exactly one half of wave length ($\lambda/2$) or integral multiple of it, the anode current becomes maximum. From the knowledge of the wave length (λ), the speed (u) can be obtained by the relation:

$$u = \lambda \times f \tag{4}$$

The ultrasonic interferometer consists of the following two parts:

(i) the high frequency generator, and (ii) the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal. The micrometer is slowly moved till the anode current on the meter on the high frequency generator deflects a maximum. A number of maxima of anode current are observed and their number (n) is counted. The total distance (d) thus moved by the micrometer gives the value of the wavelength (λ) with the following relation.

$$d = n \times \lambda/2 \tag{5}$$

Further, the speed (u) determined thus is used for the calculation of the isentropic compressibility (K_S) using the following formula:

$$K_S = 1/(u^2 \rho) \tag{6}$$

where ρ is the density of the experimental liquid.

Experimental Section

Figure 2 shows a Multi-frequency Ultrasonic Interferometer i.e. (A) Cross-section of the measuring cell and (B) Position of reflector vs. crystal current.

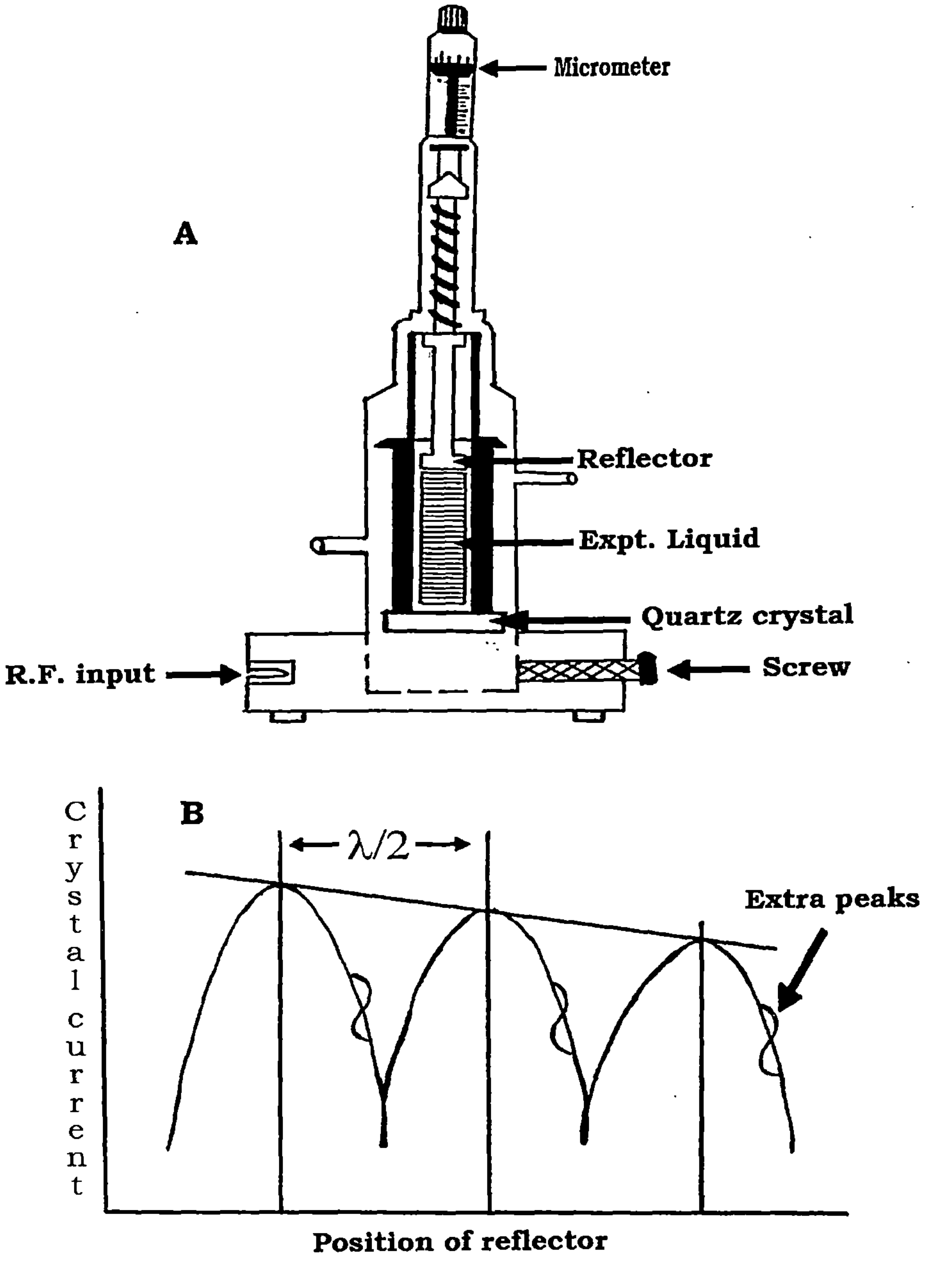

Figure 2. A Multi-frequency Ultrasonic Interferometer- (A) Cross-section of the measuring cell and (B) Position of reflector vs. crystal current.

3.2.4.. *Measurement of Conductance*

Systronics Conductivity meter- 306 is used for measuring specific conductivity of electrolytic solutions. It is a microprocessor based instrument and can provide both automatic and manual temperature compensation. The instrument shows the conductivity of the solution under test at the existing temperature or with temperature compensation. Provision for storing the cell constant and the calibrating solution type, is provided with the help of battery back-up. This data can be further used for measuring the conductivity of an unknown solution, without recalibrating the instrument even after switching it off.

The conductance measurements were carried out on this conductivity bridge using a dip-type immersion conductivity cell, CD-10 with a cell constant of 1.0 ± 10% cm^{-1}. The instrument was standardized using 0.1(M) KCl solution. The cell was calibrated by the method of Lind and co-workers.[40] The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of ± 0.01 K, described earlier.

Solutions were prepared by weight precise to ± 0.02 %. The weights were taken on a Mettler electronic analytical balance (AG 285, Switzerland). The molarities being converted to molalities as required. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvents at desired temperatures.

Figure 3 on next page shows the Systronics Conductivity meter- 306 i.e. (A) Isometric view and (B) Block diagram of the instrument.

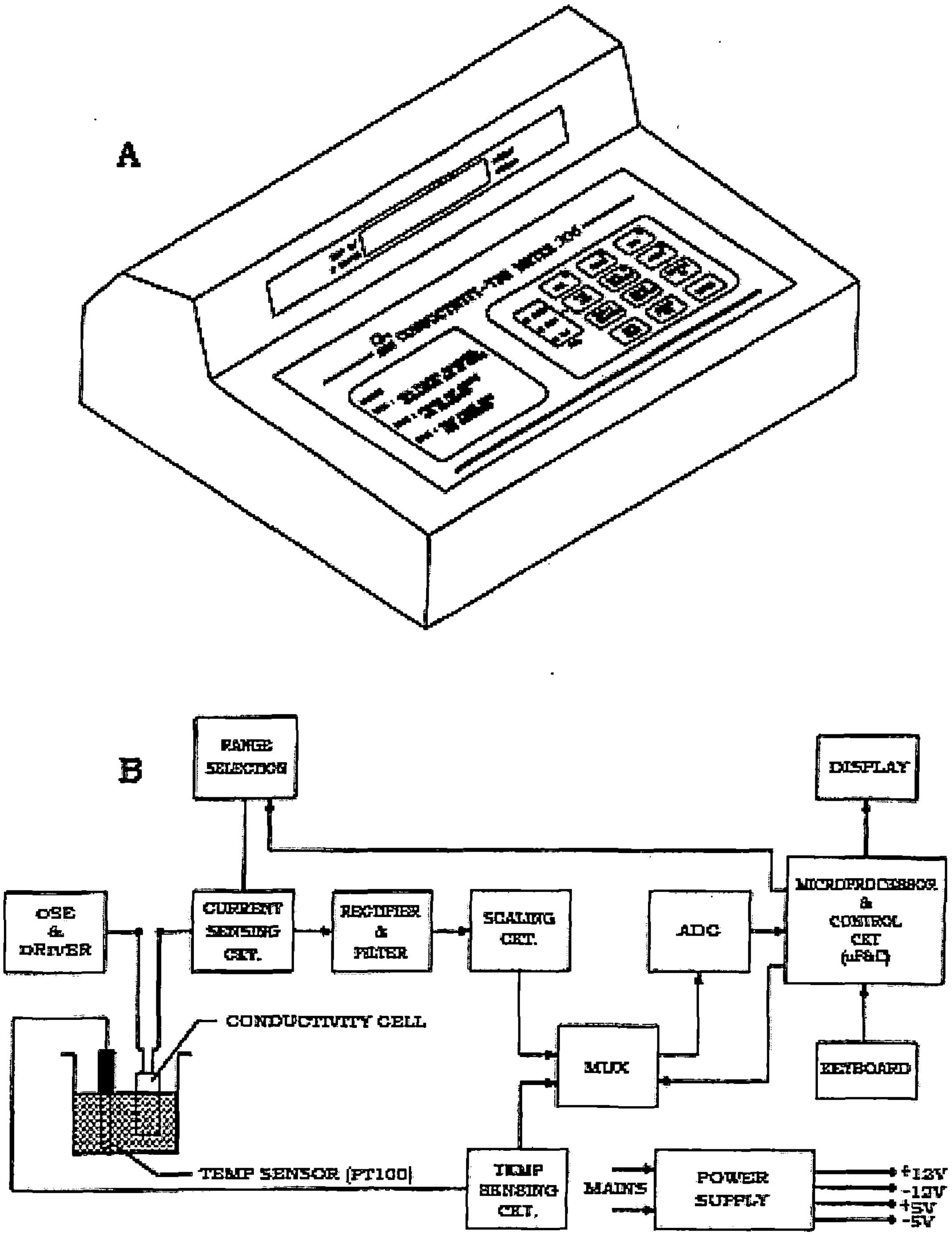

Figure 3. The Systronics Conductivity meter 306- (A) Isometric view and (B) Block diagram of the instrument.

References:

1. N. Saha, B. Das, *J. Chem. Eng. Data*, **1997**, *42*, 227.
2. M. N. Roy, B. Sinha, V. K. Dakua, *J. Chem. Eng. Data*, **2006**, *51*, 590.
3. T. M. Aminabhavi, V. B. Patil, *J. Chem. Eng. Data*, **1998**, *43*, 497.
4. J. A.; Riddick, W. B.; Bunger, T. K.; Sakano, *Organic solvents. Techniques of Chemistry*, Vol-2, 4th ed., Wiley Interscience, New York, **1986**.
5. I. Gascon, A. M. Mainar, F. M. Royo, J. S. Urieta, *J. Chem. Eng. Data*, **2000**, *45*, 751.
6. M. N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data*, **2001**, *46*,1327.
7. A. Sinha, M.N. Roy, *Phys. and Chem. Of Liquids*, **2006**, *44*, 303.
8. D.D. Perrin, W.L.F.Armarego, Purification of Laboratory Chemicals, 3rd Ed., Pergamon Press, Oxford, England. **1988**
9. Hsu-Chen Ku, Chein - HsuinTu, *J.Chem.Eng Data*. **2005**, 50, 1060.
10. I. Johnson, M. Kalidoss, R. Srinavasamorthy., *J. Chem. Eng. Data*. **2002**, *47*, 1388.
11. M.N. Roy, B.B. Gurung, and A. Choudhury, *J. T. R. Chem*, **11(2)**, 7-17 (2005).
12. D. S. Gill, A. Sharma, M. S. Chauhan, A. N. Sharma, J.S. Cheema, *Electrochemica Acta*. **1985**, *30*, 15.
13. A.Pal, R. K.Bhardwaj, *Z. Phys. Chem.,* **2002**, *216*, 1033.
14. A. Ali, A. K. Nain, D. Chand and R. Ahmad, Physics *and Chemistry of Liquids*, **2005**, *43*, 205.
15. E. Jimenez, H. Casas, L. Segade, and C. Franjo. *J. Chem. Eng .Data*. **2000**, *45*, 862.
16. A. K. Covington, T. Dickinson, Physical Chemistry of Organic Solvents Systems, Plenum Publishing Company Ltd., London, 1973.
17. N. V. Sastry and M. K. Voalnd, *International J. Themophysics*. **2000**, 21*(5)*, 1153.
18. G.Douheret, A. Pal. And M.I. Davis, *J. Chem. Thermodyn*. **1990**, *22*, 99.
19. David R, Lide, CSIR Handbook of Chemistry and Physics, 7th edition, **1990-1991**
20. Tasi, F. N *J. Chem. Eng. Data*, **1994**, *39*, 441.

21. Vogel, A.; "Practical Organic Chemistry", 4th ed. ELBS, London, **1978**.

22. Riddick, J.A.; Bunger, W.B.; Solanko, T.K.; "Techniques on Chemistry: Organic Solvents", 4th ed. Wiley New York, **1986**, 2.

23. David, R.L.; "CRC Handbook of Chemistry and Physics". 72nd ed. CRC Press, Florida, **1992**.

24. A.W.Quin, D. F. Hoffmann and P. Munk, *J. Chem. Eng. Data.* **1992**, *37*, 55.

25. S.Glasstone, K. J. Laidler and H.Eyring, *The Theory of Rate Process*, McGraw-Hill, New York, 514, **1941**.

26. D. S. Gill, T. S. Kaur, H. Kaur, I. M. Joshi and J. Singh, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1737.

27. A.J. Treszczanowicz, O. Kiyohara, G. C. Benson. *J. Chem. Thermodyn.* **1981**, *13*, 253.

28. Y. Marcus, Introduction to Liquid State Chemistry (Wiley Interscience, New York, **1977**.

29. S. K. Ghosh, D. K. Hazra. Ind. J. Chem. **1990**, *29A*, 656.

30. K. N. Marsh, "*Recommended Reference Materials for the Realisation of Physicochemical Properties*", Blackwell Scientific Publications, Oxford, U. K., **1987**.

31. J. A. Dean, "*Lange's Handbook of Chemistry*", 11th ed., McGraw-Hill Book Company, New York, **1973**.

32. D. Dasgupta, S. Das, D. K. Hazra. J. Chem. Soc. Faraday Trans I. **1988**, *84*, 1057.

33. B. Das, M.N. Roy, D.K.Hazra, Ind. J. Chem. Tech., **1994**, *1*, 93.

34. P. S. Nikam, M. Hosan, J. Chem. Eng. Data., **1988**, *33*, 165.

35. R. D. Peralta, R. Infante, G. Cortez, G. Cadenas, J. Wisniak, Int. J. Thermophys., **2003**, *24*, 1061.

36. S. Martin Contreras, J. Chem. Eng. Data., **2001**, *46*, 1149.

37. R. Francesconi, F. Comelli, J. Chem. Eng. Data., **1995**, *40*, 31.

38. J. R. Suindells, J. R. Coe Jr., T. B. Godfray. J. Res. Natd. Bus. Stand., **1952**, *48*, 1.

39. M.N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data*, **2004**, *49*, 291.

40. J. E. Lind Jr., J. J. Zwolenik, R. M. Fuoss, *J. Chem. Soc. Faraday Trans I.*, **1959**, *81*, 1557.

CHAPTER IV

Studies on Thermodynamic and Transport Properties of Binary Mixtures of Acetonitrile with Some Cyclic Ethers at Different Temperatures by Volumetric, Viscometric, and Interferometric Techniques*

4.1. *Introduction*

The mixing of different solvents gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute-solute, solute-solvent, and solvent-solvent species.[1]

This work is a part of our program to provide data for the characterization of the molecular interactions between solvents in binary systems.[2,3] Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole-dipole forces predominate,[4,5] and tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are cyclic ethers differing in the number and position of oxygen atom and methylene group.[6,7] Tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are versatile solvents used in the separation of saturated and unsaturated hydrocarbons, in pharmaceutical synthesis, and serve as solvents for many polymers. Acetonitrile has important technological applications, namely, in battery industry and plating techniques.[8,9]

In the present chapter, we report densities, viscosities, and ultrasonic speeds for the binary systems of acetonitrile + tetrahydrofuran,, acetronitrile +1,3-dioxolane, and acetronitrile +1,4-dioxane at the temperatures of (298.15, 308.15, and 318.15) K and atmospheric pressure over the entire composition range. The experimental data are used to calculate excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), and deviations in isentropic compressibility (ΔK_S) of the mixtures. Various thermodynamic parameters

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(e.g., intermolecular free length, specific acoustic impedance, etc.) and their deviations have also been derived from the density and ultrasonic speed data. These results are useful for the interpretation of the nature of interactions that occur between acetonitrile and the cyclic ethers. The work also provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

4.2. *Experimental Section*

4.2.1. *Materials*

Acetonitrile (Merck, India) was distilled from P_2O_5 and then from CaH_2 in an all-glass distillation apparatus,[10] the middle fraction was collected. 1,4-Dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminum hydride ($LiAlH_4$) as described earlier.[2] 1,3-Dioxolane (LR) was purified by standard methods. It was refluxed with PbO_2 and then fractionally distilled after addition of xylene.[12] Tetrahydrofuran (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over $LiAlH_4$ as described earlier.[11] The methods of purification of the chemicals are also discussed in details under chapter III. The purity of the solvents was ascertained by comparing experimental values of densities and viscosities with available literature as listed in Table 1.

4.2.2. *Apparatus and Procedure*

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1cm, calibrated at (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at $\pm$0.01 K of the desired temperature, removed from the bath, properly dried, and weighed in an electronic balance. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The mixtures were prepared by mixing known volume of pure liquids in airtight stoppered bottles. The reproducibility in mole fraction was within $\pm$0.0002. The mass measurements, accurate to $\pm$0.01 mg, were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty of density is $\pm 3 \times 10^{-4}$ $gm.cm^{-3}$, and that of temperature is $\pm$0.01 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer, which was calibrated at 298.15 K with triple-distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was with-in ± 0.03 % of the reported value. Details of the methods and techniques of density and viscosity measurements have been described earlier.[11,13,14] Speeds of sound were determined by a multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 5 MHz, calibrated with water, methanol, and benzene at 298.15 K. The details of the methods[11,13] and techniques have been described earlier in chapter III. The uncertainty of ultrasonic speed measurements is ± 0.2 m.s^{-1}.

4.3. *Results and Discussion*

The physical properties of the pure liquids along with their literature values are recorded in Table 1. However no literature data for viscosity of 1,3-dioxolane at (308.15 K and 318.15 K) and sound speed of acetonitrile at 298.15 K were available to us. Table 2 lists the experimental values of densities (ρ_i) and viscosities (η_i) of the binary mixtures along with the corresponding mole fractions of acetronitrile (x_1), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and interaction parameters (d_{12}, T_{12}, H_{12}) at all the experimental temperatures. The plots of V^E and $\Delta\eta$ against x_1 at 298.15 K are represented in Figure 1 and Figure 2 respectively. Because of similarity in nature, the plots at the other two temperatures are not presented here. The excess molar volumes (V^E) were calculated using equation (1): [15, 16]

$$V^E = \sum_{i=1}^{j} x_i M_i (1/\rho - 1/\rho_i) \qquad (1)$$

where ρ is the density of the mixture, M_i, x_i and ρ_i are the molecular weight, *mole fraction, and density of ith component. The estimated uncertainty for* V^E is from (0.001 to 0.014) cm^3·mol^{-1}. $\Delta\eta$ can be computed using equation (2), [16,17]

$$\Delta\eta = \eta - \sum_{i=1}^{j} (x_i \eta_i) \qquad (2)$$

where η is the absolute viscosity of the mixture and x_i, η_i are the mole fraction and viscosity of ith component in the mixture, respectively. The estimated uncertainty for

$\Delta\eta$ ranges from (0.001 to 0.003) mPa·s.

It is seen that, the values of V^E and $\Delta\eta$ (see Table 2) for all the experimental binary mixtures are negative over the entire range of composition and temperature. The negative values of V^E for the three systems are in the following order:

Acetronitrile + 1,4-dioxane > Acetronitrile + 1,3-dioxolane > Acetronitrile + tetrahydrofuran

Negative values of V^E[18] indicate a specific interaction between the mixing components. The chemical or specific interaction between the mixing molecules results in a volume decrease. The negative values of V^E for the binary mixtures of acetonitrile with the ethers may be attributed to the dipole-induced dipole interactions between the mixing components.[19]

The molar volumes of acetonitrile are (52.84, 53.63, 54 $cm^3 \cdot mol^{-1}$) and those of tetrahydrofuran, 1,3-dioxolane and 1,4-dioxane are (81.87, 82.74, 83.77, $cm^3 \cdot mol^{-1}$); (70.03, 70.80, 71.62 $cm^3 \cdot mol^{-1}$) and (85.65, 86.66, 87.70 $cm^3 \cdot mol^{-1}$) at 298.15 K, 308.15 K and 318.15 K, respectively. It is clear that, the molar volume values of acetonitrile and the other components differ considerably; hence, nonassociated acetonitrile molecules are interstitially accommodated into clusters of ethers yielding a negative contribution to observed V^E values. This implies that the complex-forming interactions are almost absent in the experimental binary systems and therefore observed $\Delta\eta$ values are also negative.[20]

From close observation of Table 2, it is seen that the negative V^E values are much higher than those of $\Delta\eta$ for all the binary systems under consideration. This clearly supports mere addition of acetonitrile molecules into aggregates of the other components.[20]

Isentropic compressibility (K_S) values were calculated from experimental densities, ρ and speeds of sound u, using equation (3)

$$K_S = 1/(u^2 \rho) \qquad (3)$$

Where K_S gives the isentropic compressibility for the *i*th component of the mixture.

We also derived the deviations in isentropic compressibility (ΔK_S), deviations in intermolecular free length (ΔL_f) and deviations in specific acoustic impedance (ΔZ) for the binary mixtures using equations (4), (5) and (6).

$$\Delta K_s = K_s - \sum_{i=1}^{2} x_i K_{s,i} \tag{4}$$

$$\Delta L_f = L_f - \sum_{i=1}^{2} x_i L_{fi} \tag{5}$$

$$\Delta Z = Z - \sum_{i=1}^{2} x_i Z_i \tag{6}$$

Where K_S, L_f and Z are the isentropic compressibility, intermolecular free length and specific acoustic impedance of the mixture and x_i, K_{S_i}, L_{f_i} and Z_i are the mole fraction, isentropic compressibility, intermolecular free length and specific acoustic impedance of *i*th component in the mixture, respectively. Experimental values of u, K_S, ΔK_S, ΔL_f, ΔZ are listed in Table 3 and the plots of ΔK_S, ΔL_f and ΔZ against x_1 are shown in Figure 3 to Figure 5.

For the investigated binary mixtures, the deviations in isentropic compressibility are negative. The composition dependence of ΔK_S for the investigated binary mixtures is shown in Figure 3; it shows that ΔK_S decrease in the order:

Acetronitrile + 1, 4-dioxane > acetonitrile + 1, 3-dioxolane > acetonitrile + tetrahydrofuran

These results can be explained in terms of molecular interactions and structural effects. There is a parallel in the qualitative behaviour of the ΔK_S and V^E curves (Figure 1 and Figure 3).

Figure (4) and Figure (5) shows that ΔL_f are positive for all the binary mixture and ΔZ behaves in opposite manner to ΔL_f. Positive and negative deviations in these functions from linear dependence on composition of the mixtures indicate the extent of association or dissociation between the mixing components.[21] The observed values of

ΔK_S and ΔL_f can be qualitatively explained by considering the factors - (i) the mutual disruption of associates present in pure liquids, (ii) dipole-induced dipole interaction between the mixing liquids and (iii) interstitial accommodation of one component into another. The second two factors contribute negative ΔK_S and ΔL_f values. Observed negative value of ΔK_S and ΔL_f for the mixtures over the entire range of composition implies that the weak dipole-induced dipole interactions are predominant between the unlike molecules along with interstitial accommodation between the components.[22, 15] Thus the graded behaviors of these functions support the results obtained earlier.

In an attempt to explore the nature of the interactions occurring between the mixing components, various thermodynamic parameters [21-25] such as intermolecular free length (L_f), specific acoustic impedance (Z), Vander Waal's constant (b), molecular radius (r), geometrical volume (B), molar surface area (Y), available volume (V_a), molar speed of sound (R), relative association (R_A) and molecular association (M_A) of the binary mixtures have been calculated using

$$L_f = K\sqrt{K_S} \tag{7}$$

$$Z = u\rho \tag{8}$$

$$b = \left(M/\rho\right) - \left(RT/\rho^2 u^2\right)\left\{\left[1 + \left(Mu^2/3RT\right)\right]^{\frac{1}{2}} - 1\right\} \tag{9}$$

$$r = \left(3b/16\pi N\right)^{\frac{1}{3}} \tag{10}$$

$$B = \frac{4}{3}\pi r^3 N \tag{11}$$

$$Y = \left(36\pi N B^2\right)^{\frac{1}{3}} \tag{12}$$

$$V_a = V - \left(1 - \frac{u}{u_\infty}\right) \tag{13}$$

$$V_0 = V - V_a \tag{14}$$

$$R = {Mu^{\frac{1}{3}}}\Big/{\rho} \tag{15}$$

$$R_A = \left({\rho_{mix}}\big/{\rho}\right)\left({u}\big/{u_{mix}}\right)^{\frac{1}{3}} \tag{16}$$

$$M_A = \left({u_{mix}}\Big/{\sum_{i=1}^{2} x_i u_i} \right)^2 - 1 \tag{17}$$

where K is a temperature dependent constant, V_0 is volume at absolute zero, u_∞ is taken as 1600 ms^{-1}. These parameters are listed in Table 4 for the pure components and in Table 5 for the binary mixtures. Plots of Z, L_f, R, M_A and R_A against x_1 are shown in Figure 6 to Figure 10.

The values of Z and L_f for the mixtures behave in opposite manner and the Figures do not exhibit any sudden variation in their behaviour. This implies the absence of any complex formation[24] between the mixing components; that is further supported by the linear variations of R, R_A and M_A of the binary mixtures against mole fraction of acetonitrile.[24] M_A and R_A values decrease for the mixtures with increasing mole fraction of acetonitrile. This implies strongly dissociative interactions between the unlike molecules in the mixtures. [24, 25]

The mixing functions V^E, $\Delta\eta$, ΔK_S, ΔL_f and ΔZ were represented *mathematically by the following type of Redlich-Kister equation* [26] *[equation (18)] for* correlating the experimental data:

$$Y_{ij}^{E} = x_i x_j \sum_{k=1}^{m} a_k (x_i - x_j)^k) \tag{18}$$

where Y_{ij}^{E} *refers to an excess property* (V^e, $\Delta\eta$, ΔK_S, ΔL_f *and* ΔZ) *for each* i-j binary pair, and x_i is the mole fraction of *i*th component, and a_k represents the coefficients. The values of coefficients (a_k) were determined by a multiple-regression *analysis based on the least-squares method and were summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 6. The standard deviation was calculated using equation (19).*

$$\sigma = \left[\sum_{i=1}^{n} \frac{(Y_{i,\exp}^{E} - Y_{i,cal}^{E})^2}{n-p} \right]^{\frac{1}{2}} \qquad (19)$$

where n is the number of experimental points and p is the number of adjustable parameters. The small σ values for excess properties indicates that the fits are good for the present study,

Several semi-empirical models have been proposed from time to time to estimate the dynamic viscosity of the binary liquid mixtures in terms of pure-component data[16, 17] and to interpret the molecular interactions in these mixtures. Some of them we examined are as follows:

Grunberg and Nissan[27] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp\left[\sum_{i=1}^{j} (x_i \ln\eta_i) + d_{12} \prod_{i=1}^{j} x_i \right] \qquad (20)$$

where d_{12} is a constant proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The values of the interchange parameter (d_{12}) have been calculated using equation (20) as a function of the composition of the binary liquid mixtures of acetronitrile with tetrahydrofuran, 1, 3-dioxolane and 1,4-dioxane and were listed in Table 2.

Tamura-Kurata [28] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \qquad (21)$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of ith pure component in the mixture.

The following viscosity model of Hind et al [29] may also interpret the molecular interactions:

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \qquad (22)$$

where H_{12} is Hind interaction parameter. In the present study, the values of interaction parameter T_{12} and H_{12} have been calculated from equation (21) and (22), respectively and were listed in Table 2. It is observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other; this is in agreement with the view put forward by Fort and Moore[15] in regard to the nature of parameter T_{12} and H_{12}.

McAllister multibody interaction model[30] is widely used to correlate the kinematic viscosities $\left(\upsilon = \eta/\rho\right)$ of the binary mixtures with mole fraction.

The three-body model is defined as:

$$\ln\upsilon = x_1^3\ln\upsilon_1 + x_2^3\ln\upsilon_2 + 3x_1^2x_2\ln\upsilon_{12} + 3x_2^3x_1\ln\upsilon_{21} - \ln\left[x_1 + \frac{x_2M_2}{M_1}\right] + 3x_1^2x_2\ln\left[\frac{2}{3}+\frac{M_2}{3M_1}\right] + 3x_2^2x_1\ln\left[\frac{1}{3}+\frac{2M_2}{3M_1}\right] + x_2^3\ln\left[\frac{M_2}{M_1}\right] \qquad (23)$$

The four-body model is given by

$$\ln\upsilon = x_1^4\ln\upsilon_1 + 4x_1^3x_2\ln\upsilon_{1112} + 6x_1^2x_2^2\upsilon_{1122} + 4x_1x_2^3\ln\upsilon_{2221} + x_2^4\ln\upsilon_2 - \ln\left[x_1 + x_2\left(\frac{M_2}{M_1}\right)\right] + 4x_1^3x_2\ln\left[\frac{3}{4}+\frac{M_2}{4M_1}\right] + 6x_1^2x_2^2\ln\left[\frac{1}{2}+\frac{M_2}{2M_1}\right] + 4x_1x_2^3\ln\left[\frac{1}{3}+\frac{3M_2}{4M_1}\right] + x_2^4\ln\left[\frac{M_2}{M_1}\right] \qquad (24)$$

Where υ, υ_1 and υ_2 are kinematic viscosities of the mixture, the pure component 1 and 2 respectively, υ_{12}, υ_{21}, υ_{1112}, υ_{1122}, υ_{2221} are model parameters and M_i are the mole fraction and molecular weight of the *i*th pure component in the mixture, respectively.

Table 7 records the parameters calculated using equation (23) and (24) along with the standard deviations. It is seen that the values of both the parameters are positive and adequate for all of the binary mixtures.

Heric and Brewer[31] have proposed an equation for the kinematic viscosity of the binary liquid mixtures

$$\upsilon = x_1\upsilon_1 + x_2\upsilon_2 + x_1x_2\{a + b(x_1 - x_2) + c(x_1 - x_2)^2\} \qquad (25)$$

Where, a , b and c are model parameters and M_i, x_i are the molecular weight and mole fraction of the *i*th pure component in the mixture, respectively.

The percentage standard deviation[24] was calculated by using equation (26).

$$\sigma\% = \left[\frac{\sum\left(100\left(\upsilon_{\exp tl} - \upsilon_{calcd}\right)\Big/\upsilon_{\exp tl}\right)^2}{(n-m)}\right]^{\frac{1}{2}} \qquad (26)$$

where n represents the number of experimental points and m the number of coefficients.

The values of parameters a, b, c have been calculated using equation (25) and listed in Table 7 along with the standard deviations. A perusal of this Table 7 shows that the values of a, b are negative for all of the binary mixtures.

4.4. *Conclusion:*

In summary, the study provided us with some idea about the type and nature of molecular interactions between the mixing components. Strong specific interaction between acetonitrile and ethers molecules seems to be present. Dipole-induced dipole interactions are present between the unlike molecules along with the interstitial accommodation of non associated acetonitrile molecules in to the clusters of ether molecules. This type of interaction is largest in acetonitritle 1,4-00 mixture and least in case of accetonitrile tetrahydrofuran mixture. This study on excess or deviation properties along with acoustic properties seems to be of much use in exploring the nature of interactions present in the experimental binary mixtures, however, more extensive study will have a better in this field.

References

1. E. S. Kim, K. N. Marsh, *J. Chem. Eng. Data,* **1988**, *33*, 288.
2. M. N. Roy, B. Sinha, V. K. Dakua, *J. Chem. Eng. Data,* **2006**, *51*, 590.
3. M. N. Roy, A. Sinha, B. Sinha, **2005**, *34 (11), 1311.*
4. G. Moumouzias, D. K. Panopoulos, G. Ritzoulis, *J. Chem. Eng. Data,* **1991**, *36*, 20.
5. B. Das, N. Saha, *J. Chem. Eng. Data,* **2000**, *45*, 2.
6. P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo, *J. Chem. Eng. Data.* **1999**, *44*, 1341.
7. D. G. Leaist, K. MacEwan, A. Stefan, M. Zamari, *J. Chem. Eng. Data.* **2000**, *45*, 815.
8. G. G. Janz, R.P.T. Tomkins, *Nonaqueous Electrolytes Handbook*, Academic Press, New York, **1973**, vol-2
9. R. Jasinski, *High Energy Batteries.* Plenum Press. New York. **1967**.
10. N. Saha, B. Das, *J. Chem. Eng. Data,* **1997**, *42*, 227.
11. M. N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data,* **2001**, *46*,1327.
12. J. A.; Riddick, W. B.; Bunger, T. K.; Sakano, *Organic solvents. Techniques of Chemistry,* Vol-2, 4th ed., Wiley Interscience, New York, **1986**.
13. M. N. Roy, D. K. Hazra, *Indian J. Chem. Technol.* **1994**, *1*, 93.
14. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data,* **2004**, *49*, 291.
15. R. J. Fort, W. R. Moore, *Trans. Faraday Soc.* **1966**, *62*, 1112.
16. R. C. Reid, J. M. Prausnitz, B. E. Poling, *The properties of Gases and Liquids,* 4th ed., McGraw-Hill International, **1987**.
17. J. B. Irving, *Viscosities of Liquid Mixtures. NEL Report No 630 and 631,* National Engineering Laboratory, East Kilbride, Glassgow, **1977**.
18. A. J. Treszczanowicz, O. Kiyohara, G. C. Benson, *J. Chem. Thermodyn.* **1981**, *13*, 253.
19. P. Jain, M. Singh, *J.Chem. Eng. Data,* **2004**, 49, 1214.
20. P. S. Nikam, S. J. Kharat, *J. Chem. Eng. Data,* **2003**, *48*, 972.
21. A. Pal, R. K. Bhardwaj, *Z. Phys. Chem.* **2002**, *216*, 1033.
22. H-C. Ku, C-H. Tu, *J. Chem. Eng. Data,* **2005**, *50*, 608.
23. B. Jacobson, *J. Chem. Phys.* **1952**, *20*, 927.

24. S. K. Mehta, R. K. Chauhan, R. K. Dewan, *J. Chem. Soc. Faraday Trans.* **1996**, *92,* 1167.
25. N. V. Shastry, S.R. Patel, *Int. J of Thermophy.* **2000**, *21,* 1153.
26. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* **1948**, *40,* 345.
27. L. Grunberg, A. H. Nissan, *Nature,* **1949**, *164,* 799.
28. M. Tamura, M. Kurata, *Bull. Chem. Soc. Jpn.* **1952**, *25,* 32.
29. R. K. Hind, E. McLaughlin, A. R. Ubbelohde, *Trans. Faraday. Soc.* **1960**, *56,* 328.
30. R. A. McAllister, *AIChE J.* **1960**, *6,* 427.
31. E. L. Heric, J. G. Brewer, *J. Chem. Eng. Data,* **1967**, *12,* 574.
32. P, S. Nikam, S. J. Kharat, *Chem. Eng. Data,* **2003**, *48,* 1291.
33. A. Sinha, M.N. Roy, *Phys. and Chem. Of Liquids,* **2006**, *44,* 303.
34. T. M. Aminabhavi, V. B. Patil, *J. Chem. Eng. Data,* **1998**, *43,* 497.
35. I. Gascon, A. M. Mainar, F. M. Royo, J. S. Urieta, *J. Chem. Eng. Data,* **2000**, *45,* 751.
36. B. Giner, A. Villares, P. Gascon, P. Cea, C. Lafuente, *Int. J. of Thermophy.* **2004**, *25(6),* 1735.
37. A. Inglese, J.E. Groller, E. Wllhelm, *J. Chem. Eng. Data* **1983**, *28,* 124.
38. K.P. Rao, K.S. Reddy, *J. Chem. Eng. Data* **1988**, *33,* 130.

TABLE 1

Comparison of density (*ρ*), viscosity (*η*) and sound speed (*u*) with Literature Data at the experimental temperatures

Pure Solvent	T / K	$\rho \times 10^3$ / (kg·m^{-3})		η /(mPa·s)		u /(m·s^{-1})	
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Acetonitrile	298.15	0.7768	0.77686[10]	0.3443	0.3446 [10]	1713.2	-
	308.15	0.7654	0.76564[10]	0.3124	0.3125 [10]		
	318.15	0.7547	0.75498[10]	0.2891	0.2893 [10]		
Tetrahydro-furan	298.15	0.8808	0.8807[33]	0.4631	0.4630 [33]	1292.2	1294[34]
	308.15	0.8715	0.8712[33]	0.4276	0.4277 [33]		
	318.15	0.8608	0.8614[33]	0.3903	0.3902 [33]		
1,4-Dioxane	298.15	1.0287	1.0282[34]	1.1779	1.178[34]	1344.4	1358[34]
	308.15	1.0168	1.0168[34]	0.9985	0.999[34]		
	318.15	1.0047	1.00526[37]	0.8909	0.901[38]		
1,3 Dioxolane	298.15	1.0577	1.05862[35]	0.5878	0.5886[35]	1338.2	1338.8[36]
	308.15	1.0463	1.04620[37]	0.5128			
	318.15	1.0344	1.03364[37]	0.4580			

TABLE 2

Values of density (ρ), viscosity (η,) excess molar volume (V^E), viscosity deviation ($\Delta\eta$,) Grunberg-Nissan, Tamura-Kurata and Hind interaction parameter (d_{12}, T_{12}, H_{12}) for binary mixtures

x_1	$\rho \times 10^3$ / $(kg \cdot m^{-3})$	η / $(mPa \cdot s)$	$V^E \times 10^6$/ $(m^3 \cdot mol^{-1})$	$\Delta\eta$ / $(mPa \cdot s)$	d_{12}	T_{12}	H_{12}
Acetonitrile + Tetrahydrofuran 298.15 K							
0	0.8808	0.4631	0	0	0	0	0
0.1633	0.8703	0.4419	-0.104	-0.002	0.011	0.393	0.397
0.3052	0.8595	0.4236	-0.142	-0.003	0.006	0.392	0.396
0.4295	0.8486	0.4075	-0.145	-0.005	-0.002	0.390	0.394
0.5394	0.8376	0.3932	-0.124	-0.006	-0.015	0.389	0.392
0.6372	0.8268	0.3808	-0.093	-0.007	-0.029	0.387	0.389
0.7249	0.8162	0.3701	-0.062	-0.007	-0.047	0.384	0.387
0.8039	0.8058	0.3611	-0.037	-0.007	-0.067	0.382	0.383
0.8754	0.7959	0.3539	-0.020	-0.005	-0.087	0.380	0.380
0.9405	0.7862	0.3481	-0.007	-0.003	-0.119	0.376	0.375
1	0.7768	0.3443	0	0	0	0	0
Acetonitrile + Tetrahydrofuran 308.15 K							
0	0.8715	0.4276	0	0	0	0	0
0.1633	0.8604	0.4066	-0.070	-0.002	0.006	0.357	0.361
0.3052	0.8492	0.3875	-0.099	-0.005	-0.013	0.353	0.358
0.4295	0.8380	0.3701	-0.110	-0.008	-0.039	0.349	0.354
0.5394	0.8270	0.3550	-0.106	-0.012	-0.067	0.345	0.349
0.6372	0.8162	0.3425	-0.096	-0.012	-0.095	0.342	0.345
0.7249	0.8057	0.3321	-0.082	-0.012	-0.126	0.338	0.339
0.8039	0.7953	0.3242	-0.066	-0.011	-0.155	0.336	0.336
0.8754	0.7852	0.3184	-0.049	-0.008	-0.184	0.333	0.332

Contd.

0.9405	0.7752	0.3145	-0.028	-0.005	-0.214	0.331	0.328
1	0.7654	0.3124	0	0	0	0	0

Acetonitrile + Tetrahydrofuran

318.15 K

0	0.8608	0.3903	0	0	0	0	0
0.1633	0.8510	0.3683	-0.201	-0.005	-0.106	0.313	0.319
0.3052	0.8405	0.3497	-0.290	-0.010	-0.135	0.311	0.317
0.4295	0.8296	0.3340	-0.311	-0.013	-0.169	0.309	0.313
0.5394	0.8184	0.3202	-0.288	-0.016	-0.218	0.305	0.308
0.6372	0.8073	0.3089	-0.245	-0.017	-0.277	0.301	0.303
0.7249	0.7963	0.3001	-0.196	-0.017	-0.349	0.298	0.298
0.8039	0.7855	0.2938	-0.141	-0.015	-0.443	0.294	0.292
0.8754	0.7750	0.2901	-0.094	-0.012	-0.581	0.291	0.287
0.9405	0.7647	0.2879	-0.045	-0.007	-0.960	0.284	0.276
1	0.7547	0.2890	0	0	0	0	0

Acetonitrile + 1,3-Dioxolane

298.15 K

0	1.0577	0.5878	0	0	0	0	0
0.1670	1.0227	0.5233	-0.124	-0.024	-0.193	0.355	0.380
0.3109	0.9899	0.4737	-0.233	-0.038	-0.231	0.355	0.376
0.4361	0.9585	0.4360	-0.277	-0.046	-0.266	0.355	0.373
0.5461	0.9282	0.4046	-0.268	-0.0502	-0.328	0.350	0.364
0.6435	0.8994	0.3783	-0.239	-0.053	-0.421	0.340	0.351
0.7302	0.8721	0.3591	-0.197	-0.051	-0.519	0.330	0.337
0.8081	0.8465	0.3444	-0.160	-0.047	-0.660	0.314	0.315
0.8783	0.8221	0.3380	-0.111	-0.036	-0.782	0.301	0.298
0.9420	0.7989	0.3366	-0.062	-0.022	-0.982	0.277	0.266
1	0.7768	0.3443	0	0	0	0	0

Contd.

Acetonitrile + 1,3-Dioxolane

298.15 K

0	0	0	0	0	0	0	0
0.1670	0.1670	0.1670	0.1670	0.1670	0.1670	0.1670	0.1670
0.3109	0.9792	0.4235	-0.295	-0.027	-0.174	0.333	0.349
0.4361	0.9478	0.3913	-0.352	-0.034	-0.221	0.329	0.343
0.5461	0.9177	0.3646	-0.357	-0.034	-0.284	0.323	0.334
0.6435	0.8890	0.3419	-0.334	-0.042	-0.377	0.312	0.321
0.7302	0.8619	0.3251	-0.297	-0.041	-0.477	0.302	0.307
0.8081	0.8361	0.3134	-0.248	-0.038	-0.593	0.290	0.292
0.8783	0.8116	0.3077	-0.190	-0.029	-0.706	0.279	0.277
0.9420	0.7882	0.3070	-0.114	-0.017	-0.845	0.264	0.257
1	0.7654	0.3124	0	0	0	0	0

Acetonitrile + 1,3-Dioxolane

318.15 K

0	1.0344	0.4580	0	0	0	0	0
0.1670	1.0003	0.4132	-0.202	-0.017	-0.188	0.297	0.313
0.3109	0.9679	0.3791	-0.336	-0.026	-0.215	0.298	0.311
0.4361	0.9366	0.3502	-0.390	-0.034	-0.275	0.292	0.304
0.5461	0.9065	0.3263	-0.392	-0.039	-0.354	0.284	0.293
0.6435	0.8780	0.3065	-0.369	-0.043	-0.460	0.274	0.280
0.7302	0.8511	0.2910	-0.342	-0.044	-0.597	0.260	0.262
0.8081	0.8255	0.2817	-0.290	-0.040	-0.737	0.246	0.245
0.8783	0.8009	0.2780	-0.219	-0.032	-0.890	0.231	0.225
0.9420	0.7775	0.2797	-0.128	-0.019	-1.093	0.210	0.198
1	0.7547	0.2891	0	0	0	0	0

Acetonitrile + 1,4-Dioxane

298.15 K

0	1.0287	1.1780	0	0	0	0	0
0.1926	0.9976	0.9468	-0.100	-0.071	0.119	0.53	0.41

Contd.

0.3492	0.9686	0.7720	-0.193	-0.115	0.031	0.51	0.40
0.4791	0.9410	0.6349	-0.258	-0.144	-0.115	0.47	0.38
0.5886	0.9146	0.5315	-0.289	-0.156	-0.297	0.44	0.36
0.6822	0.8891	0.4573	-0.275	-0.152	-0.494	0.41	0.35
0.7630	0.8645	0.4099	-0.237	-0.132	-0.648	0.40	0.35
0.8336	0.8412	0.3679	-0.191	-0.115	-0.998	0.35	0.32
0.8957	0.8185	0.3482	-0.115	-0.0831	-1.253	0.32	0.31
0.9508	0.7972	0.3389	-0.057	-0.0464	-1.632	0.27	0.28
1	0.7768	0.3443	0	0	0	0	0

Acetonitrile + 1,4-Dioxane

308.15 K

0	1.0168	0.9985	0	0	0	0	0
0.1926	0.9812	0.8244	-0.194	-0.042	0.207	0.432	0.520
0.3492	0.9484	0.6862	-0.288	-0.073	0.135	0.415	0.495
0.4791	0.9187	0.5802	-0.342	-0.090	0.055	0.405	0.475
0.5886	0.8914	0.5030	-0.357	-0.092	-0.007	0.405	0.466
0.6822	0.8661	0.4477	-0.331	-0.083	-0.044	0.412	0.464
0.7630	0.8430	0.4079	-0.301	-0.067	-0.048	0.424	0.469
0.8336	0.8212	0.3775	-0.229	-0.049	-0.029	0.438	0.478
0.8957	0.8014	0.3531	-0.168	-0.031	0.014	0.453	0.490
0.9508	0.7828	0.3340	-0.090	-0.012	0.207	0.486	0.525
1	0.7654	0.3124	0	0	0	0	0

Acetonitrile + 1,4-Dioxane

318.15 K

0	1.0047	0.8909	0	0		0	0
0.1926	0.9755	0.7189	-0.254	-0.056	0.015	0.322	0.409
0.3492	0.9468	0.5994	-0.364	-0.081	-0.014	0.337	0.411
0.4791	0.9194	0.5014	-0.430	-0.101	-0.143	0.324	0.387
0.5886	0.8930	0.4305	-0.450	-0.106	-0.268	0.318	0.370

Contd.

0.6822	0.8675	0.3854	-0.421	-0.095	-0.324	0.328	0.371
0.7630	0.8430	0.3542	-0.364	-0.078	-0.352	0.341	0.375
0.8336	0.8193	0.3354	-0.276	-0.054	-0.279	0.366	0.395
0.8957	0.7968	0.3194	-0.188	-0.033	-0.190	0.389	0.416
0.9508	0.7752	0.3076	-0.093	-0.011	0.142	0.438	0.471
1	0.7547	0.2891	0	0		0	0

TABLE 3.

Values of Ultrasonic Speeds *u*, isentropic compressibility K_s, Deviations in isentropic compressibility ΔK_s for binary mixtures at 298.15 K.

x_1	u / (m· s^{-1})	$Ks \times 10^{12}$ / Pa^{-1}	$\Delta K_S \times 10^{12}$ / Pa^{-1}	ΔL_f / Å	ΔZ / (Kg·m^2·s^{-1})
		Acetonitrile + Tetrahydrofuran			
0	1292.2	679.94	0	0	0
0.1633	1344.3	635.81	-4.72	-0.0004	0.3119
0.3052	1395.2	597.70	-8.16	-0.0013	2.2063
0.4295	1443.9	565.25	-10.64	-0.0020	4.3811
0.5394	1490.4	537.47	-12.11	-0.0025	6.2800
0.6372	1533.8	514.14	-11.73	-0.0027	7.2298
0.7249	1573.6	494.81	-9.96	-0.0023	6.5553
0.8039	1610.3	478.56	-7.36	-0.0015	4.5467
0.8754	1645.5	464.04	-4.62	-0.0008	2.8429
0.9405	1679.0	451.20	-1.75	-0.0001	0.6821
1	1713.2	438.59	0	0	0
		Acetonitrile + 1,3-Dioxolane			
0	1338.2	527.95	0	0	0
0.1670	1388.9	506.89	-6.14	-0.0006	2.7010
0.3109	1436.2	489.75	-10.42	-0.0013	8.2001
0.4361	1481.5	475.34	-13.65	-0.0024	15.5741
0.5461	1524.4	463.62	-15.54	-0.0039	25.0101
0.6435	1563.5	454.83	-15.63	-0.0048	29.1401
0.7302	1597.8	449.15	-13.56	-0.0045	27.6649
0.8081	1628.8	445.28	-10.47	-0.0037	23.1053
0.8783	1658.2	442.39	-7.09	-0.0026	16.1342
0.9420	1686.4	440.14	-3.65	-0.0015	8.6832
1	1713.2	438.61	0	0	0
		Acetonitrile + 1,4-Dioxane			
0	1344.4	537.84	0	0	0

Contd.

0.1926	1399.3	511.94	-6.79	-0.0007	3.7000
0.3492	1451.0	490.37	-12.82	-0.0015	9.1001
0.4791	1498.4	473.32	-16.98	-0.0025	15.5741
0.5886	1540.2	460.91	-18.52	-0.0036	25.0101
0.6822	1575.7	453.00	-17.15	-0.0045	29.1401
0.7630	1606.5	448.20	-13.93	-0.0042	27.6649
0.8336	1633.5	445.52	-9.60	-0.0034	23.1053
0.8957	1660.1	443.32	-5.64	-0.0023	16.1342
0.9508	1686.3	441.13	-2.36	-0.0012	8.6832
1	1713.2	438.61	0	0	0

TABLE 4.

Vander Wall's Constant *b*, Molecular Radius *r* , Geometrical Volume *B*, Collision Factor *S*, Molar Speed of Sound *R*, Available Volume V_a , Intermolecular Free Length L_f, Molar Volume at Absolute Zero V_0 , Molar Surface Area *Y* and Specific Acoustic Impedance *Z* of the Pure Components at 298.15 K.

Pure Solvent	$b\times10^5$ $/m^3$	r $/nm$	$B\times10^5$ $/(m^3\cdot mol^{-1})$	S	$R\times10^6$ $/\{m^3\cdot mol^{-1}$ $(m\cdot s^{-1})^{1/3}\}$	$V_a\times10^5$ $/(cu\cdot m)$	L_f $/\,Å$	$V_0\times10^5$ $/(cu\cdot m)$	$Y\times10^{-4}$ $/\,Å$	$Z\times10^{-3}$ $/(Kg\cdot m^2\cdot s^{-1})$
Acetonitrile	4.94	0.170	1.24	4.58	632.32	-3.74	0.431	5.658	21.82	1330.81
Tetrahydrofuran	7.66	0.197	1.91	3.45	891.72	1.57	0.536	6.612	29.22	1138.17
1,3-Dioxolane	6.57	0.187	1.64	3.57	771.81	1.15	0.473	5.858	26.38	1415.41
1,4-Dioxane	8.07	0.200	2.02	3.57	945.32	1.37	0.477	7.197	30.26	1382.98

TABLE5.

Intermolecular Free Length *L_f*, Molar Speed of Sound *R*, Relative association R_A, *Molecular association M_A, Available Volume V_a, Specific Acoustic Impedance Z of* Binary Mixtures at 298.15 K

x_1	L_f / Å	$R \times 10^6$ /{$m^3 \cdot mol^{-1}$ $(m \cdot s^{-1})^{1/3}$}	R_A	M_A	$V_a \times 10^5$ / (cu·m)	$Z \times 10^{-3}$ /($Kg \cdot m^2 \cdot s^{-1}$)
Acetonitrile + Tetrahydrofuran						
0.1633	0.5186	911.85	1.2147	-0.5911	1.18	1169.94
0.3052	0.5029	842.69	1.1848	-0.634	8.72	1199.17
0.4295	0.4890	791.88	1.1565	-0.6681	6.26	1225.29
0.5394	0.4768	753.03	1.1295	-0.6961	4.19	1248.36
0.6372	0.4664	722.31	1.1043	-0.7193	2.43	1268.15
0.7249	0.4575	697.28	1.0809	-0.7389	9.41	1284.37
0.8039	0.4500	676.55	1.059	-0.7558	-3.58	1297.58
0.8754	0.4431	659.27	1.0385	-0.7703	-1.55	1309.65
0.9405	0.4369	644.61	1.0189	-0.7831	-2.65	1320.03
Acetonitrile + 1,3-Dioxolane						
0.1670	0.4654	937.98	1.3773	-0.4928	8.64	1403.98
0.3109	0.4587	860.66	1.3224	-0.5567	6.26	1397.31
0.4361	0.4523	804.77	1.2715	-0.6074	4.32	1394.09
0.5461	0.4462	762.5	1.2241	-0.6487	2.66	1394.22
0.6435	0.4412	729.26	1.1801	-0.6831	1.25	1390.11
0.7302	0.4378	702.28	1.1391	-0.7124	7.42	1381.30
0.8081	0.4354	679.94	1.1013	-0.7373	-9.61	1370.15
0.8783	0.4335	661.37	1.0652	-0.7591	-1.93	1357.24
0.9420	0.4319	645.71	1.0317	-0.7779	-2.85	1344.40
Acetonitrile + 1,4-Dioxane						
0.1926	0.4654	1039.22	1.3739	-0.5033	9.08	1395.94
0.3492	0.4555	917.01	1.3179	-0.5677	6.05	1405.44

Contd.

0.4791	0.4475	837.8	1.2667	-0.6173	3.84	1409.99
0.6822	0.4378	740.65	1.1769	-0.6897	8.45	1400.95
0.7630	0.4354	708.61	1.1370	-0.7173	-2.21	1388.82
0.8336	0.4341	683.07	1.1002	-0.7407	-1.12	1374.1
0.8957	0.4331	662.64	1.0648	-0.7611	-2.00	1358.79
0.9508	0.4320	645.97	1.0317	-0.7788	-2.85	1344.32

TABLE 6

Redlich-Kister coefficients a_n and standard deviations σ for the binary mixtures

Binary mixture	Excess property	T/K	a_0	a_1	a_2	a_3	σ
Acetonitrile + Tetrahydrofuran	$V^E \times 10^6$ / $(m^3 \cdot mol^{-1})$	298.15	-0.535	0.439	0.238	-0.157	0.004
		308.15	-0.435	0.081	0.000	-0.046	0.000
		318.15	-1.198	0.489	0.054	-0.116	0.001
	$\Delta\eta$ / $(mPa \cdot s)$	298.15	-0.023	-0.023	-0.014	-	0.000
		308.15	-0.041	-0.044	-	-	0.001
		318.15	-0.060	0.047	-0.023	-	0.000
	$\Delta K_S \times 10^{12}$ / (Pa^{-1})	298.15	-46.921	-20.28	16.041	28.30	0.101
	ΔL_f / Å	298.15	-0.001	-0.0096	0.008	0.0125	0.000
	ΔZ / $(Kg \cdot m^2 \cdot s^{-1})$	298.15	22.952	33.3804	-8.691	-31.4791	0.195
Acetonitrile + 1,3-Dioxolane.	$V^E \times 10^6$ / $(m^3 \cdot mol^{-1})$	298.15	-1.104	0.187	0.333	-0.650	0.002
		308.15	-1.431	-0.288	-	-	0.014
		318.15	-1.580	-0.014	-0.254	-0.777	0.002
	$\Delta\eta$ / $(mPa \cdot s)$	298.15	-0.195	-0.080	-0.108	-0.059	0.001
		308.15	-0.141	-0.090	-0.090	-	0.002
		318.15	-0.148	-0.105	-0.111	-0.022	0.000
	$\Delta K_S \times 10^{12}$ / (Pa^{-1})	298.15	-59.821	-34.96	6.201	66.24	0.063
	ΔL_f / Å	298.15	-0.013	0.015	-	-	0.001
	ΔZ / $(Kg \cdot m^2 \cdot s^{-1})$	298.15	86.912	106.635	-	-	1.712

Contd.

Acetonitrile + 1,4-Dioxane	$V^E \times 10^6$ / $(m^3 \cdot mol^{-1})$	298.15	-1.069	-0.714	0.219	0.424	0.005
		308.15	-1.380	-0.368	-0.180	-	0.006
		318.15	-1.771	-0.377	-	-	0.009
	$\Delta\eta$ / $(mPa \cdot s)$	298.15	-0.583	-0.279	-0.115	-	0.003
		308.15	-0.365	-0.112	0.131	0.102	0.001
		318.15	-0.408	-0.168	0.066	0.332	0.001
	$\Delta K_S \times 10^{12}$ / (Pa^{-1})	298.15	-70.221	-41.531	31.130	46.671	0.101
	ΔL_f /Å	298.15	-0.031	-0.021	0.014	0.023	0.001
	ΔZ / $(Kg \cdot m^2 \cdot s^{-1})$	298.15	213.983	113.683	-36.983	-77.647	0.163

Table 7

Parameters of McAllister Model, Herric and Brewer Parameters and Standard Deviations for Kinematic Viscosities at Various Temperatures.

Binary System	T/K	McAllister (three body model)			McAllister (four body model)				Herric and Brewer parameter			
		υ_{12}	υ_{21}	σ	υ_{1112}	υ_{1122}	υ_{2221}	σ	$a \times 10^2$ / $cm^2\,s^{-1}$	$b \times 10^2$ / $cm^2\,s^{-1}$	$c \times 10^2$ / $cm^2\,s^{-1}$	σ
Acetonitrile + Tetrahydrofuran	298.15	0.4472	0.4953	0.004	0.4422	0.4809	0.3976	0.001	-0.1092	-0.0851	-0.1719	0.009
	308.15	0.3992	0.4621	0.004	0.3961	0.4358	0.4554	0.001	-0.6990	-0.0797	-0.0048	0.002
	318.15	0.3481	0.4175	0.015	0.3499	0.3967	0.1921	0.003	-0.2939	-0.2417	-0.4706	0.025
Acetonitrile + 1,3-Dioxolane	298.15	0.3181	0.4772	0.025	0.3339	0.4365	0.0950	0.011	-0.7160	-0.5678	-1.2469	0.063
	308.15	0.3028	0.4280	0.021	0.3204	0.4244	0.2383	0.005	-0.4759	-0.2327	-0.7290	0.026
	318.15	0.2541	0.3887	0.023	0.2739	0.3861	0.1297	0.006	-0.4963	-0.4096	-0.9001	0.042

Contd.

Acetonitrile + 1,4-Dioxane	298.15	0.3131	0.8765	0.054	0.2817	0.5868	0.0175	0.025	-1.8590	-2.0151	-2.7610	0.187
	308.15	0.4955	0.0428	0.031	0.4467	0.2183	0.8251	0.025	-0.5120	-3.4702	-2.8854	0.154
	318.15	0.3815	0.2167	0.046	0.3034	0.0921	0.6748	0.046	-0.7564	-5.1889	-4.3310	0.230

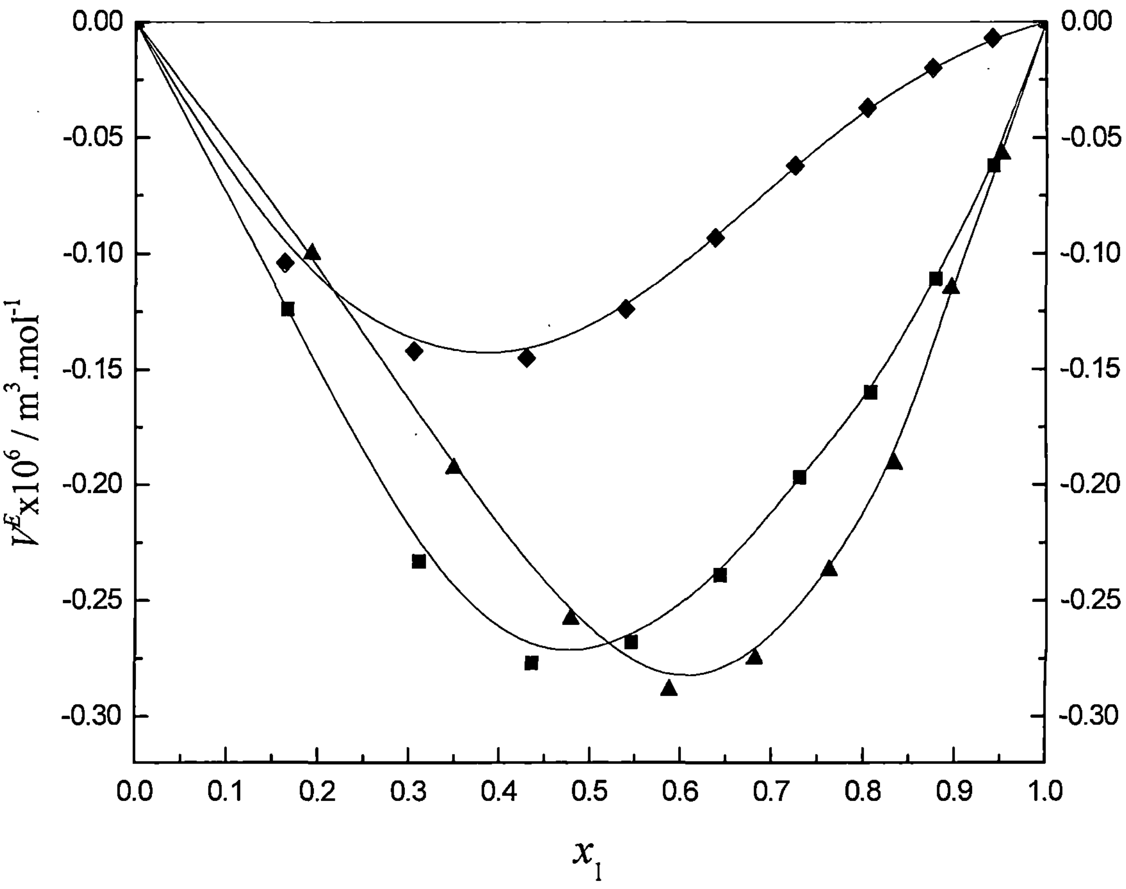

Figure1.
Excess molar volumes (V^E) for binary mixtures of Acetonitrile (1) with◆, Tetrahydrofuran; ▪, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

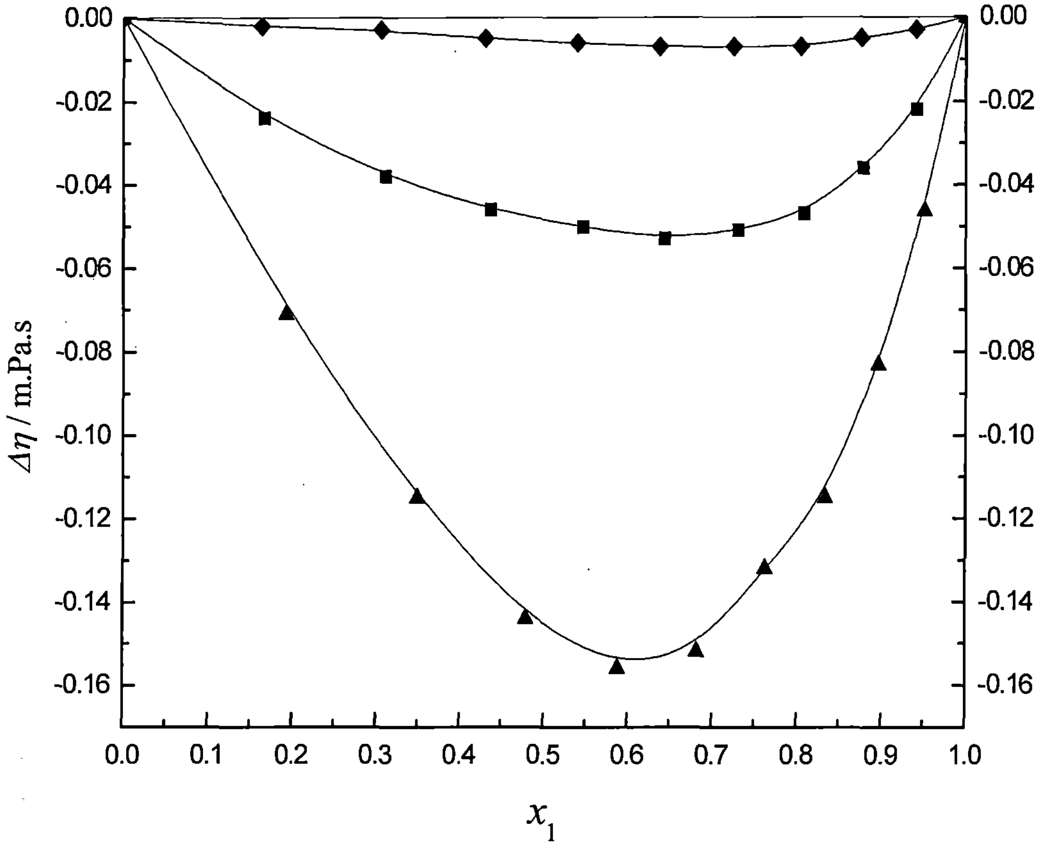

Figure2.

Viscosity deviations ($\Delta\eta$) for binary mixtures of Acetonitrile (1) with◆, Tetrahydrofuran; ■, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

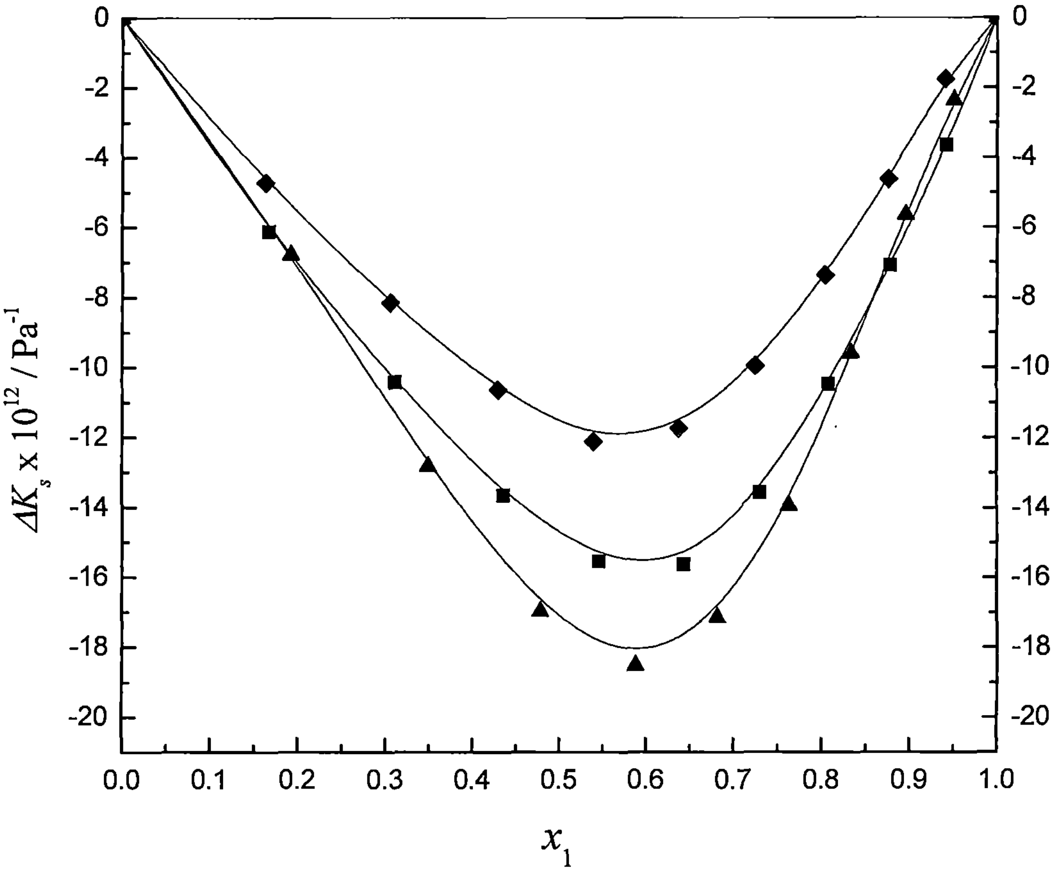

Figure3.

Deviations in isentropic compressibility (ΔK_S) for binary mixtures of Acetonitrile (1) with◆, Tetrahydrofuran; ▪, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

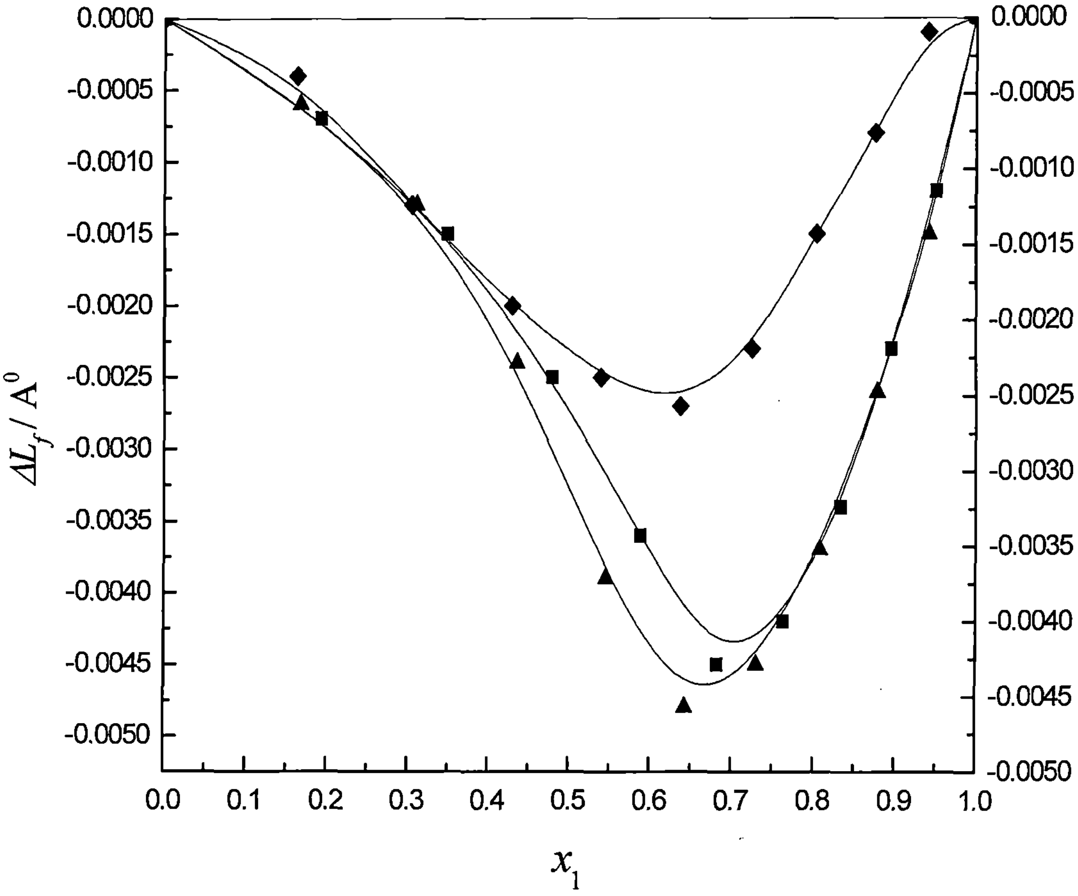

Figure4. Deviations in intermolecular free length (ΔL_f) for binary mixtures of *Acetonitrile (1) with◆, Tetrahydrofuran; ■, 1,3-Dioxolane; ▲, 1,4-Dioxane at* 298.15 K.

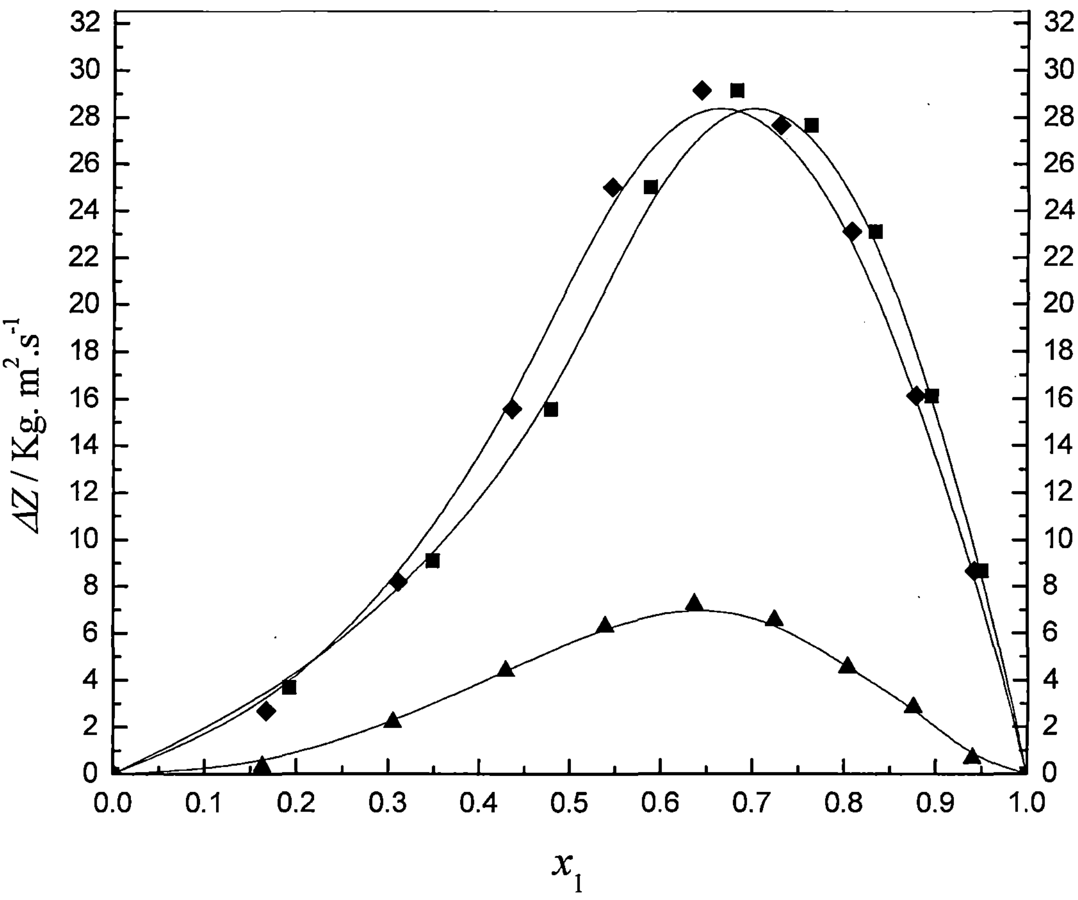

Figure5. Deviations in specific acoustic impedance (*ΔZ*) for binary mixtures of Acetonitrile (1) with ◆, Tetrahydrofuran; ■, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

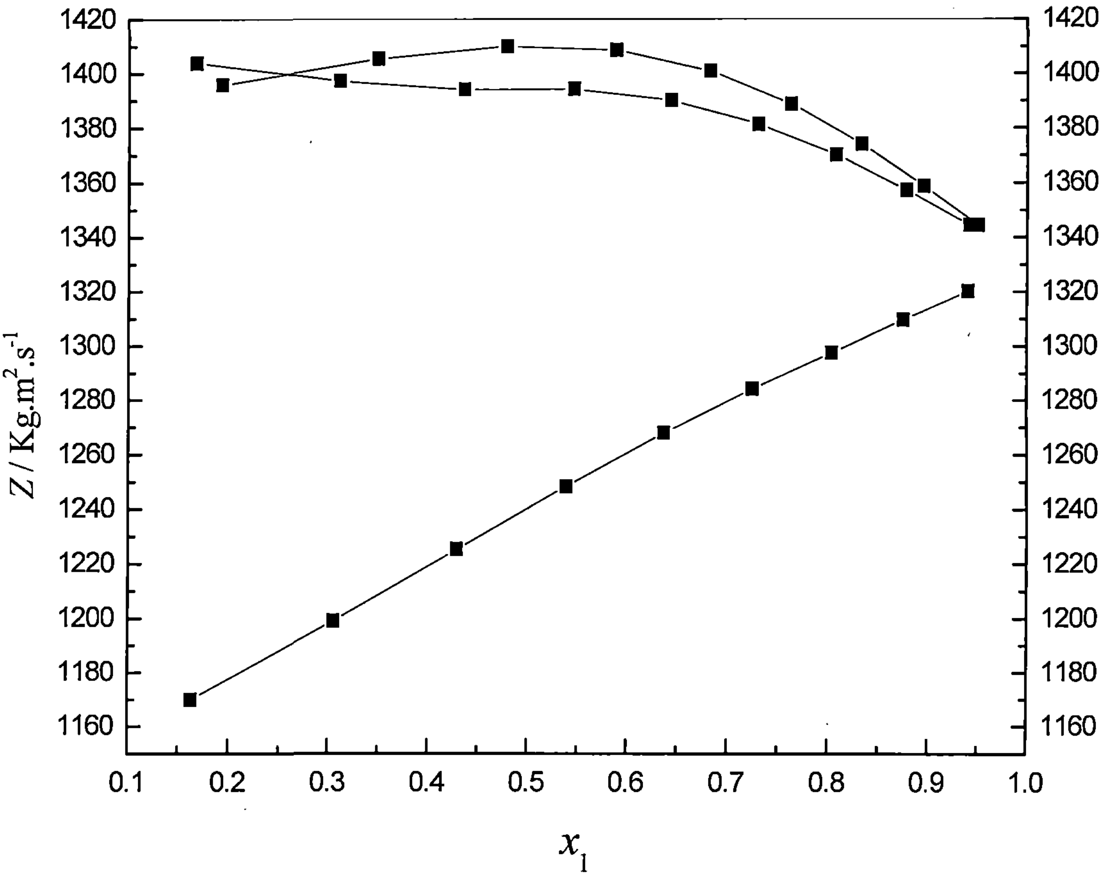

Figure6. Z values for binary mixtures of Acetonitrile (1) with ♦, Tetrahydrofuran; ■, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

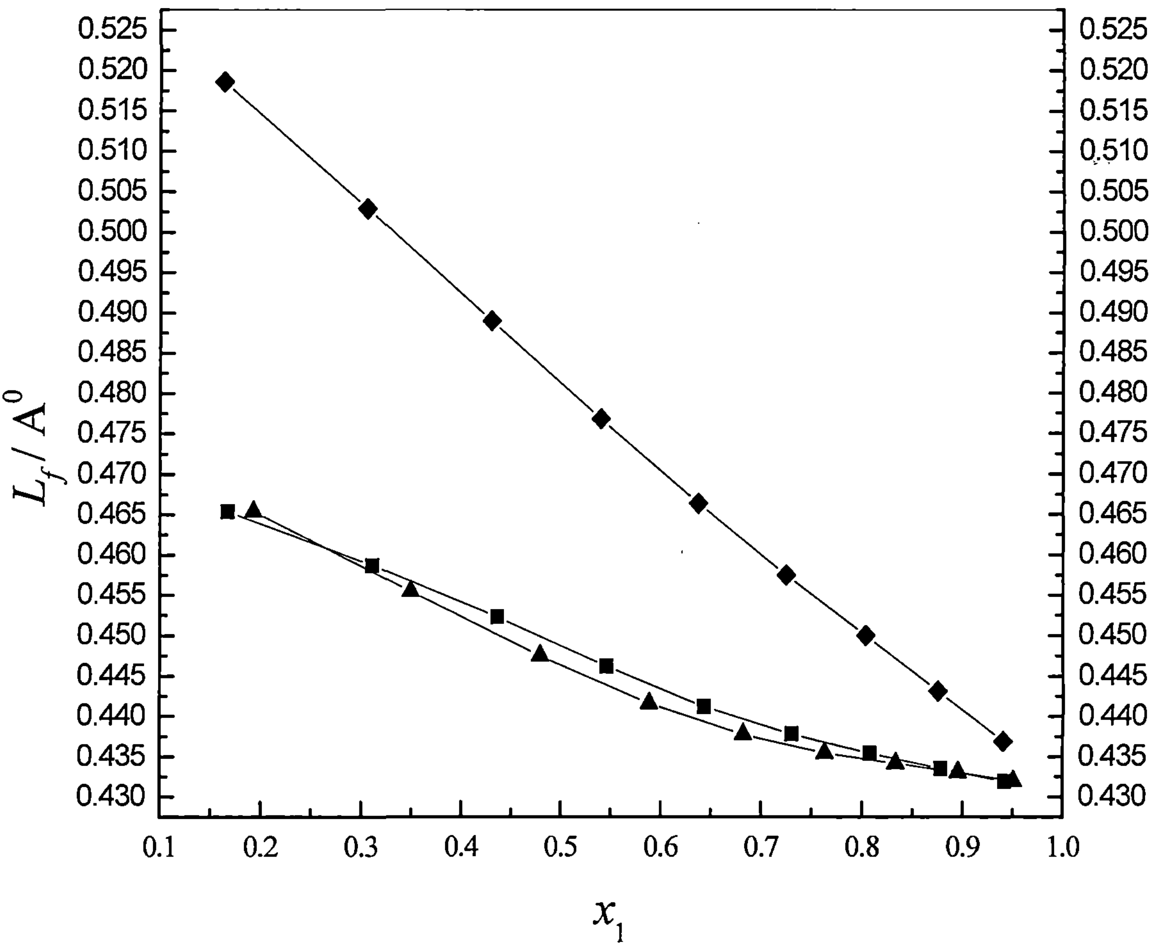

Figure7. L_f values for binary mixtures of Acetonitrile (1) with ◆, Tetrahydrofuran; ■, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

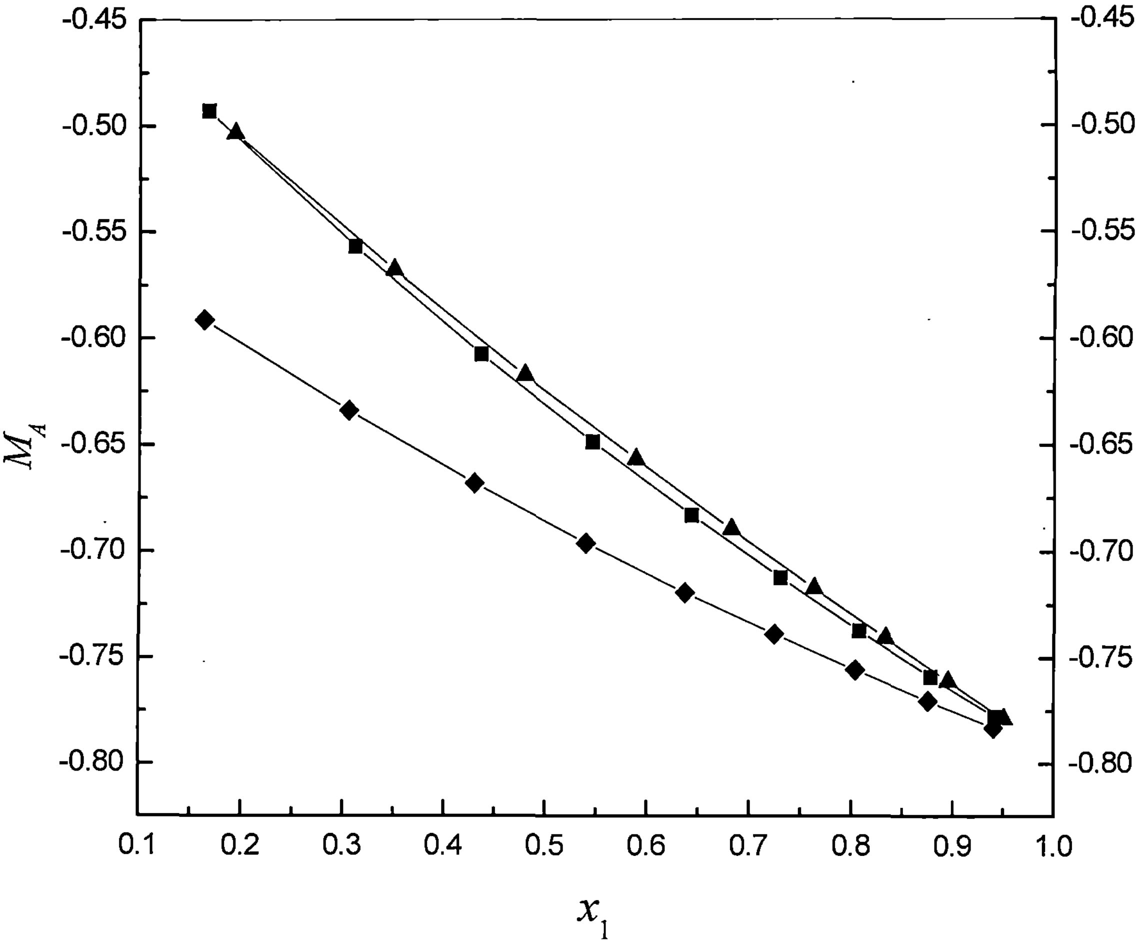

Figure9. M_A values for binary mixtures of Acetonitrile (1) with◆, Tetrahydrofuran; ▪, 1,3-Dioxolane; ▲, 1,4-Dioxane at 298.15 K.

CHAPTER V

Volumetric, viscometric and acoustic studies of binary mixtures of 2-ethoxy ethanol with 1-alkanols at 298.15 K*

5.1. Introduction

The volumetric and viscometric properties of mixed solvent systems and their dependence on composition find applications in many important chemical, industrial, and biological processes. Such systems find industrial applications such as heat transfer, fluid flow, and so forth. The study of functions such as excess molar volume, deviation in viscosity, excess free energy of activation of viscous flow, excess isentropic compressibility, etc. of binary liquid mixtures are useful in understanding the nature and strength of molecular interactions between the component molecules [1-3].

The present work deals with the study of excess thermodynamic and transport properties of some non - aqueous binary liquid mixtures. The liquids under investigation have been chosen on the basis of their industrial applications. The alkoxyethanols and alkanols are good industrial solvents which occupiers an important place in many industrial processes such as pharmaceutical and cosmetics industry and have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures.[4-9]

In this chapter, we extend our studies to the binary mixtures formed by 2-Ethoxy ethanol represented as (1) with eight monoalcohols, represented as (2), including Methanol, Ethanol, 1-Propanol, 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Heptanol and 1-Octanol at 298.15 K. The various thermodynamic properties such as excess molar volume (V^E), viscosity deviations($\Delta\eta$) and Gibbs excess free energy of activation for viscous flow (ΔG^{*E}) obtained from experimental observations have been rationalized. 2-Ethoxy ethanol and the monoalcohols have both a proton donor and a proton acceptor group. It is expected that there will be a significant degree of H-bonding leading to self-association in pure state in addition to mutual association in. their binaries. [10]

Besides this, isentropic compressibilities as well as deviations in isentropic compressibility (ΔK_S) calculated from measured speed of sound (u) of 2-Ethoxy ethanol

Published in Physics and Chemistry of Liquids and monoalchol mixtures are presented at 298.15K. The measurement of ultrasonic speed enables the accurate determination of isentropic compressibility coefficients (K_S) which can be used to provide qualitative information about the physical nature of the aggregates occurring in the liquid phase. To investigate the nature of the interactions, various thermodynamic parameters such as specific acoustic impedance [11](Z), intermolecular free length (L_f) [12], Vander Wall's constant (b) [13], molecular radius (r) [12], geometrical volume (B), molar surface area (Y), available volume (V_a) [12], molar speed of sound (R) [14], collision factor (S)[15] and molecular association (M_A), [16] has been calculated using the sound speed and density of the mixtures and pure solvents which are sensitive to interaction between solute and solvent. These properties for the mixtures studied are presented, compared and analyzed. A comparative study of the sound speeds calculated using different theoretical formulations and equations with the experimentally measured value is also performed, the results are represented graphically and the standard deviation in each case has been reported.

5.2. Experimental Section

5.2.1. *Materials*

2-Ethoxy ethanol, Merck, India, was purified as described elsewhere [17] and is also mentioned chapter III. Methanol, Ethanol, Propanol, 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Heptanol and 1-Octanol (S. D. Fine Chemicals, Analytical Reagent, Purity > 99%) were used. Their methods of purification are also mentioned in chapter III. The liquids were stored over molecular sieves. The density, viscosity and the sound speeds of the mixtures were determined immediately after mixing. The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature as listed in Table 1.

5.2.2. *Apparatus and Procedure*

The details of the methods and techniques for determination of the parameters i.e. density (ρ), viscosity (η) and ultrasonic speed (u) were described in earlier papers[17-19]and have been included in Chapter III. The weights were taken accurate to 0.0002 g. The precision of the speed of sound, density and viscosity measurements are ± 0.2 m. s^{-1}, ± 3 × 10^{-4} kg. m^{-3} and ± 2 × 10^{-4} poise (P) respectively.

5.3. *Results and Discussion*

The experimentally measured densities (ρ) and viscosities (η) of the pure liquids at 298.15 K along with the reference values are recorded in table 1.

The values of experimental density (ρ) and viscosity (η), the excess properties, (V^E, $\Delta\eta$ and ΔG^{*E}) along with the interaction parameters (d_{12}, T_{12}, H_{12}) of the studied mixtures are recorded in table 2 and the corresponding graphs for V^E and $\Delta\eta$ against the mole fractions of 2-ethoxy ethanol (x_1) are marked as Figure 1 and Figure 2 respectively.

5.3.1 *Excess molar volume*

The excess molar volumes (V^E) were calculated using the molar masses (M_i) and densities of the pure liquids and the mixtures using the following equation, [6, 23]

$$V^E = \sum_{i=1}^{j} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \tag{1}$$

where, M_i, ρ_i, x_i are the molar mass, density, mole fraction of the ith component and ρ is the density of the mixture respectively.

From figure1, we observe that, for the binary mixtures studied here, the V^E values gradually changes from higher negative to less negative values and finally turns positive with the increase of chain length along the alcohol homologous series. It has the highest negative value for methanol and ultimately turns positive for the higher alkanols. V^E values are negative for Methanol, Ethanol, 1-Propanol and then they turn gradually more and more positive from 1-Butanol to 1-Octanol. Positive V^E values for higher alkanols and negative V^E values for lower alkanols were also reported by some other workers [21-23]. The observed trend in terms of negative values of V^E in 1- alkanol + 2-Ethoxy ethanol mixture is:

Methanol > Ethanol > 1-Propanol > 1-Butanol >1-Pentanol > 1-Hexanol > 1-Heptanol >1-Octanol

Such behavior is the result of contribution from several contraction and expansion processes which proceed simultaneously when 2-Ethoxy ethanol-- alkan-1-ol molecules are formed. The following effects can be considered: (a) disruption of liquid order on mixing and unfavorable interactions between unlike molecules producing a positive contribution of V^E; (b) contraction due to free volume difference of unlike molecules and (c) possible association through hydrogen bond formation between alkan-1-ol and 2-Ethoxy ethanol producing a negative contribution to V^E.

The alkanols are known to be extremely self associated through H- bonding and *in 2-Ethoxy ethanol also self association through H- bonding is present.* [24]. *Mixing of 1-*Alkanols to 2- Ethoxy ethanol can be expected to bring changes in the H-bonding equilibria and electrostatic interactions with different resultant contributions in the volume of mixing. *The negative values obtained for lower 1- alkanols suggest that the* interaction between the unlike molecules exceed the structure breaking effect between the like molecules. These interactions are relatively strong between 2-Ethoxy ethanol *and Methanol molecule thereby showing the highest negative* V^E *value for their binary mixture. . Increasing the chain length of the alkanols tends to dilute this unlike* interaction and finally for the higher alkanols this unlike interaction becomes *unfavorable producing a positive contribution of* V^E.

5.3.2 *Viscosity deviations*

The deviation in viscosities from linearity ($\Delta\eta$) can be computed using the relationship,

$$\Delta\eta = \eta - \sum_{i=1}^{j} (x_i \eta_i) \qquad (2)$$

The values of $\Delta\eta$ Figure2 are positive for Methanol and Ethanol and decreases *regularly as the size of the alkan-1-ol is increased. The positive* $\Delta\eta$ *values indicate the* predominance of H-bonding interactions between the unlike molecules over the dissociation effects of the mixing components[25, 26]. This results in a liquid structure *where the flow is rather difficult than would be expected on the basis of the viscosities* of the pure components.

It is known that the strength of the molecular hydrogen bonding is not only factor influencing the viscosity deviations in liquid mixtures. [27, 28] The molecular size and shape of the components and average degree of association of the mixture are equally important factors. The negative values of $\Delta\eta$ for higher alkanols indicate that the average degree of cross- association of mixtures gradually decreases as the chain length of alkan-1-ol is increased [27, 29]. Thus, larger the chain length of 1-alkanol, the greater is the decrease in the average degree of association, as a result more negative deviations in viscosity versus mole fraction curve are observed. These conclusions are supported by the conclusions drawn from V^E values.

5.3.3 *Excess Gibbs energies for activation of viscous flow (ΔG^{*E}):*

It has been reported that, ΔG^{*E} parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. [38, 30]

On the basis of the theories of absolute reaction rates [40], the excess Gibbs energy of activation for viscous flow (ΔG^{*E}) was calculated from the equation, [41]

$$\Delta G^{*E} = RT\,[\,\ln\eta V - \sum_{i=1}^{j}(x_i \ln\eta_i V_i)] \tag{3}$$

According to Reed and Taylor and Meyer et. al. positive ΔG^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces [38,39].

The magnitude of the positive value of ΔG^{*E} is an excellent indicator of the strength of specific interactions. From the ΔG^{*E} values recorded in table2, it is seen that, these values are negative or positive keeping similarity with the $\Delta\eta$ values and thereby supports our conclusion drawn from V^E and $\Delta\eta$ considerations.

5.3.4 *Correlating equations:*

Apart from expressing η as a polynomial fit, several semi empirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure component data. [39, 31] We have examined equations proposed by Grunberg-Nissan, Tamura-Kurata and Hind et al.

The single parameter Grunberg-Nissan equation [32] reads as:

$$\eta = \exp[\sum_{i=1}^{j}(x_i \ln\eta_i) + d_{12}\prod_{i=1}^{j} x_i] \tag{4}$$

where d_{12} is a parameter proportional to the interchange energy and has been regarded as an approximate measure for the non-ideal behaviors of binary mixtures.

Tamura-Kurata [33] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i\phi_i\eta_i + 2T_{12}\prod_{i=1}^{j}[x_i\phi_i]^{1/2} \qquad (5)$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of ith pure component in the mixture.

The following viscosity model of Hind et al [34] may also interpret molecular interactions

$$\eta = \sum x_i^2\eta_i + 2H_{12}\prod_{i=1}^{j} x_i \qquad (6)$$

where H_{12} is the interaction parameter.

The interaction parameters have their merits in ascertaining the strength of molecular interactions in binary mixtures. Among the three parameters determined here, the Grunberg-Nissan parameter provides the best measure to ascertain the strength of interaction. At any given composition, the variation of d_{12} with strength of interaction is similar to that of $\Delta\eta$, being negative for systems in which dispersion forces are dominant, becoming less negative and then increasingly positive as the strength of interaction increases[25,34-36].

According to Fort and Moore [25] the values of T_{12} and H_{12} are not very different except where the values of the components differ considerably. Further T_{12} and H_{12} show some variation with composition although this is only large for systems where there is a strong specific interaction between the components. There is a tendency of T_{12} and H_{12} at a certain composition to increase with the strength of interaction of the components but this is not well defined and T_{12} and H_{12} can not generally be regarded as a measure of the strength of interaction. [37]

A perusal of table2 shows that the variations and signs of d_{12} are similar to those of $\Delta\eta$ and thereby supports our conclusion. It is also seen that, T_{12} and H_{12} values are positive for all binary mixtures and are almost identical and do not change appreciably with the change of composition of binary mixtures.

5.3.5 *Isentropic compressibility*

Table 5 contains the sound velocity (u), isentropic compressibility (K_S) and deviations in isentropic compressibility (ΔK_S) data for the binary mixtures at 298.15 K.

Isentropic compressibility K_S and deviations in isentropic compressibility ΔK_S were calculated from experimental densities, ρ, and speeds of sound u , using the following equations

$$K_S = (u^2 \rho)^{-1} \tag{7}$$

$$\Delta K_S = K_S - \sum_{i=1}^{j} (x_i K_{s,i}) \tag{8}$$

where, K_S, gives the isentropic compressibility for the i th component of the mixture

The ultrasonic speeds are given in table 3, together with the isentropic compressibility K_S and deviations in isentropic compressibility ΔK_S for 2-Ethoxy ethanol + 1-alkanol mixtures at 298.15 K. Experimental values for ΔK_S are plotted against mole fraction of 2-Ethoxy ethanol in Fig. 3

We have attempted to explain the physico-chemical behavior of the mixtures in order to know the nature of molecular interactions between the components by various acoustical parameters calculated using the speeds of sound and density data. Various parameters such as specific acoustic impedance Z, intermolecular free length L_f, Vander Waal's constant b, molecular radius r, geometrical volume B, molar surface area Y, available volume V_a, molar speed of sound R, relative association, R_A, collision factor S and molecular association M_A has been calculated using the following relations:

$$L_f = K \sqrt{K_S} \tag{9}$$

$$Z = u\rho \tag{10}$$

$$b = \left(\frac{M}{\rho}\right) - \left(\frac{RT}{\rho^2 u^2}\right)\left\{\left[1 + \left(\frac{Mu^2}{3RT}\right)\right]^{\frac{1}{2}} - 1\right\} \tag{11}$$

$$r = \left(\frac{3b}{16\pi N}\right)^{\frac{1}{3}} \tag{12}$$

$$B = \frac{4}{3}\pi r^3 N \tag{13}$$

$$Y = \left(36\pi N B^2\right)^{\frac{1}{3}} \tag{14}$$

$$V_a = V - \left(1 - \frac{u}{u_\infty}\right) \tag{15}$$

$$V_0 = V - V_a \tag{16}$$

$$R = \frac{Mu^{\frac{1}{3}}}{\rho} \tag{17}$$

$$R_A = \left(\frac{\rho_{mix}}{\rho}\right)\left(\frac{u}{u_{mix}}\right)^{\frac{1}{3}} \tag{18}$$

$$M_A = \left(\frac{u_{mix}}{\sum_{i=1}^{2} x_i u_i}\right)^2 - 1 \tag{19}$$

where K is a temperature dependent constant, V_0 is volume at absolute zero, u_∞ is taken as 1600 ms^{-1}. These parameters are listed in Table 4for the pure components and in Table 5 for the binary mixtures. Plots of L_f, Z, V_a and R against the mole fraction of 2-Ethoxy ethanol (x_1) are shown in figures (4), (5), (6) and (7) respectively.

It is observed that, the value of specific acoustic impedance Z increases with increasing x_1 for all the mixtures, while the L_f behaves in an opposite manner. The graphs do not show any sudden variation in their behaviour, thereby implying the absence of complex formation. [16]

The R_A values increase with increasing x_1 for all the mixtures which signifies that the 1-2 interactions in these mixtures are not strongly dissociative. The decrease in L_f and V_a with increase in x_1 indicates significant interaction between the mixing molecules. [28]

From Fig 3, it is evident that the ΔK_S values are negative for lower monoalcohols but the magnitude of negative values diminishes and the positive values increases with the increasing chain length of the alcohols. The values of ΔK_S in terms of negativity are enhanced by the following order: -

Methanol > Ethanol > 1-Propanol > 1-Butanol >1-Pentanol > 1-Hexanol > 1-Heptanol >1-Octanol

These results can be explained in terms of molecular interactions and structural effects. Positive ΔK_S values are due to the breaking of interactions and the corresponding disruption of molecular order in the pure components [42]. The donor-acceptor interaction between the 2-Ethoxy ethanol and the alcohols play an important part for the mixtures containing lower alcohols like Methanol, Ethanol, 1-Propanol where there is strong specific interaction between the component molecules leading to negative value of ΔK_S. Interactions between the molecules of 2-Ethoxy ethanol or monoalcohols are broken in the mixing process; the breaking leads to positive ΔK_S values for the mixtures containing higher chain length of alcohols as compared to the lower alcohols. There is a parallel in the qualitative behaviour of $\Delta\eta$ and V^E curves.

5.3.6 *Redlich-Kister polynomial equation*

The excess properties (V^E, $\Delta\eta$, ΔG^{*E} and ΔK_S) were fitted to the Redlich-Kister polynomial equation [43],

$$Y^E = x_1 x_2 \sum_{i=1}^{K} A_i (x_1 - x_2)^i \qquad (20)$$

where Y^E refers to excess properties, x_1 is the mole fraction of 2-Ethoxy ethanol and x_2 is that of the other component of the binary mixtures respectively. The coefficients (A_i) were obtained by fitting eqn. 20 to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The calculated values of A_i along with the tabulated standard deviations (σ) are listed in Table 6. The standard deviation (σ) was calculated using the equation,

$$\sigma = \left[\frac{(Y^E_{\exp} - Y^E_{cal})^2}{(n - m)} \right]^{\frac{1}{2}} \qquad (21)$$

where *n* is the number of data points and *m* is the number of coefficients.

5.3.7 *Predictions of sound speeds*

The sound speeds of binary mixtures are often predicted by free length theory (FLT), collision factor theory (CFT), the Nomoto Equation, the Vandeal Vangael ideal mixing relation (V V), the impedance dependence relation (I D) etc. For comparison, the theoretical values of the sound speed u has been calculated by using the above five theories and empirical equations. The following final relations were used for calculating sound speeds:

According to FLT [12], the speed of sound is given by,

$$u_{FLT} = K_s / L_f \rho^{1/2} \tag{22}$$

The free length L_f is obtained by:

$$L_f = \frac{(V - \sum_i x_i V_{0i})}{\sum_i x_i y_i} \tag{23}$$

where, V_{0i} is the molar volume of the pure component i at absolute zero and is given by Sugden's formula,

$$V_{0i} = V_i \left(\frac{1-T}{T_{ci}} \right)^{0.3} \tag{24}$$

where T_c is the critical temperature for the pure components. Y_i is the surface area per mole for the pure component I and is given by,

$$Y_i = \left(36 \pi N V_{0i}^2 \right)^{1/3} \tag{25}$$

Collision factor theory [15],

$$u_{CFT} = u_\infty [x_1 S_1] + [(x_1 B_1 + x_2 B_2)/V_{12}] \tag{26}$$

Nomoto equation, [56]

$$u_N = [(x_1 R_1 + x_2 R_2)/(x_1 V_1 + x_2 V_2)]^3 \tag{27}$$

Vandeal Vangael [57] ideal mixing relation

$$\frac{1}{x_1 M_1 + x_2 M_2} - \frac{1}{u_{mix}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \tag{28}$$

Impedance dependence relation [58, 59]

$$u = \frac{\sum x_i Z_i}{x_i \rho_i} \tag{29}$$

where, K_S, S, B, R, Z, ρ are the isentropic compressibility, collision factor, geometrical volume, molar speed of sound, specific acoustic impedance and density respectively for pure 2-ethoxy ethanol (1), 1-alkanols (2), and the mixtures (12) respectively. u_∞ is a constant value taken as1600ms^{-1}.

The compositional dependence of the experimental and sound speeds calculated by the free length theory(FLT),collision factor theory(CFT)and the Nomoto Equation of the binary mixtures of 2-ethoxy ethanol and 1-alkanols are shown in figures 9 (a - h).The results show that, the Nomoto equation and the Collision factor theory predicts the experimental data extremely well, whereas the Free length theory gives the maximum deviation for the present set of binary mixtures. Table 7 summarizes the deviations for different prediction methods. Based on deviation values obtained, the following order for the relative predictive capability for each of the methods is obtained,

Nomoto ≥ CFT > I D ≥ V V > FLT

5.4. *Conclusions*

In this work, eight binary mixtures formed by 2-Ethoxy ethanol with eight monoalcohols have been studied in terms of excess molar volumes, viscosity deviations, acoustic impedance, intermolecular free length , isentropic compressibility and interaction parameters. It is seen that, increasing the chain length of the alkanols tends to dilute the unlike interaction and finally for the higher alkanols this unlike interaction becomes unfavorable. The theoretical values of the sound speed were calculated by using the free length theory, collision factor theory, the Nomoto Equation, the Vandeal Vangael ideal mixing relation, the impedance dependence relation and compared with the experimentally measured sound speed. The results showed that, the Nomoto equation and the Collision factor theory predicts the experimental data extremely well, whereas the Free length theory gives the maximum deviation for the experimental set of binary mixtures.

References

1. B. Gracia, R. Alcalde, J. M. Leal, and J. S. Matos, *J. Chem. Soc. Faraday Trans.* **1996** *92*, 3347.

2. Y. Mahan, C. N. Liew, and A. E. Mather, *J. Solution Chem.* **2002**,*31,* 743.

3. A. Ali, Abida, S. Hyder, and A. K. Nain, *Collect. Czech. Chem. Comm.* **2002**, *67,* 1125.

4. M. N. Roy, A. Choudhury, and A. Sinha, *J. Teach. Res. Chem.* **2004**, *11,* 12.

5. D. K. Hazra, M. N. Roy, and B. Das, *Indian J. Chem. Techno.* **1994**, *1,* 93.

6. M. N. Roy and A. Choudhury, *J. Teach. Res. Chem.* **2000**, *1,* 17.

7. M. N. Roy, B. B. Gurung, and A. Choudhury, *J. Indian Chem. Soc.* **2004**, *81,* 1.

8. S. L. Oswal and H. S. Desai, *Fluid Phase Equilib.* **1999**, *161,* 191.

9. S. L. Oswal and H. S. Desai, *Fluid Phase Equilib.* **2001**, *186,* 81.

10. S. L. Oswal, and K.D.Prajapati, *J. Chem. Eng. Data.* **1998**, *43,* 367.

11. R. K. Dewan, C. M. Gupta, and S. K. Mehta, *Acoustica.* **1998**, *65,* 245.

12. . B. Jacobson *J. Chem. Phys.* **1952**, *20,* 927.

13. W. Schaaffs, *Acoustica.* **1975**, *33,* 272 .

14. M. R. Rao *Indian J. Chem.*, **1940**, *14,* 109.

15. W. Schaaffs, *Z. Phys.* **1974**, *114,* 110.

16. S. K. Mehta, R. K. Chauhan ,and R. K. Dewan, *J. Chem. Soc. Faraday Trans.* 1. **1966**, *92,* 1167.

17. D.D. Perrin, W.L.F.Armarego, Purification of Laboratory Chemicals, Great Britain, 3rd ed., **1988**

18. J. R.Suindells and T. B.Godfray, *J. Res. Natd. Bur. Stand.* **1952**,*48,* 1.

19. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data,* **2001**, *46* , 1247.

20. M.N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data,* **2004**, *49* , 291.

21 P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo,, A. H. Roux and G. Desgranges *J. Chem. Eng. Data,* **1999**, *44,* 1341.

22. Prandharinath S. Nikam, Laxman N. Shirsat and Mehdi Hassan. *J. Chem. Eng. Data.* **2000**, *77,* 244.

23. S. K. Mehta,R. K. Chauhan and R. K. Dewan. *J Chem. Soc.,Faraday Trans.* **1996**, *92 (7),* 1167.

24. N. V. Shastry. And S. R. Patel., *International Journal of Thermophysics.* **2000**, *21,* 1153.

25. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.* **1966**, *62,* 1112.
26. R. K. Nigam & P.P. Singh., *Indian J. Chem,* **1971**, *9,* 1691.
27. S. L. Oswal, H. S. Desai, *Fluid Phase Equilibria*. **2001**, *186,* 81.
28. A. Pal and R. K. Bhardwaj, *Z. Phys. Chem.* **2002**, *216,* 1033.
29. S. L. Oswal, P. Oswal, A. T. Patel *J. Chem. Eng .Data.* **1995**, *40,* 607.
30. R. C. Reid,J.M. Prausnitz, B.E. Poling. The properties of gases and liquids, 4th Mcgraw-Hill International, **1987**
31. L. Grunberg and A. H. Nissan, *Nature.* **1949**, *164,* 799.
32. M. Tamura, M. Kurata, *Bull. Chem. Soc. Jpn.* **1952**, *25,* 32.
33. R. K. Hind, E. McLaughlin, A. R. Ubbelohde *Trans. Faraday. Soc,* **1960**, *56,* 328.
34. K. Ramamoorthy. *J of Pure and Appl. Phys.* **1973**, *11,* 556.
35. J.B. Irving,Viscosity of liquid mixtures NEL Report No. 630 and 631,National Engineering Laboratory,East Kilbride,Glassgow,**1977**.
36. T. M. Reed and T. E. Taylor, *J. Phys. Chem,* **1959**, *63,* 58.
37. R. Meyer, M. Meyer and J. Metzer, A. Peneloux. *Chem. Phys,* **1971**, *62,* 406.
38. A.W.Quin, D. F. Hoffmann and P. Munk, *J. Chem. Eng. Data.* **1992**, *37,* 55.
39. S.Glasstone, K. J. Laidler and H.Eyring, The Theory of Rate Process, McGraw-Hill, New York, **1941**, 514.
40. . R. J. Fort and W. R. Moore, *Trans. Faraday. Soc.* **1965**, *61,* 2102.
41. O. Redlich and A. J. Kister, *Ind. Eng. Chem.* **1948**, *40,* 345.
42. T.M.Aminabhabiand B. Gopalkrishna., *J.Chem.Eng. Data,* **1995**, *40,* 632.
43. Hidekazu Doe, Toyokichi Kitagawa, Kiyomi Sasabe, *J.Phys. Chem.* **1984**, *88,* 3341.
44. Hsu-Chen Ku, Chein - HsuinTu, *J.Chem.Eng Data.* **2005**, 50, 1060.
45. A. Ali, A. K. Nain, D. Chand and R. Ahmad, Physics *and Chemistry of Liquids,* **2005**, *43,* 205.
46. E. Jimenez, H. Casas, L. Segade, and C. Franjo. *J. Chem. Eng .Data.* **2000**, *45,* 862.
47. A. K. Covington, T. Dickinson, Physical Chemistry of Organic Solvents Systems, Plenum Publishing Company Ltd., London, 1973.
48. N. V. Sastry and M. K. Voalnd, *International J. Themophysics.* **2000**, 21*(5),* 1153.
49. G.Douheret, A. Pal. And M.I. Davis, *J. Chem. Thermodyn.* **1990**, *22,* 99.
50. David R, Lide, CSIR Handbook of Chemistry and Physics, 7th edition, **1990-1991**

51. J. M. Resa, C. Gonzalez, and J. M. Goenaga Mixtures of . *Chem. Eng. Data.* **2005**, *50* 1570.

52. T.A.Aminabhabi, T.S. Aralaguppi, S. B. Hargoppad,and R.H. Balangdi, J.Chem. Eng. Data **1983**, *28*, 324.

53. George Ritzoulis, Doukeni Missopolinou, Stauroula Doulami, and Costas Panayiotou*,*J. Chem. Eng. Data*, **2000**,*45,* 636 .

54. T. M. Aminabhavi, V. B. Patil *J. Chem. Eng. Data.,* **1998**, *43,* 504.

55. O. Nomoto, *J. Phys. Soc. Jpn.* **1958**, *13*, 298.

56. V. Tiwari. And L. R. Mishra. *Acoustica,* **1981**, *48*, 257.

57. M. Kalidoss., R. Srinavasamorthy.,*J. Pure Appl. Ultrason.* **1997**, *9*, 4.

58. J. D. Pandey and K. Shukla., *J. Pure Appl, Phys.* **1993**, *15*, 37.

59. Tasi, F. N *J. Chem. Eng. Data,* **1994**, *39*, 441.

60. I. Johnson, M. Kalidoss, R. Srinavasamorthy., *J. Chem. Eng. Data.* **2002**, *47*, 1388.

TABLE 1.

Comparison of density (ρ), viscosity (η) and sound speeds (u) with Literature Data at 298.15 K.

Pure Liquid	$\rho \times 10^3$ / (kg·m^{-3})		η /(mPa·s)		u /(m·s^{-1})	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
2-ETHOXY ETHANOL	0.9254	0.9253[44]	1.8506	1.851[60]	1309.00	1300.40[51]
METHANOL	0.7866	0.78656[45]	0.5509	0.5422[45]	1104.2	1103.0[52]
ETHANOL	0.7857	0.7851[46]	1.0892	1.088[46]	1142.0	1145.00[53]
1-PROPANOL	0.7993	0.7995[47]	2.0074	2.004[49]	1209.4	1206.5[47]
1-BUTANOL	0.8062	0.8058[48]	2.5571	2.5600[49]	1240.2	1240.00[54]
1-PENTANOL	0.8112	0.8111[48]	3.5104	3.510[50]	1277.2	1277.00[54]
1-HEXANOL	0.8151	0.81515[48]	4.5917	4.590[50]	1328.3	1328.00[56]
1-HEPTANOL	0.82068	0.818 7[59]	5.9368	-	1331.5	1330.00[54]
1-OCTANOL	0.8218	0.8216[48]	7.3646	7.363[50]	1347.7	1347.4[55]

TABLE 2.

Values of density (ρ), viscosity (η), excess molar volume (V^E), viscosity deviation ($\Delta\eta$), excess Gibbs energy of activation for viscous flow (ΔG^{*E}), Grunberg-Nissan, Tamura Kurata and Hind interaction parameters (d_{12}, T_{12}, H_{12}) for binary mixtures of 2-Ethoxy ethanol + Methanol, Ethanol, Propanol, Butanol, Pentanol, Hexanol, Heptanol and Octanol at 298.15 K

x_1	ρ x10^{-3} /(kg.m^3)	η /(mPa.s)	V^E x10^6 /(m^3.mol^{-1})	$\Delta\eta$ /(mPa.s)	ΔG^{*E} /(J.mol^{-1})	d_{12}	T_{12}	H_{12}
2-Ethoxy ethanol + Methanol								
0	0.7866	0.5509	0	0	0			
0.0380	0.7997	0.6216	-0.058	0.021	227.32	1.66	1.22	1.49
0.0816	0.8131	0.7062	-0.118	0.049	454.06	1.81	1.26	1.53
0.1322	0.8267	0.7916	-0.176	0.069	625.16	1.65	1.25	1.50
0.1916	0.8406	0.8844	-0.231	0.085	758.35	1.48	1.25	1.47
0.2623	0.8550	0.9885	-0.298	0.097	852.25	1.32	1.24	1.45
0.3478	0.8694	1.1144	-0.349	0.111	914.00	1.21	1.26	1.45
0.4534	0.8839	1.2555	-0.379	0.115	898.30	1.07	1.27	1.43
0.5871	0.8981	1.4225	-0.350	0.109	787.40	0.95	1.29	1.42
0.7619	0.9117	1.6248	-0.211	0.084	531.16	0.85	1.33	1.43
1	0.9254	1.8506	0	0	0			
2-Ethoxy ethanol + Ethanol								
0	0.7857	1.0892	0	0	0			
0.0538	0.7985	1.1465	-0.058	0.016	72.83	0.45	1.55	1.63
0.1133	0.8115	1.2067	-0.104	0.031	137.4	0.42	1.55	1.63
0.2542	0.8382	1.3413	-0.165	0.059	241.19	0.39	1.56	1.62

Contd...

0.3383	0.8521	1.4165	-0.186	0.070	274.98	0.37	1.57	1.63
0.4341	0.8662	1.4966	-0.194	0.077	290.16	0.36	1.58	1.63
0.5440	0.8806	1.5810	-0.185	0.078	280.19	0.34	1.58	1.63
0.6716	0.8953	1.6690	-0.159	0.068	236.54	0.32	1.59	1.63
0.8215	0.9103	1.7613	-0.099	0.047	150.98	0.31	1.61	1.63
1	0.9254	1.8506	0	0	0			

2-Ethoxy ethanol + Propanol

0	0.7993	2.0074	0	0	0			
0.0690	0.8108	1.9415	-0.037	-0.055	-64.37	-0.43	1.57	1.50
0.1429	0.8224	1.8906	-0.066	-0.094	-111.04	-0.39	1.60	1.54
0.2223	0.8344	1.8521	-0.100	-0.121	-142.92	-0.36	1.63	1.58
0.3078	0.8466	1.8256	-0.114	-0.134	-158.58	-0.33	1.65	1.62
0.4001	0.8591	1.8108	-0.126	-0.135	-158.41	-0.30	1.68	1.65
0.5001	0.8717	1.8056	-0.113	-0.123	-144.40	-0.26	1.71	1.68
0.6088	0.8844	1.8105	-0.075	-0.102	-116.02	-0.23	1.73	1.72
0.7273	0.8976	1.8226	-0.049	-0.071	-78.28	-0.19	1.76	1.75
0.8572	0.9113	1.8386	-0.022	-0.034	-35.95	-0.15	1.80	1.79
1	0.9254	1.8506	0	0	0			

2-Ethoxy ethanol + Butanol

0	0.8062	2.5571	0	0	0			
0.0837	0.8166	2.4339	0.011	-0.064	-54.64	-0.29	1.81	1.79
0.1706	0.8272	2.3117	0.030	-0.125	-112.00	-0.32	1.78	1.76
0.2606	0.8381	2.2060	0.054	-0.167	-154.92	-0.33	1.79	1.77
0.3541	0.8493	2.1129	0.076	-0.194	-186.25	-0.33	1.79	1.78

Contd…

0.4513	0.8609	2.0349	0.088	-0.203	-201.16	-0.33	1.81	1.79
0.5523	0.8729	1.9838	0.087	-0.183	-183.33	-0.30	1.84	1.83
0.6574	0.8854	1.9489	0.074	-0.144	-143.54	-0.26	1.89	1.88
0.7669	0.8984	1.9249	0.048	-0.090	-87.34	-0.20	1.96	1.95
0.8810	0.9117	1.9016	0.019	-0.033	-27.22	-0.11	2.05	2.05
1	0.9254	1.8506	0	0	0			

2-Ethoxy ethanol + Butanol

0	0.8112	3.5104	0	0	0			
0.0980	0.8210	3.1674	0.045	-0.180	-54.64	-0.45	1.57	1.66
0.1965	0.8309	2.8637	0.103	-0.321	-112.00	-0.50	1.59	1.67
0.2954	0.8412	2.6191	0.148	-0.401	-154.92	-0.50	1.65	1.72
0.3947	0.8518	2.4305	0.187	-0.425	-186.25	-0.48	1.74	1.79
0.4945	0.8628	2.2827	0.212	-0.407	-201.16	-0.46	1.82	1.87
0.5947	0.8742	2.1783	0.222	-0.345	-183.33	-0.40	1.93	1.96
0.6953	0.8861	2.0992	0.203	-0.257	-143.54	-0.33	2.04	2.07
0.7964	0.8986	2.0275	0.161	-0.161	-87.34	-0.24	2.16	2.18
0.8980	0.9117	1.9541	0.093	-0.066	-27.22	-0.12	2.29	2.32
1	0.9254	1.8506	0	0	0			

2-Ethoxy ethanol + Hexanol

0	0.8151	4.5917	0	0	0			
0.1119	0.8244	3.9460	0.080	-0.339	-114.65	-0.50	2.10	1.52
0.2209	0.8340	3.4770	0.147	-0.509	-175.78	-0.45	2.08	1.74
0.3270	0.8440	3.0803	0.191	-0.615	-232.06	-0.46	2.04	1.82
0.4305	0.8543	2.7757	0.221	-0.636	-254.08	-0.46	2.01	1.92
0.5314	0.8649	2.5612	0.240	-0.574	-225.06	-0.40	1.97	2.07

Contd...

0.6297	0.8758	2.3806	0.254	-0.485	-185.27	-0.36	1.93	2.18
0.7257	0.8873	2.2425	0.237	-0.360	-119.92	-0.29	1.89	2.32
0.8193	0.8992	2.1213	0.209	-0.225	-51.23	-0.19	1.85	2.46
0.9108	0.9119	2.0053	0.126	-0.090	7.83	-0.01	1.81	2.67
1	0.9254	1.8506	0	0	0			
2-Ethoxy ethanol + Heptanol								
0	0.8207	5.9368	0	0	0			
0.1253	0.8277	4.9665	0.125	-0.435	-55.68	-0.30	1.16	1.80
0.2438	0.8367	4.2073	0.238	-0.712	-110.60	-0.33	1.36	1.90
0.3559	0.8464	3.6548	0.320	-0.811	-126.78	-0.31	1.64	2.08
0.4623	0.8561	3.2302	0.377	-0.818	-120.28	-0.28	1.88	2.25
0.5632	0.8661	2.9021	0.414	-0.733	-92.86	-0.24	2.10	2.40
0.6592	0.8771	2.6169	0.410	-0.626	-75.95	-0.23	2.24	2.50
0.7505	0.8882	2.3828	0.372	-0.487	-51.16	-0.20	2.38	2.59
0.8376	0.8995	2.1996	0.296	-0.315	-7.38	-0.12	2.55	2.74
0.9207	0.9118	2.0410	0.168	-0.134	32.75	0.07	2.79	2.98
1	0.9254	1.8506	0	0	0			
2-Ethoxy ethanol + Octanol								
0	0.8218	7.3646	0	0	0			
0.1384	0.8302	6.0618	0.169	-0.540	24.99	-0.03	1.33	2.34
0.2654	0.8389	5.0613	0.289	-0.840	36.69	-0.04	1.60	2.45
0.3825	0.8481	4.2677	0.366	-0.988	29.89	-0.07	1.79	2.52
0.4907	0.8576	3.6490	0.409	-1.010	19.57	-0.10	1.98	2.59
0.5910	0.8675	3.1718	0.428	-0.934	16.36	-0.11	2.16	2.68
0.6843	0.8778	2.8054	0.416	-0.786	26.02	-0.09	2.36	2.79
0.7713	0.8887	2.5039	0.370	-0.608	30.75	-0.08	2.52	2.88

Contd…

0.8525	0.9002	2.2662	0.291	-0.398	45.28	-0.01	2.71	3.03
0.9286	0.9123	2.0779	0.177	-0.166	69.42	0.26	3.04	3.35
1	0.9254	1.8506	0	0	0			

TABLE 3.

Values of Ultrasonic Speeds (u), Isentropic compressibility (Ks), Deviations in isentropic compressibility (Δ Ks) for binary mixtures of 2-Ethoxy ethanol + Methanol, Ethanol, Propanol, Butanol, Pentanol, Hexanol, Heptanol and Octanol at 298.15

x_1	u /m sec^{-1}	Ks $x10^{12}$ /Pa^{-1}	ΔK_s $x10^{12}$ /Pa^{-1}	x_1	u /m sec^{-1}	Ks $x10^{12}$ /Pa^{-1}	ΔKs$x10^{12}$ /Pa^{-1}
2-Ethoxy ethanol + Methanol				2-Ethoxy ethanol + Ethanol			
0	1104.2	1042.63	0	0	1142.0	975.89	0
0.0380	1130.9	981.86	-45.11	0.0538	1174.6	907.67	-49.66
0.0816	1151.5	931.90	-77.10	0.1133	1199.2	856.88	-79.88
0.1322	1167.5	886.36	-101.80	0.1798	1220.6	813.83	-100.01
0.1916	1188.6	842.09	-121.60	0.2542	1238.6	777.63	-110.49
0.2623	1205.1	803.78	-130.80	0.3383	1253.7	746.68	-112.40
0.3478	1220.5	771.62	-127.72	0.4341	1265.2	721.24	-104.80
0.4534	1233.1	744.02	-111.81	0.5440	1275.7	697.77	-90.30
0.5871	1246.9	716.60	-84.14	0.6716	1288.2	673.06	-70.96
0.7619	1266.2	684.13	-44.62	0.8215	1301.4	648.68	-43.60
1	1309.0	630.65	0	1	1309.0	630.65	0
2-Ethoxy ethanol + Propanol				2-Ethoxy ethanol + Butanol			
0	1209.4	806.49	0	0	1240.2	806.49	0
0.0690	1224.6	790.01	-17.36	0.0837	1245.0	790.01	-1.76
0.1429	1238.7	770.83	-30.71	0.1706	1252.3	770.83	-5.67
0.2223	1249.6	749.95	-37.90	0.2606	1261.4	749.95	-10.71
0.3078	1259.5	728.42	-41.50	0.3541	1271.4	728.42	-15.80
0.4001	1268.0	708.33	-41.43	0.4513	1280.6	708.33	-18.81
0.5001	1276.6	689.16	-39.01	0.5523	1289.3	689.16	-20.21
0.6088	1285.0	672.37	-33.70	0.6574	1296.1	672.37	-18.52

Contd…

0.7273	1293.6	657.40	-26.11	0.7669	1301.2	657.40	-14.24
0.8572	1302.5	644.23	-15.88	0.8810	1304.8	644.23	-7.35
1	1309.0	630.65	0	1	1309.0	630.65	0
2-Ethoxy ethanol + Pentanol				2-Ethoxy ethanol + Hexanol			
0	1277.2	755.71	0	0	1328.3	695.34	0
0.0980	1281.8	741.34	-2.11	0.1119	1324.3	691.70	3.60
0.1965	1286.5	727.16	-3.98	0.2209	1320.9	687.23	6.18
0.2954	1291.0	713.23	-5.54	0.3270	1318.0	682.02	7.83
0.3947	1295.1	699.89	-6.46	0.4305	1315.7	676.16	8.67
0.4945	1298.8	687.10	-6.77	0.5314	1314.2	669.44	8.47
0.5947	1301.6	675.20	-6.14	0.6297	1313.1	662.24	7.64
0.6953	1303.8	663.86	-4.89	0.7257	1312.2	654.55	6.15
0.7964	1305.6	652.85	-3.26	0.8193	1311.5	646.56	4.22
0.8980	1307.1	641.99	-1.42	0.9108	1310.7	638.33	1.91
1	1309.0	630.65	0	1	1309.0	630.65	0
2-Ethoxy ethanol + Heptanol				2-Ethoxy ethanol + Octanol			
0	1331.5	687.28	0	0	1347.7	669.96	0
0.1253	1326.4	686.72	6.54	0.1384	1339.3	671.52	7.01
0.2438	1322.3	683.52	10.04	0.2654	1332.8	671.02	11.49
0.3559	1319.2	678.85	11.73	0.3825	1327.3	669.33	14.40
0.4623	1316.5	673.94	12.84	0.4907	1322.5	666.64	15.97
0.5632	1314.2	668.51	13.12	0.5910	1318.7	662.89	16.16
0.6592	1312.5	661.87	11.92	0.6843	1315.6	658.17	15.11
0.7505	1311.1	655.00	10.22	0.7713	1313.3	652.39	12.75
0.8376	1309.9	647.96	8.11	0.8525	1311.5	645.84	9.39
0.9207	1309.7	639.34	4.20	0.9286	1310.2	638.54	5.08
1	1309.0	630.65	0	1	1309.0	630.65	0

TABLE 4.

Vander Wall's Constant *b*, Molecular Radius *r*, Geometrical Volume *B*, Collision Factor *S*, Molar Speed of Sound *R*, Available Volume V_a , Intermolecular Free Length L_f, Molar Volume at Absolute Zero V_0 , Molar Surface Area *Y* and Specific Acoustic Impedance *Z* of the Pure Components at 298.15 K.

Component	$b \times 10^5$ /(m^3)	r /(nm)	$B \times 10^5$ /$(m^3 mol^{-1})$	S	$R \times 10^6$ /{ $m^3 mol^{-1}$ $(ms^{-1})^{1/3}$}	$V_a \times 10^5$ /(cu m)	L_f (A^0)	$V_0 \times 10^5$ /(cu m)	$Y \times 10^{-4}$ /(A^0)	$Z \times 10^{-3}$ /Kgm^2s^{-1}
2-Ethoxy ethanol	9.17	0.209	2.29	3.48	1065.30	1.77	0.5165	7.97	32.94	1211.3
Methanol	3.69	0.154	0.92	3.05	420.98	1.26	0.6641	2.81	17.95	868.61
Ethanol	5.38	0.174	1.34	3.11	613.01	1.67	0.6425	4.19	23.08	897.29
Propan-1-ol	6.97	0.190	1.74	3.26	801.07	1.84	0.6015	5.68	27.45	966.71
Butan-1-ol	8.59	0.204	2.15	3.32	987.77	2.07	0.5841	7.13	31.54	999.79
Pentan-1-ol	10.21	0.216	2.55	3.40	1179.00	2.19	0.5654	8.67	35.40	1036.06
Hexan-1-ol	11.84	0.227	2.96	3.52	1378.00	2.13	0.5424	10.41	39.08	1082.70
Heptan-1-ol	13.42	0.237	3.35	3.51	1557.70	2.38	0.5392	11.78	42.47	1092.76
Octan-1-ol	15.06	0.246	3.77	3.54	1750.42	2.50	0.5323	13.35	45.87	1107.54

TABLE 5.

Speeds of Sound, Isentropic Compressibility and Excess Isentropic Compressibility, Deviation of Speed of Sound, Excess Intermolecular Free Length and Excess Acoustic Impedance of Alkan-1-ol +2-Ethoxy ethanol at 298.15 K

2-Ethoxy ethanol + Methanol

x_1	k_s /TPa^{-1}	L_f /(A^0)	R × 10^6 /{$m^3 mol^{-1}$ $(ms^{-1})^{1/3}$}	R_A	M_A	V_ax10^5 /(cu m)	Z × 10^{-3}
0.0380	977.74	0.6431	370.86	0.9073	-0.4828	1.20	904.38
0.0816	927.53	0.6264	384.99	0.9170	-0.4738	1.17	936.28
0.1322	887.44	0.6127	402.39	0.9281	-0.4660	1.15	965.17
0.1916	842.05	0.5969	424.43	0.9381	-0.4596	1.12	999.14
0.2623	805.36	0.5837	451.84	0.9497	-0.4548	1.11	1030.36
0.3478	772.16	0.5715	488.29	0.9617	-0.4529	1.13	1061.10
0.4534	744.05	0.5610	539.29	0.9744	-0.4548	1.18	1089.94
0.5871	716.16	0.5504	617.87	0.9864	-0.4620	1.27	1119.84
0.7619	684.14	0.5380	756.05	0.9962	-0.4766	1.44	1154.39
2-Ethoxy ethanol + Ethanol							
0.0538	907.71	0.6197	539.56	0.8946	-0.5187	1.58	937.92
0.1133	856.90	0.6021	560.05	0.9029	-0.5114	1.51	973.15
0.1798	813.87	0.5868	583.40	0.9122	-0.5049	1.45	1006.63
0.2542	777.66	0.5736	610.62	0.9226	-0.4992	1.42	1038.19
0.3383	746.66	0.5620	643.28	0.9341	-0.4945	1.40	1068.28
0.4341	721.21	0.5524	683.56	0.9467	-0.4913	1.41	1095.92
0.5440	697.79	0.5433	735.61	0.9598	-0.4898	1.45	1123.38
0.6716	673.08	0.5336	806.51	0.9727	-0.4904	1.49	1153.33
0.8215	648.63	0.5238	908.28	0.9856	-0.4936	1.58	1184.66

Contd.

TABLE5.

Speeds of Sound, Isentropic Compressibility and Excess Isentropic Compressibility, Deviation of Speed of Sound, Excess Intermolecular Free Length and Excess Acoustic Impedance of Alkan-1-ol +2-Ethoxy ethanol at 298.15 K

2-Ethoxy ethanol + Methanol

x_1	k_s /TPa^{-1}	L_f /(A^0)	R x 10^6 /{m^3mol^{-1} ($ms^{-1})^{1/3}$}	R_A	M_A	V_ax10^5 /(cu m)	Z x 10^{-3}
0.0380	977.74	0.6431	370.86	0.9073	-0.4828	1.20	904.38
0.0816	927.53	0.6264	384.99	0.9170	-0.4738	1.17	936.28
0.1322	887.44	0.6127	402.39	0.9281	-0.4660	1.15	965.17
0.1916	842.05	0.5969	424.43	0.9381	-0.4596	1.12	999.14
0.2623	805.36	0.5837	451.84	0.9497	-0.4548	1.11	1030.36
0.3478	772.16	0.5715	488.29	0.9617	-0.4529	1.13	1061.10
0.4534	744.05	0.5610	539.29	0.9744	-0.4548	1.18	1089.94
0.5871	716.16	0.5504	617.87	0.9864	-0.4620	1.27	1119.84
0.7619	684.14	0.5380	756.05	0.9962	-0.4766	1.44	1154.39
2-Ethoxy ethanol + Ethanol							
0.0538	907.71	0.6197	539.56	0.8946	-0.5187	1.58	937.92
0.1133	856.90	0.6021	560.05	0.9029	-0.5114	1.51	973.15
0.1798	813.87	0.5868	583.40	0.9122	-0.5049	1.45	1006.63
0.2542	777.66	0.5736	610.62	0.9226	-0.4992	1.42	1038.19
0.3383	746.66	0.5620	643.28	0.9341	-0.4945	1.40	1068.28
0.4341	721.21	0.5524	683.56	0.9467	-0.4913	1.41	1095.92
0.5440	697.79	0.5433	735.61	0.9598	-0.4898	1.45	1123.38
0.6716	673.08	0.5336	806.51	0.9727	-0.4904	1.49	1153.33
0.8215	648.63	0.5238	908.28	0.9856	-0.4936	1.58	1184.66
2-Ethoxy ethanol + Propanol							
0.0690	822.43	0.5899	711.17	0.8958	-0.5556	1.78	992.91

Contd.

0.1429	792.47	0.5790	732.34	0.9052	-0.5483	1.73	1018.71
0.2223	767.51	0.5698	755.46	0.9157	-0.541	1.70	1042.67
0.3078	744.60	0.5613	781.48	0.9267	-0.5339	1.68	1066.29
0.4001	723.97	0.5534	811.03	0.9383	-0.5271	1.68	1089.34
0.5001	703.92	0.5457	845.34	0.9499	-0.5208	1.67	1112.81
0.6088	684.77	0.5382	885.67	0.9616	-0.5151	1.68	1136.45
0.7273	665.77	0.5307	933.91	0.9738	-0.5097	1.69	1161.12
0.8572	646.86	0.5231	992.71	0.9863	-0.5047	1.72	1186.90

2-Ethoxy ethanol + Butanol

0.0837	790.05	0.5781	874.65	0.8973	-0.5705	2.04	1016.67
0.1706	770.86	0.5711	890.28	0.9072	-0.5634	2.01	1035.90
0.2606	749.89	0.5632	907.40	0.9169	-0.5562	1.96	1057.18
0.3541	728.41	0.5551	925.91	0.9267	-0.5489	1.91	1079.80
0.4513	708.30	0.5474	945.54	0.9371	-0.5414	1.87	1102.47
0.5523	689.17	0.5400	966.52	0.9480	-0.5336	1.83	1125.43
0.6574	672.33	0.5333	988.67	0.9599	-0.5256	1.80	1147.57
0.7669	657.42	0.5274	1012.20	0.9728	-0.5172	1.78	1169.00
0.8810	644.26	0.5221	1037.50	0.9863	-0.5088	1.78	1189.59

2-Ethoxy ethanol + Pentanol

0.0980	741.34	0.5600	1036.97	0.8934	-0.5888	2.14	1052.36
0.1965	727.16	0.5546	1040.48	0.9031	-0.5809	2.09	1068.95
0.2954	713.26	0.5493	1043.95	0.9132	-0.5725	2.04	1085.99
0.3947	699.93	0.5442	1047.35	0.9237	-0.5638	1.99	1103.17
0.4945	687.08	0.5391	1050.66	0.9348	-0.5547	1.94	1120.60
0.5947	675.20	0.5345	1053.74	0.9465	-0.5451	1.91	1137.86
0.6953	663.89	0.5300	1056.69	0.9588	-0.5349	1.87	1155.30

Contd.

0.7964	652.85	0.5255	1059.56	0.9719	-0.5241	1.84	1173.21
0.8980	641.99	0.5212	1062.36	0.9857	-0.5125	1.81	1191.68

2-Ethoxy ethanol + Hexanol

0.1119	691.65	0.5409	1194.66	0.8874	-0.6135	1.20	1091.75
0.2209	687.22	0.5392	1176.73	0.8985	-0.6032	1.17	1101.63
0.3270	682.07	0.5372	1159.86	0.9099	-0.5924	1.15	1112.39
0.4305	676.20	0.5349	1144.01	0.9216	-0.5811	1.12	1124.00
0.5314	669.44	0.5322	1129.16	0.9334	-0.5694	1.11	1136.65
0.6297	662.22	0.5293	1115.14	0.9454	-0.5572	1.13	1150.01
0.7257	654.53	0.5262	1101.84	0.9580	-0.5442	1.18	1164.32
0.8193	646.56	0.5230	1089.20	0.9711	-0.5306	1.27	1179.30
0.9108	638.33	0.5197	1077.11	0.9850	-0.5160	1.44	1195.23

2-Ethoxy ethanol + Heptanol

0.1253	686.72	0.5390	1331.37	0.8905	-0.6119	2.32	1097.86
0.2438	683.55	0.5378	1287.40	0.9011	-0.6019	2.25	1106.37
0.3559	678.90	0.5359	1248.55	0.9123	-0.5910	2.18	1116.57
0.4623	673.96	0.5340	1213.83	0.9233	-0.5801	2.12	1127.06
0.5632	668.51	0.5318	1182.65	0.9347	-0.5687	2.06	1138.23
0.6592	661.84	0.5291	1154.56	0.9470	-0.5562	1.99	1151.19
0.7505	654.96	0.5264	1129.09	0.9593	-0.5435	1.94	1164.52
0.8376	647.92	0.5236	1105.85	0.9718	-0.5304	1.89	1178.26
0.9207	639.38	0.5201	1084.81	0.9851	-0.5161	1.83	1194.18

2-Ethoxy ethanol + Octanol

0.1384	671.52	0.5330	1461.25	0.8903	-0.6175	2.41	1109.65
0.2654	671.06	0.5328	1385.10	0.9011	-0.6066	2.32	1114.39

Contd.

0.3825	669.29	0.5321	1321.61	0.9122	-0.5951	2.24	1122.97
0.4907	666.69	0.5311	1267.83	0.9236	-0.5834	2.16	1131.60
0.5910	662.89	0.5296	1221.83	0.9351	-0.5712	2.09	1142.32
0.6843	658.20	0.5277	1182.02	0.9470	-0.5586	2.02	1154.83
0.7713	652.40	0.5254	1147.29	0.9593	-0.5452	1.96	1167.13
0.8525	645.84	0.5227	1116.70	0.9722	-0.5312	1.89	1180.61
0.9286	638.54	0.5197	1089.59	0.9855	-0.5163	1.83	1195.30

TABLE 6

Redlich-Kister coefficients and standard deviations (σ) for the binary mixtures of 2-Ethoxy ethanol + Methanol, Ethanol, 1-Propanol, 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Heptanol and 1-Octanol at T = 298.15 K.

Binary mixture	Excess property	A_0	A_1	A_2	A_3	A_4	σ
2-Ethoxy ethanol + Methanol	$V^E \times 10^6$ /$(m^3.mol^{-1})$	3.16995	-0.19613	9.25258	-	-	0.49292
	$\Delta\eta$ /(mPa S)	0.45326	-0.06186	0.15702	-	-	0.00207
	ΔG^{*E} /$(J.mol^{-1})$	3479.34	-1432.39	1298.143	-2197.38	-1306.92	2.65174
	$\Delta K_S \times 10^{12}$ /(Pa^{-1})	-410.03	418.665	-260.832	-231.895	186.4851	0.26013
2-Ethoxy ethanol + Ethanol	$V^E \times 10^6$ /$(m^3.mol^{-1})$	-0.7623	0.1832	-0.14364	-0.26987	0.10883	0.0013
	$\Delta\eta$ /(mPa S)	0.31223	0.00246	-	-	-	0.00039
	ΔG^{*E} /$(J.mol^{-1})$	1146.97	-231.093	71.5142	-	-	0.69754
	$\Delta K_S \times 10^{12}$ (Pa^{-1})	-384.08	270.833	-468.176	-422.724	1819.404	0.0000
2-Ethoxy ethanol + 1-Propanol	$V^E \times 10^6$ /$(m^3.mol^{-1})$	-0.4525	0.63921	0.95591	-4.03612	-7.6092	0.0000
	$\Delta\eta$ /(mPa S)	-0.4924	0.31418	-0.06658	0.06129	-	0.00028
	ΔG^{*E} /$(J.mol^{-1})$	-576.47	417.062	-40.3791	4.6357	-17.0632	0.29871
	$\Delta K_S \times 10^{12}$ (Pa^{-1})	-155.20	77.5243	-64.4247	9.7579	-	0.2561

Contd.

2-Ethoxy ethanol + 1-Butanol	$V^E \times 10^6$ /(m^3.mol^{-1})	0.35678	0.0052	-0.31737	-	-	0.00057
	$\Delta\eta$ /(mPa S)	-0.7822	0.34872	0.3328	-	-	0.00137
	ΔG^{*E} /(J.mol^{-1})	-778.52	278.131	472.5683	71.41829	-	1.65605
	$\Delta K_S \times 10^{12}$ /(Pa^{-1})	-79.574	-24.6251	50.09514	-3.56549	-	0.13396
2- Ethoxy ethanol + 1-Pentanol	$V^E \times 10^6$ /(m^3.mol^{-1})	0.8571	0.30517	-0.11772	-	-	0.00185
	$\Delta\eta$ /(mPa S)	-1.6096	0.90572	0.24544	-0.11007	0.1719	0.00167
	ΔG^{*E} /(J.mol^{-1})	-794.99	56.0249	511.5964	241.345	-	1.67093
	$\Delta K_S \times 10^{12}$ (Pa^{-1})	-27.041	4.06096	24.6518	6.48988	-105.956	0.0000
2-Ethoxy ethanol + 1-Hexanol	$V^E \times 10^6$ /(m^3.mol^{-1})	0.9441	0.36152	0.52195	0.15616	-0.25529	0.00331
	$\Delta\eta$ /(mPa S)	-2.4006	1.13292	0.20876	0.37026	-	0.0073
	ΔG^{*E} /(J.mol^{-1})	-958.04	416.3159	634.288	439.316	-	5.67164
	$\Delta K_S \times 10^{12}$ (Pa^{-1})	34.552	-5.8076	-7.03454	4.42241	7.98105	0.03121
2-Ethoxy ethanol + 1-Heptanol	$V^E \times 10^6$ /(m^3.mol^{-1})	1.58018	0.71001	0.21536	-	-	0.00249
	$\Delta\eta$ /(mPa S)	-3.1936	1.24977	0.13886	-	-	0.01012
	ΔG^{*E} /(J.mol^{-1})	-436.66	432.54	-307.04	-728.23	1304.31	2.29942

Contd.

	$\Delta K_S \times 10^{12}$ (Pa^{-1})	51.664	3.5555	12.7633	-7.78112	-	0.19454
2-Ethoxy ethanol + 1-Octanol	$V^E \times 10^6$ $/(m^3.mol^{-1})$	1.6506	0.51687	0.46603	0.26796	-	0.00234
	$\Delta\eta$ /(mPa S)	-4.0219	0.70295	0.44447	0.61789	-	0.00719
	ΔG^{*E} $/(J.mol^{-1})$	74.122	-213.353	649.694	2647.44	-2950.2	0.0000
	$\Delta K_S \times 10^{12}$ (Pa^{-1})	64.149	14.7396	3.89818	-6.8375	2.27945	0.0169

TABLE 7

Values of standard deviation (%) for sound speeds by various methods.

Solvent mixture	σ%				
	u_{CFT}	u_{FLT}	u_{nomoto}	$U_{V\ V}$	u_{ID}
2-Ethoxy ethanol + Methanol	0.11	0.85	0.1	0.63	0.15
2-Ethoxy ethanol + Ethanol	0.20	1.19	0.12	0.35	0.16
2-Ethoxy ethanol +1-Propanol	0.04	1.35	0.05	0.13	0.05
2-Ethoxy ethanol +1- Butanol	0.05	1.44	0.04	0.07	0.04
2-Ethoxy ethanol + 1-Pentanol	0.02	1.59	0.02	0.02	0.02
2-Ethoxy ethanol + 1-Hexanol	0.01	1.79	0.02	0.01	0.01
2-Ethoxy ethanol +1-Heptanol	0.01	1.71	0.02	0.02	0.01
2-Ethoxy ethanol +1- Octanol	0.01	1.76	0.04	0.02	0.02

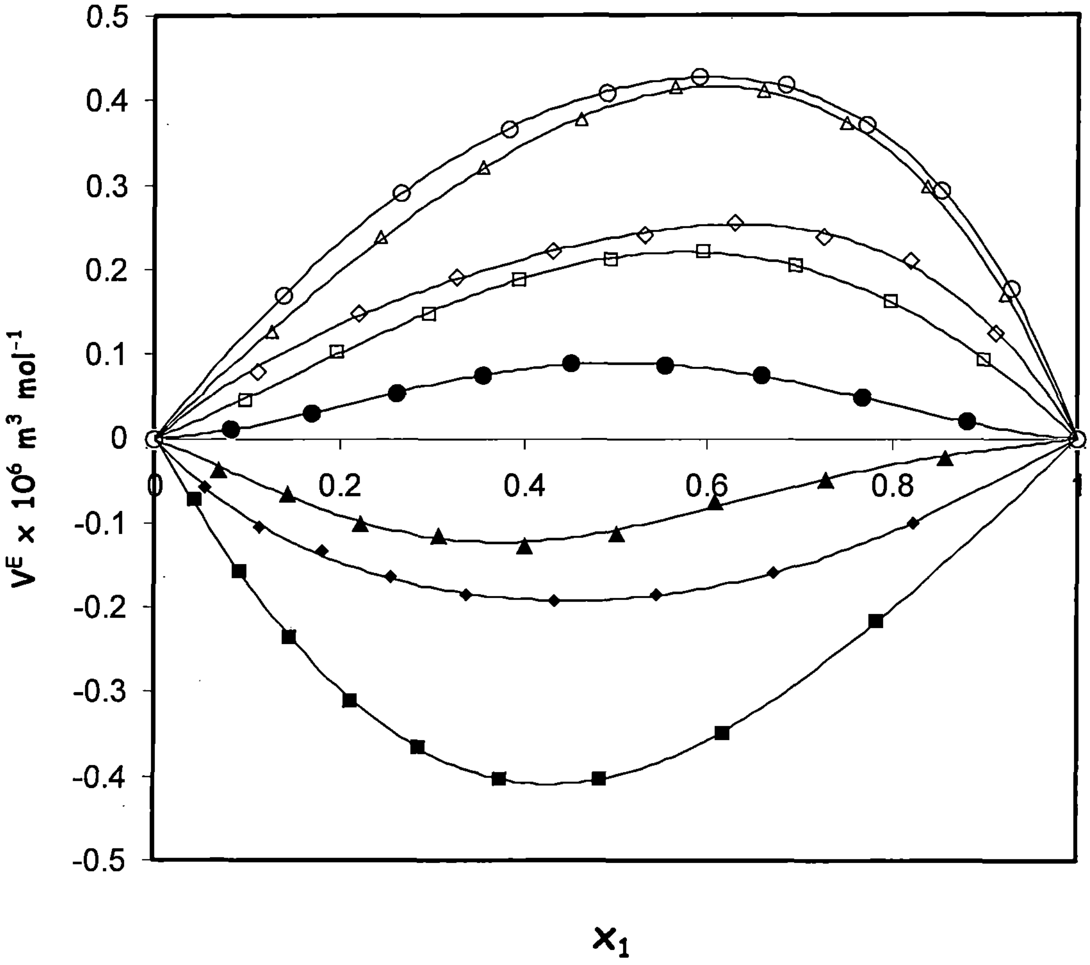

Figure1. Excess molar volumes (V^E) for binary mixtures of 2-Ethoxy ethanol with Methanol (■), Ethanol (♦), 1-Propanol (▲), 1-Butanol (●), 1-Pentanol (□), 1-Hexanol (◇), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

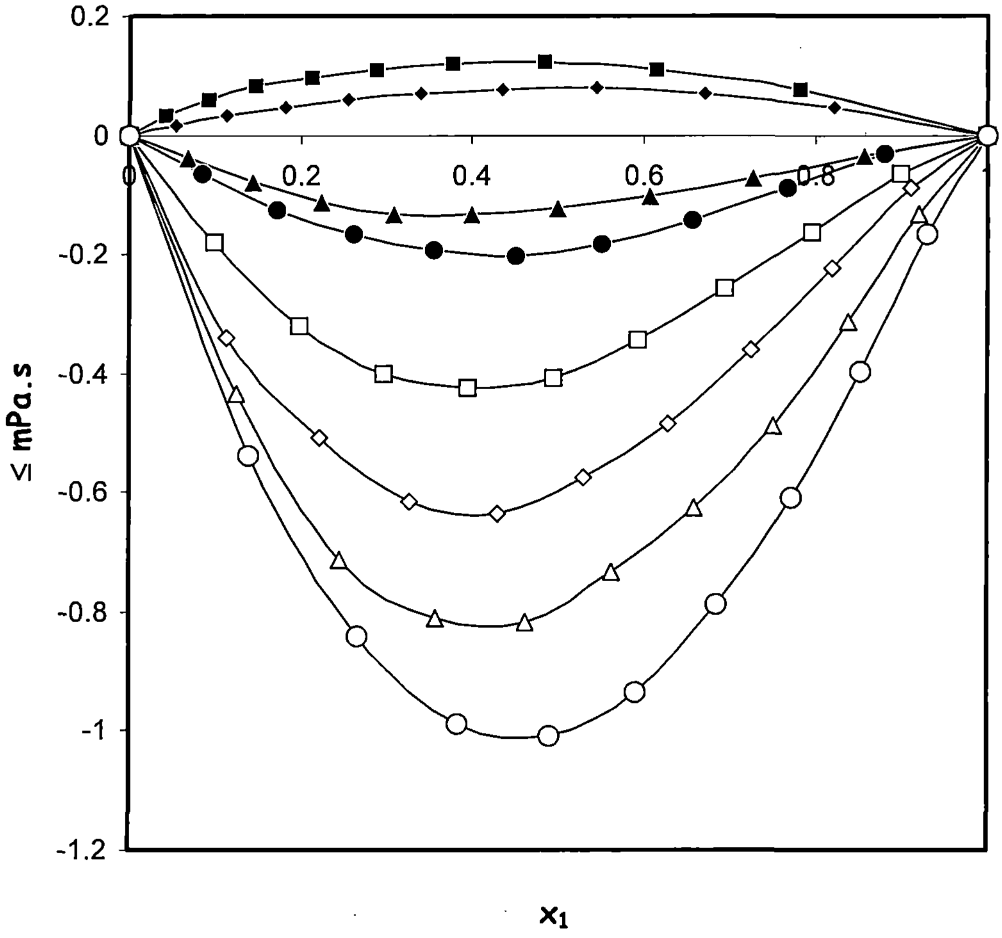

Figure2. Viscosity deviations (Δη) for binary mixtures of 2-Ethoxy ethanol with Methanol (▪), Ethanol (♦), 1-Propanol (▲), 1-Butanol (•), 1-Pentanol (□), 1-Hexanol (◇), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

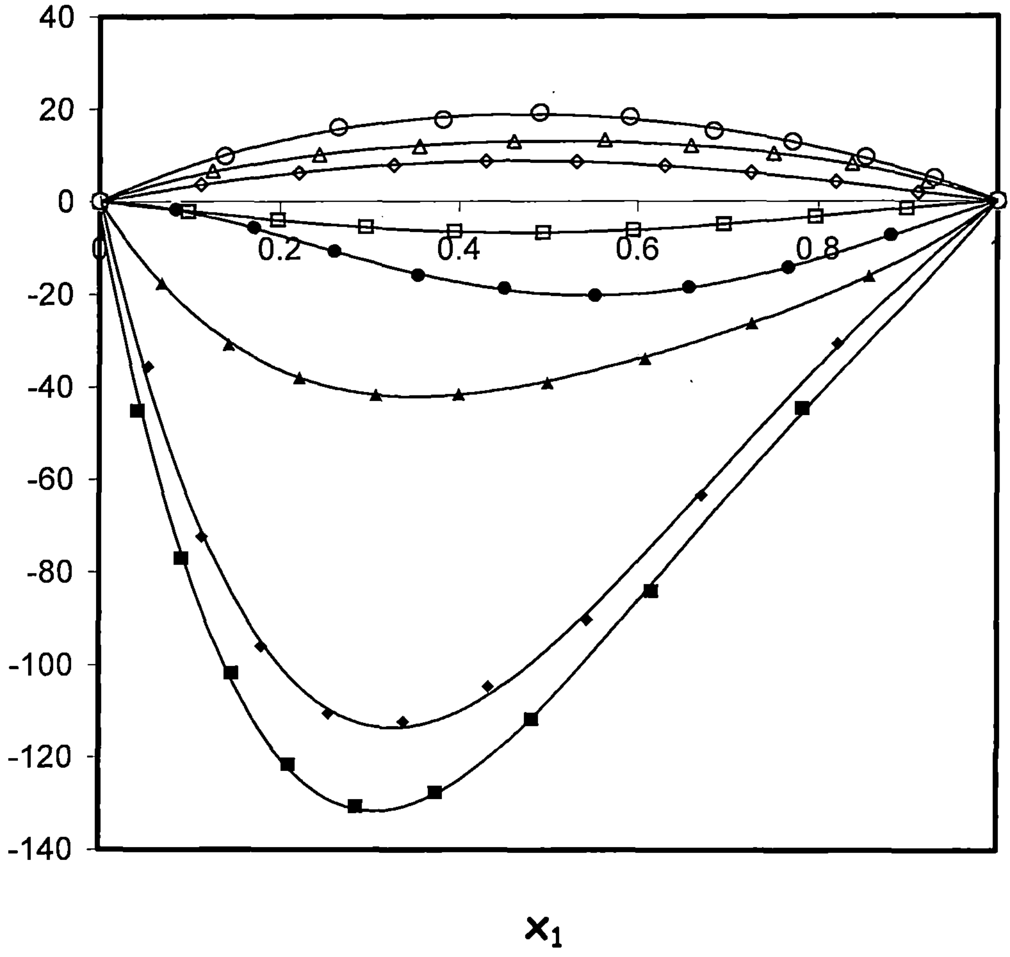

Figure3. Deviations in isentropic compressibility (Δ K_S) for binary mixtures of 2-Ethoxy ethanol with Methanol (■), Ethanol (♦), 1-Propanol (▲), 1-Butanol (●), 1-Pentanol (□), 1-Hexanol (◇), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

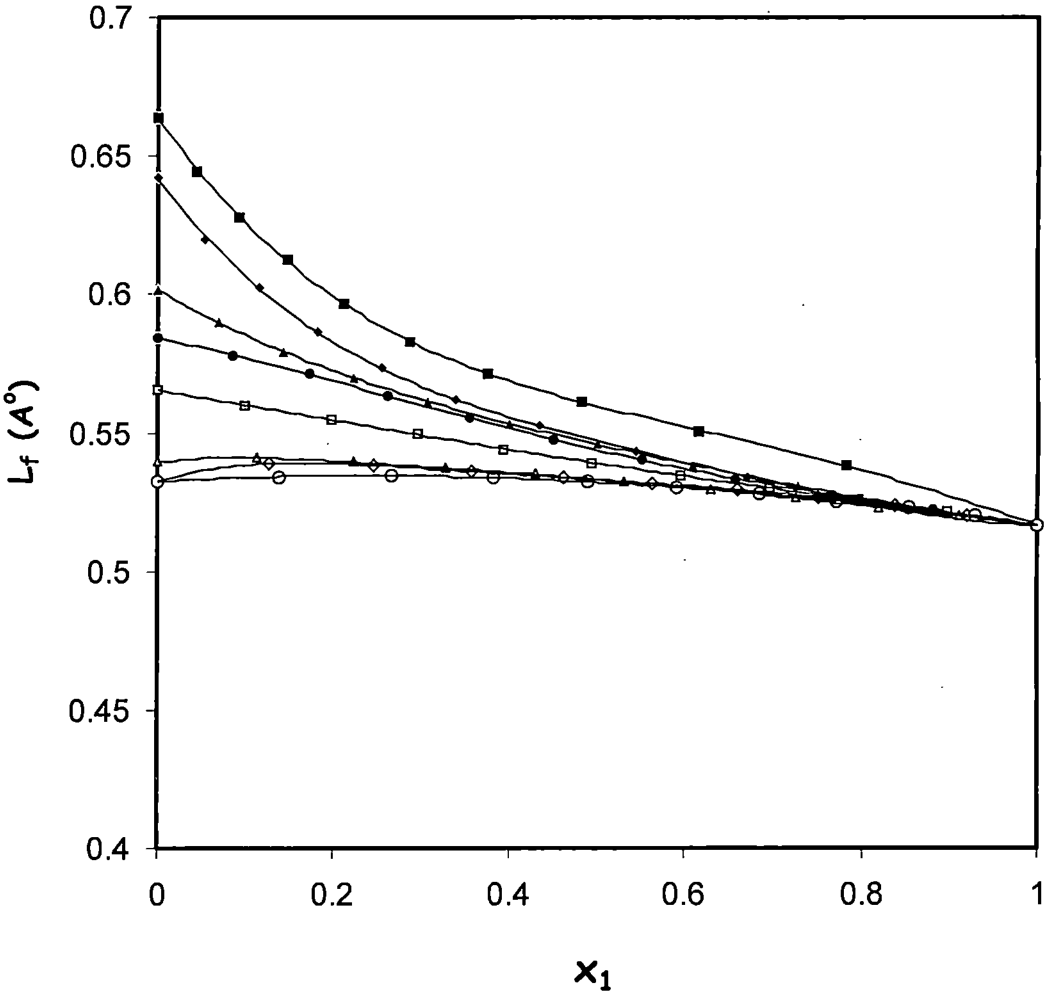

Figure4. Lf values for the experimental mixtures against the mole fraction of2-ethoxy ethanol with Methanol (■), Ethanol (♦), 1-Propanol (▲), 1-Butanol (●), 1-Pentanol (□), 1-Hexanol (◇), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

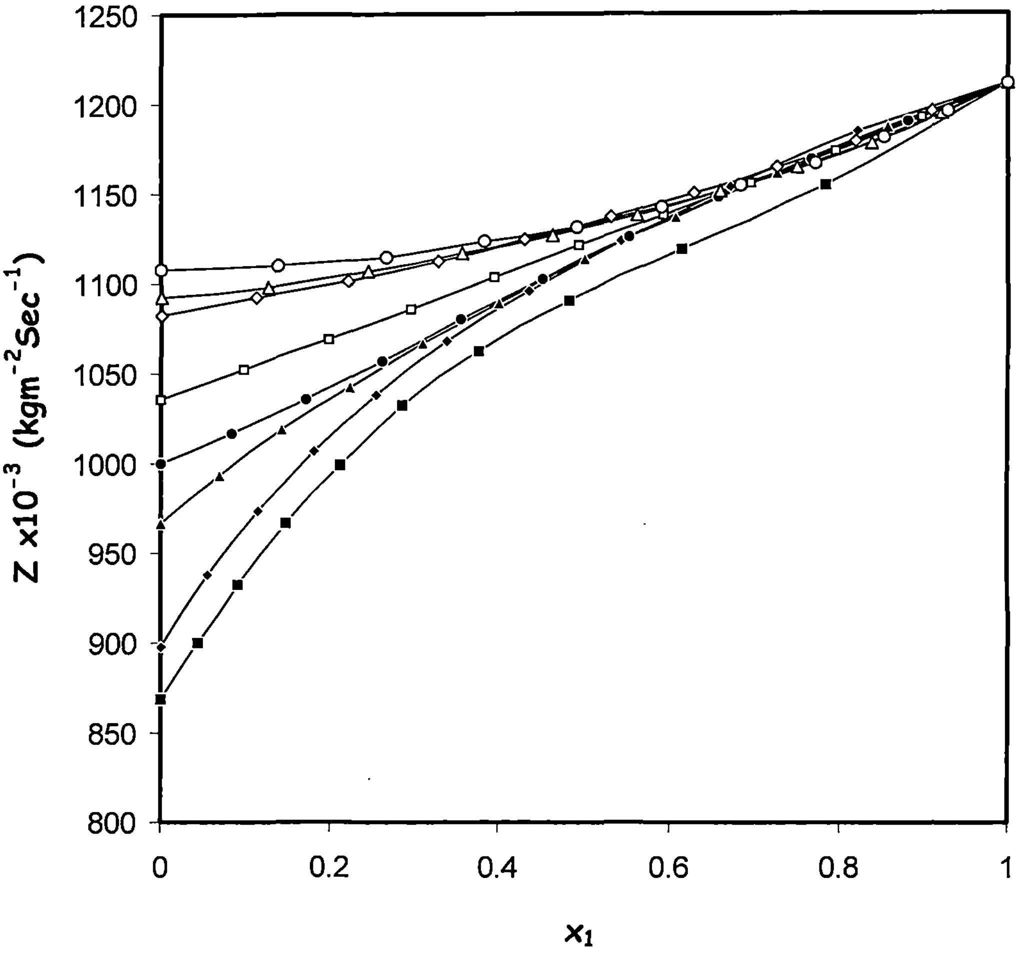

Figure5. Z values for the experimental mixtures against the mole fraction of2-ethoxy ethanol with Methanol (■), Ethanol (♦), 1-Propanol (▲), 1-Butanol (●), 1-Pentanol (□), 1-Hexanol (◇), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

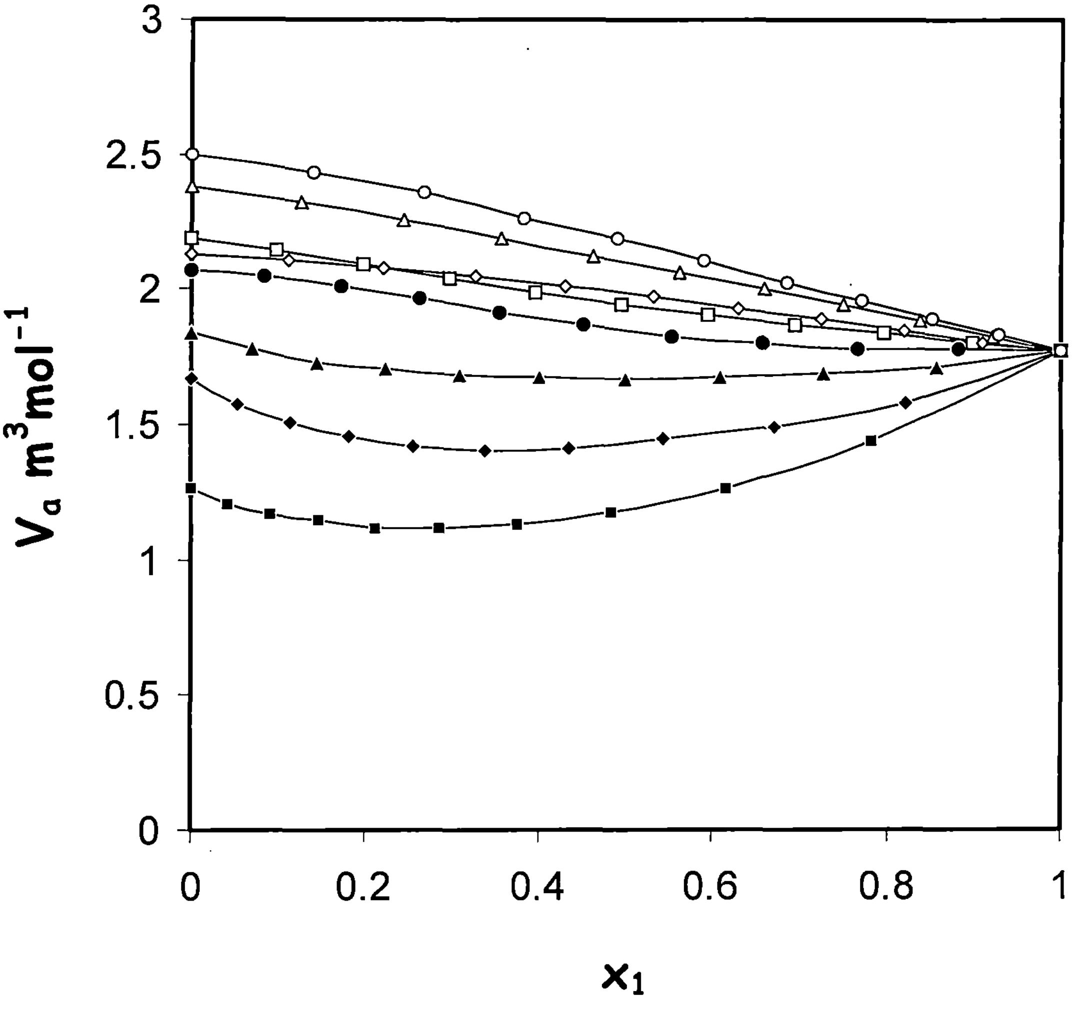

Figure6. Va values for the experimental mixtures against the mole fraction of 2-ethoxy ethanol with Methanol (■), Ethanol (♦), 1-Propanol (▲), 1-Butanol (●), 1-Pentanol (□), 1-Hexanol (◇), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

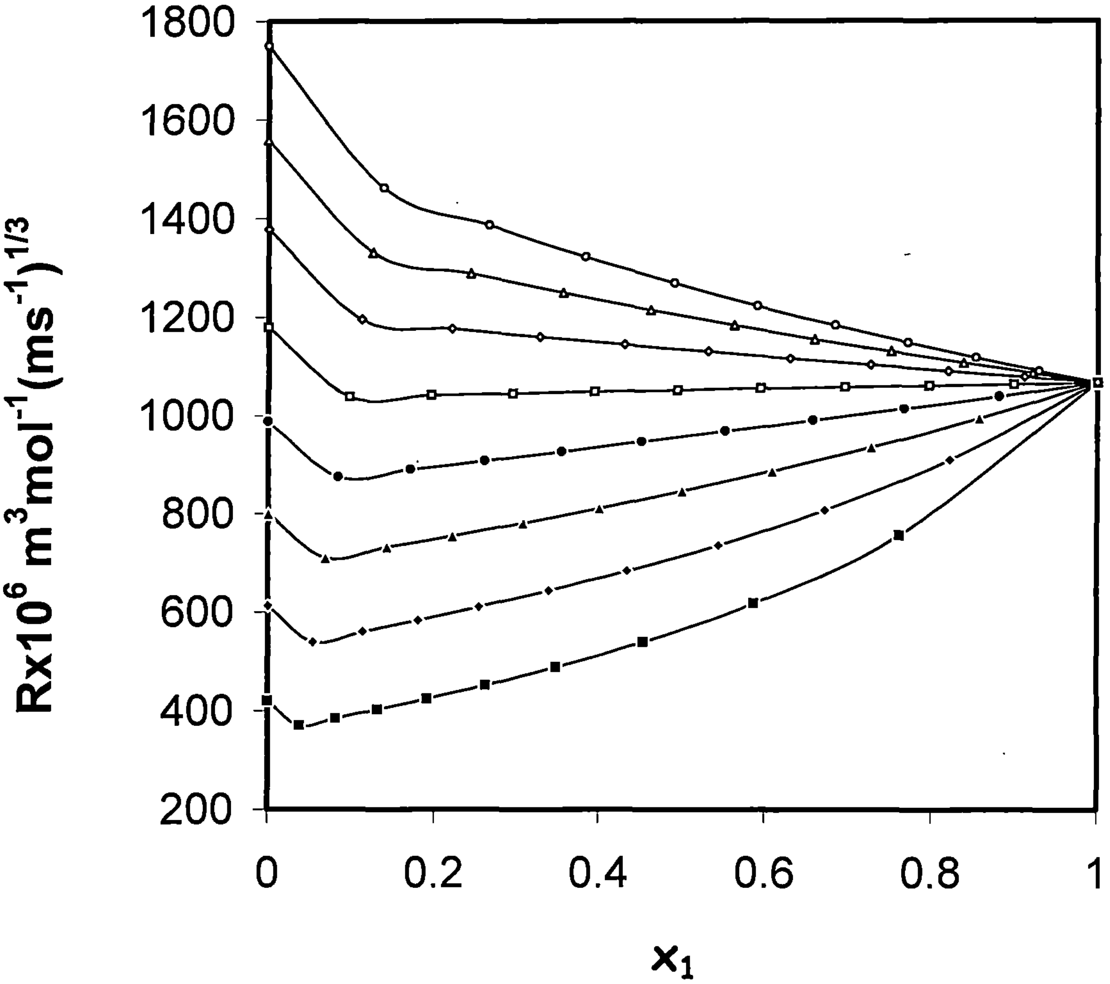

Figure7. R-values for the experimental mixtures against the mole fraction of 2-ethoxy ethanol with Methanol (■), Ethanol (♦), 1-Propanol (▲), 1-Butanol (●), 1-Pentanol (□), 1-Hexanol (◊), 1-Heptanol (Δ) and 1-Octanol (○) at 298.15

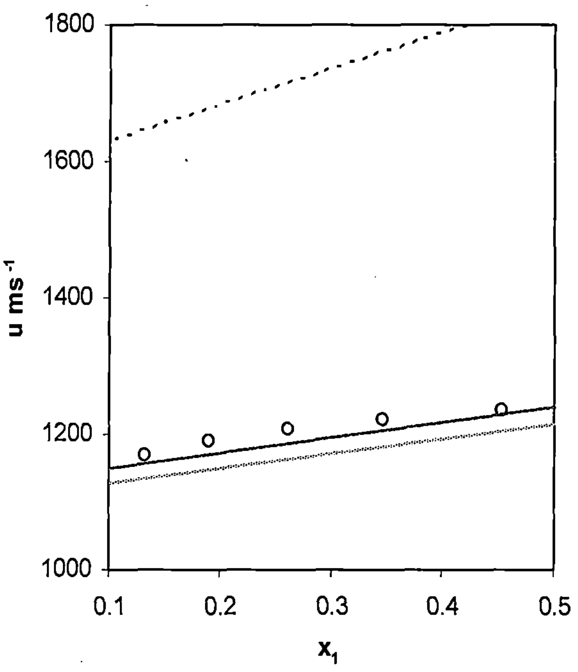

fig 9(a)

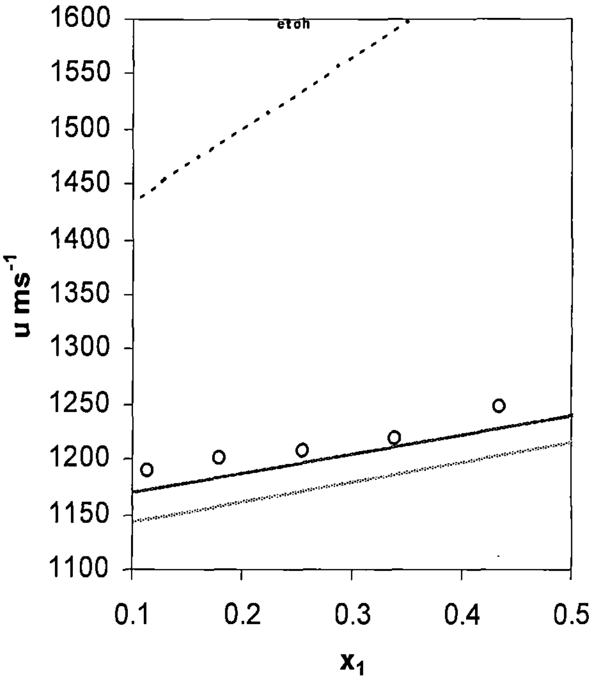

fig9(b)

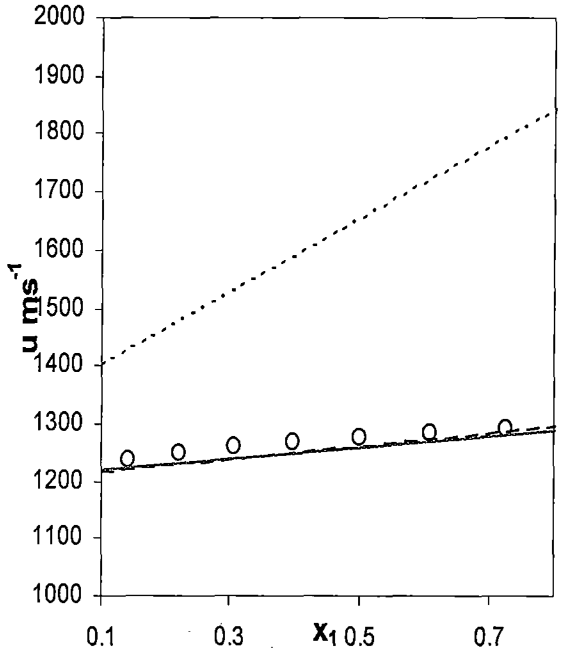

fig 9(c)

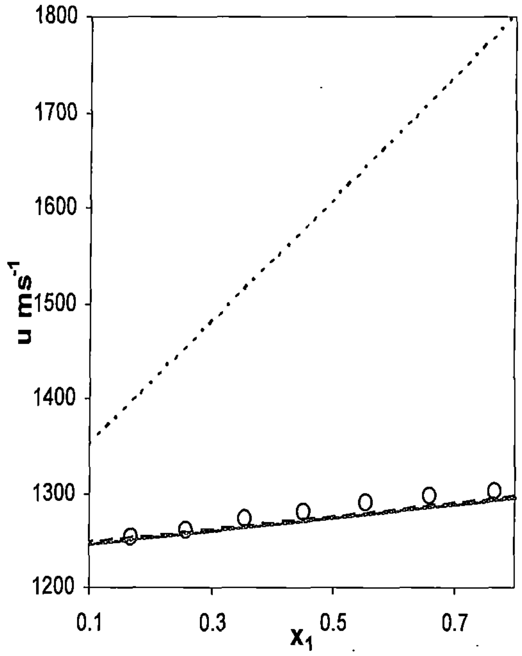

fig 9(d)

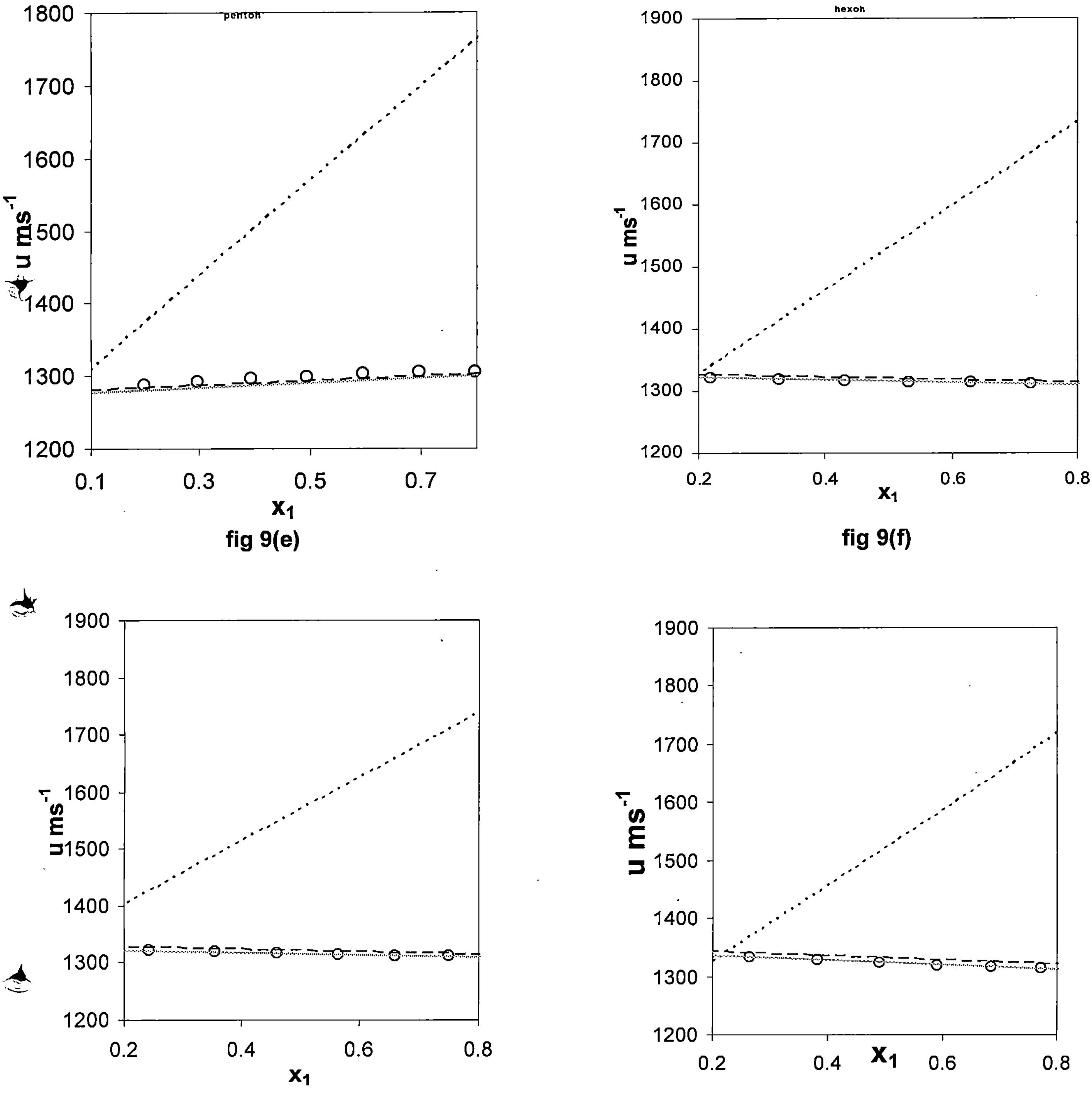

fig 9(e)

fig 9(f)

fig9(g)

fig9(h)

fig 9 (a-h): Experimental and calculated ultrasonic speed u of [2-ethoxy ethanol]+[Methanol (a), Ethanol (b), 1- Propanol (c), 1-Butanol (d), 1-Pentanol (e), 1-Hexanol (f), 1-Heptanol (g) and 1-Octanol (h)]at 298.15 K. [$u_{experimental}$ (ooooo); u_{FLT} (---------); u_{nomoto} (——————); u_{CFT} (...............).]

Chapter - VI

Excess Molar Volume, Excess Energy and Viscosity Deviation of Binary Mixtures of Tetrahydrofuran with Some Hydrocarbons at Various Temperatures

6.1. *Introduction*

Grouping of solvents into classes often is based on the nature of the intermolecular forces because the nature of association between the solute and solvent molecules brings about a marked effect on the resulting properties. After the introduction of the concept of ionization power of solvent,[1] much work has been devoted to the solvent effects on the rate and equilibrium processes.[2] Because of the close relation between liquid structure and macroscopic properties, determination of volumetric and viscometric properties is a valuable tool to learn the liquid state.[3] On the other hand, the obtaining of reliable measurements of solvent properties over a wide range of composition, pressure and temperature often is not feasible; hence, prediction and correlation methods constitute a valuable option to overcome such difficulties.[4,5]

The present work contributes to the study of the structure and interactions of ether (THF) containing binary mixtures. Tetrahydrofuran (THF) is a good industrial solvent. It figures prominently in the high energy battery industry and has found its applications in organic syntheses as manifested from the physicochemical studies.[6,7] Since no reports are available of density and viscosity studies of tetrahydrofuran (THF) with normal aliphatic hydrocarbons, the effect of chain-length of hydrocarbons (C_5, C_6, C_7) on these properties of binary mixtures of tetrahydrofuran with normal hydrocarbons at 288.15, 293.15 and 298.15 K is reported in the present investigation.

6.2. *Experimental Section*

6.2.1 Materials

Tetrahydrofuran (THF, Merck) was kept for several days over KOH, refluxed for 24 h and distilled over $LiAlH_4$ as described earlier.[8] Normal pentane, hexane and heptane were purified according to the standard procedures.[9,10] The purities were

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checked by density determination dilafometrically[11] at (288.15, 293.15 and 298.15 K) ± 0.1 K which almost agreed within the accuracy of ± 1×10^{-4} g cm^{-3} with the available literature[12,13] values. All the studies were prepared volumetrically[14] in stoppered bottles.

6.2.2. *Apparatus and Procedure*

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (288.15, 293.5 and 298.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ± 0.01 K of the desired temperature by means of a mercury in glass thermoregulator, and the temperature was determined with a calibrated thermometer and an Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The density values were reproducible to ±3×10^{-4} g cm^{-3}. Details have been described earlier.[15]

The viscosities were measured by means of suspended-level Ubbelohde[16] viscometer at the desired temperature (accuracy ± 0.01 K). The precision of the viscosity measurements was 0.05%. Details have been described earlier.[17]

The physical properties of tetrahydrofuran (THF), normal pentane, hexane and heptane at various temperatures are given in Table 1. The experimental values of mole-fractions, densities, viscosities and various derived parameters of various binary mixtures of solvents studied here at different temperatures are recorded in Table 2.

6.3. *Results and Discussion*

The experimental density (ρ) values (Table 1) have been used to calculate the excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$) excess Gibbs free energy (G^{*E}) and interaction parameter (d) using the following equations[16] (1-4):

$$V_m{}^E = \frac{M}{\rho} - \sum_{i=1}^{c} x_i \frac{M_i}{\rho_i} \quad (1)$$

$$\Delta\eta = \eta - \sum_{i=1}^{c} x_i\eta_i \quad (2)$$

$$G^{*E} = RT\ln\frac{\eta M}{\rho} - RT\sum_{i=1}^{c} x_i \ln\frac{\eta_i M_i}{\rho_i} \quad (3)$$

$$\ln\eta = \sum_{i=1}^{c} x_i \ln\eta_i + d\prod_{i=1}^{c} x_i \quad (4)$$

Where c stands for the number of components of the mixture, M and M_i are the molar masses of the mixture and of the pure components, ρ and ρ_i represent the density of the mixture and pure components, η and η_i are the corresponding viscosities, R is the gas constant T is the temperature in Kelvin and x_1 is the mole fraction. The values of these functions and d are recorded in Table 2 along with the values of ρ, η and x_1.

The excess molar volume were correlated by Redlich kister *equation.*

$$V_m^E = X_1X_2\Sigma a_j(x_1 - x_2)^i \quad (5)$$

The coefficient in eqn. (5) was estimated by the least-squares fit method, where the squares of the difference between the calculated and experimental excess molar volumes results is minimized. The optimal values of the coefficients in eqn. (5) are listed in table 3. The standard deviation was calculated by

$$\sigma(V_m^E) = \frac{\left[\Sigma(V_{m\,\exp t}^E - V_{mcalc}^E)^2\right]}{(D-N)^{0.5}} \quad (6)$$

where D and N are the number of data points and parameters, respectively. The experimental values of $\Delta\eta$ are also reported in Table 1. The viscosity deviations were correlated by the following equation:

$$Q = X_1X_2\Sigma H_j(x_1 - x_2)^j \quad (7)$$

Where Q = $\Delta\eta$ /(m pa. S). The coefficient in equation (7) are also regressed by employing the least square fit method. Standard deviations for the viscosity calculations were determined by equation (8).

$$\sigma(\Delta\eta) = \frac{\left[\Sigma(\Delta\eta_{\exp t} - \Delta\eta_{calc})^2\right]}{(D-N)^{0.5}} \quad (8)$$

The optimal parameters in correlating deviations of viscosity are listed in Table 4.

From Table-2 it is observed that the values of V_m^E for all binary mixtures THF + n-pentane, THF + n-hexane and THF + n-heptane at different temperatures over the entire composition are positive indicating the mutual dissociation of the component molecules. Because of the small difference in the molar volumes of the components, tetrahydrofuran will not fit into the structure of the normal aliphatic hydrocarbons (C_5H_{12}, C_6H_{14}, C_7H_{16}), thereby increasing the volume of the mixture.[19] Positive V_m^E also suggests that the dispersion forces prevail between THF and normal hydrocarbons.

It is also found from Table-2 that the difference in the molar volumes of the mixtures of the components follows the following order:

THF + n-heptane > THF + n-hexane > THF + n-pentane

at any temperature studied here. This indicates the higher value of V_m^E for THF + n-pentane mixture than that of THF + n-hexane mixture which is in turn higher than that of THF + n-heptane (shown in figures. 1, 2 and 3).

There is a systematic increase in V_m^E with a rise in temperature for all mixtures studied here and such changes or variations are included in Figs. 1, 2 and 3. This increase in V_m^E with temperature is as expected from Theoretical considerations.[20]

Deviations in viscosity ($\Delta\eta$) shown in Figs. 4, 5 and 6 for the mixtures of tetrahydrofuran (THF) with normal aliphatic hydrocarbons (C_5 - C_7) are negative which increase with increasing size of hydrocarbons. The trend in $\Delta\eta$ is

THF - C_5H_{12} < THF - C_6H_{14} < THF - C_7H_{16}.

The dominance of exothermic enthalpy of mixing over endothermic mixing resulting THF-hydrocarbon interaction, leads to less negative $\Delta\eta$ values for higher aliphatic hydrocarbons than for lower ones.[21] It seems that in tetrahydrofuran + hydrocarbon systems, the forces between pairs of unlike molecules are far less than that between pairs of like molecules. Therefore, the binary mixtures of tetrahydrofuran with higher hydrocarbons are less fluid due to enhanced non-covalent forces between like molecules. Negative $\Delta\eta$ values in the present investigation can also be attributed due to unequal molecular sizes of the constituent molecules of the mixture where dispersion forces are dominant.[22]

The effect of temperature increase is to disrupt hetero and homo association of the molecules which causes increase in fluidity of the liquid. So, $\Delta\eta$ values are higher at higher temperatures. Similar results was obtained as reported earlier.[23]

The negative values of excess Gibbs free energy of flow (shown in Figs. 7, 8, 9) for tetrahydrofuran + n-hydrocarbons over the entire range of composition and temperature which indicate the formation of molecular complex between unlike molecules through non-covalent bonds. Subba *et al.*[24] made a similar observation from G^{*E} studies for the binary mixtures of some solvents.

The negative values of Grünberg and Nissan parameter (d) indicates the presence of strong molecular interactions due to appreciable dipole-dipole and dipole-induced dipole interactions[23] while the negative values of d may be attributed to dominance of dispersion type of forces[22] between the like molecules. The last conclusion is in excellent agreement with the values of d (shown in Table-2) obtained from the experiment in our investigation.

6.4 *Conclusion*

. In this chapter , we studied the interactions occurring in binary mixtures of ethers with some members of the normal hydrocarbon series. The work reveals the dominance of dispersive forces between the ethers and hydrocarbons. It seems that, in the Ether+ Hydrocarbon binary systems, the forces between the unlike pairs of molecules are far less than that between like pair of molecules. The effect of temperature increase is to disrupt the homo and hetero association of component molecules in the mixtures. There is scope of improvisation of the conducted study covering the detailed nature of the interacting forces between the mixing components

References

1. F.J. Millero, In Structure and transport Process in water and Aqueous Solutions, Horne R.A. ed. New York, **1972**.
2. R.W. Curney, Ionic Process in Solutions; McGraw-Hill: New York, **1952**.
3. M.N. Roy, D.K. Hazra,. *North Bengal Univ. Rev.* **1997**, *8*, 54.
4. N. Saha, B. Das, *J. Chem. Eng. Data.* **1997**, *42*, 277.
5. C.R. Reid, B.E. Poling, The Properties of Gases and Liquids; McGraw Hill, New York, **1998**, Chapter 1.
6. C.G. Janz,. R.P.T. Tomkins, Non-aqueous Electrolytes Handbook; Academic Press, New York, **1973**, vol. 2.
7. R. Jasinki, High Energy Batteries, Plenum Press, New York, **1967**.
8. A. Choudhuri, A. Jha, M.N. Roy, *J. Indian. Chem. Soc.* **2003**, *80*, 632.
9. A. Vogel, "Practical Organic Chemistry", 4th ed. ELBS, London, **1978**.
10. J.A. Riddick, W.B. Bunger, T.K Solanko, "Techniques on Chemistry: Organic Solvents", 4th ed. Wiley New York, **1986**, 2.
11. R.L David, "CRC Handbook of Chemistry and Physics". 72nd ed. CRC Press, Florida, **1992**.
12. A.K. Covington, T. Dickinson, "Physical Chemistry of Organic Solvent Systems", Plenum: New York, **1973**.
13. J.A. Dean, "Langes Handbook of Chemistry", 12th ed. McGraw Hill, New York, **1979**.
14. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data.* **2001**, *46*, 1247.
15. P.S. Nikam, M. Hogan, *J. Chem. Eng. Data.* **1988**, *33*, 165.
16. M.N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, *49*, 291.
17. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, *1*, 93.
18. D.S. Gill, T.S. Cheema, *Z. Phys. Chem.* (N.F.), **1983**, *134*, 205.
19. A. Assarsson, F.R. Eirich, *J. Phys. Chem.* **1968**, *72*, 2710.
20. T.N. Aminabhavi, B. Gopalkrishna, *J. Chem. Eng. Data.* **1994**, *39*, 529.
21. R.J. Fort, H. Moore, *Trans. Faraday. Soc.* **1965**, *61*, 2102.
22. A. Choudhury, Gurung, B.B., M.N. Roy, *J Indian Chemical Society.* **2004**, 81, 330.
23. M. Singh, *J Indian Chemical Society.* **2002**, *79*, 659.
24. M.C.S. Subba, K.C. Rao, *J. Phys. Chem. Liq.* **1988**, *18*, 185.

Table 1

Physical Properties of Tetrahydrofuran, n-Pentane, n-Hexane and n-Heptane at Various Temperatures

T/K	$\rho \times 10^{-3}$ /kg m^{-3}		η /m. Pa. S	
	This Work	Literature	This Work	Literature
		Tetrahydrofuran (THF)		
288.15	0.88720	0.88720 [12]	0.50924	0.50923 [12]
293.15	0.88358	0.88357 [12]	0.49107	0.49106 [12]
298.15	0.87888	0.87888 [12]	0.45999	0.45999 [12]
		n-Pentane		
288.15	0.62528	0.62527 [9,10,11]	0.23145	0.23144[9,10,11]
293.15	0.62131	0.62132[9,10,11]	0.21996	0.21995[9,10,11]
298.15	0.61883	0.61883[9,10,11]	0.21210	0.21210[9,10,11]
		n-Hexane		
288.15	0.66125	0.66124[9,10,11]	0.33381	0.33381[9,10,11]
293.15	0.65472	0.65471[9,10,11]	0.31256	0.31255[9,10,11]
298.15	0.65253	0.65252[9,10,11]	0.29191	0.29190[9,10,11]
		n-Heptane		
288.15	0.68192	0.68192 [9,10,11]	0.42121	0.42121 [9,10,11]
293.15	0.67951	0.67950 [9,10,11]	0.40020	0.40010 [9,10,11]
298.15	0.67669	0.67669 [9,10,11]	0.38450	0.38450 [9,10,11]

Table 2

Density (ρ), viscosity (η), excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), excess free energy of activation of viscous flow (G^{*E}), interaction parameter (d) and mole fractions of tetrahydrofuran (x_1) with different normal hydrocarbons at various temperatures

x_1	$\rho \times 10^{-3}$ /kg. m^{-3}	η /m. Pa. S	V_m^E /Cm^{3}mol^{-1}	$\Delta\eta$ /m. Pa. S	G^{*E} / J mol^{-1}	d
288.15 K						
THF + n-Pentane						
0	0.62528	0.23145	0	0	0	0
0.10005	0.64384	0.24404	0.08012	-0.01520	-48.30241	-0.28795
0.20009	0.66314	0.25863	0.22501	-0.02841	-85.07026	-0.29207
0.30012	0.68356	0.27829	0.38213	-0.03653	-87.33218	-0.24928
0.40013	0.70536	0.29859	0.52531	-0.04401	-98.96688	-0.25388
0.50014	0.72910	0.32188	0.60112	-0.04850	-103.4397	-0.25829
0.60013	0.75389	0.34765	0.75452	-0.05051	-104.1155	-0.27671
0.70012	0.78256	0.38240	0.65501	-0.04354	-70.39536	-0.23806
0.80009	0.81536	0.41850	0.35254	-0.03521	-57.71623	-0.24135
0.90005	0.85002	0.46314	0.15231	-0.01833	-19.71319	-0.17868
1	0.88720	0.50924	0	0	0	0
THF + n-Hexane						
0	0.66125	0.33381	0	0	0	0
0.11713	0.67683	0.34235	0.31001	-0.01201	-27.52968	-0.23410
0.22998	0.69396	0.35205	0.47510	-0.02211	-52.41408	-0.24807
0.33863	0.71227	0.36440	0.58502	-0.03002	-63.79133	-0.24709
0.44335	0.73168	0.37894	0.67511	-0.03265	-65.71838	-0.24491
0.54436	0.75343	0.39784	0.59002	-0.03147	-50.21391	-0.21945
0.64184	0.77676	0.41661	0.47512	-0.02980	-43.40952	-0.21533
0.73598	0.80164	0.43672	0.36013	-0.02631	-36.22659	-0.21676
0.82695	0.82184	0.45847	0.25003	-0.02041	-27.60456	-0.22318
0.91491	0.85643	0.48214	0.14561	-0.01217	-17.23062	-0.24081
1	0.88720	0.50924	0	0	0	0

Contd.

THF + n-Heptane						
0	0.68192	0.42121	0	0	0	0
0.13376	0.69798	0.42314	0.01801	-0.00984	-7.43921	-0.17964
0.25784	0.71408	0.42721	0.16810	-0.01670	-7.72454	-0.18181
0.37327	0.73105	0.43232	0.29111	-0.02175	-9.27331	-0.19153
0.48091	0.74900	0.43746	0.38112	-0.02608	-17.43592	-0.21398
0.58153	0.76886	0.44679	0.32102	-0.02561	-12.01893	-0.21126
0.67580	0.78996	0.45649	0.24515	-0.02421	-11.42528	-0.21828
0.76430	0.81226	0.46761	0.17321	-0.02088	-9.62714	-0.22511
0.84753	0.83579	0.47985	0.11213	-0.01597	-8.13692	-0.23610
0.92597	0.86066	0.49304	0.06122	-0.00968	-7.39667	-0.26666
1	0.88720	0.50924	0	0	0	0
293.15 K						
THF + n-Pentane						
0	0.62131	0.21996	0	0	0	0
0.10005	0.63975	0.23307	0.10009	-0.01401	-40.13625	-0.24946
0.20009	0.65882	0.24979	0.28215	-0.02442	-52.82306	-0.20946
0.30012	0.67932	0.26882	0.42501	-0.03250	-58.50596	-0.19254
0.40013	0.70091	0.28943	0.60002	-0.03901	-64.64248	-0.19537
0.50014	0.72427	0.31156	0.72551	-0.04399	-74.89723	-0.21415
0.60013	0.74962	0.33706	0.80432	-0.04560	-76.91300	-0.22744
0.70012	0.77846	0.36856	0.68511	-0.04121	-61.08626	-0.21975
0.80009	0.81076	0.40335	0.44004	-0.03352	-50.21842	-0.22649
0.90005	0.84594	0.44846	0.18603	-0.01551	-5.25559	-0.11664
1	0.88358	0.49107	0	0	0	0
THF +n-Hexane						
0	0.65472	0.31256	0	0	0	0
0.11713	0.67030	0.32340	0.34011	-0.01001	-13.78878	-0.18204
0.22998	0.68750	0.33559	0.52012	-0.01802	-24.35637	-0.18527
0.33863	0.70596	0.34898	0.63510	-0.02403	-31.96879	-0.19098
0.44335	0.72573	0.36001	0.70001	-0.03169	-61.24642	-0.23893
0.54436	0.74763	0.37971	0.62503	-0.03002	-41.13155	-0.20693
0.64184	0.77130	0.40073	0.50002	-0.02640	-22.50561	-0.18047

Contd.

0.73598	0.79649	0.42074	0.38215	-0.02320	-18.26332	-0.18161
0.82695	0.82346	0.44201	0.26002	-0.01817	-14.90494	-0.18918
0.91491	0.385273	0.46499	0.10003	-0.01089	-11.68659	-0.20717
1	0.88358	0.49107	0	0	0	0
THF + n-Heptane						
0	0.67951	0.40020	0	0	0	0
0.13376	0.69541	0.40303	0.03211	-0.00932	-6.19986	-0.17964
0.25784	0.71116	0.40749	0.23101	-0.01614	-6.62451	-0.18181
0.37327	0.72815	0.41302	0.32905	-0.02110	-8.97066	-0.19153
0.48091	0.74110	0.41907	0.39811	-0.02483	-14.95693	-0.21398
0.58153	0.76587	0.42849	0.33521	-0.02455	-10.38316	-0.21126
0.67580	0.78682	0.43850	0.26115	-0.02302	-9.17771	-0.21828
0.76430	0.80901	0.44949	0.18522	-0.02016	-8.91551	-0.22511
0.84753	0.83246	0.46185	0.11609	-0.01537	-7.42920	-0.23610
0.92597	0.85715	0.47507	0.06713	-0.00927	-7.24725	-0.26666
1	0.88358	0.49107	0	0	0	0
298.15 K						
THF +n-Pentane						
0	0.61884	0.21210	0	0	0	0
0.10005	0.63627	0.22409	0.25510	-0.01281	-37.51550	-0.24948
0.20009	0.65502	0.24048	0.46001	-0.02122	-39.51000	-0.18319
0.30012	0.67532	0.25800	0.59870	-0.02850	-45.81660	-0.17346
0.40013	0.69680	0.27677	0.75420	-0.03452	-54.29800	-0.18177
0.50014	0.71991	0.29768	0.88000	-0.03840	-59.58580	-0.19288
0.60013	0.74504	0.32036	0.94801	-0.04051	-67.55300	-0.21753
0.70012	0.77317	0.34700	0.87505	-0.03865	-66.34380	-0.23686
0.80009	0.80424	0.38003	0.71900	-0.03040	-43.53820	-0.22629
0.90005	0.84004	0.42120	0.34599	-0.01401	-1.44872	-0.11918
1	0.87888	0.45999	0	0	0	0

Contd.

THF + n-Hexane						
0	0.65253	0.29191	0	0	0	0
0.11713	0.66764	0.30251	0.40111	-0.00909	-10.00730	-0.17017
0.22998	0.68449	0.31417	0.61002	-0.01546	-19.08990	-0.17560
0.33863	0.70279	0.32582	0.71502	-0.02155	-34.60930	-0.19689
0.44335	0.72236	0.33805	0.77501	-0.02838	-51.08960	-0.24782
0.54436	0.74425	0.35700	0.66541	-0.02748	-28.97290	-0.18652
0.64184	0.76770	0.37358	0.53021	-0.02621	-17.33250	-0.17095
0.73598	0.79261	0.39434	0.41001	-0.02127	-15.01330	-0.17459
0.82695	0.81936	0.41503	0.27512	-0.01587	-7.93677	-0.16881
0.91491	0.84793	0.43648	0.15003	-0.00921	-4.84634	-0.17684
1	0.87888	0.45999	0	0	0	0
THF + n-Heptane						
0	0.67669	0.38450	0	0	0	0
0.13376	0.69246	0.38606	0.05512	-0.00854	-5.49011	-0.17200
0.25784	0.70808	0.38915	0.26102	-0.01481	-5.70903	-0.17872
0.37327	0.72492	0.39354	0.35621	-0.01914	-6.60921	-0.18669
0.48091	0.74273	0.39842	0.41111	-0.02238	-11.48670	-0.20288
0.58153	0.76231	0.40609	0.35005	-0.02231	-8.35571	-0.20388
0.67580	0.78308	0.41463	0.28106	-0.02089	-6.83200	-0.20859
0.76430	0.80505	0.42423	0.19514	-0.01797	-5.56499	-0.21470
0.84753	0.82828	0.43559	0.13008	-0.01289	-4.67554	-0.21027
0.92597	0.85272	0.44651	0.07201	-0.00789	-3.80617	-0.24030
1	0.87888	0.45999	0	0	0	0

Table 3

Regression results for the excess volumes of THF + Normal Hydrocarbons mixture at various temperatures

System	Temp (K)	a_0	a_1	a_2	a_3	a_4	a_5	σ
THF + n-Pentane	288.15	2.6628	2.0239	-2.0835	2.8456	-	-	0.0405
	293.15	2.9725	1.8899	-2.0609	-2.3361	-	-	0.0187
	298.15	3.5424	1.3472	-	-	-	-	0.0341
THF + n-Hexane	288.15	2.5410	-1.2884	-2.0980	2.6035	3.2279	-2.9888	0.0138
	293.15	2.6047	-1.0650	0.4984	-	-	-	0.0173
	298.15	2.8035	-1.3676	-	-	-	-	0.0200
THF + n-Heptane	288.15	1.4462	-0.0143	-2.6272	1.1404	1.6129	-	0.0115
	293.15	1.5076	-0.4841	-1.6890	1.6837	-	-	0.0113
	298.15	1.5802	-0.5575	-1.5346	1.6635	-	-	0.0096

Table 4
Regression results for the deviation of viscosity of THF +Normal Hydrocarbons mixture at various temperatures

System	Temp (K)	a_0	a_1	a_2	a_3	a_4	a_5
THF + n-Pentane	288.15	0.1945	-0.0376	-	-	-	0.0011
	293.15	0.1761	-0.0428	-	-	-	0.0015
	298.15	-0.1572	-0.0444	-	-	-	0.0016
THF + n-Hexane	288.15	-0.1311	-0.0102	-	-	-	0.0009
	293.15	-0.1168	-0.0165	-	-	-	0.0014
	298.15	-0.1103	-0.0198	0.0274	-	-	0.0010
THF + n-Heptane	288.15	-0.1021	-0.0288	-	-	-	0.0005
	293.15	-0.0986	-0.0236	0.0206	-0.0097	-0.0487	0.0003
	298.15	-0.0884	-0.0213	-	-	-	0.0003

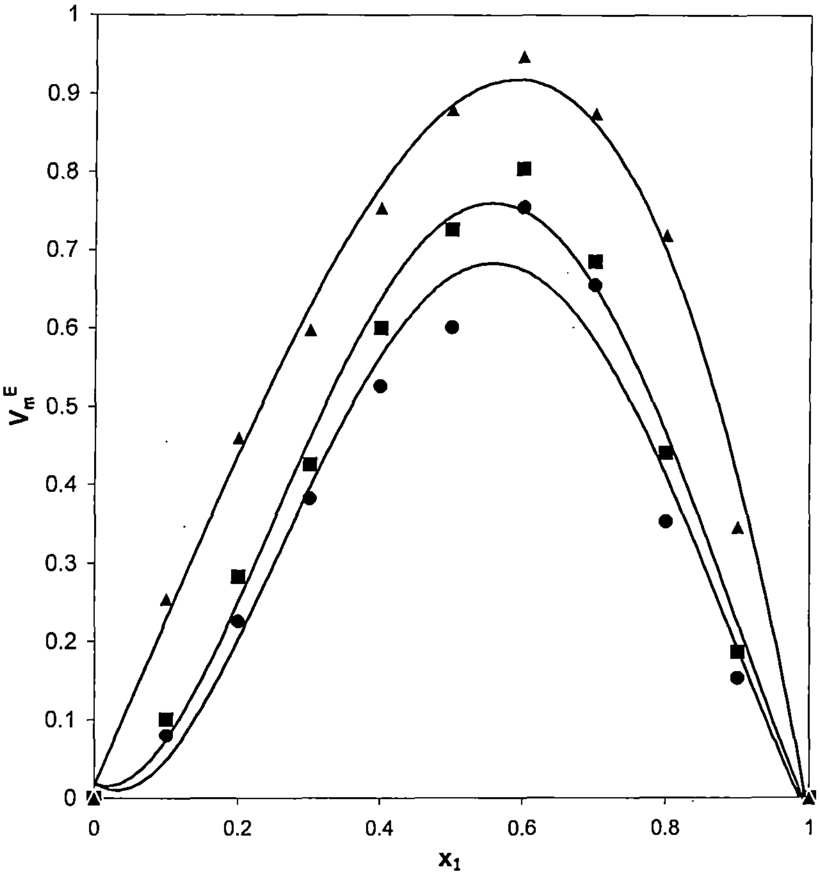

Fig. 1: Plot of excess molar volume (V_m^E) vs. mole fraction (x_1) of THF + n-Pentane mixtures at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

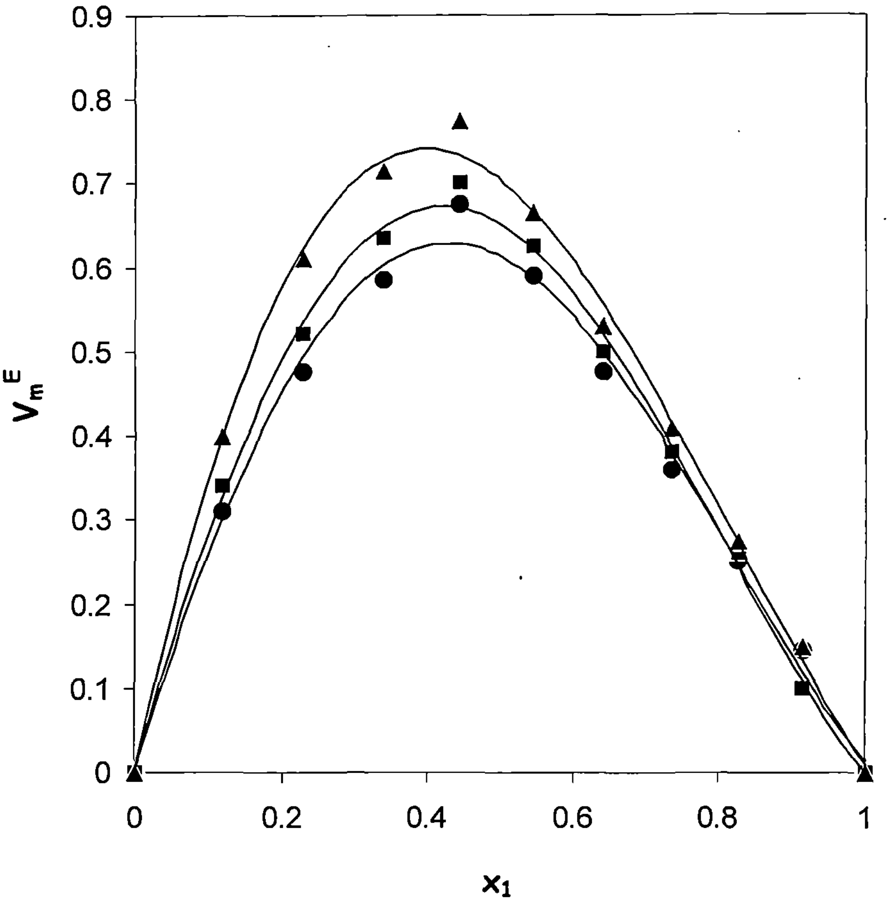

Fig. 2: Plot of excess molar volume (V_m^E) vs. mole fraction (x_1) of THF + n-Hexane mixtures at at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

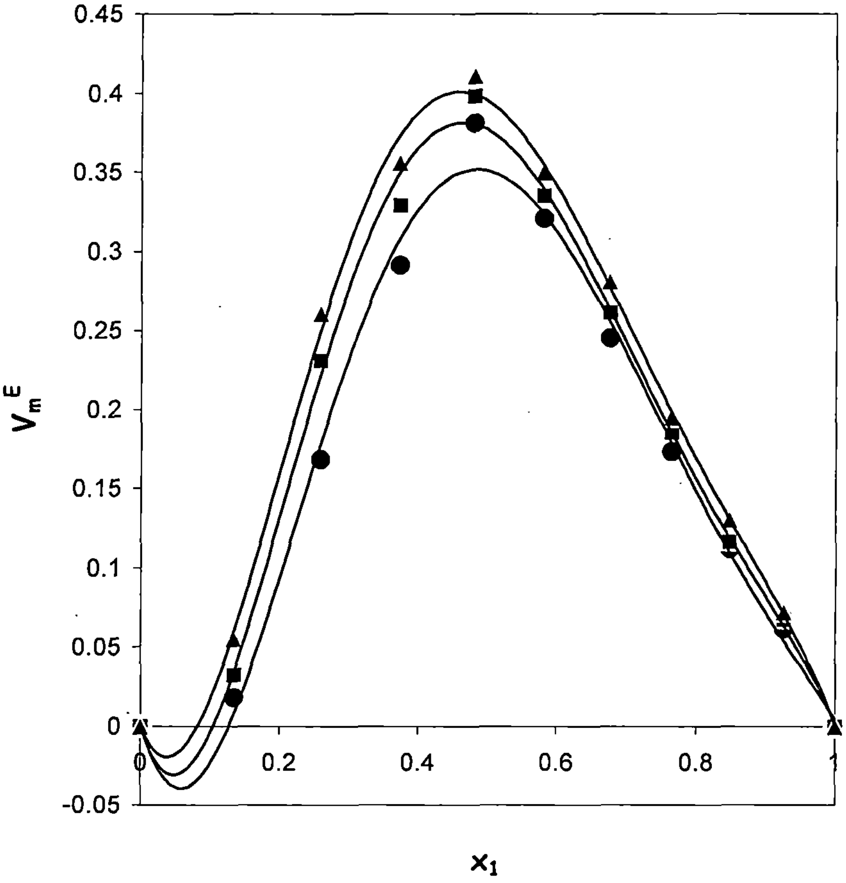

Fig. 3: Plot of excess molar volume (V_m^E) vs. mole fraction (x_1) of THF + n-Heptane mixtures at at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

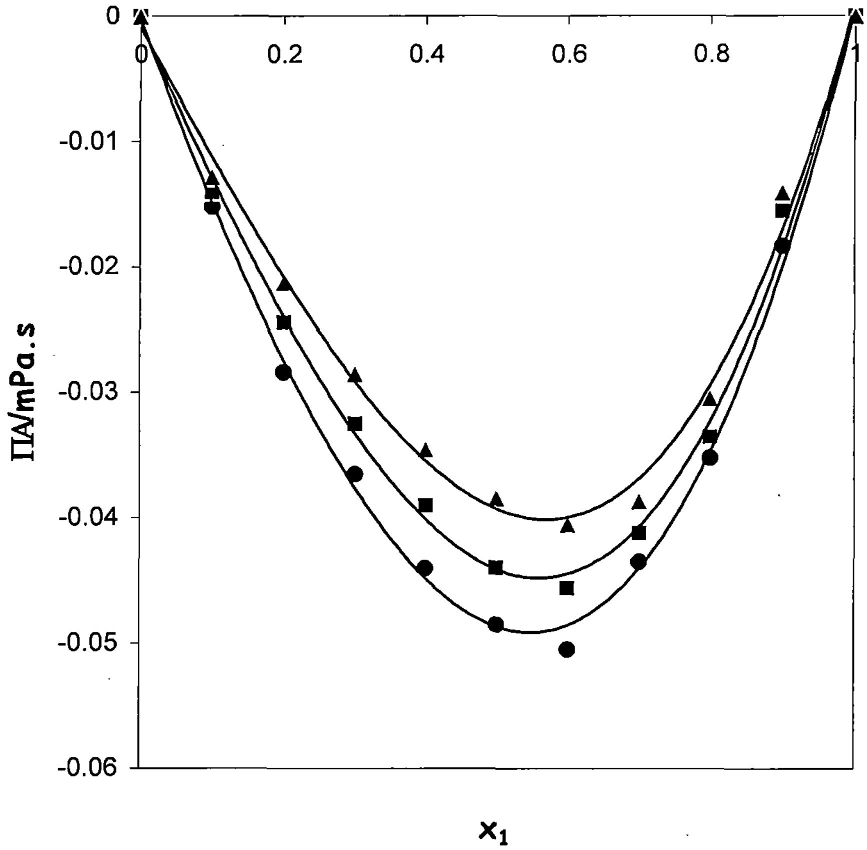

Fig. 4: Plot of viscosity deviation ($\Delta\eta$/m. Pa. S) vs. mole fraction (x_1) of THF + n-Pentane mixtures at at 288.15 K (•); 293.15 K (▪) and 298.15 K (▲).

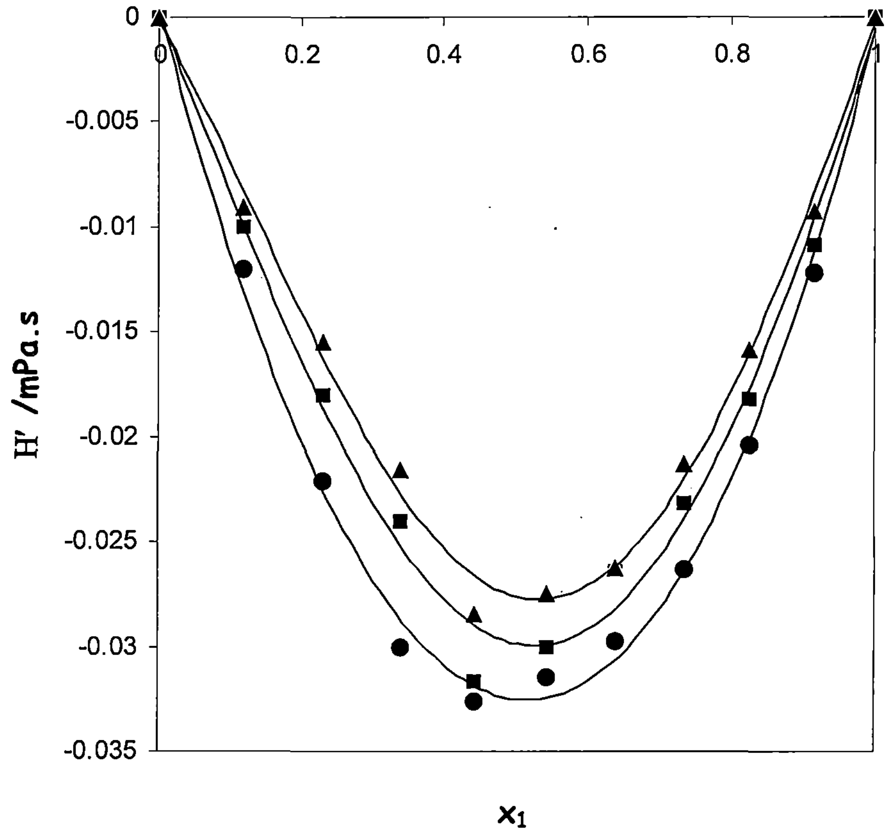

Fig. 5: Plot of viscosity deviation ($\Delta\eta$/m. Pa. S) vs. mole fraction (x_1) of THF + n-Hexane mixtures at at 288.15 K (•); 293.15 K (▪) and 298.15 K (▲).

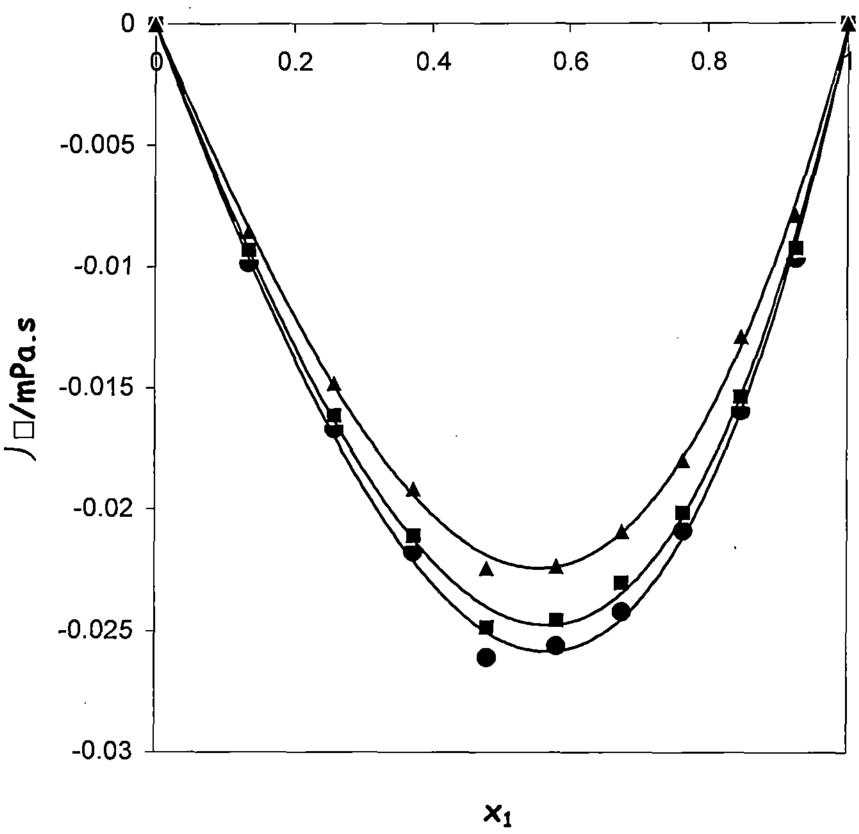

Fig. 6: Plot of viscosity deviation ($\Delta\eta$/m. Pa. S) vs. mole fraction (x_1) of THF + n-Heptane mixtures at at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

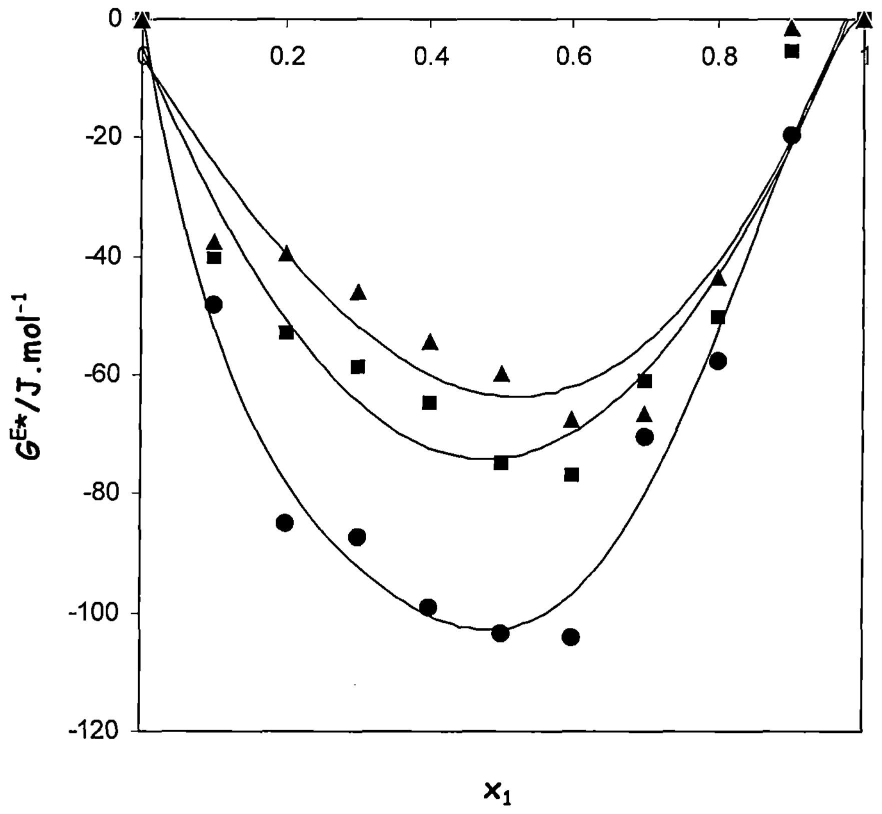

Fig. 7: Plot of excess free energy of activation of viscous flow (G^{*E} /J. mol^{-1}) vs. mole fraction (x_1) of THF + n-Pentane mixtures at at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

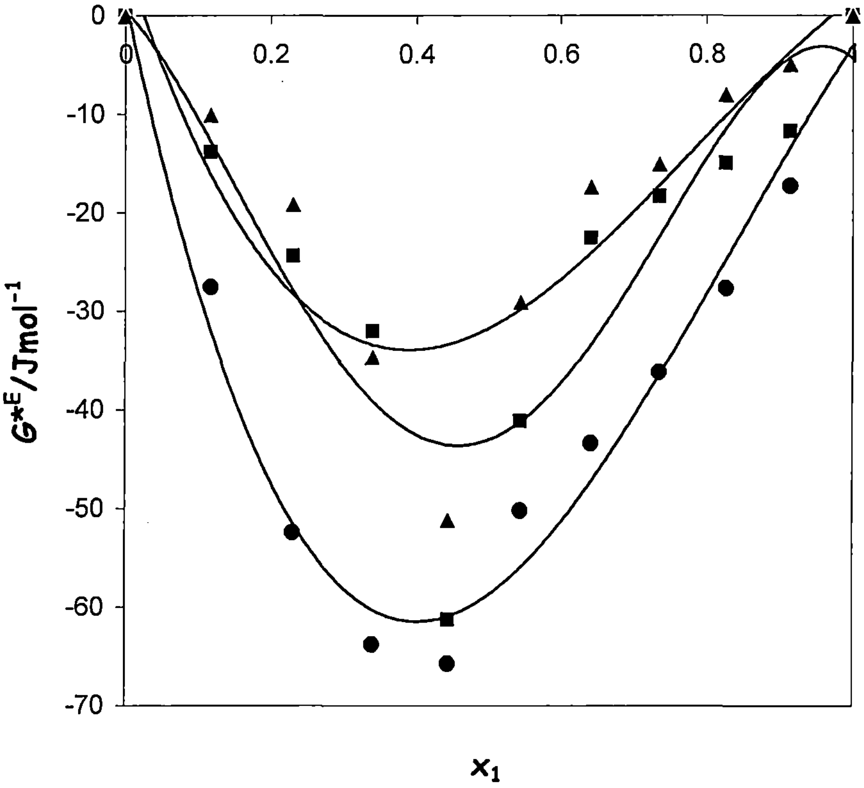

Fig. 8: Plot of excess free energy of activation of viscous flow (G^{*E}/J. mol^{-1}) vs. mole fraction (x_1) of THF + n-Hexane mixtures at at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

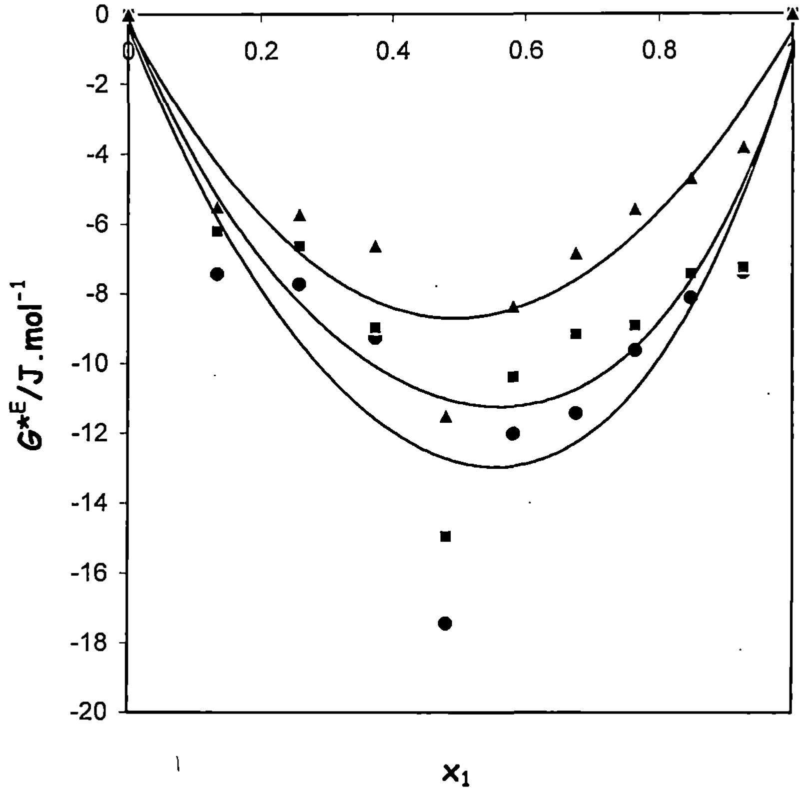

Fig 9 excess free energy of activation of viscous flow (G^{*E} /J. mol^{-1}) vs. mole fraction (x_1) of THF + n-Heptane mixtures at at 288.15 K (•); 293.15 K (■) and 298.15 K (▲).

CHAPTER VII

Physico-Chemical Studies on the Solute-Solvent Interactions and Ultrasonic Speed of Resorcinol in 2-Methoxyethanol and Tetrahydrofuran at Different Temperatures*

7.1. *Introduction*

Studies on viscosities, densities and ultrasonic speeds of solutions help in characterizing the structure and thermodynamic properties of solutions. Various types of interactions exist between the solutes in solutions and of these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Tetrahydrofuran (THF) and 2-methoxyethanol (ME) are very important solvents widely used in various industries. These are industrial solvents and figure prominently in the high-energy battery technology and have also found wide application in the organic synthesis as manifested from the physico-chemical studies in these media [1-10]. In this present work, an attempt has been made to provide an unequivocal interpretation of solute-solvent and solute-solute interactions prevailing in the studied solutions. Several workers have reported volumetric, Viscometric and ultrasonic studies of this compound in non-aqueous solutions [11-15] but such studies in pure THF and 2-methoxyethanol is still scanty.

7.2. *Experimental Section*

7.2.1. *Materials*

Tetrahydrofuran (Merck, India] was kept several days over KOH, refluxed for 24 hours and distilled over $LiAlH_4$ described earlier [1]. 2-Methoxyethanol was allowed to stand overnight with $CaSO_4$ and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenyhydrazine to remove aliphatic ketones. Resorcinol (A.R.) was purified by the reported procedure [11] and the compound was dried and stored in a vacuum desiccator.

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7.2.2. *Apparatus and Procedure*

Densities, ρ at 303.15, 313.15 and 323.15 K were measured with Ostwald-Sprengel type Pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of ~ 0.1 cm. It was calibrated at 303.15, 313.15 and 323.15 K with double-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at the desired temperature (± 0.01^0C) by means of a mercury-in-glass thermo-regulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during time of actual measurements. An average of triplicate measurement was taken into account. The density values were reproducible to ± 3×10^{-4} g cm^{-3}. Details have been described earlier [16]. The viscosity was measured by means of a suspended level Ubbelohde [17] viscometer at the desired temperature with a thermostat bath controlled to $\pm0.01^0C$.

Sound speeds were determined with an accuracy of 0.3% using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz which was calibrated with water, methanol and benzene at each temperature, described in detail elsewhere [18-19]. The solutions studied here were made by mass and the conversion of molality into molarity was done [20].

7.3. *Results and Discussion*

The experimental values of concentration c, densities ρ, viscosities η and derived parameters at 303.15, 313.15 and 323.15 K are recorded in table 2.

The apparent molar volumes V_ϕ were determined from the solution densities using the following equation,

$$V_\varphi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \qquad (1)$$

Where, M is the molar mass of the solute, c is the molarity of the solution and the other symbols have their usual significance.

The limiting apparent molar volumes V_ϕ^0 were calculated using the least-squares treatment of the plot of V_ϕ vs. $c^{\frac{1}{2}}$ using the Masson equation [21],

$$V_\varphi = V_\varphi^0 + S_v^* c^{1/2} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_v^* the experimental slope.

The values of V_ϕ^0 and S_v^* along with temperature of resorcinol in solvents follows the polynomial ,

$$V_\varphi^0 = a_0 + a_1 T + a_2 T^2 \tag{3}$$

over the temperature range under investigation, where A is the temperature in degree Kelvin.

Values of coefficients of the above equation for resorcinol in pure THF and 2-methoxyethanol are recorded in table 3.

From the values of coefficients the following equations are obtained

Resorcinol in THF

$$\begin{aligned} V_\varphi^0 &= -643.0947/c\,m^3 mol^{-1} + 3.6120T/cm\ ^3 mol^{-1} K^{-1} \\ &- 4.9985 \times 10^{-3} T^2 / cm^3 mol^{-1} K^{-2} \end{aligned} \tag{4}$$

Resorcinol in ME

$$\begin{aligned} V_\varphi^0 &= -548.53663/\ cm^3 mol^{-1} + 2.50172T/c\,m^3 mol^{-1} K^{-1} \\ &- 2.0465 \times 10^{-3} /cm^3 mol^{-1} K^{-2} \end{aligned} \tag{5}$$

The apparent molar expansibilities ϕ_E^0 can be obtained by the following equation,

$$\varphi_E^0 = (\frac{\delta V_\varphi^0}{\delta T})_p = a_1 + 2a_2 T \tag{6}$$

The values of ϕ_E^0 of the studied compound at 303.13, 313.15 and 323.15 K are determined and reported in table 4.

Hepler [22] developed a technique of examining the magnitudes of $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ for solute in terms of long range structure-making and breaking capacity of the solutes in mixed solvent systems using the general thermodynamic expression.

$$\left(\delta c_P / \delta P\right) = \left(\delta^2 V_\phi^0 / \delta T^2\right)_P \qquad (7)$$

The viscosity of resorcinol in pure THF and in pure 2-methoxyethanol has been analyzed using the Jones-Dole [23] equation:

$$\left.\begin{aligned} \frac{\eta}{\eta_0} &= 1 + Ac^{1/2} + Bc \\ \left(\frac{\eta}{\eta_0} - 1\right)/c^{1/2} &= A + Bc^{1/2} \end{aligned}\right] \qquad (8)$$

Where $\eta = (Kt - \frac{L}{t})\rho$

where, η_0 and η are the viscosities of solvent and solution respectively. K and L are the constant for a particular viscometer. The values of A and B are estimated by computerized lest square method and recorded in table 1.

Isentropic compressibility, K_S was calculated from the following relation.

$$K_S = \frac{1}{u^2 \rho} \qquad (9)$$

where ρ is the solution density and u is the speeds of sound in the solution. The apparent molal isentropic compressibility ϕ_K of the solution was determined from the relation

$$\phi_K = MK_S / \rho_0 + 1000\left(K_S\rho_0 - K_S^0\rho\right) / m\rho\rho_0 \qquad (10)$$

The limiting apparent molal isentropic compressibility, ϕ_K^0 was obtained by extrapolating the plots of ϕ_K versus the square root of molal concentration of the solute to zero concentration by the computerized least square method:

$$\varphi_K = \varphi_K^0 + S_K^* m^{1/2} \tag{11}$$

where S_K^* is the experimental slope.

The values of u, β, ϕ_K, ϕ_K^0 and S_K^* are recorded in table 2.

We have determined the ρ and η and calculated the V_ϕ, V_ϕ^0, S_v^*, ϕ_K, ϕ_K^0, B and A at 303.15, 313.15 and 323.15 K using appropriate equations and graphical representations.

As the investigated systems are characterized by hydrogen bond, the solute-solvent and solute-solute interactions can be interpreted in terms of structural changes, which arise due to hydrogen bond interactions present between various components of the solvent and solution systems.

To examine the solute-solvent interactions, the V_ϕ can be used. Table1 and Figs.1 and 3 in case of ME reveal that the V_ϕ^0 values are positive and increases with rise in temperature. This indicates the presence of strong solute-solvent interaction and these interactions are strengthened with rise in temperature. Whereas in case of THF the V_ϕ values are small at various temperatures and the values of V_ϕ increases with increase of temperature. This indicates the presence of weak solute-solvent interaction and such interaction increases with rise of temperature. Similar results were obtained for some 1:1 electrolyte in aqueous DMF [24] and aqueous THF [1].

It is also evident (Table1 and Figs. 1 and 3) that S_v^* are positive in both system at different temperatures. Since S_v^* is a measure of solute-solute interactions, the results indicate the presence of strong solute-solute interactions. As expected, the S_v^* values decrease with increasing temperature in these solvents for the studied solute, which is attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of solute-solute interactions [25].

It is found from table4 that the value of ϕ_E^0 of solute decreases with rise in temperature in studied solvents, which can be ascribed to the absence of caging or packing effect [26].

In our present investigations, it is evident from table 4 that the $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ values are negative for resorcinol in studied solvents, suggesting thereby that resorcinol acts as a structure-breaker in such solvents.

It is observed (table 1 and Figs.2 and 4) that the values of B of resorcinol in the studied solvent systems are positive and these values increase with increasing temperature. This indicates that this solute acts as structure-breaker in such solvents. These conclusions are excellent agreement with that drawn from magnitude of $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ illustrated earlier.

It has been reported by a number of workers that $\left(\delta B / \delta T\right)$is a better criterion [27-28] for determining the structure making/breaking nature of any solute rather than simply the value of B. It is found from table 1 that the values of B increase with rise in temperature [positive $\left(\delta B / \delta T\right)$] suggesting structure-breaking tendency. A similar result was reported by some workers [29] studied solvents in case of viscosity of some salts in propionic acid + ethanol mixtures.

A perusal of table 2 and Figs. 5 and 6 show that the values of ϕ_K^0 are negative and become more negative on increasing the temperature. Negative ϕ_K^0 values of resorcinol can be interpreted in terms of the loss of compressibility of solvents due to electrostrictive forces in the vicinity of the solute particles. On raising the temperature of the system, the solute particles lose some solvent molecules from their first coordination sphere in a process, which is expected to increase the compressibility. But at higher temperature, breakdown of the non-covalent bonding between the solvent molecules also takes place more effectively resulting in a loss of compressibility. Thus it may be concluded that for the solute solution under study, the later effect is growing faster and overriding the former as far as the present temperature range is concerned. From Table 2 (figs.5 and 6), it is evident that S_K^* have positive values indicating the existence of strong solute - solute interactions in the studied solvent system which resembles the agreement drawn from S_v^* discussed earlier. A similar result was reported by worker [30] in the case of ultrasonic studies of some alkali metal halides and nitrates in THF + Water mixture.

7.4 *Conclusion:*

The study shows the nature of interactions occurring in solution of Resorcinol in ME and THF were probed with the aid of their apparent molar volume and apparent molar isentropic compressibility at three different temperatures in this chapter. It appears that weak solute-solvent (Resorcinol-ME/THF) interactions were present here, and such interactions increases with rise of temperature whereas the solute-solute interaction in the above case is very strong but diminishes with rise of temperature due to the breaking of non covalent bonding between the solute molecules. These are the notable points as obtained from the above work.

References

1. M.N. Roy, A. Jha, and R. Dey, *J. Chem. Eng. Data.* **2001**, *46*, 1247.
2. M.N. Roy and B.B. Gurung, *J. Indian Chem. Soc.* **2004**, *81*, 1.
3. K. Masayuki and N. Kastutosh, *J. Chem. Eng. Data.* **1995**, *46*, 935.
4. F.J. Millero, *Structure and Transport process in water and aqueous solution*, R.A. Horne, New York, **1972**.
5. R. Jasinki, *High Energy Batteries*, Plenum Press, New York, **1967**.
6. M.N. Roy and D.K. Hazra, *Indian J. Chem. Technol.* **1994**, *1*, 93.
7. M.N. Roy, *J. Teach. and Res.* **2000**, *7*, 17.
8. A. Sacco, M.D. Monika and A.D. Giglio, *J. Chem. Soc. Faraday Trans.*1 **1983**, *9*, 2631.
9. C.G. Janz and R.P.T. Tomkins, N*on-aqueous Electrolytes Handbook*, Academic Press, New York, Vol. 2 **1973**.
10. M.L. Parmar, V.N. Rao and S.K. Bhardwaj, *J. Indian. Chem. Soc.* **1990**, *67*, 591.
11. P. Franzosini and F.W. Falgar, *J. Chem. Thermodynamics.* **1984**, *16*, 81.
12. T.V. Chalkian, A.P. Sarvasyan and K.J. Breslauer, *J. Phys. Chem.* **1993**, *97*, 1301.
13. M.N. Roy, D. Nandi and D.K. Hazra, *J. Indian Chem. Soc.* **1993**, *70*, 1123.
14. D.P. Kharakoz, *Biophys. Chem.* **1989**, *34*, 115.
15. T.S. Banipal and P. Kapoor; *J. Indian Chem.* **1999**, *76*, 341.
16. M.N. Roy, B. Das and D.K. Hazra; *Indian J. Chem. Technol.* **1994**, *1*, 93.
17. J.R. Suindells and T.B. Godfray, *J. Res. Natt. Bur. Stand.* **1952**, *1*, 48.
18. K. Tamura, K. Ohomura, and S. Murakami, *J. Chem. Thermodyn.* **1983**, *15*, 859.
19. M.N. Roy and B.B. Gurung, *J. Indian Chem. Soc.* **2003**, *80*, 1.
20. D.P. Shoemaker and C.W.S. Gorland, *Experiments in Physical Chemistry*, McGraw Hill, New York. **1967**, *131*.
21. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.

22. L.G. Hepler, *Can. J. Chem.* **1969**, *47*, 4617.

23. G. Johnes and M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950.

24. E. Gorland-Paneda, C. Yanes, and J.J. Calventa, *J. Chem. Soc. Faraday Trans.*, **94**, 573 **1994**.

25. F.J. Millero, *Structure and Transport process in water and aqueous solution*, R.A. Horne, New York, **1973**.

26. P.R. Misra and B. Das, *Indian J. Chem.* **1978**, *16*, 348.

27. R. Gopal and M.A. Siddique, *J. Phy. Chem.* **1969**, *72*, 1814.

28. N. Saha and B. Das, *J. Chem. Eng. Data.* **1997**, *42*, 277.

29. M.L. Parmer and M.K. Chouhan, *Indian J. Chem.* **1995**, *34A*, 434.

30. M.N. Roy and D.K. Hazra; *N.B. Univ. Rev.* (Sci and Technol.) **1997**, *8*, 54.

Table 1

Molar Concentration (c), Densities (ρ), Viscosities (η), Apparent Molar Volumes (V_ϕ), Limiting Apparent Molar Volume (V_ϕ^0), Experimental Slope (S_v^*) and Values of A and B of Resorcinol in Various Solvents at Different Temperatures.

c / mol. dm^{-3}	$\rho \times 10^3$/ kg.m^{-3}	$\eta \times 10^3$/ Pa. s	$V_\phi \times 10^6$/ m^3.mol^{-1}	$V_\phi^0 \times 10^6$/ m^3.mol^{-1}	$S_v^* \times 10^6$/ (m^9.mol^{-3})$^{1/2}$	A / m$^{3/2}$mol$^{1/2}$	B / m^3 mol^{-1}.
Resorcinol in ME							
303.15 K							
0.00803	0.9583	1.4015	34.2162	21.7866	135.4508	0.02071	0.4634
0.0562	0.9610	1.4359	53.2808				
0.1044	0.9627	1.4683	65.0445				
0.1526	0.9635	1.5013	75.5418				
0.2007	0.9638	1.5372	83.2368				
0.2489	0.9640	1.5706	88.5811				
313.15K							
0.00795	0.9494	1.2159	44.3659	34.1912	118.3329	-0.0273	0.4847
0.0557	0.9517	1.2383	62.0655				
0.1033	0.9530	1.2629	72.9971				
0.1511	0.9540	1.2893	80.1794				
0.1987	0.9542	1.3167	87.5660				
0.2464	0.9544	1.3438	91.9686				
323.15 K							
0.00789	0.9421	1.0468	55.0455	46.1865	106.6030	-0.0344	0.4940
0.0552	0.9440	1.0660	70.9719				
0.1025	0.9451	1.0867	80.9737				
0.1497	0.9456	1.1088	88.9894				
0.1970	0.9458	1.1320	94.1862				
0.2448	0.9462	1.1548	96.8548				
Resorcinol in THF							
303.15 K							
0.00806	0.8768	0.4495	5.3602	-7.4616	145.6027	0.0794	0.2191
0.0564	0.8808	0.4590	26.9953				

Contd.

0.1048	0.8838	0.4668	40.0985				
0.1532	0.8861	0.4738	49.9931				
0.2016	0.8879	0.4808	58.1998				
0.2500	0.8893	0.4884	64.5511				
				313.15 K			
0.00797	0.8671	0.41034	9.8467	-2.1468	140.2331	0.0152	0.2508
0.0558	0.8709	0.41594	31.3241				
0.1036	0.8738	0.42164	43.1172				
0.1542	0.8760	0.4268	53.0209				
0.1993	0.8776	0.4323	61.2416				
0.2472	0.8793	0.4374	66.2484				
				323.15 K			
0.007906	0.8613	0.3894	14.4522	2.16829	139.4083	-0.0199	0.2806
0.05542	0.8649	0.3933	35.0664				
0.10291	0.8677	0.3978	46.9925				
0.15039	0.8698	0.4026	56.0956				
0.19782	0.8713	0.4074	64.6902				
0.24526	0.8726	0.4125	70.7684				

Table 2

Molal Concentration (m), Sound Velocity (u), Isentropic Compressibility (K_S), Apparent Molal Isentropic Compressibility (ϕ_K), Limiting Apparent Molal Isentropic Compressibility (ϕ_K^0) and Experimental Slope (S_K^*) of Resorcinol in Various Solvents at Different Temperatures

m / Mol.Kg^{-1}	u/ (m·s^{-1})	K_S × 10^7/ Pa^{-1}	ϕ_K × 10^7 / m^{3}mol^{-1}Pa^{-1}	ϕ_K^0 × 10^7 / m^{3}mol^{-1}Pa^{-1}	S_K^* × 10^7/ (m^9.mol^{-3})$^{1/2}$Pa^{-1}
			Resorcinol in ME		
			303.15 K		
0.008389	1302.4	6.1514	-3.5306	-4.0555	6.0166
0.0589	1315.1	6.0164	-2.6057		
0.1097	1323.7	5.9283	-2.0206		
0.1612	1329.9	5.8684	-1.5810		
0.2132	1335.4	5.8183	-1.2911		
0.2658	1338.1	5.7938	-1.0056		
			313.15 K		
0.008386	1268.7	6.5438	-4.1709	-4.8330	7.2967
0.05887	1282.8	6.3855	-3.0711		
0.10973	1292.5	6.2807	-2.4066		
0.16115	1299.0	6.2119	-1.9011		
0.21316	1301.8	6.1837	-1.4104		
0.26576	1304.9	6.1525	-1.1225		
			323.15K		
0.008386	1240.7	6.8960	-4.9125	-5.7239	8.7415
0.58870	1256.4	6.7110	-3.6126		
0,10973	1267.2	6.5897	-2.8322		
0.16115	1274.5	6.5108	-2.2314		
0.21316	1277.5	6.4782	-1.6762		
0.26576	1279.8	6.4526	-1.3099		
			Resorcinol in THF		
			303.15 K		
0.0092057	1252.9	7.2654	-4.5522	-5.2802	7.9261

Contd.

0.06453	1263.8	7.1076	-3.2512		
0.12017	1270.9	7.0051	-2.5363		
0.17625	1273.7	6.9564	-1.8841		
0.23287	1274.8	6.9304	-1.4088		
0.29005	1276.1	6.9050	-1.1056		
			313.15 K		
0.0092057	1193.6	8.0952	-5.3215	-6.1470	8.9247
0.06453	1205.2	7.9056	-3.9084		
0.12017	1211.9	7.7915	-2.9865		
0.17625	1216.3	7.7167	-2.3412		
0.23287	1218.3	7.6765	-1.8060		
0.29005	1219.7	7.6452	-1.4413		
			323.15K		
0.0092057	1148.1	8.8090	-7.3286	-8.5072	13.0257
0.06453	1162.0	8.5620	-5.2087		
0.12017	1169.8	8.4220	-3.9104		
0.17625	1173.0	8.3554	-2.9009		
0.23287	1174.4	8.3514	-2.1771		
0.29005	1175.1	8.3339	-1.6740		

Table 3

Values of Coefficient for Resorcinol in THF and ME

Solvent	$a_0 \times 10^6$ (m^3mol^{-1})	$a_1 \times 10^6$ ($m^3mol^{-1}K^{-1}$)	$a_2 \times 10^6$ ($m^3mol^{-1}K^{-2}$)
THF	-643.0947	3.6121	-4.9985×10^{-3}
ME	-548.5366	2.0517	-2.0465×10^{-3}

Table 4

Limiting Apparent Molar Expansibilities (ϕ_E^0) for Resorcinol in THF and ME at Different Temperatures

	ϕ_E^0 x 10^6 / ($m^3mol^{-1}K^{-1}$)			$\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$
Solvents	**303.15 K**	**313.15 K**	**323.15 K**	
THF	0.5726	0.4904	0.4081	Negative
ME	1.2609	1.2199	1.1791	Negative

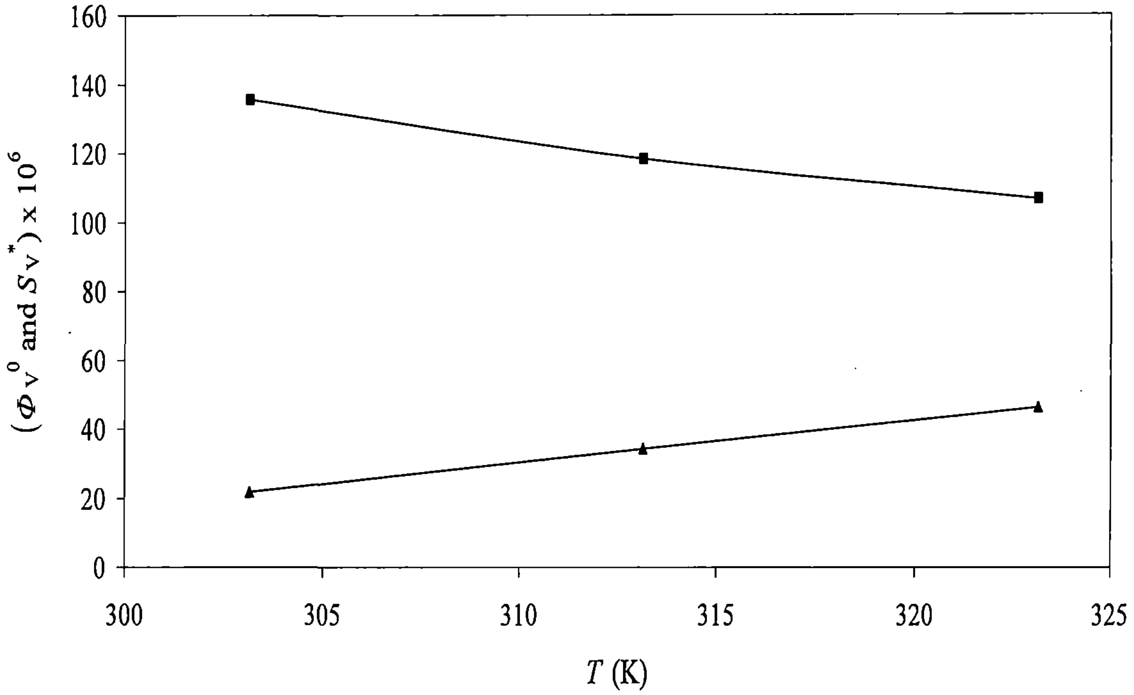

Fig.1. Plots of $\Phi_V{}^0$ and $S_V{}^*$ *versus* temperature *T* for resorcinol in ME. Experimental points: $\Phi_V{}^0$ (▲), $S_V{}^*$ (■).

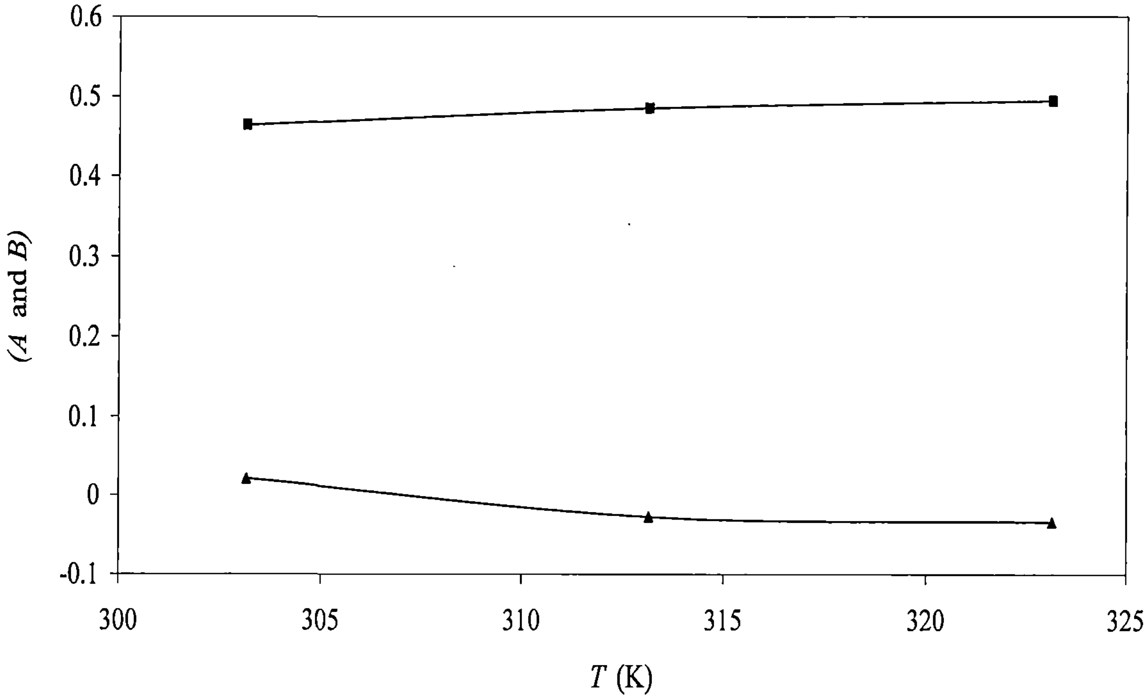

Fig.2. Plots of *A* and *B* *versus* temperature *T* for resorcinol in ME. Experimental points: A (▲), B(■).

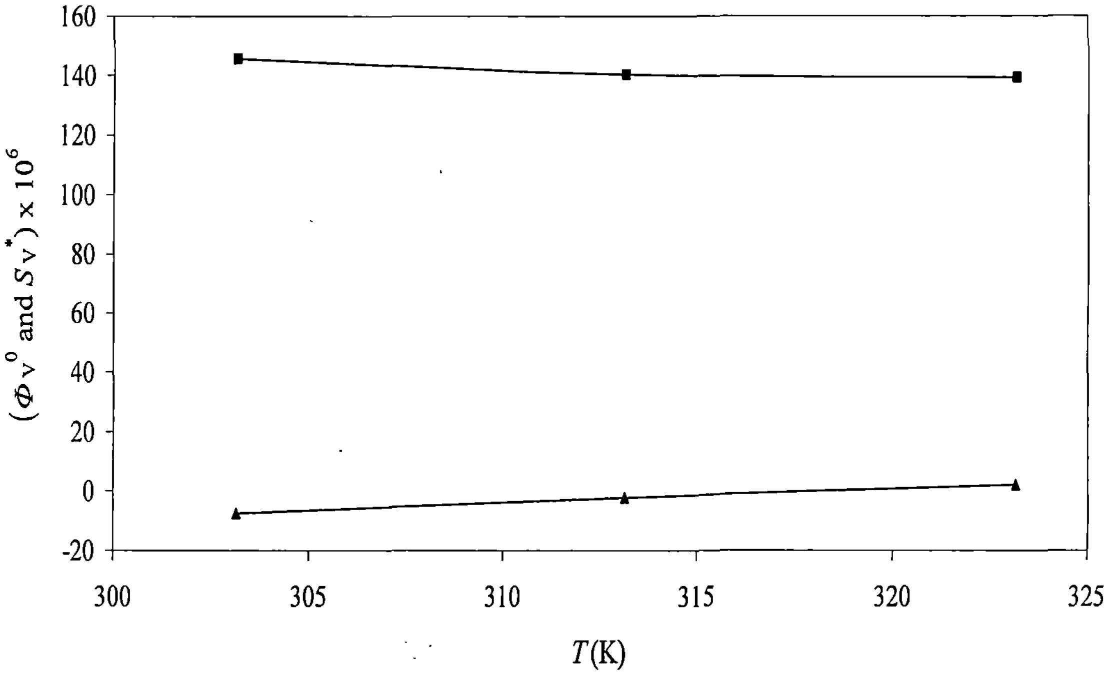

Fig.3. Plots of Φ_V^0 and S_V^* *versus* temperature T for resorcinol in THF. Experimental points: Φ_V^0(▲), S_V^* (■)

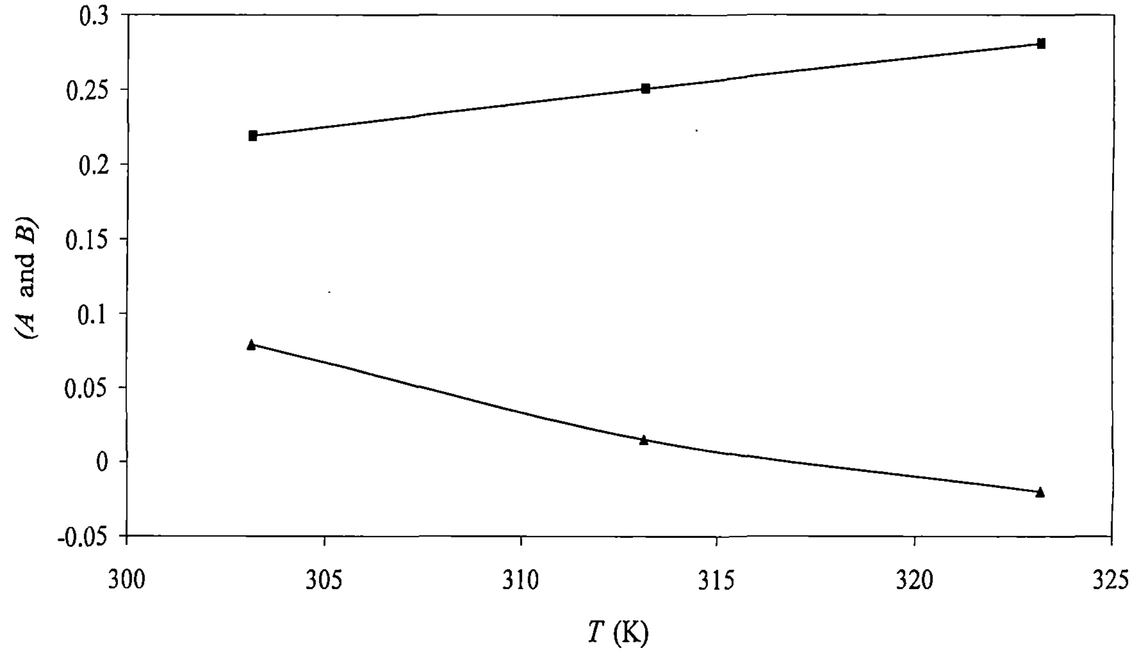

Fig.4. Plots of A and B *versus* temperature T for resorcinol in THF. Experimental points: A (▲), B (■).

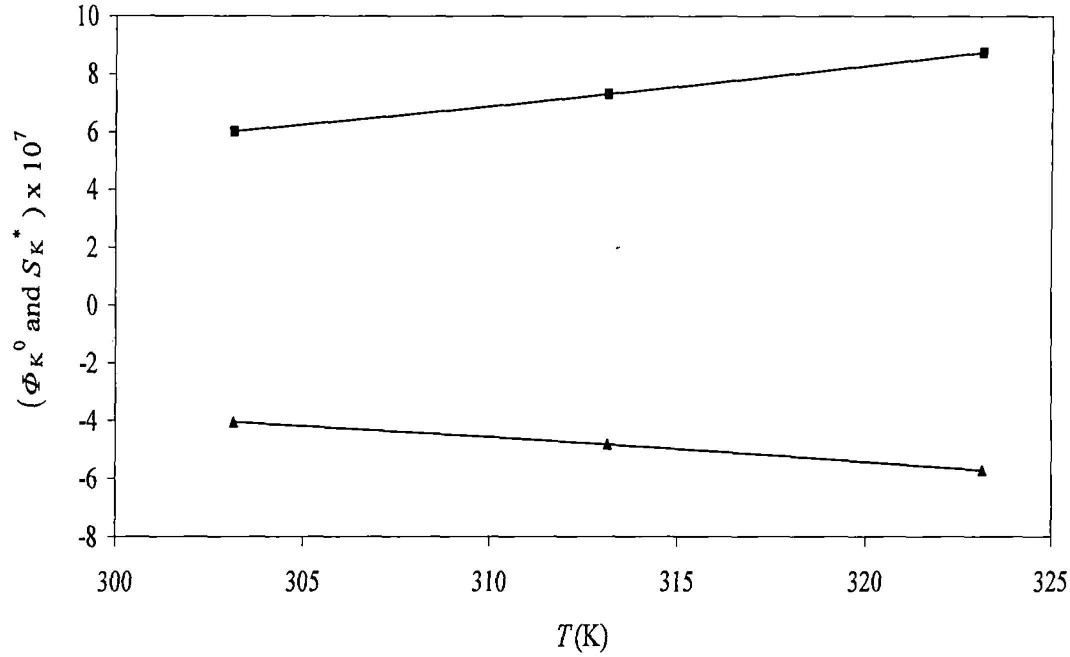

Fig.5. Plots of Φ_K^0 and S_K^* *versus* temperature T for resorcinol in ME. Experimental points: Φ_K^0 (▲), S_K^* (■).

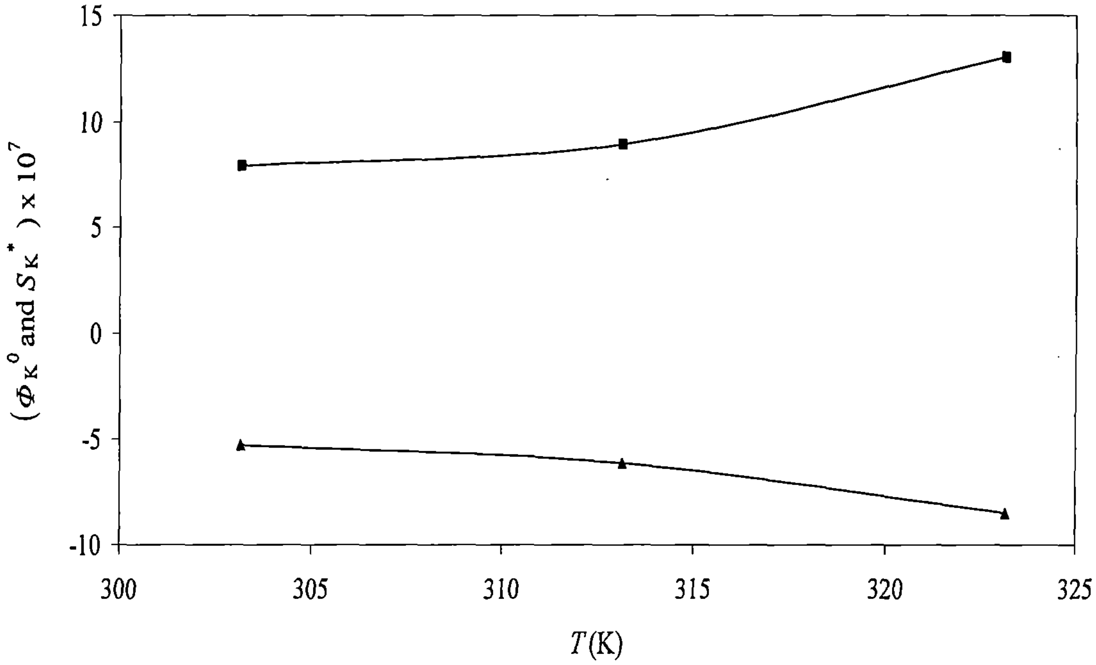

Fig.6. Plots of Φ_K^0 and S_K^* *versus* temperature T for resorcinol in THF. Experimental points: Φ_K^0 (▲), S_K^* (■).

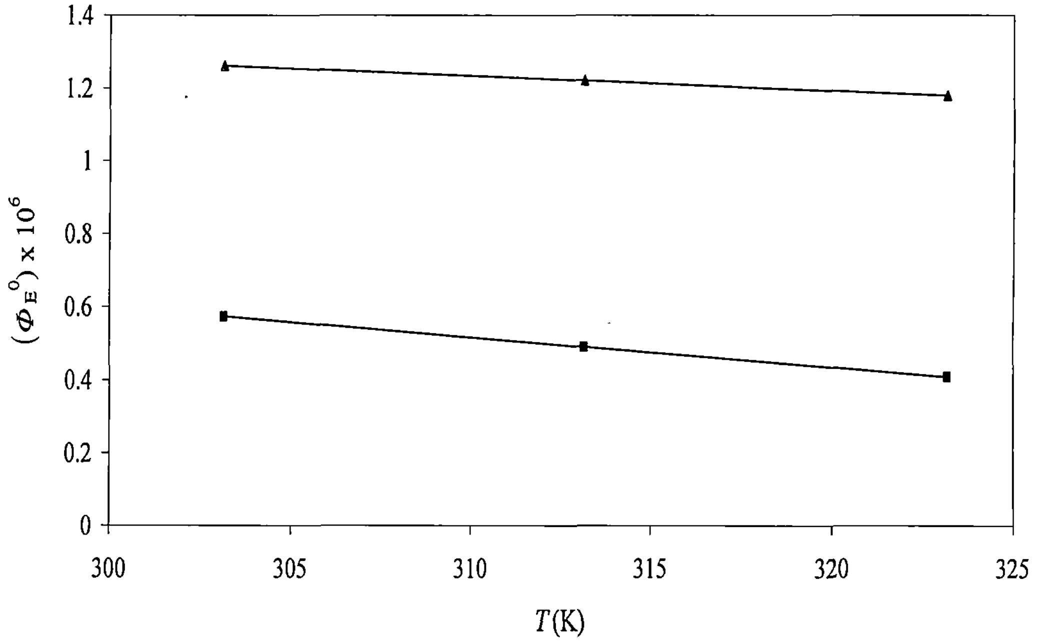

Fig.7. Plots of Φ_E^0 *versus* temperature T for resorcinol in different solvents.
Experimental points: ME (▲), THF (■)

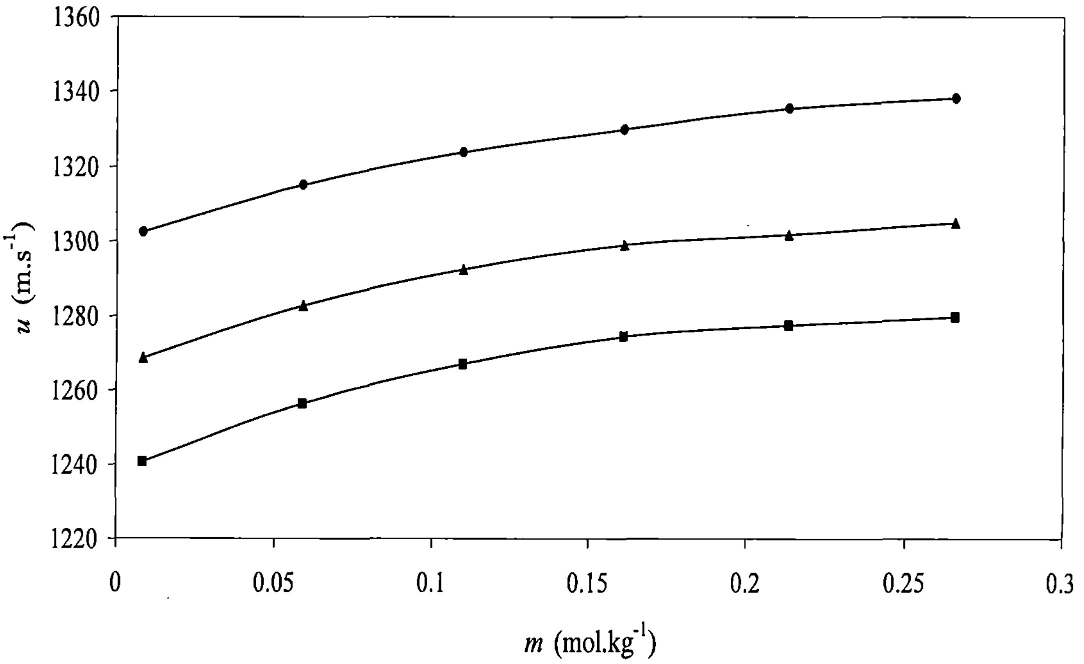

Fig.8. Variation of ultasonic speeds u with concentration m of resorcinol in ME.
Experimental points: 303.15 K (●), 313.15 K (▲), 323.15 K (■).

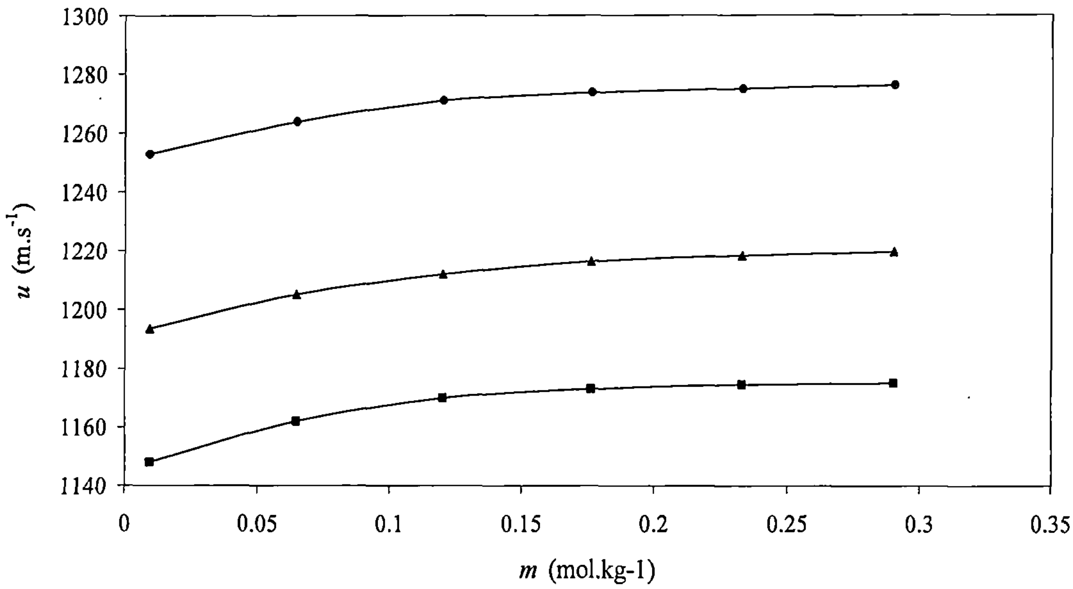

Fig.9. Variation of ultrasonic speeds *u* with concentration *m* of resorcinol in THF. Experimental points: 303.15 K (●), 313.15 K (▲), 323.15 K (■).

CHAPTER VIII

Electrical Conductance of Alkali Chlorides in Mixed Solvents: Methanol + Carbon Tetrachloride and Methanol + 1,4-Dioxane at 298.15 K*

8.1. *Introduction*

Study of electrical conductance of mixed organic solvent systems plays a significant role in examining the nature and magnitude of ion-ion and ion-solvent interactions.[1-7] Other solvent properties such as viscosity and permittivity have also been taken into account in determining the extent of these interactions.

1, 4-dioxane is a good industrial solvent and figures prominently in the high-energy battery technology [8] and has also found its application in the organic syntheses.[9,10,11,12] Carbon tetrachloride is used to make compounds such as Chlorofluoromethanes, used as refrigerants and aerosol-spray propellants, in fire extinguishers and for dry cleaning of fabrics. Methanol is very widely used in industry, including the manufacture of pharmaceuticals and cosmetic products, in enology and as an energy source.[13]

The alkali metal salts, specially, Li salts has been used for many years in non-aqueous batteries.[8] In such systems, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte possessing high specific conductivity and, hence, minimal ion-ion interaction is required to maintain the cell at low resistance. Knowledge of the application of the solvent and solute studied and the state of association of the electrolytes and their interactions with solvent molecules is essential for the optimal choice of solvent and electrolyte[14].

Methanol is extremely self-associated by hydrogen bonding in pure state[15]. But, this type of strong intermolecular forces are either very week or totally absent in case of carbon tetrachloride or 1,4-dioxane while the dipole-induced dipole forces along with dispersive forces predominate in these cases.

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The conductance and viscosity of three alkali chlorides is studied to reveal the nature of ionic association and mobility of ions in these mixed solvent systems, which have not been studied earlier as per available literature.

In the present work, an attempt has been made to ascertain the complete nature of ion-solvent, solvent-solvent interactions of the alkali metal chlorides in solvent mixtures of methanol with carbon tetrachloride and 1,4-dioxane at 298.15 K. A comparison between the natures of interactive forces operating in these two different solvent systems is also analyzed.

8.2 Experimental Section

8.2.1. *Materials*

Lithium chloride (Merck, India), Sodium chloride (Loba Chemie) and Potassium chloride (Merck, India) was recrystallized, dried by the procedures mentioned in Chap III and stored in desiccators before use.

Methanol (Merck, India, Uvasol grade, 99.5% pure) was dried over 3Å molecular sieves and distilled fractionally. Carbon tetrachloride (Merck, India) was dried, and destilled as mentioned procedures (vide Chap III). 1,4-dioxane (Merck, India) with initial water content of 120 ppm found by Karl-Fischer titration and 0.15% impurities found by gas chromatography was used after redistillation[10].

The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature as listed in Table 1.

8.2.2. *Apparatus and Procedure*

Digital Temperature controller BP-41 (Bose-Panda Instruments, India) (± 0.1K) was used to maintain the temperature.

Conductance measurements of the solvent systems were executed in a Systronic 308 conductivity-TDS meter (accuracy ± 0.1%) working at a frequency of 1kHz, using a dip type immersion cell (cell constant 1.07at 298.15 K).

Densities (ρ) were measured at the mentioned temperatures with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. Viscosities (η) have been measured by means of a suspended Ubbelohde type viscometer [31]. The details of density and viscosity measurements were described earlier[9, 23] in Chap III. The precision of the density and viscosity measurements is ± 3×10^{-4} g.cm^{-1} and ± 2×10^{-4} m.Pa.s respectively.

All the solvent mixtures were prepared by mass. Three sets of each binary solvent mixtures (90.6%, 82.31%, 66.89%) of methanol with carbon tetrachloride and 1,4-dioxane having mole fractions of methanol (x_1) as 1.0000, 0.97885, 0.95712, 0.90657 and 1.0000, 0.96364, 0.92747, 0.84752 respectively were chosen as the solvent media for present study. A stock solution of each salt was prepared by mass and working solutions were prepared by weight dilution.

8.3. *Results and Discussion*

The physical properties of the pure solvent and solvent mixtures are given in Table 1, where ε is the dielectric constant, ρ_0 is the density (Kg.m^{-3}) and η_0 is the viscosity (m.Pa.s). Conductivities of electrolyte solutions as a function of molar concentration (c) are given in Table 2 in different solvent mixtures at 298.15K.

Permittivity (ε) of the solvent-mixtures were estimated by a computerized extrapolation programme, using ε and *W%* values from literature[14]. The conductance data have been analyzed by Fuoss conductance- concentration equation. (Fuoss, 1978 a, b).[16,17]

$$\Lambda = P[\Lambda_0(1+R_X)+E_L] \tag{1}$$

$$P = 1-\alpha(1-\gamma) \tag{2}$$

$$\gamma = 1-K_A c\gamma^2 f^2 \tag{3}$$

$$-\ln f = \beta\kappa / 2(1+\kappa R) \tag{4}$$

$$\beta = e^2 / \varepsilon kT \tag{5}$$

$$K_A = K_R / (1-\alpha) = K_R(1+K_S) \tag{6}$$

Where, R_X is the relaxation field effect, E_L is the electrophoretic counter current, κ^{-1} is the radius of the ion atmosphere, ε is the relative permittivity of the solvent, e is the electron charge, k is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, f is the activity coefficient, c is the molarity of the solution, T is the absolute temperature, β is twice the Bjerrum distance, and α denotes the fraction of the paired ions, K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter R around cations, and K_S is a constant describing the short range process by which contact pairs form and dissociate. K_R and K_S are given as follows,

$$K_R = \frac{(1-\alpha)(1-\gamma)}{c\gamma^2 f^2} \qquad (7)$$

$$K_S = \frac{\alpha}{(1-\alpha)} \qquad (8)$$

The computations were performed in a computer using the programme suggested by Fuoss. The initial Λ_0 values for iteration procedure were obtained from Shedlovsky extrapolation[19] of the data. Input for the program is the set,

$$(C_j, \Lambda_j, j = 1,\ldots\ldots\ldots\ldots, n), n, \eta, \varepsilon, T,$$

initial value of Λ_0 and a set of instructions to cover a protected range of R values.

In practice calculations were performed by fitting the values of Λ_0 and σ, which minimize the standard deviation (σ),

$$\sigma^2 = \sum \left[\frac{(\Lambda_{jcalc} - \Lambda_{jobs})^2}{(n-2)} \right] \qquad (9)$$

For a sequence of R values and then plotting σ against the best-fit R corresponds the minimum of σ versus R curve. First, approximate run over a fairly wide range of R values are made to locate the minimum and then a fine scan around the minimum was made. Finally with this minimizing value of R, corresponding Λ_0 and K_A were calculated.

In the present analysis, however, since a rough scan of R values gave no significant minima in the (σ % vs. R) curves, the R value was assumed to be, $R = a + d$ where, a is the sum of crystallographic radii and d, the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance 'd' is given by, [17]

$$d(A^0) = 1.183\left(\frac{M}{\rho_0}\right)^{\frac{1}{3}} \qquad (10)$$

Where, M is the molar weight of the solvent and ρ_0 is its density. In mixed solvent studies M is replaced by the mole fraction average molecular weight M_{AV}, given by,

$$M_{AV} = M_1M_2 \Big/ (W_1M_2 + W_2M_1) \qquad (11)$$

Where, W_1, W_2 and M_1, M_2 are the weight fraction and molecular weight of the first and second component respectively. Though, this is an over simplification ignoring possible selective solvation, it at least provides a self consistent way to obtain an acceptable value for the parameter when a broad range of R values fits the data.

The limiting equivalent conductance, (Λ_0), the association constant (K_A), and the Walden products ($\Lambda_0\eta_0$) for the three salts at all the mole fractions of the solvent mixtures studied here are recorded in Table 3. These data are interpreted in terms of ion-solvent and ion-ion interactions and structural changes in the mixed solvent systems.

It is observed from Table 3 that, the limiting equivalent conductance Λ_0 values for alkali chlorides increases with the increase in size of the cation for any mole fraction of the mixed solvent systems. For the three alkali chlorides, having common anion, the Λ_0 value is enhanced by the following order:

$Li^+ < Na^+ < K^+$

The trend of variation of Λ_0 values predicts the relative actual sizes of these ions as they exist in solution.[18] Thus the actual sizes of the cations as they exist in solution, follow the order:

$Li^+ > Na^+ > K^+$.

This is due to solvation of the ions by the solvent mixtures. For these electrolytes having the common anion, as the size of the cation increases, the solvation decreases. So, it can be said that, Li^+, which has the largest size in solution, is the most solvated one, and K^+, having the smallest size is the least solvated one.[19]

The conductivity enhancement in case of solvent mixtures can qualitatively be well explained by a favorable combination of high permittivity and low viscosity of solvents as observed by some researchers [20]. In the discussed solvent mixtures, methanol is the common solvent having higher permittivity compared to 1,4-Dioxane or Carbon tetrachloride. In both the solvent mixtures the conductivity measurements were done by taking the same salts. So, the combination of a solvent of higher permittivity (Methanol) with the one having low viscosity of (1,4-Dioxane) has comparatively higher mobility resulting in higher conductivity values.

The associations constant (K_A), as recorded in Table 3 indicates that, all the salts are highly associated in both the solvent mixtures. This is expected because of the lower permittivity of the components added.[21] For the alkali metal chlorides studied here, the K_A values decreases with increasing size of the cations in the order:

$Li^+ < Na^+ < K^+$,

This is due to an apparent decrease in ion dipole interactions.[5,22,23]

It is further seen from Table 3 that Λ_0 values decrease gradually with the addition of CCl_4 or 1,4 Dioxane to pure methanol with corresponding increase in K_A values. This indicates that association of ions increase with the addition of 1,4-dioxane or CCl_4 to pure methanol rendering to the decrease of the mobility of ions in the mixture and thereby decreasing Λ_0 values. The significantly large values of K_A and exothermic ion-pair formation in the solvent mixture indicate the presence of specific short-range interaction within the ion-pair.

The values of Walden product ($\Lambda_0\eta_0$) for the studied electrolytes pass through a maximum at about 0.97885 mole fraction of methanol, in methanol carbon tetrachloride solvent system, whereas for, methanol, 1,4-dioxane solvent system, the Walden product is maximum at 0.96364 mole fraction of methanol (table 3). The Walden products then decrease continuously for all the lower mole fractions. The representative plots for the selected chlorides for solvent mixture1, (methanol+ carbon tetrachloride) is given in figure 1, and that for solvent mixture 2, (methanol + 1,4- dioxane) is given figure 2.

There are lots of models to account for the dependence of the Walden product on solvent composition. The theory based on "gel effect,"[24,25] proposes that, the initial increment in $\Lambda_0\eta_0$ is due to migration process, occurring free of viscous force through the interstices created by long range order in the solvent. Some researchers[26] have also put forward a 'sorting mechanism' depending upon the 'acid base properties' of the organic solvent. It is suggested that, in this experiment, ion- methanol interactions are stronger than ion- carbon tetrachloride or ion- 1,4-dioxane interactions presumably because of the weaker acid- base properties of the later two solvent components. The theory envisages a comparative enrichment of methanol in the ionic co sphere and this causes the local viscosity near the ions to be lower than the bulk viscosity of the solvent medium, which in turn increases the mobility and as a result the Walden product appears higher for the next solvent mixtures. The theories based on solvent- dipole relaxation effects [27,28] can be used to explain the decrease in Walden product ($\Lambda_0\eta_0$) as the carbon tetrachloride or 1,4-dioxane concentration in the solvent mixture increases. It is generally accepted that, retardation due to relaxation of solvent dipoles around the ions in motion can decrease their mobility and the dielectric-shifting coefficient can be computed. However, to obtain meaningful data, it is essential to take into account the microscopic nature of the solvent in the vicinity of the ions as also the influence of the ions in the structure of the solvent.

There is another proposed scheme based on the assumption that, the progressive addition of carbon tetrachloride or 1,4-dioxane to methanol causes initial contraction of the solvation sheath around the ions present in solvent media. This "desolvation effect" [24,29] decreases the effective size of the cations and anions and as a result, the ionic mobility and Walden product of the salts can increase initially in the methanol rich region of the mixture. Gluekuf, [30] has noted that, as the ion size decreases, its first solvation sheath also contracts and therefore the friction between this layer and the ion increases. It appears that, this enhanced drag of the solvation layer decreases the mobility and so the Walden product ($\Lambda_0\eta_0$) shows a maximum at a particular solvent composition and then decreases monotonously. Extensive solvation of the ions with carbon tetrachloride or 1,4-dioxane can also decrease the mobility of the ions but this process is significant at higher concentration of carbon tetrachloride or 1,4-dioxane in the solvent mixture and helps in the continuous decrease of Walden product ($\Lambda_0\eta_0$).

It should still be mentioned[25] that, the theories discussed here or other contemporary theories do not predict quantitatively either the value of the maximum or its enhanced dependence for certain electrolytes in different solvent medium.

8.4 *Conclusion:*

In this chapter, the conductance and viscosity of three alkali chlorides is studied to reveal the nature of ionic association and mobility of ions in methanol+ carbon tetrachloride and methanol + 1,4- dioxane mixed solvent systems. It is found that, for these electrolytes having the common anion, as the size of the cation increases, the solvation decreases. All the salts are highly associated in both the solvent mixtures. Also the combination of a solvent of higher permittivity with the one having low viscosity of has comparatively higher mobility resulting in higher conductivity values. The values of Walden product for the studied electrolytes pass through a maximum at a particular mole fraction and then decrease continuously for all the lower mole fractions. These are the main conclusions drawn from the above conductance study.

References

1. P. K. Muhuri and D. K. Hazra, *J. Phys. Chem.* **1995**, *190*, 111.
2. A.K. Srivastava, R. A. Samanta, *J. Chem Engg, Data.* **1994**, *39*, 358.
3. H.Doe, H.Ohe, H.Matuba, A.Ichimura, T.Kitagawa, *Bull. Chem. Soc. Japan,* **1990**, *63*, 2785.
4. S.Taniewska-Osinska, A. Piekarska, A. Bald, A. Szeigis, *J. Chem. Soc., Faraday Trans,* **1989**, *85*, 3709.
5. N. Islam, S. B.A. Jaldi, A.A.Ansari, *Bull. Chem. Soc. Japan,* **1989**, *62,* 309.
6. N. Papadopoulos, *Can. J. Chem,* **1989**, *67*, 1624.
7. M.S.K. Niazi, *Bull. Chem. Soc. Japan,* **1989**, *62,* 309.
8. R. Jasinski, 'High Energy Batteries', Plenum Press, New York, **1967**.
9. M.N. Roy, A. Jha, R. Dey, *J. Chem Engg Data,* **2001**,*46*, 1247.
10. Janz C.G, Tomkins R.P.T. *Non-aqueous Electrolytes Handbook.* Academic Press. New York. **1973** Vol-2,
11. M.N. Roy, *J.Teach. Res. in chem.,* **2000**, *7*, 17.
12. M.N Roy and Hazra D.K., *Indian. J. Chem. Technology.* **1994**, *1*, 93.
13. B. Sinha, A. Sinha, A. Jha and M. N. Roy, *J. Ind. Chem. Soc.* **2005**, *82*, 814.
14. A.K. Covington. T. Dickinson, ' Physical Chemistry of Organic Solvent Systems', (ch 5,appendix 5.1,table 5.1.5, page 606,608).Plenum Press, New York, **1973**.
15. L. Pikkaranien, *J. Chem Engg. Data,* **1988**, *33*, 299.
16. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 16.
17. R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.,* **1978**, *75,* 16.
18. R. M. Fuoss, *J. Phys. Chem.,* **1978**, *82*, 2427.
19. M.N. Roy, D. Nandi, D. K. Hazra, *J. Indian Chem. Soc.,* **1993**, *70*, 121
20. R. M. Fuoss and T. Shedlovsky, *J. Amer. Chem. Soc.,* **1949**, *71*, 1496.
21. Y. Matsuda, M. Morita, F. Tachihara, *Bull. Chem. Soc. Japan.* **1986**,*59*, 1967.
22. Robert. C West (editor), Handbook of Chemistry and Physics, 67th edition, C.R.C. Press, Florida **1986-1987**.
23. R.L. Kay and D.F. Evans. *J. Phys. Chem.* **1965**,*69*, 4208.
24. B. Das, N. Saha, *J. Chem Engg. Data.* **2000**,*45*, 2.
25. R.L. Kay, T.L. Broadwater. *ElectrcChim. Acta,* **1971**, *16*, 667.
26. Jomma. S. Chazhoor, T. P. Radhakrishnan, *Proc. Indian Acad. Sc.* **1979**, *88A*, 53.

27. R.L. Kay, T.L. Broadwater, *J. Solution. Chem.* **1976**, *5*, 57.

28. R. H. Boyd, *J. Chem. Phys.* **1961**, *35*, 1281.

29. R. Zwanzig, *J. Chem. Phys.* **1970**,*52*, 3625.

30. T.L. Broadwater, R.L. Kay. *J. Phys. Chem.*, **1970**,*74*, 3802.

31. E. Gluekauf, *Trans Faraday Society*. **1964**, *60*, 1637.

32. J. R.Suindells and T. B.Godfray, *J. Res. Natd. Bur. Stand.* **1952**, *48*, 1

Table 1.

Physical Properties of solvent Mixtures at 298.15 K.

Methanol + Carbon tetrachloride

Mass% of Methanol	x_1	ε	$\rho_0 \times 10^{-3}$ /Kg .m^{-3}	η_0 / mPa.s
100.00	1	32.66	0.7866	0.5470
90.60	0.97885	26.72	1.0313	0.5672
82.31	0.95712	22.22	1.0401	0.5875
66.89	0.90657	15.31	1.0405	0.6438
Methanol + 1,4-Dioxane				
100.00	1	32.66	0.7866	0.5470
90.60	0.96364	29.12	0.8058	0.5589
82.31	0.92747	26.41	0.8225	0.5488
66.89	0.84752	21.25	0.8570	0.5684

Table 2.

Electrical conductance Λ as a function of concentration c for alkali chlorides in mixed solvents at 298.15 K.

$c \times 10^4$ /mol.dm^{-3}	Λ /S.cm^{3}mol^{-1}	$c \times 10^4$ /mol.dm^{-3}	Λ /S.cm^{3}mol^{-1}	$c \times 10^4$ /mol.dm^{-3}	Λ /S.cm^{3}mol^{-1}
		Methanol + Carbon tetrachloride			
		x_1= 1.0000			
LiCl		NaCl		KCl	
12.35,	83.2	12.54,	89.1	13.53,	94.2
21.17,	76.8	21.49,	83.3	23.20,	87.7
27.79,	72.6	28.21,	79.4	30.45,	84.5
32.94,	69.2	33.43,	76.6	36.09,	81.4
37.06,	67.5	37.61,	74.3	40.06,	79.4
40.43,	65.8	41.03,	73.1	44.29,	78.2
43.24,	64.9	43.88,	71.8	47.37,	77.2
45.62,	63.6	46.29,	70.6	49.97,	75.6
47.66,	62.6	48.36,	69.6	52.20,	74.9
49.42,	62.4	50.15,	68.7	54.13,	74.6
50.96,	61.8	51.72,	67.7	55.82,	74.1
52.32,	60.9	53.10,	67.1	57.31,	73.5
		x_1= 0.97885			
6.37,	82.7	7.76,	86.8	7.74,	92.3
10.92,	76.6	13.30,	80.3	13.26,	85.5
14.33,	72.9	17.46,	76.8	17.40,	82.0
16.99,	70.2	20.69,	74.1	20.62,	79.8
19.11,	67.8	23.28,	71.7	23.20,	77.6
20.85,	66.2	25.39,	70.0	25.31,	75.8
22.30,	65.1	27.15,	68.7	27.07,	74.8
23.53,	63.8	28.64,	67.4	28.56,	74.0
24.58,	62.9	29.92,	67.2	29.84,	73.3
25.49,	62.4	31.03,	66.0	30.94,	72.7
26.29,	61.6	32.00,	65.3	31.91,	72.0
26.99,	61.0	32.86,	65.0	32.76,	71.5
		x_1= 0.95712			
4.44,	80.5	4.40,	83.4	4.50,	87.6
7.61,	76.6	7.54,	78.5	7.72,	80.8
9.99,	74.4	9.86,	76.0	10.13,	76.8
11.84,	72.9	11.73,	73.2	12.01,	74.0
13.32,	71.9	13.20,	72.0	13.51,	72.2
14.53,	70.8	14.40,	71.0	14.74,	70.5
15.54,	70.1	15.40,	69.8	15.76,	69.4
16.39,	69.5	16.25,	69.1	16.63,	68.6
17.12,	69.1	16.98,	68.5	17.37,	68.3
17.75,	68.7	17.61,	68.0	18.01,	66.9
18.30,	68.3	18.16,	67.4	18.57,	66.6

Contd.

18.79,	68.1	18.64,	66.8	19.07,	66.0
x_1= 0.90657					
1.57,	50.8	6.1	47.5	1.53,	70.6
2.69,	47.4	10.5	37.3	2.61,	67.1
3.53,	45.6	13.8	31.3	3.64,	63.8
4.19,	44.0	16.3	27.3	4.26,	61.8
4.71,	43.3	18.4	24.6	4.74,	60.0
5.13,	42.3	20.0	21.6	5.14,	58.9
5.49,	42.0	21.4	20.0	5.48,	58.0
5.79,	41.8	22.6	18.6	5.76,	57.3
6.05,	41.5	23.6	17.5	6.02,	57.0
6.28,	40.7	24.5	16.0	6.21,	56.0
6.48,	40.7	25.3	15.2	6.40,	55.2
6.65,	40.3	26.0	14.6	6.56,	55.4
Methanol + 1,4-Dioxane					
x_1= 0.96364					
LiCl		NaCl		KCl	
10.11	102.1	10.22	97.3	9.52	100.4
17.33	100.5	17.51	91.2	16.32	95.8
22.75	99.5	22.98	89.1	21.42	92.9
26.96	98.6	27.23	86.7	25.39	91.1
30.30	98.1	30.63	85.1	28.57	89.5
33.09	97.7	33.42	84.1	31.17	88.3
35.39	97.4	35.74	83.1	33.33	87.5
37.34	97.2	37.70	82.3	35.16	86.8
39.01	96.9	38.38	81.8	36.73	86.1
40.45	96.7	40.48	81.3	38.09	85.9
41.71	96.5	42.12	80.9	39.28	85.3
42.83	96.4	43.25	80.5	40.33	85.1
x_1= 0.97747					
9.68	96.8	9.84	98.3	7.89	96.9
16.60	93.3	46.86	93.6	13.52	92.9
21.79	91.1	22.13	90.6	17.75	90.5
25.82	89.5	26.23	88.8	21.04	88.5
29.05	88.5	29.51	87.1	23.67	87.0
31.69	87.3	32.19	85.8	25.82	86.1
33.89	86.9	34.43	84.9	27.61	85.5
35.75	86.2	36.32	84.1	29.13	84.5
37.35	85.7	37.94	83.6	30.43	84.1
38.73	85.5	39.34	83.1	31.56	83.6
39.94	85.2	40.57	82.6	32.55	83.1
41.01	84.9	41.65	82.3	33.42	82.7
x_1= 0.97747					
3.62	87.9	3.59	89.5	3.85	91.4
6.20	84.7	6.16	85.9	6.60	87.0
8.14	82.7	8.09	83.5	8.66	84.6
9.65	81.2	9.59	81.8	10.26	82.6
10.85	80.2	10.79	81.2	11.54	81.6

Contd.

Electrical Conductance of ……………… Methanol + 1,4-Dioxane at 298.15 K.

11.84	79.4	11.77	80.0	12.59	80.5
12.66	78.7	12.59	79.2	13.46	79.7
13.35	78.2	13.28	78.7	14.20	79.0
13.94	77.7	13.87	78.2	14.83	78.7
14.46	77.2	14.38	77.8	15.38	78.2
14.91	76.8	14.83	77.3	15.86	77.9
15.31	76.5	15.23	77.1	16.28	77.5

Table 3.

Values of derived conductance parameters (Λ_0, K_A, R, $\Lambda_0\eta_0$, σ) for alkali chlorides in mixed solvents at 298.15 K.

Mass% of Methanol	x_1	Λ_0 /S.cm^{3}mol^{-1}	K_A /dm^{3}mol^{-1}	R / Å	$\Lambda_0\eta_0$	σ
		LiCl / Methanol + Carbon Tetrachloride				
100.00	1	108.25±0.50	328.34±0.51	6.38	59.21	0.51
90.60	0.97885	106.79±0.71	492.40±0.71	6.14	60.57	0.71
82.31	0.95712	90.54±0.10	570.23±0.10	6.23	53.19	0.10
66.89	0.90657	60.22±0.18	642.41±0.18	6.43	38.77	0.18
		NaCl / Methanol+ Carbon Tetrachloride				
100.00	1	111.85±0.79	253.35±0.79	6.73	61.18	0.50
90.60	0.97885	110.79±0.67	447.99±0.67	6.49	62.84	0.33
82.31	0.95712	98.23±0.33	460.91±0.10	6.58	57.71	0.10
66.89	0.90657	72.23±1.31	481.35±1.31	6.78	46.50	1.31
		KCl / Methanol+ Carbon Tetrachloride				
100.00	1	113.77± .15	187.62± .15	7.11	62.22	0.15
90.60	0.97885	112.18± .31	344.69± .31	6.87	63.63	0.31
82.31	0.95712	103.22± .49	565.86± .49	6.96	60.64	0.49
66.89	0.90657	86.32± .34	776.44± .34	7.16	55.57	0.34
		LiCl / Methanol + 1,4-Dioxane				
100.00	1	108.65± .51	328.34± .51	6.38	59.21	0.51
90.60	0.96364	107.35± .04	335.18± .04	6.43	59.99	0.04
82.31	0.92747	103.39± .11	341.24± .11	6.48	56.75	0.11
66.89	0.84752	96.85± .17	434.19± .17	6.69	55.05	0.17
		NaCl / Methanol + 1,4-Dioxane				
100.00	1	111.85± .79	253.35± .79	6.73	61.18	0.79
90.60	0.96364	110.92± .26	241.87± .26	6.78	61.99	0.26
82.31	0.92747	106.21± .16	284.22± .16	6.83	58.29	0.16
66.89	0.84752	99.22± .28	370.31±. 17	6.94	56.40	0.17
		KCl / Methanol + 1,4-Dioxane				
100.00	1	113.77±0 .15	187.62± 0.15	7.11	62.22	0.15
90.60	0.96364	112.72±0 .16	248.24± 0.16	7.16	63.02	0.16
82.31	0.92747	108.63± 0.21	254.63± 0.21	7.21	59.62	0.21
66.89	0.84752	101.45± 0.08	429.15± 0.08	7.32	57.66	0.08

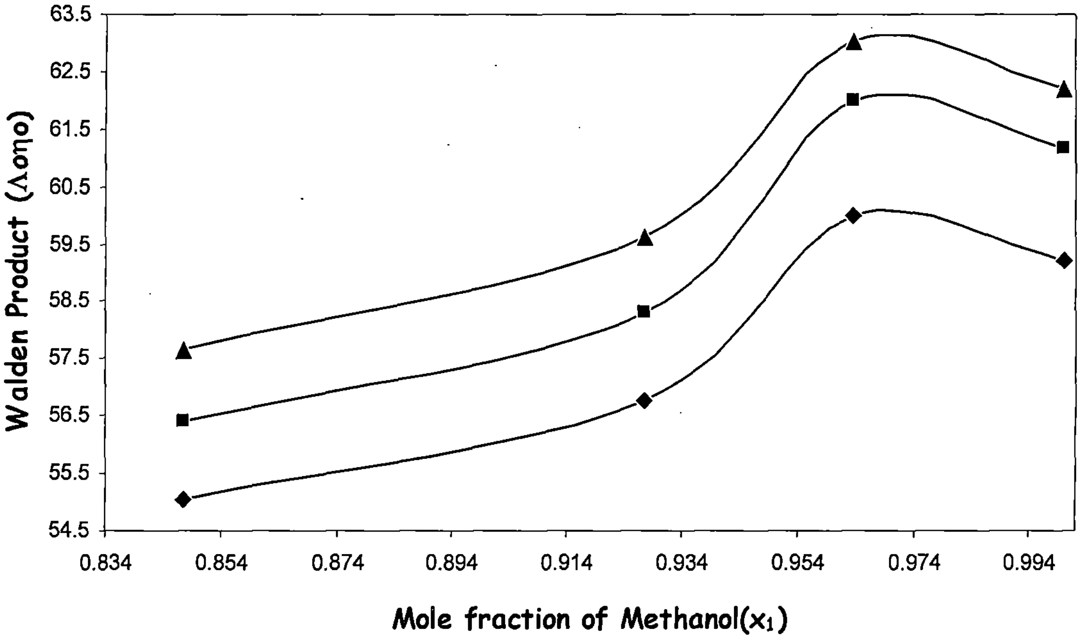

Fig1: Walden products for several alkali metal cations (♦ = LiCl, ■ = NaCl, ▲= KCl) as a function of the mole fraction of methanol in Methanol-CCl4 solvent mixture.

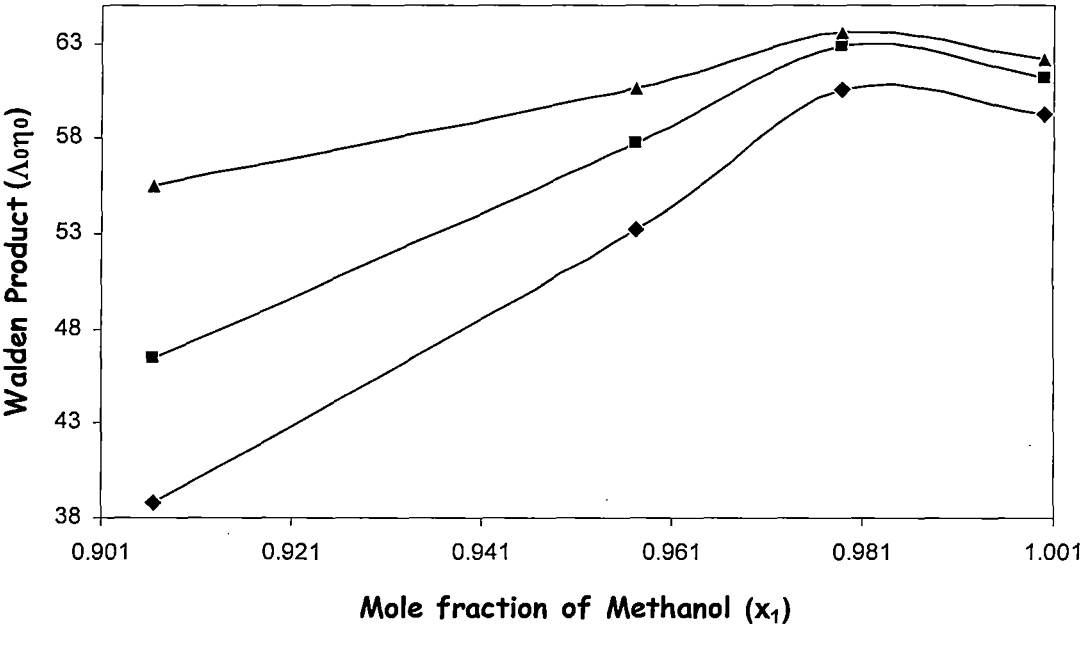

Fig2: Walden products for several alkali metal cations (♦ = LiCl, ■ = NaCl, ▲= KCl) as a function of the mole fraction of methanol in Methanol- 1,4-DO solvent mixture.

CHAPTER IX

Physicochemical investigation on interactions of some amino acids with aqueous tetra butyl ammonium bromide solution at 298.15 K*

9.1. Introduction

Amino acids are monomers that constitute proteins and are considered to be the model compounds of proteins. The behavior of proteins in mixtures is highly influenced by many factors such as p_H, solvent properties, chemical structure and surface charge distribution of proteins, and type and concentration of the electrolyte. The influence of electrolyte on the behavior of protein is one of the important topics in physical chemistry of the substances. It has long been known that there is a strong interaction between electrolytes and proteins, [1] which causes a departure from ideal behavior. To understand the finer details, the interactions of the monomers of the protein i.e. the interactions of the amino acids with electrolytes must be studied owing to the complex structural organization of the biological macromolecules.

There are investigations on the changes of thermodynamic behaviour of proteins by the effect of various co-solutes/co-solvents, such as guanidine hydrochloride, sodium thiocyanate, magnesium chloride, urea and alcohols.[2-7] However, there are few measurements on interactions between amino acid and organic salts. [8-4]

Better insight can be gained into the effect of electrostatic and hydrophobic interactions on the stability of proteins with the help of tetraalkylammonium salts as these salts are expected to influence the macromolecular conformation by weakening attractive or repulsive inter- and intra-chain, charge-charge interactions and by affecting hydrophobic interactions through the side chains of the alkyl groups. Tetraalkylammonim salts orient water molecules around them depending on their alkyl side chain due to their bulkiness.

In this work we studied the volumes, viscosities and sound speeds of some amino acids in aqueous tetraalkylammonimbromide solutions. All of these properties are sensitive to specific interactive changes in solutions. In order to understand the finer details of the interactions of functional groups of amino acids with the experimentally

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**Communicated in Physics and Chemistry of Liquids* selected salt we studied the standard partial molar volumes, the corresponding volume of transfer at infinite dilution and B coefficients of viscosity.

9.2. *Experimental Section*

9.2.1 *Source and purity of samples*

The amino acids, glycine (Analar, >99%), L-alanine (S.D. Fine Chemicals, >98.5%), L-Valine (Loba Chemie, India, >99%) and L-leucine (Loba Chemie, India, >99%), Tetra butyl ammonium bromide (Thomas Baker, India, >98%) were used for the present study. These were used without further purification and dried over anhydrous P_2O_5 in a vacuum desiccator before use. Deionized, doubly distilled, degassed water with a specific conductance of less than 10^{-6} Ω cm^{-1} was used for all of the measurements.The density, viscosity and sound speeds of the solutions were measured immediately after mixing. The purity of the samples were ascertained by GLC.

9.2.2 *Method*

The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The densities (ρ) were measured with an Ostwald-Sperngel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01K of the desired temperature. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The density values were reproducible to $\pm 3 \times 10^{-4}$ $g.cm^{-3}$.

The viscosity was measured by means of a suspended Ubbelohde type viscometer calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [15-17]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ±0.01K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1s. At least three repetitions of each data reproducible to ± 0.1s were taken to average the flow times. The precision of the viscosity measurements was ±0.003mPa.s. Details have been described earlier.[18-19]

The accuracy of the viscosity measurements, based on our work on several pure liquids, was ± 0.003 mPa s.

Ultrasonic speeds of sound (*u*) were measured with an accuracy of ± 0.03% using a single crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi, M-81) working at 2 MHz, which was calibrated with doubly distilled water, purified methanol and benzene at 298.15 K. The details of the methods and measurement have been described earlier.[18,19]

9.3 *Results and Discussion*

9.3.1 *Standard partial molar volume and compressibility:*

The measured densities of aqueous amino acid solutions were used to calculate the value of apparent molar volume $V_{\phi,2}$, using equation (1)

$$V_{\phi,2} = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m\rho\rho_0} \tag{1}$$

Where, M is the molar mass of the solute, m is the molality of the amino acid in aqueous TBAB solution, ρ and ρ_0 are the densities of the water-TBAB-amino acid ternary mixture and aqueous TBAB solution. The experimentally measured densities (ρ) and the apparent molar volumes ($V_{\phi,2}$) are listed in table 1.

The apparent molar isentropic compressibility ($K_{\phi,2}$) of the solutions is determined from equation (2):

$$K_{\phi,2} = \frac{M\kappa}{\rho} - \frac{(\kappa_0\rho - \kappa\,\rho_0)}{m\rho\rho_0} \tag{2}$$

where, κ and κ_0 are the isentropic compressibilities of the amino acid solution and the co-solute solution respectively. The calculated $K_{\phi,2}$ values are reported in table 1.

Isentropic compressibility (κ) values were calculated from experimental densities (ρ) and speeds of sound (u), using equation (3)

$$\kappa = (u^2\rho)^{-1} \tag{3}$$

In the case of negligible concentration dependence (i.e., within the uncertainty limits of the measurements) the variation of the apparent molar quantities $Q_{\phi,2}$, with molality can adequetly be represented by equation (4):

$$Q_{\phi,2} = Q^{0}_{2,m} + S_{q}m \tag{4}$$

Where is the infinite dilution value that is equal to the partial molar quantity $Q_{\phi,2}$ at infinite dilution and S_q is the experimental slope.

Equation 4 was fitted to our $V_{\phi,2}$ and $K_{\phi,2}$ data by the least squares method outlined earlier [20]. The $V^{0}_{2,m}$ and $K^{0}_{2,m}$ values together with their standard deviation percents are summarized in table2 and table 3 along with the concentration dependence of these thermodynamic functions S_v and S_k. The standard deviations for all the quantities are given within first bracket.

The slopes for the compressibility data behave similarly to the slopes of the volume data, i.e., positive S_{k_s} and S_v slopes are observed for all amino acids studied.

The sign of S_q (S_v or S_{k_s}) is determined by the interaction between the solute species. It is seen from table 2 and table 3 that, the S_q values for all the amino acids are positive. The positive S_q values indicate the dominance of the interaction of the charged functional groups of the zwitterionic amino acids over the pair wise interaction. With the introduction of additional methyl groups in the side chains of the amino acids, the S_q values also change indicating that, the methyl groups modulates the interaction of the charged end groups in pair wise interaction.

$V^{0}_{2,m}$ and $K^{0}_{2,m}$ values are by definition free from solute-solute interactions and therefore provide information regarding solute-solvent interactions.

The values of $V^{0}_{2,m}$ are positive for all the amino acids at all the concentration of TBAB solution studied. The $V^{0}_{2,m}$ value increases gradually with the increase in concentration of TBAB in the aqueous solution for all the TBAB concentration studied. For Valine, there is a slight decrease in $V^{0}_{2,m}$ value for 0.125 (M) TBAB concentrations, however the value increases finally.

A similar work was reported by Banerjee et. al. in aqueous tetra ethyl ammonium bromide solution [14]. All the $V_{2,m}^{0}$ values obtained by them are positive like ours and the trend of changes in $V_{2,m}^{0}$ values observed by them are similar to that observed by us.

From, table3, it is seen that, the value of isentropic compressibilities at infinite dilution ($K_{2,m}^{0}$) also increases gradually with the increase in concentration of TBAB in the aqueous solution for all the TBAB concentration studied. But, the values of the isentropic compressibilities at infinite dilution are negative for all the solutions.

At neutral pH, amino acids exist as zwitterions and on dissolution in water there is an overall decrease in the volume of the water. This is due to the contraction of the water near the end groups, and is termed as electrostriction. As a result, the electrostricted water is much less compressible than bulk water and leads to a large decrease in the compressibility of aqueous solution. [20] Thus, the values of ($K_{2,m}^{0}$) for all the studied amino acids are negative.

Moreover it is seen that, the negative nature of $K_{2,m}^{0}$ values for the studied amino acids increases in the order,

Glycine < L-alanine < L- valine < L-leucine

Since the contribution of a methylene group to the partial compressibility is negative at ambient temperature [21], the ions having larger hydrophobic groups may be expected to have more negative values of the partial molar compressibility. So, L-leucine having the largest negative group shows the highest negative $K_{2,m}^{0}$ value.

9.3.2 *Group contributions:*

The $V_{2,m}^{0}$ values of studied amino acids vary linearly with the number of C-atoms in their alkyl side chain. Similar correlation has been reported for some series of ω-amino acids in aqueous potassium thiocyanate [22] and guanidine hydrochloride solutions.[9]

A linear regression analysis of $V_{2,m}^{0}$ values of amino acids vs. number of carbon atoms in 0.062, 0.125, 0.256 (M) TBAB solution was carried out using the following equation

$$V_{2,m}^{0} = V_{2,m}^{0}\left(NH_3^{+}, COO^{-}\right) + n_c V_{2,m}^{0}\left(CH_2\right) \qquad (5)$$

where, n_c is the number of carbon atoms in the alkyl side chain of the amino acid, $V_{2,m}^0(NH_3^+, COO^-)$and $V_{2,m}^0(CH_2)$ are contribution of the zwitterionic end groups and methylene group to $V_{2,m}^0$respectively. Since the alkyl side chains of homologous series of α- amino acids studied in this work are: CH_2-(glycine); CH_3CH-(alanine), CH_3CH_3CHCH-(valine), $CH_3CH_3CHCH_2CH-$(leucine), the value of (CH_2) obtained by this method characterizes the mean contribution of the $CH-$ and CH_3- groups to

$V_{2,m}^0$of the α- amino acids. To calculate the contribution of other alkyl chains, the method of Hakin et.al. [19,20] was used. According to them,

$$V_{2,m}^0(CH_3) = 1.5V_{2,m}^0(CH_2) \tag{6}$$

$$V_{2,m}^0(CH) = 0.5V_{2,m}^0(CH_2) \tag{7}$$

$V_{2,m}^0$values of amino acids are listed in table 4. It is observed from table 4 that, the contribution of the (NH_3^+, COO^-) to $V_{2,m}^0$ of the amino acids is larger compared to that of the (CH_2) group and increases with the increase of TBAB concentration in the solution, thereby indicating that, the interaction of the ions of TBAB with the zwitterionic end groups of amino acids dominate over those of the hydrophobic group-TBAB interaction. However, the contribution from the side chain of amino acids increases with the increase in chain length.

9.3.3 *Water of hydration*

The number of water molecules hydrated to amino acids (N_w) can be estimated from the electrostriction partial molar volume, using the equation, [23]

$$N_w = V_{2,m}^0(elect) \Big/ \left(V_E^0 - V_B^0\right) \tag{8}$$

where, V_E^0 is the molar volume of the electrostricted water and V_B^0 is the molar volume of the bulk water. The value of ($V_E^0 - V_B^0$) ≈ -3.0 cm^3·mol^{-1}, [23] for electrolytes at 298.15 K. The $V_{2,m}^0(elect)$ value was calculated using the following equation,

$$V_{2,m}^0 = V_{2,m}^0(in) + V_{2,m}^0(elect) \tag{9}$$

where $V_{2,m}^{0}(in)$ is the intrinsic partial molar volume due to the hydration of the amino acids. The $V_{2,m}^{0}(in)$ term can further be divided into two terms, one for the vanderwall's volume and the other for the volume of the packing effects. The values of $V_{2,m}^{0}(in)$ for amino acids were obtained from their molar crystal volumes using the following relationship,

$$V_{2,m}^{0}(in)=\frac{0.7}{0.634}V_{2,m}^{0}(cryst) \tag{10}$$

where, 0.7 is the packing density for the molecule in an organic crystal and 0.634 is the packing density for the randomly packed spheres. The molar volume of the crystals were calculated using the crystal densities of the amino acids represented by Berlin and Pallansh [24] at 298.15 K. The values of $V_{2,m}^{0}(elect)$ were obtained from the intrinsic partial molar volume of the amino acid $V_{2,m}^{0}(in)$ and the $V_{2,\phi}^{0}$ values determined experimentally.

The obtained N_w values are listed in table 5. It can be seen that, for glycine, L-alanine and L-valine, the values the N_w values vary with the solvent composition, showing a tendency to decrease with the increase in the concentration of TBAB solution. This indicates that, with the addition of electrolytes introduces dehydration effect on amino acids in solution.[25] However, for L-Leucine, the N_w values remain unaltered by TBAB concentration. This indicates that, the hydrophobic group of leucine reduces the ion-ion interaction between the amino acid and the salt.

The N_w values obtained by us are lower than those obtained by Banerjee et. al. [14]. This may be due to the replacement of the ethyl group of co-solute molecule by the bulkier butyl group. The possible explanation may be due to lesser solvation of the bulkier butyl group compared to the smaller ethyl group. [26]

9.3.4 *Transfer volume and compressibility*

Transfer volumes and transfer compressibilities ($\Delta_{tr}V_{2,m}^{0}$ and $\Delta_{tr}K_{2,m}^{0}$) for each amino acid [27]from pure water to TBAB solutions is determined by the equations,

$$\Delta_{tr}V_{\phi,2}^{0}=V_{2,m}^{0}(TBAB)-V_{2,m}^{0}(water) \tag{11}$$

$$\Delta_{tr}K_{2,m}^{0}=K_{2,m}^{0}(TBAB)-K_{2,m}^{0}(water) \tag{12}$$

The results obtained are listed in table 6 and table9 and are illustrated in figure 1 and figure 2.

Different types of interactions which take place in the ternary systems of (amino acid +TBAB+ water) are; (a) ion-ion interaction between the Br^- ion of TBAB and the NH_3^+ group of the amino acid; (b) ion-ion interaction between the $(C_4H_9)_4N^+$ ion of TBAB and the COO^- group of amino acid; (c) hydrophobic-hydrophobic interaction between the butyl group o The f TBAB and hydrophobic group of amino acid.

Applying the co-sphere overlap model [28] as the guideline, it may be inferred that, (a) and (b) type of interactions will lead to a positive $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ since there is a reduction in the electrostriction effect and the overall water structure is enhanced. Interactions of type (c) will lead to a negative $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ because the introduction of an alkyl group provides an additional scope of hydrophobic-hydrophobic and hydrophilic-hydrophobic interactions. As a result, there will be a reduction in the structure of water formed as a result of their co-spheres overlapping.

Both positive and negative values of volume of transfer for the amino acids were observed. The $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ values for glycine and L-alanine increases with the increase in concentration of TBAB in the solution. But for L-valine, the volume of transfer increases from negative to positive values with rise in TBAB concentration. For L-leucine, all of the $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ values are negative, but with the rise in TBAB concentration, the values shift to lower negative values.

The value of $\Delta_{tr}V_{2,m}^0$ for glycine from water to 0.025(M) TBAB is negative, but, very small. This indicates a balance between the interactions (a) and (c). With increasing concentration of co-solute TBAB, a positive $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ results indicating an enhancement in the ion-ion interaction between the zwitterionic centers of the amino acid and the ion of the salt. Similar is the case of alanine, but, here, the presence of an additional alkyl group increases the hydrophobic interaction leading to a decrease in the positive nature of $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ values. With the increase in the number of hydrophobic group from L- valine to L-leucine, the $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ values become more and more negative. The increased number of hydrophobic groups in these amino acids interacts strongly with the hydrophobic groups of TBAB thereby leading to negative volumes of transfer, which increases with the increasing concentration of TBAB.

The comparison of our work with the work of Banerjee et. al. shows that, the $\Delta_{tr}V_{2,m}^{0}$ values for amino acids shifts towards the positive side in aqueous TBAB solution. This is due to the predominance of (a) and (b) type of forces in case of TBAB solution

9.3.5 *Viscosity B coefficients*

The relative viscosities, η_r of the studied amino acids in the selected concentrations of co-solute solutions were calculated using the following relation and are summarized in table 1.

$$\eta_r = \eta/\eta_0 \tag{13}$$

where η and η_0 are the viscosities of solution and solvent, respectively. The B coefficients of viscosity were determined by fitting the η_r values to the Jones-Dole equation by least squares method as follows,

$$\eta_r = \eta/\eta_0 = 1 + Bc \tag{14}$$

where c is the molarity of the solution calculated from molality values. The values of the B coefficients along with their standard deviation percents are listed in table 8.

The B-coefficient measures the size and shape effects as well as the structural effect induced by solute-solvent interactions. [29] The B-coefficient values for amino acids in aqueous TBAB solutions follow the order

Glycine < L-alanine < L- valine < L-leucine

From the above order, it is clear that magnitude of the B coefficient increases with increasing molar mass and size of the alkyl side chains of amino acids. The values increase with the concentration of TBAB indicating the promotion of liquid structure in the presence of TBAB.

In fact, the B-coefficient values for the amino acids reflect the net structural effects of the charged end and the hydrophobic (CH_2) groups on the amino acids. *B*-coefficients for the homologous series of R-amino acids vary linearly with the number of carbon atoms on their alkyl chains at a given temperature. [22, 30, 31] Similar to equation 4, the linear relation can be represented by the regression parameters

$$B = B\left(NH_3^+, COO^-\right) + n_c B(CH_2) \tag{15}$$

The regression parameters $B\left(NH_3^+, COO^-\right)$ and $B(CH_2)$ indicate the contributions of the zwitterionic and the methylene groups to the B-coefficient. It should be pointed out that $B(CH_2)$obtained here characterizes the mean contribution of$CH-$ and CH_3- groups to B-coefficients of the amino acids. Such linear correlation [20, 31] has also been observed in other solutes for these amino acids. The values of the charged end-groups contribution, $B\left(NH_3^+, COO^-\right)$and the methylene group contribution, $B(CH_2)$to the B-coefficients are given in table 9. It can be seen from table 7 that values of $B\left(NH_3^+, COO^-\right)$decrease while $B(CH_2)$values increase with increasing concentration of TBAB in solutions, indicating that the zwitterionic groups break while (CH_2) groups enhance the structures of the aqueous salt solutions.

9.4. *Conclusion:*

In summary, volume, viscosity and compressibility data have been determined for aqueous amino acids solutions and the results have been used to estimate the volume and compressibility of transfer, number of hydrated water molecules and the viscosity B-coefficient values. From the values obtained for the above mentioned parameters the following conclusions may be drawn.

With the increase in concentration of aqueous TBAB in solution, the partial molar quantities also increases. The contribution of the $\left(NH_3^+, COO^-\right)$ group to $V_{2,m}^0$ of the amino acids is larger compared to that of the (CH_2) group and increases with the increase of TBAB concentration in the solution. The number of water molecules hydrated to amino acids increases with the increase in hydrophobic content of the amino acids, indicating the predominance of hydrophobic interactions between the amino acid and TBAB with increasing number Carbon atoms in the former. The partial isentropic compressibilities of the amino acids behave in the similar way as that of the $V_{2,m}^0$ and same conclusions are drawn as above.

From the considerations of the volume of transfer, it is concluded that, for Glycine and L-alanine, with increasing concentration of co-solute TBAB, more positive

$\Delta_{tr}V_{2,m}^{0}$ and $\Delta_{tr}K_{2,m}^{0}$ values result indicating an enhancement in the ion-ion interaction. The increased number of hydrophobic groups in these amino acids leads to stronger interaction between the hydrophobic groups of amino acids with hydrophobic groups of TBAB thereby leading to negative volumes of transfer.

The magnitude of the B coefficient values increase with the concentration of TBAB indicating the promotion of liquid structure in the presence of TBAB.

References

1. J. G. Kirkwood, *Chem. Rev.* **1939**, *24*, 233.
2. G.I. Makhatadze, P.L.Privalov, *J. Mol. Biol.* **1992**, *226*, 491.
3. T.E. Creighton,. *Curr. Opin. Struct. Biol.* **1991**, *1*, 5.
4. T. Arakawa, S.N.Timasheff, Biochem. **1984**, *3*, 5912.
5. G. Velicelebi, J.M.Sturtevant, *Biochem.* **1979**, *18*, 1180.
6. J.A. Schellman, *Biopolymers.* **1987**, 26, 549.
7. Jr.Greene, C.N.Pace, *J. Biol. Chem.* **1974**, *249*, 5388.
8. K. B. Belibagli, E. Ayranci, *J. Solution Chem.* **1990**, *19*, *867.*
9. Z.Yan, J.Wang, H.Zheng, D. Liu, *J. Solution Chem.* **1998**, *27*, 473.
10. Z.Yan, J.Wang, D. Liu, J. Lu, *Z. Phys Chem.* **1999**, *211*, 121.
11. Z.Yan, J.Wang, H.Zhang, ,J.Lu, Biophys. Chem. **2000**, *86*, 71.
12. T. S.Banipal, D.Kuar, P. K Banipal, *J. Chem. Eng. Data.* **2004**, *49*, 1236.
13. Z. Yan, J. Wang, H. Zhang, X. Xuan, *J. Chem. Eng. Data.* **2005**, *50*, 1864.
14. T. Banerjee, N. Kishore, *J Solution Chem.* **2005**, *34(2)*, 137.
15. K. N. Marsh, Recommended Reference Materials for the Realisation of Physicochemical Properties, Blackwell Scientific Publications, Oxford, U. K **1987**.
16. J. A. Dean, Lange's Handbook of Chemistry, 11th edn., McGraw-Hill Book Company, New York **1973**.
17. A. Chatterjee and B. Das, *J. Chem. Eng. Data.* **2006**, *51*, 1352.
18. M. N. Roy, A Jha, R.Dey, *J. Chem. Eng. Data.* **2001**, *46*, 1327.
19. M. N. Roy, A Jha, A.Choudhury, *J. Chem. Eng. Data.* **2004**, *49*, 291.
20. M.Sakurai, K.Nakamura, N. Takenaka, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 352.
21. R. K. Wadi, P. Ramasami, *J. Chem. Soc., Faraday Trans.* **1997**, *93(2)*, 243.
22. R. K. Wadi, R. K. Goyal, *J. Solution Chem.* **1992**, *21*, 163.
23. F. J. Millero, A. L. Surdo, C. Shin. *J. Phys. Chem.* **1978**, *82*, 784.
24. E. Berlin and M. J. Pallansch, *J. Phys. Chem* . **1968**, *72*, 1887.
25. T.Owaga, K. Mizutani, M. Yasuda. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2064.
26. A . Mukhopadhyay, M. Pal, *Indian J. Chem.* **2002**, *41A*, 1120.
27. L. Xu, C.Ding, R. Lin. *J. Solution Chem.* **2006**, *35(2)*, 191.
28. Z. Yan, J.Wang, W.Liu, J. Lu. *Thermochim. Acta.* **1999**, *17*, 334.

29. R. H. Stokes, R. Milles. International Encyclopedia of Physical Chemistry and Chemical Physics; Pergamon: New York, **1965**.
30. Z. Yan, J.Wang, , J.Lu. *Biophys. Chem.* **2002**, *99*, 199.
31. J. Yan, J. Wang, J. Lu. *J. Chem. Eng. Data.* **2001**, *46*, 217.
32. S.K.Singh, A.Kundu, N.Kishore. *J.Chem.Thermdyn.* **2004**, *5*, 703.

Table 1

Experimental densities (ρ), viscosities (η), sound speed (u) of aqueous TBAB solutions at all the experimental concentration at 298.15 K

Molality of TBAB in water	$\rho \times 10^{-3}$/ kg·m^{-3}	η / mPa.s	u/ ms^{-1}
m_s =0.062	1.0062	0.9506	1685.2
m_s =0.125	1.0165	0.9698	1888.4
m_s =0.256	1.0179	1.0796	2016.4

Table 2

Experimental molalities (c), densities (ρ), viscosities (η),sound speed (u), *apparent molar volumes* ($V_{2,\phi}$) *and apparent isentropic compressibilities* ($K_{s,\phi}$) *along* with the concentration (c) of glycine, L-alanine, L- valine, L-leucine in water and in aqueous TBAB solution as a function of the molalities of Amino Acids.

m_s =0.062					
c/ mol·kg^{-1}	$\rho \times 10^{-3}$/ kg·m^{-3}	η_r	u/ ms^{-1}	$V_{\phi,2} \times 10^{6}$/ m^3·mol^{-1}	$K_{\phi,2} \times 10^{10}$/ m^3·mol^{-1}Pa^{-1}
Glycine					
0.0241	1.0070	1.0028	1583.7	41.68	-25.12
0.0320	1.0072	1.0243	1918.6	43.55	-24.88
0.0561	1.0081	1.0280	2155.2	42.72	-24.11
0.0721	1.0085	1.0308	2368.5	42.90	-23.77
0.0881	1.0091	1.0337	2638.0	41.89	-23.30
0.1001	1.0094	1.0357	2916.5	42.84	-23.06
Alanine					
0.0266	1.0072	1.0290	1861.0	60.64	-23.61
0.0354	1.0072	1.0314	1929.0	60.66	-23.31
0.0621	1.0080	1.0382	2182.9	60.71	-22.63
0.0799	1.0085	1.0424	2409.2	60.74	-22.23
0.0976	1.0091	1.0469	2717.9	60.78	-21.89
0.1109	1.0094	1.0503	3039.0	60.79	-21.64

Contd.

		Valine			
0.0257	1.0069	1.0136	1896.3	90.18	-28.51
0.0342	1.0071	1.0170	1982.0	90.19	-28.18
0.0599	1.0078	1.0276	2310.6	90.12	-27.06
0.0770	1.0082	1.0347	2642.5	90.22	-26.64
0.0942	1.0087	1.0417	3139.9	90.23	-26.11
0.1070	1.0090	1.0474	3759.8	90.24	-25.74
		Leucine			
0.0261	1.0068	1.0214	1942.3	106.31	-32.66
0.0348	1.0070	1.0265	2052.2	106.38	-32.30
0.0609	1.0077	1.0408	2516.7	106.48	-31.24
0.0782	1.0081	1.0505	3065.2	106.52	-30.68
0.0956	1.0085	1.0604	4170.5	106.61	-30.06
0.1087	1.0088	1.0684	7170.2	106.65	-29.81
		m_s =**0.125**			
		Glycine			
0.0245	1.0172	0.9854	2043.4	43.83	-16.69
0.0326	1.0175	0.9867	2097.2	43.88	-16.22
0.0570	1.0182	0.9903	2255.8	43.95	-14.63
0.0734	1.0187	0.9930	2378.2	44.01	-14.00
0.0896	1.0192	0.9956	2494.2	44.08	-13.23
0.1018	1.0196	0.9975	2585.7	44.10	-12.72
		Alanine			
0.0262	1.0172	0.9899	2110.9	61.32	-21.26
0.0349	1.0175	0.9926	2198.5	61.41	-20.92
0.0611	1.0182	0.9993	2536.4	61.61	-20.27
0.0785	1.0186	1.0044	2851.5	61.72	-19.82
0.0960	1.0191	1.0092	3316.6	61.82	-19.48
0.1090	1.0195	1.0128	3836.5	61.88	-19.20
		Valine			
0.0261	1.0172	1.0017	2151.9	90.42	-24.55
0.0348	1.0174	1.0047	2257.2	90.46	-23.99
0.0608	1.0180	1.0148	2672.1	90.57	-22.75
0.0782	1.0185	1.0215	3008.3	90.65	-21.35
0.0956	1.0189	1.0282	3604.8	90.70	-20.86
0.1086	1.0192	1.0337	4338.2	90.74	-20.49
		Leucine			
0.0166	1.0169	1.0390	2103.3	106.19	-32.31
0.0222	1.0170	1.0423	2187.6	106.20	-31.85
0.0388	1.0174	1.0514	2508.8	106.23	-30.99
0.0498	1.0177	1.0582	2809.7	106.25	-30.39
0.0610	1.0179	1.0645	3246.0	106.26	-29.95
0.0692	1.0181	1.0689	3729.1	106.28	-29.62
		m_s =**0.256**			
		Glycine			
0.0245	1.0186	0.9818	2146.3	45.03	-11.53
0.0326	1.0188	0.9832	2179.3	45.13	-10.62

Contd

0.0571	1.0195	0.9878	2260.6	45.38	-8.63
0.0735	1.0211	0.9915	2313.9	45.49	-7.89
0.0898	1.0205	0.9946	2323.2	45.62	-6.62
0.1021	1.0208	0.9971	2351.9	44.69	-6.26
Alanine					
0.0262	1.0186	0.9872	2196.0	61.97	-14.59
0.0349	1.0188	0.9895	2254.9	62.10	-13.96
0.0611	1.0195	0.9971	2484.3	62.47	-13.55
0.0786	1.0201	1.0024	2651.1	62.62	-13.01
0.0961	1.0204	1.0070	2833.4	62.75	-12.43
0.1092	1.0208	1.0101	2992.1	62.84	-12.09
Valine					
0.0262	1.0185	1.0020	2342.4	92.59	-24.08
0.0349	1.0188	1.0054	2481.6	89.75	-23.69
0.0611	1.0194	1.0166	3011.5	90.97	-21.90
0.0786	1.0198	1.0243	3570.7	91.34	-21.00
0.0961	1.0202	1.0318	4510.6	91.52	-20.15
0.1092	1.0205	1.0374	5904.0	91.62	-19.56
Leucine					
0.0262	1.0185	0.9956	2379.1	106.28	-26.18
0.0349	1.0187	0.9997	2516.6	106.31	-24.94
0.0612	1.0193	1.0149	3094.0	106.37	-22.75
0.0786	1.0197	1.0261	3643.8	106.38	-21.27
0.0961	1.0201	1.0356	4623.5	106.38	-20.26
0.1092	1.0204	1.0434	5711.3	106.39	-19.25

Table 3.
Standard partial molal volumes of amino acids in Aqueous TBAB solution at 298.15 K

Amino acids	Parameters	$V^0_{2,m}$ x 10^6 / $m^3 \cdot mol^{-1}$			
		Water	m_s =0.0622	m_s =0.125	m_s =0.256
Glycine	$V^0_{2,m}$ x10^6 $m^3 \cdot mol^{-1}$	43.14(±0.06)[32]	42.52(±0.01)	43.57(±0.03)	44.40(±0.02)
	S_v	0.86	0.9078	0.9912	0.5812
Alanine	$V^0_{2,m}$ x10^6 $m^3 \cdot mol^{-1}$	60.43(±0.04)[32]	60.23(±0.03)	60.78(±0.01)	61.14(±0.02)
	S_v	0.73	0.7218	0.6955	0.1045
Valine	$V^0_{2,m}$ x10^6 $m^3 \cdot mol^{-1}$	90.39(±0.14)[32]	90.12(±0.01)	90.10(±0.04)	91.01(±0.04)
	S_v	-	0.3613	0.8618	0.6759
Leucine	$V^0_{2,m}$ x10^6 $m^3 \cdot mol^{-1}$	107.72(±0.24)[32]	106.01(±0.02)	106.11(±0.01)	106.20(±0.02)
	S_v	-	0.9891	0.7995	0.1589

Table 4.

Standard partial isentropic compressibilities of amino acids in Aqueous TBAB solution at 298.15 K

Amino Acids	Parameters	$K_{2,m}^{0}$ x 10^{10} / $m^3 \cdot mol^{-1}Pa^{-1}$			
		Water	m_s = 0.0622	m_s = 0.125	m_s = 0.256
Glycine	$K_{2,m}^{0}$ x 10^{10}/ $m^3 \cdot mol^{-1}Pa^{-1}$	-27.00[23]	-27.14(±0.07)	-20.54(±0.09)	-16.53(±0.11)
	S_K	4.56	12.81	24.74	32.73
L-alanine	$K_{2,m}^{0}$ x 10^{10}/ $m^3 \cdot mol^{-1}Pa^{-1}$	-25.26[23]	-25.47(±0.08)	-23.18(±0.11)	-16.75(±0.13)
	S_K	4.75	11.46	12.12	13.93
L-valine	$K_{2,m}^{0}$ x 10^{10}/ $m^3 \cdot mol^{-1}Pa^{-1}$	-30.62[23]	-31.17(±0.11)	-30.95(±0.09)	-28.61(±0.07)
	S_K	8.43	16.50	23.73	27.54
L-leucine	$K_{2,m}^{0}$ x 10^{10}/ $m^3 \cdot mol^{-1}Pa^{-1}$	-31.78[23]	-35.45(±0.09)	-34.83(±0.11)	-32.46(±0.12)
	S_K	13.61	17.11	19.98	40.04

Table 5.
Contribution of zwitterionic groups (NH_3^+, COO^-) and CH_2 group, and other alkyl chains to the infinite dilution apparent molar volume in aqueous TBAB at 298.15 K.

Group	$V_{2,m}^0$ x 10^6 / $m^3 \cdot mol^{-1}$			
	Water	m_s = 0.0622	m_s = 0.125	m_s = 0.256
NH_3^+, COO^-	27.68(±0.92)	27.80(±0.86)	29.07(±0.72)	30.65(±0.51)
CH_2	15.91(±0.33)	15.66(±0.29)	15.40(±0.21)	15.17(±0.19)
CH_3CH-	31.82(±0.52)	31.32(±0.44)	30.80(±0.31)	30.34(±0.25)
CH_3CH_2CH-	47.73(±0.42)	93.96(±0.36)	92.40(±0.21)	91.02(±0.28)
CH_3 CH_3CH CH_2CH-	79.45(±0.41)	78.30(±0.32)	77.00(±0.56)	75.85(±0.41)

Table 6
Hydration number (N_W) of amino acids in aqueous TBAB at 298.15 K

Amino Acids	N_W		
	m_s = 0.0622	m_s = 0.125	m_s = 0.256
Glycine	3.1	2.8	2.5
L-Alanine	3.8	3.7	3.5
L-Valine	4.0	4.0	3.7
L-Leucine	6.0	6.0	6.0

Table 7
Transfer volumes of amino acids ($\Delta_{tr}V_{2,m}^0$ x10^6 / $m^3 \cdot mol^{-1}$) from water to aqueous TBAB at 298.15 K.

Amino Acids	$\Delta_{tr}V_{2,m}^0$ x 10^6 / $m^3 \cdot mol^{-1}$		
	m_s = 0.0622	m_s = 0.125	m_s = 0.256
Glycine	-0.09(±0.03)	0.43(±0.02)	1.26(±0.02)
L-alanine	-0.20(±0.08)	0.34(±0.07)	0.70(±0.08)
L-valine	-0.27(±0.05)	-0.29(±0.04)	0.62(±0.05)
L-leucine	-1.34(±0.21)	-1.36(±0.21)	-0.45(±0.23)

Table 8

Transfer compressibilities of amino acids ($\Delta_{tr}K_{2,m}^{0}$ x10^{6} / $m^{3}\cdot mol^{-1}$) from water to aqueous TBAB at 298.15 K.

Amino Acids	$\Delta_{tr}K_{2,m}^{0}$ x 10^{6} / $m^{3}\cdot mol^{-1}$		
	m_s = 0.0622	m_s = 0.125	m_s = 0.256
Glycine	-0.14(±0.06)	6.46(±0.13)	10.47(±0.27)
L-Alanine	-0.21(±0.03)	2.08(±0.08)	8.51(±0.19)
L-Valine	-0.55(±0.07)	-0.33(±0.03)	2.01(±0.13)
L-Leucine	-3.67(±0.13)	-3.05(±0.23)	-0.68(±0.11)

Table 9

Viscosity B coefficients (B / $dm^{3}mol^{-1}$) for amino acids in aqueous TBAB solutions at 298.15 K.

Amino Acids	B / $dm^{3}mol^{-1}$		
	m_s = 0.0622	m_s = 0.125	m_s = 0.256
Glycine	0.1473(±0.09)	0.1681(±0.06)	0.1986(±0.06)
L-Alanine	0.2728(±0.02)	0.2761(±0.02)	0.2796(±0.01)
L-Valine	0.4144(±0.03)	0.4175(±0.05)	0.4285(±0.04)
L-Leucine	0.5647(±0.05)	0.5769(±0.04)	0.5824(±0.02)

Table 10

Contributions of (NH_3^+, COO^-) and CH_2 groups to viscosity *B*-coefficients of the amino acids in aqueous TBAB Sasolutions at 298.15 K

Group	B / $dm^{3}mol^{-1}$		
	m_s = 0.0622	m_s = 0.125	m_s = 0.256
NH_3^+, COO^-	0.098(±0.18)	0.096(±0.08)	0.092(±0.11)
CH_2	0.057(±0.04)	0.072(±0.05)	0.097(±0.05)

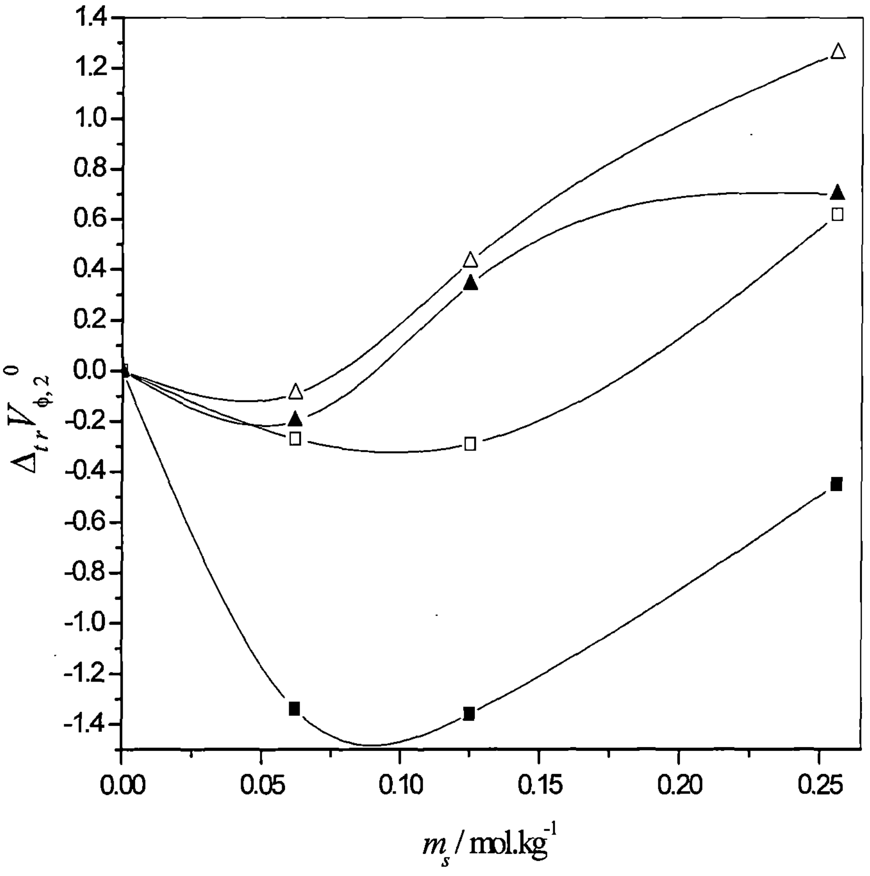

Figure1: The transfer volumes of the experimental amino acids from water to aqueous TBAB solutions plotted against the molarity ms of the TBAB solutions at 298.15 K. Δ, *Glycine;* ▲, *L-Alanine;* □, L-Valine; ■, L-Leucine.

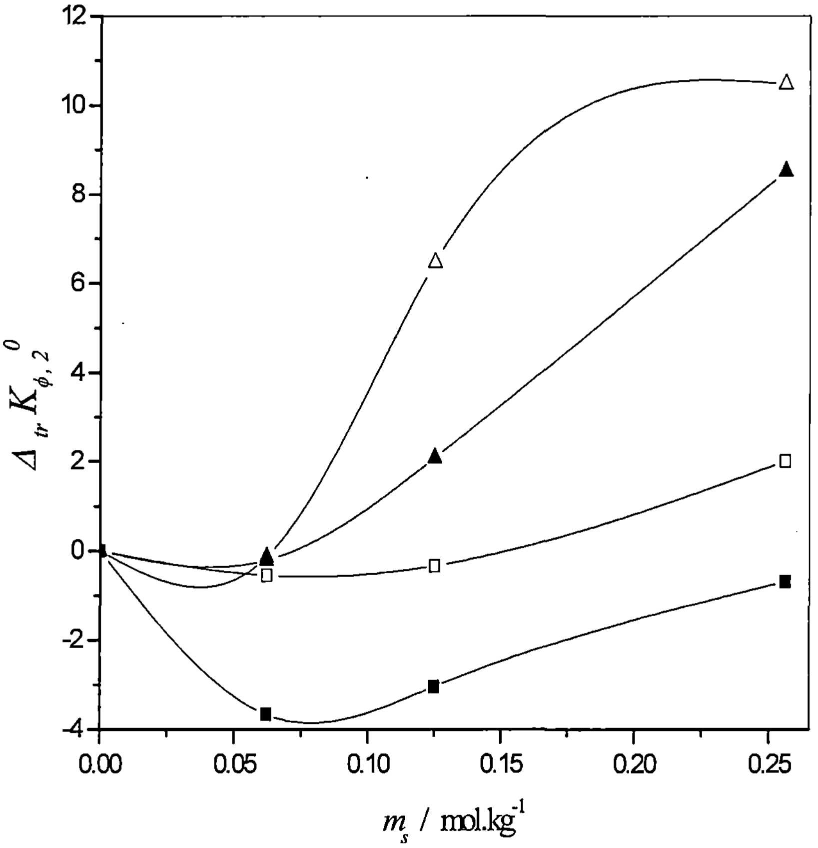

Figure 2: The transfer volumes of the experimental amino acids from water to aqueous TBAB solutions plotted against the molarity ms of the TBAB solutions at 298.15 K. Δ, Glycine; ▲, L-Alanine; □, L-Valine; ■, L-Leucine.

CHAPTER X

Thermodynamic and Transport Properties of Some Monobasic Acetate Salts in Aqueous Binary Mixtures of Methanol at Different Temperatures*

10.1. *Introduction*

Studies on the thermodynamic transport properties and ultrasonic speeds of different electrolytes in different solvents are of great importance to obtain information on the behavior of ions in solutions. Among the various type of interactions occurring between solute molecules in solution, these solute- solute and solute- solvent interactions are of current interest in all branches of chemistry.[1-7] These interactions help in better understanding of the nature of solutes and solvents, i.e., whether the solute modifies or distorts the structure of the solvent. The inferences regarding these interactions are derived from density, viscosity and ultrasonic speed data measured experimentally. The literature is full of such data in pure solvents but investigations on mixed solvent systems are scanty. Partial molar volume, viscosity coefficients and adiabatic compressibilities reflects the cumulative effects[25,26] of solute-solvent and solute-solute interactions, it would be of interest to study these factors of acetate salts in binary aqueous mixtures of methanol. Such data are expected to highlight the role of acetate salts in influencing the partial molar volume, viscosity coefficients and adiabatic compressibilities in mixed solvent systems. These considerations prompted us to undertake the present study.

10.2. *Experimental Section*

10.2.1. *Materials*

Ammonium and sodium acetate (Riedel A.R.) were used as received. Lithium and potassium acetates were prepared and purified by the reported procedures.[8] The salts were dried and stored in vacuum desiccators.

Methanol (E. Merck, India, Uvasol grade 99.5% pure) was dried over 3 Å molecular sieves and distilled fractionally. The middle fraction was collected and

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redistilled. The purified solvent had a density of 0.9799 g. cm^{-3} and a viscosity of 1.5809 m Pa. s at 298.15 K. These values agree well with the literature values.[27,24] The details have been reported earlier in chapter III.

10.2.2. *Apparatus and Procedure*

The densities (ρ) were measured with an Ostwald Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298, 308 and 318) K with doubly distilled water and benzene. An average of triplicate measurements was taken into account. The density values are reproducible to ±3×10^{-4} g. cm^{-3}. Details have been discussed earlier.[9]

The viscosities were measured by means of suspended level Ubbelohde type viscometer[□□] at the derived temperature (accuracy ± 0.01K). The precision of the viscosity measurement was 0.05%. Details have been described earlier.[9]

Sound velocities were determined with an accuracy of 0.3% using a single crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz, which was calibrated, with water, methanol and benzene at the required temperature.

The details of these experimental measurements have been included earlier in chapter III.

10.3. *Results and Discussion*

The apparent molar volumes V_ϕ were determined from the solution densities using the following equation,

$$V_\varphi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \tag{1}$$

where M is the molar mass of the solute, c is the molarity of the solution and the other symbols have their usual significance.

The limiting apparent molar volumes V_ϕ^0 were calculated using the least-squares treatment of the plot of V_ϕ vs. $c^{\frac{1}{2}}$ using the Masson equation [10,11],

$$V_{\varphi} = V_{\varphi}^{0} + S_{v}^{*} c^{1/2} \qquad (2)$$

where V_{ϕ}^{0} is the partial molar volume at infinite dilution and S_{v}^{*} the experimental slope. The variation of V_{ϕ} with temperature of the salts in the solvents follows the polynomial equation,

$$V_{\varphi}^{0} = a_{0} + a_{1}T + a_{2}T^{2} \qquad (3)$$

Over the temperature range under the investigation. The apparent molar *expansibilities are calculated from equation,*

$$\varphi_{E}^{0} = (\frac{\delta V_{\varphi}^{0}}{\delta T})_{P} \qquad (4)$$

The sign of $(\frac{\delta V_{\varphi}^{0}}{\delta T})_{P}$ was also determined to ascertain whether the chosen acetate salts are structure breaker or maker in methanol water mixtures.

The sign of $\left(\delta^{2}V_{\phi}^{0} \middle/ \delta T^{2}\right)_{P}$ was also determined to ascertain whether the chosen acetate salts are structure breaker or maker in methanol water mixtures.

Here, the general thermodynamic expression,

$$\left(\delta c_{P} \middle/ \delta P\right) = \left(\delta^{2}V_{\phi}^{0} \middle/ \delta T^{2}\right)_{P} \qquad (5)$$

is used for this explanation.

The plots of V_{ϕ} against √c are all linear and the slopes and intercepts of these lines are taken as V_{ϕ}^{0} and S_{v}^{*} respectively and their values are recorded in table-(2).

The V_{ϕ}^{0} values are interpreted in terms of solute-solvent interactions (as ionic interactions vanish at infinite dilution).

Table-2 shows that the values of V_{ϕ}^{0} are positive and large and decreases with increase of temperature as well as with increase of mass% of methanol in the solvent mixture. This indicates the presence of strong solute-solvent interaction. These interactions are weakened with rise in temperature, suggesting more electrostrictive solvation at higher temperature. Similar results are reported for some 1:1 electrolytes in aqueous DMF.[18,19]

The values of experimental slope, (S_v^*) shown in Table-2 are negative for all investigated salts and increase with rise in temperature. This indicates the presence of weak solute-solute interactions and these interactions, however, increase with the increase of temperature which may be attributed to the solvation of solutes, *i.e.*, more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the increase of temperature.

The variation of V_ϕ^0 with temperature of the salts in the solvents follows according to equation (3) over the temperature range under the investigation. The coefficients (a_is) are presented in Table 3.

The limiting apparent molar expansibilities (ϕ_E^0) calculated from equation (4) are recorded in table-(4). The ϕ_E^0 values for lithium acetate and sodium acetate in methanol solutions increase with increase of temperature, whereas for ammonium acetate and potassium acetate the values decrease with increase of temperature. The increase in magnitude of ϕ_E^0 values with temperature may be ascribed to 'caging or packing effect'.[19] It also indicates that the behavior of these two salts in methanol are similar to that of some symmetrical Tetra alkyl ammonium salts.[12] On the other hand, the decrease in ϕ_E^0 values with increase of temperature, for ammonium acetate and potassium acetate indicates that they behave just like common salts, because in case of common salts, the molar expansibility decrease with increase of temperature.[12,15]

During the past few years it has been emphasized by some workers that S_v^* is not the sole criterion for determining the structure making / breaking nature of any electrolyte. Hepler[13] developed a technique of examining the sign of $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ for various electrolytes in terms of long range structure making and structure breaking capacity of the electrolytes in methanol water mixtures. The structure making solutes should have positive value, whereas structure breaking ones have negative value $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$. These values of the selected acetates are recorded in table (4). It is seen from table (4) that, the $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ values for lithium acetate and sodium acetate are positive, indicating that they are structure makers in methanol water mixture whereas for ammonium acetate and potassium acetate the values are negative, indicating that they are structure breakers in this mixed solvent system.

The viscosity data of solutions for various electrolytes studied here have been analyzed using Jones-Dole equation.[16]

$$\left.\begin{aligned}\frac{\eta}{\eta_0} &= 1 + Ac^{1/2} + Bc \\ \left(\frac{\eta}{\eta_0} - 1\right)/c^{1/2} &= A + Bc^{1/2}\end{aligned}\right] \quad (6)$$

$$\text{Where } \eta = \left(Kt - \frac{L}{t}\right)\rho$$

where η and η_0 are the viscosities of solution and solvent mixture respectively. A and B are constants for the above equation, ρ is the density of the solution and K and L are constants for a particular viscometer. The values of A and B are estimated by least squares method.

The viscosity data for various solutions of electrolytes were analyzed according to Jones-Dole equation[16]. The values of A and B are recorded in Table (2).

Table (2) shows that the values of A are very small for all salts studied in methanol water mixtures at various temperatures thereby showing the presence of weak solute-solute interactions. In other words these results indicate that all the salts mix ideally with methanol + water mixtures and there is a perfect solvation of these molecules resulting in either the absence or weak solute-solute interactions.

Table (2) shows that two types of trends are observed in the change of B-coefficients with temperature. B values for lithium acetate and sodium acetate in methanol solutions decreases with increase of temperature, thereby showing that solute- solvent interactions are weakened with rise of temperature, whereas for ammonium and potassium acetate, value of B coefficient increases with the increase in temperature indicating improved solute-solvent interactions for the solutions with the increase in temperature which may be attributed to solvation of ions by the solvent system studied here.

It has been reported by a number of workers that dB/dT is a better criterion[10,20,21] for determining the structure making/braking capacity of any electrolyte rather than simply the B-coefficient values. It is evident from Table (2) that for lithium acetate and sodium acetate the B values decrease with increase of temperature (negative dB/dT) indicating that they are structure makers in methanol water mixture. On the other hand, for ammonium acetate and potassium acetate the B values increase with increase of temperature (positive dB/dT) indicating that they are structure breakers in methanol water mixture. These conclusions are in excellent agreement with that drawn from $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ values explained earlier.

Adiabatic compressibility coefficients β, were derived from the following relation

$$\beta = \frac{1}{u^2 \rho} \qquad (7)$$

Where ρ is the density of solution and u is the ultrasonic speed in the solution.

The apparent molar adiabatic compressibilities (ϕ_K) of the solutions was calculated from the following equation

$$\phi_k = \beta \times \frac{M}{\rho_0} + \frac{1000(\beta\rho_0 - \beta_0\rho)}{m\rho\rho_0} \qquad (8)$$

where, m is the molality of the solution, β_0 is the adiabatic compressibility of the solvent mixture and the other terms are described earlier.

The limiting apparent molar adiabatic compressibilities ϕ_K^0 and experimental slopes (S_K^*) were obtained[4,17] by extrapolating the plots of ϕ_K versus the square root of molar concentration ($\sqrt{m}$) of the electrolyte by the computerized least squares method using the following equation.

$$\varphi_K = \varphi_K^0 + S_K^* m^{1/2} \qquad (9)$$

The values of ultrasonic speed (u), adiabatic compressibility (β), molality (m), limiting apparent molal adiabatic compressibility (ϕ_K^0), density (ρ), apparent molal adiabatic compressibility (ϕ_K) and experimental slope (S_K^*) are given in Table-5.

A perusal of Table-5 shows that the ϕ_K^0 values decrease whereas S_K^* value increase with the increase of mass % of Methanol in the mixtures at a particular temperature (298.15 K) for all the salts studied here. Since the values of ϕ_K^0 and S_K^* are measure of solute- solute and solute- solvent interactions respectively, the results are in good agreement with that drawn from the conclusion based on the values of V_ϕ^0 and S_v^* mentioned earlier. Negative values of ϕ_K^0 of the salts are interpreted in terms of the loss of compressibility of solvent-mixture due to the electrostrictive forces in the vicinity of the ions and hence the extent of compressibility electrostriction decreases with the increase of the amount of Methanol in the mixture for all the salts under investigation. Same results were observed for some electrolytes in aqueous ethanol, and in 2-Methoxyethanol[23] in case of the studies on sound velocities of some alkali metal halides in the THF + H_2O mixtures.[22]

9.4. *Conclusion:*

In the above chapter, inferences regarding solute- solute and solute- solvent interactions are derived from density, viscosity and ultrasonic speed data measurements. It is seen that, strong solute-solvent interaction are present here. These interactions are weakened with rise in temperature, suggesting more electrostrictive solvation at higher temperature. For lithium acetate and sodium acetate in methanol solutions 'caging or packing effect' seems to be present whereas, ammonium acetate and potassium acetate behaves just like common salts in methanol solutions. Lithium acetate and sodium acetate are structure makers in methanol water mixture whereas ammonium acetate and potassium acetate are structure breakers in this mixed solvent system. However, there is scope of improvement of the study by considering more parameters in details.

References

1. M.N. Roy, A Jha., *J. Chem. Eng. Data.* **2001**, *46*, 1247.
2. M.N Roy. and D.K. Hazra *N.B. Univ. Rev.* (Sci and technol), **1997**, *8*, 45.
3. G.G. Janz Non aqueous electrolytes hand book, Academic Press, New York, **1973**, Vol. 2.
4. M Iqbal. and R.E Verral., *Can. J. Chem.* **1989**, *76*, 727.
5. B Das. and D.K., Hazra *J. Chem. Eng. Data.* **1991**, 36, 405.
6. O Popovych. and R.P.T. Tomkins, 'Non-Aqueous Solution Chemistry', Wiley Interscience, New York. **1981**
7. M.N., Roy, A Jha and S Roy Chowdhury., *J. Indian Chem. Soc*, **2002**, *79*, 623.
8. P Franzosini. and F.W. Falgar *J. Chem. Thermodyn.* **1984**, *16*, 81.
9. P.S Nikam., A.B Sawant., J.S. Ather and R.S Khairmar. *J. Indian Chem. Soc.* **2000**, *77*, 197.
10. D.O. Mason, *Phil. Mag.* **1929**, *8*, 218.
11. D. Nandi , M.N Roy. and D.K. Hazra, *J. Indian Chem. Soc.* **1993**, *70*, 305.
12. F.J Millero. and H.W. Drost *J. Phys. Chem.* **1968**, 72, 1758.
13. D.S Hepler L.G. *Can. J. Chem.* **1969**, **1968**, *47*, 4613.
14. Gill. and T.S. Cheema *Z. Phys. Chem.* (Neue Iolge), **1984**, *140*, 139.
15. B.N Prasad. and M.C.S Subba. *J. Indian Chem. Soc.* **2000**, *77*, 8.
16. G. Jones, and M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950.
17. S Bhowmik., A.K Das. and R.K Mohanty,. *Indian J. Chem. Sect.* **1985**, *24(A)*, 1018.
18. C Calvente., J.J Maestre., E. Yanes and Panedo Carcia. *J. Chem. Soc. Faraday Trans.* **1994**, *94*, 573.
19. F.J. Millero, 'In structure and transport processes in water and aqueous solutions', R.A. Horne, New York. **1972**
20. R Gopal. and M.A. Siddiqui, *J. Phys. Chem.* **1969**, *72*, 1814.
21. N Saha. and B Das. *J. Chem. Eng. Data.* **1997**, *42*, 277.
22. M.N Roy. and D.K Hazra. *N.B. Univ. Rev.* (Sci and technol), **1997**, *8*, 45.
23. B Das. and D.K Hazra *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3740.
24. H.Doe., H. Ohe Matoba and A. Ichimura *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2785.
25. E.J Kind. *J. Phys. Chem.* **1969**, *78*, 1221.
26. M.L., Parmar R.K. Awasthi and M.K Guleria. *J. Chem. Sci.* **2004**, *116*, 33.

Table 1

Concentration (c), Density (ρ), Viscosity (η), Apparent Molar Volume (V_ϕ) and $(\frac{\eta}{\eta_0}-1)/c^{1/2}$ of some acetate salts in various mass % of Methanol at different temperature

10% Methanol + H_2O mixture

c / mol. dm^{-3}	$\rho \times 10^3$/ $kg.m^{-3}$	$\eta \times 10^3$/ Pa. s	$V_\phi \times 10^6$/ $m^3.mol^{-1}$	$(\frac{\eta}{\eta_0}-1)/c^{1/2}$	c / mol. dm^{-3}	$\rho \times 10^3$/ $kg.m^{-3}$	$\eta \times 10^3$/ Pa. s	$V_\phi \times 10^6$/ $m^3.mol^{-1}$	$(\frac{\eta}{\eta_0}-1)/c^{1/2}$
298.15K									
CH_3COONH_4					CH_3COONa				
0.0061	0.9799	1.1690	78.87	0.1208	0.0060	0.9799	1.1761	143.15	0.2001
0.0428	0.9800	1.1847	76.64	0.1112	0.0423	0.9799	1.2105	137.90	0.2203
0.0794	0.9801	1.1913	75.34	0.1017	0.0789	0.9803	1.2323	135.21	0.2280
0.1161	0.9803	1.1970	74.32	0.0985	0.1148	0.9806	1.2489	133.12	0.2311
0.1528	0.9805	1.2004	73.46	0.0935	0.1511	0.9801	1.2648	132.03	0.2372
0.1894	0.9808	1.2020	72.70	0.0872	0.1873	0.9815	1.2794	130.34	0.2424
CH_3COOLi					CH_3COOK				
0.0060	0.9799	1.1769	105.80	0.2101	0.0061	0.9799	1.1835	101.20	0.2611
0.0421	0.9801	1.2202	102.74	0.2615	0.0425	0.9800	1.2163	97.52	0.2020
0.0781	0.9802	1.2500	100.83	0.2840	0.0790	0.9803	1.2313	95.66	0.1723
0.1141	0.9805	1.2789	99.23	0.3086	0.1155	0.9806	1.2384	94.29	0.1432
0.1502	0.9808	1.3035	98.63	0.3240	0.1519	0.9809	1.2443	93.53	0.1201
0.1862	0.9812	1.3265	96.86	0.3371	0.1884	0.9817	1.2456	90.86	0.0960
308.15									

Contd.

		CH_3COONH_4					CH_3COONa		
0.0061	0.9742	0.9140	78.15	0.0756	0.0060	0.9772	0.9281	142.58	0.2770
0.0426	0.9743	0.9136	76.43	0.0801	0.0421	0.9773	0.9569	138.60	0.2587
0.0791	0.9745	0.9302	75.23	0.0844	0.0785	0.9775	0.9691	136.09	0.2377
0.1156	0.9747	0.9355	74.64	0.0872	0.1144	0.9778	0.9794	134.49	0.2301
0.1521	0.9750	0.9407	73.62	0.09061	0.1505	0.9781	0.9860	133.46	0.2195
0.1885	0.9524	0.9449	73.36	0.0923	0.1867	0.9785	0.9936	132.05	0.2163
		CH_3COOLi					CH_3COOK		
0.0060	0.9772	0.9253	104.93	0.2380	0.0061	0.9774	0.9188	140.70	0.1440
0.0419	0.9729	0.9588	103.18	0.2702	0.0423	0.9787	0.9395	137.29	0.1653
0.0778	0.9774	0.9827	101.61	0.2922	0.0785	0.9801	0.9535	135.73	0.1765
0.1137	0.9776	1.0042	101.03	0.3120	0.1147	0.9815	0.9656	133.62	0.1851
0.1495	0.9778	1.0232	100.82	0.3262	0.1512	0.9830	0.9771	133.52	0.1940
0.1854	0.9780	1.0412	98.58	0.3390	0.1875	0.9845	0.9862	130.95	0.1972
					318.15				
		CH_3COONH_4					CH_3COONa		
0.0061	0.9714	0.7406	76.69	0.0966	0.0060	0.9714	0.7559	140.70	0.3679
0.0425	0.9715	0.7510	75.63	0.1052	0.0419	0.9715	0.7833	137.29	0.3211
0.0788	0.9716	0.7580	75.20	0.1112	0.0781	0.9717	0.7985	135.73	0.2960
0.1152	0.9718	0.7640	74.89	0.1161	0.1139	0.9721	0.8040	133.62	0.2782
0.1495	0.9720	0.7689	74.65	0.1183	0.1497	0.9723	0.8094	133.52	0.2614
0.1878	0.9723	0.7733	74.42	0.1201	0.1858	0.9730	0.8136	130.95	0.2480

Contd.

		CH_3COOLi					CH_3COOK		
0.0059	0.9714	0.7493	104.20	0.2524	0.0060	0.9715	0.7388	99.35	0.0666
0.0417	0.9715	0.7766	102.48	0.2771	0.0422	0.9724	0.7489	98.04	0.0921
0.0774	0.9717	0.7955	101.41	0.2960	0.0782	0.9733	0.7568	96.80	0.1059
0.1131	0.9719	0.8143	100.42	0.3207	0.1143	0.9742	0.7639	95.89	0.1160
0.1448	0.9722	0.8291	99.75	0.3316	0.1506	0.9752	0.7711	94.37	0.1265
0.1844	0.9725	0.8426	98.68	0.3407	0.1864	0.9782	0.7780	93.71	0.1353
				20% Methanol + H_2O Mixture					
				298.15K					
		CH_3COONH_4					CH_3COONa		
0.0063	0.9644	1.4190	78.30	0.1696	0.0060	0.9652	1.4015	143.61	0.1288
0.0443	0.9645	1.4398	77.37	0.1345	0.0421	0.9653	1.4450	139.44	0.1562
0.0823	0.9647	1.4461	76.88	0.1144	0.0782	0.9655	1.4655	137.63	0.1669
0.1203	0.9648	1.4481	76.34	0.0988	0.1142	0.9658	1.4843	136.00	0.1779
0.1583	0.9650	1.4486	75.87	0.0871	0.1503	0.9663	1.5005	134.16	0.1850
0.1962	0.9653	1.4485	75.21	0.0780	0.1864	0.9668	1.5180	132.74	0.1951
		CH_3COOLi					CH_3COOK		
0.0061	0.9653	1.4241	106.24	0.2201	0.0063	0.9652	1.4415	100.08	0.3710
0.0423	0.9653	1.4664	104.37	0.2324	0.0443	0.9653	1.4756	98.51	0.2561
0.0786	0.9654	1.4928	103.19	0.2362	0.0823	0.9655	1.4740	97.50	0.1842

Contd.

0.1149	0.9657	1.5145	102.09	0.2411	0.1203	0.9658	1.4613	96.53	0.1262
0.1511	0.9659	1.5335	101.56	0.2451	0.1583	0.9662	1.4464	95.57	0.0830
0.1874	0.9661	1.5504	101.05	0.2480	0.1962	0.9666	1.4287	94.60	0.0463
308.15K									
CH_3COONH_4					CH_3COONa				
0.0063	0.9604	1.0664	78.28	0.1342	0.0060	0.96040	1.06816	143.08	0.1590
0.0441	0.9605	1.0816	78.07	0.1194	0.0419	0.96048	1.09117	139.63	0.1667
0.0819	0.9606	1.0887	77.94	0.1111	0.0778	0.96064	1.10567	137.77	0.1716
0.1196	0.9607	1.0935	77.81	0.1050	0.1137	0.96100	1.11752	136.18	0.1752
0.1574	0.9608	1.0968	77.69	0.0993	0.1495	0.96136	1.12788	135.01	0.1781
0.1953	0.9609	1.0992	77.59	0.0944	0.1853	0.96180	1.13713	133.81	0.1804
CH_3COOLi					CH_3COOK				
0.00602	0.96041	1.07687	104.68	0.2648	0.0063	0.9604	1.0728	104.31	0.2101
0.04217	0.96051	1.09823	103.57	0.1986	0.0475	0.9605	1.0956	100.63	0.1761
0.07179	0.96062	1.02963	102.90	0.1691	0.0817	0.9607	1.1035	98.96	0.1609
0.09670	0.96078	1.10375	102.13	0.1482	0.1192	0.9610	1.1071	97.15	0.1424
0.15122	0.96111	1.09786	101.28	0.1041	0.1570	0.9614	1.1099	95.63	0.1309
0.18760	0.96142	1.09312	100.51	0.0833	0.1947	0.9619	1.1105	93.97	0.1211
318.15K									
CH_3COONH_4					CH_3COONa				
0.0063	0.9543	0.8433	77.39	0.1160	0.0059	0.9543	0.8552	141.09	0.3036

Contd.

0.0438	0.9544	0.8577	77.43	0.1259	0.0416	0.9544	0.8754	139.90	0.2330
0.0814	0.9545	0.8668	77.44	0.1305	0.0773	0.9545	0.8809	138.98	0.1950
0.1189	0.9546	0.8748	77.45	0.1361	0.1128	0.9547	0.8805	138.56	0.1599
0.1565	0.9547	0.8816	77.46	0.1391	0.1486	0.9549	0.8808	137.85	0.1340
0.1942	0.9547	0.8877	77.46	0.1415	0.1858	0.9730	0.8136	130.95	0.2480
		CH_3COOLi					CH_3COOK		
0.0060	0.9543	0.8633	103.52	0.4281	0.0063	0.9543	0.8445	99.42	0.1335
0.0420	0.9544	0.8931	102.41	0.3363	0.0438	0.9543	0.8601	97.54	0.1398
0.0714	0.9545	0.9004	101.80	0.2901	0.0813	0.9546	0.8698	96.41	0.1435
0.0885	0.9544	0.9023	101.54	0.2680	0.1186	0.9549	0.8777	95.60	0.1462
0.1506	0.9547	0.9034	100.12	0.2092	0.1563	0.9552	0.8849	94.40	0.1490
0.1867	0.9548	0.9021	99.90	0.1841	0.1936	0.9556	0.8914	93.53	0.1515
				30% Methanol + H_2O Mixture					
				298.15K					
		CH_3COONH_4					CH_3COONa		
0.0062	0.9606	1.4208	78.32	0.1809	0.0060	0.9606	1.41131	143.60	0.0970
0.0436	0.9607	1.4417	77.83	0.1400	0.0423	0.9607	1.43791	139.44	0.1290
0.0810	0.9608	1.4482	77.50	0.1206	0.0786	0.9609	1.46028	137.63	0.1516
0.1184	0.9609	1.4518	77.27	0.1059	0.1148	0.9612	1.47956	136.00	0.1660
0.1158	0.9611	1.4516	76.99	0.0920	0.1511	0.9617	1.49930	134.16	0.1810
0.1931	0.9612	1.4475	76.79	0.0760	0.1874	0.9622	1.51751	132.74	0.1925

Contd.

		CH_3COOLi					CH_3COOK		
0.0061	0.9606	1.4294	104.09	0.2610	0.0061	0.9606	1.4517	99.80	0.4640
0.0429	0.9608	1.4543	102.30	0.2020	0.0429	0.9607	1.4922	97.91	0.3150
0.0796	0.9610	1.4687	101.05	0.1720	0.0798	0.9609	1.4945	96.70	0.2370
0.1164	0.9612	1.4691	100.86	0.1430	0.1166	0.9613	1.4825	95.47	0.1711
0.1531	0.9614	1.4665	100.17	0.1200	0.1534	0.9617	1.4666	94.71	0.1201
0.1898	0.9620	1.4593	99.32	0.0960	0.1902	0.9622	1.4412	93.14	0.0711
					308.15K				
		CH_3COONH_4					CH_3COONa		
0.0062	0.9542	1.1113	77.17	0.1511	0.0060	0.9542	1.1380	140.70	0.4650
0.0434	0.9543	1.1305	77.10	0.1413	0.0421	0.9543	1.1744	138.49	0.3381
0.0806	0.9544	1.1399	77.06	0.1336	0.0781	0.9546	1.1767	137.11	0.2562
0.1177	0.9546	1.1464	77.04	0.1280	0.1142	0.9549	1.1706	136.11	0.1951
0.1549	0.9547	1.5205	77.03	0.1245	0.1501	0.9552	1.1620	134.91	0.1501
0.1922	0.9549	1.5569	77.00	0.1194	0.1861	0.9558	1.4559	133.63	0.1001
		CH_3COOLi					CH_3COOK		
0.0061	0.9542	1.1306	103.77	0.3781	0.0061	0.9541	1.1947	98.01	0.2470
0.0427	0.9543	1.1602	102.45	0.2730	0.0428	0.9542	1.4227	96.67	0.1941
0.0794	0.9545	1.1632	101.60	0.2102	0.0794	0.9545	1.4648	95.86	0.1562
0.1161	0.9548	1.1580	100.73	0.1596	0.1146	0.9549	1.4691	96.35	0.1311
0.1530	0.9551	1.1519	100.57	0.1253	0.1525	0.9553	1.1441	94.43	0.1070

Contd.

0.1898	0.9556	1.1413	99.06	0.0902	0.1892	0.9560	1.1398	92.63	0.0872
318.15K									
CH_3COONH_4					CH_3COONa				
0.0062	0.9503	0.8558	76.48	0.0717	0.0060	0.9503	0.8764	140.47	0.3851
0.0431	0.9504	0.8665	77.11	0.0871	0.0418	0.9504	0.9040	138.95	0.3041
0.0801	0.9505	0.8742	77.50	0.0962	0.0778	0.9506	0.9139	137.83	0.2653
0.1171	0.9506	0.8815	77.81	0.1043	0.1137	0.9509	0.9168	136.81	0.2290
0.1542	0.9507	0.8876	77.83	0.1092	0.1494	0.9512	0.9165	136.30	0.1991
0.1911	0.9508	0.8932	78.24	0.1131	0.1853	0.9513	0.9152	135.54	0.1753
CH_3COOLi					CH_3COOK				
0.0061	0.9503	0.8881	104.02	0.4530	0.0061	0.9502	0.8637	99.15	0.1901
0.0424	0.9504	0.9077	103.88	0.3231	0.0425	0.9503	0.8809	98.09	0.1704
0.0790	0.9505	0.9097	103.82	0.2454	0.0789	0.9505	0.8890	97.69	0.1588
0.1155	0.9506	0.9069	103.77	0.1933	0.1152	0.9508	0.8950	97.89	0.1520
0.1522	0.9508	0.8979	103.70	0.1412	0.1516	0.9512	0.8992	96.92	0.1454
0.1907	0.9509	0.8904	103.66	0.1061	0.1881	0.9516	0.9017	96.51	0.1372

Table 2

Limiting apparent molar volume (V_ϕ^0), experimental slope (S_v^*), A and B parameters of viscosity for acetate salts in different mass % of Methanol at different temperatures

Mass % of CH_3OH	V_ϕ^0 at			S_v^* at			A at			B at		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
CH_3COONa												
10	145.54	144.34	142.75	-35.66	-28.78	-26.03	0.1937	0.2918	0.3921	0.1138	-0.1807	-0.3380
20	144.05	143.62	142.06	-25.50	-21.78	-10.64	0.1261	0.1541	0.3461	0.1536	-0.0625	-0.5505
30	143.45	142.78	141.86	-22.96	-20.09	-14.14	0.0750	0.5460	0.4219	0.2711	-0.1028	-0.5934
CH_3COOLi												
10	107.28	106.35	105.53	-23.61	-16.29	-15.31	0.1845	0.2133	0.2283	0.3596	0.2902	0.2624
20	106.53	105.81	104.50	-12.54	-11.74	-10.63	0.2137	0.3050	0.4728	0.0799	-0.5121	-0.6924
30	104.72	105.07	104.12	-12.50	-12.28	-1.01	0.2977	0.4369	0.5251	-0.4563	-0.8085	-0.9759
CH_3COOK												
10	103.30	101.48	101.03	-17.20	-18.09	-16.30	0.3053	0.1331	0.0519	-0.2967	0.1529	0.1923
20	101.64	101.02	100.83	-14.92	-9.31	-16.04	0.4434	0.2303	0.1295	-0.9036	-0.2505	0.0494
30	100.67	99.414	99.668	-14.71	-13.02	-6.80	0.5524	0.2842	0.2009	-1.1116	-0.4527	-0.1456
CH_3COONH_4												
10	80.22	79.23	78.35	-14.45	-13.82	-8.86	0.1289	0.0711	0.0916	-0.0925	0.0479	0.0683
20	79.07	78.06	77.39	-8.18	-1.86	0.19	0.1886	0.1426	0.1106	-0.2545	-0.1093	0.0715
30	78.68	77.21	76.15	-4.68	-0.46	4.59	0.2019	0.1587	0.0628	-0.2832	-0.0883	0.1178

Table 3

Values of various coefficients (a_0, a_1, a_2) of acetate salts in various mass % of water methanol mixtures

Mass % of CH_3OH	a_0/ $cm^3\ mol^{-1}$	a_1/ $cm^3\ mol^{-1}\ K^{-1}$	a_2/ $cm^3\ mol^{-1}\ K^{-1}$
		CH_3COONa	
10	480.47	-2.12	0.0034
20	791.35	-3.86	0.0057
30	458.06	-1.42	0.0013
		CH_3COOLi	
10	244.49	-0.83	0.0013
20	476.18	-2.38	0.0039
30	573.27	-3.50	0.0065
		CH_3COOK	
10	16.59	2.33	-0.0069
20	88.96	0.68	-0.0022
30	-218.51	3.32	-0.0076
		CH_3COONH_4	
10	59.20	0.23	-0.0006
20	-47.00	0.93	-0.0017
30	-65.83	1.10	-0.0021

Table 4

Limiting apparent molar compressibilities (ϕ_E^0) for acetate salts in various mass % of methanol at different temperature

Mass % of Methanol	ϕ_E^0 / cm^3 mol^{-1} K^{-1}			$\left(\delta\phi_E^0 / \delta T\right)_P$
	298.15 K	308.15 K	318.15 K	
		CH_3COONa		
10	-0.1255	-0.0585	0.0085	Positive
20	-0.4856	-0.3735	-0.2605	Positive
30	-0.6825	-0.6575	-0.6325	Positive
		CH_3COOLi		
10	-0.0875	-0.0625	-0.0375	Positive
20	-0.0926	-0.0156	0.0615	Positive
30	0.3665	0.4965	0.6265	Positive
		CH_3COOK		
10	-1.7515	-1.8885	-2.0253	Negative
20	-0.5985	-0.6415	-0.6845	Negative
30	-1.1805	-1.3315	-1.4825	Negative
		CH_3COONH_4		
10	-0.0935	-0.1045	-0.1155	Negative
20	-0.0840	-0.1180	-0.1520	Negative
30	-0.1265	-0.1675	-0.2085	Negative

Table 6

Mass % THF, Molality (m), Density (ρ), Sound Velocity (u), Adiabatic Compressibility (β), Apparent Molal Adiabatic Compressibility (ϕ_K), Limiting Apparent Molal Adiabatic Compressibility (ϕ_K^0) and Experimental Slope (S_K^*) of some acetate salts in methanol water mixtures (10%, 20%, 30%) at 298.15 K

Mass % of Methanol	m / mol kg^{-1}	ρ / kg m^{-3}	u / m sec^{-1}	$\beta \times 10^{10}$/Pa^{-1}	$\phi_K \times 10^{10}$/m^{3}mol^{-1}Pa^{-1}	$\phi_K^0 \times 10^{10}$/ M^{3}mol^{-1}Pa^{-1}	$S_K^* \times 10^{10}$/ M^{3}mol$^{-3/2}$Pa^{-1}kg$^{1/2}$
				CH_3COONH_4			
10	0.0062	979.9	1465.23	4.7533	-33.379	-38.670	78.605
	0.0437	980.0	1500.36	4.5329	-9.660		
	0.0813	980.1	1547.72	4.2631	-8.443		
	0.1192	980.3	1647.72	3.9965	-7.940		
	0.1571	980.6	1715.00	3.8625	-6.854		
	0.1952	980.8	1748.27	3.7589	-5.010		
20	0.0066	964.4	1653.54	3.7923	-47.195	-55.103	117.50
	0.0460	964.5	1698.45	3.5941	-10.954		
	0.0857	964.5	1745.18	3.4037	-8.075		
	0.1254	964.8	1796.78	3.2104	-7.047		
	0.1655	965.0	1825.32	3.1102	-5.920		
	0.2057	965.3	1872.11	2.9558	-5.494		
30	0.0065	960.6	1695.00	3.6234	-96.108	-113.32	247.06
	0.0455	960.7	1732.15	3.4693	-58.400		
	0.0847	960.8	1758.36	3.3663	-40.001		
	0.1240	960.9	1789.92	3.2483	-25.202		
	0.1636	961.1	1821.02	3.1377	-11.503		
	0.2033	961.2	1867.36	2.9834	-6.121		
				CH_3COOK			
10	0.0062	979.9	1453.23	4.8321	-20.872	-24.399	44.699
	0.0435	980.0	1541.92	4.2917	-15.330		
	0.0801	980.3	1598.56	3.9920	-11.961		

Contd.

	0.1185	980.6	1629.16	3.8422	-9.265		
	0.1563	980.9	1637.14	3.0836	-7.182		
	0.1940	981.7	1636.49	3.8039	-5.714		
20	0.0066	965.2	1619.35	3.9508	22.549	-27.062	58.330
	0.0460	965.3	1734.89	3.4418	14.400		
	0.0855	965.5	1770.48	3.3041	9.264		
	0.1231	965.8	1801.66	3.1897	7.185		
	0.1650	966.2	1724.37	3.4808	3.510		
	0.2050	966.6	1672.79	3.6973	1.640		
30	0.0064	960.6	1605.78	4.0373	-27.501	-32.667	65.64
	0.0448	960.7	1759.84	3.3610	-18.890		
	0.0834	960.9	1829.67	3.1086	-13.610		
	0.1219	961.3	1843.05	3.0854	-9.412		
	0.1609	961.7	1781.83	3.2143	-6.201		
	0.1999	962.2	1736.83	3.4439	-3.700		
				CH$_3$COOLi			
10	0.0061	979.9	1455.54	4.8168	-23.665	-27.507	49.642
	0.0430	980.0	1557.53	4.2062	-17.500		
	0.0800	980.2	1627.16	3.8533	-13.731		
	0.1173	980.5	1630.54	3.8362	-9.414		
	0.1548	980.8	1648.45	3.7521	-7.607		
	0.1923	981.2	1671.72	3.6469	-6.614		
20	0.0063	965.2	1641.36	3.8455	-41.001	-52.751	115.67
	0.0440	965.3	1890.99	2.8971	-27.900		
	0.0819	965.4	2060.49	2.4397	-20.700		
	0.1013	965.7	2120.69	2.3027	-18.100		
	0.1592	965.9	2039.72	2.4880	-10.200		
	0.1981	966.1	1977.51	2.6470	-7.300		
30	0.0064	960.6	1630.67	3.9149	-50.010	-61.574	136.72
	0.0448	960.7	1996.90	2.6104	37.201		
	0.0836	960.9	2357.73	1.8720	29.103		
	0.1226	961.2	2668.21	1.4614	23.300		

Contd.

	0.1619	961.4	2770.96	1.3547	18.312		
	0.2013	962.0	2918.87	1.2201	15.400		
				CH_3COONa			
10	0.0062	979.9	1449.22	4.8590	-16.370	-20.21	38.896
	0.0433	980.0	1518.30	4.4265	-12.000		
	0.0810	980.3	1563.00	4.1757	-9.327		
	0.1184	980.6	1586.60	4.0512	-7.290		
	0.1563	980.9	1588.07	4.0425	-5.440		
	0.1945	981.5	1590.77	4.0262	-4.350		
20	0.0062	965.2	1614.56	3.9779	-19.700	-24.049	51.253
	0.0438	965.3	1720.34	3.5005	-13.600		
	0.0816	965.5	1785.67	3.2491	-10.300		
	0.1196	965.8	1808.63	3.1569	-7.690		
	0.1579	966.3	1814.23	3.1476	-5.780		
	0.1965	966.8	1831.61	3.0881	-4.880		
30	0.0063	960.6	1581.20	4.1638	-9.369	-32.161	70.184
	0.0442	960.7	1585.75	4.1395	-1.408		
	0.0824	960.9	1712.98	3.5467	-8.134		
	0.1208	961.2	1726.96	3.4058	-5.902		
	0.1595	961.7	1747.32	3.3249	-4.908		
	0.1984	962.2	1767.98		-4.289		

CHAPTER XI

Thermodynamic and transport properties of binary mixtures of dimethyl sulfoxide with t-butyl alcohol, butyl acetate, 2-butanone and butyl amine at different temperatures*

11.1. Introduction

Dimethyl sulfoxide (DMSO), a typical aprotic solvent having both polar and nonpolar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells.[1]

This solvent was chosen particularly for this study because of its wide range of applicability as a solvent in chemical and biological processes. Viscosity and density of binary liquid mixtures are extensively used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications.[4,5] These have been extensively used to obtain information on intermolecular interactions and stereo chemical effects in these systems.[6] In this paper we extend our studies to the binary mixtures of DMSO, with butyl acetate, tert-butyl alcohol, n-butyl amine and 2-butanone.The various thermodynamic properties such as excess molar volume (V^E) and viscosity deviations ($\Delta\eta$) obtained from experimental observations have been rationalized.

To our knowledge, the experimental data reported in this paper are not available in the literature.

11.2. *Experimental Section*

11.2.1. *Materials*

Dimethylsulfoxide, Merck, India, was kept several days over anhydrous $CaSO_4$, refluxed for four hours over CaO. Finally, it was distilled at low pressure. Details[11] have been described in chapter III. tert-butanol, n-butyl acetate, 2-butanone, n-butylamine (S. D. Fine Chemicals, Analytical Reagent, Purity > 99%) were used. The purity of the solvents was ascertained by comparing experimental values of densities and viscosities with those reported in the literature [12-17] as listed in Table 1.

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11.2.2. *Apparatus and Procedure*

Viscosities (η) have been measured at 298.15 K, 308.15 K and 318.15 K by means of a suspended Ubbelohde type viscometer [7]. Calibration was done at all the experimental temperatures with triply distilled water and purified methanol using density and viscosity values from the literature. Densities (ρ) were measured at the mentioned temperatures with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was $\pm 2 \times 10^{-4}$ mPa.s. The measurements were done in a thermostatic bath controlled to ± 0.01 K. The details of the methods and techniques for determination of these parameters have been described in earlier papers. [6,8,9,10]

The mixtures were prepared by mixing known volumes of pure liquids in air-tight stoppered bottles. The reproducibility in mole fraction was within ± 0.0002 units. The weights were taken on a Mettler electronic analytical balance (AG 285) accurate to 0.02 mg. The precision of the density and viscosity measurements is $\pm 3 \times 10^{-4}$ g cm^{-1} and $\pm 2 \times 10^{-4}$ m Pa s respectively. The details of all the experimental methods are described in chapter III.

8.3. *Results and Discussion*

Table 2 lists the experimental values of densities (ρ_i) and viscosities (η_i) of the binary mixtures along with the corresponding mole fractions of DMSO (x_1), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), excess Gibbs energy of activation for viscous flow (G^{*E}) and interaction parameters (d_{12}, T_{12}, H_{12}) at all the experimental temperatures. The plots of V^E, $\Delta\eta$, G^{*E} against x_1 at 298.15 K are represented in fig. 1, 2, 3 respectively. Because of similarity of nature the plots at the other two temperatures are not presented here.

The experimental ρ values have been used to calculate the excess molar volumes (V^E) using the following equation, [5,18]

$$V^E = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \qquad (1)$$

Where, M_i, ρ_i, ρ are mol. Wt., density of the pure components and density of the mixtures respectively.

The deviation in viscosities from linearity ($\Delta\eta$) can be computed using the relationship,

$$\Delta\eta = \eta - \sum_{i=1}^{2} (x_i \eta_i) \tag{2}$$

Where, η_i, η and are the viscosities of the pure components and of the mixtures respectively.

On the basis of the theories of absolute reaction rates [19], the excess Gibbs energy of activation for viscous flow (G^{*E}) was calculated from the equation, [20]

$$\Delta G^{*E} = RT\ [\ \ln \eta V - \sum_{i=1}^{2} (x_i \ln \eta_i V_i)] \tag{3}$$

R, T, V, V_i are the Universal gas constant, experimental temperature in absolute scale and molar volumes of pure component and the mixtures respectively. The excess properties (V^E, $\Delta\eta$ and G^{*E}) were fitted to the Redlich-Kister polynomial equation[21],

$$Y^E = x_1 x_2 \sum_{i=1}^{K} a_i (x_1 - x_2)^i \tag{4}$$

where Y^E refers to excess properties, x_1 is the mole fraction DMSO and x_2 is that of the other component. The coefficients (a_i) were obtained by fitting eq.6 to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The estimated values of a_i along with the tabulated standard deviations (σ) are summarized for all mixtures in table 3. The standard deviation (σ) was calculated using the equation,

$$\sigma = \left[\frac{(Y^E_{\exp} - Y^E_{cal})^2}{(n - m)} \right]^{\frac{1}{2}} \tag{5}$$

where n is the number of data points and m is the number of coefficients.

The value of the excess molar volume, V^E are found to be negative for mixtures containing DMSO and butyl acetate, butyl amine and 2-butanone and their magnitudes follow the order given below;

Butyl amine > 2-Butanone> Butyl acetate,

But for the mixture of DMSO with tert-butyl alcohol, values of V^E are positive. This indicates that, the interaction occurring between DMSO and butyl amine is the strongest followed by butanone and butyl acetate. Whereas dispersive force plays the main role in case of tert-butyl alcohol.

The values of V^E may be regarded as the result of contributions from several opposing effects[22], namely, physical, chemical, and structural. Physical contributions are nonspecific interactions and contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease. The structural contributions arise especially from geometrical fitting (interstitial accommodation), of one component into other due to the differences in the free volume and molar volume between components lead to negative contribution to V^E.

The largest negative excess volume of DMSO and n- butyl amine system is due to strong interaction between the oxygen atom of DMSO and hydrogen atom of n- butyl amine. This indicates formation of intermolecular hydrogen bonded complexes. The parabolic shapes of V^E versus x_1 plots with well defined minima also indicate the presence of complex formation. It is seen that the values of V^E for the binary mixtures of DMSO with 2-butanone are also negative over the entire range of composition, suggesting specific interactions between the mixing components. These negative values of V^E may be attributed to the dipole-dipole interactions resulting in the formation of electron-transfer complexes between the molecules of mixing components. The molar volumes of DMSO and butyl acetate differ considerably. Hence, smaller DMSO molecules are interstitially accommodated into aggregates of butyl acetate, yielding negative V^E values for DMSO and butyl acetate mixtures .

DMSO+ tert-butyl alcohol mixture is the only exception among the experimental binary mixtures showing positive values of V^E over the entire composition and temperature range. Mixing of DMSO with tert-butyl alcohol would induce dissociation of the hydrogen bonds in the self associated alcohol[23] leading to expansion in volume, and thus a positive contribution to V^E values. Another equally important contribution leading to the positive V^E values for this mixture arises from the close molecular sizes of DMSO and tert-butyl alcohol. Assarson and Eirich [23] suggested that the liquids of similar molecular sizes usually mix with positive excess volumes.

Large negative values of viscosity deviations $\Delta\eta$ are observed for the binary mixtures of DMSO with t-Butyl alcohol and Butyl acetate. For 2- butanone and butyl amine the $\Delta\eta$ values are negative for lower mole fractions of DMSO but ultimately they turn positive at *higher mole fractions of* DMSO *thereby resulting sigmoid type plots* (fig-2).

In general, for systems where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative, whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules, thereby resulting in positive values[36]. The negative $\Delta\eta$ values of DMSO and t-Butyl alcohol mixtures indicates the dominance of dispersion forces between the unlike molecules in this mixture [35, 36] and supports the conclusion drawn from V^E values.. According to Fort and Moore also $\Delta\eta$ values are negative in systems of unequal molecular size in which dispersion forces are predominant. [39] This explains the negative $\Delta\eta$ values for DMSO and Butyl acetate mixture which also supports the conclusion drawn from V^E values. For 2- butanone and butyl amine mixtures with DMSO positive $\Delta\eta$ values indicate presence of charge transfer interactions leading to the formation of complex species between unlike molecules, [40] This conclusion is in excellent agreement with that drawn from V^E values.

According to Reed and Taylor and Meyer *et al.* positive G^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces. [25,27]

It is seen that, for DMSO+ t-butyl alcohol and DMSO+ butyl acetate, the G^{*E} values are negative over the entire range of composition and temperature indicating that, in these mixtures forces of dispersion are dominating. The large and positive G^{*E} values for DMSO + butylamine mixture supports strong specific interactions through complex formation in the system. The value of G^{*E} for DMSO+ 2-butanone mixture is less positive suggesting the presence of weaker interactions.

There is a systematic rise in V^E and $\Delta\eta$ values with a rise in temperature for all the components studied here suggesting an increase in interaction between the component molecules. The effect of temperature increase is to disrupt hetero and homo association of the molecules which causes increase in fluidity of the liquid. So, $\Delta\eta$ values are higher at higher temperatures. Similar results were reported earlier [28].

Apart from expressing η as a polynomial fit, several semi empirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure component data. [29,30] We have examined equations proposed by Grunberg-Nissan, Tamura-Kurata and Hind et al.

The single parameter Grunberg-Nissan equation [31] reads as:

$$\eta = \exp[\sum_{i=1}^{2}(x_i \ln \eta_i) + x_1 x_2 d_{12}] \tag{6}$$

where d_{12} is a parameter proportional to the interchange energy and has been regarded as an approximate measure for the non-ideal behaviors of binary mixtures.

Tamura-Kurata [32] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{2} x_i \phi_i \eta_i + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} T_{12} \tag{7}$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of i^th^ pure component in the mixture.

Molecular interactions may also be interpreted by the viscosity model of Hind *et al* [32]

$$\eta = \sum_{i=1}^{2} x_i^2 \eta_i + 2(x_1 x_2 H_{12})$$

(8)

where H_{12} is interaction parameter.

Among the three parameters determined here, the Grunberg-Nissan parameter provides the best measure to ascertain the strength of interaction. At any given composition, the variation of d_{12} with strength of interaction is similar to that of $\Delta\eta$, being negative for systems in which dispersion forces are dominant, becoming less negative and then increasingly positive as the strength of interaction increases.[26,37,38]

According to Fort and Moore [26] the values of T_{12} and H_{12} are not very different except where the values of the components differ considerably. There is a tendency of T_{12} and H_{12} at a certain composition to increase with the strength of interaction of the components but this is not well defined and T_{12} and H_{12} can not generally be regarded as a measure of the strength of interaction. [38]

A perusal of this table shows that the variations and signs of d_{12} are similar to those of $\Delta\eta$ and thereby supports our conclusion. DMSO + n-butylamine mixture, which involves large specific interaction, shows positive d_{12} values.

T_{12} and H_{12} values are positive for all binary mixtures, almost identical and do not change appreciably with the change of composition of binary mixtures.

4.4. *Conclusion:*

In summary, we can draw some conclusion about the type and nature of molecular interactions occurring in the binary mixtures of DMSO with butyl acetate, tert-butyl alcohol, n-butyl amine and 2-butanone. Specific interaction is present between DMSO and n- butyl amine, DMSO + butyl acetate, DMSO + 2-butanone solvent system but in DMSO + t-butyl alcohol solvent system dispersion forces are prevailing. This study on excess or deviation properties along with acoustic properties seems to be of much use in exploring the nature of interactions present in the experimental binary mixtures; however, more extensive study will have a better in this field.

References:

1) T. Kamiyama, M. Morita, and T. Kimura, *J. Chem. Eng. Data,* **2004**, *49,* 1350.

2) M. K. Pasha, J. R. Dimmock, M.D. Hollenberg, Sharma, R. K. *Biochem., Pharmacol,* **2002**, *64,* 1461.

3) R. Francesconi, A. Bigi, K. Rubini, F. Comelli, J. *Chem. Eng. Data,* **2005**, *50,* 1932.

4) C.Lafuente,B.Giner, A.Villares, I.Gascon P. Cea, *Int. J. of Thermophysics.* **2004**, *25,*1735.

5) P. S.Nikam, L.N.Shirsat, M.Hasan, *J. Indian. Chem. Soc.* **2000**, *77,* 244.

6) M.N.Roy and A.Choudhury, *J. Teaching and Res in Chem*. **2000**, *1,* 17.

7) J. R.Suindells and T. B.Godfray, *J. Res. Natd. Bur. Stand.* **1952**, *48,* 1.

8) D.K.Hazra, M.N.Roy and B.Das, *Ind. J. Chem. Techno.* **1994**,*1,*93.

9) M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data,* **2001**. *46* , 1247.

10) M.N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data,* **2004**, *49* , 291.

11) D. S. Gill, A. Sharma, M. S. Chauhan, A. N. Sharma, J.S. Cheema, *Electrochemica Acta.* **1985**, *30,* 15.

12) J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic solvents: physical properties and methods of purification, 4th ed.;* Wiley-Interscience: New York, **1986**

13) N.V. Sastry, M.C. Patel. *J. Chem. Eng. Data.* **2003**, *48,* 1019.

14) Anson, R. Garriga, S.Martinez, P. Pelez, M. J. Gracia, *Chem. Eng. Data.* **2005**,*50,* 677.

15) C.M. Kinart, W. J.Kinart, D. J.Checinska-Majak, *Chem. Eng. Data* **2003**,*48,*1037. .

16) Hsu-Chen, Ku.; Chein-Hsiun, Tu. K. *J. Chem. Eng. Data* **2005**,*50,* 608.

17) A.Pal, R. K.Bhardwaj, *Z. Phys. Chem.,* **2002**, *216,* 1033.

18) A.W.Quin, D. F. Hoffmann and P. Munk, *J. Chem. Eng. Data.* **1992**, *37,* 55.

19) S.Glasstone, K. J. Laidler and H.Eyring, *The Theory of Rate Process,* McGraw-Hill, New York, 514, **1941**.

20) D. S. Gill, T. S. Kaur, H. Kaur, I. M. Joshi and J. Singh, *J. Chem. Soc. Faraday Trans.* **1993**,*89,*1737.

21) A.J. Treszczanowicz, O. Kiyohara, G. C. Benson. *J. Chem. Thermodyn.* **1981**, *13,* 253.

22) Y. Marcus, Introduction to Liquid State Chemistry (Wiley Interscience, New York, **1977**.

23) P. Assarson and F. R. Eirich, *J. Phys. Chem.* **1968**, *72*, 2710.

24) T. M. Reed and T. E. Taylor, *J. Phys. Chem,* **1959**, *63*, 58.

25) R. J.Fort, W. R. Moore. *Trans Faraday Society.* **1996**, *62*, 1112.

26) R. Meyer, M. Meyer and J. Metzer, A. Peneloux. *Chem. Phys,* **1971**, *62*, 406.

27) M. Singh. *J Indian Chemical Society.* **2002**, *79*,659.

28) R. C. Reid,J.M. Prausnitz, B.E. Poling. The properties of gases and liquids, 4th Mcgraw-Hill International, **1987**

29) J.B. Irving, *NEL Report No. 630 and 631*,National Engineering Laboratory,East Kilbride,Glassgow

30) L. Grunberg and A. H. Nissan, Nature. **1949**, *164*, 799.

31) M. Tamura, M. Kurata, *Bull. Chem. Soc. Jpn.* **1952**,*25*, 32.

32) R. K. Hind, E. McLaughlin, A. R. Ubbelohde *Trans. Faraday. Soc.* **1960**,*56*, 328.

33) D. S. Gill and T. S. Cheema*, Z. Phys. Chem (N.F).* **1983**, 134, 205.

34) Y. Marcus, Ion Solvation, Wiley, New York, **1985**.

35) M. G. Prolongo, R. M. Masegosa, H. I. Fuentes and A. Horta, *J. Phy. Chem.* **1984** *88*, 2163.

36) K. Ramamoorthy. *J of Pure and Appl. Phys.* **1973**, *11*, 554.

37) K. Ramamoorthy. *J of Pure and Appl. Phys.* **1973**, *11*, 556.

38) D Agarwal. and M Singh., *J Indian Chemical Society,* **2004**, *81*, 850,.

Table 1

Comparison of density (ρ), viscosity (η) of the Pure Liquids with Literature Data at 298.15 K.

	Temperature	$\rho \times 10^{-3}$/ (kg.m^{-3})		η / (m Pa.s)	
		Expt.	Lit.	Expt.	Lit.
DMSO	298.15 K	1.0951	1.09568[17]	1.9923	1.991[17]
	308.15 K	1.0839	-	1.7052	-
	318.15 K	1.0757	-	1.4504	-
Butyl acetate	298.15 K	0.8754	0.8761[18]	0.6738	0.674[18]
	308.15 K	0.8646	-	0.6684	-
	318.15 K	0.8565	-	0.5342	-
t-Butyl alchohol	298.15 K	0.7807	0.7799[19]	4.4338	4.433[19]
	308.15 K	0.7705	-	2.7910	-
	318.15 K	0.7610	-	1.8099	-
Butyl amine	298.15 K	0.7312	0.7331[20]	0.4960	0.496[22]
	308.15 K	0.7199	-	0.4195	-
	318.15 K	0.7136	-	0.3600	-
2-Butanone	298.15 K	0.7984	0.7996[21]	0.3784	0.378[21]
	308.15 K	0.7883	-	0.3235	-
	318.15 K	0.7796	-	0.3138	-

Table 2

Measured and Derived Parameters for Various Studied Binary Mixtures at 298.15 K, 308.15 K And 318.15 K

x_1	ρ x 10^{-3}/ (kg.m^{-3})	η / (mPa.s)	V^E x10^6 / (m^3.mol^{-1})	$\Delta\eta$/ (mPa.s)	G^{*E} / J.mol^{-1})	d_{12}	T_{12}	H_{12}
				298.15 K				
			tert-Butyl alcohol + DMSO					
0.0953	0.8031	3.6683	0.068	-0.533	-270.70	-1.31	-0.41	0.12
0.1917	0.8269	3.0119	0.145	-0.954	-559.55	-1.51	-0.31	0.14
0.2890	0.8521	2.5592	0.225	-1.169	-762.96	-1.55	0.03	0.37
0.3874	0.8791	2.2505	0.276	-1.238	-881.15	-1.55	0.35	0.61
0.4868	0.9083	2.0714	0.296	-1.174	-887.18	-1.49	0.69	0.86
0.5872	0.9399	1.9671	0.281	-1.033	-816.73	-1.41	0.97	1.08
0.6888	0.9743	1.9624	0.222	-0.790	-625.17	-1.23	1.31	1.37
0.7914	1.0115	1.9556	0.148	-0.546	-437.31	-1.12	1.54	1.56
0.8951	1.0518	1.9423	0.065	-0.306	-258.69	-1.16	1.61	1.58
			Butyl acetate + DMSO					
0.1418	0.8943	0.6508	-0.140	-0.210	-419.83	-1.55	0.51	0.47
0.2710	0.9137	0.6822	-0.212	-0.349	-617.16	-1.42	0.55	0.45
0.3893	0.9335	0.7441	-0.238	-0.443	-698.62	-1.34	0.56	0.40
0.4979	0.9539	0.8413	-0.226	-0.489	-675.80	-1.27	0.58	0.36
0.5980	0.9750	0.9732	-0.192	-0.489	-583.06	-1.17	0.60	0.32
0.6905	0.9968	1.1292	-0.141	-0.455	-470.78	-1.09	0.62	0.27
0.7763	1.0195	1.3174	-0.089	-0.382	-334.72	-0.99	0.65	0.24
0.8561	1.0434	1.5356	-0.051	-0.267	-192.35	-0.85	0.71	0.25
0.9305	1.0686	1.7657	-0.019	-0.135	-76.24	-0.70	0.80	0.29
			Butanone + DMSO					
0.0930	0.8234	0.4384	-0.302	-0.090	-20.99	-0.09	0.70	0.65
0.1875	0.8492	0.5180	-0.520	-0.163	1.37	0.02	0.71	0.65
0.2834	0.8762	0.6758	-0.693	-0.160	263.84	0.54	0.87	0.79
0.3809	0.9041	0.8631	-0.800	-0.130	467.78	0.81	1.00	0.91
0.4799	0.9333	1.0880	-0.854	-0.065	632.84	1.04	1.16	1.06
0.5806	0.9635	1.3404	-0.837	0.025	735.31	1.23	1.34	1.24
0.6829	0.9947	1.5525	-0.737	0.072	679.11	1.28	1.45	1.35
0.7868	1.0274	1.7503	-0.589	0.102	549.37	1.34	1.57	1.49
0.8925	1.0608	1.9089	-0.345	0.090	332.04	1.42	1.72	1.65
			Butyl Amine +DMSO					
0.0942	0.7595	0.5608	-0.403	-0.076	-19.60	-0.10	0.87	0.80
0.1896	0.7892	0.6836	-0.711	-0.096	143.36	0.37	1.04	0.93
0.2862	0.8207	0.8842	-0.948	-0.040	448.01	0.88	1.28	1.15
0.3841	0.8540	1.1108	-1.109	0.040	675.78	1.15	1.48	1.32
0.4834	0.8892	1.3283	-1.191	0.109	776.10	1.25	1.61	1.55
0.5839	0.9265	1.5437	-1.185	0.174	801.06	1.33	1.74	1.74

Contd

0.6858	0.9658	1.7132	-1.073	0.191	706.96	1.33	1.81	1.93
0.7891	1.0070	1.8558	-0.845	0.179	548.66	1.34	1.88	2.13
0.8939	1.0503	1.9775	-0.501	0.144	345.03	1.48	2.06	2.07
308.15 K								
tert- Butyl alcohol + DMSO								
0.0953	0.7932	2.4965	0.026	-0.191	-156.14	-0.75	0.95	1.14
0.1917	0.8173	2.2559	0.054	-0.327	-286.22	-0.76	1.03	1.19
0.2890	0.8430	2.0712	0.077	-0.406	-376.30	-0.76	1.13	1.26
0.3874	0.8703	1.9334	0.098	-0.437	-423.97	-0.74	1.23	1.33
0.4868	0.8996	1.8355	0.111	-0.427	-429.55	-0.72	1.33	1.39
0.5872	0.9310	1.7704	0.110	-0.383	-395.46	-0.68	1.41	1.46
0.6888	0.9648	1.7292	0.099	-0.314	-330.22	-0.65	1.49	1.51
0.7914	1.0014	1.6867	0.075	-0.245	-270.22	-0.69	1.51	1.51
0.8951	1.0411	1.6621	0.034	-0.157	-186.23	-0.82	1.44	1.41
Butyl acetate + DMSO								
0.1418	0.8842	0.7177	-0.244	-0.098	-111.00	-0.51	0.90	0.79
0.2710	0.9037	0.7848	-0.335	-0.165	-158.04	-0.47	0.91	0.77
0.3893	0.9238	0.8663	-0.357	-0.206	-167.64	-0.44	0.92	0.75
0.4979	0.9438	0.9507	-0.339	-0.234	-178.27	-0.46	0.92	0.72
0.5980	0.9649	1.0476	-0.299	-0.241	-169.13	-0.46	0.91	0.69
0.6905	0.9869	1.1548	-0.258	-0.229	-149.89	-0.47	0.91	0.65
0.7763	1.0096	1.2712	-0.203	-0.202	-125.88	-0.48	0.90	0.61
0.8561	1.0334	1.4053	-0.144	-0.151	-84.19	-0.48	0.91	0.58
0.9305	1.0580	1.5465	-0.069	-0.087	-47.14	-0.50	0.89	0.52
Butanone + DMSO								
0.0930	0.8124	0.4090	-0.215	-0.043	204.19	0.95	0.82	0.76
0.1875	0.8380	0.5575	-0.440	-0.025	593.52	1.53	1.01	0.93
0.2834	0.8655	0.7461	-0.692	0.031	927.48	1.80	1.18	1.09
0.3809	0.8940	0.9258	-0.860	0.076	1061.92	1.77	1.27	1.18
0.4799	0.9233	1.1266	-0.940	0.14	1141.60	1.80	1.39	1.29
0.5806	0.9533	1.3117	-0.906	0.186	1102.61	1.79	1.48	1.40
0.6829	0.9842	1.4620	-0.786	0.195	946.45	1.72	1.54	1.46
0.7868	1.0165	1.5877	-0.613	0.177	716.86	1.69	1.60	1.54
0.8925	1.0498	1.6767	-0.360	0.120	409.58	1.69	1.68	1.64
Butyl Amine + DMSO								
0.0942	0.7489	0.5155	-0.529	-0.025	298.88	0.98	1.02	0.92
0.1896	0.7793	0.6382	-0.927	-0.025	614.32	1.06	1.10	0.98
0.2862	0.8111	0.8425	-1.212	0.055	1091.99	1.49	1.34	1.20
0.3841	0.8451	1.0464	-1.440	0.133	1408.81	1.62	1.49	1.34
0.4834	0.8804	1.2390	-1.509	0.198	1601.54	1.64	1.59	1.46
0.5839	0.9177	1.4212	-1.480	0.251	1709.70	1.67	1.70	1.58
0.6858	0.9567	1.5703	-1.320	0.269	1719.63	1.68	1.78	1.69
0.7891	0.9978	1.6681	-1.056	0.234	1543.01	1.66	1.83	1.77
0.8939	1.0403	1.6887	-0.618	0.12	1078.02	1.48	1.74	1.69
318.15 K								
tert-Butyl alcohol + DMSO								

Contd.

0.0953	0.7837	1.7142	0.032	-0.078	-78.06	-0.39	1.22	1.27
0.1917	0.8078	1.5876	0.060	-0.153	-216.16	-0.57	1.08	1.14
0.2890	0.8335	1.4874	0.080	-0.211	-325.19	-0.64	1.05	1.10
0.3874	0.8610	1.4069	0.092	-0.245	-410.41	-0.70	1.04	1.07
0.4868	0.8904	1.3750	0.096	-0.252	-410.63	-0.67	1.09	1.11
0.5872	0.9221	1.3684	0.087	-0.230	-365.21	-0.61	1.15	1.15
0.6888	0.9562	1.3737	0.069	-0.189	-298.64	-0.58	1.20	1.19
0.7914	0.9930	1.3890	0.043	-0.136	-215.40	-0.54	1.24	1.21
0.8951	1.0327	1.4189	0.020	-0.069	-107.35	-0.48	1.29	1.26
Butyl acetate + DMSO								
0.1418	0.8758	0.5781	-0.212	-0.086	-116.05	-0.51	0.74	-2.39
0.2710	0.8955	0.6605	-0.348	-0.122	-70.40	-0.30	0.82	-0.66
0.3893	0.9158	0.7569	-0.426	-0.134	-1.55	-0.17	0.87	-0.07
0.4979	0.9365	0.8393	-0.443	-0.151	-4.94	-0.18	0.87	0.19
0.5980	0.9579	0.9280	-0.426	-0.154	-3.73	-0.19	0.87	0.34
0.6905	0.9799	1.0308	-0.383	-0.136	20.96	-0.15	0.89	0.45
0.7763	1.0026	1.1374	-0.312	-0.108	38.02	-0.11	0.91	0.54
0.8561	1.0261	1.2444	-0.222	-0.074	41.28	-0.08	0.94	0.61
0.9305	1.0504	1.3507	-0.113	-0.036	31.38	-0.03	0.97	0.68
Butanone + DMSO								
0.0930	0.8051	0.3725	-0.389	-0.047	71.81	0.35	0.65	0.60
0.1875	0.8312	0.4369	-0.662	-0.091	107.63	0.29	0.64	0.59
0.2834	0.8584	0.5429	-0.870	-0.093	290.81	0.56	0.71	0.65
0.3809	0.8866	0.6887	-1.009	-0.058	523.03	0.86	0.83	0.76
0.4799	0.9161	0.8739	-1.093	0.015	749.95	1.16	0.99	0.91
0.5806	0.9472	1.0807	-1.142	0.107	901.39	1.43	1.17	1.10
0.6829	0.9797	1.2410	-1.128	0.151	989.72	1.76	1.44	1.39
0.7868	1.0127	1.3732	-0.979	0.165	932.08	2.15	1.77	1.75
0.8925	1.0455	1.3853	-0.657	0.057	641.73	2.59	2.14	2.18
Butyl Amine + DMSO								
0.0942	0.7422	0.4387	-0.510	-0.024	174.36	0.78	0.85	0.76
0.1896	0.7728	0.5147	-0.960	-0.052	242.39	0.61	0.82	0.74
0.2862	0.8050	0.6441	-1.316	-0.028	476.63	0.90	0.94	0.84
0.3841	0.8396	0.8489	-1.623	0.070	841.07	1.36	1.17	1.05
0.4834	0.8762	1.0931	-1.826	0.206	1138.80	1.75	1.43	1.32
0.5839	0.9143	1.2867	-1.866	0.290	1196.30	1.89	1.60	1.50
0.6858	0.9541	1.4169	-1.760	0.309	1073.30	1.92	1.69	1.62
0.7891	0.9945	1.4255	-1.423	0.205	710.87	1.66	1.58	1.52
0.8939	1.0359	1.4277	-0.886	0.093	334.24	1.39	1.44	1.40

Table 3
Redlich-Kister coefficients and standard deviations (σ) for the binary mixtures at 298.15 K, 308.15 K And 318.15 K

Binary mixture	Excess property	Temp. (/K)	a_0	a_1	a_2	a_3	a_4	σ
DMSO + Tert-But. Alcohol.	V^E x10^6/ (m^3.mol^{-1})	298.15	1.183	-0.074	-0.722			0.002
		308.15	0.442	0.121	-0.087	-0.126	-0.124	0.002
		318.15	0.378	-0.100	-0.147	-	-	0.001
	$\Delta\eta$/ (mPa S)	298.15	-4.664	2.294	-	-	-	0.023
		308.15	-1.689	0.711	-0.094	-0.588	-0.502	0.002
		318.15	-0.998	0.220	0.272	-0.182	-	0.001
	G^{*E} /(J.mol^{-1})	298.15	-3553.20	981.45	1660.60	-1224.24	-2480.93	9.21
		308.15	-1707.49	454.38	311.26	-1252.91	-710.67	3.22
		318.15	-1639.09	485.49	-1006.67	-	-	7.39
DMSO + But. Acet.	V^E x10^6/ (m^3.mol^{-1})	298.15	-0.889	0.518	0.257	-	-	0.002
		308.15	-1.351	0.541	-0.436	0.116	-	0.003
		318.15	-1.778	-0.024	-	-	-	0.002
	$\Delta\eta$/ (mPa.S)	298.15	-1.958	-0.373	-	-	-	0.006
		308.15	-0.933	-0.305	-0.177	-	-	0.001
		318.15	-0.615	-0.001	-	-	-	0.007
	G^{*E} /(J.mol^{-1})	298.15	-2688.68	1090.97	370.72	419.07	-	5.51
		308.15	-702.389	35.529	-217.51	218.25	-	3.37
		318.15	-28.83	46.12	675.66			3.57
DMSO + 2-Butanone	V^E x10^6/ (m^3.mol^{-1})	298.15	-3.402	-0.052	-0.205	-	-	0.006
		308.15	0.599	0.931	-0.324	0.215	-	0.005
		318.15	-4.445	-1.210	-0.390	-	-	0.006
	$\Delta\eta$/ (mPa.S)	298.15	-0.177	1.396	-	-	-	0.010
		308.15	0.599	0.931	0.214	-	-	0.005

Contd.

		318.15	0.011	1.886	0.262	-	-	0.004
	G^{*E} /(J.mol^{-1})	298.15	2668.48	2379.35	-2772.74	-999.62		11.44
		308.15	4545.82	-180.14	-242.60	-563.24	-2344.28	16.42
		318.15	3125.33	3726.60	114.70	1235.00	-	6.95
DMSO + n-But.Amine	V^E x10^6/ (m^3.mol^{-1})	298.15	-4.787	-0.437	-0.191			0.003
		308.15	0.858	1.293	-0.563	-0.362	-	0.011
		318.15	-7.327	-2.062	-0.404	-	-	0.012
	$\Delta\eta$ / (mPa.S)	298.15	0.510	1.266	-1.046	0.391	1.166	0.005
		308.15	1.121	1.783	-1.050	-1.39	-	0.014
		318.15	0.890	2.385	-1.662	-3.650	1.228	0.007
	G^{*E} /(J.mol^{-1})	298.15	3205.28	866.70	-2967.24	2496.09	976.64	16.87
		308.15	3808.74	2767.12	-518.58	999.67	-	16.24
		318.15	4644.68	3325.08	-2269.01	6206.62	-2316.12	17.05

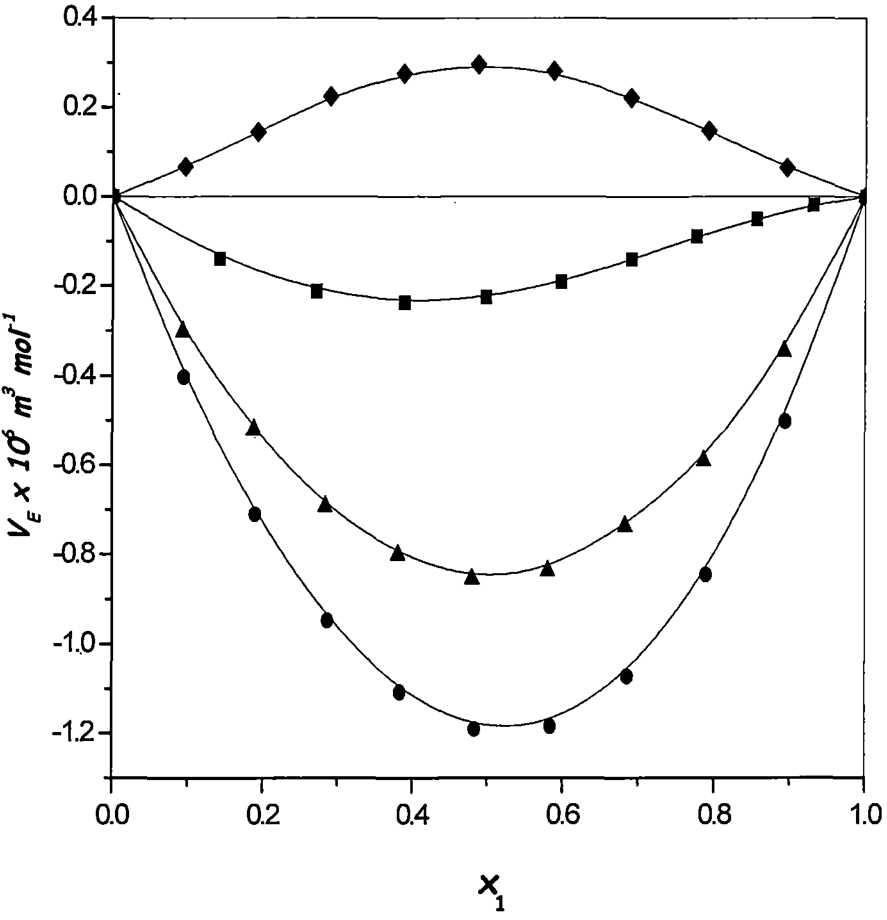

Figure1.

Excess molar volumes (V^E) for binary mixtures of DMSO(x_1) with t-butyl alcohol (♦) n-butyl acetate (■),2-Butanone (▲)and n-butylamine(●);at 298.15K

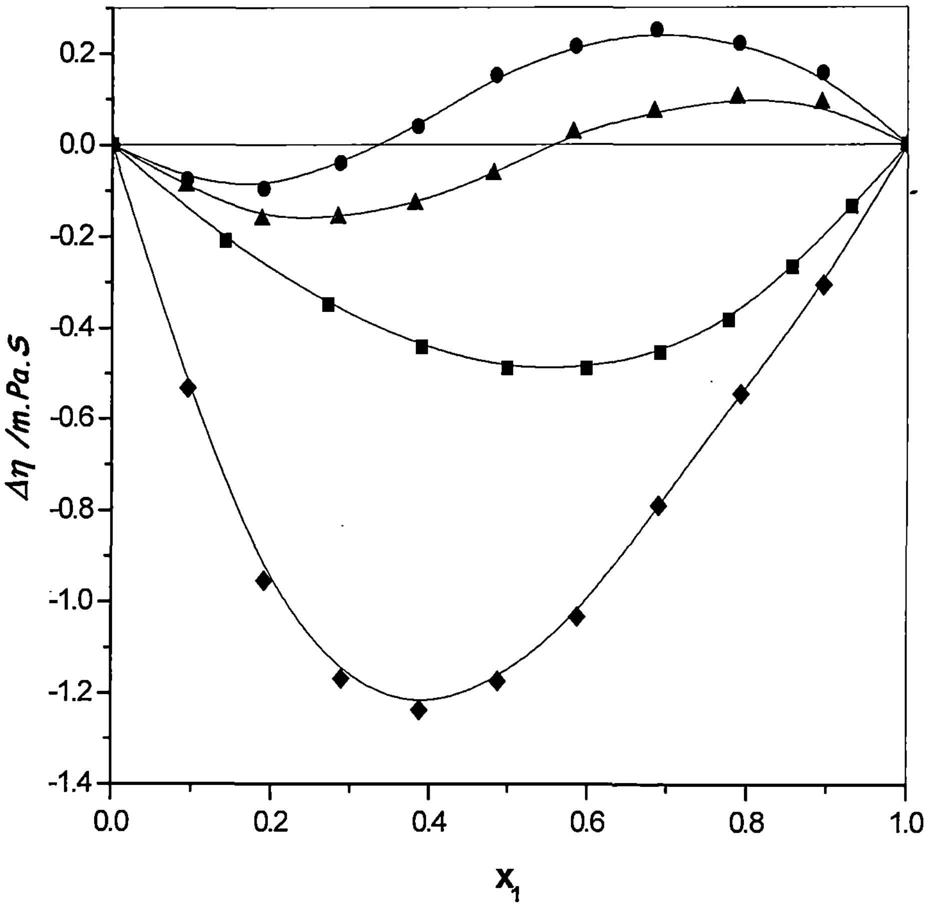

Figure2.

Viscosity deviations ($\Delta\eta$) for binary mixtures of DMSO(x_1) with t-butyl alcohol (◆) n-butyl acetate (■),2-Butanone (▲)and n-butylamine(●);at 298.15K

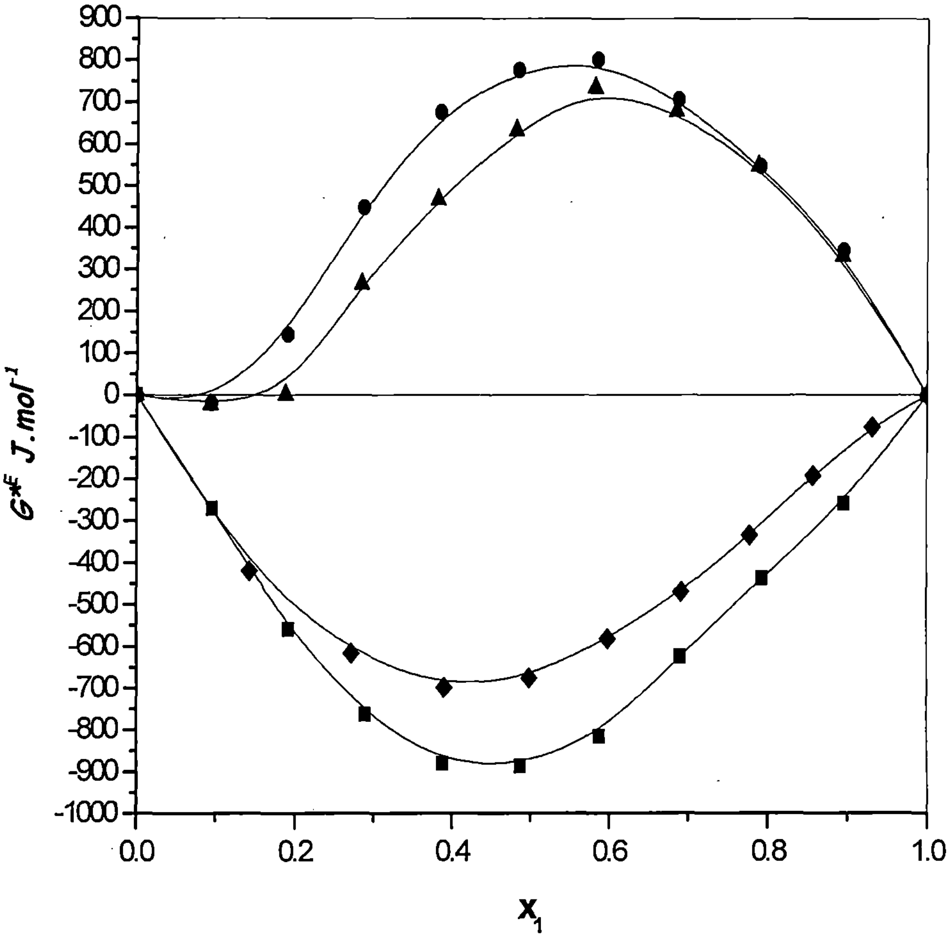

Figure3.

Excess Gibbs free energies for activation of viscous flow (G^{*E}) for binary mixtures of DMSO(x_1) with t-butyl alcohol (♦) n-butyl acetate (■),2-Butanone (▲)and n-butylamine(●);at 298.15K

Chapter XII

Concluding Remarks

The aim of the present work was to study the physicochemical properties and to collect new experimental data on properties such as densities, viscosities, conductivities and speeds of sound for various binary liquid systems and salt solutions over the entire range of compositions and at different temperatures. Furthermore, the study involved the evaluation of the apparent molar properties, excess functions, interaction parameters from the experimental data and interpretation of the intermolecular interactions and tesing various existing models of speed of sound. The study was undertaken covering a wide range of solvents and solutes of varying physical and chemical properties. The various solvents and solutes used in the investigation had been chosen mainly on the basis of their industrial applications.

Tetrahydrofuran, and its mixtures are the very important solvents widely used in various industries. This is a good industrial solvent and figures prominently in the high-energy battery technologies and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium. The alkoxyethanols (2-ethoxyethanol and 2-Methoxyethanol) occupies an important place in many industrial processes such as pharmaceutical and cosmetics industry. Alcohols have varied applications in chemical and cosmetic industries. These are useful in enology and as an alternative energy source. Dimethyl sulfoxide (DMSO) has a wide range of applicability as a solvent in chemical and biological processes. Some alkali metal halides and acetate salts show numerous interesting properties that are now being actively investigated in many laboratories.

A study of densities, viscosities, and ultrasonic speeds for the binary systems of acetonitrile with tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane at various temperatures over the entire composition range lead to the conclusion that, strong specific interaction is present between acetonitrile and ethers molecules. Dipole-induced dipole interactions are present between the unlike molecules along with the interstitial accommodation of non associated acetonitrile molecules in to the clusters of ether molecules.

The study of excess thermodynamic and transport properties for binary mixtures formed by 2-Ethoxy ethanol with eight monoalcohols suggest that with the increasing chain length, the alkanols tends to dilute the unlike interaction and finally for the higher alkanols this unlike interaction becomes unfavorable. The theoretical values of the sound speed were calculated by using the free length theory, collision factor theory, the Nomoto Equation, the Vandeal Vangael ideal mixing relation, the impedance dependence relation and compared with the experimentally measured sound speed. The results showed that, the Nomoto equation and the Collision factor theory predicts the experimental data extremely well, whereas the Fee length theory gives the maximum deviation for the experimental set of binary mixtures.

The measurement of viscosities and densities of binary liquid mixtures of Tetrahydrofuran with normal hydrocarbons (n-pentane, n-hexane, n-heptane) demonstrates that, the forces between the unlike pairs of molecules are far less than that between like pair of molecules. The effect of temperature increase is to disrupt the homo and hetero association of component molecules in the mixtures.

The examination of the ion-solvent and ion-ion interactions of Resorcinol in 2-Methoxyethanol and Tetrahydrofuran reveals that weak solute-solvent (Resorcinol-ME/THF) interactions are present here, and such interactions increases with rise of temperature whereas the solute-solute interaction in the above case is very strong but diminishes with rise of temperature due to the breaking of non covalent bonding between the solute molecules.

The comparative study of electrical conductance of some alkali chlorides in Methanol - Carbon tetrachloride and - 1,4-dioxane systems gives a clear distinction between the nature of ionic association and mobility of ions in these two systems. It is found that, for these electrolytes having the common anion, as the size of the cation increases, the solvation decreases. All the salts are highly associated in both the solvent mixtures. Also the combination of a solvent of higher permittivity with the one having low viscosity of has comparatively higher mobility resulting in higher conductivity values. The values of Walden product for the studied electrolytes pass through a maximum at a particular mole fraction and then decrease continuously for all the lower mole fractions.

Density, viscosity and compressibility data have been determined for amino acids in aqueous TBAB solutions and the results have been used to estimate the volume and compressibility of transfer, number of hydrated water molecules and the viscosity B-coefficient values. With the increase in concentration of aqueous TBAB in solution, the partial molar quantities also increase. The contribution of the $\left(NH_3^+, COO^-\right)$ group to $V_{2,m}^0$ of the amino acids is larger compared to that of the $\left(CH_2\right)$ group and increases with the increase of TBAB concentration in the solution. The number of water molecules hydrated to amino acids increases with the increase in hydrophobic content of the amino acids indicating the predominance of hydrophobic interactions between the amino acid and TBAB with increasing number Carbon atoms in the former. It s concluded that, for Glycine and L-alanine, with increasing concentration of co-solute TBAB, more positive $\Delta_{tr}V_{2,m}^0$ and $\Delta_{tr}K_{2,m}^0$ values result indicating an enhancement in the ion-ion interaction. The increased number of hydrophobic groups in these amino acids leads to stronger interaction between the hydrophobic groups of amino acids with hydrophobic groups of TBAB thereby leading to negative volumes of transfer.

We have investigated the molecular interactions of four acetate salts i.e. ammonium acetate, potassium acetate, sodium acetate and lithium acetate in different mass % of water methanol binary solvent mixtures at different temperatures. The study indicates the presence of strong solute-solvent interactions which weakens with rise in temperature, suggesting more electrostrictive solvation at higher temperature. For lithium acetate and sodium acetate in methanol solutions 'caging or packing effect' seems to be present whereas, ammonium acetate and potassium acetate behaves just like common salts in methanol solutions. Lithium acetate and sodium acetate are structure makers in methanol water mixture whereas ammonium acetate and potassium acetate are structure breakers in this mixed solvent system.

A study conducted on the excess thermodynamic and transport properties of binary mixtures of DMSO with butyl acetate, tert-butyl alcohol, n-butyl amine and 2-butanone indicates the presence of Specific interaction between DMSO and n- butyl amine, DMSO + butyl acetate, DMSO + 2-butanone solvent system but in DMSO + t-butyl alcohol solvent system dispersion forces are prevailing.

Concluding Remarks

Most of the present day knowledge on non-aqueous solutions have come from studies on various thermodynamic properties, e.g., density, transport properties, e.g., viscosity, conductance as well as acoustic properties, e.g., ultrasonic speed.

However, it is necessary to remember that molecular interactions are very complex in nature. There are strong forces existing in the molecule and it is not really possible to separate them all. Nevertheless, if careful judgement is used, valid conclusions can be drawn in many cases relating to degree of structure and order of the system.

Extensive studies of the different physico-chemical, biological or pharmaceutical activity between different components of a given mixture will be of sufficient help in understanding the nature of the different interactions prevailing in systems.

APPENDIX

List of Publications

[1] Studies on Thermodynamic and Transport Properties of Binary Mixtures of Acetonitrile with Some Cyclic Ethers at Different Temperatures by Volumetric, Viscometric, and Interferometric Techniques. ***Journal of Chemical Engineering & Data***, **2006**, *51*, 2225-2232.

[2] Volumetric, viscometric and acoustic studies of binary mixtures of 2-ethoxy ethanol with 1-alkanols at 298.15 K. ***Physics and Chemistry of Liquids***, **2007**, *44(6)*, 663-685.

[3] Excess Molar Volume, Excess Energy and Viscosity Deviation of Binary Mixtures of Tetrahydrofuran with Some Hydrocarbons at Various Temperatures. ***Journal of the Indian Chemical Society***, **2005**, *82 (7)*, 625-631.

[4] Physico-Chemical Studies on the Solute-Solvent Interactions and Ultrasonic Speed of Resorcinol in 2-Methoxyethanol and Tetrahydrofuran at Different Temperatures. ***Journal of Teaching and Research in Chemistry***, **2005**, *11(2)*, 7-17.

[5] Electrical Conductance of Alkali Chlorides in Mixed Solvents: Methanol + Carbon Tetrachloride and Methanol + 1,4-Dioxane at 298.15 K. ***Journal of the Indian Chemical Society***, **2006**, *83(12)*, 1223-1229.

[6] Thermodynamic and Transport Properties of Some Monobasic Acetate Salts in Aqueous Binary Mixtures of Methanol at Different Temperatures. ***Journal of Teaching and Research in Chemistry***, **2005**, *12(2)*, 24-43.

[7] Thermodynamic and transport properties of binary mixtures of dimethyl sulfoxide with t-butyl alcohol, butyl acetate, 2-butanone and butyl amine at different temperatures. ***Russian Journal of Physical Chemistry***, 2006, *80*, **163-171**.

Seminar/Symposium/Convention attended

[1] 42nd Annual Convention of Chemists 2005, Santiniketan, February 9-13, 2006 organized by Indian Chemical Society and hosted by the Department of Chemistry, Visva-Bharati, India.

Reprints of the Published Papers

J. Chem. Eng. Data **2006,** *51,* 2225−2232 **2225**

Studies on Thermodynamic and Transport Properties of Binary Mixtures of Acetonitrile with Some Cyclic Ethers at Different Temperatures by Volumetric, Viscometric, and Interferometric Techniques

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Densities and viscosities of the binary mixtures of acetronitrile with tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane were measured over the entire range of composition at (298.15, 308.15, and 318.15) K. Ultrasonic speeds of these binary mixtures have also been measured at 298.15 K. From the experimental data, values of excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and deviations in isentropic compressibility (ΔK_s) have been calculated. These results were fitted to Redlich−Kister polynomial equation. The density and viscosity data were analyzed by some semiempirical viscosity models, and the results have been discussed in terms of molecular interactions and structural effects. The excess properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures. To explore the nature of the interactions, various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) have also been derived from the density and ultrasonic speed data.

Introduction

The mixing of different solvents gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute−solute, solute−solvent, and solvent−solvent species.[1]

This work is a part of our program to provide data for the characterization of the molecular interactions between solvents in binary systems.[2,3] Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole−dipole forces predominate,[4,5] and tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are cyclic ethers differing in the number and position of oxygen atom and methylene group.[6,7] Tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are versatile solvents used in the separation of saturated and unsaturated hydrocarbons, in pharmaceutical synthesis, and serve as solvents for many polymers. Acetonitrile has important technological applications, namely, in battery industry and plating techniques.[8,9]

In the present paper, we report densities, viscosities, and ultrasonic speeds for the binary systems of acetonitrile + tetrahydrofuran, acetronitrile +1,3-dioxolane, and acetronitrile +1,4-dioxane at the temperatures of (298.15, 308.15, and 318.15) K and atmospheric pressure over the entire composition range. The experimental data are used to calculate excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), and deviations in isentropic compressibility (ΔK_s) of the mixtures. Various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) and their deviations have also been derived from the density and ultrasonic speed data. These results are useful for the interpretation of the nature of interactions that occur between acetonitrile and the cyclic ethers. The work also provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

Experimental Section

Materials. Acetonitrile (Merck, India) was distilled from P_2O_5 and then from CaH_2 in an all-glass distillation apparatus.[10] The middle fraction was collected. 1,4-Dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminum hydride ($LiAlH_4$) as described earlier.[2] 1,3-Dioxolane (LR) was purified by standard methods. It was refluxed with PbO_2 and then fractionally distilled after addition of xylene.[12] Tetrahydrofuran (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over $LiAlH_4$ as described earlier.[11] The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with available literature as listed in Table 1.

Apparatus and Procedure. The densities were measured with an Ostwald−Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm, calibrated at (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at ± 0.01 K of the desired temperature, removed from the bath, properly dried, and weighed in an electronic balance. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account.

The mixtures were prepared by mixing known volume of pure liquids in air-tight stoppered bottles. The reproducibility in mole fraction was within ± 0.0002. The mass measurements, accurate to ± 0.01 mg, were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty of density is $\pm 3 \times 10^{-4}$ $g\cdot cm^{-3}$, and that of temperature is ± 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, which was calibrated at 298.15 K with triple-distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was with-

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Table 1. Comparison of Density ρ, Viscosity η, and Sound Speeds u with Literature Data at the Experimental Temperatures

	T	$\rho \times 10^{-3}$/(kg·m^{-3})		η/(mPa·s)		u/(m·s^{-1})	
pure solvent	K	expt	lit.	expt	lit.	expt	lit.
acetonitrile	298.15	0.7768	0.77686^{10}	0.3443	0.3446^{10}	1713.2	
	308.15	0.7654	0.76564^{10}	0.3124	0.3125^{10}		
	318.15	0.7547	0.75498^{10}	0.2891	0.2893^{10}		
tetrahydrofuran	298.15	0.8808	0.8807^{33}	0.4631	0.4630^{33}	1292.2	1294^{34}
	308.15	0.8715	0.8712^{33}	0.4276	0.4277^{33}		
	318.15	0.8608	0.8614^{33}	0.3903	0.3902^{33}		
1,4-dioxane	298.15	1.0287	1.0282^{34}	1.1779	1.178^{34}	1344.4	1358^{34}
	308.15	1.0168	1.0168^{34}	0.9985	0.999^{34}		
	318.15	1.0047	1.00526^{37}	0.8909	0.901^{38}		
1,3 dioxolane	298.15	1.0577	1.05862^{35}	0.5878	0.5886^{35}	1338.2	1338.8^{36}
	308.15	1.0463	1.04620^{37}	0.5128			
	318.15	1.0344	1.03364^{37}	0.4580			

Table 2. Values of Density ρ, Viscosity η, Excess Molar Volume V^E, Viscosity Deviation $\Delta\eta$, and Grunberg−Nissan, Tamura−Kurata, and Hind Interaction Parameters d_{12}, T_{12}, and H_{12} for Binary Mixtures

	$\rho \times 10^{-3}$	η	$V^E \times 10^6$	$\Delta\eta$					$\rho \times 10^{-3}$	η	$V^E \times 10^6$	$\Delta\eta$			
x_1	kg·m^{-3}	mPa·s	m^3·mol^{-1}	mPa·s	d_{12}	T_{12}	H_{12}	x_1	kg·m^{-3}	mPa·s	m^3·mol^{-1}	mPa·s	d_{12}	T_{12}	H_{12}
Acetonitrile + Tetrahydrofuran															
298.15 K															
0	0.8808	0.4631	0	0	0	0	0	0.7249	0.8162	0.3701	−0.062	−0.007	−0.047	0.384	0.387
0.1633	0.8703	0.4419	−0.104	−0.002	0.011	0.393	0.397	0.8039	0.8058	0.3611	−0.037	−0.007	−0.067	0.382	0.383
0.3052	0.8595	0.4236	−0.142	−0.003	0.006	0.392	0.396	0.8754	0.7959	0.3539	−0.020	−0.005	−0.087	0.380	0.380
0.4295	0.8486	0.4075	−0.145	−0.005	−0.002	0.390	0.394	0.9405	0.7862	0.3481	−0.007	−0.003	−0.119	0.376	0.375
0.5394	0.8376	0.3932	−0.124	−0.006	−0.015	0.389	0.392	1	0.7768	0.3443	0	0	0	0	0
0.6372	0.8268	0.3808	−0.093	−0.007	−0.029	0.387	0.389								
308.15 K															
0	0.8715	0.4276	0	0	0	0	0	0.7249	0.8057	0.3321	−0.082	−0.012	−0.126	0.338	0.339
0.1633	0.8604	0.4066	−0.070	−0.002	0.006	0.357	0.361	0.8039	0.7953	0.3242	−0.066	−0.011	−0.155	0.336	0.336
0.3052	0.8492	0.3875	−0.099	−0.005	−0.013	0.353	0.358	0.8754	0.7852	0.3184	−0.049	−0.008	−0.184	0.333	0.332
0.4295	0.8380	0.3701	−0.110	−0.008	−0.039	0.349	0.354	0.9405	0.7752	0.3145	−0.028	−0.005	−0.214	0.331	0.328
0.5394	0.8270	0.3550	−0.106	−0.012	−0.067	0.345	0.349	1	0.7654	0.3124	0	0	0	0	0
0.6372	0.8162	0.3425	−0.096	−0.012	−0.095	0.342	0.345								
318.15 K															
0	0.8608	0.3903	0	0	0	0	0	0.7249	0.7963	0.3001	−0.196	−0.017	−0.349	0.298	0.298
0.1633	0.8510	0.3683	−0.201	−0.005	−0.106	0.313	0.319	0.8039	0.7855	0.2938	−0.141	−0.015	−0.443	0.294	0.292
0.3052	0.8405	0.3497	−0.290	−0.010	−0.135	0.311	0.317	0.8754	0.7750	0.2901	−0.094	−0.012	−0.581	0.291	0.287
0.4295	0.8296	0.3340	−0.311	−0.013	−0.169	0.309	0.313	0.9405	0.7647	0.2879	−0.045	−0.007	−0.960	0.284	0.276
0.5394	0.8184	0.3202	−0.288	−0.016	−0.218	0.305	0.308	1	0.7547	0.2890	0	0	0	0	0
0.6372	0.8073	0.3089	−0.245	−0.017	−0.277	0.301	0.303								
Acetonitrile + 1,3-Dioxolane															
298.15 K															
0	1.0577	0.5878	0	0	0	0	0	0.7302	0.8721	0.3591	−0.197	−0.051	−0.519	0.330	0.337
0.1670	1.0227	0.5233	−0.124	−0.024	−0.193	0.355	0.380	0.8081	0.8465	0.3444	−0.160	−0.047	−0.660	0.314	0.315
0.3109	0.9899	0.4737	−0.233	−0.038	−0.231	0.355	0.376	0.8783	0.8221	0.3380	−0.111	−0.036	−0.782	0.301	0.298
0.4361	0.9585	0.4360	−0.277	−0.046	−0.266	0.355	0.373	0.9420	0.7989	0.3366	−0.062	−0.022	−0.982	0.277	0.266
0.5461	0.9282	0.4046	−0.268	−0.0502	−0.328	0.350	0.364	1	0.7768	0.3443	0	0	0	0	0
0.6435	0.8994	0.3783	−0.239	−0.053	−0.421	0.340	0.351								
308.15 K															
0	1.0463	0.5128	0	0	0	0	0	0.7302	0.8619	0.3251	−0.297	−0.041	−0.477	0.302	0.307
0.1670	1.0116	0.4618	−0.160	−0.018	−0.158	0.330	0.349	0.8081	0.8361	0.3134	−0.248	−0.038	−0.593	0.290	0.292
0.3109	0.9792	0.4235	−0.295	−0.027	−0.174	0.333	0.349	0.8783	0.8116	0.3077	−0.190	−0.029	−0.706	0.279	0.277
0.4361	0.9478	0.3913	−0.352	−0.034	−0.221	0.329	0.343	0.9420	0.7882	0.3070	−0.114	−0.017	−0.845	0.264	0.257
0.5461	0.9177	0.3646	−0.357	−0.034	−0.284	0.323	0.334	1	0.7654	0.3124	0	0	0	0	0
0.6435	0.8890	0.3419	−0.334	−0.042	−0.377	0.312	0.321								
318.15 K															
0	1.0344	0.4580	0	0	0	0	0	0.7302	0.8511	0.2910	−0.342	−0.044	−0.597	0.260	0.262
0.1670	1.0003	0.4132	−0.202	−0.017	−0.188	0.297	0.313	0.8081	0.8255	0.2817	−0.290	−0.040	−0.737	0.246	0.245
0.3109	0.9679	0.3791	−0.336	−0.026	−0.215	0.298	0.311	0.8783	0.8009	0.2780	−0.219	−0.032	−0.890	0.231	0.225
0.4361	0.9366	0.3502	−0.390	−0.034	−0.275	0.292	0.304	0.9420	0.7775	0.2797	−0.128	−0.019	−1.093	0.210	0.198
0.5461	0.9065	0.3263	−0.392	−0.039	−0.354	0.284	0.293	1	0.7547	0.2891	0	0	0	0	0
0.6435	0.8780	0.3065	−0.369	−0.043	−0.460	0.274	0.280								
Acetonitrile + 1,4-Dioxane															
298.15 K															
0	1.0287	1.1780	0	0	0	0	0	0.7630	0.8645	0.4099	−0.237	−0.132	−0.648	0.396	0.353
0.1926	0.9976	0.9468	−0.100	−0.071	0.119	0.534	0.414	0.8336	0.8412	0.3679	−0.191	−0.115	−0.998	0.346	0.322
0.3492	0.9686	0.7720	−0.193	−0.115	0.031	0.509	0.403	0.8957	0.8185	0.3482	−0.115	−0.083	−1.253	0.316	0.310
0.4791	0.9410	0.6349	−0.258	−0.144	−0.115	0.473	0.383	0.9508	0.7972	0.3389	−0.057	−0.046	−1.632	0.265	0.280
0.5886	0.9146	0.5315	−0.289	−0.156	−0.297	0.440	0.365	1	0.7768	0.3443	0	0	0	0	0
0.6822	0.8891	0.4573	−0.275	−0.152	−0.494	0.411	0.352								
308.15 K															
0	1.0168	0.9985	0	0	0	0	0	0.7630	0.8430	0.4079	−0.301	−0.067	−0.048	0.424	0.469
0.1926	0.9812	0.8244	−0.194	−0.042	0.207	0.432	0.520	0.8336	0.8212	0.3775	−0.229	−0.049	−0.029	0.438	0.478
0.3492	0.9484	0.6862	−0.288	−0.073	0.135	0.415	0.495	0.8957	0.8014	0.3531	−0.168	−0.031	0.014	0.453	0.490
0.4791	0.9187	0.5802	−0.342	−0.090	0.055	0.405	0.475	0.9508	0.7828	0.3340	−0.090	−0.012	0.207	0.486	0.525
0.5886	0.8914	0.5030	−0.357	−0.092	−0.007	0.405	0.466	1	0.7654	0.3124	0	0	0	0	0
0.6822	0.8661	0.4477	−0.331	−0.083	−0.044	0.412	0.464								
318.15 K															
0	1.0047	0.8909	0	0		0	0	0.7630	0.8430	0.3542	−0.364	−0.078	−0.352	0.341	0.375
0.1926	0.9755	0.7189	−0.254	−0.056	0.015	0.322	0.409	0.8336	0.8193	0.3354	−0.276	−0.054	−0.279	0.366	0.395
0.3492	0.9468	0.5994	−0.364	−0.081	−0.014	0.337	0.411	0.8957	0.7968	0.3194	−0.188	−0.033	−0.190	0.389	0.416
0.4791	0.9194	0.5014	−0.430	−0.101	−0.143	0.324	0.387	0.9508	0.7752	0.3076	−0.093	−0.011	0.142	0.438	0.471
0.5886	0.8930	0.4305	−0.450	−0.106	−0.268	0.318	0.370	1	0.7547	0.2891	0	0		0	0
0.6822	0.8675	0.3854	−0.421	−0.095	−0.324	0.328	0.371								

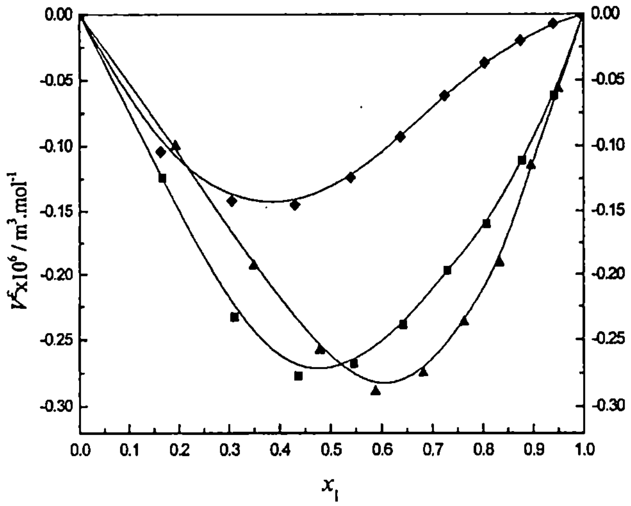

Figure 1. Excess molar volumes (V^E) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

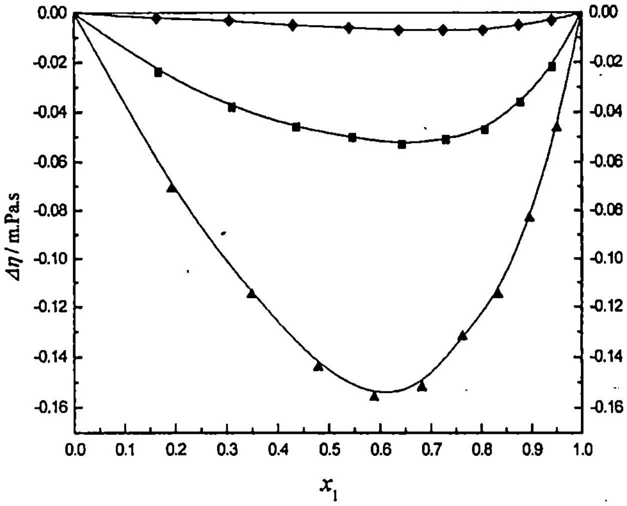

Figure 2. Viscosity deviations ($\Delta\eta$) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

Table 3. Values of Ultrasonic Speeds *u*, Isentropic Compressibility K_s, Deviations in Isentropic Compressibility ΔK_s, Deviations in Intermolecular Free Length (ΔL_f), and Deviations in Specific Acoustic Impedance (ΔZ) for Binary Mixtures at 298.15 K

x_1	u / m·s^{-1}	$K_s \times 10^{12}$ / Pa^{-1}	$\Delta K_s \times 10^{12}$ / Pa^{-1}	ΔL_f / Å	ΔZ / kg·m^2·s^{-1}
		Acetonitrile + Tetrahydrofuran			
0	1292.2	679.94	0	0	0
0.1633	1344.3	635.81	−4.72	−0.0004	0.3119
0.3052	1395.2	597.70	−8.16	−0.0013	2.2063
0.4295	1443.9	565.25	−10.64	−0.0020	4.3811
0.5394	1490.4	537.47	−12.11	−0.0025	6.2800
0.6372	1533.8	514.14	−11.73	−0.0027	7.2298
0.7249	1573.6	494.81	−9.96	−0.0023	6.5553
0.8039	1610.3	478.56	−7.36	−0.0015	4.5467
0.8754	1645.5	464.04	−4.62	−0.0008	2.8429
0.9405	1679.0	451.20	−1.75	−0.0001	0.6821
1	1713.2	438.59	0	0	0
		Acetonitrile + 1,3-Dioxolane			
0	1338.2	527.95	0	0	0
0.1670	1388.9	506.89	−6.14	−0.0006	2.7010
0.3109	1436.2	489.75	−10.42	−0.0013	8.2001
0.4361	1481.5	475.34	−13.65	−0.0024	15.5741
0.5461	1524.4	463.62	−15.54	−0.0039	25.0101
0.6435	1563.5	454.83	−15.63	−0.0048	29.1401
0.7302	1597.8	449.15	−13.56	−0.0045	27.6649
0.8081	1628.8	445.28	−10.47	−0.0037	23.1053
0.8783	1658.2	442.39	−7.09	−0.0026	16.1342
0.9420	1686.4	440.14	−3.65	−0.0015	8.6832
1	1713.2	438.61	0	0	0
		Acetonitrile + 1,4-Dioxane			
0	1344.4	537.84	0	0	0
0.1926	1399.3	511.94	−6.79	−0.0007	3.7000
0.3492	1451.0	490.37	−12.82	−0.0015	9.1001
0.4791	1498.4	473.32	−16.98	−0.0025	15.5741
0.5886	1540.2	460.91	−18.52	−0.0036	25.0101
0.6822	1575.7	453.00	−17.15	−0.0045	29.1401
0.7630	1606.5	448.20	−13.93	−0.0042	27.6649
0.8336	1633.5	445.52	−9.60	−0.0034	23.1053
0.8957	1660.1	443.32	−5.64	−0.0023	16.1342
0.9508	1686.3	441.13	−2.36	−0.0012	8.6832
1	1713.2	438.61	0	0	0

in ± 0.03 % of the reported value. Details of the methods and techniques of density and viscosity measurements have been described earlier.[11,13,14]

Speeds of sound were determined by a multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 5 MHz, calibrated with water, methanol, and benzene at 298.15 K. The details of the methods and techniques have been described earlier.[11,13] The uncertainty of ultrasonic speed measurements is ± 0.2 m s^{-1}.

Results and Discussion

The physical properties of the pure liquids along with their literature values are recorded in Table 1. However no literature data for viscosity of 1,3-dioxolane at (308.15 and 318.15) K and sound speed of acetonitrile at 298.15 K were available to us. Table 2 lists the experimental values of densities (ρ_i) and viscosities (η_i) of the binary mixtures along with the corresponding mole fractions of acetronitrile (x_1), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and interaction parameters (d_{12}, T_{12}, and H_{12}) at all the experimental temperatures. The plots of V^E and $\Delta\eta$ against x_1 at 298.15 K are represented in Figures 1 and 2, respectively. Because of similarity in nature, the plots at the other two temperatures are not presented here.

The excess molar volumes (V^E) were calculated using eq 1:[15,16]

$$V^E = \sum_{i=1}^{j} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \qquad (1)$$

where ρ is the density of the mixture; M_i, x_i, and ρ_i are the molecular weight, mole fraction, and density of *i*th component, respectively. The estimated uncertainty for V^E is from (0.001 to 0.014) cm^3·mol^{-1}.

Δn can be computed using eq 2:[16,17]

$$\Delta\eta = \eta - \sum_{i=1}^{j} (x_i \eta_i) \qquad (2)$$

where η is the absolute viscosity of the mixture; x_i and η_i are the mole fraction and viscosity of *i*th component in the mixture, respectively. The estimated uncertainty for $\Delta\eta$ is from (0.001 to 0.003) mPa·s.

It is seen that, the values of V^E and $\Delta\eta$ (see Table 2) for all the experimental binary mixtures are negative over the entire range of composition and temperature. The negative values of V^E for the three systems are in the following order:

acetronitrile + 1,4-dioxane > acetronitrile + 1,3-dioxolane >
acetronitrile + tetrahydrofuran

Negative values of V^E[18] indicate a specific interaction between the mixing components. The chemical or specific interaction between the mixing molecules results in a volume decrease. The negative values of V^E for the binary mixtures of acetonitrile with the ethers may be attributed to the dipole-induced dipole interactions between the mixing components.[19]

The molar volumes of acetonitrile are (52.84, 53.63, and 54) cm^3·mol^{-1}, and those of tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane are (81.87, 82.74, and 83.77) cm^3·mol^{-1}; (70.03, 70.80,

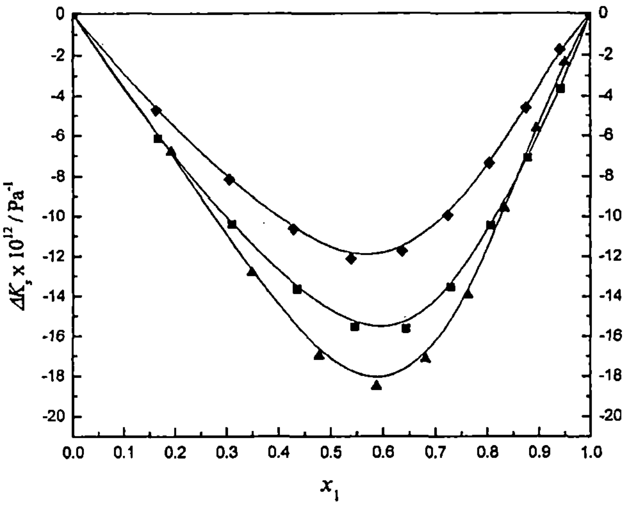

Figure 3. Deviations in isentropic compressibility (ΔK_s) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

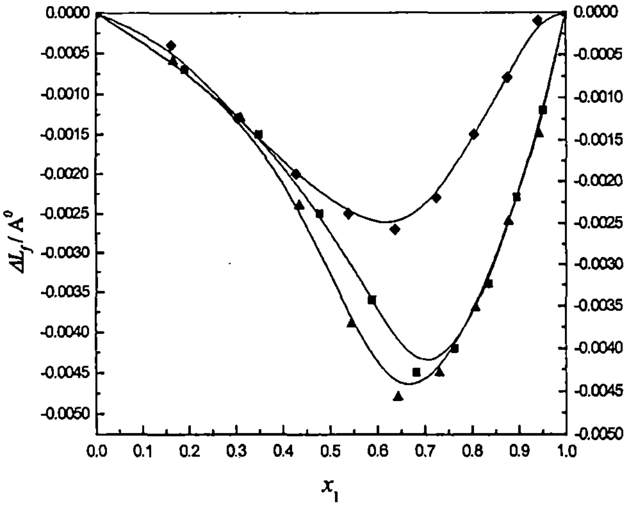

Figure 4. Deviations in intermolecular free length (ΔL_f) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

and 71.62) cm^3·mol^{-1}; and (85.65, 86.66, and 87.70) cm^3·mol^{-1} at (298.15, 308.15, and 318.15) K, respectively. It is clear that the molar volume values of acetonitrile and the other components differ considerably; hence, nonassociated acetonitrile molecules are interstitially accommodated into clusters of ethers yielding a negative contribution to observed V^E values. This implies that the complex-forming interactions are almost absent in the experimental binary systems; therefore, observed $\Delta\eta$ values are also negative.[20]

From close observation of Table 2, it is seen that the negative V^E values are much higher than those of $\Delta\eta$ for all the binary systems under consideration. This clearly supports mere addition of acetonitrile molecules into aggregates of the other components.[20]

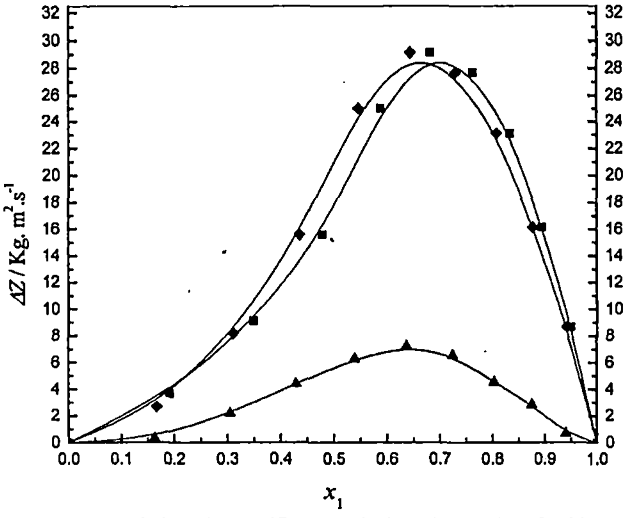

Figure 5. Deviations in specific acoustic impedance (ΔZ) for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

Isentropic compressibility (K_s) values were calculated from experimental densities ρ and speeds of sound u, using

$$K_s = (u^2\rho)^{-1} \tag{3}$$

where K_s gives the isentropic compressibility for the ith component of the mixture. We also derived the deviations in isentropic compressibility (ΔK_s), deviations in intermolecular free length (ΔL_f), and deviations in specific acoustic impedance (ΔZ) for the binary mixtures using

$$\Delta K_s = K_s - \sum_{i=1}^{2} x_i K_{s,i} \tag{4}$$

$$\Delta L_f = L_f - \sum_{i=1}^{2} x_i L_{fi} \tag{5}$$

$$\Delta Z = Z - \sum_{i=1}^{2} x_i Z_i \tag{6}$$

where K_s, L_f, and Z are the isentropic compressibility, intermolecular free length, and specific acoustic impedance of the mixture and x_i, K_{si}, L_{fi}, and Z_i are the mole fraction, isentropic compressibility, intermolecular free length, and specific acoustic impedance of ith component in the mixture, respectively. Experimental values of u, K_s, ΔK_s, ΔL_f, and ΔZ are listed in Table 3, and the plots of ΔK_s, ΔL_f, and ΔZ against x_1 are shown in Figures 3 to 5.

For the investigated binary mixtures, the deviations in isentropic compressibility are negative. The composition dependence of ΔK_s for the investigated binary mixtures is shown in Figure 3; it shows that ΔK_s decrease in the following order:

acetronitrile + 1,4-dioxane > acetonitrile + 1,3-dioxolane > acetonitrile + tetrahydrofuran

These results can be explained in terms of molecular interactions

Table 4. van der Waals Constant b, Molecular Radius r, Geometrical Volume B, Collision Factor S, Molar Speed of Sound R, Available Volume V_a, Intermolecular Free Length L_f, Molar Volume at Absolute Zero V_0, Molar Surface Area Y, and Specific Acoustic Impedance Z of the Pure Components at 298.15 K

pure solvent	$b \times 10^5$ / m^3	r / nm	$B \times 10^5$ / m^3·mol^{-1}	S	$R \times 10^6$ / m^3·mol^{-1}·(m·s^{-1})$^{1/3}$	$V_a \times 10^5$ / m^3	L_f / Å	$V_0 \times 10^5$ / m^3	$Y \times 10^{-4}$ / Å	$Z \times 10^{-3}$ / kg·m^2·s^{-1}
acetonitrile	4.94	0.170	1.24	4.58	632.32	−3.74	0.431	5.658	21.82	1330.81
tetrahydrofuran	7.66	0.197	1.91	3.45	891.72	1.57	0.536	6.612	29.22	1138.17
1,3-dioxolane	6.57	0.187	1.64	3.57	771.81	1.15	0.473	5.858	26.38	1415.41
1,4-dioxane	8.07	0.200	2.02	3.57	945.32	1.37	0.477	7.197	30.26	1382.98

and structural effects. There is a parallel in the qualitative behavior of the ΔK_s and the V^E curves (Figures 1 and 3).

Figures 4 and 5 shows that ΔL_f values are positive for all the binary mixture and that ΔZ behaves in a manner opposite to ΔL_f. Positive and negative deviations in these functions from linear dependence on composition of the mixtures indicate the extent of association or dissociation between the mixing components.[21] The observed values of ΔK_s and ΔL_f can be qualitatively explained by considering the following factors: (i) the mutual disruption of associates present in pure liquids, (ii) dipole-induced interaction between the mixing liquids, and (iii) interstitial accommodation of one component into another. The second two factors contribute negative ΔK_s and ΔL_f values. Observed negative value of ΔK_s and ΔL_f for the mixtures over the entire range of composition implies that the weak dipole-induced interactions are predominant between the unlike molecules along with interstitial accommodation between the components.[22,15] Thus the graded behaviors of these functions support the results obtained earlier.

In an attempt to explore the nature of the interactions occurring between the mixing components, various thermodynamic parameters[21−25] such as intermolecular free length (L_f), specific acoustic impedance (Z), van der Waals constant (b), molecular radius (r), geometrical volume (B), molar surface area (Y), available volume (V_a), molar speed of sound (R), relative association (R_A), and molecular association (M_A) of the binary mixtures have been calculated using

$$L_f = K\sqrt{K_S} \tag{7}$$

$$Z = u\rho \tag{8}$$

$$b = \left(\frac{M}{\rho}\right) - \left(\frac{RT}{\rho^2 u^2}\right)\left\{\left[1 + \left(\frac{Mu^2}{3RT}\right)\right]^{1/2} - 1\right\} \tag{9}$$

$$r = \left(\frac{3b}{16\pi N}\right)^{1/3} \tag{10}$$

$$B = \frac{4}{3}\pi r^3 N \tag{11}$$

$$Y = (36\pi N B^2)^{1/3} \tag{12}$$

$$V_a = V - \left(1 - \frac{u}{u_\infty}\right) \tag{13}$$

$$V_0 = V - V_a \tag{14}$$

$$R = \frac{Mu^{1/3}}{\rho} \tag{15}$$

$$R_A = \left(\frac{\rho_{\text{mix}}}{\rho}\right)\left(\frac{u}{u_{\text{mix}}}\right)^{1/3} \tag{16}$$

$$M_A = \left(\frac{u_{\text{mix}}}{\sum_{i=1}^{2} x_i u_i}\right)^2 - 1 \tag{17}$$

where K is a temperature-dependent constant, V_0 is volume at absolute zero, and u_∞ is taken as 1600 ms^{-1}. These parameters are listed in Table 4 for the pure components and in Table 5 for the binary mixtures. Plots of Z, L_f, R, M_A, and R_A against x_1 are shown in Figures 6 to 10.

The plots of Z and L_f for the mixtures behave in opposite manner, and these figures do not exhibit any sudden variation in their behavior. This implies the absence of any complex formation[24] between the mixing components, which is further supported by the linear variations of R, R_A, and M_A of the binary mixtures against mole fractions of acetonitrile.[24] M_A and R_A values decrease for the mixtures with increasing mole fraction of acetonitrile. This implies strongly dissociative interactions between the unlike molecules in the mixtures.[24,25]

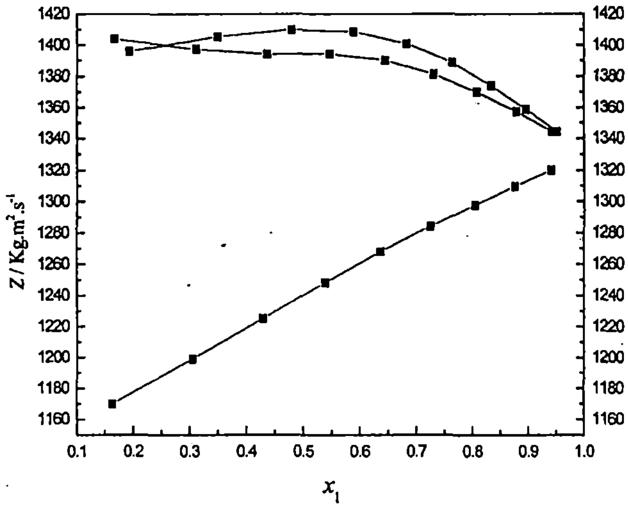

Figure 6. Z values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

Table 5. Intermolecular Free Length L_f, Molar Speed of Sound R, Relative Association R_A, Molecular Association M_A, Available Volume V_a, and Specific Acoustic Impedance Z of Binary Mixtures at 298.15 K

x_1	L_f Å	$R \times 10^6$ m^3·mol^{-1}·(m·s^{-1})$^{1/3}$	R_A	M_A	$V_a \times 10^5$ m^3	$Z \times 10^{-3}$ kg·m^2·s^{-1}
		Acetonitrile + Tetrahydrofuran				
0.1633	0.5186	911.85	1.2147	−0.5911	1.18	1169.94
0.3052	0.5029	842.69	1.1848	−0.634	8.72	1199.17
0.4295	0.4890	791.88	1.1565	−0.6681	6.26	1225.29
0.5394	0.4768	753.03	1.1295	−0.6961	4.19	1248.36
0.6372	0.4664	722.31	1.1043	−0.7193	2.43	1268.15
0.7249	0.4575	697.28	1.0809	−0.7389	9.41	1284.37
0.8039	0.4500	676.55	1.059	−0.7558	−3.58	1297.58
0.8754	0.4431	659.27	1.0385	−0.7703	−1.55	1309.65
0.9405	0.4369	644.61	1.0189	−0.7831	−2.65	1320.03
		Acetonitrile + 1,3-Dioxolane				
0.1670	0.4654	937.98	1.3773	−0.4928	8.64	1403.98
0.3109	0.4587	860.66	1.3224	−0.5567	6.26	1397.31
0.4361	0.4523	804.77	1.2715	−0.6074	4.32	1394.09
0.5461	0.4462	762.5	1.2241	−0.6487	2.66	1394.22
0.6435	0.4412	729.26	1.1801	−0.6831	1.25	1390.11
0.7302	0.4378	702.28	1.1391	−0.7124	7.42	1381.30
0.8081	0.4354	679.94	1.1013	−0.7373	−9.61	1370.15
0.8783	0.4335	661.37	1.0652	−0.7591	−1.93	1357.24
0.9420	0.4319	645.71	1.0317	−0.7779	−2.85	1344.40
		Acetonitrile + 1,4-Dioxane				
0.1926	0.4654	1039.22	1.3739	−0.5033	9.08	1395.94
0.3492	0.4555	917.01	1.3179	−0.5677	6.05	1405.44
0.4791	0.4475	837.8	1.2667	−0.6173	3.84	1409.99
0.5886	0.4416	782.14	1.2199	−0.6569	2.15	1408.67
0.6822	0.4378	740.65	1.1769	−0.6897	8.45	1400.95
0.7630	0.4354	708.61	1.1370	−0.7173	−2.21	1388.82
0.8336	0.4341	683.07	1.1002	−0.7407	−1.12	1374.1
0.8957	0.4331	662.64	1.0648	−0.7611	−2.00	1358.79
0.9508	0.4320	645.97	1.0317	−0.7788	−2.85	1344.32

The mixing functions V^E, $\Delta\eta$, ΔK_s, ΔL_f, and ΔZ were represented mathematically by the following type of Redlich–Kister equation[26] (eq 18) for correlating the experimental data:

$$Y_{ij}^E = x_i x_j \sum_{k=1}^{m} a_k (x_i - x_j)^k \tag{18}$$

where Y_{ij}^E refers to an excess property (V^E, $\Delta\eta$, ΔK_s, ΔL_f, and ΔZ) for each i–j binary pair, and x_i is the mole fraction of ith component, and a_k represents the coefficients. The values of

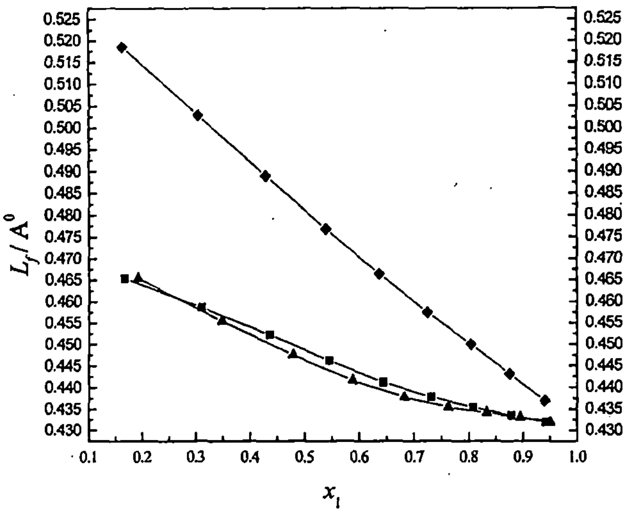

Figure 7. L_f values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

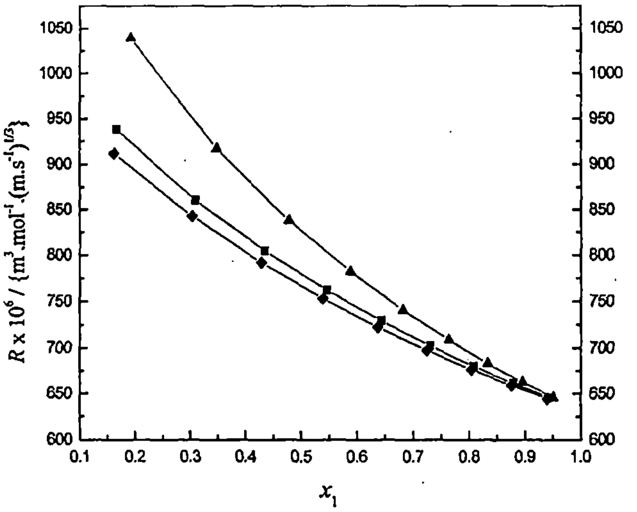

Figure 8. R values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

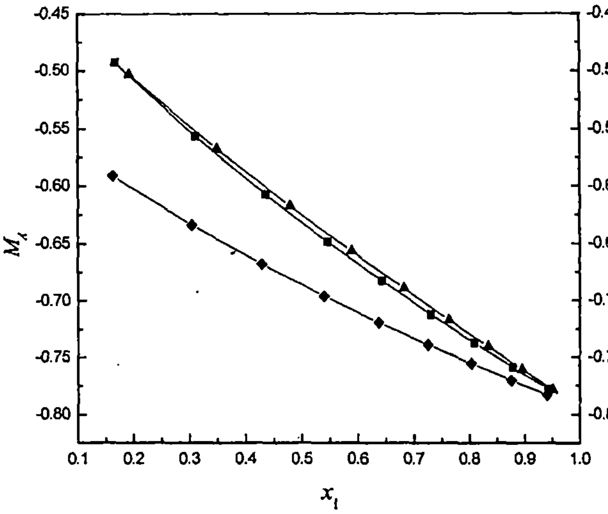

Figure 9. M_A values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

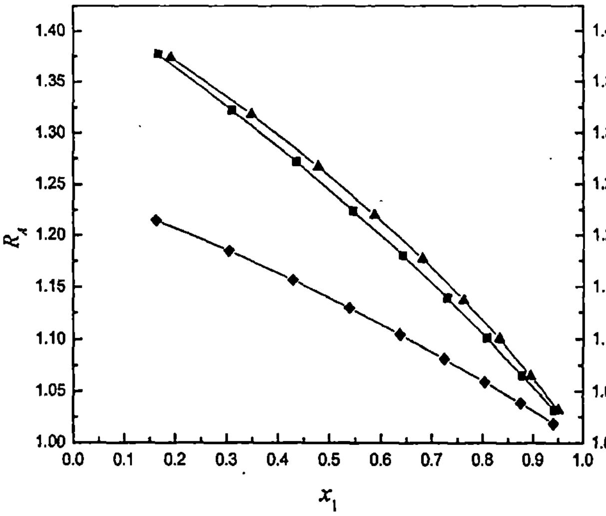

Figure 10. R_A values for binary mixtures of acetonitrile (1) with ◆, tetrahydrofuran; ■, 1,3-dioxolane; and ▲, 1,4-dioxane at 298.15 K.

coefficients (a_k) were determined by a multiple-regression analysis based on the least-squares method and were summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 6. The standard deviation was calculated using

$$\sigma = \left[\sum_{i=1}^{n} \frac{(Y^{E}_{i,\mathrm{exp}} - Y^{E}_{i,\mathrm{cal}})^2}{n-p}\right]^{1/2} \tag{19}$$

where n is the number of experimental points and p is the number of adjustable parameters. The small σ values for excess properties indicate that the fits are good for the present study.

Several semiempirical models have been proposed from time to time to estimate the dynamic viscosity of the binary liquid mixtures in terms of pure-component data[16,17] and to interpret the molecular interactions in these mixtures. Some of them we examined are as follows:

Grunberg and Nissan[27] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp[\sum_{i=1}^{j} (x_i \ln \eta_i) + d_{12}\prod_{i=1}^{j}[x_i] \tag{20}$$

where d_{12} is a constant proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The values of the interchange parameter (d_{12}) have been calculated using eq 20 as a function of the composition of the binary liquid mixtures of acetronitrile with tetrahydrofuran (1,3-dioxolane and 1,4-dioxane) and are listed in Table 2.

Tamura and Kurata[28] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i\phi_i\eta_i + 2T_{12}\prod_{i=1}^{j} [x_i\phi_i]^{1/2} \tag{21}$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of ith pure component in the mixture.

Table 6. Redlich−Kister Coefficients a_k and Standard Deviations σ for the Binary Mixtures

excess property	T/K	a_0	a_1	a_2	a_3	σ
		Acetonitrile + Tetrahydrofuran				
$V^E \times 10^6/(\mathrm{m^3 \cdot mol^{-1}})$	298.15	−0.535	0.439	0.238	−0.157	0.004
	308.15	−0.435	0.081	0.0001	−0.046	0.000
	318.15	−1.198	0.489	0.054	−0.116	0.001
$\Delta\eta/(\mathrm{mPa \cdot s})$	298.15	−0.023	−0.023	−0.014		0.000
	308.15	−0.041	−0.044			0.001
	318.15	−0.060	0.047	−0.023		0.000
$\Delta K_s \times 10^{12}/(\mathrm{Pa^{-1}})$	298.15	−46.92	−20.28	16.04	28.30	0.101
ΔL_f/Å	298.15	−0.0097	−0.0096	0.0979	0.0125	0.000
$\Delta Z/(\mathrm{kg \cdot m^2 \cdot s^{-1}})$	298.15	22.9517	33.3804	−8.6910	−31.4791	0.195
		Acetonitrile + 1,3-Dioxolane				
$V^F \times 10^6/(\mathrm{m^3 \cdot mol^{-1}})$	298.15	−1.104	0.187	0.333	−0.650	0.002
	308.15	−1.43	−0.288			0.014
	318.15	−1.58	−0.014	−0.254	−0.777	0.002
$\Delta\eta/(\mathrm{mPa \cdot s})$	298.15	−0.195	−0.080	−0.108	−0.059	0.001
	308.15	−0.141	−0.090	−0.090		0.002
	318.15	−0.148	−0.105	−0.111	−0.022	0.000
$\Delta K_s \times 10^{12}/(\mathrm{Pa^{-1}})$	298.15	−59.82	−34.96	6.20	66.24	0.063
ΔL_f/Å	298.15	−0.0134	0.0150			0.001
$\Delta Z/(\mathrm{kg \cdot m^2 \cdot s^{-1}})$	298.15	86.9118	106.6348			1.712
		Acetonitrile + 1,4-Dioxane				
$V^E \times 10^6/(\mathrm{m^3 \cdot mol^{-1}})$	298.15	−1.069	−0.714	0.219	0.424	0.005
	308.15	−1.38	−0.368	−0.180		0.006
	318.15	−1.77	−0.377			0.009
$\Delta\eta/(\mathrm{mPa \cdot s})$	298.15	−0.583	−0.279	−0.115		0.003
	308.15	−0.365	−0.112	0.131	0.102	0.001
	318.15	−0.408	−0.168	0.066	0.332	0.001
$\Delta K_s \times 10^{12}/(\mathrm{Pa^{-1}})$	298.15	−70.22	−41.53	31.13	46.67	0.101
ΔL_f/Å	298.15	−0.0306	−0.0213	0.0143	0.0232	0.001
$\Delta Z/(\mathrm{kg \cdot m^2 \cdot s^{-1}})$	298.15	213.9833	113.6827	−36.9828	−77.6469	0.163

Table 7. Parameters of McAllister Model, Heric and Brewer Parameters, and Standard Deviations for Kinematic Viscosities at Various Temperatures

T	McAllister (three-body model)			McAllister (four-body model)				Heric and Brewer parameter			
K	u_{12}	υ_{21}	σ	υ_{1112}	υ_{1122}	υ_{2221}	σ	$a \times 10^2/\mathrm{cm^2 \cdot s^{-1}}$	$b \times 10^2/\mathrm{cm^2 \cdot s^{-1}}$	$c \times 10^2/\mathrm{cm^2 \cdot s^{-1}}$	σ
				Acetonitrile + Tetrahydrofuran							
298.15	0.4472	0.4953	0.004	0.4422	0.4809	0.3976	0.001	−0.1092	−0.0851	−0.1719	0.009
308.15	0.3992	0.4621	0.004	0.3961	0.4358	0.4554	0.001	−0.6990	−0.0797	−0.0048	0.002
318.15	0.3481	0.4175	0.015	0.3499	0.3967	0.1921	0.003	−0.2939	−0.2417	−0.4706	0.025
				Acetonitrile + 1,3-Dioxolane							
298.15	0.3181	0.4772	0.025	0.3339	0.4365	0.0950	0.011	−0.7160	−0.5678	−1.2469	0.063
308.15	0.3028	0.4280	0.021	0.3204	0.4244	0.2383	0.005	−0.4759	−0.2327	−0.7290	0.026
318.15	0.2541	0.3887	0.023	0.2739	0.3861	0.1297	0.006	−0.4963	−0.4096	−0.9001	0.042
				Acetonitrile + 1,4-Dioxane							
298.15	0.3131	0.8765	0.054	0.2817	0.5868	0.0175	0.025	−1.8590	−2.0151	−2.7610	0.187
308.15	0.4955	0.0428	0.031	0.4467	0.2183	0.8251	0.025	−0.5120	−−3.4702	−2.8854	0.154
318.15	0.3815	0.2167	0.046	0.3034	0.0921	0.6748	0.046	−0.7564	−5.1889	−4.3310	0.230

The following viscosity model of Hind et al.[29] may also interpret the molecular interactions:

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \tag{22}$$

where H_{12} is the Hind interaction parameter.

In the present study, the values of interaction parameters T_{12} and H_{12} have been calculated from eqs 21 and 22, respectively, and are listed in Table 2. It is observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other; this is in agreement with the view put forward by Fort and Moore[15] in regard to the nature of parameters T_{12} and H_{12}.

The McAllister multibody interaction model[30] is widely used to correlate the kinematic viscosities ($\upsilon = \eta/\rho$) of the binary mixtures with mole fraction. The three-body model is defined as

$$\ln \upsilon = x_1^3 \ln \upsilon_1 + x_2^3 \ln \upsilon_2 + 3x_1^2 x_2 \ln \upsilon_{12} + 3x_2^3 x_1 \ln \upsilon_{21} - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3x_2^2 x_1 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3 \ln\left[\frac{M_2}{M_1}\right] \tag{23}$$

The four-body model is given by

$$\ln \upsilon = x_1^4 \ln \upsilon_1 + 4x_1^3 x_2 \ln \upsilon_{1112} + 6x_1^2 x_2^2 \ln \upsilon_{1122} + 4x_1 x_2^3 \ln \upsilon_{2221} - \ln \upsilon_{2221} + x_2^4 \ln \upsilon_2 - \ln\left[x_1 + x_2\left(\frac{M_2}{M_1}\right)\right] + 4x_1^3 x_2 \ln\left[\frac{3}{4} + \frac{M_2}{4M_1}\right] + 6x_1^2 x_2^2 \ln\left[\frac{1}{2} + \frac{M_2}{2M_1}\right] + 4x_1 x_2^3 \ln\left[\frac{1}{3} + \frac{3M_2}{4M_1}\right] + x_2^4 \ln\left[\frac{M_2}{M_1}\right] \tag{24}$$

where v, v_1, and v_2 are kinematic viscosities of the mixture, the pure acetonitrile and the corresponding second component, respectively. v_{12}, v_{21}, v_{1112}, v_{1122}, and v_{2221} are model parameters; M_i and x_i are the molecular weight and mole fraction of the *i*th pure component in the mixture.

Table 7 records the parameters calculated using eqs 23 and 24 along with the standard deviations. It is seen that the values of both the parameters are positive and adequate for all of the binary mixtures.

Heric and Brewer[31] have proposed an equation for the kinematic viscosity of the binary liquid mixtures:

$$v = x_1v_1 + x_2v_2 + x_1x_2\{a + b(x_1 - x_2) + c(x_1 - x_2)^2\} \quad (25)$$

where a, b, and c are model parameters and M_i and x_i are the molecular weight and mole fraction of the *i*th pure component in the mixture, respectively.

The percentage standard deviation[24] was calculated using

$$\sigma\,\% = \left[\frac{\sum(100(v_{\text{exptl}} - v_{\text{calcd}})/v_{\text{exptl}})^2}{(n - m)}\right]^{1/2} \quad (26)$$

where n represents the number of experimental points and m is the number of coefficients.

The values of parameters a, b, and c have been calculated using eq 25 and are listed in Table 7 along with the standard deviations. A perusal of Table 7 shows that the values of a and b are negative for all of the binary mixtures.

Literature Cited

(1) Kim, E. S.; Marsh, K. N. Isothermal vapor−liquid equilibria for the ternary ethanol−acetonitrile−chloroform system. *J. Chem. Eng. Data* **1988**, *33*, 288−292.

(2) Roy, M. N.; Sinha, B.; Dakua, V. K. Excess molar volumes and viscosity deviations of binary liquid mixtures of 1,3-dioxolane and 1,4-dioxane with butyl acetate, butyric acid, butyl amine, and 2-butanone at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 590−594.

(3) Roy, M. N.; Sinha, A.; Sinha, B. Excess molar volumes, viscosity deviations and isentropic compressibility of binary mixtures containing 1,3-dioxolane and monoalcohols at 303.15 K. *J. Solution Chem.* **2005**, *34* (11), 1311−1325.

(4) Moumouzias, G.; Panopoulos, D. K.; Ritzoulis, G. Excess properties of the binary liquid system propylene carbonate + acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20−23.

(5) Das, B.; Saha, N. Electrical conductances of some symmetrical tetraalkylammonium salts in methanol, acetonitrile, and methanol (1) + acetonitrile (2) mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 2−5.

(6) Brocos, P; Calvo, E; Pineiro, A; Bravo, R; Amigo, A. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 5. Binary systems {1,3-dioxolane + 1-alkanols}. *J. Chem. Eng. Data* **1999**, *44*, 1341−1347.

(7) Leaist, D. G.; MacEwan, K.; Stefan, A.; Zamari, M. Binary mutual diffusion coefficients of aqueous cyclic ethers at 25° C. Tetrahydrofuran, 1,3-dioxolane, 1,4-dioxane, 1,3-dioxane, tetrahydropyran, and trioxane. *J. Chem. Eng. Data* **2000**, *45*, 815−818.

(8) Janz, G. G.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1973; Vol. 2.

(9) Jasinski, R. *High Energy Batteries*; Plenum Press: New York, 1967.

(10) Saha, N.; Das, B. Apparent molar. volumes of some symmetrical tetraalkylammonium bromides in acetonitrile at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **1997**, *42*, 227−229.

(11) Roy, M. N.; Jha, A.; Dey, R. Study of ion−solvent interactions of some alkali metal chlorides in tetrahydrofuran + water mixture at different temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1327−1329.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Techniques of Chemistry*, Vol. 2, 4th ed.; Wiley-Interscience: New York, 1986.

(13) Roy, M. N.; Hazra, D. K. Densities and viscosities of the binary aqueous mixture of tetrahydrofuran and 1,2 dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* **1994**, *1*, 93−97.

(14) Roy, M. N.; Jha, A.; Choudhury, A. Densities and viscosities and adiabatic compressibilities of some mineral salts in water at different temperatures. *J. Chem. Eng. Data* **2004**, *49*, 291−296.

(15) Fort, R. J.; Moore, W. R. Viscosities of binary liquid mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−1119.

(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: 1987.

(17) Irving, J. B. *Viscosities of Liquid Mixtures*; NEL Reports 630 and 631; National Engineering Laboratory: East Kilbride, Glassgow, 1977.

(18) Treszczanowicz, A. J.; Kiyohara, O.; Benson, G. C. Excess molar volumes for *n*-alkanes binary mixtures of decan-1-ol + *n*-pentane, + *n*-hexane, + *n*-octane, + *n*-decane, and + *n*-hexadecane. *J. Chem. Thermodyn.* **1981**, *13*, 253−260.

(19) Jain, P.; Singh, M, Density, viscosity, and excess properties of binary liquid mixtures of propylene carbonate with polar and nonpolar Solvents. *J. Chem. Eng. Data* **2004**, *49*, 1214−1217.

(20) Nikam, P. S.; Kharat, S. J. Excess molar volumes and deviations in viscosity of binary mixtures of *N,N*-dimethylformamide with aniline and benzonitrile at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 972−976.

(21) Pal, A.; Bhardwaj, R. K. Ultrasonic speeds and volumetric properties of dipropylene glycol monomethyl ether−*n*-alkylamine mixtures at 298.15 K. *Z. Phys. Chem.* **2002**, *216*, 1033−1051.

(22) Ku, H.-C.; Tu, C.-H. Densities and viscosities of binary and ternary mixtures of ethanol, 2-butanone, and 2,2,4-trimethylpentane at T = (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2005**, *50*, 608−615.

(23) Jacobson, B. Ultrasonic velocity of liquids and liquid mixtures. *J. Chem. Phys.* **1952**, *20*, 927−928.

(24) Mehta, S. K.; Chauhan, R. K.; Dewan, R. K. Excess volumes and isentropic compressibilities of pyrrolidin-2-one-alkanol (C_1−C_5) binary mixtures. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 1167−1173.

(25) Shastry, N. V.; Patel, S. R. Densities, viscosities, sound speeds and excess properties of binary mixtures of methyl methacrylate with alkoxyethanols and 1-alchohols at 298.15 and 308.15 K. *Int. J. Thermophys.* **2000**, *21*, 1153−1174.

(26) Redlich, O.; Kister, A. T. Algebric representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(27) Grunberg, L.; Nissan, A. H. Mixture law for viscosity. *Nature* **1949**, *164*, 799−800.

(28) Tamura, M.; Kurata, M. Viscosity of binary mixture of liquids. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 32−37.

(29) Hind, R. K.; McLaughlin, E.; Ubbelohde. A. R. Structure and viscosity of liquid-camphor and pyrene mixtures. *Trans. Faraday. Soc.* **1960**, *56*, 328−334.

(30) McAllister, R. A. The viscosity of liquid mixtures. *AIChE J.* **1960**, *6*, 427.

(31) Heric, E. L.; Brewer, J. G. Viscosity of some binary liquid nonelectrolyte mixtures. *J. Chem. Eng. Data* **1967**, *12*, 574−583.

(32) Nikam, P., S.; Kharat, S. J. Densities and viscosities of binary mixtures of *N,N*-dimethylformamide with benzyl alcohol and acetophenone at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 1291−1295.

(33) Sinha, A.; Roy, M. N. Studies on viscous antagonism, excess molar volume and isoentropic compressibility in aqueous mixed solvent systems at different temperatures. *Phys. Chem. Liq.* **2006**, *44*, 303−314.

(34) Aminabhavi, T. M.; Patil, V. B. Density, viscosity, refractive index, and speed of sound in binary mixtures of ethenylbenzene with *N,N*-dimethylacetamide, tetrahydrofuran, *N,N*-dimethylformamide, 1,4-dioxane, dimethyl sulfoxide, chloroform, bromoform, and 1-chloronaphthalene in the temperature interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 497−503.

(35) Gascon, I.; Mainar, A. M.; Royo, F. M.; Urieta, J. S. Experimental viscosities and viscosity predictions of the ternary mixture (cyclohexane + 1,3-dioxolane + 2-butanol) at 298.15 and 313.15 K. *J. Chem. Eng. Data* **2000**, *45*, 751−755.

(36) Giner, B.; Villares, A.; Gascon, P.; Cea, P.; Lafuente, C. Speeds of sound and isentropic compressibilities of binary mixtures containing cyclic ethers and haloalkanes at 298.15 and 313.15 K. *Int. J. Thermophys.* **2004**, *25* (6), 1735−1746.

(37) Inglese, A.; Groller, J. E.; Wilhelm, E. Excess volumes of mixtures of oxolane, oxane, 1,3-dioxolane, and 1,4-dioxane with *n*-alkanes at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1983**, *28*, 124−127.

(38) Rao, K. P.; Reddy, K. S. Viscosities of trichloroethylene with ketones and 1,4-dioxane at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1988**, *33*, 130−133.

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Volumetric, viscosimetric and acoustic studies of binary mixtures of 2-ethoxyethanol with 1-alkanols at 298.15 K

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Densities, viscosities and sound speeds of eight binary mixtures of 2-ethoxyethanol with methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol are determined over the entire range of mole fractions at 298.15 K. The excess molar volume (V^E), viscosity deviations ($\Delta\eta$) and Gibbs excess free energy of activation for viscous flow (ΔG^{*E}) have been investigated from these experimental density (ρ) and viscosity (η) values. The viscosity data have been correlated by Grunberg and Nissan, Tamura–Kurata and Hind correlation equation. The deviations in isentropic compressibility (ΔK_S) were also calculated using the measured speeds of sound. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding. The sound speeds were predicted by using free length and collision factor theoretical formulations, by Nomotto equation, by Vandeal Vangael ideal mixing relation and the impedance dependence relation. The deviations have been fitted to a Redlich–Kister equation and the results are discussed in terms of molecular interactions and structural effects. The excess properties are found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

Keywords: Densities; Viscosities; Excess molar volume; Viscosity deviation; Excess Gibbs energy of activation of viscous flow; 2-Ethoxyethanol; Monoalcohols; Sound speed; Isentropic compressibility; Excess isentropic compressibility; Hydrogen bonding; Specific interactions

1. Introduction

The volumetric and viscometric properties of mixed solvent systems and their dependence on composition find applications in many important chemical, industrial and biological processes. Such systems find industrial applications such as heat transfer, fluid flow and so forth. The study of quantities such as excess molar volume, deviation in viscosity, excess free energy of activation of viscous flow, excess isentropic compressibility, etc. of binary liquid mixtures are useful in understanding the nature and strength of molecular interactions between the component molecules [1–3].

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The present work deals with the study of excess thermodynamic and transport properties of some non-aqueous binary liquid mixtures. The liquids under investigation have been chosen on the basis of their industrial applications. The alkoxyethanols and alkanols are good industrial solvents which occupy an important place in many industrial processes such as pharmaceutical and cosmetics industry. These applications have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures [4–9].

In this article, we extend our studies to the binary mixtures formed by 2-ethoxyethanol represented as (**1**) with eight monoalcohols, represented as (**2**), including methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol at 298.15 K. The various thermodynamic properties such as excess molar volume (V^E), viscosity deviations ($\Delta\eta$) and Gibbs excess free energy of activation for viscous flow (ΔG^{*E}) obtained from experimental observations have been rationalized. 2-Ethoxyethanol and the monoalcohols have both a proton donor and a proton acceptor group. It is expected that there will be a significant degree of H-bonding leading to self-association in pure state in addition to mutual association in their binaries [10].

Besides this, isentropic compressibilities as well as deviations in isentropic compressibility (ΔK_S) calculated from measured speed of sound (u) of 2-ethoxyethanol and monoalcohol mixtures are presented at 298.15 K. The measurement of ultrasonic speed enables the accurate determination of isentropic compressibility coefficients (K_S) which can be used to provide qualitative information about the physical nature of the aggregates occurring in the liquid phase. To investigate the nature of the interactions, various thermodynamic parameters such as specific acoustic impedance [11] Z, intermolecular free length L_f [12], van der Waal's constant b [13], molecular radius r [12], geometrical volume B, molar surface area Y, available volume V_a [12], molar speed of sound R [14], collision factor S [15] and molecular association M_A [16] has been calculated using the sound speed and density of the mixtures and pure solvents which are sensitive to interaction between solute and solvent. These properties for the mixtures studied are presented, compared and analyzed. A comparative study of the sound speeds calculated using different theoretical formulations and equations with the experimentally measured value is also performed, the results are represented graphically and the standard deviation in each case has been reported.

2. Experiments

2.1. *Source and purity of samples*

2-Ethoxyethanol (Merck, India) was kept several days over anhydrous $CaSO_4$, refluxed for 4 h over CaO. Finally, it was distilled at low pressure. Details have been described elsewhere [17]. Methanol, ethanol, propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol (S.D. Fine Chemicals, Analytical Reagent, Purity >99%) were used. The liquids were stored over molecular sieves. The density, viscosity and the sound speeds of the mixtures were determined immediately after mixing. The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature as listed in table 1.

Table 1. Comparison of density (ρ), viscosity (η) and sound speeds (u) with literature data at 298.15 K.

	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		u (m s^{-1})	
Pure liquid	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
2-Ethoxyethanol	0.9254	0.9253 [44]	1.85061	1.851 [60]	1309.00	1300.40 [51]
Methanol	0.7866	0.78656 [45]	0.5509	0.5422 [45]	1104.2	1103.00 [52]
Ethanol	0.7857	0.7851 [46]	1.0892	1.088 [46]	1142	1145.00 [53]
1-Propanol	0.7993	0.7995 [47]	2.0074	2.004 [49]	1209.4	1206.50 [47]
1-Butanol	0.8062	0.8058 [48]	2.5571	2.5600 [49]	1240.2	1240.00 [54]
1-Pentanol	0.8112	0.8111 [48]	3.5104	3.510 [50]	1277.2	1277.00 [54]
1-Hexanol	0.8151	0.81515 [48]	4.5917	4.590 [50]	1328.3	1328.00 [56]
1-Heptanol	0.82068	0.81870 [59]	5.93678	–	1331.5	1330.00 [54]
1-Octanol	0.8218	0.8216 [48]	7.3646	7.363 [50]	1347.7	1347.40 [55]

2.2. *Method*

Viscosities (η) have been measured at 298.15 K, by means of a suspended Ubbelohde-type viscometer [18] which was calibrated at the experimental temperature. The flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was $\pm 2 \times 10^{-4}$ mPa s. Densities (ρ) were measured at the mentioned temperature with an Ostwald–Sprengel-type pycnometer having bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at ±0.01 K of the desired temperature. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The density values were reproducible to $\pm 3 \times 10^{-5}$ g cm^{-3}. The measurements were done in a thermostatic bath controlled to ±0.01 K. The details of the methods and techniques for determination of these parameters have been described in earlier papers [4–6,19,20]. Speeds of sound were determined by a multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 5 MHz. The meter was calibrated with water, methanol, and benzene at 298.15 K. The precisions of the speed of sound measurements are ±0.2 m s^{-1}. The details of the methods and techniques have been described previously [19,20].

The mixtures were prepared by mixing known volumes of pure liquids in airtight stoppered bottles. The reproducibility in mole fraction was within ±0.0002 units. The weights were taken on a Mettler electronic analytical balance (AG 285, made in Switzerland) accurate to 0.02 mg.

3. Results and discussion

The experimentally measured densities (ρ) and viscosities (η) of the pure liquids at 298.15 K along with the reference values are recorded in table 1.

The values of experimental density (ρ) and viscosity (η), the excess properties, (V^E, $\Delta\eta$ and ΔG^{*E}) along with the interaction parameters (d_{12}, T_{12} and H_{12}) of the studied mixtures are recorded in table 2 and the corresponding graphs for V^E and $\Delta\eta$ against the mole fractions of 2-ethoxyethanol (x_1) are marked as figures 1 and 2, respectively.

Table 2. Values of density (ρ), viscosity (η), excess molar volume (V^E), viscosity deviation ($\Delta\eta$), excess Gibbs energy of activation for viscous flow (ΔG^{*E}), Grunberg–Nissan, Tamura Kurata and Hind interaction parameters (d_{12}, T_{12}, H_{12}) for binary mixtures of 2-Ethoxy ethanol+Methanol, Ethanol, Propanol, Butanol, Pentanol, Hexanol, Heptanol and Octanol at 298.15 K.

x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	$V^E \times 10^6$ (m^3 mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})	d_{12}	T_{12}	H_{12}
2-Ethoxyethanol + methanol								
0	0.7866	0.5509	0	0	0			
0.0380	0.7997	0.6216	−0.058	0.021	227.32	1.66	1.22	1.49
0.0816	0.8131	0.7062	−0.118	0.049	454.06	1.81	1.26	1.53
0.1322	0.8267	0.7916	−0.176	0.069	625.16	1.65	1.25	1.50
0.1916	0.8406	0.8844	−0.231	0.085	758.35	1.48	1.25	1.47
0.2623	0.8550	0.9885	−0.298	0.097	852.25	1.32	1.24	1.45
0.3478	0.8694	1.1144	−0.349	0.111	914.00	1.21	1.26	1.45
0.4534	0.8839	1.2555	−0.379	0.115	898.30	1.07	1.27	1.43
0.5871	0.8981	1.4225	−0.350	0.109	787.40	0.95	1.29	1.42
0.7619	0.9117	1.6248	−0.211	0.084	531.16	0.85	1.33	1.43
1	0.9254	1.8506	0	0	0			
2-Ethoxyethanol + ethanol								
0	0.7857	1.0892	0	0	0			
0.0538	0.7985	1.1465	−0.058	0.016	72.83	0.45	1.55	1.63
0.1133	0.8115	1.2067	−0.104	0.031	137.4	0.42	1.55	1.63
0.1798	0.8247	1.2721	−0.135	0.046	195.57	0.41	1.56	1.63
0.2542	0.8382	1.3413	−0.165	0.059	241.19	0.39	1.56	1.62
0.3383	0.8521	1.4165	−0.186	0.070	274.98	0.37	1.57	1.63
0.4341	0.8662	1.4966	−0.194	0.077	290.16	0.36	1.58	1.63
0.5440	0.8806	1.5810	−0.185	0.078	280.19	0.34	1.58	1.63
0.6716	0.8953	1.6690	−0.159	0.068	236.54	0.32	1.59	1.63
0.8215	0.9103	1.7613	−0.099	0.047	150.98	0.31	1.61	1.63
1	0.9254	1.8506	0	0	0			
2-Ethoxyethanol + propanol								
0	0.7993	2.0074	0	0	0			
0.0690	0.8108	1.9415	−0.037	−0.047	−64.37	−0.43	1.57	1.50
0.1429	0.8224	1.8906	−0.066	−0.094	−111.04	−0.39	1.60	1.54
0.2223	0.8344	1.8521	−0.100	−0.121	−142.92	−0.36	1.63	1.58
0.3078	0.8466	1.8256	−0.114	−0.134	−158.58	−0.33	1.65	1.62
0.4001	0.8591	1.8108	−0.126	−0.135	−158.41	−0.30	1.68	1.65
0.5001	0.8717	1.8056	−0.113	−0.123	−144.40	−0.26	1.71	1.68
0.6088	0.8844	1.8105	−0.075	−0.102	−116.02	−0.23	1.73	1.72
0.7273	0.8976	1.8226	−0.049	−0.071	−78.28	−0.19	1.76	1.75
0.8572	0.9113	1.8386	−0.022	−0.034	−35.95	−0.15	1.80	1.79
1	0.9254	1.8506	0	0	0			
2-Ethoxyethanol + butanol								
0	0.8062	2.5571	0	0	0			
0.0837	0.8166	2.4339	0.011	−0.064	−54.64	−0.29	1.81	1.79
0.1706	0.8272	2.3117	0.030	−0.125	−112.00	−0.32	1.78	1.76
0.2606	0.8381	2.2060	0.054	−0.167	−154.92	−0.33	1.79	1.77
0.3541	0.8493	2.1129	0.076	−0.194	−186.25	−0.33	1.79	1.78
0.4513	0.8609	2.0349	0.088	−0.203	−201.16	−0.33	1.81	1.79
0.5523	0.8729	1.9838	0.087	−0.183	−183.33	−0.30	1.84	1.83
0.6574	0.8854	1.9489	0.074	−0.144	−143.54	−0.26	1.89	1.88
0.7669	0.8984	1.9249	0.048	−0.090	−87.34	−0.20	1.96	1.95
0.8810	0.9117	1.9016	0.019	−0.033	−27.22	−0.11	2.05	2.05
1	0.9254	1.8506	0	0	0			

(*Continued*)

Table 2. Continued.

x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	$V^E \times 10^6$ (m^3 mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})	d_{12}	T_{12}	H_{12}
2-Ethoxyethanol + pentanol								
0	0.8112	3.5104	0	0	0			
0.0980	0.8210	3.1674	0.045	−0.180	−54.64	−0.45	1.57	1.66
0.1965	0.8309	2.8637	0.103	−0.321	−112.00	−0.50	1.59	1.67
0.2954	0.8412	2.6191	0.148	−0.401	−154.92	−0.50	1.65	1.72
0.3947	0.8518	2.4305	0.187	−0.425	−186.25	−0.48	1.74	1.79
0.4945	0.8628	2.2827	0.212	−0.407	−201.16	−0.46	1.82	1.87
0.5947	0.8742	2.1783	0.222	−0.345	−183.33	−0.40	1.93	1.96
0.6953	0.8861	2.0992	0.203	−0.257	−143.54	−0.33	2.04	2.07
0.7964	0.8986	2.0275	0.161	−0.161	−87.34	−0.24	2.16	2.18
0.8980	0.9117	1.9541	0.093	−0.066	−27.22	−0.12	2.29	2.32
1	0.9254	1.8506	0	0	0			
2-Ethoxyethanol + hexanol								
0	0.8151	4.5917	0	0	0			
0.1119	0.8244	3.9460	0.080	−0.339	−114.65	−0.50	2.10	1.52
0.2209	0.8340	3.4770	0.147	−0.509	−175.78	−0.45	2.08	1.74
0.3270	0.8440	3.0803	0.191	−0.615	−232.06	−0.46	2.04	1.82
0.4305	0.8543	2.7757	0.221	−0.636	−254.08	−0.46	2.01	1.92
0.5314	0.8649	2.5612	0.240	−0.574	−225.06	−0.40	1.97	2.07
0.6297	0.8758	2.3806	0.254	−0.485	−185.27	−0.36	1.93	2.18
0.7257	0.8873	2.2425	0.237	−0.360	−119.92	−0.29	1.89	2.32
0.8193	0.8992	2.1213	0.22	−0.225	−51.23	−0.19	1.85	2.46
0.9108	0.9119	2.0053	0.126	−0.090	7.83	−0.40	1.81	2.67
1	0.9254	1.8506	0	0	0			
2-Ethoxyethanol + heptanol								
0	0.8207	5.9368	0	0	0			
0.1253	0.8277	4.9665	0.125	−0.435	−55.68	−0.30	1.16	1.80
0.2438	0.8367	4.2073	0.238	−0.712	−110.60	−0.33	1.36	1.90
0.3559	0.8464	3.6548	0.320	−0.811	−126.78	−0.31	1.64	2.08
0.4623	0.8561	3.2302	0.377	−0.818	−120.28	−0.28	1.88	2.25
0.5632	0.8661	2.9021	0.414	−0.733	−92.86	−0.24	2.10	2.40
0.6592	0.8771	2.6169	0.410	−0.435	−75.95	−0.23	1.16	2.50
0.7505	0.8882	2.3828	0.372	−0.487	−51.16	−0.20	2.38	2.59
0.8376	0.8995	2.1996	0.296	−0.315	−7.38	−0.12	2.55	2.74
0.9207	0.9118	2.0410	0.168	−0.134	32.75	0.07	2.79	2.98
1	0.9254	1.8506	0	0	0			
2-Ethoxyethanol + octanol								
0	0.8218	7.3646	0	0	0			
0.1384	0.8302	6.0618	0.169	−0.540	24.99	−0.03	1.33	2.34
0.2654	0.8389	5.0613	0.289	−0.840	36.69	−0.04	1.60	2.45
0.3825	0.8481	4.2677	0.366	−0.988	29.89	−0.07	1.79	2.52
0.4907	0.8576	3.6490	0.409	−1.010	19.57	−0.10	1.98	2.59
0.5910	0.8675	3.1718	0.428	−0.934	16.36	−0.11	2.16	2.68
0.6843	0.8778	2.8054	0.416	−0.786	26.02	−0.09	2.36	2.79
0.7713	0.8887	2.5039	0.370	−0.608	30.75	−0.08	2.52	2.88
0.8525	0.9002	2.2662	0.291	−0.398	45.28	−0.01	2.71	3.03
0.9286	0.9123	2.0779	0.177	−0.166	69.42	0.26	3.04	3.35
1	0.9254	1.8506	0	0	0			

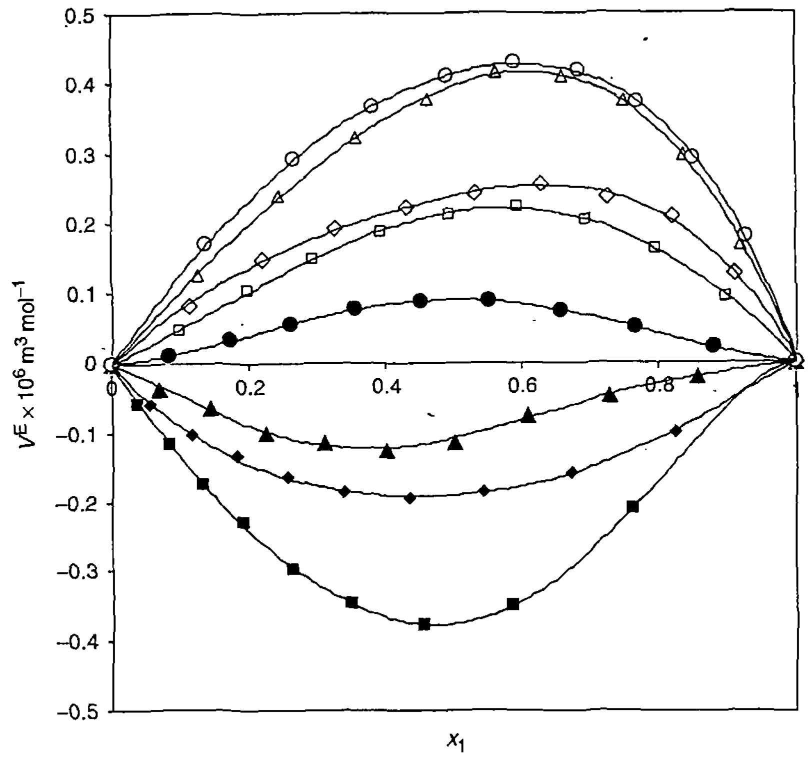

Figure 1. Excess molar volumes (V^E) for binary mixtures of 2-ethoxyethanol with methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

3.1. *Excess molar volume*

The excess molar volumes (V^E) were calculated using the molar masses (M_i) and densities of the pure liquids and the mixtures using the following equation [6,23].

$$V^E = \sum_{i=1}^{j} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \tag{1}$$

where, M_i, ρ_i, x_i are the molar mass, density, mole fraction of the *i*th component and ρ is the density of the mixture, respectively.

From figure 1, we observe that, for the binary mixtures studied here, the V^E values gradually change from highly negative to less negative and finally turn positive with the increase of chain length along the alcohol homologous series. It has highest negative value for methanol and ultimately turns positive for the higher alkanols. V^E values are negative for methanol, ethanol, 1-propanol and then they turn gradually more and more positive from 1-butanol to 1-octanol. Positive V^E values for higher alkanols and negative V^E values for lower alkanols were also reported

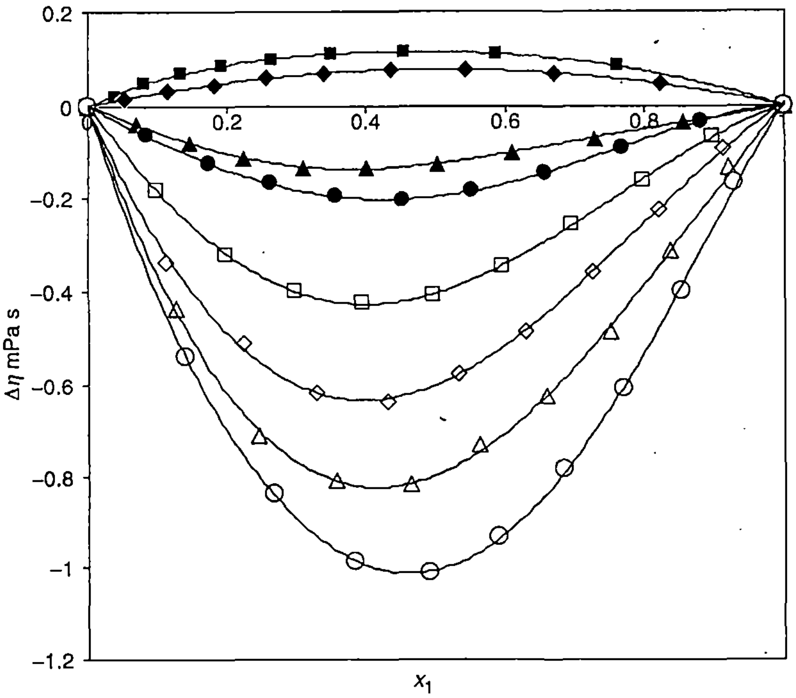

Figure 2. Viscosity deviations (Δη) for binary mixtures of 2-ethoxyethanol with methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

by some other workers [21–23]. The observed trend in terms of negative values of V^E in 1-alkanol + 2-ethoxyethanol mixture is:

Methanol > Ethanol > 1-Propanol > 1-Butanol > 1-Pentanol
> 1-Hexanol > 1-Heptanol > 1-Octanol

Such a behavior is the result of the contribution from several contraction and expansion processes which proceed simultaneously when 2-ethoxyethanol-alkan-1-ol molecules are formed. The following effects can be considered: (a) disruption of liquid order on mixing and unfavorable interactions between unlike molecules producing a positive contribution of V^E; (b) contraction due to free volume difference of unlike molecules and (c) possible association through hydrogen bond formation between alkan-1-ol and 2-ethoxyethanol producing a negative contribution to V^E.

The alkanols are known to be extremely self associated through H-bonding and in 2-ethoxyethanol also self association through H-bonding is present [24]. Mixing of 1-alkanols to 2-ethoxyethanol can be expected to bring changes in the H-bonding equilibria and electrostatic interactions with different resultant contributions in the volume of mixing. The negative values obtained for lower 1-alkanols suggest that the interaction between the unlike molecules exceed the structure breaking effect between the like molecules. These interactions are relatively strong between

2-ethoxyethanol and methanol molecules thereby showing the highest negative V^E value for their binary mixture. Increasing the chain length of the alkanols tends to dilute this unlike interaction and finally for the higher alkanols this unlike interaction becomes unfavorable producing a positive contribution of V^E.

3.2. *Viscosity deviations*

The deviation in viscosities from linearity ($\Delta\eta$) can be computed using the relationship,

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i\eta_i) \tag{2}$$

The values of $\Delta\eta$ (figure 2) are positive for methanol and ethanol and decrease regularly as the size of the alkan-1-ol is increased. The positive $\Delta\eta$ values indicate the predominance of H-bonding interactions between the unlike molecules over the dissociation effects of the mixing components [25,26]. This results in a liquid structure where the flow is rather difficult than would be expected on the basis of the viscosities of the pure components.

It is known that the strength of the molecular hydrogen bonding is not the only factor influencing the viscosity deviations in liquid mixtures [27,28]. The molecular size and shape of the components and average degree of association of the mixture are equally important factors. The negative values of $\Delta\eta$ for higher alkanols indicate that the average degree of cross-association of mixtures gradually decreases as the chain length of alkan-1-ol is increased [27,29]. Thus, larger the chain length of 1-alkanol, the greater is the decrease in the average degree of association, as a result more negative deviations in viscosity *versus* mole fraction curve are observed. These conclusions are supported by the conclusions drawn from V^E values.

3.3. *Excess Gibbs energies for activation of viscous flow (ΔG^{*E})*

It has been reported that ΔG^{*E} parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules [30,38].

On the basis of the theories of absolute reaction rates [40], the excess Gibbs energy of activation for viscous flow (ΔG^{*E}) was calculated from the equation [41],

$$\Delta G^{*E} = RT\left[\ln \eta V - \sum_{i=1}^{j}(x_i \ln \eta_i V_i)\right] \tag{3}$$

According to Reed and Taylor and Meyer *et al.*, positive ΔG^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces [38,39].

The magnitude of the positive value of ΔG^{*E} is an excellent indicator of the strength of specific interactions. From the ΔG^{*E} values recorded in table 2, it is seen that these values are negative or positive keeping similarity with the $\Delta\eta$ values and thereby supports our conclusion drawn from V^E and $\Delta\eta$ considerations.

3.4. *Correlating equations*

Apart from expressing η as a polynomial fit, several semi-empirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure component data [31,39]. We have examined equations proposed by Grunberg–Nissan, Tamura–Kurata and Hind *et al.*

The single parameter Grunberg–Nissan equation [31] reads as:

$$\eta = \exp\left[\sum_{i=1}^{j}(x_i \ln \eta_i) + d_{12}\prod_{i=1}^{j} x_i\right] \tag{4}$$

where d_{12} is a parameter proportional to the interchange energy and has been regarded as an approximate measure for the non-ideal behaviors of binary mixtures.

Tamura–Kurata [32] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i\phi_i\eta_i + 2T_{12}\prod_{i=1}^{j}[x_i\phi_i]^{1/2} \tag{5}$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of *i*th pure component in the mixture.

Molecular interactions may also be interpreted by the following viscosity model of Hind *et al.* [33]

$$\eta = \sum x_i^2\eta_i + 2H_{12}\prod_{i=1}^{j} x_i \tag{6}$$

where H_{12} is the interaction parameter.

The interaction parameters have their merits in ascertaining the strength of molecular interactions in binary mixtures. Among the three parameters determined here, the Grunberg–Nissan parameter provides the best measure to ascertain the strength of interaction. At any given composition, the variation of d_{12} with strength of interaction is similar to that of $\Delta\eta$, being negative for systems in which dispersion forces are dominant, becoming less negative and then increasingly positive as the strength of interaction increases [25,34,35,36].

According to Fort and Moore [25], the values of T_{12} and H_{12} are not very different except where the values of the components differ considerably. Furthermore, T_{12} and H_{12} show some variation with composition although this is only large for systems where there is a strong specific interaction between the components. There is a tendency of T_{12} and H_{12} at a certain composition to increase with the strength of interaction of the components, but this is not well-defined and T_{12} and H_{12} cannot generally be regarded as a measure of the strength of interaction [37].

A perusal of table 2 shows that the variations and signs of d_{12} are similar to those of $\Delta\eta$ and thereby supports our conclusion. It is also seen that, T_{12} and H_{12} values are positive for all binary mixtures and are almost identical and do not change appreciably with the change of composition of binary mixtures.

3.5. *Isentropic compressibility*

Table 5 contains the sound velocity (u), isentropic compressibility (K_S) and deviations in isentropic compressibility (ΔK_S) data for the binary mixtures and calculated at 298.15 K.

Isentropic compressibility K_S and deviations in isentropic compressibility ΔK_S were calculated from experimental densities (ρ) and speed of sound (u) using the following equations

$$K_S = (u^2\rho)^{-1} \tag{7}$$

$$\Delta K_S = K_S - \sum_{i=1}^{j}(x_i K_{S,i}) \tag{8}$$

where K_S gives the isentropic compressibility for the ith component of the mixture.

The ultrasonic speeds are given in table 3, together with the isentropic compressibility K_S and deviations in isentropic compressibility ΔK_S for 2-ethoxyethanol + 1-alkanol mixtures at 298.15 K. Experimental values for ΔK_S are plotted against mole fraction of 2-ethoxyethanol in figure 3.

We have attempted to explain the physico-chemical behavior of the mixtures in order to know the nature of molecular interactions between the components by various acoustical parameters calculated using the speed of sound and density data. Various parameters such as specific acoustic impedance Z, intermolecular free length L_f, van der Waal's constant b, molecular radius r, geometrical volume B, molar surface area Y, available volume V_a, molar speed of sound R, relative association R_A, collision factor S and molecular association M_A has been calculated using the following relations:

$$Z = u\rho \tag{9}$$

$$b = \left(\frac{M}{\rho}\right) - \left(\frac{RT}{\rho^2 u^2}\right)\left\{\left[1 + \left(\frac{Mu^2}{3RT}\right)\right]^{1/2} - 1\right\} \tag{10}$$

$$r = \left(\frac{3b}{16\pi N}\right)^{1/3} \tag{11}$$

$$L_f = \frac{K}{u\rho^{1/2}} \tag{12}$$

$$B = \frac{4}{3}\pi r^3 N \tag{13}$$

$$Y = (36\pi N B^2)^{1/3} \tag{14}$$

$$V_a = V - V_0 \tag{15}$$

$$R = \frac{Mu^{1/3}}{\rho} \tag{16}$$

$$S = \frac{uV}{u_\infty B} \tag{17}$$

Table 3. Values of ultrasonic speeds (u), isentropic compressibility (K_S), deviations in isentropic compressibility (ΔK_S) for binary mixtures of 2-ethoxyethanol + methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and octanol at 298.15 K.

x_1	u (m s^{-1})	$K_S \times 10^{12}$ (Pa^{-1})	$\Delta K_S \times 10^{12}$ (Pa^{-1})	x_1	u (m s^{-1})	$K_S \times 10^{12}$ (Pa^{-1})	$\Delta K_S \times 10^{12}$ (Pa^{-1})
2-Ethoxyethanol + methanol				2-Ethoxyethanol + ethanol			
0	1104.2	1042.63	0	0	1142.0	975.89	0
0.0380	1130.9	981.86	−45.11	0.0538	1174.6	907.67	−49.66
0.0816	1151.5	931.90	−77.10	0.1133	1199.2	856.88	−79.88
0.1322	1167.5	886.36	−101.80	0.1798	1220.6	813.83	−100.01
0.1916	1188.6	842.09	−121.60	0.2542	1238.6	777.63	−110.49
0.2623	1205.1	803.78	−130.80	0.3383	1253.7	746.68	−112.40
0.3478	1220.5	771.62	−127.72	0.4341	1265.2	721.24	−104.80
0.4534	1233.1	744.02	−111.81	0.5440	1275.7	697.77	−90.30
0.5871	1246.9	716.60	−84.14	0.6716	1288.2	673.06	−70.96
0.7619	1266.2	684.13	−44.62	0.8215	1301.4	648.68	−43.60
1	1309.0	630.65	0	1	1309.0	630.65	0
2-Ethoxyethanol + propanol				2-Ethoxyethanol + butanol			
0	1209.4	806.49	0	0	1240.2	806.49	0
0.0690	1224.6	790.01	−17.36	0.0837	1245.0	790.01	−1.76
0.1429	1238.7	770.83	−30.71	0.1706	1252.3	770.83	−5.67
0.2223	1249.6	749.95	−37.90	0.2606	1261.4	749.95	−10.71
0.3078	1259.5	728.42	−41.50	0.3541	1271.4	728.42	−15.80
0.4001	1268.0	708.33	−41.43	0.4513	1280.6	708.33	−18.81
0.5001	1276.6	689.16	−39.01	0.5523	1289.3	689.16	−20.21
0.6088	1285.0	672.37	−33.70	0.6574	1296.1	672.37	−18.52
0.7273	1293.6	657.40	−26.11	0.7669	1301.2	657.40	−14.24
0.8572	1302.5	644.23	−15.88	0.8810	1304.8	644.23	−7.35
1	1309.0	630.65	0	1	1309.0	630.65	0
2-Ethoxyethanol + pentanol				2-Ethoxyethanol + hexanol			
0	1277.2	755.71	0	0	1328.3	695.34	0
0.0980	1281.8	741.34	−2.11	0.1119	1324.3	691.70	3.60
0.1965	1286.5	727.16	−3.98	0.2209	1320.9	687.23	6.18
0.2954	1291.0	713.23	−5.54	0.3270	1318.0	682.02	7.83
0.3947	1295.1	699.89	−6.46	0.4305	1315.7	676.16	8.67
0.4945	1298.8	687.10	−6.77	0.5314	1314.2	669.44	8.47
0.5947	1301.6	675.20	−6.14	0.6297	1313.1	662.24	7.64
0.6953	1303.8	663.86	−4.89	0.7257	1312.2	654.55	6.15
0.7964	1305.6	652.85	−3.26	0.8193	1311.5	646.56	4.22
0.8980	1307.1	641.99	−1.42	0.9108	1310.7	638.33	1.91
1	1309.0	630.65	0	1	1309.0	630.65	0
2-Ethoxyethanol + heptanol				2-Ethoxyethanol + octanol			
0	1331.5	687.28	0	0	1347.7	669.96	0
0.1253	1326.4	686.72	6.54	0.1384	1339.3	671.52	7.01
0.2438	1322.3	683.52	10.04	0.2654	1332.8	671.02	11.49
0.3559	1319.2	678.85	11.73	0.3825	1327.3	669.33	14.40
0.4623	1316.5	673.94	12.84	0.4907	1322.5	666.64	15.97
0.5632	1314.2	668.51	13.12	0.5910	1318.7	662.89	16.16
0.6592	1312.5	661.87	11.92	0.6843	1315.6	658.17	15.11
0.7505	1311.1	655.00	10.22	0.7713	1313.3	652.39	12.75
0.8376	1309.9	647.96	8.11	0.8525	1311.5	645.84	9.39
0.9207	1309.7	639.34	4.20	0.9286	1310.2	638.54	5.08
1	1309.0	630.65	0	1	1309.0	630.65	0

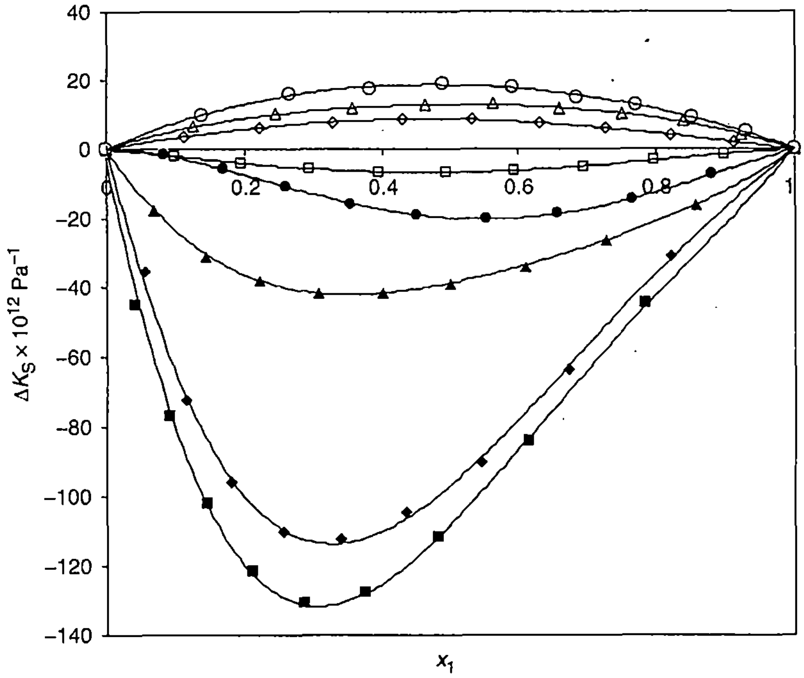

Figure 3. Deviations (ΔK_S) for binary mixtures of 2-ethoxyethanol with methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

$$M_A = \left[\left(\frac{u_{\text{mix}}}{\Sigma x_i u_i}\right)^2 - 1\right] \tag{18}$$

$$R_A = \left(\frac{L_f}{L_f'}\right)^3 \tag{19}$$

where K is a temperature-dependent constant, V_0 is volume at absolute zero, u_∞ is taken as 1600 m s^{-1}. These parameters are listed in table 4 for the pure components and in table 5 for the binary mixtures. Plots of L_f, Z, V_a and R against the mole fraction of 2-ethoxyethanol (x_1) are shown in figures 4–7, respectively.

It is observed that, the value of specific acoustic impedance Z, increases with increasing x_1 for all the mixtures, while the L_f behaves in an opposite manner. The graphs do not show any sudden variation in their behavior, thereby implying the absence of complex formation [16].

The R_A values increase with increasing x_1 for all the mixtures which signifies that the 1–2 interactions in these mixtures are not strongly dissociative. The decrease in L_f and V_a with increase in x_1 indicates significant interaction between the mixing molecules [28].

From figure 3, it is evident that the ΔK_S values are negative for lower monoalcohols but the magnitude of negative values diminishes and the positive values increases with

Table 4. van der Waal's constant b, molecular radius r, geometrical volume B, collision factor S, molar speed of sound R, available volume V_a, intermolecular free length L_f, molar volume at absolute zero V_0, molar surface area Y and specific acoustic impedance Z of the pure components at 298.15 K.

Component	$b \times 10^5$ (m^3)	r (nm)	$B \times 10^5$ (m^{3}mol^{-1})	S	$R \times 10^6$ [m^{3}mol^{-1}(m s^{-1})$^{1/3}$]	$V_a \times 10^5$ (m^3)	L_f (Å)	$V_0 \times 10^5$ (m^3)	$Y \times 10^{-4}$ (Å)	$Z \times 10^{-3}$ (Kg m^2 s^{-1})
2-Ethoxyethanol	9.17	0.209	2.29	3.48	1065.30	1.77	0.5165	7.97	32.94	1211.35
Methanol	3.69	0.154	0.92	3.05	420.98	1.26	0.6641	2.81	17.95	868.61
Ethanol	5.38	0.174	1.34	0.92	613.01	1.67	0.6425	4.19	23.08	897.29
Propan-1-ol	6.97	0.190	1.74	3.26	801.07	1.84	0.6015	5.68	27.45	966.71
Butan-1-ol	8.59	0.204	2.15	3.32	987.77	2.07	0.5841	7.13	31.54	999.79
Pentan-1-ol	10.21	0.216	2.55	3.40	1179.00	2.19	0.5654	8.67	35.40	1036.06
Hexan-1-ol	11.84	0.227	2.96	3.52	1378.00	2.13	0.5424	10.41	39.08	1082.70
Heptan-1-ol	13.42	0.237	3.35	3.51	1557.70	2.38	0.5392	11.78	42.47	1092.76
Octan-1-ol	15.06	0.246	3.77	3.54	1750.42	2.50	0.5323	13.351	45.87	1107.54

Table 5. Speeds of sound, isentropic compressibility and excess isentropic compressibility, deviation of speed of sound, excess intermolecular free length and excess acoustic impedance of alkan-1-ol + 2-ethoxyethanol at 298.15 K.

x_1	K_S (TPa^{-1})	L_f (Å)	$R \times 10^6$ [m^3 mol^{-1} (m s^{-1})$^{1/3}$]	R_A	M_A	$V_a \times 10^5$ (m^3)	$Z \times 10^{-3}$
2-Ethoxyethanol + methanol							
0.0380	977.74	0.6431	370.86	0.9073	−0.4828	1.20	904.38
0.0816	927.53	0.6264	384.99	0.9170	−0.4738	1.17	936.28
0.1322	887.44	0.6127	402.39	0.9281	−0.4660	1.15	965.17
0.1916	842.05	0.5969	424.43	0.9381	−0.4596	1.12	999.14
0.2623	805.36	0.5837	451.84	0.9497	−0.4548	1.11	1030.36
0.3478	772.16	0.5715	488.29	0.9617	−0.4529	1.13	1061.10
0.4534	744.05	0.5610	539.29	0.9744	−0.4548	1.18	1089.94
0.5871	716.16	0.5504	617.87	0.9864	−0.4620	1.27	1119.84
0.7619	684.14	0.5380	756.05	0.9962	−0.4766	1.44	1154.39
2-Ethoxyethanol + ethanol							
0.0538	907.71	0.6197	539.56	0.8946	−0.5187	1.58	937.92
0.1133	856.90	0.6021	560.05	0.9029	−0.5114	1.51	973.15
0.1798	813.87	0.5868	583.40	0.9122	−0.5049	1.45	1006.63
0.2542	777.66	0.5736	610.62	0.9226	−0.4992	1.42	1038.19
0.3383	746.66	0.5620	643.28	0.9341	−0.4945	1.40	1068.28
0.4341	721.21	0.5524	683.56	0.9467	−0.4913	1.41	1095.92
0.5440	697.79	0.5433	735.61	0.9598	−0.4898	1.45	1123.38
0.6716	673.08	0.5336	806.51	0.9727	−0.4904	1.49	1153.33
0.8215	648.63	0.5238	908.28	0.9856	−0.4936	1.58	1184.66
2-Ethoxyethanol + propanol							
0.0690	822.43	0.5899	711.17	0.8958	−0.5556	1.78	992.91
0.1429	792.47	0.5790	732.34	0.9052	−0.5483	1.73	1018.71
0.2223	767.51	0.5698	755.46	0.9157	−0.541	1.70	1042.67
0.3078	744.60	0.5613	781.48	0.9267	−0.5339	1.68	1066.29
0.4001	723.97	0.5534	811.03	0.9383	−0.5271	1.68	1089.34
0.5001	703.92	0.5457	845.34	0.9499	−0.5208	1.67	1112.81
0.6088	684.77	0.5382	885.67	0.9616	−0.5151	1.68	1136.45
0.7273	665.77	0.5307	933.91	0.9738	−0.5097	1.69	1161.12
0.8572	646.86	0.5231	992.71	0.9863	−0.5047	1.72	1186.90
2-Ethoxyethanol + butanol							
0.0837	790.05	0.5781	874.65	0.8973	−0.5705	2.04	1016.67
0.1706	770.86	0.5711	890.28	0.9072	−0.5634	2.01	1035.90
0.2606	749.89	0.5632	907.40	0.9169	−0.5562	1.96	1057.18
0.3541	728.41	0.5551	925.91	0.9267	−0.5489	1.91	1079.80
0.4513	708.30	0.5474	945.54	0.9371	−0.5414	1.87	1102.47
0.5523	689.17	0.5400	966.52	0.9480	−0.5336	1.83	1125.43
0.6574	672.33	0.5333	988.67	0.9599	−0.5256	1.80	1147.57
0.7669	657.42	0.5274	1012.20	0.9728	−0.5172	1.78	1169.00
0.8810	644.26	0.5221	1037.50	0.9863	−0.5088	1.78	1189.59
2-Ethoxyethanol + pentanol							
0.0980	741.34	0.5600	1036.97	0.8934	−0.5888	2.14	1052.36
0.1965	727.16	0.5546	1040.48	0.9031	−0.5809	2.09	1068.95
0.2954	713.26	0.5493	1043.95	0.9132	−0.5725	2.04	1085.99
0.3947	699.93	0.5442	1047.35	0.9237	−0.5638	1.99	1103.17
0.4945	687.08	0.5391	1050.66	0.9348	−0.5547	1.94	1120.60
0.5947	675.20	0.5345	1053.74	0.9465	−0.5451	1.91	1137.86
0.6953	663.89	0.5300	1056.69	0.9588	−0.5349	1.87	1155.30
0.7964	652.85	0.5255	1059.56	0.9719	−0.5241	1.84	1173.21
0.8980	641.99	0.5212	1062.36	0.9857	−0.5125	1.81	1191.68

(*Continued*)

Table 5. Continued.

x_1	K_S (TPa^{-1})	L_f (Å)	$R \times 10^6$ [$m^3 mol^{-1} (m s^{-1})^{1/3}$]	R_A	M_A	$V_a \times 10^5$ (m^3)	$Z \times 10^{-3}$
2-Ethoxyethanol + hexanol							
0.1119	691.65	0.5409	1194.66	0.8874	−0.6135	1.20	1091.75
0.2209	687.22	0.5392	1176.73	0.8985	−0.6032	1.17	1101.63
0.3270	682.07	0.5372	1159.86	0.9099	−0.5924	1.15	1112.39
0.4305	676.20	0.5349	1144.01	0.9216	−0.5811	1.12	1124.00
0.5314	669.44	0.5322	1129.16	0.9334	−0.5694	1.11	1136.65
0.6297	662.22	0.5293	1115.14	0.9454	−0.5572	1.13	1150.01
0.7257	654.53	0.5262	1101.84	0.9580	−0.5442	1.18	1164.32
0.8193	646.56	0.5230	1089.20	0.9711	−0.5306	1.27	1179.30
0.9108	638.33	0.5197	1077.11	0.9850	−0.5160	1.44	1195.23
2-Ethoxyethanol + heptanol							
0.1253	686.72	0.5390	1331.37	0.8905	−0.6119	2.32	1097.86
0.2438	683.55	0.5378	1287.40	0.9011	−0.6019	2.25	1106.37
0.3559	678.90	0.5359	1248.55	0.9123	−0.5910	2.18	1116.57
0.4623	673.96	0.5340	1213.83	0.9233	−0.5801	2.12	1127.06
0.5632	668.51	0.5318	1182.65	0.9347	−0.5687	2.06	1138.23
0.6592	661.84	0.5291	1154.56	0.9470	−0.5562	1.99	1151.19
0.7505	654.96	0.5264	1129.09	0.9593	−0.5435	1.94	1164.52
0.8376	647.92	0.5236	1105.85	0.9718	−0.5304	1.89	1178.26
0.9207	639.38	0.5201	1084.81	0.9851	−0.5161	1.83	1194.18
2-Ethoxyethanol + octanol							
0.1384	671.52	0.5330	1461.25	0.8903	−0.6175	2.41	1109.65
0.2654	671.06	0.5328	1385.10	0.9011	−0.6066	2.32	1114.39
0.3825	669.29	0.5321	1321.61	0.9122	−0.5951	2.24	1122.97
0.4907	666.69	0.5311	1267.83	0.9236	−0.5834	2.16	1131.60
0.5910	662.89	0.5296	1221.83	0.9351	−0.5712	2.09	1142.32
0.6843	658.20	0.5277	1182.02	0.9470	−0.5586	2.02	1154.83
0.7713	652.40	0.5254	1147.29	0.9593	−0.5452	1.96	1167.13
0.8525	645.84	0.5227	1116.70	0.9722	−0.5312	1.89	1180.61
0.9286	638.54	0.5197	1089.59	0.9855	−0.5163	1.83	1195.30

the increasing chain length of the alcohols. The values of ΔK_S in terms of negativity are enhanced by the following order:

Methanol > Ethanol > 1-Propanol > 1-Butanol > 1-Pentanol

> 1-Hexanol > 1-Heptanol > 1-Octanol

These results can be explained in terms of molecular interactions and structural effects. Positive ΔK_S values are due to the breaking of interactions and the corresponding disruption of molecular order in the pure components [42]. The donor–acceptor interaction between the 2-ethoxyethanol and the alcohols play an important part for the mixtures containing lower alcohols like methanol, ethanol, 1-propanol where there is strong specific interaction between the component molecules leading to negative value of ΔK_S. Interactions between the molecules of 2-ethoxyethanol or monoalcohols are broken in the mixing process; the breaking leads to positive K_S^E values for the mixture containing higher chain length of alcohols as compared to the lower alcohols. There is a parallel in the qualitative behavior of ΔK_S and V^E curves.

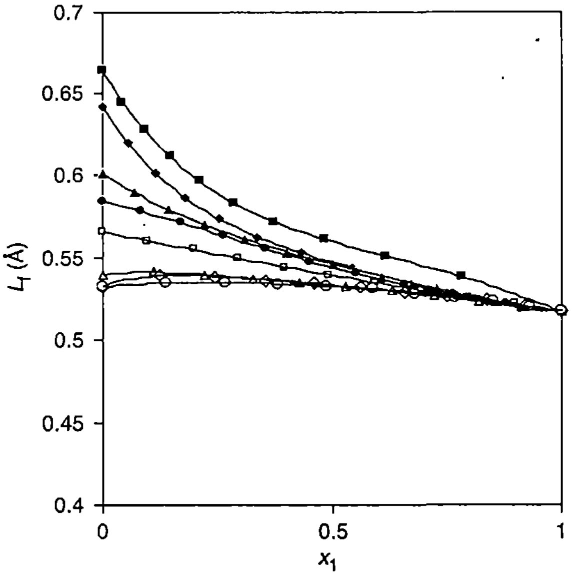

Figure 4. L_f values for the experimental mixtures against the mole fraction of 2-ethoxyethanol, methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

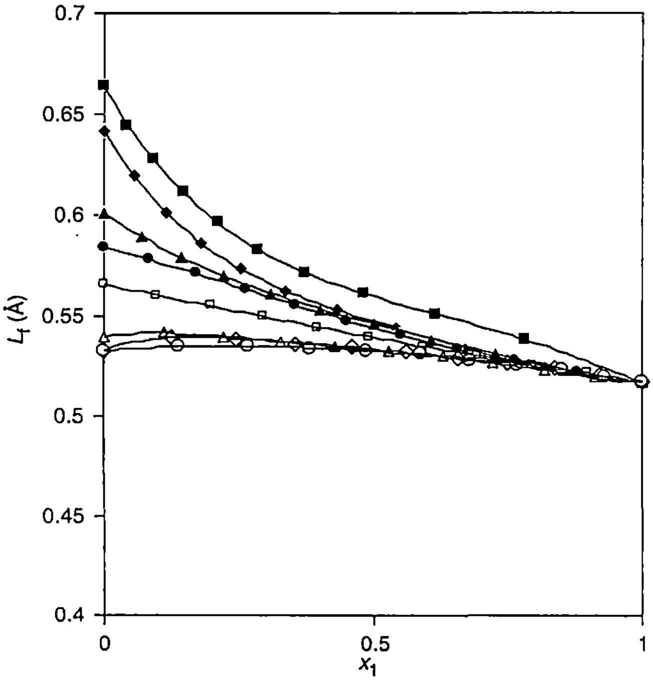

Figure 5. Z values for the experimental mixtures against the mole fraction of 2-ethoxyethanol, methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

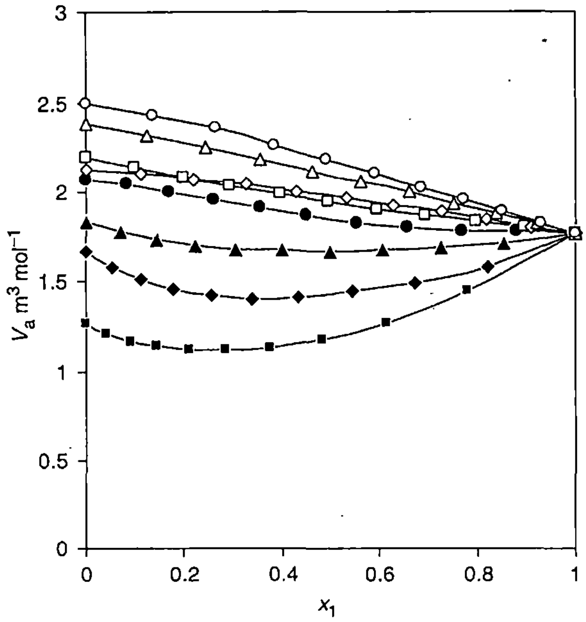

Figure 6. V_a values for the experimental mixtures against the mole fraction of 2-ethoxyethanol, methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

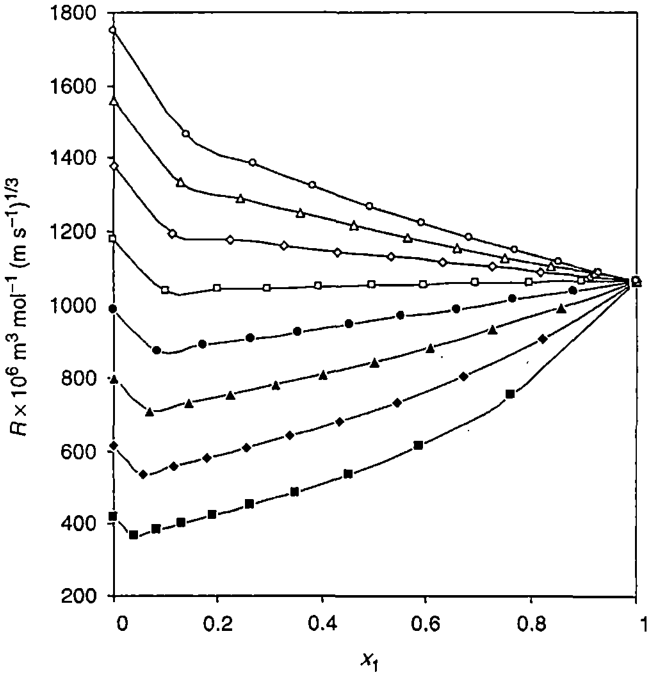

Figure 7. R values for the experimental mixtures against the mole fraction of 2-ethoxyethanol, methanol (■), ethanol (◆), 1-propanol (▲), 1-butanol (●), 1-pentanol (□), 1-hexanol (◇), 1-heptanol (△) and 1-octanol (○) at 298.15 K.

3.6. *Redlich–Kister polynomial equation*

The excess properties (V^E, $\Delta\eta$, ΔG^{*E} and ΔK_S) were fitted to the Redlich–Kister polynomial equation [43],

$$Y^E = x_1 x_2 \sum_{i=1}^{K} A_i (x_1 - x_2)^i \tag{20}$$

where Y^E refers to excess properties, x_1 is the mole fraction of 2-ethoxyethanol and x_2 is that of the other component of the binary mixtures, respectively. The coefficients (A_i) were obtained by fitting equation (20) to experimental results using a least squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The calculated values of A_i along with the tabulated standard deviations (σ) are listed in table 6. The standard deviation (σ) was calculated using the equation,

$$\sigma^2 = \frac{1}{n-m}\left(Y^E_{\text{exp}} - Y^E_{\text{cal}}\right)^2 \tag{21}$$

where n is the number of data points and m is the number of coefficients.

3.7. *Predictions of sound speeds*

The sound speeds of binary mixtures are often predicted by free length theory (FLT), collision factor theory (CFT), the Nomoto equation, the Vandeal Vangael (VV) ideal mixing relation, the impedance dependence (ID) relation, etc. For comparison, the theoretical values of the sound speed u has been calculated by using the above five theories and empirical equations. The following final relations were used for calculating sound speeds.

According to FLT [12], the speed of sound is given by,

$$u_{\text{FLT}} = \frac{K_S}{L_f \rho^{1/2}} \tag{22}$$

The free length L_f is obtained by:

$$L_f = \frac{V - \sum_i x_i V_{0i}}{\sum_i x_i y_i} \tag{23}$$

where, V_{0i} is the molar volume of the pure component i at absolute zero and is given by Sugden's formula,

$$V_{0i} = V_i\left(\frac{1-T}{T_{ci}}\right)^{0.3} \tag{24}$$

where T_c is the critical temperature for the pure components.

Y_i is the surface area per mole for the pure component i and is given by,

$$Y_i = \left(36\pi N V_{0i}^2\right)^{1/3} \tag{25}$$

Collision factor theory [15],

$$u_{\text{CFT}} = u_\infty[x_1 S_1] + \left[\frac{x_1 B_1 + x_2 B_2}{V_{12}}\right] \tag{26}$$

Nomoto equation [56],

$$u_N = \left[\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2}\right]^3 \tag{27}$$

Vandeal Vangael [57] ideal mixing relation

$$\frac{1}{x_1 M_1 + x_2 M_2} - \frac{1}{u_{\text{mix}}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \tag{28}$$

Table 6. Redlich–Kister coefficients and standard deviations (σ) for the binary mixtures of 2-ethoxyethanol + methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol at $T = 298.15$ K.

Excess property	A_0	A_1	A_2	A_3	A_4	σ
2-Ethoxyethanol + methanol						
$V^E \times 10^6$ (m^3 mol^{-1})	3.16995	−0.19613	9.25258	–	–	0.49292
$\Delta\eta$ (mPa S)	0.45326	−0.06186	0.15702	–	–	0.00207
ΔG^{*E} (J mol^{-1})	3479.34	−1432.39	1298.143	−2197.38	−1306.92	2.65174
$\Delta K_S \times 10^{12}$ (Pa^{-1})	−410.03	418.6652	−260.832	−231.895	186.4851	0.26013
2-Ethoxyethanol + ethanol						
$V^E \times 10^6$ (m^3 mol^{-1})	−0.7623	0.1832	−0.14364	−0.26987	0.10883	0.0013
$\Delta\eta$ (mPa s)	0.31223	0.00246	–	–	–	0.00039
ΔG^{*E} (J mol^{-1})	1146.97	−231.093	71.5142	–	–	0.69754
$\Delta K_S \times 10^{12}$ (Pa^{-1})	−384.08	270.8331	−468.176	−422.724	1819.404	0.0000
2-Ethoxyethanol + 1-propanol						
$V^E \times 10^6$ (m^3 mol^{-1})	−0.4525	0.63921	0.95591	−4.03612	−7.6092	0.0000
$\Delta\eta$ (mPa s)	−0.4924	0.31418	−0.06658	0.06129	–	0.00028
ΔG^{*E} (J mol^{-1})	−576.47	417.0622	−40.3791	4.6357	−17.0632	0.29871
$\Delta K_S \times 10^{12}$ (Pa^{-1})	−155.20	77.52434	−64.4247	9.7579	–	0.2561
2-Ethoxyethanol + 1-butanol						
$V^E \times 10^6$ (m^3 mol^{-1})	0.35678	0.0052	−0.31737	–	–	0.00057
$\Delta\eta$ (mPa s)	−0.7822	0.34872	0.3328	–	–	0.00137
ΔG^{*E} (J mol^{-1})	−778.52	278.1309	472.5683	71.41829	–	1.65605
$\Delta K_S \times 10^{12}$ (Pa^{-1})	−79.574	−24.6251	50.09514	−3.56549	–	0.13396
2-Ethoxyethanol + 1-pentanol						
$V^E \times 10^6$ (m^3 mol^{-1})	0.85714	0.30517	−0.11772	–	–	0.00185
$\Delta\eta$ (mPa s)	−1.6096	0.90572	0.24544	−0.11007	0.1719	0.00167
ΔG^{*E} (J mol^{-1})	−794.99	56.02497	511.5964	241.3453	–	1.67093
$\Delta K_S \times 10^{12}$ (Pa^{-1})	−27.041	4.06096	24.65183	6.48988	−105.956	0.0000
2-Ethoxyethanol + 1-hexanol						
$V^E \times 10^6$ (m^3 mol^{-1})	0.94412	0.36152	0.52195	0.15616	−0.25529	0.00331
$\Delta\eta$ (mPa s)	−2.4006	1.13292	0.20876	0.37026	–	0.0073
ΔG^{*E} (J mol^{-1})	−958.04	416.3159	634.2876	439.3159	–	5.67164
$\Delta K_S \times 10^{12}$ (Pa^{-1})	34.5516	−5.80756	−7.03454	4.42241	7.98105	0.03121
2-Ethoxyethanol + 1-heptanol						
$V^E \times 10^6$ (m^3 mol^{-1})	1.58018	0.71001	0.21536	–	–	0.00249
$\Delta\eta$ (mPa s)	−3.1936	1.24977	0.13886	–	–	0.01012
ΔG^{*E} (J mol^{-1})	−436.66	432.5375	−307.039	−728.232	1304.31	2.29942
$\Delta K_S \times 10^{12}$ (Pa^{-1})	51.6636	3.55552	12.76334	−7.78112	–	0.19454
2-Ethoxyethanol + 1-octanol						
$V^E \times 10^6$ (m^3 mol^{-1})	1.65059	0.51687	0.46603	0.26796	–	0.00234
$\Delta\eta$ (mPa s)	−4.0219	0.70295	0.44447	0.61789	–	0.00719
ΔG^{*E} (J mol^{-1})	74.1220	−213.353	649.6937	2647.439	−2950.2	0.0000
$\Delta K_S \times 10^{12}$ (Pa^{-1})	64.1492	14.7396	3.89818	−6.8375	2.27945	0.0169

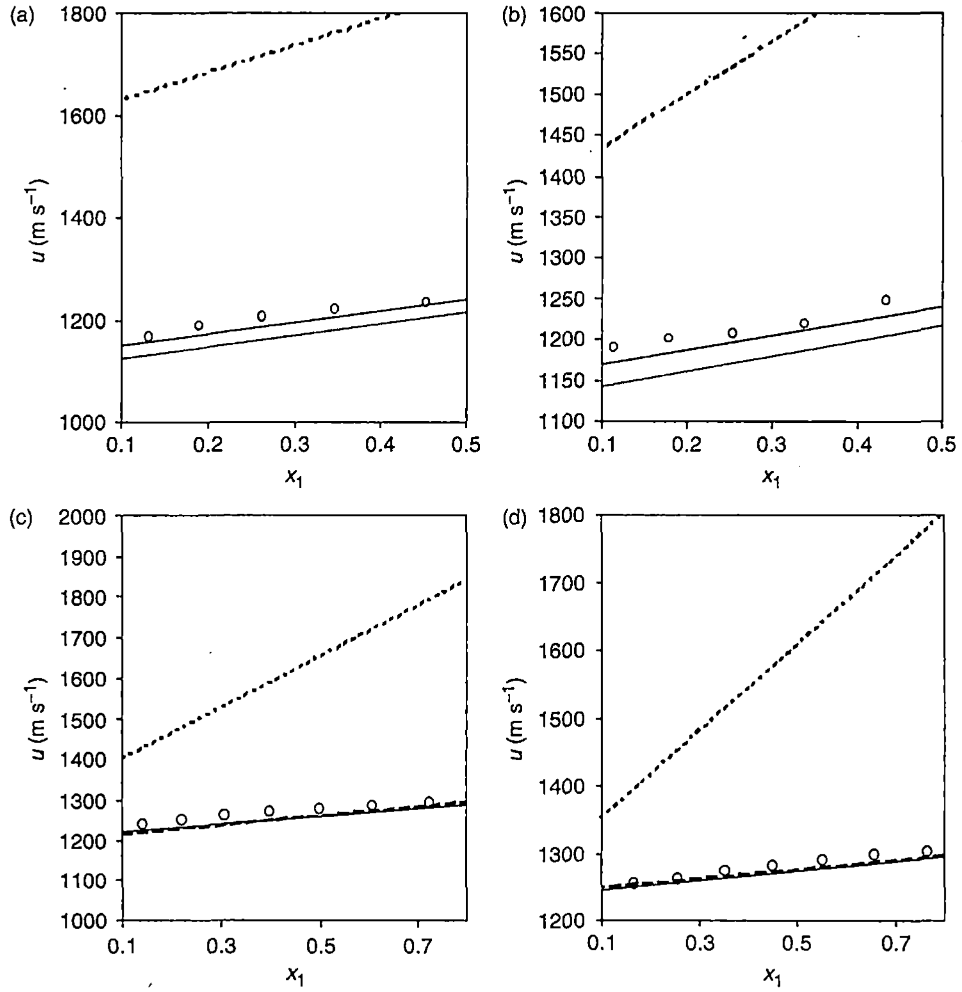

Figure 8(a–h). Experimental and calculated ultrasonic speed u of [2-ethoxyethanol] + [methanol (a), ethanol (b), 1-propanol (c), 1-butanol (d), 1-pentanol (e), 1-hexanol (f), 1-heptanol (g) and 1-octanol (h)] at 298.15 K. [$u_{\text{experimental}}$ (OOOOO); u_{FLT} (-------); u_{Nomoto} (– – – –); u_{CFT} (·········)].

Impedance dependence relation [58,59]

$$u = \frac{\sum x_i Z_i}{x_i \rho_i} \tag{29}$$

where, K_S, S, B, R, Z, ρ are the isentropic compressibility, collision factor, geometrical volume, molar speed of sound, specific acoustic impedance and density respectively for pure 2-ethoxyethanol (**1**), 1-alkanols (**2**), and the mixtures (12), u_∞ is a constant value taken as 1600 m s^{-1}.

The compositional dependence of the experimental and sound speeds calculated by the free length theory (FLT), collision factor theory (CFT) and the Nomoto equation of the binary mixtures of 2-ethoxyethanol and 1-alkanols are shown in figure 8(a–h). The results show that the Nomoto equation and the collision factor theory predicts the

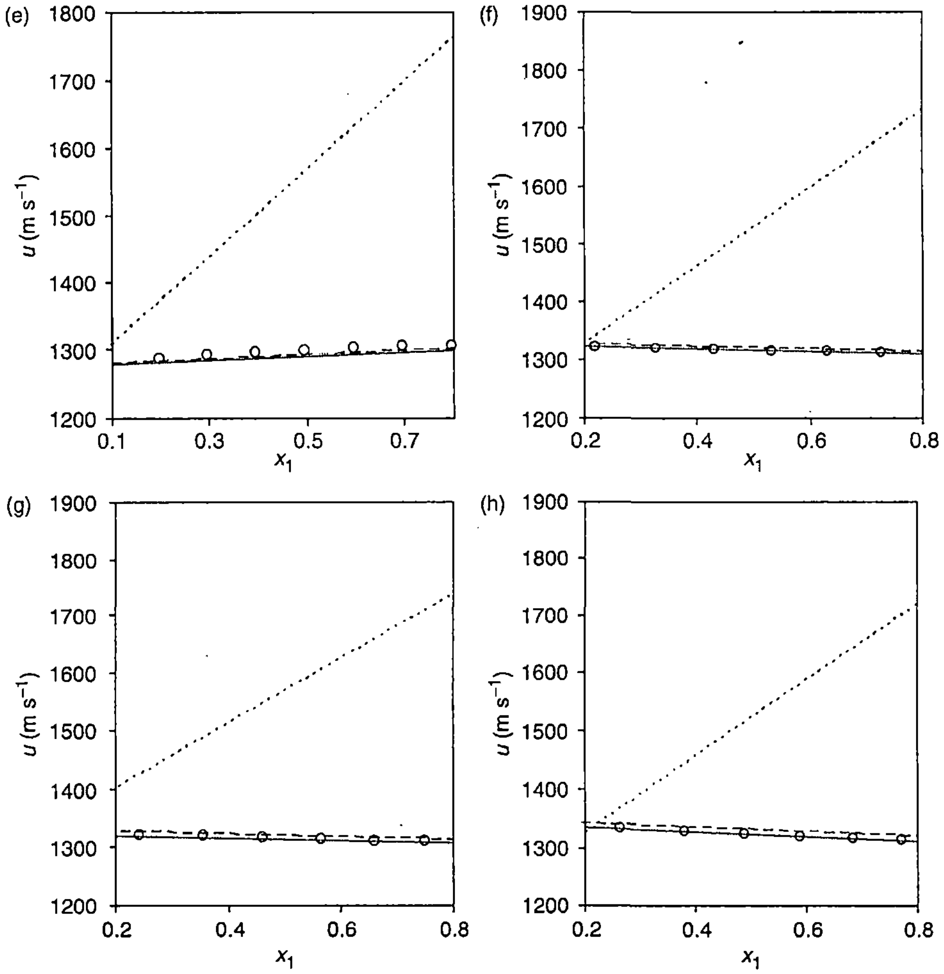

Figure 8(a–h). Continued.

experimental data extremely well, whereas the free length theory gives the maximum deviation for the present set of binary mixtures. Table 7 summarizes the deviations for different prediction methods. Based on deviation values obtained, the following order for the relative predictive capability for each of the methods is obtained,

$$\text{Nomoto} \geq \text{CFT} > \text{ID} \geq \text{VV} > \text{FLT}$$

4. Conclusions

In this work, eight binary mixtures have been studied in terms of excess molar volumes, viscosity deviations, acoustic impedance, intermolecular free length, isentropic

Table 7. Values of standard deviation (%) for sound speeds by various methods.

	σ (%)				
Solvent mixture	u_{CFT}	u_{FLT}	u_{Nomoto}	U_{VV}	u_{ID}
2-Ethoxyethanol + methanol	0.11	0.85	0.10	0.63	0.15
2-Ethoxyethanol + ethanol	0.20	1.19	0.12	0.35	0.16
2-Ethoxyethanol + 1-propanol	0.04	1.35	0.05	0.13	0.05
2-Ethoxyethanol + 1-butanol	0.05	1.44	0.04	0.07	0.04
2-Ethoxyethanol + 1-pentanol	0.02	1.59	0.02	0.02	0.02
2-Ethoxyethanol + 1-hexanol	0.01	1.79	0.02	0.01	0.01
2-Ethoxyethanol + 1-heptanol	0.01	1.71	0.02	0.02	0.01
2-Ethoxyethanol + 1-octanol	0.01	1.76	0.04	0.02	0.02

compressibility and interaction parameters. The investigation was carried out to explore the nature of interactions between the mixing components. It may be concluded from our effort that, the strength of associative interaction between the unlike molecules weakens with the increase of chain length of the 1-alkanols.

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References

[1] B. Gracia, R. Alcalde, J.M. Leal, J.S. Matos. *J. Chem. Soc. Faraday Trans.*, **92**, 3347 (1996).
[2] Y. Mahan, C.N. Liew, A.E. Mather. *J. Solu. Chem.*, **31**, 743 (2002).
[3] A. Ali, Abida, S. Hyder, A.K. Nain. *Collect. Czech. Chem. Comm.*, **67**, 1125 (2002).
[4] M.N. Roy, A. Choudhury, A. Sinha. *J. Teach. Res. Chem.*, **11**, 12 (2004).
[5] D.K. Hazra, M.N. Roy, B. Das. *Indian J. Chem. Technol.*, **1**, 93 (1994).
[6] M.N. Roy, A. Choudhury. *J. Teach. Res. Chem.*, **1**, 17 (2000).
[7] M.N. Roy, B.B. Gurung, A. Choudhury. *J. Indian Chem. Soc.*, **81**, 1 (2004).
[8] S.L. Oswal, H.S. Desai. *Fluid Phase Equilib.*, **61**, 191 (1999).
[9] S.L. Oswal, H.S. Desai. *Fluid Phase Equilib.*, **186**, 81 (2001).
[10] S.L. Oswal, K.D. Prajapati. *J. Chem. Eng. Data*, **43**, 367 (1998).
[11] R.K. Dewan, C.M. Gupta, S.K. Mehta. *Acoustica*, **65**, 245 (1998).
[12] B. Jacobson. *J. Chem. Phys.*, **20**, 927 (1952).
[13] W. Schaaffs. *Acoustica*, **33**, 272 (1975).
[14] M.R. Rao. *Indian J. Chem.*, **14**, 109 (1940).
[15] W. Schaaffs. *Z. Phys.*, **114**, 110 (1974).
[16] S.K. Mehta, R.K. Chauhan, R.K. Dewan. *J. Chem. Soc. Faraday Trans.*, **92**, 1167 (1966).
[17] D.D. Perrin, W.L.F. Armarego. *Purification of Laboratory Chemicals*, 3rd Edn, Pergamon Press, Oxford (1988).
[18] J.R. Suindells, T.B. Godfray. *J. Res. Naid. Bur. Stand.*, **48**, 1 (1952).
[19] M.N. Roy, A. Jha, R. Dey. *J. Chem. Eng. Data*, **46**, 1247 (2001).
[20] M.N. Roy, A. Jha, A. Choudhury. *J. Chem. Eng. Data*, **49**, 291 (2004).
[21] P. Brocos, E. Calvo, A.Ä. Piñeiro, R. Bravo, A.A.A.H. Roux, G. Roux-Desgranges. *J. Chem. Eng. Data*, **44**, 1341 (1999).
[22] P.S. Nikam, L.N. Shirsat, M. Hassan. *J. Chem. Eng. Data*, **77**, 244 (2000).

[23] S.K. Mehta, R.K. Chauhan, R.K. Dewan. *J. Chem. Soc. Faraday Trans.*, **92**(7), 1167 (1996).
[24] N.V. Shastry, S.R. Patel. *Int. J. Thermophys.*, **21**(5), 1153 (2000).
[25] R.J. Fort, W.R. Moore. *Trans. Faraday Soc.*, **62**, 1112 (1966).
[26] R.K. Nigam, P.P. Singh. *Indian J. Chem.*, **9**, 1691 (1971).
[27] S.L. Oswal, H.S. Desai. *Fluid Phase Equilib.*, **186**, 81 (2001).
[28] A. Pal, R.K. Bhardwaj. *Z. Phys. Chem.*, **216**, 1033 (2002).
[29] S.L. Oswal, P. Oswal, A.T. Patel. *J. Chem. Eng. Data*, **40**, 607 (1995).
[30] R.C. Reid, J.M. Prausnitz, B.E. Poling. *The Properties of Gases and Liquids*, 4th Edn, Mcgraw-Hill International, New York (1987).
[31] L. Grunberg, A.H. Nissan. *Nature*, **164**, 799 (1949).
[32] M. Tamura, M. Kurata. *Bull. Chem. Soc. Jpn.*, **25**, 32 (1952).
[33] R.K. Hind, E. McLaughlin, A.R. Ubbelohde. *Trans. Faraday Soc.*, **328**, 56 (1960).
[34] K. Ramamoorthy. *J. Pure Appl. Phys.*, **11**, 556 (1973).
[35] J.B. Irving. *Viscosity of Liquid Mixtures*, NEL Report Nos 630 and 631, National Engineering Laboratory, East Kilbride, Glasgow (1977).
[36] T.M. Reed, T.E. Taylor. *J. Phys. Chem.*, **63**, 58 (1959).
[37] R. Meyer, M. Meyer, J. Metzer, A. Peneloux. *Chem. Phys.*, **62**, 406 (1971).
[38] A.W. Quin, D.F. Hoffmann, P. Munk. *J. Chem. Eng. Data*, **37**, 55 (1992).
[39] S. Glasstone, K.J. Laidler, H. Eyring. *The Theory of Rate Process*, p. 514, McGraw-Hill, New York (1941).
[40] R.J. Fort, W.R. Moore. *Trans. Faraday. Soc.*, **61**, 2102 (1965).
[41] O. Redlich, A.J. Kister. *Ind. Eng. Chem.*, 40, 345 (1948).
[42] T.M. Aminabhabi, B. Gopalkrishna. *J. Chem. Eng. Data*, **40**, 632 (1995).
[43] H. Doe, T. Kitagawa, K. Sasabe. *J. Phys. Chem.*, **88**, 3341 (1984).
[44] H.-C. Ku, C.-H. Tu. *J. Chem. Eng. Data*, **50**, 1060 (2005).
[45] A. Ali, A.K. Nain, D. Chand, R. Ahmad. *Phys. Chem. Liq.*, **43**, 205 (2005).
[46] E. Jimenez, H. Casas, L. Segade, C. Franjo. *J. Chem. Eng. Data*, **45**, 862 (2000).
[47] A.K. Covington, T. Dickinson. *Physical Chemistry of Organic Solvents Systems*, Plenum Publishing Company Ltd., London (1973).
[48] N.V. Sastry, M.K. Voalnd. *Int. J. Themophys.*, **21**(5), 1153 (2000).
[49] G. Douheret, A. Pal, M.I. Davis. *J. Chem. Thermodyn.*, **22**, 99 (1990).
[50] D.R. Lide. *CSIR Handbook of Chemistry and Physics*, 7th Edn (1990–1991).
[51] J.M. Resa, C. Gonzalez, J.M. Goenaga. *J. Chem. Eng. Data*, **50**, 1570 (2005).
[52] T.A. Aminabhabi, T.S. Aralaguppi, S.B. Hargoppad, R.H. Balangdi. *J. Chem. Eng. Data*, **28**, 324 (1983).
[53] G. Ritzoulis, D. Missopolinou, S. Doulami, C. Panayiotou. *J. Chem. Eng. Data*, **45**, 636 (2000).
[54] T.M. Aminabhavi, V.B. Patil. *J. Chem. Eng. Data*, **43**, 504 (1998).
[55] O. Nomoto. *J. Phys. Soc. Jpn.*, **13**, 298 (1958).
[56] V. Tiwari, L.R. Mishra. *Acoustica*, **48**, 257 (1981).
[57] M. Kalidoss, R. Srinavasamorthy. *J. Pure Appl. Ultrason.*, **9**, 4 (1997).
[58] J.D. Pandey, K. Shukla. *J. Pure Appl. Phys.*, **15**, 37 (1993).
[59] F.N. Tasi. *J. Chem. Eng. Data*, **39**, 441 (1994).
[60] I. Johnson, M. Kalidoss, R. Srinavasamorthy. *J. Chem. Eng. Data*, **47**, 1388 (2002).

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Excess molar volume, excess energy and viscosity deviation of binary mixtures of tetrahydrofuran with some hydrocarbons at various temperatures

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The density and viscosity of the binary mixtures of tetrahydrofuran with normal pentane, hexane and heptane have been measured as a function of the composition at 288.15, 293.15 and 298.15 K. From these data, excess molar volume, excess free energy, deviation in viscosity of the composition and the interaction parameter of Grunberg and Nissan have been calculated. All the derived parameters are found to be either negative or positive over the entire range of composition depending on the molecular interactions and the nature of the binary liquid mixtures. The results have been interpreted in terms of possible molecular interactions existing between the components of these mixtures.

Grouping of solvents into classes often is based on the nature of the intermolecular forces because the manner whereby solute and solvent molecules are associated with one another brings about a marked effect on the resulting properties. After the introduction of the concept of ionization power of solvent[1], much work has been devoted to the solvent effects on the rate and equilibrium processes[2]. Because of the close connection between liquid structure and macroscopic properties, determination of volumetric and viscometric properties is a valuable tool to learn the liquid state[3]. On the other hand, the obtaining of reliable measurements of solvent properties over a wide range of composition, pressure and temperature often is not feasible; hence, prediction and correlation methods constitute a valuable option to overcome such difficulties[4,5].

The present work deals with the study of the structure and interactions in THF + hydrocarbon mixtures. Tetrahydrofuran (THF) is a good industrial solvent. It figures prominently in the high energy battery industry and has found its applications in organic syntheses as evident from its physicochemical studies[6,7]. Since no reports are available of density and viscosity studies of tetrahydrofuran (THF) with normal aliphatic hydrocarbons, the effect of chain-length of hydrocarbons (C_5, C_6, C_7) on these properties of binary mixtures of tetrahydrofuran with normal hydrocarbons at 288.15, 293.15 and 298.15 K is reported in the present investigation.

Results and discussion

The physical properties of tetrahydrofuran (THF), normal pentane, hexane and heptane at various temperatures are given in Table 1. The experimental values of mole-fractions (X_1), densities (ρ), viscosities and various derived parameters of the different binary mixtures of solvents studied here at different temperatures are recorded in Table 2.

The experimental density (ρ) values (Table 1) have been used to calculate the excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), excess Gibbs free energy (G^{*E}) and interaction parameter (d) using the following eqs.[8] (1–4) :

$$V_m^E = \frac{M}{\rho} - \sum_{i=1}^{c} x_i \frac{M_i}{\rho_i} \tag{1}$$

$$\Delta\eta = \eta - \sum_{i=1}^{c} x_i \eta_i \tag{2}$$

$$G^{*E} = RT \ln \frac{\eta M}{\rho} - RT \sum_{i=1}^{c} x_i \ln \frac{\eta_i M_i}{\rho_i} \tag{3}$$

$$\ln \eta = \sum_{i=1}^{c} x_i \ln \eta_i + d \prod_{i=1}^{c} x_i \tag{4}$$

where c stands for the number of components of the mixture, M and M_i are the molar mass of the mixture and of the pure components, ρ and ρ_i represent the density of the mixture and pure components, η and η_i are the corresponding viscosities, R is the gas constant and T is the temperature in Kelvin. The values of these functions and d are presented in Table 2 along with the values of ρ, η and mole fraction.

Table 1. Physical properties of tetrahydrofuran, n-pentane, n-hexane and n-heptane at various temperatures

T/K	$\rho \times 10^{-3}$ kg m^{-3}		η/m.Pa.S	
	This Work	Literature	This Work	Literature
		Tetrahydrofuran (THF)		
288.15	0.88720	0.88720[19]	0.50924	0.50923[19]
293.15	0.88358	0.88357[19]	0.49107	0.49106[19]
298.15	0.87888	0.87888[19]	0.45999	0.45999[19]
		n-Pentane		
288.15	0.62528	0.62527[16-18]	0.23145	0.23144[16-18]
293.15	0.62131	0.62132[16-18]	0.21996	0.21995[16-18]
298.15	0.61883	0.61883[16-18]	0.21210	0.21210[16-18]
		n-Hexane		
288.15	0.66125	0.66124[16-18]	0.33381	0.33381[16-18]
293.15	0.65472	0.65471[16-18]	0.31256	0.31225[16-18]
298.15	0.65253	0.65252[16-18]	0.29191	0.29190[16-18]
		n-Heptane		
288.15	0.68192	0.68192[16-18]	0.42121	0.42121[16-18]
293.15	0.67951	0.67950[16-18]	0.40020	0.40010[16-18]
298.15	0.67669	0.67669[16-18]	0.38450	0.38450[16-18]

The excess molar volume were correlated by Redlich-Kister equation.

$$V_m^E = X_1 X_2 \Sigma a_i (x_1 - x_2)^i \qquad (5)$$

The coefficient in eq. (5) was estimated by the least-squares fit method, where the squares of the difference between the calculated and experimental excess molar volumes results is minimized. The optimal values of the coefficients in eq. (5) are listed in Table 3. The standard deviation was calculated by

$$\sigma (V_m^E) = [(V_{m\,expt}^E - V_{m\,cal}^E)]^2/(D - N)^{0.5} \qquad (6)$$

where D and N are the number of data points and parameters, respectively. The experimental values of $\Delta\eta$ are also reported in Table 1. The viscosity deviations were correlated by the following equation :

$$Q = X_1 X_2 \Sigma H_i (x_1 - x_2)^i \qquad (7)$$

where $Q = \Delta\eta/(\text{m.Pa.S})$. The coefficient in eq. (7) are also regressed by employing the least square fit method. Standard deviations for the viscosity calculations were determined by eq. (8).

$$\sigma (\Delta\eta) = [\Sigma(\Delta\eta_{expt} - \Delta\eta_{cal})]^2/(D - N)^{0.5} \qquad (8)$$

The optimal parameters in correlating deviations of viscosity are listed in Table 4.

From Table 2 it is observed that the values of V_m^E for all binary mixtures THF + n-pentane, THF + n-hexane and THF + n-heptane at different temperatures over the entire composition are positive indicating the mutual dissociation of the component molecules. Because of the small difference in the molar volumes of the components, tetrahydrofuran will not fit into the structure of the normal aliphatic hydrocarbons (C_5H_{12}, C_6H_{14}, C_7H_{16}), thereby increasing the volume of the mixture[9]. Positive V_m^E also suggests that the dispersion forces prevail between THF and normal hydrocarbons.

It is also found from Table 2 that the difference in the molar volumes of the mixtures of the components follows the following order : THF + n-heptane > THF + n-hexane > THF + n-pentane at any temperature studied here. This indicates the higher value of V_m^E for THF + n-pentane mixture than that of THF + n-hexane mixture which is in turn higher than that of THF + n-heptane (shown in Table 2).

There is a systematic increase in V_m^E with a rise in temperature for all mixtures studied here and such changes or variations are evident from Table 2. This increase in V_m^E with temperature is as expected from theoretical considerations[10].

Deviations in viscosity ($\Delta\eta$) shown in Table 2 for the mixtures of tetrahydrofuran (THF) with normal aliphatic hydrocarbons (C_5-C_7) are negative which increase with increasing size of hydrocarbons. The trend in $\Delta\eta$ is THF-C_5H_{12} < THF-C_6H_{14} < THF-C_7H_{16}. The dominance of exo-

Table 2. Density (ρ), viscosity (η), excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), excess free energy of activation of viscous flow (G^{*E}), interaction parameter (d) and mole fractions of tetrahydrofuran (X_1) with different normal hydrocarbons at various temperatures

X_1	$\rho \times 10^{-3}$ kg m^{-3}	η/m.Pa.S	V_m^E /cm^{3}mol^{-1}	$\Delta\eta$/m.Pa.S	G^{*E} J mol^{-1}	d
			288.15 K			
			THF + n-Pentane			
0	0.62528	0.23145	0	0	0	0
0.10005	0.64384	0.24404	0.08012	0.01520	–48.30241	–0.28795
0.20009	0.66314	0.25863	0.22501	0.02841	–85.07026	–0.29207
0.30012	0.68356	0.27829	0.38213	-0.03653	–87.33218	–0.24928
0.40013	0.70536	0.29859	0.52531	–0.04401	–98.96688	–0.25388
0.50014	0.72910	0.32188	0.60112	–0.04850	–103.43975	–0.25829
0.60013	0.75389	0.34765	0.75452	–0.05051	–104.11553	–0.27671
0.70012	0.78256	0.38240	0.65501	–0.04354	–70.39536	–0.23806
0.80009	0.81536	0.41850	0.35254	–0.03521	–57.71623	–0.24135
0.90005	0.85002	0.46314	0.15231	–0.01833	–19.71319	–0.17868
1	0.88720	0.50924	0	0	0	0
			THF + n-Hexane			
0	0.66125	0.33381	0	0	0	0
0.11713	0.67683	0.34235	0.31001	–0.01201	–27.52968	–0.23410
0.22998	0.69396	0.35205	0.47510	–0.02211	–52.41408	–0.24807
0.33863	0.71227	0.36440	0.58502	–0.03002	–63.79133	–0.24709
0.44335	0.73168	0.37894	0.67511	–0.03265	–65.71838	–0.24491
0.54436	0.75343	0.39784	0.59002	–0.03147	–50.21391	–0.21945
0.64184	0.77676	0.41661	0.47512	–0.02980	–43.40952	–0.21533
0.73598	0.80164	0.43672	0.36013	–0.02631	–36.22659	–0.21676
0.82695	0.82184	0.45847	0.25003	–0.02041	–27.60456	–0.22318
0.91491	0.85643	0.48214	0.14561	–0.01217	–17.23062	–0.24081
1	0.88720	0.50924	0	0	0	0
			THF + n-Heptane			
0	0.68192	0.42121	0	0	0	0
0.13376	0.69798	0.42314	0.01801	–0.00984	–7.43921	–0.17964
0.25784	0.71408	0.42721	0.16810	–0.01670	–7.72454	–0.18181
0.37327	0.73105	0.43212	0.29111	–0.02175	–9.27331	–0.19153
0.48091	0.74900	0.43746	0.38112	-0.02608	–17.43592	–0.21398
0.58153	0.76886	0.44679	0.32102	–0.02561	–12.01893	–0.21126
0.67580	0.78996	0.45649	0.24515	–0.02421	–11.42528	–0.21828
0.76430	0.81226	0.46761	0.17321	–0.02088	–9.62714	–0.22511
0.84753	0.83579	0.47985	0.11213	–0.01597	–8.13692	–0.23610
0.92597	0.86066	0.49304	0.06122	–0.00968	–7.39667	–0.26666
1	0.88720	0.50924	0	0	0	0
			293.15 K			
			THF + n-Pentane			
0	0.62131	0.21996	0	0	0	0
0.10005	0.63975	0.23307	0.10009	–0.01401	–40.13625	–0.24946
0.20009	0.65882	0.24979	0.28215	–0.02442	–52.82306	–0.20946
0.30012	0.67932	0.26882	0.42501	–0.03250	–58.50596	–0.19254

Table 2 (contd.)

0.40013	0.70091	0.28943	0.60002	–0.03901	–64.64248	–0.19537
0.50014	0.72427	0.31156	0.72551	–0.04399	–74.89723	–0.21415
0.60013	0.74962	0.33706	0.80432	–0.04560	–76.91300	–0.22744
0.70012	0.77846	0.36856	0.68511	0.04121	61.08626	–0.21975
0.80009	0.81076	0.40335	0.44004	–0.03352	–50.21842	–0.22649
0.90005	0.84594	0.44846	0.18603	0.01551	5.25559	0.11064
1	0.88358	0.49107	0	0	0	0
				THF + n-Hexane		
0	0.65472	0.31256	0	0	0	0
0.11713	0.67030	0.32340	0.34011	–0.01001	–13.78878	–0.18204
0.22998	0.68750	0.33559	0.52012	–0.01802	–24.35637	–0.18527
0.33863	0.70596	0.34898	0.63510	–0.02403	–31.96879	–0.19098
0.44335	0.72573	0.36001	0.70001	–0.03169	–61.24642	–0.23893
0.54436	0.74763	0.37971	0.62503	–0.03002	–41.13155	–0.20693
0.64184	0.77130	0.40073	0.50002	–0.02640	–22.50561	–0.18047
0.73598	0.79649	0.42074	0.38215	–0.02320	–18.26332	–0.18161
0.82695	0.82346	0.44201	0.26002	–0.01817	–14.90494	–0.18918
0.91491	0.385273	0.46499	0.10003	–0.01089	–11.68659	–0.20717
1	0.88358	0.49107	0	0	0	0
				THF + n-Heptane		
0	0.67951	0.40020	0	0	0	0
0.13376	0.69541	0.40303	0.03211	–0.00932	–6.19986	–0.17964
0.25784	0.71116	0.40749	0.23101	–0.01614	–6.62451	–0.18181
0.37327	0.72815	0.41302	0.32905	–0.02110	–8.97066	–0.19153
0.48091	0.74110	0.41907	0.39811	–0.02483	–14.95693	–0.21398
0.58153	0.76587	0.42849	0.33521	–0.02455	–10.38316	–0.21126
0.67580	0.78682	0.43850	0.26115	–0.02302	–9.17771	–0.21828
0.76430	0.80901	0.44949	0.18522	–0.02016	–8.91551	–0.22511
0.84753	0.83246	0.46185	0.11609	–0.01537	–7.42920	–0.23610
0.92597	0.85715	0.47507	0.06713	–0.00927	–7.24725	–0.26666
1	0.88358	0.49107	0	0	0	0
				298.15 K		
				THF + n-Pentane		
0	0.61884	0.21210	0	0	0	0
0.10005	0.63627	0.22409	0.25510	–0.01281	–37.51550	–0.24948
0.20009	0.65502	0.24048	0.46001	–0.02122	–39.51000	–0.18319
0.30012	0.67532	0.25800	0.59870	–0.02850	–45.81660	–0.17346
0.40013	0.69680	0.27677	0.75420	–0.03452	–54.29800	–0.18177
0.50014	0.71991	0.29768	0.88000	–0.03840	59.58580	–0.19288
0.60013	0.74504	0.32036	0.94801	–0.04051	67.55308	–0.21753
0.70012	0.77317	0.34700	0.87505	–0.03865	–66.34380	–0.23686
0.80009	0.80424	0.38003	0.71900	–0.03040	–43.53820	–0.22629
0.90005	0.84004	0.42120	0.34599	–0.01401	–1.44872	–0.11918
1	0.87888	0.45999	0	0	0	0

Table-2 (contd.)

			THF + n-Hexane			
0	0.65253	0.29191	0	0	0	0
0.11713	0.66764	0.30251	0.40111	−0.00909	−10.00730	−0.17017
0.22998	0.68449	0.31417	0.61002	−0.01546	−19.08990	−0.17560
0.33863	0.70279	0.32582	0.71502	−0.02155	−34.60930	−0.19689
0.44335	0.72236	0.33805	0.77501	−0.02838	−51.08960	−0.24782
0.54436	0.74425	0.35700	0.66541	−0.02748	−28.97290	−0.18652
0.64184	0.76770	0.37358	0.53021	−0.02621	−17.33250	−0.17095
0.73598	0.79261	0.39434	0.41001	−0.02127	−15.01330	−0.17459
0.82695	0.81936	0.41503	0.27512	−0.01587	−7.93677	−0.16881
0.91491	0.84793	0.43648	0.15003	−0.00921	−4.84634	−0.17684
1	0.87888	0.45999	0	0	0	0
			THF + n-Heptane			
0	0.67669	0.38450	0	0	0	0
0.13376	0.69246	0.38606	0.05512	−0.00854	−5.49011	−0.17200
0.25784	0.70808	0.38915	0.26102	−0.01481	−5.70903	−0.17872
0.37327	0.72492	0.39354	0.35621	−0.01914	−6.60921	−0.18669
0.48091	0.74273	0.39842	0.41111	−0.02238	−11.48670	−0.20288
0.58153	0.76231	0.40609	0.35005	−0.02231	−8.35571	−0.20388
0.67580	0.78308	0.41463	0.28106	−0.02089	−6.83200	−0.20859
0.76430	0.80505	0.42423	0.19514	−0.01797	−5.56499	−0.21470
0.84753	0.82828	0.43559	0.13008	−0.01289	−4.67554	−0.21027
0.92597	0.85272	0.44651	0.07201	−0.00789	−3.80617	−0.24030
1	0.87888	0.45999	0	0	0	0

Table 3. Regression results for the excess volumes of THF + normal hydrocarbons mixture at various temperatures

System	Temp. K	a_0	a_1	a_2	a_3	a_4	a_5	δ
THF + n-Pentane	288.15	2.66282	2.02386	−2.08350	2.84555	–	–	0.04050
	293.15	2.97246	1.88985	−2.06088	−2.33610	–	–	0.018708
	298.15	3.54241	1.34718	–	–	–	–	0.034120
THF + n-Hexane	288.15	2.54097	−1.28838	−2.09799	2.60345	3.22786	−2.98877	0.013813
	293.15	2.60473	−1.06502	0.49835	–	–	–	0.017298
	298.15	2.80351	−1.36760	–	–	–	–	0.019951
THE + n-Heptane	288.15	1.44615	−0.014286	−2.62717	1.14038	1.61289	–	0.011453
	293.15	1.50759	−0.48406	−1.68899	1.68368	–	–	0.011274
	298.15	1.58020	−0.55754	−1.53455	1.66353	–	–	0.009582

thermic enthalpy of mixing over endothermic mixing resulting tetrahydrofuran (THF)-hydrocarbon interaction, leads to less negative Δη values for higher aliphatic hydrocarbons than for lower ones[21]. It seems that in tetrahydrofuran + hydrocarbon systems, the forces between pairs of unlike molecules are far less than that between pairs of like molecules. Therefore, the binary mixtures of tetrahydrofuran with higher hydrocarbons are less fluid due to enhanced non-covalent forces between like molecules. Negative Δη values in the present investigation can also be attributed to unequal molecular sizes of the constituent molecules of the mixture where dispersion forces are dominant[12].

The effect of temperature increase is to disrupt hetero and homo association of the molecules which causes increase in fluidity of the liquid. So, Δη values are higher at higher temperatures. Similar results was obtained as reported earlier[13].

Table 4. Regression results for the deviation of viscosity of THF + normal hydrocarbons mixture at various temperatures

System	Temp. K	a_0	a_1	a_2	a_3	a_4	δ
THF + n-Pentane	288.15	0.19448	–0.03755	–	–	–	0.001113
	293.15	0.17614	–0.04281	–	–	–	0.001459
	298.15	–0.15715	–0.04444	–	–	–	0.001574
THF + n-Hexane	288.15	–0.13108	–0.01022	–	–	–	0.000923
	293.15	–0.11682	–0.01651	–	–	–	0.001417
	298.15	–0.11033	–0.01977	0.02744	–	–	0.000948
THE + n-Heptane	288.15	–0.10213	–0.02881	–	–	–	0.000533
	293.15	0.09863	–0.02359	0.02062	–0.00971	–0.04866	0.000267
	298.15	–0.08840	–0.02129	–	–	–	0.000322

The negative values of excess Gibbs free energy of flow (shown in Table 2) for tetrahydrofuran + n-hydrocarbons over the entire range of composition and temperature which indicate the formation of molecular complex between unlike molecules through non-covalent bonds. Subba *et al.*[14] made a similar observation from G^{*E} studies for the binary mixtures of propionic acid and alcohols.

The positive values of Grunberg and Nissan parameter (*d*) indicates the presence of strong molecular interactions due to appreciable dipole-dipole and dipole-induced dipole interactions[13] while the negative values of *d* may be attributed to dominance of dispersion type of forces[12] between the like molecules. The last conclusion is in excellent agreement with the values of *d* (shown in Table 2) obtained from the experiment in our investigation.

Experimental

Tetrahydrofuran (THF, Merck) was kept for several days over KOH, refluxed for 24 h and distilled over $LiAlH_4$ as described earlier[15]. Normal pentane, hexane and heptane were purified according to the standard procedures[16,17]. The purities were checked by density determination dilatometrically[18] at (288.15, 293.15 and 298.15 K) ± 0.1 K which almost agreed within the accuracy of $\pm 1 \times 10^{-4}$ g cm^{-3} with the available literature[19,20] values. All the mixtures were prepared volumetrically[21] in stoppered bottles.

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (288.15, 293.5 and 298.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K of the desired temperature by means of a mercury in glass thermoregulator, and the temperature was determined with a calibrated thermometer and a Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The density values were reproducible to $\pm 3 \times 10^{-5}$ g cm^{-3}. Details have been described earlier[22].

The viscosities were measured by means of suspended-level Ubbelohde[24] viscometer at the desired temperature (accuracy ±0.01 K). The precision of the viscosity measurements was 0.05%. Details have been described earlier[24].

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References

1. F. J. Millero, in "Structure and Tansport Process in Water and Aqueous Solutions", ed. R. A. Horne, New York, 1972.
2. R. W. Gurney, "Ionic Process in Solutions", McGraw-Hill, New York, 1952.
3. M. N. Roy and D. K. Hazra, *North Bengal Univ. Rev.*, 1997, **8**, 54.
4. N. Saha and B. Das, *J. Chem. Eng. Data*, 1997, **42**, 277.
5. C. R. Reid and B. E. Poling, "The Properties of Gases and Liquids", McGraw-Hill, New York, 1998, Chap. 1.
6. C. G. Janz and R. T. P. Tomkins, "Non-aqueous Electrolytes Handbook", Academic Press, New York, 1973, Vol. 2.
7. R. Jasinki, "High Energy Batteries", Plenum Press, New York, 1967.

8. D. S. Gill and T. S. Cheema, *Z. Phys. Chem. (N.F.)*, 1983, **134**, 205.

9. A. Assarsson and F. R. Eirich, *J. Phys. Chem*, 1968, **72**, 2710.

10. T. N. Aminabhavi and B. Gopalkrishna, *J. Chem. Eng. Data*, 1994, **39**, 529.

11. R. J. Fort and H. Moore, *J. Indian Chem. Soc.*, 1965, **61**, 2102.

12. A. Choudhury, B. B. Gurung and M. N. Roy, *J. Indian Chem. Soc.*, 2004, **81**, 330.

13. M. Singh, *J. Indian Chem. Soc.*, 2002, **79**, 659.

14. M. C. S. Subba and K. C. Rao *J. Phys. Chem. Liq.*, 1988, **18**, 185.

15. A. Choudhuri, A. Jha and M. N. Roy, *J. Indian Chem. Soc.*, 2003, **80**, 632.

16. A. Vogel, "Practical Organic Chemistry", 4th ed., ELBS, London, 1978.

17. J. A. Riddick, W. B. Bunger and T. K. Solanko, "Techniques on Chemistry : Organic Solvents", 4th ed., Wiley, New York, 1986, 2.

18. R. L. David, "CRC Handbook of Chemistry and Physics", 72nd ed., CRC Press, Florida, 1992.

19. A. K. Covington and T. Dickinson, "Physical Chemistry of Organic Solvent Systems", Plenum, New York, 1973.

20. J. A. Dean, "Langes Handbook of Chemistry", 12th ed., McGraw-Hill, New York, 1979.

21. M. N. Roy, A. Jha and R. Dey, *J. Chem. Eng. Data*, 2001, **46**, 1247.

22. M. N. Roy and A. Choudhury, *J. Tech. Res. Chem.*, 2003, **1**, 17.

23. M. N. Roy, A. Jha and A. Choudhury, *J. Chem. Eng. Data*, 2004, **49**, 291.

24. M. N. Roy and D. K. Hazra, *Indian J. Chem. Technol.*, 1994, **1**, 93.

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Physico-Chemical Studies on the Solute-Solvent Interactions and Ultrasonic Speed of Resorcinol in 2-Methoxy Ethanol and Tetrahydrofuran at Different Temperatures

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ABSTRACT

The densities, viscosities and ultrasonic speeds of resorcinol in pure 2-methoxy ethanol and pure tetrahydrofuran have been investigated in 303.15K, 313.15K and 323.15K. Apparent molar volume (V_ϕ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_v^*) derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The structure making/breaking capacity of this solute investigated here has been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the solute particles.

Introduction

Studies on viscosities, densities and ultrasonic speeds of solutions assist in characterizing the structure and thermodynamic properties of solutions. Various types of interactions exist between the solutes in solutions and of these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Tetrahydrofuran (THF), and 2-methoxy enthanol (ME) are very important solvents widely used in various industries. These are industrial solvents and figure prominently in the high-energy battery technology and have also found wide applications in the organic synthesis as manifested from the physico-chemical studies in these media[1-10]. In this present work, an attempt has been made to provide an unequivocal interpretation of solute-solvent and solute-solute interactions prevailing in the studied solutions. Several workers have reported volumetric, viscometric and ultrasonic studies of this compound in non-aqueous solutions[11-15] but such studies in pure THF and 2-methoxy ethanol are still scanty.

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Experiments

Method

Densities, ρ at 303.15, 313.15 and 323.15 K were measured with Sprengel type Pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of ~0.1 cm. It was calibrated at 303.15, 313.15 and 323.15 K with double-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at the desired temperature ($\pm$0.01K) by means of a mercury-in-glass thermo-regulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The pycnometer was then removed from the thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during time of actual measurements. An average of triplicate measurements was taken into account. The density values were reproducible to $\pm$ 3 x 10^{-5} g cm^{-3}. Details have been described earlier[16]. The viscosity was measured by means of a suspended level Ubbelohde[17] viscometer at the desired temperature with a thermostat bath controlled to $\pm$0.01 K.

Sound velocities were determined with an accuracy of 0.3% using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz which was calibrated with water, methanol and benzene at each temperature, described in detail elsewhere[18,19]. The solutions studied here were made by mass, the conversion of molality into molarity was done[20].

Source and purity of samples

Tetrahydrofuran (Merck, India) was kept several days over KOH, refluxed for 24 hours and distilled over $LiAlH_4$ described earlier[1]. 2-Methoxy ethanol was allowed to stand overnight with $CaSO_4$ and distilled from sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenhydrazine to remove aliphatic ketones. Resorcinol (A.R.) was purified by the reported procedure[11] and the compound was dried and stored in a vacuum desiccator.

Results

The experimental values of concentration(c), densities (ρ), viscosities (η) and derived parameters at 303.15, 313.15 and 323.15 K are recorded in Table – 1.

The apparent molar volume (V_ϕ) were determined from the solution densities using the following equation,

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \qquad (1)$$

Table -1

Molar concentration, densities, viscosities, apparent molar volumes (v_ϕ), limiting apparent molar volume (v_ϕ^0), experimental slope (S_v^*) and values of A and B of resorcinol in various solvents at different temperatures

Resorcinol in ME

c/mol dm^{-3}	ρ/g cm^{-3}	η/cp	v_ϕ /cm^3 mol^{-1}	v_ϕ^0/cm^3 mol^{-1}	S_v^*/cm^3 $dm^{1/2}$ $mol^{-3/2}$	A/$dm^{3/2}$ $mol^{-1/2}$	B/dm^3 mol^{-1}
			303.15K				
0.008029	0.95834	1.40147	34.21621	21.7866	135.4508	0.02071	0.46342
0.05621	0.96104	1.43588	53.28075				
0.10438	0.96271	1.46825	65.04447				
0.15256	0.96348	1.50134	75.54179				
0.20074	0.96382	1.53721	83.23679				
0.24891	0.96401	1.57063	88.58110				
			313.15Ks				
0.007954	0.94935	1.21587	44.36590	34.1912	118.3329	-0.0273	0.48472
0.05566	0.95166	1.23826	62.06549				
0.10333	0.95303	1.26285	72.99709				
0.15105	0.95395	1.28926	80.17937				
0.19873	0.95418	1.31665	87.56597				
0.24644	0.95444	1.34376	91.96859				
			323.15K				
0.007893	0.94208	1.04675	55.04547	46.1865	106.6030	-0.0344	0.4940
0.05522	0.94401	1.06603	70.97192				
0.10247	0.94509	1.08673	80.97367				
0.14972	0.94556	1.10875	88.98941				
0.19699	0.94584	1.13195	94.18618				
0.24482	0.94624	1.15483	96.85475				
			Resorcinol in THF				
			303.15K				
0.0080634	0.8768	0.44945	5.36021	-7.46164	145.60272	0.079406	0.21908
0.05644	0.88083	0.45897	26.99526				
0.10482	0.88381	0.46680	40.09853				
0.15320	0.88611	0.47375	49.99311				
0.20159	0.88787	0.48075	58.19976				
0.24997	0.88934	0.48838	64.55114				

				313.15K			
0.007974	0.86708	0.41034	9.84666	-2.14684	140.23313	0.0152	0.25078
0.05580	0.87090	0.41594	31.32406				
0.10363	0.87381	0.42164	43.11721				
0.15415	0.87599	0.42677	53.02089				
0.19927	0.87764	0.43228	61.24157				
0.24715	0.87930	0.43740	66.24838				
				323.15K			
0.007906	0.86129	0.38944	14.45223	2.16829	139.40834	-0.01988	0.28058
0.05542	0.86494	0.39331	35.06637				
0.10291	0.86768	0.39780	46.99245				
0.15039	0.86981	0.40258	56.09555				
0.19782	0.87128	0.40736	64.69020				
0.24526	0.87258	0.41245	70.76840				

where M is the molecular weight of the solute, c is the molarity of the solution and the other symbols have their usual significance.

The limiting apparent molar volumes (V_ϕ^0) were calculated using the lease squares treatment of the plot of V_ϕ^* vs $c^{1/2}$ using the Masson equation[21].

$$V_\varphi = V_\varphi^0 + S_\upsilon^* c^{1/2} \tag{2}$$

Table – 2

Molal concentration (m), sound velocity (u), adiabatic compressibility (β), apparent molal adiabatic compressibility (ϕ_k), limiting apparent molal adiabatic compressibility (ϕ_k^0) and experimental slope (S_k^*) of resorcinol in various solvents at different temperatures

Resorcinol in ME

m/mol kg^{-1}	u/ms^{-1}	β x10^{10}/pa^{-1}	ϕ_k x10^7/m^3 mol^{-1} pa^{-1}	ϕ_k^0x 107/m^3 mol^{-1} pa^{-1}	S_k^*x10^7/m^3 $mol^{-3/2}$ pa^{-1} kg^{-1}
			303.15K		
0.008386	1302.42222	6.15144	-3.53056	-4.0552	6.01661
0.05889	1315.10976	0.01637	-2.60571		
0.10973	1323.69716	5.92826	-2.02055		
0.16115	1329.89488	5.86844	-1.58099		
0.21316	1335.37726	5.81830	-1.29114		
0.26576	1338.06352	5.79382	-1.00556		

			313.15K		
0.008386	1268.73567	6.54382	-4.17088		
0.05887	1282.8593	6.38552	-3.07110		
0.10973	1292.53715	6.28069	-2.4066	-4.8330	7.2967
0.16115	1299.04835	6.21189	-1.90114		
0.21316	1301.84487	6.18374	-1.4104		
0.26576	1304.96485	6.15253	-1.12253		
			323.15K		
0.008386	1240.67703	6.89596	-4.91245		
0.58870	1256.37339	6.71098	-3.61256		
0.10973	1267.15845	6.58969	-2.83223	-5.7239	8.7415
0.16115	1274.50031	6.51075	-2.23143		
0.21316	1277.51300	6.47816	-1.67623		
0.26576	1279.76619	6.45264	-1.30988		
			Resorcinol in THF		
			303.15K		
0.0092057	1252.90681	7.26544	-4.55220		
0.06453	1263.84373	7.10757	-3.25120		
0.12017	1270.90584	7.00510	-2.5363	-5.2802	7.9261
0.17625	1273.69507	6.95635	-1.8841		
0.23287	1274.80837	6.93044	-1.4088		
0.29005	1276.09679	6.90502	-1.10556		
			313.15K		
0.0092057	1193.59694	8.09516	-5.32146		
0.06453	1205.16882	7.90562	-3.90844		
0.12017	1211.94033	7.79149	-2.9865	-6.1470	8.9247
0.17625	1216.28610	7.71666	-2.3412		
0.23287	1218.31345	7.67654	-1.80601		
0.29005	1219.65271	7.64523	-1.4413		
			323.15K		
0.0092057	1148.06843	8.80897	-7.32857		
0.06453	1162.03754	8.56198	-5.20866		
0.12017	1169.80470	8.42197	-3.91044	-8.5072	13.02574
0.17625	1173.01666	8.35540	-2.90088		
0.23287	1174.41862	8.3514	-2.17714		
0.29005	1175.04828	8.33394	-1.67397		

Where V_ϕ^0 is the partial molar volume at infinite dilution and S_v^* the experimental slope.

The values of V_ϕ^0 and S_v^* along with temperature of resorcinol in solvents follows the polynomial-

$$V_\varphi^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Over the temperature range under investigation, where T is the temperature in Kelvin.

Values of coefficients of the above equation for resorcinol in pure THF and 2-methoxy ethanol are recorded in Table - 3.

Table – 3

Values of coefficient for resorcinol in THF and ME

Solvent	a_0/cm^3 mol^{-1}	a_1/cm^3 mol^{-1} K^{-1}	A_2/cm^3 mol^{-1}K^{-2}
THF	-643.094	3.61205	-4.9985×10^{-3}
ME	-548.5366	2.05172	-2.0465×10^{-3}

From the values of coefficients the following equations are obtained

Resorcinol in THF

$$V_\varphi^0 = -643.0947 / \text{cm}^3\text{mol}^{-1} + 2.50172\text{T} / \text{cm}^3\text{mol}^{-1}\text{K}^{-1} - 4.9985 \times 10^{-3} / \text{cm}^3\text{mol}^{-1}\text{K}^{-2} \quad (4)$$

Resorcinol in ME

$$V_\varphi^0 = -548.53663 / \text{cm}^3\text{mol}^{-1} + 2.50172\text{T} / \text{cm}^3\text{mol}^{-1}\text{K}^{-1} - 2.0465 \times 10^{-3} / \text{cm}^3\text{mol}^{-1}\text{K}^{-2} \quad (5)$$

The apparent molar expansibilities (ϕ_E^0) can be obtained by the following equation.

$$\varphi_E^0 = \left(\frac{\delta V_\varphi^0}{\delta T}\right)p = a_1 + 2a_2 T \quad (6)$$

The values of ϕ_E^0 of the studied compound at 303.13, 313.15 and 323.15K are determined and reported in table – 4.

Table – 4

Limiting apparent molar expansibilities (ϕ_E^0) for resorcinol in THF and ME at different temperatures

Solvents	303.15K	313.15K	323.15K	$(\delta^2 V_\phi^0/dT^2)\rho$
THF	0.57262	0.49035	0.40809	Negative
ME	1.26093	1.21999	1.17907	Negative

Helper[22] developed a technique of examining the magnitudes of $(\delta^2V_\phi^0/\delta T^2)_p$ for solute in terms of long range structure-making and breaking capacity of the solutes in mixed solvent systems using the general thermodynamic expression.

$$(\delta c_p/\delta P) = -(\delta^2V_\phi^0/\delta T^2)_p \qquad (7)$$

The viscosity of resorcinol in pure THF and in pure-2-methoxy ethanol have been analyzed using the Jones-Dole[23] equation:

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \qquad (8)$$

$$\left(\frac{\eta}{\eta_0} - 1\right)/c^{1/2} = A + Bc^{1/2}$$

where $\eta = \left(Kt - \frac{L}{t}\right)\rho$

where, η_0 and η are the viscosities of solvent and solution respectively. K and L are the constants for a particular viscometer. The values of A and B are estimated by computerized least square method and recorded in table 1.

Adiabatic compressibility (β) was calculated from the following relation.

$$\beta = \frac{1}{u^2\rho} \qquad (9)$$

where ρ is the solution density and u is the sound velocity in the solution. The apparent molal adiabatic compressibility (ϕ_k) of the solution was determined from the relation.

$$\phi_K = M\beta/\rho_0 + 1000(\beta\rho_0 - \beta_0\rho)/m\rho\rho_0 \qquad (10)$$

The limiting apparent molal adabatic compressibility (ϕ_k^0) was obtained by extraploting the plots of (ϕ_k) versus the square root of molal concentration of the solute to zero concentration by the computerized least square method.

$$\varphi_K = \varphi_K^0 + S_K^* m^{1/2} \qquad (11)$$

where Sk^* is the experimental slope.

The values of u, β, ϕ_k, ϕ_k^0 and Sk^* are recorded in Table 2.

Discussion

We have determined the ρ and η and calculated the V_ϕ, V_ϕ^0, S_V^*, ϕ_k, ϕ_k^0, B and A at 303.15, 313.15 and 323.15K using appropriate equations and graphical diagrams.

As the investigated systems are characterized by hydrogen bond, the solute-solvent and solute-solute interactions can be interpreted in terms of structural changes which arise due to hydrogen bond interactions present between various components of the solvent and solute-solute interactions can be interpreted in terms of structural changes which arise due to hydrogen bond interactions present between various components of the solvent and solution systems.

To examine the solute-solvent interactions, the V_ϕ^0 can be used. Table-1 and Figs. I and III in case of ME reveals that the V_ϕ^0 values are positive and increase with rise in temperature. This indicates the presence of strong solute-solvent interaction and these interactions are strengthened with rise in temperature. Whereas in case of THF the V_ϕ^0 values are small at various temperatures and the values of V_ϕ^0 increase with increase of temperature. This indicates the presence of weak solute-solvent interaction and such interaction increases with rise of temperature. Similar results were obtained for some 1:1 electrolyte in aqueous DMF[24] and aqueous THF[1].

Fig. I: Plot of ϕ_V^0 and S_V^* vs. Temperature of resorcinol in ME

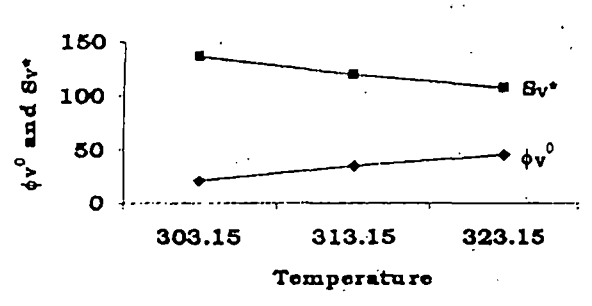


Fig. II: Plot of A and B vs. Temperature of resorcinol in ME

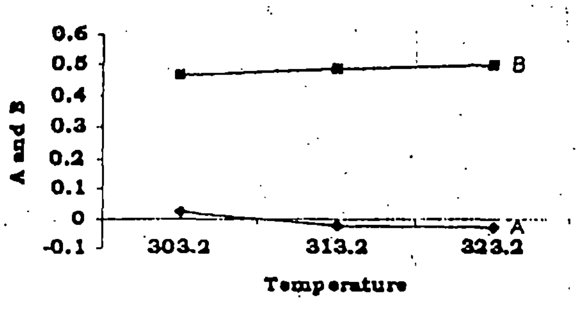


Fig. III: Plot of ϕ_V^0 and S_V^* vs. Temperature of resorcinol in THF

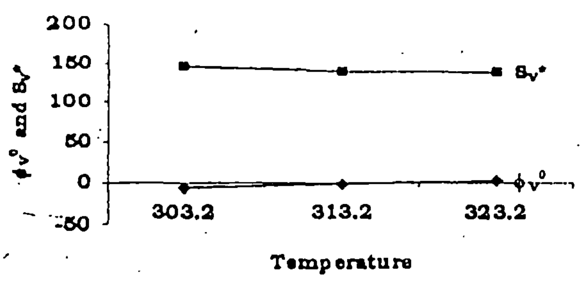
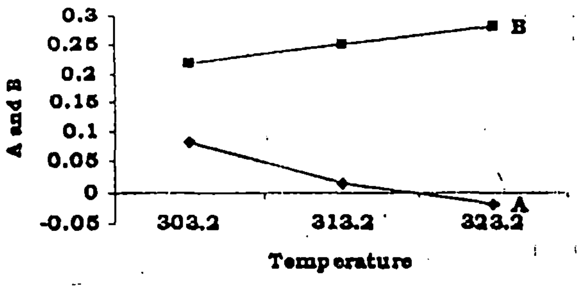


Fig. IV: Plot of A and B vs. Temperature of resorcinil in THF



It is also evident (Table-1 and Figs. I and III) that S_V^* are positive in both systems at different temperatures. Since S_V^* is a measure of solute-solute interactions, the results indicate the presence of strong solute-solute interaction. As expected, the S_V^* values decrease with increasing temperature in these solvents for the studied solute, which is attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of solute-solute interactions[25].

It is found from Table 4 that the value of ϕ_E^0 of solute decreases with rise in temperature in studied solvents, which can be ascribed to the absence of caging or packing effect.[26]

In our present investigations, it is evident from Table 4 that the $(\delta^2 V_\phi^0/\delta T^2)\rho$ values are negative for resorcinol in studied solvents, suggesting thereby that resorcinol acts as a structure-breaker in such solvents.

It is observed (Table 1 and Figs. II and IV) that the values of B of resorcinol in the studied solvent systems are positive and these values increase with increasing temperature. This indicates that this solute acts structure-breaker in such solvents. These conclusions are excellent agreement with that drawn from magnitude of $(\delta^2 V_\phi^0/\delta T^2)$ illustrated earlier.

It has been reported by a number of workers that dB/dT is a better criterion [27,28] determining the structure making/breaking nature of any solute rather than simply the value of B. It is found from Table 1 that the values of B increase with rise in temperature (positive dB/dT) suggesting structure-breaking tendency.

A similar result was reported by some workers[29] in studied solvents in case of viscosity of some salts in propionic acid + ethanol mixtures.

Fig. V: Plot of ϕ_k^0 and S_k^* vs. Temperature of resorcinol in ME

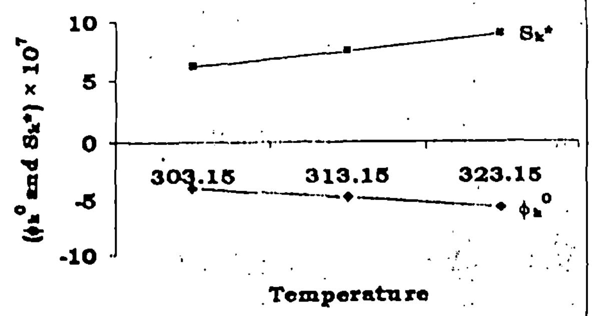
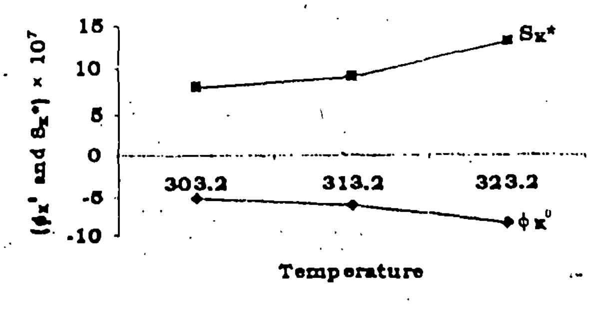


Fig. VI: Plot of ϕ_K^0 and S_K^* vs. Temperature of resorcinol in THF



A perusal of Table 2 and Figs. V and VI show that the values of ϕ_K^0 are negative and become more negative on increasing the temperature. Negative ϕ_K^0 values of resorcinol can be interpreted in terms of the loss of compressibility of solvents due to electrostrictive forces in the vicinity of the solute particles. On raising the temperature of the system, the solute particles lose some solvent molecules from their first coordination sphere in a process, which is expected to increase the compressibility. But at higher temperature, breakdown of the non-covalent bonding between the solvent molecules also takes place more effectively resulting in a loss of compressibility. Thus it may be concluded that for the solute solution under study, the latter effect is growing faster and overriding the former as far as the present temperature range is concerned. From Table 2 (figs. V and VI), it is evident that S_K^* have positive values indicating the existence of strong solute-solute interactions in the studied solvent system which resembles the agreement drawn from S_v^* discussed earlier. A similar results were reported by work[30] in the case of ultrasonic studies of some alkali metal halides and nitrates in THF + Water mixture.

List of Symbols

ρ : Density of solution
ρ_0 : Density of solvent
η : Viscosity of solution
η_0 : Viscosity of solvent
c : Molar concentration of solution
m : Molal concentration of solution
u : Sound velocity of solution
u_0 : Sound velocity of solvent
β : Adiabatic compressibility of solution
β_0 : Adiabatic compressibility of solvent
ϕ_K : Apparent molal adiabatic compressibility
ϕ_K^0 : Limiting apparent molal adiabatic compressibility
S_K^* : Experimental slope
V_ϕ : Apparent molar volume
V_ϕ^0 : Limiting apparent molar volume
S_V^* : Experimental slope
M : Molecular weight of solute
ϕ_E : Apparent molar expansibility
ϕ_E^0 : Limiting apparent molar expansibility
ME : 2-Methoxy ethanol
THF : Tetrahydrofuran

References

1. M.N. Roy, A. Jha and R. Dey; J. Chem. Eng. Data, 46 (2001) 1247.
2. M.N. Roy and B.B. Gurung; J. Indian Chem. Soc. 81 (2004) 1.
3. K. Masayuki and N. Kastutosh; J. Chem. Eng. Data, 46 (1995) 935.
4. F.J. Millero; 'In structure and transport process in water and aqueous solution'; R.A. Horne, New York, 1972.
5. R. Jasinki; High Energy Batteries, Plenum Press, New York, 1967.
6. M.N. Roy and D.K. Hazra, Indian J. Chem. Technol. 1 (1994) 93.
7. M.N. Roy; J. Tech. and Res., 7 (2000) 17.
8. A. Sacco, M.D. Monika and A.D. Giglio; J. Chem. Soc. Faraday Trans. 1, 9 (1983) 2631.
9. C.G. Janz and R.P.T. Tomkins; Non-aqueous Electrolytes Handbook, Academic Press, New York, 2 (1973)
10. M.L. Parmar, V.N. Rao and S.K. Bhardwaj; J. Indian. Chem. Soc. 97 (1990) 591.
11. P. Franzosini and F.W. Falgar; J. Chem. Thermodynamics, 16 (1984) 81.
12. T.V. Chalkian, A.P. Sarvasyan and K.J. Breslauer; J. Phys. Chem. 97 (1993) 1301.
13. M.N. Roy, D. Nandi and D.K. Hazra; J. Indian Chem. Soc., 70 (1993) 1123.
14. D.P. Kharakoz; Biophys. Che,. 34 (1989) 115.
15. T.S. Banipal and P. Kanpoor; J. Indian Chem. 76 (1999) 341
16. M.N. Roy, B. Das and D.K. Hazra; Indian Chem. 76 (1999) 341.

17. J.R. Sunindells and T.B. Godfray; J. Res. Natt. Bur. Stand. 1 (1952) 48.

18. K. Tamura, K. Ohomura and S. Murakami; J. Chem. Thermodyn. 15 (1983) 859.

19. M.N. Roy and B.B. Gurung; J. Indian Chem. Soc. 80 (2003) 1.

20. D.P. Shoemaker and C.W.S. Gorland; "Experiments in Physical Chemistry"; McGraw Hill, New York, 131 (1967).

21. D.O. Masson; Phil. Mag. 8 (1929) 218.

22. L.G. Hepler; Can. J. Chem. 47 (1969) 4617.

23. G. Johnes and M. Dole, J. Am. Chem. Soc. 51 (1929) 2950.

24. E. Gorland-Paneda, C. Yanes and J.J. Calventa; J. Chem. Soc. Faraday Trans. 94 (1994)573.

25. F.J. Millero; 'In structure and transport process in water and aqueous solution'; R.A. Horne, New York, 1973.

26. P.R. Misra and B. Das; Indian J. Chem. 16 (1978) 348.

27. R. Gopal and M.A. Siddique; J. Phy. Chem. 72 (1997) 1814.

28. N. Saha and B. Das; J. Chem. Eng. Data, 42 (1997) 277.

29. M.L. Parmer and M.K. Chouhan; Indian J. Chem. 34A (1995) 434.

30. M.N. Roy and D.K. Hazra; N.B. Univ. Rev. (Sci and Technol.), 8 (1997) 54.

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Electrical conductance of alkali chlorides in mixed solvents : Methanol + carbon tetrachloride and methanol + 1,4-dioxane at 298.15 K

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Abstract : Conductance measurements for selected alkali metal chlorides, MCl (M^+ = Li, Na, K) are performed in the binary mixtures of methanol with carbon tetrachloride and 1,4-dioxane at 298.15 K. The limiting equivalent conductance (Λ_0), the association constant (K_A), and the Walden products ($\Lambda_0\eta_0$) for the three salts are evaluated at all the mole fractions of the solvent mixtures using the 1978 Fuoss conductance-concentration equation. Analysis of data indicates presence of strong association of the electrolytes in the solvent mixtures studied here. The results have been discussed and interpreted in terms of ion-solvent interactions and structural changes in the mixed solvent systems.

Keywords : Methanol, mixed solvents, association constant, ion-solvent interactions, ion-ion interactions.

Study of electrical conductance of mixed organic solvent systems plays a significant role in examining the nature and magnitude of ion-ion and ion-solvent interactions[1-7]. Other solvent properties such as the viscosity and permittivity have also been taken into account in determining the extent of these interactions.

1,4-Dioxane is a good industrial solvent and figures prominently in the high-energy battery technology[8] and has also found its application in the organic syntheses[9,10-12]. Carbon tetrachloride is used to make compounds such as chlorofluoromethanes, used as refrigerants and aerosol-spray propellants, in fire extinguishers and for dry cleaning of fabrics. Methanol is very widely used in industry, including the manufacture of pharmaceuticals and cosmetic products, in enology and as an energy source[13].

The alkali metal salts, specially, Li salts has been used for many years in non-aqueous batteries[8]. In such systems, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte possessing high specific conductivity and, hence, minimal ion-ion interaction is required to maintain the cell at low resistance. Knowledge of the application of the solvent and solute studied and the state of association of the electrolytes and their interactions with solvent molecules is essential for the optimal choice of solvent and electrolyte[14].

Methanol is extremely self-associated by hydrogen bonding in pure state[15]. But, this type of strong intermolecular forces are either very week or totally absent in case of carbon tetrachloride or 1,4-dioxane while the dipole-induced dipole forces along with dispersive forces predominate in these cases.

The conductance and viscosity of three alkali chlorides is studied to reveal the nature of ionic association and mobility of ions in these mixed solvent systems, which have not been studied earlier as per available literautre.

In the present work, an attempt has been made to ascertain the complete nature of ion-solvent, solvent-solvent interactions of the alkali metal chlorides in solvent mixtures of methanol with carbon tetrachloride and 1,4-dioxane at 298.15 K. A comparison between the natures of interactive forces operating in these two different solvent systems is also analyzed.

Results and discussion

The physical properties of the pure solvent and solvent mixtures are given in Table 1, where ε is the dielectric constant, ρ_0 is the density (kg m^{-3}) and η_0 is the viscosity (mPa.s). Conductivities of electrolyte solutions as a function of molar concentration (*c*) are given in Table 2 in different solvent mixtures at 298.15 K.

Permittivity (ε) of the solvent-mixtures were estimated by a computerized extrapolation programme, using ε and W% values from literature[14]. The conductance data have

Table 1. Physical properties of solvent mixtures at 298.15 K

Mass% of methanol	x_1	ε	$\rho_0 \times 10^{-3}$ /Kg m^{-3}	η_0 /mPa.s
Methanol + carbon tetrachloride				
100.00	1	32.66	0.7866	0.5470
90.60	0.97885	26.72	1.0313	0.5672
82.31	0.95712	22.22	1.0401	0.5875
66.89	0.90657	15.31	1.0405	0.6438
Methanol + 1,4-dioxane				
100.00	1	32.66	0.7866	0.5470
90.60	0.96364	29.12	0.8058	0.5589
82.31	0.92747	26.41	0.8225	0.5488
66.89	0.84752	21.25	0.8570	0.5684

Table 2. Electrical conductance Λ as a function of concentration c for alkali chlorides in mixed solvents at 298.15 K

$c \times 10^4$ mol dm^{-3}	Λ/S cm^2 mol^{-1}	$c \times 10^4$ mol dm^{-3}	Λ/S cm^2 mol^{-1}	$c \times 10^4$ mol dm^{-3}	Λ/S cm^2 mol^{-1}
Methanol + carbon tetrachloride					
x_1 = 1.0000					
LiCl		NaCl		KCl	
12.35	83.2	12.54	89.1	13.53	94.2
21.17	76.8	21.49	83.3	23.20	87.7
27.79	72.6	28.21	79.4	30.45	84.5
32.94	69.2	33.43	76.6	36.09	81.4
37.06	67.5	37.61	74.3	40.06	79.4
40.43	65.8	41.03	73.1	44.29	78.2
43.24	64.9	43.88	71.8	47.37	77.2
45.62	63.6	46.29	70.6	49.97	75.6
47.66	62.6	48.36	69.6	52.20	74.9
49.42	62.4	50.15	68.7	54.13	74.6
50.96	61.8	51.72	67.7	55.82	74.1
52.32	60.9	53.1	67.1	57.31	73.5
x_1 = 0.97885					
6.37	82.7	7.76	86.8	7.74	92.3
10.92	76.6	13.3	80.3	13.26	85.5
14.33	72.9	17.46	76.8	17.40	82.0
16.99	70.2	20.69	74.1	20.62	79.8
19.11	67.8	23.28	71.7	23.20	77.6
20.85	66.2	25.39	70.0	25.31	75.8
22.30	65.1	27.15	68.7	27.07	74.8
23.53	63.8	28.64	67.4	28.56	74.0
24.58	62.9	29.92	67.2	29.84	73.3
25.49	62.4	31.03	66.0	30.94	72.7
26.29	61.6	32.00	65.3	31.91	72.0
26.99	61.0	32.86	65.0	32.76	71.5
x_1 = 0.95712					
LiCl		NaCl		KCl	
4.44	80.5	4.40	83.4	4.50	87.6
7.61	76.6	7.54	78.5	7.72	80.8
9.99	74.4	9.86	76.0	10.13	76.8
11.84	72.9	11.73	73.2	12.01	74.0
13.32	71.9	13.20	72.0	13.51	72.2
14.53	70.8	14.40	71.0	14.74	70.5
15.54	70.1	15.40	69.8	15.76	69.4
16.39	69.5	16.25	69.1	16.63	68.6
17.12	69.1	16.98	68.5	17.37	68.3
17.75	68.7	17.61	68.0	18.01	66.9
18.30	68.3	18.16	67.4	18.57	66.6
18.79	68.1	18.64	66.8	19.07	66.0
x_1 = 0.90657					
1.57	50.8	6.1	47.5	1.53	70.6
2.69	47.4	10.5	37.3	2.61	67.1
3.53	45.6	13.8	31.3	3.64	63.8
4.19	44.0	16.3	27.3	4.26	61.8
4.71	43.3	18.4	24.6	4.74	60.0
5.13	42.3	20.0	21.6	5.14	58.9
5.49	42.0	21.4	20.0	5.48	58.0
5.79	41.8	22.6	18.6	5.76	57.3
6.05	41.5	23.6	17.5	6.02	57.0
6.28	40.7	24.5	16.0	6.21	56.0
6.48	40.7	25.3	15.2	6.40	55.2
6.65	40.3	26.0	14.6	6.56	55.4
Methanol + 1,4-dioxane					
x_1 = 0.96364					
10.11	102.1	10.22	97.3	9.52	100.4
17.33	100.5	17.51	91.2	16.32	95.8
22.75	99.5	22.98	89.1	21.42	92.9
26.96	98.6	27.23	86.7	25.39	91.1
30.30	98.1	30.63	85.1	28.57	89.5
33.09	97.7	33.42	84.1	31.17	88.3
35.39	97.4	35.74	83.1	33.33	87.5
37.34	97.2	37.70	82.3	35.16	86.8
39.01	96.9	38.38	81.8	36.73	86.1
40.45	96.7	40.48	81.3	38.09	85.9
41.71	96.5	42.12	80.9	39.28	85.3
42.83	96.4	43.25	80.5	40.33	85.1
x_1 = 0.97747					
9.68	96.8	9.84	98.3	7.89	96.9
16.60	93.3	46.86	93.6	13.52	92.9
21.79	91.1	22.13	90.6	17.75	90.5
25.82	89.5	26.23	88.8	21.04	88.5

Table-2 (contd.)

Table-2 (contd.)

LiCl		NaCl		KCl	
29.05	88.5	29.51	87.1	23.67	87.0
31.69	87.3	32.19	85.8	25.82	86.1
33.89	86.9	34.43	84.9	27.61	85.5
35.75	86.2	36.32	84.1	29.13	84.5
37.35	85.7	37.94	83.6	30.43	84.1
38.73	85.5	39.34	83.1	31.56	83.6
39.94	85.2	40.57	82.6	32.55	83.1
41.01	84.9	41.65	82.3	33.42	82.7
		$x_1 = 0.97747$			
3.62	87.9	3.59	89.5	3.85	91.4
6.20	84.7	6.16	85.9	6.60	87.0
8.14	82.7	8.09	83.5	8.66	84.6
9.65	81.2	9.59	81.8	10.26	82.6
10.85	80.2	10.79	81.2	11.54	81.6
11.84	79.4	11.77	80.0	12.59	80.5
12.66	78.7	12.59	79.2	13.46	79.7
13.35	78.2	13.28	78.7	14.20	79.0
13.94	77.7	13.87	78.2	14.83	78.7
14.46	77.2	14.38	77.8	15.38	78.2
14.91	76.8	14.83	77.3	15.86	77.9
15.31	76.5	15.23	77.1	16.28	77.5

been analyzed by Fuoss conductance-concentration equation (Fuoss, 1978a,b)[16,17].

$$\Lambda = P\,[\Lambda_0\,(1 + R_x) + E_L] \qquad (1)$$

$$P = 1 - \alpha\,(1 - \gamma) \qquad (2)$$

$$\gamma = 1 - K_A\, c\gamma^2 f^2 \qquad (3)$$

$$-\ln f = \beta\kappa/2\,(1 + \kappa R) \qquad (4)$$

$$\beta = e^2/\varepsilon k T \qquad (5)$$

$$K_A = K_R/(1 - \alpha) = K_R\,(1 + K_s) \qquad (6)$$

where, R_x is the relaxation field effect, E_L is the electrophoretic counter current, κ^{-1} is the radius of the ion atmosphere, ε is the relative permittivity of the solvent, e is the electron charge, k is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, f is the activity coefficient, c is the molarity of the solution, T is the absolute temperature, β is twice the Bjerrum distance, and a denotes the fraction of the paired ions, K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter 'R' around cations, and K_s is the constant describing the short range process by which contact pairs form and dissociate. K_R and K_s are given as follows,

$$K_R = (1 - \alpha)\,(1 - \gamma)/c\,\gamma^2 f^2 \qquad (7)$$

$$K_s = \alpha/(1 - \alpha) \qquad (8)$$

The computations were performed in a computer using the programme suggested by Fuoss. The initial Λ_0 values for iteration procedure were obtained from Shedlovsky extrapolation[19] of the data. Input for the program is the set, $(C_j, \Lambda_j; j = 1, \text{-----}, n)$, n, ε, η, T, initial value of Λ_0, and a set of instructions to cover a protected range of R values.

In practice, calculations were performed by fitting the values of Λ_0 and σ, which minimize the standard deviation (σ),

$$\sigma^2 = \Sigma\,[(\Lambda_{j\,\text{calc.}} - \Lambda_{j\,\text{obs.}})^2/(n - 2)] \qquad (9)$$

for a sequence of R values and then plotting σ against the best-fit R corresponds the minimum of σ versus R curve. First, approximate run over a fairly wide range of R values are made to locate the minimum and then a fine scan around the minimum was made. Finally with this minimizing value of R, corresponding Λ_0 and K_A were calculated.

In the present analysis, however, since a rough scan of R values gave no significant minima in the (σ% vs R) curves, the R value was assumed to be, $R = a + d$ where, a is the sum of crystallographic radii and d, the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by[17],

$$d\,(\text{Å}) = 1.183\,(M/\rho_0)^{1/3} \qquad (10)$$

where, M is the molar weight of the solvent and ρ_0 is its density. In mixed solvent studies M is replaced by the mole fraction average molecular weight (M_{AV}). given by,

$$M_{AV} = M_1 M_2/(W_1 M_2 + W_2 M_1) \qquad (11)$$

where, W_1, W_2 and M_1, M_2 are the weight fraction and molecular weight of the first and second component respectively. Though, this is an over simplification ignoring possible selective solvation, it at least provides a self consistent way to obtain an acceptable value for the parameter when a broad range of R values fits the data.

The limiting equivalent conductance, (Λ_0) , the association constant (K_A), and the Walden products ($\Lambda_0\eta_0$) for the three salts at all the mole fractions of the solvent mixtures studied here are given in Table 3. These data are interpreted in terms of ion-solvent and ion-ion interactions and structural changes in the mixed solvent systems.

It is observed from Table 3 that, the limiting equivalent conductance (Λ_0) values for alkali chlorides increases with the increase in size of the cation for any mole fraction of the mixed solvent systems. For the three alkali chlorides, having common anion, the Λ_0 value is enhanced by the following order :

$Li^+ < Na^+ < K^+$

The trend of variation of Λ_0 values predicts the relative actual sizes of these ions as they exist in solution[18]. Thus the actual sizes of the cations as they exist in solution, follow the order ;

$Li^+ > Na^+ > K^+$

This is due to solvation of the ions by the solvent mixtures. For these electrolytes having the common anion, as the size of the cation increases, the solvation decreases. So, it can be said that, Li^+, which has the largest size in solution, is the most solvated one, and K^+, having the smallest size is the least solvated one[19].

The conductivity enhancement in case of solvent mixtures can qualitatively be well explained by a favorable combination of high permittivity and low viscosity of solvents as observed by some researchers[20]. In the discussed solvent mixtures, methanol is the common solvent having higher permittivity compared to 1,4-dioxane or

Table 3. Values of derived conductance parameters (Λ_0, K_A, R, $\Lambda_0\eta_0$, σ) for alkali chlorides in mixed solvents at 298.15 K

Mass% of methanol	x_1	Λ_0 /S cm^2 mol^{-1}	K_A /dm^3 mol^{-1}	R /Å	Walden product ($\Lambda_0\eta_0$)	σ
			LiCl/methanol + carbon tetrachloride			
100.00	1	108.25 ± 0.50	328.34 ± 0.51	6.38	59.21	0.51
90.60	0.97885	106.79 ± 0.71	492.40 ± 0.71	6.14	60.57	0.71
82.31	0.95712	90.54 ± 0.10	570.23 ± 0.10.	6.23	53.19	0.10
66.89	0.90657	60.22 ± 0.18	642.41 ± 0.18	6.43	38.77	0.18
			NaCl/methanol + carbon tetrachloride			
100.00	1	111.85 ± 0.79	253.35 ± 0.79	6.73	61.18	0.50
90.60	0.97885	110.79 ± 0.67	447.99 ± 0.67	6.49	62.84	0.33
82.31	0.95712	98.23 ± 0.33	460.91 ± 0.10	6.58	57.71	0.10
66.89	0.90657	72.23 ± 1.31	481.35 ± 1.31	6.78	46.50	1.31
			KCl/methanol + carbon tetrachloride			
100.00	1	113.77 ± 0.15	187.62 ± 0.15	7.11	62.22	0.15
90.60	0.97885	112.18 ± 0.31	344.69 ± 0.31	6.87	63.63	0.31
82.31	0.95712	103.22 ± 0.49	565.86 ± 0.49	6.96	60.64	0.49
66.89	0.90657	86.32 ± 0.34	776.44 ± 0.34	7.16	55.57	0.34
			LiCl/methanol + 1,4-dioxane			
100.00	1	108.65 ± 0.51	328.34 ± 0.51	6.38	59.21	0.51
90.60	0.96364	107.35 ± 0.04	335.18 ± 0.04	6.43	59.99	0.04
82.31	0.92747	103.39 ± 0.11	341.24 ± 0.11	6.48	56.75	0.11
66.89	0.84752	96.85 ± 0.17	434.19 ± 0.17	6.69	55.05	0.17
			NaCl/methanol + 1,4-dioxane			
100.00	1	111.85 ± 0.79	253.35 ± 0.79	6.73	61.18	0.79
90.60	0.96364	110.92 ± 0.26	241.87 ± 0.26	6.78	61.99	0.26
82.31	0.92747	106.21 ± 0.16	284.22 ± 0.16	6.83	58.29	0.16
66.89	0.84752	99.22 ± 0.28	370.31 ± 0.17	6.94	56.40	0.17
			KCl/methanol + 1,4-dioxane			
100.00	1	113.77 ± 0.15	187.62 ± 0.15	7.11	62.22	0.15
90.60	0.96364	112.72 ± 0.16	248.24 ± 0.16	7.16	63.02	0.16
82.31	0.92747	108.63 ± 0.21	254.63 ± 0.21	7.21	59.62	0.21
66.89	0.84752	101.45 ± 0.08	429.15 ± 0.08	7.32	57.66	0.08

carbon tetrachloride. In both the solvent mixtures the conductivity measurements were done by taking the same salts. So, the combination of a solvent of higher permittivity (methanol) with the one having low viscosity (1,4-dioxane) has comparatively higher mobility resulting in higher conductivity values.

The associations constant (K_A), as recorded in Table 3 indicates that, all the salts are highly associated in both the solvent mixtures. This is as expected because of the lower permittivity of the components added[21]. For the alkali metal chlorides studied here, the K_A values decreases with increasing size of the cations in the order :

$Li^+ < Na^+ < K^+$.

This is due to an apparent decrease in ion dipole interactions[5,22,23].

It is further seen from Table 3 that Λ_0 values decrease gradually with the addition of CCl_4 or 1,4-dioxane to pure methanol with corresponding increase in K_A values. This indicates that association of ions increase with the addition of 1,4-dioxane or CCl_4 to pure methanol rendering to the decrease of the mobility of ions in the mixture and thereby decreasing Λ_0 values. The significantly large values of K_A and exothermic ion-pair formation in the solvent mixture indicate the presence of specific short-range interaction within the ion-pair.

The values of Walden product ($\Lambda_0\eta_0$) for the studied electrolytes pass through a maximum at about 0.97885 mole fraction of methanol, in methanol carbon tetrachloride solvent system, whereas for, methanol, 1,4-dioxane solvent system, the Walden product is maximum at 0.96364 mole fraction of methanol (Table 3). The Walden products then decrease continuously for all the lower mole fractions. The representative plots for the selected chlorides for solvent mixture 1, (methanol + carbon tetrachloride) is given in Fig. 1, and that for solvent mixture 2, (methanol + 1,4-dioxane) is given in Fig. 2.

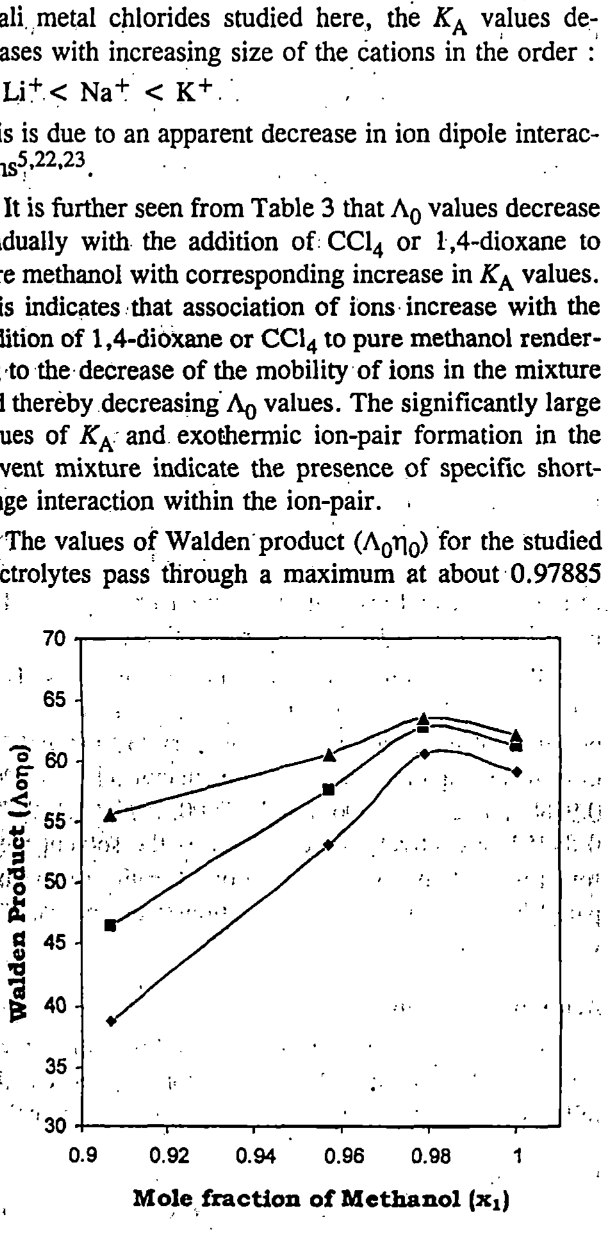

Fig. 1. Walden products for several alkali metal cations (◆ = LiCl, ■ = NaCl, ▲ = KCl) as a function of the mole fraction of methanol in methanol-CCl_4 solvent mixture.

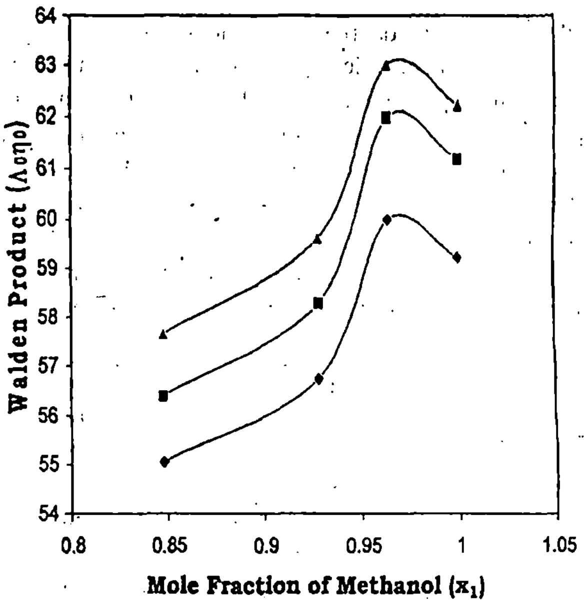

Fig. 2. Walden products for several alkali metal cations (◆ = LiCl, ■ = NaCl, ▲ = KCl) as a function of the mole fraction of methanol in methanol-DO solvent mixture.

There are lots of models to account for the dependence of the Walden product on solvent composition. The theory based on "gel effect"[24,25], proposes that, the initial increment in ($\Lambda_0\eta_0$) is due to migration process, occurring free of viscous force through the interstices created by long range order in the solvent. Some researchers[26] have also put forward a 'sorting mechanism' depending upon the 'acid base properties' of the organic solvent. It is suggested that, in this experiment, ion-methanol interactions are stronger than ion-carbon tetrachloride or ion-1,4-dioxane interactions presumably because of the weaker acid-base properties of the later two solvent components. The theory envisages a comparative enrichment of methanol in the ionic cosphere and this causes the local viscosity near the ions to be lower than the bulk viscosity of the solvent medium, which in turn increases the mobility and as a result the Walden product appears higher for the next solvent mixtures. The theories based on solvent-dipole relaxation effect[27,28] can be used to explain the decrease in Walden product ($\Lambda_0\eta_0$) as the carbon tetrachloride or 1,4-dioxane concentration in the solvent mixture increases. It is generally accepted that, retardation due to relaxation of solvent dipoles around the ions in motion can decrease their mobility and the dielectric-shifting coefficient can be computed. However, to obtain meaningful data, it is essential to take into account the microscopic nature of the solvent in the vicinity of the ions as also the influence of the ions in the structure of the solvent.

There is another proposed scheme based on the assumption that, the progressive addition of carbon tetrachloride or 1,4-dioxane to methanol causes initial contraction of the solvation sheath around the ions present in solvent media. This "desolvation effect"[24,29] decreases the effective size of the cations and anions and as a result, the ionic mobility and Walden product of the salts can increase initially in the methanol rich region of the mixture. Gluekuf[30], has noted that, as the ion size decreases, its first solvation sheath also contracts and therefore the friction between this layer and the ion increases. It appears that, this enhanced drag of the solvation layer decreases the mobility and so the Walden product ($\Lambda_0\eta_0$) shows a maximum at a particular solvent composition and then decreases monotonously. Extensive solvation of the ions with carbon tetrachloride or 1,4-dioxane can also decrease the mobility of the ions but this process is significant at higher concentration of carbon tetrachloride or 1,4-dioxane in the solvent mixture and helps in the continuous decrease of Walden product ($\Lambda_0\eta_0$).

It should still be mentioned[25] that, the theories discussed here or other contemporary theories do not predict quantitatively either the value of the maximum or its enhanced dependence for certain electrolytes in different solvent medium.

Experimental

Lithium chloride (Merck, India) was recrystallized from conductivity water, dried for several hours at 403 K and stored in a vacuum desiccator. Sodium chloride (Loba Chemie) was dried for 48 h under reduced pressure in presence of P_2O_5 at 473 K without preceding purification and stored under dry nitrogen. Potassium chloride (Merck, India); crystals were dissolved in conductivity water, filtered, saturated with chlorine and precipitated by HCl after boiling off excess chlorine. The precipitate was washed, dissolved in conductivity water, recrystallized by cooling to 268 K, dried at room temperature in a vacuum desiccator, fused under dry nitrogen, cooled and stored in a desiccator.

Methanol (Merck, India, Uvasol grade, 99.5% pure) was dried over 3 Å molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. Carbon tetrachloride (Merck, India) was shaken vigorously with potassium hydroxide for several hours and was washed with water. This step was repeated for several times and then shaking was done with concentrated sulphuric acid until there was no further coloration, washed again with water, dried with $CaCl_2$, and distilled over P_2O_5. 1,4-Dioxane (Merck, India) with initial water content of 120 ppm found by Karl-Fischer titration and 0.15% impurities found by gas chromatography was used after redistillation[10].

Digital Temperature controller BP-41 (Bose-Panda Instruments, India) (±0.01K) was used to maintain the temperatures. Conductance measurements of the solvent systems were executed in a Systronic 308 conductivity-TDS meter (accuracy ±0.1%) working at a frequency of 1 kHz, using a dip type immersion cell (cell constant 1.07 at 298.15 K). Densities (ρ) were measured at the mentioned temperatures with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. Viscosities (η) have been measured by means of a suspended Ubbelohde type viscometer[31]. The details of density and viscosity measurements were described earlier[9,23]. The precision of the density and viscosity measurements is $\pm 3 \times 10^{-4}$ g cm^{-1} and $\pm 2 \times 10^{-4}$ mPa.s respectively.

All the solvent mixtures were prepared by mass. Three sets of each binary solvent mixtures (90.6%, 82.31%, 66.89%) of methanol with carbon tetrachloride and 1,4-dioxane having mole fractions of methanol (x_1) as 1.0000, 0.97885, 0.95712, 0.90657 and 1.0000, 0.96364, 0.92747, 0.84752 respectively were chosen as the solvent media for present study. A stock solution of each salt was prepared by mass and working solutions were prepared by weight dilution.

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References

1. P. K. Muhuri and D. K. Hazra, *J. Phys. Chem.*, 1995, **190**, 111.
2. A. K. Srivastava and R. A. Samanta, *J. Chem. Engg. Data*, 1994, **39**, 358.

3. H. Doe, H. Ohe, H. Matuba, A. Ichimura and T. Kitagawa, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2785.
4. S. Taniewska-Osinska, A. Piekarska, A. Bald and A. Szeigis, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 3709.
5. N. Islam, S. B. A. Jaldi and A. A. Ansari, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 309.
6. N. Papadopoulos, *Can. J. Chem.*, 1989, **67**, 1624.
7. M. S. K. Niazi, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 309.
8. R. Jasinski, "High Energy Batteries", Plenum Press, New York, 1967.
9. M. N. Roy, A. Jha and R. Dey, *J. Chem. Engg. Data*, 2001, **46**, 1247.
10. C. G. Janz and R. P. T. Tomkins, "Non-aqueous Electrolytes Handbook", Academic Press, New York, Vol. 2, 1973.
11. M. N. Roy, *J. Teach. Res. in Chem.*, 2000, **7**, 17.
12. M. N. Roy and D. K. Hazra, *Indian J. Chem. Technol.*, 1994, **1**, 93.
13. B. Sinha, A. Sinha, A. Jha and M. N. Roy, *J. Indian Chem. Soc.*, 2005, **82**, 814.
14. A. K. Covington and T. Dickinson, "Physical Chemistry of Organic Solvent Systems", Plenum Press, New York, 1973, Chap. 5, Appendix 5.1, Table 5.1.5, pp. 606, 608.
15. L. Pikkaranien, *J. Chem. Engg. Data*, 1988, **33**, 299; R. M. Fuoss, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 16.
16. R. M. Fuoss, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 16.
17. R. M. Fuoss, *J. Phys. Chem.*, 1978, **82**, 2427.
18. M. N. Roy, D. Nandi and D. K. Hazra, *J. Indian Chem. Soc.*, 1993, **70**, 121.
19. R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, 1949, **71**, 1496.
20. Y. Matsuda, M. Morita and F. Tachihara, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1967.
21. Robert C. West (ed.), "Handbook of Chemistry and Physics", 67th ed., C.R.C. Press, Florida, 1986-1987.
22. R. L. Kay and D. F. Evans. *J. Phys. Chem.*, 1965, **69**, 4208.
23. B. Das and N. Saha, *J. Chem. Engg. Data*, 2000, **45**, 2.
24. R. L. Kay and T. L. Broadwater, *Electrochim. Acta*, 1971, **16**, 667.
25. Jomma S. Chazhoor and T. P. Radhakrishnan, *Proc. Indian Acad. Sci.*, 1979, **88A**, 53.
26. R. L. Kay and T. L. Broadwater, *J. Solution Chem.*, 1976, **5**, 57.
27. R. H. Boyd, *J. Chem. Phys.*, 1961, **35**, 1281.
28. R. Zwanzig, *J. Chem. Phys.*, 1970, **52**, 3625.
29. T. L. Broadwater and R. L. Kay. *J. Phys. Chem.*, 1970, **74**, 3802.
30. E. Gluekauf, *Trans. Faraday Soc.*, 1964, **60**, 1637.
31. J. R. Suindells and T. B. Godfray, *J. Res. Natd. Bur. Stand.*, 1952, **48**, 1.

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Thermodynamic and transport properties of some monobasic acetate salts in aqueous binary mixtures of methanol at different temperatures

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ABSTRACT

The densities, viscosities and ultrasonic speeds of some monobasic acetate salts, viz. ammonium acetate (CH_3COONH_4), lithium acetate (CH_3COOLi), sodium acetate (CH_3COONa) and potassium acetate (CH_3COOK) in methanol water mixtures (10%, 20%, 30%) have been measured at 298.15, 308.15 and 318.15 K. The limiting apparent molar volumes (V_{ϕ}°), the experimental slope (S_v^*), supplemented with the measured density data have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The parameters B and A obtained from viscosity data analyzed using Jones-Dole equation have also been interpreted in terms of solute- solute and solute-solvent interactions respectively. The structure making or structure breaking nature of the acetates in the solvent-mixtures studied here has been discussed. The compressibility data supplemented with the ultrasonic speeds explain the electrostriction of the solvent molecules around the positive ions.

Key words: Density, viscosity, ultrasonic speed, methanol + water mixtures, acetate salts, solute-solute and solute-solvent interactions.

Introduction

Studies on the thromodynamic transport properties and ultrasonic speeds of different electrolytes in different solvents are of great importance to obtain information of the behavior of ions in solutions. Among the various type of interactions occurring between solute molecules in solution, these solute-solute and solute- solvent interactions are of current interest in all branches of chemistry[1-7]. These interactions help in better understanding of the nature of solutes and solvents, i.e., whether the solute modifies or distorts the structure of the solvent. The inferences regarding these interactions is derived from density, viscosity and ultrasonic speed data measured experimentally. The literature is full of such data in pure solvents but investigations on mixed solvent systems are scanty. Partial molar volume, viscosity coefficients and adiabatic compressibilities reflect the cumulative effects[25,26] of solute-solvent and solute-solute interactions in mixtures of methanol. Such data are expected to highlight the role of acetate salts in binary aqueous mixtures of methanol. Such data are expected to highlight the role of acetate salts in influencing the partial molar volume, viscosity coefficients and adiabatic compressibilities in mixed solvent systems. These considerations prompted us to undertake the present study.

Experimental

Ammonium and sodium acetate (Riedel A.R.) were used as received. Lithium and potassium acetates were prepared and purified by the reported procedures[8] The salts were dried and stored in vacuum desiccators.

Methanol (E. Merck, India, Uvasol grade 99.5% pure) was dried over 3 A molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density of 0.979935 $g.cm^{-3}$ and a viscosity of 1.58089 m Pa. s at 298.15 K. These values agree well with the literature values[27,24]. The purities as checked by gas chromatography were found to be 99.8% for methanol.

The densities (ρ) were measured with an Ostwald Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298, 308 and 318) K with double distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ± 0.01 K of the desired temperature by means of a mercuty in glass Thermo-regulator and the temperature was determined by a calibrated Thermometer and Muller bridge. The pycnometer was then removed form the Thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. An average of triplicate measurements were taken into account. The density values are reproducible to $\pm 3 \times 10^{-5}$ g . cm^3 . Details have been discussed earlier.[9]

The apparent molar volumes ($V\phi$) were calculated from the solution densities using to following relation,

$$V_\phi = M/\rho_0 - 10^3(\rho - \rho_0)/c\rho_0 \quad ....(1)$$

where M is the molecular weight of the solute, c the molarity of the solution, ρ is the density of the solution, ρ_0 is the density of the solvent mixture.

The limiting apparent molar volumes (v_ϕ^0) and experimental slopes

(S_v*) were determined applying the least square method to the plots of V_ϕ vs.c½ using the Masson equation.[10,11]

$$V_\phi = V_\phi^0 + S_v^* c^{1/2} \quad .... (2)$$

where ($V\phi^0$) is the partial molar volume at infinite dilution and S_v^* the experimental slope. The variation of (V_ϕ) with temperature of the salts in the solvents follows the polynomial equation, $V_\phi^0 = a_0 + a_1 T + a_2 T^2$ ...... (3) over the temperature range under the investigation.

The apparent molar expansibilities are calculated from equation,

$$\phi^0{}_E = \left[\delta V_\phi^0 / \delta T\right]_p \quad .... (4)$$

The sign of $\left(\delta^2 V_\phi^0 / \delta T^2\right)_p$ was also determined to ascertain whether the chosen acetate salts are structure breaker or maker in methanol water mixtures.

Here, the general thermodynamic expression, $\left(\delta c_p / \delta_P\right)_T = -\left(\delta^2 V_\phi^0 / \delta T^2\right)_p$..(5) is used for this explanation.

The viscosities were measured by means of suspended level Ubbelohde type viscometer [11] at the derived temperature (accuracy ±0.01 K). The precision of the viscosity measurement was 0.05%. Details have been described earlier. [9]

The viscosity data of solutions for various electrolytes studied here have been analyzed using Jones-Dole equation. [16]

$$\eta / \eta_0 = 1 + A\sqrt{c} + Bc$$

$$(\eta . \eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad .... (6)$$

$$\text{where, } \eta = (K + -L/t) \times \rho$$

where η and η_0 are the viscosities of solution and solvent mixture respectively. A and B are constants for the above equation, ρ is the density of the solution and K and L are constants for a particular viscometer. The values of A and B are estimated by least squares method.

Sound velocities were determined with an accuracy of 0.3% using a single crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz, which was calibrated, with water, methanol and benzene at the required temperature.

Adiabatic compressibility coefficients ß, were derived from the following relation $\beta = \frac{1}{\upsilon^2 \rho}$ .... (7)

where ρ is the density of solution and u is the ultrasonic speed in the solution.

The apparent molar adiabatic compressibilities (ϕ_k) of the solutions was calculated from the following equation,

$$(\phi_k) = \beta \times M / \rho_0 + 1000(\beta\rho_0 - \beta_0\rho)/m\rho\rho_0 \cdots(8)$$

where, m is the molality of the solution, β_0 is the adiabatic compressibility of the solvent mixture and the other terms are described earlier.

The limiting apparent molar adiabatic compressibilities (ϕ_k^0) and experimental slopes (S^*_k) were obtained [4,17] by extrapolating the plots of (ϕ_k versus the square of molar concentration $\sqrt{m}$ of the electrolyte by the computerized least squares method using the following equation.

$$\phi_k = \phi_k^0 + S^*_k\sqrt{m} \text{ ....}(9)$$

The plots of V_ϕ against $\sqrt{c}$ are all linear and the slopes and intercepts of these lines are taken as V_ϕ^0 and S_v^* respectively and their values are recorded in table - 2 .

The V_ϕ^0 values are interpreted in terms of solute –solvent interactions (as ionic interactions vanish at infinite dilution).

Table-2 shows that the values of V_ϕ^0 are positive and large and decrease with increase of temperature as well as with increase mass % of methanol in the solvent mixture. This indicates the presence of strong solute-solvent interaction.

These interactions are weakened with rise in temperature, suggesting more electrostrictive solvation at higher temperature. Similar results are reported for some 1:1 electrolytes in aqueous DMF. [18,19]

The values of experimental slope, (S_v^*) shown in Table-2 are negative for all investigated salts and increase with rise in temperature. This indicates the presence of weak solute–solute interactions and these interactions, however, increase with the increase of temperature which may be attributed to the solvation lof solutes, i.e., more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the increase of temperature.

The variation of V_ϕ with temperature of the salts in the solvents follows according to equation (3) over the temperature range under the investigation. The coefficients (a's) are presented in table 3.

The limiting apparent molar expansibilities (ϕ^0_E) calculated from equation (4) are recorded in table- 4. The ϕ_E^0 values for lithium acetate and sodium acetate in methanol solutions increase with increase of temperature, whereas for ammonium acetate and potassium acetate the values decrease with increase of temperature. The

Table 1 : Concentration (c), Density (ρ), Viscosity (η), Apparent Molar Volume (V_ϕ) and $(\eta/\eta_0-1)/\sqrt{c}$ of some acetate salts in various mass % of Methanol at different temperature

10 % Methanol + H_2O mixture

c	ρ/g.cm^{-3}	η/cp	V_ϕ/cm^3 mol^{-1}	$(\eta/\eta_0-1)/\sqrt{c}$	c	ρ/g.cm^{-3}	η/cp	V_ϕ/cm^3 mol^{-1}	$(\eta/\eta_0-1)/\sqrt{c}$
					298.15 K				
		CH_3COONH_4				CH_3COONa			
0.00611	0.97993	1.16903	0.07	0.1208	0.00604	0.97991	1.17609	143.15	0.2001
0.04277	0.98000	1.18472	0.20	0.1112	0.04230	0.97999	1.21049	137.90	0.2203
0.07943	0.98014	1.19128	0.28	0.1017	0.07886	0.98028	1.23226	135.21	0.2280
0.11609	0.98030	1.19696	0.34	0.0985	0.11482	0.98058	1.24885	133.12	0.2311
0.15275	0.98054	1.20041	0.39	0.0935	0.15108	0.98095	1.26477	132.03	0.2372
0.18941	0.98079	1.20204	0.43	0.0872	0.18733	0.98150	1.27939	130.34	0.2424
		CH_3COOLi				CH_3COOK			
0.006007	0.97992	1.17694	105.80	0.2101	0.00608	0.97993	1.18346	101.20	0.2611
0.042050	0.98001	1.22019	102.74	0.2615	0.04254	0.98004	1.21630	97.52	0.2020
0.078094	0.98019	1.25000	100.83	0.2840	0.07899	0.98028	1.23128	95.66	0.1723
0.114137	0.98047	1.27886	99.23	0.3086	0.11546	0.98060	1.23837	94.29	0.1432
0.150180	0.98078	1.30350	98.63	0.3240	0.15192	0.98092	1.24430	93.53	0.1201
0.186223	0.98117	1.32651	96.86	0.3371	0.18837	0.98165	1.24555	90.86	0.0960
					308.15 K				
		CH_3COONH_4				CH_3COONa			
0.00608	0.97419	0.91396	78.15	0.0756	0.00601	0.97720	0.92812	142.58	0.2770
0.04259	0.97429	0.91360	76.43	0.0801	0.004214	0.97728	0.95686	138.60	0.2587
0.07907	0.97448	0.93016	75.23	0.0844	0.07854	0.97746	0.96913	136.09	0.2377
0.11556	0.97468	0.93547	74.64	0.0872	0.11439	0.97775	0.97941	134.49	0.2301

0.15207	0.97500	0.94071	73.62	0.09061	0.15047	0.97807	0.98597	133.46	0.2195
0.18852	0.95237	0.94490	73.36	0.0923	0.18669	0.97853	0.99355	132.05	0.2163
		CH_3COOLi				CH_3COOK			
0.00599	0.977224	0.92534	104.93	0.2380	0.00608	0.97742	0.91880	140.70	0.1440
0.041883	0.97293	0.95880	103.18	0.2702	0.04233	0.97872	0.93950	137.29	0.1653
0.077831	0.977433	0.98269	101.61	0.2922	0.07853	0.98009	0.95354	135.73	0.1765
0.113654	0.977594	1.00418	101.03	0.3120	0.11474	0.98148	0.96557	133.62	0.1851
0.14946	0.977799	1.02321	100.82	0.3262	0.15121	0.98299	0.97714	133.52	0.1940
0.185447	0.978027	1.04124	98.58	0.3390	0.18745	0.98448	0.98617	130.95	0.1972
					318.15				
		CH_3COONH_4				CH_3COONa			
0.00605	0.97139	0.74055	140.70	0.0966	0.00598	0.97138	0.75594	140.70	0.3679
0.04248	0.97149	0.75096	137.29	0.1052	0.04194	0.97150	0.78334	137.29	0.3211
0.07878	0.97164	0.75796	135.73	0.1112	0.07811	0.97171	0.79853	135.73	0.2960
0.11516	0.97181	0.76395	133.62	0.1161	0.11391	0.97210	0.80398	133.62	0.2782
0.14946	0.97203	0.76886	133.52	0.1183	0.14973	0.97234	0.80939	133.52	0.2614
0.18783	0.97229	0.77329	130.95	0.1201	0.18583	0.97303	0.81359	130.95	0.2480
		CH_3COOLi				CH_3COOK			
0.00595	0.97139	0.74934	104.20	0.2524	0.00602	0.97151	0.73882	99.35	0.0666
0.04169	0.97149	0.77659	102.48	0.2771	0.04215	0.97236	0.74890	98.04	0.0921
0.07737	0.97165	0.79554	101.41	0.2960	0.07824	0.97327	0.75679	96.80	0.1059
0.11312	0.97189	0.81431	100.42	0.3207	0.11432	0.97423	0.76385	95.89	0.1160
0.14484	0.97215	0.82911	99.75	0.3316	0.15061	0.97520	0.77110	94.37	0.1265
0.18444	0.97252	0.84257	98.68	0.3407	0.18636	0.97821	0.77795	93.71	0.1353

20 % Methanol + H_2O mixture

298.15 K

CH_3COONH_4					CH_3COONa				
0.00633	0.96441	1.41901	78.30	0.1696	0.00601	0.96524	1.40148	143.61	0.1288
0.04431	0.96451	1.43976	77.37	0.1345	0.04208	0.96531	1.44499	139.44	0.1562
0.08230	0.96465	1.44607	76.88	0.1144	0.07816	0.96551	1.46547	137.63	0.1669
0.12028	0.96482	1.44810	76.34	0.0988	0.11423	0.96583	1.48433	136.00	0.1779
0.15826	0.96502	1.44863	75.87	0.0871	0.15030	0.96626	1.50054	134.16	0.1850
0.19624	0.96529	1.44850	75.21	0.0780	0.18637	0.96679	1.51799	132.74	0.1951

CH_3COOLi					CH_3COOK				
0.00605	0.96525	1.42408	106.24	0.2201	0.00633	0.96524	1.44145	100.08	0.3710
0.04232	0.96530	1.46637	104.37	0.2324	0.04431	0.96533	1.47557	98.51	0.2561
0.07859	0.96544	1.49275	103.19	0.2362	0.08230	0.96554	1.4703	97.50	0.1842
0.11487	0.96565	1.51453	102.09	0.2411	0.12028	0.96584	1.46130	96.53	0.1262
0.15114	0.96585	1.53353	101.56	0.2451	0.15826	0.96618	1.44635	95.57	0.0830
0.18741	0.96609	1.55044	101.05	0.2480	0.19624	0.96656	1.42865	94.60	0.0463

308.15 K

CH_3COONH_4					CH_3COONa				
0.00630	0.96041	1.06642	78.28	0.1342	0.00598	0.96040	1.06816	143.08	0.1590
0.04406	0.96049	1.08163	78.07	0.1194	0.04187	0.96048	1.09117	139.63	0.1667
0.08186	0.96058	1.08872	77.94	0.1111	0.07775	0.96064	1.10567	137.77	0.1716
0.11957	0.96067	1.09350	77.81	0.1050	0.11369	0.96100	1.11752	136.18	0.1752
0.15741	0.96079	1.09675	77.69	0.0993	0.14950	0.96136	1.12788	135.01	0.1781
0.19526	0.96090	1.09920	77.59	0.0944	0.18531	0.96180	1.13713	133.81	0.1804

		CH_3COOLi				CH_3COOK			
0.00602	0.96041	1.07687	104.68	0.2648	0.00630	0.96038	1.07277	104.31	0.2101
0.04217	0.96051	1.09823	103.57	0.1986	0.04745	0.96047	1.09564	100.63	0.1761
0.07179	0.96062	1.02963	102.90	0.1691	0.08172	0.96065	1.10345	98.96	0.1609
0.09670	0.96078	1.10375	102.13	0.1482	0.11921	0.96097	1.10706	97.15	0.1424
0.15122	0.96111	1.09786	101.28	0.1041	0.15700	0.96139	1.10991	95.63	0.1309
0.18760	0.96142	1.09312	100.51	0.0833	0.19466	0.96193	1.11049	93.97	0.1211

318.15 K

		CH_3COONH_4				CH_3COONa			
0.00626	0.95428	0.84331	77.39	0.1160	0.00594	0.95426	0.85520	141.09	0.3036
0.04382	0.95441	0.85766	77.43	0.1259	0.04159	0.95435	0.87535	139.90	0.2330
0.08142	0.95451	0.86676	77.44	0.1305	0.07728	0.95452	0.88094	138.98	0.1950
0.11893	0.95460	0.87484	77.45	0.1361	0.11280	0.95469	0.88053	138.56	0.1599
0.15652	0.95470	0.88163	77.46	0.1391	0.14863	0.95493	0.88081	137.85	0.1340
0.19415	0.95473	0.88773	77.46	0.1415	0.18583	0.97300	0.81359	130.95	0.2480
		CH_3COOLi				CH_3COOK			
0.00599	0.95427	0.86332	103.52	0.4281	0.00626	0.95425	0.84447	99.42	0.1335
0.04195	0.95438	0.89314	102.41	0.3363	0.04375	0.95433	0.86008	97.54	0.1398
0.07144	0.95446	0.90041	101.80	0.2901	0.08127	0.95457	0.86983	96.41	0.1435
0.08846	0.95442	0.90225	101.54	0.2680	0.11864	0.95485	0.87774	95.60	0.1462
0.15055	0.95472	0.90340	100.12	0.2092	0.15630	0.95519	0.88486	94.40	0.1490
0.18665	0.95483	0.90207	99.90	0.1841	0.19363	0.95556	0.89135	93.53	0.1515

30 % Methanol + H_2O mixture

298.15 K

CH_3COONH_4					CH_3COONa				
0.00623	0.96060	1.42075	78.32	0.1809	0.00604	0.96059	1.41131	143.60	0.0970
0.04361	0.96069	1.44170	77.83	0.1400	0.04231	0.96068	1.43791	139.44	0.1290
0.08099	0.96080	1.44822	77.50	0.1206	0.07857	0.96089	1.46028	137.63	0.1516
0.11837	0.96091	1.45178	77.27	0.1059	0.11483	0.96118	1.47956	136.00	0.1660
0.11575	0.96107	1.45161	76.99	0.0920	0.15110	0.96168	1.49930	134.16	0.1810
0.19313	0.96123	1.44753	76.79	0.0760	0.18736	0.96219	1.51751	132.74	0.1925

CH_3COOLi					CH_3COOK				
0.00612	0.96060	1.42936	104.09	0.2610	0.00614	0.96058	1.45166	99.80	0.4640
0.04287	0.96075	1.45433	102.30	0.2020	0.04294	0.96069	1.49218	97.91	0.3150
0.07960	0.96098	1.46872	101.05	0.1720	0.07975	0.96094	1.49450	96.70	0.2370
0.11635	0.96119	1.46907	100.86	0.1430	0.11656	0.96134	1.48253	95.47	0.1711
0.15309	0.96141	1.46651	100.17	0.1200	0.15337	0.96169	1.46658	94.71	0.1201
0.18983	0.96141	1.45934	99.32	0.0960	0.19018	0.96224	1.44118	93.14	0.0711

308.15 K

CH_3COONH_4					CH_3COONa				
0.00619	0.95418	1.11128	77.17	0.1511	0.00600	0.95417	1.13797	140.70	0.4650
0.04338	0.95431	1.13054	77.10	0.1413	0.04214	0.95428	1.17441	138.49	0.3381
0.08056	0.95444	1.13986	77.06	0.1336	0.07812	0.95457	1.17669	137.11	0.2562
0.11771	0.95458	1.14644	77.04	0.1280	0.11420	0.95488	1.17059	136.11	0.1951
0.15489	0.95471	1.52052	77.03	0.1245	0.15010	0.95522	1.16204	134.91	0.1501
0.19215	0.95485	1.55694	77.00	0.1194	0.18612	0.95575	1.45594	133.63	0.1001

		CH_3COOLi				CH_3COOK			
0.00608	0.95417	1.13059	103.77	0.3781	0.00614	0.95414	1.19467	98.01	0.2470
0.04268	0.95434	1.16015	102.45	0.2730	0.04275	0.95424	1.42266	96.67	0.1941
0.07941	0.95449	1.16321	101.60	0.2102	0.07938	0.95452	1.46483	95.86	0.1562
0.11614	0.95484	1.15795	100.73	0.1596	0.11456	0.95487	1.46909	96.35	0.1311
0.15301	0.95508	1.15191	100.57	0.1253	0.15245	0.95533	1.14410	94.43	0.1070
0.18982	0.95558	1.14128	99.06	0.0902	0.18916	0.95601	1.13977	92.63	0.0872
				318.15 K					
		CH_3COONH_4				CH_3COONa			
0.00616	0.95027	0.85584	76.48	0.0717	0.00598	0.95025	0.87640	140.47	0.3851
0.04314	0.95040	0.86645	77.11	0.0871	0.04184	0.95041	0.90397	138.95	0.3041
0.08012	0.95051	0.87423	77.50	0.0962	0.07776	0.95056	0.91394	137.83	0.2653
0.11711	0.95061	0.88145	77.81	0.1043	0.11373	0.95093	0.91678	136.81	0.2290
0.15420	0.95072	0.88755	77.83	0.1092	0.14940	0.95122	0.91650	136.30	0.1991
0.19112	0.95077	0.89315	78.24	0.1131	0.18533	0.95129	0.91517	135.54	0.1753
		CH_3COOLi				CH_3COOK			
0.00605	0.95026	0.88810	104.02	0.4530	0.00608	0.95024	0.86366	99.15	0.1901
0.04243	0.95038	0.90768	103.88	0.3231	0.04248	0.95033	0.88094	98.09	0.1704
0.07900	0.95050	0.90966	103.82	0.2454	0.07892	0.95053	0.88902	97.69	0.1588
0.11549	0.95063	0.90687	103.77	0.1933	0.11515	0.95083	0.89495	97.89	0.1520
0.15217	0.95077	0.89786	103.70	0.1412	0.15155	0.95115	0.89922	96.92	0.1454
0.19067	0.95091	0.89044	103.66	0.1061	0.18810	0.95161	0.90169	96.51	0.1372

Table 2: Limiting apparent molar volume ($V_\phi{}^0$), experimental slope ($S_v{}^*$), A and B aparameters of viscosity for acetate salts in different mass % of Methanol at different temperatures.

Mass % of CH_3OH	**$V_\phi{}^0$**			**$S_v{}^*$ at**			**A at**			**B at**		
	298.15	**308.15**	**318.15**	**298.15**	**308.15**	**318.15**	**298.15**	**308.15**	**318.15**	**298.15**	**308.15**	**318.15**
CH_3COONa												
10	145.54	144.34	142.75	-35.66	-28-78	-26.03	0.1937	0.2918	0.3921	0.1138	-0.1807	-0.3380
20	144.05	143.62	142.06	-25.50	-21.78	-10.64	0.1261	0.1541	0.3461	0.1536	-0.0625	-0.5505
30	143.45	142.78	141.86	-22.96	-20.09	-14.14	0.0750	0.5460	0.4219	0.2711	-0.1028	-.5934
CH_3COOLi												
10	107.28	106.35	105.53	-23.61	-16.29	-15.31	0.1845	0.2133	0.2283	0.3596	0.2902	0.2624
20	106.53	105.81	104.50	-12.54	-11.74	-10.63	0.2137	0.3050	0.4728	0.0799	-0.5121	-0.6924
30	104.72	105.07	104.12	-12.50	-12.28	-1.01	0.2977	0.4369	0.5251	-0.4563	-0.8085	-0.9759
CH_3COOK												
10	103.30	101.48	101.03	-17.20	-18.09	-16.30	0.3053	0.1331	0.0519	-0.2967	0.1529	0.1923
20	101.64	101.02	100.83	-14.92	-9.31	-16.04	0.4434	0.2303	0.1295	-0.9036	-0.2505	0.0494
30	100.67	99.414	99.668	-14.71	-13.02	-6.80	0.5524	0.2842	0.2009	-1.1116	-0.4527	-0.1456
CH_3COONH_4												
10	80.22	79.23	78.35	-14.45	-13.82	-8.86	0.1289	0.0711	0.0916	-0.0925	0.0479	0.0683
20	79.07	78.06	77.39	-8.18	-1.86	0.19	0.1886	0.1426	0.1106	-0.2545	-0.1093	0.0715
30	78.68	77.21	76.15	-4.68	-0.46	4.59	0.2019	0.1587	0.0628	-0.2832	-0.0883	0.1178

Table 3: Values of various coefficients (a_0, a_1, a_2) of acetate salts in various mass % of water methanol mixtures

Mass% of CH_3OH	a_0/cm^3 mol^{-1}	a_1/cm^3 mol^{-1} K^{-1}	a_2/cm^3 mol^{-1} K^{-2}
CH_3COONa			
10	480.47	-2.12	0.0034
20	791.35	-3.86	0.0057
30		-1.42	0.0013
CH_3COOLi			
10	244.49	-0.83	0.0013
20	476.18	-2.38	0.0039
30	573.27	-3.50	0.0065
CH_3COOK			
10	16.59	2.33	-0.0069
20	88.96	0.68	-0.0022
30	-218.51	3.32	-0.0076
CH_3COONH_4			
10	59.20	0.23	-0.0006
20	-47.00	0.93	-0.0017
30	-65.83	1.10	-0.0021

increase in magnitude of ϕ^0_E values with temperature may be ascribed to 'caging or packing effect',[19] It also indicates that the behavior of these two salts in methanol are similar to that of some symmetrical tetraalkyl ammonium salts.[12] On the other hand, the decrease in ϕ^0_E values with increase of temperature, for ammonium acetate and potassium acetate indicates that they behave just like common salts, because in case of common salts, the molar expansibility decreases with increase of temperature.[12,15]

During the past few years it has been emphasized by some workers that S_v^* is not the sole criterion for determining the structure making / breaking nature of any electrolyte. Hepler[13] developed a technique of examining the sign for various electrolytes in terms of long range structure making and structure breaking capacity of the electrolytes in methanol water mixtures. The structure making solutes should have positive value, whereas structure breaking ones have negative value $(\delta^2V_\phi^0/\delta T^2)_p$. These values of the selected acetates are recorded in table 4 . It is seen from table.4 that, the $\left(\delta^2 V_\phi^0/\delta T^2\right)_P$ values for lithium acetate and sodium acetate are positive, indicating that they are structure makers in methanol water mixtures whereas for ammonium acetate and potassium acetate the values are negative, indicating that they are structure breakers in this mixed solvent system.

Table-4: Limiting apparent molar compressibilities (ϕ_E^0) for acetate salts in various mass % of methanol at different temperature

Maa % of Methanol	ϕ_E^0/ cm^3 mol^{-1} K^{-1}			
	298.15 K	308.15 K	318.15 K	$(\delta\phi_E^0/\delta T)$
		CH_3COONa		
10	-0.1255	-0.0585	0.0085	Positive
20	-0.4856	-0.3735	-0.2605	Positive
30	-0.6825	-0.6575	0.6325	Positive
		CH_3COOLi		
10	-0.0875	-0.0625	-0.0375	Positive
20	-0.0926	-0.0156	0.0615	Positive
30	0.3665	0.4965	0.6265	Positive
		CH_3COOK		
10	-1.7515	-1.8885	-2.0253	Negative
20	-0.5985	-0.6415	-0.6845	Negative
30	-1.1805	-1.3315	-1.4825	Negative
		CH_3COONH_4		
10	-0.0935	-0.1045	-0.1155	Negative
20	-0.0840	-0.1180	-0.1520	Negative
30	-0.1265	-0.1675	-0.2085	Negative

The viscosity data for various solutions of electrolytes were analyzed according to Jones-Dole equation[16]. The values of A and B are recorded in table 2.

Table 2 shows that the values of A are very small for all salts studied in methanol water mixtures at various temperatures thereby showing the presence of weak solute-solute interactions. In other words these results indicate that all the salts mix ideally with methanol + water mixtures and there is a perfect solvation of these molecules resulting in either the absence or weak solute-solute interactions.

Table 2 shows that two types of trends are observed in the change of B-coefficients with temperature. B values for lithium acetate and sodium acetate in methanol solutions decrease with increase of temperature, thereby showing that solute- solvent interactions are weakened with rise of temperature, whereas for ammonium and potassium acetate, values of B-coefficient increase with the increase in temperature indicating improved solute-solvent interactions for the solutions with the increase in temperature which may be attributed to solvation of ions by the solvent system studied here.

It has been reported by a number of workers that dB/dT is a better criterion [10,20,21] for determining the structure making / braking capacity of any electrolyte rather than simply the B-coefficient values. It is evident from table 2 that for lithium acetate and sodium acetate the B values decrease with increase of temperature (negative dB/dT) indicating that they are structure makers in methanol water mixture. On the other hand, for ammonium acetate and potassium acetate the B values increase with increase of temperature (positive dB/dT) indicating that they are structure breakers in methanol water mixture. These conclusions are in excellent agreement with that drawn from $\left(\delta^2 V_\phi^0 / \delta T^2\right)_P$ values explained earlier.

The values of ultrasonic speed (u), adiabatic compressibility (β), molality (m), limiting apparent molal adiabatic comressibility (ϕ_k^0), density (ρ), apparent molal adiabatic compressibility (ϕ_k) and experimental slope (S_k^0) are given in table - 5.

A perusal of table - 5 shows that the ϕ_k^0 values decrease whereas S_k^* values increase with the increase of mass % of methanol in the mixtures at a particular temperature (298.15 K) for all the salts studied here, Since the values of ϕ_K^0 and S_k^* are measure of solute-solute and solute-solvent interactions respectively, the results are in good agreement with that drawn from the conclusion based on the values of V_ϕ^0 and S_v^* mentioned earlier. Negative values of ϕ_k^0 of the salts are interpreted in terms of the loss of compressibility of solvent-mixture due to the electrostrictive forces in the vicinity of the ions and hence the extent of compressibility electrostriction decreases with the increase of the amount of methanol in the mixture for all the salts under investigation. Same results were observed for some electrolytes in aqueous ethanol, and in 2-methoxyethanol[23] in case of the studies on sound velocities of some alkali metal halides in theTHF + H_2O mixtures.[22]

Table 5: Mass % THF, Molality (m), Density (ρ^0), Sound Velocity (u), Adiabatic Compressibility (β), Apparent Molal Adiabatic Compressibility (ϕ k), Limiting Apparent Molal Adiabatic Compressibility (ϕk^0) and Experimental Slope (S_K*) of some acetate salts in methanol water mixtures

(10%, 20%, 30%) at 298.15 K

Mass % of methanol	m/mol kg^{-1}	ρ/ kg m^{-3}	u/m sec^{-1}	$\beta \times 10^{10}$/Pa^{-1}	$\phi k \times 10^{10}$/ m^{3}mol^{-1}Pa^{-1}	$\phi k^0 \times 10^{10}$/ m^{3}mol^{-1} Pa^{-1}	$S_k^* \times 10^{10}$/ m^{3}mol$^{-3/2}$ Pa^{-1}kg$^{1/2}$
			CH_3COON_4				
	0.00623	979.931	1465.23	4.7533	-33.379		
	0.04374	980.009	1500.36	4.5329	-9.660		
10	0.08134	980.140	1547.72	4.2631	-8.443	-38.670	78.605
	0.11915	980.303	1647.72	3.9965	-7.940		
	0.15708	980.548	1715.00	3.8625	-6.854		
	0.19524	980.792	1748.27	3.7589	-5.010		
	0.00656	964.410	1653.54	3.7923	-47.195		
	0.04601	964.509	1698.45	3.5941	-10.954		
20	0.08567	964.462	1745.18	3.4037	-8.075	-55.103	117.50
	0.12544	964.816	1796.78	3.2104	-7.047		
	0.16547	965.018	1825.32	3.1102	-5.920		
	0.20566	965.292	1872.11	2.9558	-5.494		
	0.00648	960.600	1695.00	3.6234	-96.108		
	0.04550	960.689	1732.15	3.4693	-58.400		
30	0.08471	960.801	1758.36	3.3663	-40.001	-113.32	247.06
	0.12403	960.905	1789.92	3.2483	-25.202		
	0.16360	961.074	1821.02	3.1377	-11.503		
	0.20330	961.229	1867.36	2.9834	-6.121		

CH_3COOK

	0.00620	979.929	1453.23	4.8321	-22.872		
	0.04348	980.044	1541.92	4.2917	-15.330		
10	0.08008	980.282	1598.56	3.9920	-11.961	-24.339	44.699
	0.11847	980.597	1629.16	3.8422	-9.265		
	0.15633	980.920	1637.14	3.0836	-7.182		
	0.19401	981.648	1636.49	3.8039	-5.714		
	0.00656	965.241	1619.35	3.9508	22.549		
	0.04596	965.334	1734.89	3.4418	14.400		
20	0.08551	965.536	1770.48	3.3041	9.264	-27.062	58.330
	0.12313	965.841	1801.66	3.1897	7.185		
	0.16497	966.176	1724.37	3.4808	3.510		
	0.20497	966.582	1672.79	3.6973	1.640		
	0.00639	960.579	1605.78	4.0373	-27.501		
	0.04479	960.685	1759.84	3.3610	-18.890	-32.667	65.64
30	0.08339	960.938	1829.67	3.1086	-13.610		
	0.12193	961.337	1843.05	3.0854	-9.412		
	0.16091	961.686	1781.83	3.2143	-6.201		
	0.19995	962.236	1736.83	3.4439	-3.700		

CH_3COOLi

	0.00613	979.929	1455.54	4.8168	-23.665		
	0.04299	980.018	1557.53	4.2062	-17.500		
10	0.08006	980.191	1627.16	3.8533	-13.731	-27.507	49.642

	0.11728	980.466	1630.54	3.8362	-9.414		
	0.15478	980.775	1648.45	3.7521	-7.607		
	0.19231	981.168	1671.72	3.6469	-6.614		
	0.00627	965.249	1641.36	3.8455	-41.001		
	0.04404	965.300	1890.99	2.8971	-27.900		
20	0.08188	965.435	2060.49	2.4397	-20.700	-52.751	115.67
	0.10129	965.645	2120.69	2.3027	-18.100		
	0.15917	965.849	2039.72	2.4880	-10.100		
	0.19807	966.086	1977.51	2.6470	-7.300		
	0.00637	960.604	1630.67	3.9149	-50.010		
	0.04481	960.749	1996.90	2.6104	37.201		
30	0.08355	960.982	2357.73	1.8720	29.103	-61.574	136.72
	0.12259	961.185	2668.21	1.4614	23.300		
	0.16192	961.405	2770.96	1.3547	18.312		
	0.20133	962.035	2918.87	1.2201	15.400		
			CH_3COONa				
	0.00616	979.910	1449.22	4.8590	-16.370		
	0.04331	979.987	1518.30	4.4265	-12.000		
10	0.08098	980.280	1563.00	4.1757	-9.327	-20.21	38.896
	0.11835	980.581	1586.60	4.0512	-7.290		
	0.15634	980.947	1588.07	4.0425	-5440		
	0.19451	981.499	1590.77	4.0262	-4.350		
	0.00623	965.244	1614.56	3.9779	-19.700		

20	0.04378	965.312	1720.34	3.5005	-13.600	-24.049	51.253
	0.08157	965.505	1785.67	3.2491	-10.300		
	0.11961	965.827	1808.63	3.1569	-7.690		
	0.15789	966.256	1814.23	3.1476	-5.780		
	0.19646	966.788	1831.61	3.0881	-4.880		
30	0.00629	960.593	1581.20	4.1638	-9.369	-32.161	70.184
	0.04420	960.678	1585.75	4.1395	-1.408		
	0.08236	960.892	1712.98	3.5467	-8.134		
	0.12083	961.177	1726.96	3.4058	-5.902		
	0.15945	961.676	1747.32	3.3249	-4.908		
	0.19843	962.194	1767.98		-4.289		

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References

1. M.N. Roy, A. Jha. J. Chem. Eng. Data. 46, (2001), 1247-1252
2. M. N. Roy, D. K. Hazra and N.B. Univ. Rev. (Sci and technol) 8, (1997), 45.
3. G. G. Janz, 19973, Non aqueous electrolytes hand book, Academic Prss, New York, Vol-2.
4. M. Iqbal and R. E. Verral Can. J. Chem. 76, (1989), 727.
5. B. Das and D. K. Hazra., J. Chem. Eng. Data. 36, (1991), 405.
6. O. Popovych and R.P.T. Tomkins 1981, Non- Aqueous Solution Chemistry, Wiley Interscience, New York.
7. M. N. Roy, A. Jha and S. Chowdhury, J. Indian Chem. Soc, 79, (2002), 623.
8. P. Franzosini, F.W. Falgar J. Chem. Thermodyn. 16, (1984), 81.
9. P.S. Nikam, A.B. Sawant, J.S. Ather and R.S. Khairmar, J. Indian Chem. Soc 77, (2000), 197.
10. D. O.. Mason, Phil Mag. 8, (1929), 218.
11. D. Nandi, M. N. Roy and D. K. Hazra., J. Indian Chem. Soc. 70, (1993), 305.
12. F. J. Millero and H.W. Drost., J. Phys. Chem. 72, (1968), 1758.
13. L. G. Hepler Can. J. Chem. 47, (1969), 4613.
14. D. S. Gill and T.S Cheema Z. Phys. Chem. (Neue lolge), 140, (1984), 139.
15. B. N. Prasad and M.C.S. Subba J. Indian Chem. Soc. 77, (2000), 8.
16. G. Jones, and M. Dole J. Am. Chem. Soc 51, (1929), 2950.
17. S. Bhowmik and A. K. Das, R. K. Mohanty, Indian J. Chem. Sect. 24 (A), (1985), 1018.
18. C. Calvente, J. J. Maestre, E. Yanes and Carcia Panedo. J. Chem. Soc. Faraday Trans. 94, (1994), 573.
19. F. J. Millero 1972, 'In structure and tansport processes in water and aqueous solutions', R. A. Horne, New York.

20. R. Gopal and M.A. Siddiqui. J. Phys. Chem. 72, (1969), 1814.

21. N. Saha and B. Das, J. Chem. Eng. Data 42, (1997), 277.

22. M. N. Roy and D. K. Hazra. N. B. Univ. Rev. (Sci and technol), 8, (1997), 45.

23. B. Das and D. K. Hazra. Bull. Chem. Soc. Jpn. 65, (1992), 3740.

24. H. Doe., H. Ohe, H. Matoba and A Ichimura Bull. Chem. Soc. Jpn. 63, (1990), 2785.

25. E. J. Kind. J. Phys. Chem. 78, (1969), 1221.

26. M. L. Parmar, R. K. Awasthi and M. K. Guleria. J. Chem. Sci. 116, (2004), 33-38.

27. N. Saha and D. K. Hazra. J. Chem. Eng. Data. 40, (1995), 1264.

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PHASE TRANSITIONS AND THERMODYNAMIC ASPECTS OF STRUCTURE OF SUBSTANCES

Thermodynamic and Transport Properties of Binary Mixtures of Dimethyl Sulfoxide with *t*-Butyl Alcohol, Butyl Acetate, 2-Butanone and Butyl Amine at Different Temperatures[1]

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Abstract—Densities and viscosities of binary mixtures of dimethyl sulfoxide (DMSO) with *tert*-butyl alcohol, butyl acetate, butanone, and butyl amine were determined over the entire range of mole fractions at temperatures of 298.15, 308.15, and 318.15 K. At each temperature, the excess molar volume (V^E), viscosity deviations ($\Delta\eta$), and Gibbs excess free energy of activation for viscous flow (ΔG^{*E}) have been investigated from these measured density (ρ) and viscosity (η) values. The experimental viscosity data were correlated by means of the equations of Grunberg–Nissan, Tamura and Kurata, and Hind et al. The deviations have been fitted to a Redlich–Kister equation, and the results are discussed in terms of molecular interactions and structural effects.

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1. INTRODUCTION

Dimethylsulfoxide (DMSO), a typical aprotic solvent having both polar and nonpolar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells [1].

This solvent was chosen particularly for this study because of its wide range of applicability as a solvent in chemical and biological processes. Viscosity and density of binary liquid mixtures are extensively used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications [2, 3]. These have been extensively used to obtain information on intermolecular interactions and stereochemical effects in these systems [4]. In this paper we extend our studies to binary mixtures of DMSO with butyl acetate, *tert*-butyl alcohol, *n*-butyl amine, and 2-butanone. The various thermodynamic properties, such as excess molar volume (V^E) and viscosity deviations ($\Delta\eta$), obtained from experimental observations have been rationalized.

To our knowledge, the experimental data reported in this paper are not available in the literature.

2. EXPERIMENTS

Viscosities (η) have been measured at 298.15, 308.15, and 318.15 K by means of a suspended Ubbelohde-type viscometer [5]. Calibration was done at all the experimental temperatures with triply distilled water and purified methanol using density and viscosity values from the literature. Densities (ρ) were measured at the mentioned temperatures with an Ostwald–Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal capillary diameter of about 1 mm. The flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was $\pm 2 \times 10^{-4}$ mPa s. The measurements were done in a thermostatic bath controlled to ±0.01 K. The details of the methods and techniques for determination of these parameters have been described in earlier papers [6–9].

The mixtures were prepared by mixing known volumes of pure liquids in airtight stoppered bottles. The reproducibility in mole fractions was within ±0.0002 units. The weights were taken on a Mettler electronic analytical balance (AG 285) accurate to 0.02 mg. The precisions of the density and viscosity measurements are $\pm 3 \times 10^{-4}$ g cm^{-1} and $\pm 2 \times 10^{-4}$ m Pa s, respectively.

Dimethylsulfoxide (Merck, India) was kept for several days over anhydrous $CaSO_4$ and refluxed for 4 h over CaO. Finally, it was distilled at low pressure. The details have been described earlier [10]. *tert*-Butanol, *n*-butyl acetate, 2-butanone, and *n*-butylamine (S.D. Fine Chemicals, A R, purity > 99%) were used. The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature [2, 10–17], as listed in Table 1.

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[1] The text was submitted by the authors in English.

Table 1. Comparison of density (ρ) and viscosity (η) of pure liquids (I) with literature data at 298.15 K (II)

T, K	$\rho \times 10^{-3}$, kg m^{-3}		η, m Pa s	
	I	II	I	II
	DMSO			
298.15	1.0951	1.09568 [2]	1.9923	1.991 [11]
308.15	1.0839	1.08531 [2]	1.7052	1.654 [11]
318.15	1.0757	–	1.4504	–
	Butyl acetate			
298.15	0.8754	0.8761 [10]	0.6738	0.674 [10]
308.15	0.8646	0.8654 [16]	0.6684	0.593 [16]
318.15	0.8565	–	0.5342	–
	t-Butyl alchohol			
298.15	0.7807	0.7799 [12]	4.4338	4.433 [12]
308.15	0.7705	0.77024 [11]	2.7910	2.9397 [11]
318.15	0.7610	0.7594 [17]	1.8099	1.705 [15]
	Butyl amine			
298.15	0.7312	0.7331 [20]	0.4960	0.496 [15]
308.15	0.7199	–	0.4195	–
318.15	0.7136	–	0.3600	–
	2-Butanone			
298.15	0.7984	0.7996 [14]	0.3784	0.378 [14]
308.15	0.7883	0.7892 [14]	0.3235	0.341 [14]
318.15	0.7796	0.7784 [14]	0.3138	0.307 [14]

3. RESULTS AND DISCUSSIONS

Table 2 lists the experimental values of densities (ρ) and viscosities (η) of the binary mixtures along with the corresponding mole fractions of DMSO (x_1), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), excess Gibbs energy of activation for viscous flow (ΔG^{*E}), and interaction parameters (d_{12}, T_{12}, H_{12}) at all the experimental temperatures. The plots of V^E, $\Delta\eta$, ΔG^{*E} against x_1 at 298.15 K are represented in Figs. 1, 2, and 3, respectively. Because of their similarity, the plots at the other temperatures are not presented here.

The experimental densities have been used to calculate the excess molar volumes (V^E) using the following equation [4]:

$$V^E = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right), \qquad (1)$$

where M_i, ρ_i, and ρ are the molecular weight, density of the pure components, and density of the mixtures, respectively.

The deviation in viscosities from linearity ($\Delta\eta$) can be computed using the relationship

$$\Delta\eta = \eta - \sum_{i=1}^{2} (x_i \eta_i), \qquad (2)$$

where η_i and η are the viscosities of the pure components and of the mixtures, respectively.

On the basis of the theories of absolute reaction rates [18], the excess Gibbs energy of activation for a viscous flow (ΔG^{*E}) was calculated from the equation [19]

$$\Delta G^{*E} = RT\left[\ln \eta V - \sum_{i=1}^{2} (x_i \ln \eta_i V_i)\right], \qquad (3)$$

where R, T, V_i, and V are the universal gas constant, experimental temperature in absolute scale, and the molar volumes of the pure component and the mixtures, respectively.

The excess properties (V^E, $\Delta\eta$ and ΔG^{*E}) were fitted to the Redlich–Kister polynomial equation [20],

$$Y^E = x_1 x_2 \sum_{i=1}^{K} a_i (x_1 - x_2)^i, \qquad (4)$$

where Y^E refers to an excess property, x_1 is the mole fraction of DMSO and x_2 is that of the other component. The coefficients (a_i) were obtained by fitting Eq. (4) to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The estimated values of a_i along with the standard deviations (σ) are summarized for all mixtures in Table 3. The standard deviation (σ) was calculated using the equation

$$\sigma = \left[\frac{(Y^E_{\text{exp}} - Y^E_{\text{calcd}})^2}{(n-m)}\right]^{1/2}, \qquad (5)$$

where n is the number of data points and m is the number of coefficients.

The values of the excess molar volume V^E are found to be negative for mixtures of DMSO with butyl acetate, butyl amine, and 2-butanone, and their magnitudes follow the order given below:

butyl amine > 2-butanone > butyl acetate.

This indicates that specific interaction is present in the first three mixtures [21] and is strongest in the case of DMSO and butyl amine mixture followed by butanone and butyl acetate. But, for the mixture of DMSO with *tert*-butyl alcohol, the values of V^E are positive, indicating that dispersive force plays the main role [14, 22] in the case of a *tert*-butyl alcohol + DMSO mixture.

The values of V^E may be regarded as the result of contributions from several opposing effects [23], namely, physical, chemical, and structural ones. Physi-

Table 2. Measured and derived parameters for various studied binary mixtures at 298.15, 308.15, and 318.15 K

x_1	$\rho \times 10^{-3}$, kg m^{-3}	η, mPa s	$V^E \times 10^6$, m^3 mol^{-1}	$\Delta\eta$, mPa s	ΔG^{*E}, J mol^{-1}	d_{12}	T_{12}	H_{12}
tert-Butyl alcohol + DMSO, 298.15 K								
0.0953	0.8031	3.6683	0.068	−0.533	−270.70	−1.31	−0.41	0.12
0.1917	0.8269	3.0119	0.145	−0.954	−559.55	−1.51	−0.31	0.14
0.2890	0.8521	2.5592	0.225	−1.169	−762.96	−1.55	0.03	0.37
0.3874	0.8791	2.2505	0.276	−1.238	−881.15	−1.55	0.35	0.61
0.4868	0.9083	2.0714	0.296	−1.174	−887.18	−1.49	0.69	0.86
0.5872	0.9399	1.9671	0.281	−1.033	−816.73	−1.41	0.97	1.08
0.6888	0.9743	1.9624	0.222	−0.790	−625.17	−1.23	1.31	1.37
0.7914	1.0115	1.9556	0.148	−0.546	−437.31	−1.12	1.54	1.56
0.8951	1.0518	1.9423	0.065	−0.306	−258.69	−1.16	1.61	1.58
Butyl acetate + DMSO, 298.15 K								
0.1418	0.8943	0.6508	−0.140	−0.210	−419.83	−1.55	0.51	0.47
0.2710	0.9137	0.6822	−0.212	−0.349	−617.16	−1.42	0.55	0.45
0.3893	0.9335	0.7441	−0.238	−0.443	−698.62	−1.34	0.56	0.40
0.4979	0.9539	0.8413	−0.226	−0.489	−675.80	−1.27	0.58	0.36
0.5980	0.9750	0.9732	−0.192	−0.489	−583.06	−1.17	0.60	0.32
0.6905	0.9968	1.1292	−0.141	−0.455	−470.78	−1.09	0.62	0.27
0.7763	1.0195	1.3174	−0.089	−0.382	−334.72	−0.99	0.65	0.24
0.8561	1.0434	1.5356	−0.051	−0.267	−192.35	−0.85	0.71	0.25
0.9305	1.0686	1.7657	−0.019	−0.135	−76.24	−0.70	0.80	0.29
Butanone + DMSO, 298.15 K								
0.0930	0.8234	0.4384	−0.302	−0.090	−20.99	−0.09	0.70	0.65
0.1875	0.8492	0.5180	−0.520	−0.163	1.37	0.02	0.71	0.65
0.2834	0.8762	0.6758	−0.693	−0.160	263.84	0.54	0.87	0.79
0.3809	0.9041	0.8631	−0.800	−0.130	467.78	0.81	1.00	0.91
0.4799	0.9333	1.0880	−0.854	−0.065	632.84	1.04	1.16	1.06
0.5806	0.9635	1.3404	−0.837	0.025	735.31	1.23	1.34	1.24
0.6829	0.9947	1.5525	−0.737	0.072	679.11	1.28	1.45	1.35
0.7868	1.0274	1.7503	−0.589	0.102	549.37	1.34	1.57	1.49
0.8925	1.0608	1.9089	−0.345	0.090	332.04	1.42	1.72	1.65
Butylamine + DMSO, 298.15 K								
0.0942	0.7595	0.5608	−0.403	−0.076	−19.60	−0.10	0.87	0.80
0.1896	0.7892	0.6836	−0.711	−0.096	143.36	0.37	1.04	0.93
0.2862	0.8207	0.8842	−0.948	−0.040	448.01	0.88	1.28	1.15
0.3841	0.8540	1.1108	−1.109	0.040	675.78	1.15	1.48	1.32
0.4834	0.8892	1.3283	−1.191	0.109	776.10	1.25	1.61	1.55
0.5839	0.9265	1.5437	−1.185	0.174	801.06	1.33	1.74	1.74
0.6858	0.9658	1.7132	−1.073	0.191	706.96	1.33	1.81	1.93
0.7891	1.0070	1.8558	−0.845	0.179	548.66	1.34	1.88	2.13
0.8939	1.0503	1.9775	−0.501	0.144	345.03	1.48	2.06	2.07

Table 2. (Contd.)

x_1	$\rho \times 10^{-3}$, kg m^{-3}	η, mPa s	$V^E \times 10^6$, m^3 mol^{-1}	$\Delta\eta$, mPa s	ΔG^{*E}, J mol^{-1}	d_{12}	T_{12}	H_{12}
tert-Butyl alcohol + DMSO, 308.15 K								
0.0953	0.7932	2.4965	0.026	−0.191	−156.14	−0.75	0.95	1.14
0.1917	0.8173	2.2559	0.054	−0.327	−286.22	−0.76	1.03	1.19
0.2890	0.8430	2.0712	0.077	−0.406	−376.30	−0.76	1.13	1.26
0.3874	0.8703	1.9334	0.098	−0.437	−423.97	−0.74	1.23	1.33
0.4868	0.8996	1.8355	0.111	−0.427	−429.55	−0.72	1.33	1.39
0.5872	0.9310	1.7704	0.110	−0.383	−395.46	−0.68	1.41	1.46
0.6888	0.9648	1.7292	0.099	−0.314	−330.22	−0.65	1.49	1.51
0.7914	1.0014	1.6867	0.075	−0.245	−270.22	−0.69	1.51	1.51
0.8951	1.0411	1.6621	0.034	−0.157	−186.23	−0.82	1.44	1.41
Butyl acetate + DMSO, 308.15 K								
0.1418	0.8842	0.7177	−0.244	−0.098	−111.00	−0.51	0.90	0.79
0.2710	0.9037	0.7848	−0.335	−0.165	−158.04	−0.47	0.91	0.77
0.3893	0.9238	0.8663	−0.357	−0.206	−167.64	−0.44	0.92	0.75
0.4979	0.9438	0.9507	−0.339	−0.234	−178.27	−0.46	0.92	0.72
0.5980	0.9649	1.0476	−0.299	−0.241	−169.13	−0.46	0.91	0.69
0.6905	0.9869	1.1548	−0.258	−0.229	−149.89	−0.47	0.91	0.65
0.7763	1.0096	1.2712	−0.203	−0.202	−125.88	−0.48	0.90	0.61
0.8561	1.0334	1.4053	−0.144	−0.151	−84.19	−0.48	0.91	0.58
0.9305	1.0580	1.5465	−0.069	−0.087	−47.14	−0.50	0.89	0.52
Butanone + DMSO, 308.15 K								
0.0930	0.8124	0.4090	−0.215	−0.043	204.19	0.95	0.82	0.76
0.1875	0.8380	0.5575	−0.440	−0.025	593.52	1.53	1.01	0.93
0.2834	0.8655	0.7461	−0.692	0.031	927.48	1.80	1.18	1.09
0.3809	0.8940	0.9258	−0.860	0.076	1061.92	1.77	1.27	1.18
0.4799	0.9233	1.1266	−0.940	0.14	1141.60	1.80	1.39	1.29
0.5806	0.9533	1.3117	−0.906	0.186	1102.61	1.79	1.48	1.40
0.6829	0.9842	1.4620	−0.786	0.195	946.45	1.72	1.54	1.46
0.7868	1.0165	1.5877	−0.613	0.177	716.86	1.69	1.60	1.54
0.8925	1.0498	1.6767	−0.360	0.120	409.58	1.69	1.68	1.64
Butylamine + DMSO, 308.15 K								
0.0942	0.7489	0.5155	−0.529	−0.025	298.88	0.98	1.02	0.92
0.1896	0.7793	0.6382	−0.927	−0.025	614.32	1.06	1.10	0.98
0.2862	0.8111	0.8425	−1.212	0.055	1091.99	1.49	1.34	1.20
0.3841	0.8451	1.0464	−1.440	0.133	1408.81	1.62	1.49	1.34
0.4834	0.8804	1.2390	−1.509	0.198	1601.54	1.64	1.59	1.46
0.5839	0.9177	1.4212	−1.480	0.251	1709.70	1.67	1.70	1.58
0.6858	0.9567	1.5703	−1.320	0.269	1719.63	1.68	1.78	1.69
0.7891	0.9978	1.6681	−1.056	0.234	1543.01	1.66	1.83	1.77
0.8939	1.0403	1.6887	−0.618	0.12	1078.02	1.48	1.74	1.69

Table 2. (Contd.)

x_1	$\rho \times 10^{-3}$, kg m^{-3}	η, mPa s	$V^E \times 10^6$, m^3 mol^{-1}	$\Delta\eta$, mPa s	ΔG^{*E}, J mol^{-1}	d_{12}	T_{12}	H_{12}
tert-Butyl alcohol + DMSO, 318.15 K								
0.0953	0.7837	1.7142	0.032	−0.078	−78.06	−0.39	1.22	1.27
0.1917	0.8078	1.5876	0.060	−0.153	−216.16	−0.57	1.08	1.14
0.2890	0.8335	1.4874	0.080	−0.211	−325.19	−0.64	1.05	1.10
0.3874	0.8610	1.4069	0.092	−0.245	−410.41	−0.70	1.04	1.07
0.4868	0.8904	1.3750	0.096	−0.252	−410.63	−0.67	1.09	1.11
0.5872	0.9221	1.3684	0.087	−0.230	−365.21	−0.61	1.15	1.15
0.6888	0.9562	1.3737	0.069	−0.189	−298.64	−0.58	1.20	1.19
0.7914	0.9930	1.3890	0.043	−0.136	−215.40	−0.54	1.24	1.21
0.8951	1.0327	1.4189	0.020	−0.069	−107.35	−0.48	1.29	1.26
Butyl acetate + DMSO, 318.15 K								
0.1418	0.8758	0.5781	−0.212	−0.086	−116.05	−0.51	0.74	−2.39
0.2710	0.8955	0.6605	−0.348	−0.122	−70.40	−0.30	0.82	−0.66
0.3893	0.9158	0.7569	−0.426	−0.134	−1.55	−0.17	0.87	−0.07
0.4979	0.9365	0.8393	−0.443	−0.151	−4.94	−0.18	0.87	0.19
0.5980	0.9579	0.9280	−0.426	−0.154	−3.73	−0.19	0.87	0.34
0.6905	0.9799	1.0308	−0.383	−0.136	20.96	−0.15	0.89	0.45
0.7763	1.0026	1.1374	−0.312	−0.108	38.02	−0.11	0.91	0.54
0.8561	1.0261	1.2444	−0.222	−0.074	41.28	−0.08	0.94	0.61
0.9305	1.0504	1.3507	−0.113	−0.036	31.38	−0.03	0.97	0.68
Butanone + DMSO, 318.15 K								
0.0930	0.8051	0.3725	−0.389	−0.047	71.81	0.35	0.65	0.60
0.1875	0.8312	0.4369	−0.662	−0.091	107.63	0.29	0.64	0.59
0.2834	0.8584	0.5429	−0.870	−0.093	290.81	0.56	0.71	0.65
0.3809	0.8866	0.6887	−1.009	−0.058	523.03	0.86	0.83	0.76
0.4799	0.9161	0.8739	−1.093	0.015	749.95	1.16	0.99	0.91
0.5806	0.9472	1.0807	−1.142	0.107	901.39	1.43	1.17	1.10
0.6829	0.9797	1.2410	−1.128	0.151	989.72	1.76	1.44	1.39
0.7868	1.0127	1.3732	−0.979	0.165	932.08	2.15	1.77	1.75
0.8925	1.0455	1.3853	−0.657	0.057	641.73	2.59	2.14	2.18
Butylamine + DMSO, 318.15 K								
0.0942	0.7422	0.4387	−0.510	−0.024	174.36	0.78	0.85	0.76
0.1896	0.7728	0.5147	−0.960	−0.052	242.39	0.61	0.82	0.74
0.2862	0.8050	0.6441	−1.316	−0.028	476.63	0.90	0.94	0.84
0.3841	0.8396	0.8489	−1.623	0.070	841.07	1.36	1.17	1.05
0.4834	0.8762	1.0931	−1.826	0.206	1138.80	1.75	1.43	1.32
0.5839	0.9143	1.2867	−1.866	0.290	1196.30	1.89	1.60	1.50
0.6858	0.9541	1.4169	−1.760	0.309	1073.30	1.92	1.69	1.62
0.7891	0.9945	1.4255	−1.423	0.205	710.87	1.66	1.58	1.52
0.8939	1.0359	1.4277	−0.886	0.093	334.24	1.39	1.44	1.40

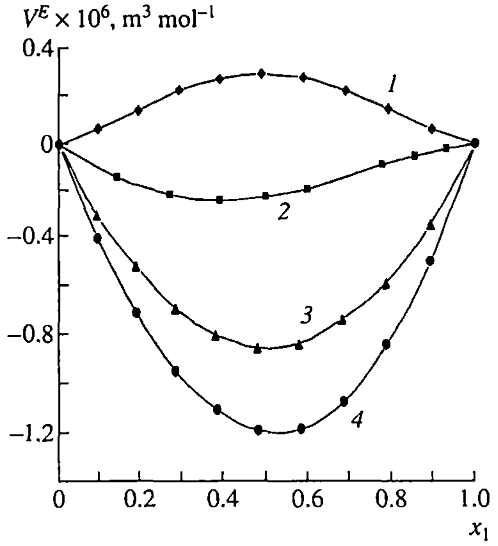

Fig. 1. Excess molar volumes (V^E) for binary mixtures of DMSO(x_1) with (*1*) *t*-butyl alcohol, (*2*) *n*-butyl acetate, (*3*) 2-butanone, and (*4*) *n*-butylamine at 298.15 K.

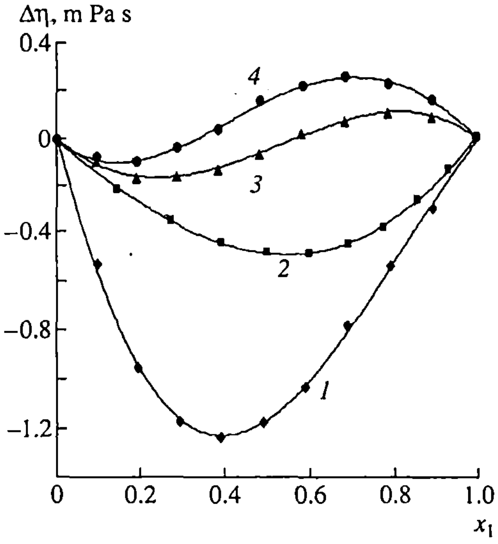

Fig. 2. Viscosity deviations (Δη) for binary mixtures of DMSO(x_1) with (*1*) *t*-butyl alcohol, (*2*) *n*-butyl acetate, (*3*) 2-butanone, and (*4*) *n*-butylamine at 298.15 K.

cal contributions are nonspecific interactions and contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease. The structural contributions arise especially from geometrical fitting (interstitial accommodation) of one component into the other due to the differences in the free volume and molar volume between the components and lead to a negative contribution to V^E.

The largest negative excess volume of DMSO and *n*-butyl amine system is due to the strong interaction between the oxygen atom of DMSO and the hydrogen atom of *n*-butyl amine. This indicates the formation of intermolecular hydrogen-bonded complexes. The parabolic shapes of V^E versus x_1 plots (Fig. 1) with well-defined minima also indicate the presence of complex formation. It is seen that the values of V^E for binary mixtures of DMSO with 2-butanone are also negative over the entire range of composition, suggesting specific interactions between the mixing components. These negative values of V^E may be attributed to dipole–dipole interactions resulting in the formation of electron-transfer complexes between the molecules of mixing components. The molar volumes of DMSO and butyl acetate differ considerably. Hence, smaller DMSO molecules are interstitially accommodated into aggregates of butyl acetate, yielding negative V^E values for DMSO and butyl acetate mixtures.

The DMSO + *tert*-butyl alcohol mixture is the only exception among the binary mixtures showing positive values of V^E over the entire composition and temperature range. Mixing of DMSO with *tert*-butyl alcohol would induce dissociation of the hydrogen bonds in the self-associated alcohol [24], leading to expansion in volume, and, thus, a positive contribution to V^E values. Another equally important contribution leading to the positive V^E values for this mixture arises from the close molecular sizes [25] of DMSO and *tert*-butyl alcohol.

Large negative values of viscosity deviations Δη are observed for the binary mixtures containing *t*-butyl alcohol and butyl acetate. For 2-butanone and butyl amine, the Δη values are negative for lower mole fractions of DMSO but become positive at higher mole fractions of DMSO, as shown in Fig. 2.

The negative Δη values of DMSO and *t*-butyl alcohol mixtures indicate the dominance of dispersion forces [25] between the unlike molecules [26]. According to Fort and Moore [27], Δη values are negative in systems of unequal molecular size, with dominant dispersive forces. This explains the negative Δη values for the DMSO and butyl acetate mixture. For 2-butanone and butyl amine mixtures with DMSO, positive Δη values indicate the presence of charge transfer interactions leading to the formation of complex species between unlike molecules [27]. These conclusions are in excellent agreement with that drawn from V^E values.

The systematic rise in V^E values with a rise in temperature (Table 2) for all the systems suggested an increase in interaction between the component molecules [28, 29]. The effect of temperature increase is to disrupt hetero and homo association of the molecules resulting in an increase in fluidity of the liquids giving higher Δη values at higher temperatures. Similar results have been reported earlier [28].

According to Reed and Taylor and Meyer et al., positive ΔG^{*E} values indicate specific interactions, while negative values indicate the dominance of dispersion forces [26, 30].

Table 3. Redlich–Kister coefficients and standard deviations (σ) for the binary mixtures at 298.15, 308.15, and 318.15 K

Excess property	T, K	A_0	A_1	A_2	A_3	A_4	σ
DMSO + *tert*-Butyl alcohol							
$V^E \times 10^6$, m^3 mol^{-1}	298.15	1.183	−0.074	−0.722			0.002
	308.15	0.442	0.121	−0.087	−0.126	−0.124	0.002
	318.15	0.378	−0.100	−0.147	–	–	0.001
Δη, mPa s	298.15	−4.664	2.294				0.023
	308.15	−1.689	0.711	−0.094	−0.588	−0.502	0.002
	318.15	−0.998	0.220	0.272	−0.182		0.001
ΔG^{*E}, J mol^{-1}	298.15	−3553.20	981.45	1660.60	−1224.24	−2480.93	9.21
	308.15	−1707.49	454.38	311.26	−1252.91	−710.67	3.22
	318.15	−1639.09	485.49	−1006.67	–	–	7.39
DMSO + butyl acetate							
$V^E \times 10^6$, m^3 mol^{-1}	298.15	−0.889	0.518	0.257	–	–	0.002
	308.15	−1.351	0.541	−0.436	0.116	–	0.003
	318.15	−1.778	−0.024	–	–	–	0.002
Δη, mPa s	298.15	−1.958	−0.373	–	–	–	0.006
	308.15	−0.933	−0.305	−0.177	–	–	0.001
	318.15	−0.615	−0.001	–	–	–	0.007
ΔG^{*E}, J mol^{-1}	298.15	−2688.68	1090.97	370.72	419.07	–	5.51
	308.15	−702.389	35.529	−217.51	218.25	–	3.37
	318.15	−28.83	46.12	675.66			3.57
DMSO + 2-Butanone							
$V^E \times 10^6$, m^3 mol^{-1}	298.15	−3.402	−0.052	−0.205	–	–	0.006
	308.15	0.599	0.931	−0.324	0.215	–	0.005
	318.15	−4.445	−1.210	−0.390	–	–	0.006
Δη, mPa s	298.15	−0.177	1.396	–	–	–	0.010
	308.15	0.599	0.931	0.214	–	–	0.005
	318.15	0.011	1.886	0.262	–	–	0.004
ΔG^{*E}, J mol^{-1}	298.15	2668.48	2379.35	−2772.74	−999.62		11.44
	308.15	4545.82	−180.14	−242.60	−563.24	−2344.28	16.42
	318.15	3125.33	3726.60	114.70	1235.00	–	6.95
DMSO + *n*-butylamine							
$V^E \times 10^6$, m^3 mol^{-1}	298.15	−4.787	−0.437	−0.191			0.003
	308.15	0.858	1.293	−0.563	−0.362	–	0.011
	318.15	−7.327	−2.062	−0.404	–	–	0.012
Δη, mPa s	298.15	0.510	1.266	−1.046	0.391	1.166	0.005
	308.15	1.121	1.783	−1.050	−1.39	–	0.014
	318.15	0.890	2.385	−1.662	−3.650	1.228	0.007
ΔG^{*E}, J mol^{-1}	298.15	3205.28	866.70	−2967.24	2496.09	976.64	16.87
	308.15	3808.74	2767.12	−518.58	999.67	–	16.24
	318.15	4644.68	3325.08	−2269.01	6206.62	−2316.12	17.05

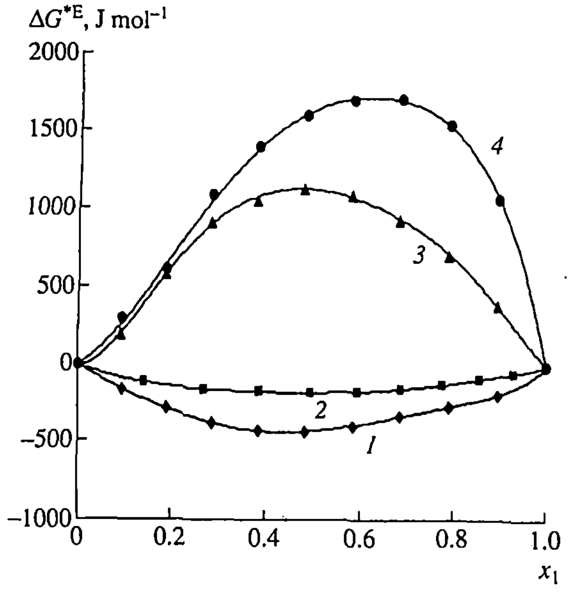

Fig. 3. Excess Gibbs energies for activation of viscous flow (ΔG^{*E}) for binary mixtures of DMSO(x_1) with (*1*) *t*-butyl alcohol, (*2*) *n*-butyl acetate, (*3*) 2-butanone, and (*4*) *n*-butylamine at 298.15 K.

It is seen that, for DMSO + *t*-butyl alcohol mixtures, the ΔG^{*E} values are negative over the entire range of the composition and temperature, indicating the dominance of dispersive forces between the mixing components. The large, positive ΔG^{*E} values for the DMSO + butylamine mixture speak in favor of strong specific interactions through complex formation in the system. The values of ΔG^{*E} for DMSO + 2-butanone system are less positive, suggesting weaker interactions in the system.

Several semiempirical relations have been proposed to estimate the dynamic viscosity (η) of liquid mixtures in terms of pure component data [30, 31]. Some of them that we examined are as follows:

The single parameter Grunberg–Nissan equation [32] reads as:

$$\eta = \exp\left[\sum_{i=1}^{2}(x_i \ln\eta_i) + x_1 x_2 d_{12}\right], \qquad (6)$$

where d_{12} is a parameter proportional to the interchange energy and has been regarded as an approximate measure for the nonideal behaviors of binary mixtures.

Tamura-Kurata [33] put forward the following equation for the viscosity of binary liquid mixtures:

$$\eta = \sum_{i=1}^{2} x_i\phi_i\eta_i + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12}, \qquad (7)$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of i^{th} pure component in the mixture.

Molecular interactions may also be interpreted by the viscosity model of Hind et al. [34],

$$\eta = \sum_{i=1}^{2} x_i^2\eta_i + 2(x_1x_2H_{12}), \qquad (8)$$

where H_{12} is the interaction parameter.

The values of the interaction parameter d_{12} have been calculated as a function of the composition of binary liquid mixtures and are listed in Table 2. From Table 2 we see that the DMSO + *n*-butylamine mixture, which involves large specific interaction, shows positive d_{12} values, whereas the DMSO + *t*-butyl alcohol system, where dispersive forces are predominant, shows negative d_{12} values [16, 35, 36].

The values of T_{12} and H_{12} have been calculated from Eqs. (4) and (5) and are listed in Table 2. It is observed from Table 2 that T_{12} and H_{12} values are positive for all binary mixtures, show almost identical values and do not change appreciably with the change of composition of binary mixtures. This is in agreement with the view put forward by Fort and Moore [27]. After a thorough study of the behavior of excess properties and interaction parameters of selected binary mixtures, it is observed that specific interaction is present in the systems of DMSO + *n*-butyl amine, + butyl acetate, and +2-butanone and that dispersive forces are dominant in the system of DMSO + *t*-butyl alcohol at all the experimental temperatures.

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REFERENCES

1. T. Kamiyama, M. Morita, and T. Kimura, J. Chem. Eng. Data **49**, 1350 (2004).
2. R. Francesconi, A. Bigi, K. Rubini, and F. Comelli, J. Chem. Eng. Data **50**, 1932 (2005).
3. C. Lafuente, B. Giner, A. Villares, et al., Int. J. Thermophys. **25**, 1735 (2004).
4. P. S. Nikam, L. N. Shirsat, and M. Hasan, J. Indian Chem. Soc. **77**, 244 (2000).
5. J. R.Suindells and T. B.Godfray, J. Res. Natl. Bur. Stand. **48**, 1, (1952).
6. M. N. Roy and A. Choudhury, J. Teach. Res. Chem. **1**, 17 (2000).
7. D. K. Hazra, M. N. Roy and B. Das, Ind. J. Chem. Technol. **1**, 93 (1994).
8. M. N. Roy, A. Jha, and R. Dey, J. Chem. Eng. Data **46**, 1247 (2001).
9. M. N. Roy, A. Jha, and A. Choudhury, J. Chem. Eng. Data **49**, 291 (2004).

10. N. V. Sastry and M. C. Patel. J. Chem. Eng. Data **48**, 1019 (2003).
11. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed. (Wiley–Interscience, New York, 1986).
12. R. Anson, S. Garriga, P. Martinez, et al., J. Chem. Eng. Data **50**, 677 (2005).
13. C. M. Kinart, W. J. Kinart, and D. J. Checinska-Majak, J. Chem. Eng. Data **48**, 1037 (2003).
14. Hsu-Chen Ku and K. Chein-Hsiun Tu, J. Chem. Eng. Data **50**, 608 (2005).
15. *TRC Thermodynamic Tables: Non-Hydrocarbons* (Thermodynamics Research Center, College Station, TX, 1971).
16. T. M Aminabhavi and K. Banerjee, J. Chem. Eng. Data **43**, 514 (1998).
17. *TRC Thermodynamic Tables: Non-Hydrocarbons* (Thermodynamics Research Center, College Station, TX, 1966).
18. A. W. Quin, D. F. Hoffmann and P. Munk, J. Chem. Eng. Data **37**, 55 (1992).
19. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Process: the Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena* (McGraw-Hill, New York, 1941), p. 514.
20. D. S. Gill, T. S. Kaur, H. Kaur, et al., J. Chem. Soc., Faraday Trans. **89**, 1737 (1993).
21. J. N. Nayak, T. M. Aminabhavi, and M. I. Aralaguppi, J. Chem. Eng. Data **48**, 1152 (2003).
22. M. N. Roy, A. Sinha, and B. Sinha, J. Solution Chem. **34**, 1311 (2005).
23. A. J. Treszczanowicz, O. Kiyohara, and G. C. Benson. J. Chem. Thermodyn. **13**, 253 (1981).
24. Y. Marcus, *Introduction to Liquid State Chemistry* (Wiley–Interscience, New York, 1977).
25. P. Assarson and F. R. Eirich, J. Phys. Chem. **72**, 2710 (1968)
26. T. M. Reed and T. E. Taylor, J. Phys. Chem, **63**, 58 (1959).
27. R. J. Fort and W. R. Moore, Trans. Faraday Soc. **62**, 1112 (1996).
28. T. N. Aminabhabi and B. Gopalkrisna, J. Chem. Eng. Data **39**, 529 (1994).
29. M. Singh, J. Ind. Chem. Soc. **79**, 659 (2002).
30. R. Meyer, M. Meyer, J. Metzer, and A. Peneloux, Chem. Phys. **62**, 406 (1971).
31. J. B. Irving, *NEL Report Nos. 630 and 631* (National Engineering Laboratory, East Kilbride, Glassgow).
32. L. Grunberg and A. H. Nissan, Nature **164**, 799 (1949).
33. M. Tamura and M. Kurata, Bull. Chem. Soc. Jpn. **25**, 32 (1952).
34. R. K. Hind, E. McLaughlin, and A. R. Ubbelohde, Trans. Faraday. Soc. **56**, 328 (1960).
35. K. Ramamoorthy, J. Pure Appl. Phys. **11**, 554 (1973).
36. K. Ramamoorthy, J. Pure Appl. Phys. **11**, 556 (1973).