PHYSICO-CHEMICAL INVESTIGATION ON VARIOUS INTERACTIONS IN 1,4-DIOXANE AND ITS BINARY SYSTEMS AND VISCOUS ANTAGONISM AND SYNERGISM PREVAILING IN SOME SOLVENT MEDIA

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Dedicated

To

My Granny,

Late Anjali Sinha

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This is to certify that **Mr. Biswajit Sinha**, M.Sc. (Chemistry) has carried out his research work embodied in the thesis entitled "**Physico-Chemical Investigation On Various Interactions In 1,4-Dioxane And Its Binary Systems And Viscous Antagonism And Synergism Prevailing In Some Solvent Media**" based on his original works, under my supervision and guidance. He is submitting his thesis for the award of Doctor of Philosophy (Science) degree in Chemistry in accordance with the rules and regulations of the University of North Bengal.

I am much impressed for his keen interest and research aptitudes on such a difficult and interesting topic. In my opinion, he is fit and proper person for the degree of Doctor of Philosophy (Ph. D.) in Chemistry of the University of North Bengal.

I wish him every success in life.

Date : March, 2007.

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CHAPTER I

1.1. Object and application of the research work

In recent years there has been an increasing interest in the study of physico-chemical properties of solvent-solvent[1-3] and solute-solvent[4-6] systems. The physico-chemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts in recent years 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[7] made the first systematic attempt in these directions by collecting a number of data on the thermodynamic and mechanical properties of liquid mixtures. 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.

Molecular behavior of a formulation[8] can influence aspects such as, patient acceptability, since it has been well demonstrated that density and viscosity both influence the absorption rate of such products in the body.[9, 10] The rheological behavior of such products is also a matter of major concern in this regards. Rheology is the branch of science[11] that studies material deformation and flow, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied to the analysis of the viscous behavior of many pharmaceutical products,[12-16] and to establish their stability and even bio-availability.

Considering the rheological behavior, the study of viscous synergy and antagonism is important, since many products are formulated with more than one component in order to yield the desired physical structure and properties.[17] Synergy and antagonism gives the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components of a given mixture. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system[18, 19] is said to lack interaction. The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

In solution chemistry the way for proper understanding of the different phenomena regarding the molecular interactions forms the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents. Estimates of ion-solvent interactions can be had thermodynamically and also from the measurement of partial molar volumes, viscosity B - coefficient and limiting ionic conductivity studies. Estimates of single-ion values enable us to refine our model of ion-solvent interactions. Acceptable values of ion-solvent interactions would enable the chemists to choose solvents that will enhance (i) the rates of chemical reactions, (ii) the solubility of minerals in leaching operations or (iii) reverse the direction of equilibrium reactions.

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are now well recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck[20], Franks[21], Popovych[22], Bates[23], Parker[24], Criss and Salomon[25], Marcus[26] and others.[27-29] The solute-solute and solute-solvent interactions have been subject of wide interest as apparent from Faraday Transactions of the chemical society.[30]

In spite of vast collections of data on the different electrolytic and non-electrolytic solutions in water, the structure of water and the different types of interactions that water undergoes with electrolytes are yet to be properly understood. However, the studies on properties of aqueous solutions have provided sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties.[21,31]

Object and application of the research work

In recent years, there has been increasing interest in the behavior of electrolytes or solutes 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 opened vistas for physical chemists and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry.[32]

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.[33-35] 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.[36,37] 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.[38]

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become evident that the majority of the solutes are significantly influenced by the solvents. Conversely, the nature of strongly structured solvents like water, is substantially modified by the presence of solutes.[39]

A knowledge of ion-solvent interactions in non-aqueous solutions[28] 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 theories. 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 in solution.

1.2. Importance and scope of Physico-chemical parameters:

The study of physico-chemical properties involves the interpretation of the excess properties as a mean of unraveling the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of characteristic departure from ideal behavior of some physical properties such as density, volume, viscosity, compressibility etc.[40, 41]

Density of solvent mixtures and related volumetric properties like excess molar volume are essential for theoretical as well as practical aspects. The sign and magnitude of excess molar volume imparts estimate of strength of unlike interactions in the binaries. The negative values of excess molar volume (V^{E}) suggest specific interactions[42,43] between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces[42,43] between them. The negative V^{E} values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. The negative

V^E values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.[42]

A knowledge of viscosity of fluids is required in most engineering calculations where fluid flow, mass transport and heat transport are important factors. Viscosity data provides valuable information about the nature and strength of forces operating within and between the unlike molecules. Recently the employment of computer simulation of molecular dynamics has led to significant improvement towards a successful molecular theory of transport properties in fluids and a proper understanding of molecular motions and interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents.[44,45] The study of physico-chemical behaviors like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. Excess isentropic compressibility, intermolecular free length etc impart valuable information about the structure and molecular interactions in pure and mixed solvents. The acoustic measurements can also be used for the test of various solvent theories and statistical models and are quite sensitive to changes in ionic concentrations as well as useful in elucidating the solute-solvent interactions.

Drugs are basically composed of organic molecules and the study of bio-molecules plays a key role in the elucidation of thermodynamic properties of bio-chemical processes in living cells. The process of drug transport, protein binding, anesthesia, etc are few examples where drug and bio-macromolecules appear to interact in an important and vitally significant way. Drug transport across biological cells and membranes is dependent on physico-chemical properties of drugs. But direct study of the physico-chemical properties in physiological media such as blood, intracellular fluids is difficult to accomplish. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as thermodynamic parameters are convenient for interpreting intermolecular interactions in solution phase. Also the study of thermodynamic properties of drug in a suitable medium can be correlated to its theraptic effects.[46, 47] These facts therefore prompted us to undertake the study of binary or ternary solvent systems with 1,4-dioxane and 1,3-dioxolane or tetrahydrofuran as primary solvents with some polar, weakly polar and non-polar solvents as well as with some solutes. Furthermore, the excess properties derived from experimental density, viscosity and speeds of sound data and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

1.3. Importance of solvents used:

1,4-Dioxane, 1,3-Dioxolane, Tetrahydrofuran, Benzene, n-Hexane, N, N-Dimethylformamide, Butyric acid, Butylamine, 2-butanone, Monoalkanols viz. Methanol, Ethanol, 1-Propanol, 2-Propanol, 1-Butanol, 2-Butanol, t-Butanol, i-Amyl alcohol some alkyl acetates viz. Methyl acetate, Ethyl acetate, i-amyl acetate, Butyl acetate along with water considered as a universal solvent have been chosen as main 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.

1,4-dioxane is very hygroscopic and miscible in all proportions with water. Its dielectric constant and dipole moment are 2.209 and 0.45D respectively at 25^{0}C. However, its dipole moment rises with increase in temperature suggesting formation of boat form.[32]

Tetrahydrofuran is moderately toxic and has been widely used as a solvent for organometallics and forms blue solutions with alkali metals and most inorganic salts except lithium and sodium perchlorates are insoluble.

1,4-dioxane, 1,3-dioxolane and tetrahydrofuran are all cyclic ethers and they figure prominently in the high-energy battery technology[48] 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.[49]

N, N-dimethylformamide is a non-associative aprotic protophilic solvent with a liquid range of –60 to 153^{0}C, low vapour pressure and good solubility for a wide range of substances. It is slightly basic and a popular solvent in visible and near u. v. spectrometry (>270 nm) and for polarographic work. It is also used in the separation of saturated and unsaturated hydrocarbons and serves as solvents for vinyl resins, acid gases, polyacrylic fibres and catalyst in carbonylation reaction as well as in organic synthesis. It has also been used as the model of peptide linkage in studies aimed at understanding of protein denaturation studies.[50, 51]

The increasing use of 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran, N, N-dimethylformamide, 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.[52, 53]

The hydrocarbons, both aromatic and aliphatic have varied applications. Benzene is used as solvents for fats and oils, dry-cleaner of woolen clothes, anti-knock gasoline and in manufacture of detergents, insecticides, etc. whereas n-hexane, which is familiar in the laboratory as the principle component of petroleum ether, is used as solvent, dry-cleaner and motor fuel.

Alcohols and their 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.[8] A knowledge of their physico-chemical characteristics helps to understand their behavior in a better way.

Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc. It is obtainable commercially in adequate purity for most purposes, the principle impurity being up to 0.05% water usually be removed by distillation, or by use of molecular sieves and calcium hydride. Ethanol has been used as a solvent in quantitative studies and 'Absolute' alcohol usually contains 0.01% water.
The importance of iso-amyl alcohol in research field is implied for its usefulness in gas chromatography. It can isolate high quality RNA from even the hardest to isolate samples for immediate use in micro array application and it is also useful in most DNA applications.[54]

However, it is worth mentioning that 1,4-dioxane differs from alcohols in its behaviour towards water. Alcohols are usually structure makers whereas 1,4-dioxane acts as a net structure breaker.[55] Aqueous 1,4-dioxane mixtures have been found to be more basic than water and the basicity has been found to be maximum in the region 45-50 mass% of 1,4-dioxane.[56]

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.

1.4. Method of Investigations

The phenomenon of synergy, antagonism, ion-ion, ion-solvent and solvent-solvent interactions are intriguing. It is desirable to explore these interactions using different experimental techniques. We have, therefore, employed four important methods, viz. densitometry, viscometry, ultrasonic interferometry and conductometry in our research works.

Viscosity and density have been used to interpret the synergic and antagonic behavior in the solvent mixtures. The values of synergic and antagonic interaction indices determine the nature of the molecular package.

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 volume, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solute and solute-solvent 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 investigations.

The excess properties such as excess molar volume, viscosity deviations and deviation in isentropic compressibility along with the correlating equations explain 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.

1.5. Summary of the works done

Chapter I

This chapter contains the object and applications of the research work, the reasons for choosing the main solvents and solutes and methods of investigation. This also includes a summary of the works associated with the thesis.

Chapter II

This chapter contains the general introduction of the thesis and forms a background of the works embodied in the thesis. Viscous synergy and antagonism have been defined along with their interaction indices. A brief review of notable works on ion-ion, ion-solvent and solvent-solvent interaction has been made. Also an attempt has been made to define these interactions. Various derived parameters dependent on density, viscosity, ultrasonic speed of sound and conductance along with their importance in solution chemistry has been discussed. Several semi-empirical models to estimate dynamic viscosity of binary liquid mixtures have been discussed.

Ionic association and its dependence on ion-size parameters as well as relation between solution viscosity and limiting conductance of an ion has been discussed using Stokes' law and Walden rule. Critical evaluations of different methods employed frequently for obtaining the single ion values (viscosity B-coefficient and limiting equivalent conductance) and their implications have been discussed.

Chapter III

This chapter contains the experimental section mainly involving 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 chapter presents a study on viscous synergy and isentropic compressibility in the systems comprising some monoalkanols (C_1-C_4) and cyclic ethers (1,4-dioxane and tetrahydrofuran) in the proportion $w/w = 1:1$, in water at different concentrations (w/w) at 298.15 K to determine the proportion of monoalkanol + cyclic ether + water, at which maximum synergy occurs. The density and viscosity data have been analyzed using the equation developed by Kaletunc-Gencer and Peleg. Also a correlation between the density and viscosity increment for all the systems has been attempted. The ratio between maximum viscosity reached by the mixtures and pure state viscosity is expressed by the enhancement index defined as: $E_n = \eta_{max}/\eta_0$.

Chapter V

In this chapter the densities, viscosities, and ultrasonic speeds of resorcinol in 1,4-dioxane + water mixtures and in pure 1,4-dioxane have been measured at 303.15, 313.15 and 323.15 K. Apparent molar volumes (V_ϕ) and viscosity B-coefficients were obtained from the experimental data. 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 the Jones-Dole equation, and the derived parameters A and B have also been interpreted in terms of solute-solute and solute-solvent interactions, respectively. The structure making/breaking capacities of resorcinol in the studied solvent systems have been discussed.

Chapter VI

In this chapter electrical conductances of some ammonium and tetraalkylammonium halides have been measured in different mass% of 1,4-dioxane + water mixtures (20%, 40%, 60% and 80%) at 298.15 K. The limiting molar conductivity (Λ_0), the association constant (K_A) and association distance (R) in the solvent mixtures have been evaluated using Fuoss conductance equation (1978). 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 VII

In this chapter the densities and viscosities of ternary mixtures of tetrahydrofuran + methanol + benzene and isopropanol + benzene + n-hexane have been measured at 303.15, 313.15 and 323.15 K over the entire range of composition. The data have been analyzed using the equation developed by Kaletune-Gencer and Peleg. The experimental results have been discussed and explained in terms of molecular package and electrostriction.

Chapter VIII

In this chapter 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 density (ρ) and viscosity (η) measurements of eight binary mixtures of 1,3-dioxolane with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, t-butanol and iso-amyl alcohol over the entire range of mole fractions at 303.15 K. The viscosity data have been correlated with Grunberg-Nissan equation. The excess or deviation properties have been fitted to Redlich–Kister polynomial equation and the results have been discussed in terms of molecular interactions and structural effects.

Chapter IX

In this chapter apparent molar volumes (V_ϕ) and viscosity B-coefficients of sodium molybdate in aqueous binary mixtures of 1,4-dioxane have been determined from density and viscosity measurements at 303.15, 313.15 and 323.15 K and at various electrolyte concentrations. Adiabatic compressibility (β) of different solutions have been determined from the measurement of ultrasonic speeds of sound at 303.15 K. Experimental density data were evaluated using the Masson equation and the derived parameters interpreted in terms of ion-solvent and ion-ion interactions. Partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane mixtures have also been calculated and discussed. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of the sign of $(\delta^2 V_\phi^0 / \delta T^2)_p$.

Chapter X

In this chapter the densities and viscosities have been measured for the binary mixtures of butylamine and N, N- dimethylformamide with methyl acetate, ethyl acetate, butyl acetate and iso-amyl acetate at 298.15 K over the entire range of composition. From density and viscosity data, the values of excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) have been determined. These results have been fitted to Redlich–Kister polynomial equation to estimate the binary coefficients and standard errors between the experimental and the computed values. The density and viscosity data have been analyzed in terms of some semiempirical viscosity models and the results have been discussed in terms of molecular interactions and structural effects.

Chapter XI

In this chapter the densities and viscosities were measured for the binary mixtures of 1,4-dioxane and 1,3-dioxolane with butyl acetate, butyric acid, butylamine and 2-butanone at 298.15 K over the entire range of composition. From density and viscosity data, the values of excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) have been determined. These results were fitted to Redlich–Kister polynomial equation. The density and viscosity data have also been analyzed in term of some semi empirical viscosity models.

Chapter XII

This chapter contains the concluding remarks on the works related to the thesis.

References

[1] A. J. Queimade, I. M. Marrucho, J. A. P. Coutinho, E. H. Stenby, Int. J. Thermophys., 26 (2005) 47.

[2] A. Ali, Abida, A. K. Nain, S. Hyder, J. Soln. Chem., 32 (2003) 865.

[3] N. N. Wankhede, M. K. Lande, B. R. Arbad, J. Chem. Eng. Data., 50 (2005) 969.

[4] A. Sinha, M. N. Roy, J. Chem. Eng. Data., 51 (2006) 1415.

[5] L. H. Blanco, E. F. Vargas, J. Soln. Chem., 35 (2006) 21.

[6] M. N. Roy, A. Sinha, Fluid. Phase. Equilibr., 243 (2006) 133.

[7] S. T. Young, Phil. Mag., 33 (1882) 153.

[8] J. V. Herraez, R. Belda, O. Diez, Phys. Chem. Liq., 42 (2004) 467.

[9] C. Fauli-Trillo, *Tratado de Farmacia Galencia*, Ed. S.A. Lujan, Madrid, (1993).

[10] J. Swarbrik, J. C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, New York, (1993).

[11] J. V. Herraez, R. Belda, J. Soln Chem., 33 (2004) 117.

[12] C. K. Zeberg-Mikkelsen, S. E. Quinones-Cisneros, S. H. Stenby, Fluid Phase Equilibr., 194 (2002) 1191.

[13] R. Shukla, M. Cheryan, Journal of Membrane Science, 198 (2002) 104.

[14] M. J. Assael, N. K. Dalaouti, I. Metaxa, Fluid Phase Equilibr., 199 (2002) 237.

[15] J.M. Resa, C. Gonzalez, J. Lanz, J. Food Engineering, 51 (2002) 113.

[16] M. Garcia-Velarde, Revista Espanola de Fisica, 9 (1995) 12.

[17] E. R. Morris, *Food Gels - Applied Science*, Elsevier, London, (1984).

[18] J. Pellicer, *Sinergia Viscosa*, Valencia, Spain, October (1997).

[19] G. Copetti, R. Lapasin, E. R. Morris, *Proceedings of the 4th European Rheology Conference*, Seville, Spain, (1994) 215.

[20] D. K. Meck, *The Chemistry of Non-Aqueous Solvents*, Ed. J. J. Lagowski, Academic, New York, Vol-1, Chapter 1, (1966).

[21] F. Franks, *Physico-Chemical Processes in Mixed Aqueous Solvents*, Heinemann Educational Books Ltd., (1967).

[22] O. Popovych, Crit. Rev. Anal. Chem., 1 (1973) 73.

[23] R. G. Bates, *Solute-Solvent Interactions*, Eds. J. J. Coetzee, C.D. Ritchie, Marcel Dekker, New York, (1969).

[24] A. J. Parker, Electrochim. Acta., 21(1976) 671.

[25] C. M. Criss, M. Salomon, J. Chem. Edu., 53 (1976) 763.

[26] Y. Marcus, *Ion Solvation*, Wiley, Chinchester, (1986).

[27] R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation*, Elsevier, Amsterdam, (1988).

[28] O. Popovych, R. P. T. Tomkins, *Non-Aqueous Solution Chemistry*, John Wiley and Sons, New York, (1981).

[29] E. J. King, *Acid-Base Equilibria*, Pergamon, Oxford, (1965).

[30] *Faraday Discussions of the Chemical Society*, 67 (1977).

[31] G. S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport process*, Ed. R.A. Horne, Wiley, Chapters 9 &10 (1972).

[32] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).

[33] Y. Marcus, *Ion Properties*, Dekker, New York, (1997).

[34] A. Masquez, A Vargas, P. B. Balbuena, J. Electron. Soc., 45 (1998) 3328.

[35] A. F. D. Namor, M. A. L. Tanco, M. Solomon, J. Phys. Chem., 98 (1994) 11796.

[36] A. Chandra, B. Bagchi, J. Phys. Chem. B., 104 (2000) 9067.

[37] G. Atkinson, R. Garney, M. J. Taft, *Hydrogen Bonded Solvent Systems*, Eds. A. K. Covington, P. Jones, Taylor and Francis, London, (1968).

[38] W.E. Waghorne, *Chem. Soc. Rev.* (1993) 285.

[39] K. Gunaseelau, S. Dev, K. Ismail, Ind. J. Chem., 39A (2000) 761.

[40] M. Iqbal, R. E. Verral, Can. J. Chem., 67 (1989) 727.

[41] E. P. Georgios, I. Z. Ioannis, J. Chem. Eng. Data., 37 (1992) 167.

[42] J. N. Nayak, M. I. Aralaguppi, T. J. Aminabhavi, J. Chem. Eng. Data., 48 (2003) 1489.

[43] K. Hsu-Chen, T. Chein-Hsiun, J. Chem. Eng. Data., 50 (2005) 608.

[44] A. Ali, A. K. Nain, J. Pure. Appl. Ultrasonics., 22 (2000) 10.

[45] J. H. Dymond, Chem. Soc. Rev., 14 (1985) 317.

[46] E. L. Herric, J. G. Brewer, J. Chem. Eng. Data., 14 (1969) 55.

[47] P. K. Gessner, M. P. Shakarjian, J. Pharm. Exptal. Therap., 235 (1985) 32.

[48] C. G. Janz, R. P. T. Tomkins, *Non-Aqueous Electrolytes Handbook,* Academic, New York, 2 (1973).

[49] P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo, J. Chem. Eng. Data., 48 (1999) 1341.

[50] D. B. Henson, C. A. Swensen, J. Phys. Chem., 77 (1973) 2401.

[51] D. Balasubramanium, R. Shaikh, Biopolymers., 12 (1973) 1639.

[52] C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, Int. J. Thermophys., 55 (2004) 1735.

[53] P. S. Nikam, L. N. Shirsat, M. Hasan, J. Ind. Chem. Soc. 77 (2000) 244.

[54] J. Verga, E. Rinyu, E. Kevei, B. Toth, Z. Kozakiewicz, Can. J. Microbiol/ Rev. Can. Microbiol, 44 (1998) 569.

[55] K. Majumdar, S. C. Lahiri, D. C. Mukherjee, J. Ind. Chem. Soc., 70 (1993) 365.

[56] K. Majumdar, S. C. Lahiri, J. Ind. Chem. Soc., 74 (1997) 382.

CHAPTER II

2.1. Viscous Synergy and Antagonism

Rheology is the branch of science[1] that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products,[2-11] and to establish their stability and even bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.[12, 13]

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction.[14, 15]

The method most widely used to analyze the synergic and antagonic behavior of the ternary liquid mixtures used here is that developed by Kaletunc-Gencer and Peleg[16] allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp}, with the viscosity expected in the absence of interaction, η_{calc} as defined by the simple mixing rule as:

$$\eta_{calc} = \sum_{i=1}^{j} w_i \eta_i \qquad (1)$$

where w_i and η_i are the fraction by weight and the viscosity of the ith component, measured experimentally and i is an integer.

Accordingly, when $\eta_{exp} > \eta_{calc}$, viscous synergy exists, while, when $\eta_{calc} > \eta_{exp}$, the system is said to exhibit viscous antagonism.

This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other synergy indices are defined in consequence.[17]

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_S) as introduced by Howell[18] is taken into account:

$$I_S = \frac{\eta_{exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \qquad (2)$$

When the values of I_S are negative, it is termed as antagonic interaction index (I_A).

The method used to analyze volume contraction and expansion is similar to that applied to viscosity, i.e., the density of the mixture is determined experimentally, ρ_{exp}, and a calculation is made for ρ_{calc} based on the expression:

$$\rho_{calc} = \sum_{i=1}^{j} w_i \rho_i \qquad (3)$$

where ρ_i is the experimentally measured density of the ith component. Other symbols have their usual significance.

Accordingly, when $\rho_{exp} > \rho_{calc}$, volume contraction occurs, but when $\rho_{calc} > \rho_{exp}$, there is volume expansion in the system.

Also a power factor termed as the enhancement index (E_η) has also been studied.[1] The enhancement index of the viscosity given as:

$$E_\eta = \frac{\eta_{max}}{\eta_0} \qquad (4)$$

where η_{max} is the maximum viscosity attained in the mixture and η_0 is the experimental viscosity of the pure components.

The investigations have been carried out with ternary mixtures of tetrahydrofuran + methanol + benzene, isopropanol + benzene + n-hexane at 303.15, 313.15 and 323.15 K and ternary mixtures of 1,4-dioxane or tetrahydrofuran with water and monoalkanols and water + tetrahydrofuran + 1,4-dioxane at 298.15 K. The monoalkanols were methanol, Ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol.

2.2. Ion-Solvent Interaction

The formation of mobile ions in solution is a basic aspect to electrochemistry. There are two distinct ways that mobile ions form in solution to create ionically conducting phases. The first one is illustrated for aqueous acetic acid in figure 1:[19]

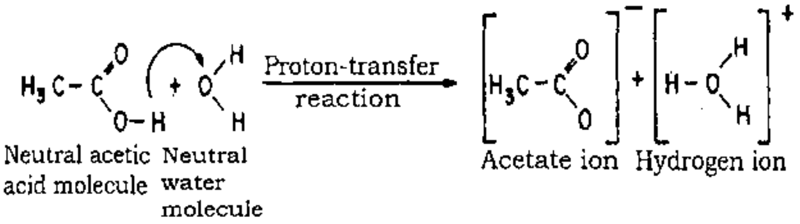

Figure1. The chemical method of producing ionic solutions.

The second one involves dissociation of a solid lattice of ions such as the lattice of sodium chloride. The ion formation, as shown in figure 2,[19] is as if the solvent colliding with the walls of the crystal gives the ions in the crystal lattice a better deal energetically than they have within the lattice. It entices them out and into the solution. Thus there is a considerable energy of interaction between the ions and the solvent molecules. These interactions are collectively termed as ion- solvent interactions.

Ions orient dipoles. The spherically symmetrical electric field of the ion may tear solvent dipoles out of the solvent lattice and orient them with appropriate charged end toward the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. The majority of reactions occurring in solutions are chemical or biological in nature. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents.[20-29]

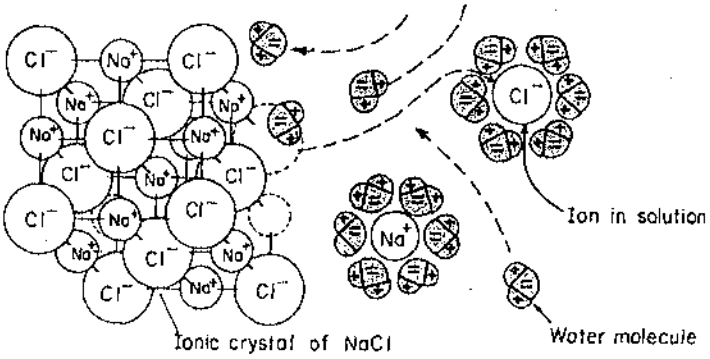

Figure 2. Dissolution of an ionic crystal by the action of a solvent.

As water is the most abundant solvent in nature and its major importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic and equilibrium studies. But still our knowledge of molecular interactions in water is extremely limited. Moreover, the uniqueness of water as a solvent has been questioned[30, 31] and it has been realized that the studies of other solvent media like non-aqueous and mixed solvents would be of great help in understanding different molecular interactions and a host of complicated phenomena. [20-29]

The organic solvents have been classified based on the dielectric constants, organic group types, acid base properties or association through hydrogen bonding,[29] donor-acceptor properties,[32, 33] hard and soft acid-base principles,[34] etc. As a result, the different solvents show a wide divergence of properties ultimately influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes or non-electrolytes in various solvents would thus provide important information in this direction. Henceforth, in the development of theories of electrolytic solutions, much attention has been devoted to the controlling forces-'ion-solvent interactions' in infinitely dilute solutions wherein ion-ion interactions are almost absent. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a key role to understand the physico-chemical properties of solutions.

One of the causes for the intricacies in solution chemistry is the uncertainty about the structure of the solvent molecules in solution. The introduction of a solute modifies the solvent structure to an uncertain magnitude, also the solute molecule is modified by the solvent molecule and the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemist.

Ion-solvent interactions can be studied by spectrometry.[35, 36] The spectral solvent shifts or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent interactions. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

It is thus apparent that the real understanding of the ion-solvent interaction is a difficult task. The aspect embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc. and such thermodynamic properties as apparent and partial molar volumes and apparent molal adiabatic compressibility.

2.3. Ion-ion interaction

Ion-solvent interactions are only a part of the story of an ion related to its environment. The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions constitute the essential part- 'ion-ion interactions'. The degree of ion-ion interactions affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions, in general, are stronger than ion-solvent interactions. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but ion-solvent interactions or ion-solvation still remains a complex process.

While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the majority of the solutes are significantly modified by the solvents. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-

solvent interactions are elucidated and thus the present dissertation is intimately related to the studies of solute-solute, solute-solvent and solvent-solvent interactions in some solvent media.

2.4. Theory of Mixed Solvents

As the mixed and non-aqueous solvents are increasingly used in chromatography, solvent extraction, in the elucidation of reaction mechanism, in preparing high density batteries, etc. a number of molecular theories, based on either the radial distribution function or the choice of suitable physical model, have been developed for mixed solvents. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. L. Jones and Devonshire[37] were first to evaluate the thermodynamic functions for a single fluid in terms of interchange energy parameters. They used "Free volume" or "Cell model". Prigogine and Garikian[38] extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans[39] developed a two fluid version of the cell model. They found that while excess molar volume (V^E) was negative for mixtures with molecules of almost same size, it was large positive for mixtures with molecules having small difference in their molecular sizes. Treszczanowicz et al.[40] suggested that V^E is the result of several contributions from several opposing effects. These may be divided arbitrarily into three types, viz. physical, chemical and structural. Physical contributions contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change would therefore depend on the relative strength of these effects. However, it is generally assumed that when V^E is negative, viscosity deviation $(\Delta\eta)$ may be positive and vise-versa. This assumption is not a concrete one, as evident from some studies.[41-42] It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi et al.[43] therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-interaction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Based on the principle of corresponding states as suggested by Pitzer,[44] L. Huggins[45] introduced a new approach in his theory of conformal solutions. Using a simple perturbation approach, he showed that the properties of mixtures could be obtained from the knowledge of intermolecular forces and thermodynamic properties of the pure components. Recently, Rowlinson et al.[46-48] reformulated the average rules for van der waals mixtures and their calculated values were in much better agreement with the experimental values even when one fluid theory was applied. The more recent independent effort is the perturbation theory of Baker and Henderson.[49] A more successful approach is due to Flory who made the use of certain features of cell theory and assumed an empirical equation for the dependence of energy on volume. Flory et al.[50-52] developed a statistical theory for predicting the excess properties of binary mixtures by using the equation of state and the properties of pure components along with some adjustable parameters. This theory is applicable to mixtures containing components with molecules of different shapes and sizes. Patterson and Dilamas[53] combined both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure etc. to the excess thermodynamic properties. Recently, Heintz[54-56] and coworkers suggested a theoretical model based on a statistical mechanical derivation and accounts for self-association and cross-association in hydrogen bonded solvent mixtures is termed as extended real associated solution model (ERAS). It combines the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory et al. [50-52] Subsequently the ERAS model has been successfully applied by many workers[57-59] to describe the excess thermodynamic properties of alkanol-amine mixtures.

2.5. 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 like electrostriction,[60] hydrophobic hydration,[61] micellization[62] and co-sphere overlap during solute-solvent interactions[63] to a large extent have been derived and interpreted from the partial molar volume data of many compounds.

2.5.1. 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[19] 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:[64]

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/(c\rho_0) \quad (5)$$

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:[65]

$$\overline{V_2} = V_\phi + (1000 - cV_\phi)\big/(2000 + c^{3/2}.\partial V_\phi/\partial\sqrt{c})\sqrt{c}.\partial V_\phi/\partial\sqrt{c} \quad (6)$$

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 a period of years – the Masson equation,[66] the Redlich-Meyer equation,[67] the Owen-Brinkley equation[68] and the Pitzer equation.[44] Masson found that the apparent molar volume of electrolyte, V_ϕ, vary with the square root of the molar concentration by the linear equation:

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

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[69] and nearly all V_ϕ data in non-aqueous[70-74] solvents have been extrapolated to infinite dilution through the use of equation (7).

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

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{8}$$

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 (8). Thus,

$$\phi_E^0 = (\partial V_\phi^0 / \partial T)_P = a_1 + 2a_2 T^2 \tag{9}$$

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

During the past few years, different workers emphasized that S_V^* is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler[75] 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:

$$(\partial C_P / \partial P)_T = -(\partial^2 V_\phi^0 / \partial T^2)_P \tag{10}$$

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[67] have shown that equation (7) cannot be more than a limiting law and for a given solvent and temperature the slope, S_V^* should depend only upon the valence type. They suggested an equation for representing V_ϕ as follows:

$$V_\phi = V_\phi^0 + S_V\sqrt{c} + b_V c \tag{11}$$

$$\text{where, } S_V = Kw^{3/2} \tag{12}$$

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

$$w = 0.5\sum_i^j \gamma_i z_i^2 \tag{13}$$

$$\text{and, } K = N^2e^2(8\pi/1000\varepsilon^3RT)^{1/2}[(\partial\ln\varepsilon/\partial P)_T - \beta/3] \tag{14}$$

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[67] extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However, studies[76-78] 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[68] 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:

$$V_\phi = V_\phi^0 + S_V\tau(Ka)\sqrt{c} + 0.5w_V\theta(Ka) + 0.5K_V c \tag{15}$$

where the symbols have their usual significance. However, equation (15) has not been widely employed for the treatment of results for non-aqueous solutions.

Recently, Pogue and Atkinson[79] used the Pitzer formalism to fit the apparent molar volume data. The Pitzer equation for the apparent molar volume of a single salt $M_{\gamma M}X_{\gamma X}$ is:

$$V_\phi = V_\phi^0 + V|z_M z_X|A_V|2b ln(I + bI^{0.5}) + 2\gamma_M \gamma_X RT[mB_{MX}^2 + m^2(\gamma_M \gamma_X)^{0.5} C_{MX}^V] \qquad (16)$$

where the symbols have their usual significance.

2.5.2. 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 salvation. The calculation of the ionic limiting partial molar volumes in organic solvents is, however, a difficult one. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions[80] to non-aqueous electrolyte solutions.

In the last few years, the method suggested by Conway et al.[80] 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, $\overline{V}^0_{R_4NX}$ for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{R_4N^+}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\overline{V}^0_{R_4NX} = \overline{V}^0_{X^-} + bM_{R_4N^+} \qquad (17)$$

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

Uosaki et al. [81] used this method for the separation of some literature values and of their own $\overline{V}^0_{R_4NX}$ values into ionic contributions in organic electrolyte solutions. Krumgalz[82] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.5.3. 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: [83, 84]

$$V^E = \sum_{i=1}^{j} x_i M_i (1/\rho - 1/\rho_i) \tag{18}$$

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 i^{th} component in the mixture, respectively.

2.6. Viscosity

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively.[84,86] Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, $\overline{V}_2^0$, i.e., the partial molar volume, gives a lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

The viscosity relationships of electrolytic solutions are highly complicated. Because ion-ion and ion-solvent interactions are occurring in the solution and separation of the related forces is a difficult task. But from careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system. As 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 thus, 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.

In 1905 Grüneisen[87] performed the first systematic measurement of viscosities of a number of electrolytic solutions over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In

1929, Jones and Dole[88] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations, c:

$$\eta/\eta_0 = \eta_r = 1 + A\sqrt{c} + Bc \tag{19}$$

The above equation can be rearranged as:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \tag{20}$$

where 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[89] of inter-ionic attractions in 1923.

The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory[90-92] and is given by the Falkenhagen Vernon[92] equation:

$$A_{Theo} = \frac{0.2577\Lambda_0}{\eta_0(\varepsilon T)^{0.5}\lambda_+^0\lambda_-^0}[1 - 0.6863(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0})^2] \tag{21}$$

where the symbols have their usual significance. In very accurate work on aqueous solutions,[93] A-coefficient has been obtained by fitting η_r to equation (20) and compared with the values calculated from equation (21), the agreement was normally excellent. The accuracy achieved with partially aqueous solutions was however poorer,[94] A-coefficient suggesting that should be calculated from conductivity measurements. Crudden et al.[95] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_P(\frac{1-\alpha}{\alpha}) \tag{22}$$

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 (20) is valid up to 0.1 (M) [85, 96, 97] within experimental errors.

At higher concentrations the extended Jones-Dole equation (23), involving an additional coefficient D, originally used by Kaminsky,[98] has been used by several workers[99, 100] and is given below:

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (23)$$

The coefficient D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (20) is used by the most of the workers.

The plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ against $\sqrt{c}$ for the electrolytes should give the value of A-coefficient. But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur.[97, 101, 102] Thus, instead of determining A- coefficient from the plots or by the least square method, the A-coefficient are generally calculated using Falkenhagen-Vernon equation (21).

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.[88]

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 influencing B - coefficients are: [103, 104]

(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 depolymeriation 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.

2.6.1. Viscosities at Higher Concentration

It had been found that the viscosity at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade: [105]

$$\eta = A\exp^{b/T} \tag{24}$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range[106-111] and the equation suggested by Angell[112, 113] 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:

$$1/\eta = A\exp[-K_1/(N_0 - N)] \tag{25}$$

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.[114-116] introducing the limiting condition, that is $N \to 0, \eta \to \eta_0$; which is the viscosity of the pure solvent. Thus, we have:

$$\ln\eta/\eta_0 = \ln\eta_{\text{Rel}} = K_1\, N/N_0(N_0 - N) \tag{26}$$

The equation (26) 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. Majumder et al. tested the equation (26) by using literature data as well as their own experimental data. 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 producing minimum deviations between η_{Rel}^{Exp} and η_{Rel}^{Theo} was accepted.

In dilute solutions, $N << N_0$ and we have:

$$\eta_{\text{Rel}} = \exp(K_1 N/N_0^2) \cong 1 + K_1\, N/N_0^2 \tag{27}$$

Equation (27) 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 (26) written in the form:

$$N/\ln\eta_{\text{Rel}} = N_0^2/K_1 - (N_0/K_1)N \qquad (28)$$

It closely resembles the Vand's equation[109] for fluidity (reciprocal for viscosity):

$$2.5c/2.3\log\eta_{\text{Rel}} = 1/V - Qc \qquad (29)$$

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.

2.6.2. 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.[102, 117-147] 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[148] 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[149] and also of Kaminsky[98] is based on:

$$B_{K^+} = B_{Cl^-} \text{(in water)} \qquad (30)$$

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 15-45°C. The assignment is supported from other thermodynamic properties. Nightingle,[150] however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron[99] is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker not a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation,[151]

$$B = 0.0025\overline{V}_0 \tag{31}$$

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 25°C.

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:

$$B_{BPh_4^-} = B_{PPh_4^+} = B_{BPh_4PPh_4}/2 \tag{32}$$

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

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \tag{33}$$

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.[152] They also adopted $B^{25}_{Me_4N^+} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss[153] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer et al.,[154] $\lambda^0_{25}(Bu_4N^+) = 61.4$ and $\lambda^0_{25}(Ph_4B^-) = 58.3$ in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \tag{34}$$

(c) Gopal and Rastogi[103] 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[102] assuming:

$$B_{[(\text{i-pe})_3\text{BuN}^+]} = B_{\text{Ph}_4\text{B}^-} = 1/2B_{[(\text{i-pe})_3\text{BuNPh}_4\text{B}]} \tag{35}$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate[155] solutions.

The methods, however, have been strongly criticized by Krumgalz.[156] 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 $\lambda_{\text{K}^+}^0 = \lambda_{\text{Cl}^-}^0$ at 25°C 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 $(\text{i-pe})_3\text{BuN}^+$ or $(\text{i-Am})_3\text{BuN}^+$ 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[156, 157] 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 [158, 159] 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:

$$B_{\text{R}_4\text{NX}} = a + br^3\text{R}_4\text{N}^+ \tag{36}$$

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

The extrapolation of the plot of $B_{\text{R}_4\text{NX}}$ (R > Pr or Bu) against $r^3\text{R}_4\text{N}$ to zero cation dimension gives directly B_{X^-} in the proper solvent and thus B-ion values can be calculated.

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

$$B_{\text{R}_4\text{N}^+} - B_{\text{R'}_4\text{N}^+} = B_{\text{R}_4\text{NX}} - B_{\text{R'}_4\text{NX}} \tag{37}$$

$$B_{\mathrm{R_4N^+}} / B_{\mathrm{R'_4N^+}} = r^3_{\mathrm{R_4N^+}} / r^3_{\mathrm{R'_4N^+}} \tag{38}$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data. [160]

Gill and Sharma[140] 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 Bu_4N^+ (5.00Å) 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:

$$B_{\mathrm{Ph_4B^-}} / B_{\mathrm{Bu_4N^+}} = r^3_{\mathrm{Ph_4B^-}} / r^3_{\mathrm{Bu_4N^+}} = (5.35/5.00)^3 \tag{39}$$

$$\text{and,} \quad B_{\mathrm{Bu_4NBPh_4}} = B_{\mathrm{Bu_4N^+}} + B_{\mathrm{Ph_4B^-}} \tag{40}$$

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:

$$B_{\mathrm{[(i-Am)_3BuN^+]}} = B_{\mathrm{Ph_4B^-}} = 1/2 B_{\mathrm{[(i-Am)_3BuNPh_4B]}} \tag{41}$$

Recently, Lawrence and Sacco[143] used tetrabutylammonium tetrabutylborate (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:

$$B_{\mathrm{Bu_4N^+}} / B_{\mathrm{Bu_4B^-}} = V_{W(\mathrm{Bu_4N^+})} / V_{W(\mathrm{Bu_4B^-})} \tag{42}$$

$$\text{or, } B_{\mathrm{Bu_4N^+}} = B_{\mathrm{Bu_4NBBu_4}} / [1 + V_{W(\mathrm{Bu_4B^-})} / V_{W(\mathrm{Bu_4N^+})}] \tag{43}$$

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[161] 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 Fajan's competition principle[162] and 'volcano plots' of Morris.[163] The principle was extended to derive absolute single ion B-coefficients for alkali metals and halides in water. They also observed that $B_{Cs^+} = B_{I^-}$ suggested by Krumgalz[158] to be more reliable than $B_{K^+} = B_{Cl^-}$ 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.

2.6.3. 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 generalisations have been made by Kaminsky. 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:

$$\text{(i) } A \text{ and } dA/dT > 0 \qquad (44)$$

$$\text{(ii) } B_{ion} < 0 \text{ and } dB_{ion}/dT > 0 \qquad (45)$$

characteristic of the structure breaking ions.

$$\text{(iii) } B_{ion} > 0 \text{ and } dB_{ion}/dT < 0 \qquad (46)$$

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,[164] A, B, C Zones of Frank and Wen[165] and hydrated radius of Nightingle.[150] 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 neighborhood. Thus, the Jones-Dole equation:

$$\eta = \eta_0 + \eta^{*} + \eta^{E} + \eta^{A} + \eta^{D} = \eta_0 + \eta(A\sqrt{c} + Bc) \tag{47}$$

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

$$\eta^{E} + \eta^{A} + \eta^{D} = \eta_0 BC \tag{48}$$

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

Following Stokes, Mills and Krumgalz[156] we can write for B_{Ion} as:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{Reinf} \tag{49}$$

where as according to Lawrence and Sacco:

$$B_{Ion} = B_{W} + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \tag{50}$$

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^{2+} 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 neighborhood 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[164] 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:

$$\overline{S}_h^0 = \overline{S}_{aq}^0 - \overline{S}_g^0 \tag{51}$$

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. mol^{-1}. deg^{-1}. Asmus[166] used the entropy of hydration to correlate ionic B-values and Nightingale[150] 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.[167] to assign single ion B-coefficients so that a plot of ΔS_e^0,[168, 169] the electrostatic entropy of solvation or $\Delta S_{I,II}^0$,[168, 169] 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$_4^-$ are structure breakers and K$^+$ is a border line case.

2.6.4. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [170] approach as:

$$\eta = Ae^{E_{vis}/RT} = (hN/V)e^{\Delta G^*/RT} = (hN/V)e^{(\Delta H^*/RT - \Delta S^*/R)} \tag{52}$$

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[171] 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:

$$R[d\ln\eta/d(1/T)] = r[d\ln\eta_0/d(1/T)] + R/(1+Bc).d(1+Bc)/d(1/T) \tag{53}$$

$$\Delta E^{\neq}_{\eta(Soln)} = \Delta E^{\neq}_{\eta_0(Solv)} + \Delta E^{\neq}_{V} \tag{54}$$

$\Delta E^{\neq}_{V}$ 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. [172] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = (\overline{V}_1^0 - \overline{V}_2^0)/1000 + \overline{V}_1^0(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/1000RT \tag{55}$$

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:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln\eta_1\overline{V}_1^0/hN \tag{56}$$

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:

$$d(\Delta\mu_2^{0\neq})/dT = -\Delta S_2^{0\neq} \tag{57}$$

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \tag{58}$$

2.6.5. 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 [151] leads to the equation:

$$\eta/\eta_0 = 1 + 2.5\phi \qquad (59)$$

where ϕ is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by (i) Sinha [173] on the basis of departures from spherical shape and (ii) Vand on the basis of dependence of the flow patterns around the neighboring 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 monatomic cations).

Thus we have from equation (58):

$$2.5\phi = A\sqrt{c} + Bc \qquad (60)$$

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

$$2.5\overline{V}_\text{I} = B \qquad (61)$$

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

$$B_\pm = 2.5\overline{V}_\pm = 2.5 \times 4/3(\pi R_\pm^3 N/1000) \qquad (62)$$

assuming that the ions behave like rigid spheres with a effective radii, $R_\pm$ moving in a continuum. $R_\pm$, calculated using the equation (62) 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: [174]

$$B_\pm = 2.5/1000(V_i + n_b V_S) \qquad (63)$$

where V_i is the molar volume of the base ion and V_S, the molar volume of the solvent. The equation (63) has been used by a number of workers to study the nature of solvation and solvation number.

2.6.6. Viscosity Deviation

Quantitatively, as per the absolute reaction rates theory,[175] the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i \eta_i) \tag{64}$$

where η is the dynamic viscosities of the mixture and x_i, η_i are the mole fraction and viscosity of ith component in the mixture, respectively.

2.6.7. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow, G^{*E} can be calculated as: [176]

$$G^{*E} = RT[\ln \eta V - \sum_{i=1}^{j} x_i \ln \eta_i V_i] \tag{65}$$

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 ith pure component, respectively.

2.7. 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.

2.7.1. 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,[177-181] measurements in non-aqueous[63, 66] 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 most convenient way to measure the compressibility of a solvent/solution is from the speed of sound in it.

The isentropic compressibility (K_S) of a solvent/solution can be calculated from the Laplace's equation: [182]

$$K_S = 1/(u^2\rho) \tag{66}$$

where ρ is the solution density and u is the ultrasonic speed in the solvent/solution. The isentropic compressibility (K_S) determined by equation (66) is adiabatic,[19] not an isothermal one, because the local compressions occurring when the ultrasound passes through the solvent/solution are too rapid to allow an escape of the heat produced.

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

$$\phi_K = MK_S/\rho_0 + 1000(K_S\rho_0 - K_S^0\rho)/m\rho\rho_0 \tag{67}$$

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:[178, 181]

$$\phi_K = \phi_K^0 + S_K^*\sqrt{m} \tag{68}$$

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.[183, 184] This is reflected by the negative values of ϕ_K^0 of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure. [64, 183]

The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved.[183] However, the poor fit of the solute molecules[185, 186] 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[187] and non-aqueous non-electrolyte[188] solutions.

2.7.2. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility, ΔK_S can be calculated using the following equation:[189-191]

$$\Delta K_S = K_S - \sum_{i=1}^{j} x_i K_{S,i} \tag{69}$$

where x_i, $K_{S,i}$ are the mole fraction and isentropic compressibility of i^{th} component in the mixture, respectively.

2.8. Correlating Equations

Several semi-empirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data.[192, 193] 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:[194]

$$\eta = \exp[\sum_{i=1}^{j} (x_i \ln \eta_i) + d_{12} \prod_{i=1}^{j} x_i] \tag{70}$$

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[195] between the mixing components in the mixtures while its positive values indicate the presence of specific interactions[195] between them.

b) Tamura-Kurata[196] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \tag{71}$$

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

c) Molecular interactions may also be interpreted by the following viscosity model of Hind et al: [197]

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \tag{72}$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[198] 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[195] in regard to the nature of parameter T_{12} and H_{12}.

Moreover, The excess or deviation properties (V^E, $\Delta\eta$, G^{*E} and ΔK_S) have been fitted to Redlich-Kister[199] polynomial equation using the method of least squares involving the Marquardt algorithm[200] and the binary coefficients, a_i were determined as follows:

$$Y^E = x_1 x_2 \sum_{i=1}^{j} a_i (x_1 - x_2)^i \qquad (73)$$

where Y^E refers to an excess or deviation 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,

$$\sigma = [(Y^E_{\exp} - Y^E_{cal})^2 / (n - m)]^{1/2} \qquad (74)$$

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

2.9. Conductance

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte of solutions.[201, 202] 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-Hückel 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.[201-214]

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[215] 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:

$$\Lambda = \Lambda_0 - S\sqrt{c} \qquad (75)$$

$$\text{where, } S = \alpha \Lambda_0 + \beta \qquad (76)$$

$$\alpha = (ze)^2 \kappa / 3(2+\sqrt{2})\varepsilon_r kT\sqrt{c} = 82.406 \times 10^4 z^3/(\varepsilon_r T)^{3/2} \qquad (77a)$$

$$\beta = z^2 e F\kappa / 3\pi\eta\sqrt{c} = 82.487 z^3/\eta\sqrt{\varepsilon_r T} \qquad (77b)$$

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.[216] In the subsequent years, Pitts (1953) [217] and Fuoss and Onsager (1957)[206, 218] 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[216] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned.[202, 219, 220] The original Fuoss-Onsager equation was further modified by Fuoss and Hsia[221] 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:

$$\Lambda = \Lambda_0 - \alpha \Lambda_0 \sqrt{c}/(1+\kappa a)(1+\kappa a/\sqrt{2}) - \beta\sqrt{c}/(1+\kappa a) + G(\kappa a) \qquad (78)$$

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2 \sqrt[3]{c} \qquad (79)$$

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.[202, 222, 223] Further correction of the equation (79) was made by Fuoss and Accascina.[206]

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2 \sqrt[3]{c} - \mathrm{F}\Lambda c \qquad (80)$$

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.[224]

2.9.1. Ionic Association

The equation (80) 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.[225]

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

$$\mathrm{M}^{z+} + \mathrm{A}^{z-} = \mathrm{MA} \tag{81}$$

$$K_A = (1-\alpha)/\alpha^2 c\gamma_\pm^2 \tag{82}$$

$$\alpha = 1 - \alpha^2 K_A c\gamma_\pm^2 \tag{83}$$

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[226] or Shedlovsky's equation:[227]

$$T(z)/\Lambda = 1/\Lambda_0 + K_A/\Lambda_0^2 . c\gamma_\pm^2 \Lambda/T(z) \tag{84}$$

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

$$F(z) = 1 - z(1 - z(1 - ....)^{-1/2})^{-1/2} \tag{85a}$$

$$\text{and } 1/T(z) \equiv S(z) = 1 + z + z^2/2 + z^3/8 + \text{ ....} \tag{85b}$$

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 (84).

The Fuoss-Hsia[221] conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_\pm^2 (\alpha c) \tag{86}$$

The equation was modified by Justice.[228] The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c}) + E(\alpha c)\ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \tag{87}$$

$$(1-\alpha)/\alpha^2 c\gamma_\pm^2 = K_A \tag{88}$$

$$\ln \gamma_\pm = -k\sqrt{q}/(1 + kR\sqrt{\alpha c}) \tag{89}$$

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 (87) 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:229

$$K_A = (4\pi N_A a^3/3000)\exp(e^2/a\varepsilon kT) \tag{90}$$

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:230

$$K_A = 4\pi N_A a/1000 \int_{r=a}^{r=q} r^2 \exp(z^2e^2/r\varepsilon kT)\,dr \tag{91}$$

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.231

2.9.2. Ion size Parameter and Ionic Association

For plotting, equation (80) can be rearranged to the 'Λ' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec\ln c = \Lambda_0 + J_1c + J_2\sqrt[3]{c} = \Lambda_0 + J_1c \tag{92}$$

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 smaller225 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' [232] but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J.[233]

Fuoss[234] 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:

$$\underset{}{A^+ + B^+} = \underset{\text{Solvent separated pair}}{(A^+ \ldots\ldots B^+)} = \underset{\text{Contact pair}}{A^+B^-} = \underset{\text{Neutral molecule}}{AB} \qquad (93)$$

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 $(r \le R)$, 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 (93) are:

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 f^2 \qquad (94)$$

$$K_S = \alpha/(1-\alpha) = \exp(-E_S/kT) = e^{-\varepsilon} \qquad (95)$$

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.

$$\text{Now,} \quad (1-\alpha) = 1/(1+K_S) \qquad (96)$$

And the conductometric pairing constant is given by:

$$K_A = (1-\alpha)/c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \qquad (97)$$

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:

$$\Lambda = p[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e] = p[\Lambda_0(1+R_X) + E_L] \qquad (98)$$

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:

$$p = 1 - \alpha(1-\gamma) \qquad (99)$$

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:

$$\Lambda = \gamma[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e \qquad (100)$$

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

$$K_A = (1-\gamma)/c\gamma^2 f^2 \approx K_R K_S \qquad (101)$$

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

$$\gamma = 1 - K_R c\gamma^2 f^2/(1-\alpha) \tag{102}$$

$$K_R = (4\pi N_A R^3/3000)\exp(\beta/R) \tag{103}$$

$$-\ln f = \beta_\kappa/2(1+\kappa R), \quad \beta = e^2/\varepsilon kT \tag{104}$$

$$\kappa^2 = 8\pi\beta\gamma n = \pi\beta N_A \gamma c/125 \tag{105}$$

$$-\varepsilon = \ln[\alpha/(1-\alpha)] \tag{106}$$

The details of the calculations are presented in the 1978 paper.[234] 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).

2.9.3. 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:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \tag{107}$$

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

$$\lambda_+^0 = t_+\Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_-\Lambda_0 \tag{108}$$

Thus, from accurate value of λ^0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions.[235] However, accurate transference number determinations are limited to few solvents only. Spiro[236] and Krumgalz[237] 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[237] and some important points are mentioned below:

(i) Walden equation,[238] $(\lambda_{\pm}^{0})_{\text{water}}^{25} \cdot \eta_{0,\text{water}} = (\lambda_{\pm}^{0})_{\text{acetone}}^{25} \cdot \eta_{0,\text{acetone}}$ (109)

(ii) $$\left.\begin{aligned} \lambda_{\text{pic}}^{0} \cdot \eta_0 &= 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^{0} \cdot \eta_0 &= 0.296 \end{aligned}\right|^{238,239} \text{based on } \Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^{0} = 0.563 \qquad (110)$$

Walden considered the products to be independent of temperature and solvent. However the $\Lambda_{\text{Et}_4N_{\text{pic}}}^{0}$ 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) $\lambda_{25}^{0}(\text{Bu}_4\text{N}^+) = \lambda_{25}^{0}(\text{Ph}_4\text{B}^-)$[239] (111)

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

(iv) $\lambda_{25}^{0}(\text{Bu}_4\text{N}^+) = \lambda_{25}^{0}(\text{Bu}_4\text{B}^-)$[240] (112)

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[241] is:

$$\lambda_{25}^{0}(\text{R}_4\text{N}^+) = zF^2/6\pi N_A \eta_0 [r_i - (0.0103\varepsilon_0 + r_y)] \qquad (113)$$

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.[237(a)] In a paper,[237(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) $\lambda_{25}^{0}[(\text{i}-\text{Am})_3\text{BuN}^+] = \lambda_{25}^{0}(\text{Ph}_4\text{B}^-)$[242] (114)

It has been found from transference number measurements that the $\lambda_{25}^{0}[(\text{i}-\text{Am})_3\text{BuN}^+]$ and $\lambda_{25}^{0}(\text{Ph}_4\text{B}^-)$ values differ from one another by 1%.

(vii) $\lambda_{25}^{0}(\text{Ph}_4\text{B}^-) = 1.01\lambda_{25}^{0}(\text{i}-\text{Am}_4\text{B}^-)$[243] (115)

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

Krumgalz[237] 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:

$$r_S = |z|F^2 / A\pi\eta_0\lambda^0_\pm \tag{116}$$

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:

$$\lambda^0_\pm\eta_0 = \text{constant} \tag{117}$$

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.

2.9.4. 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:

$$V_S = (4\pi/3)(r_S^3 - r_C^3) \tag{118}$$

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

$$n_S = V_S / V_0 \tag{119}$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects[244] from:

$$V_S^0 = 4.35 r_S^3 \tag{120}$$

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[207] and theoretical corrections [245-248] have been suggested to make the general method.

2.9.5. 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:

$$\lambda_i^0 = |z_i e| \hat{e} F / 6\pi \eta_0 R_i = 0.819 |z_i| / \eta_0 R_i \tag{121}$$

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:

$$\lambda_i^0 \eta_0 = 0.819 |z_i| / R_i = \text{constant} \tag{122}$$

This is known as Walden's rule.[249] 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,[207] Nightingale[150] and others[250-252] 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[253] was invoked without much success[254, 255] but it has been found that:

$$\lambda_i^0 \eta^p = \text{constant} \tag{123}$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions.[256, 257]

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[258] 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:

$$\lambda_{i,0}^{0}=Fe|z_i|/6\pi R_{\propto}(1+A/\varepsilon R_{\propto}^{2}) \tag{124}$$

$$\text{or, } R_i=R_{\propto}+A/\varepsilon \tag{125}$$

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[227] gave the expression:

$$\lambda_i^0=Fe|z_i|/6\pi\eta_0 r_i[1+(2/27\pi\eta_0.Z_i^2e^2\tau/r_i^4\varepsilon_0)] \tag{126}$$

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

Zwanzig[247] 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:

$$\lambda_i^0=z_i^2eF/\{A_V\pi\eta_0r_i+A_D[z_i^2e^2(\varepsilon_r^0-\varepsilon_r^{\propto})\tau/\varepsilon_r^0(2\varepsilon_r^0+1)r_i^3]\} \tag{127}$$

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[245] and Zwanzig's[247] equations are very similar and both may be written in the form:

$$\lambda_i^0=Ar_i^3/(r_i^4+B) \tag{128}$$

The theory predicts[259] 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 (127) can be rearranged as:[260]

$$z_i^2 eF/\lambda_i^0 \eta_0 = A_V \pi r_i + A_D z_i^2/r_i^3 . e^2(\varepsilon_r^0 - \varepsilon_i^\infty)/\varepsilon_r^0(2\varepsilon_r^0 + 1).\tau/\eta_0 \qquad (129)$$

$$\text{or}, L^* = A_V \pi r_i + A_D z_i^2/r_0^3 P^* \qquad (130)$$

In order to test Zwanzig's theory, the equation (130) was applied for Me_4N^+ and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol.[259-264] 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.[235]

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,[260] 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.[261]

(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.[260]

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[259-269] mixtures and other aqueous binary mixtures.[270-273] To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts[246, 247, 274] 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,[275] 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[276] 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[277, 278] 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.

2.10. 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.[19] 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,[19] 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.[279-283] 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.[284, 285] 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.[286] of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

2.11. Conductance- Some Recent Trends

Recently Blum, Turq and coworkers[287-288] 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.[289] 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[290] 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] J. V. Herraez, R. Belda, J. Soln Chem., 33 (2004) 117.

[2] J. Ferguson, Z. Kamblonski, *Applied Fluid Rheology*, Elsevier Science, University Press, Cambridge, (1991).

[3] C. K. Zeberg-Mikkelsen, S. E. Quinones-Cisneros, S.H. Stenby, Fluid Phase Equilibr., 194 (2002) 1191.

[4] R. Shukla, M. Cheryan, J. Membrane Science., 198 (2002) 104.

[5] R. Voight, *Tratado de Tecnologia Farmaceutica*, Ed. S.A. Acribia, Zaragoza, (1982).

[6] M. J. Assael, N. K. Dalaouti, I. Metaxa, Fluid Phase Equilibr.,199 (2002) 237.

[7] A. Darr, *Technologia Farmaceutica*, Ed. S. A. Acribia, Zaragoza, (1979).

[8] H. A. Barnes, J. F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier Science Publishers BV, Amsterdam, (1993).

[9] J. M. Resa, C. Gonzalez, J. Lanz, J. Food Engineering., 51 (2002) 113.

[10] M. Garcia-Velarde, Revista Espanola de Fisica., 9 (1995) 12.

[11] C. W. Macosk, *Rheology: Principles, Measurements and Applications*, VCH Publishers, New York, (1994).

[12] C. Fauli-Trillo, *Tratado de Farmacia Galencia*, Ed. S. A. Lujan, Madrid, (1993).

[13] J. Swarbrik, J. C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, New York, (1993).

[14] J. Pellicer, *Sinergia Viscosa*, Valencia, Spain, October (1997).

[15] G. Copetti, R. Lapasin, E. R. Morris, *Proceedings of the 4th European Rheology Conference*, Seville, Spain, 215 (1194).

[16] G. Kaletunc-Gencer, M.Peleg, J. Texture Studies, 17 (1986) 61.

[17] D. D. Christianson, *Hydrocolloidal Interactions with Starches*, Wesport. Conn., 399 (1982).

[18] N. K. Howell, *Proceedings of the 7th International Conference*, Wales, (1993).

[19] J. O'M. Bockris, A. K. N. Reddy, Modern Electrochemistry, 2nd ed., Plenum Press, New York, (1923).

[20] H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, *3rd ed.*, (1958).

[21] J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents, Academic*, New York, (1966).

[22] B. E. Conway, R. G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York, (1966).

[23] J. S. Muishead-Gould, K. J. Laidler, *Chemical Physics of Ionic Solutions*, Wiley, New York, 75 (1966).

[24] J. F. Coetzee, C. D. Ritchie, *Solute-Solvent Interactions*, Marcel Dekker, New York, (1969).

[25] R. G. Bates, J. Electroanal. Chem., 29 (1972) 1.

[26] G. S. Kell, C. M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport process*, Ed. R. A. Horne, Wiley, Chapters 9 &10, (1972).

[27] E. S. Amis, J. F. Hinton, *Solvent effects on Chemical Phenomena*, Academic, New York, (1973).

[28] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).

[29] J. E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley-Interscience, (1975).

[30] F. Franks, *Physico-Chemical processes in Mixed Aqueous Solvents*, Heinemann, 141(1967).

[31] F. Franks, *Water–A Comprehensive Treatise*, Plenum, New York, 1 (1973).

[32] V. Gutmann, Electrochim. Acta., 21 (1967) 661.

[33] U. Mayer, V. Gutmann, Adv. Inorg.Chem. Radiochem., 17 (1975) 189.

[34] R. G. Pearson, *Hard and Soft Acids and Bases*, Dowdon, Hutchinson and Ross, Strondsburgh, (1973).

[35] G. R. Behbehani, M. Dillon, J. Symth, W. E. Waghorne, J. Solution. Chem, 31 (2002) 811.

[36] C. Guha, J. M. Chakraborty, S. Karanjai, B. Das, J. Phys. Chem B, 107 (2003) 12814.

[37] L. Jones, J. F. Devonshire, A. F. Proc. Royal. Soc., (1937).

[38] I. Prigogine, S. Garikian, Physica., 16 (1950) 239.

[39] I. Prigogine, A. Belleman, J. Phys. Chem., 21 (1953) 561.

[40] A. J. Treszczanowicz, G. C. Benson, Fluid Phase Equilibr., 23 (1985) 117.

[41] Wen-Lu Weng, J. Chem. Eng. Data, 45 (2002) 606.

[42] P. S. Nikam, S. J. Kharat, J. Chem. Eng. Data, 50 (2005) 455.

[43] R. P. Rastogi, J. Nath, J. Mishra, J. Phys. Chem., 71 (1966) 1277.

[44] K. S. Pitzer, G. Mayora, J. Phys. Chem., 77 (1973) 2300.

[45] D. Cook, L-Higgins, H. C. Proc. Royal. Soc., A209 (1951) 28.

[46] J. S. Rowlinson, *Liquid and Liquid Mixtures*, Butterworths, London, pp. 17 (1959).

[47] J. S. Rowlinson, Proc. Royal. Soc., A214 (1952) 192.

[48] J. L. Lebowitz, J. S. Rowlinson, J. Chem. Phys., 41 (1964) 133.

[49] J. A. Barker, D. J. Henderson, J. Phys. Chem., 47 (1967) 4714.

[50] P. J. Flory, R. A. Orwoll, A. Vrij, J. Am. Chem. Soc., 86 (1964) 3507.

[51] P. J. Flory, A. Abe, J. Am. Chem. Soc., 86 (1964) 3563.

[52] P. J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.

[53] D. Patterson, G. Delmas, Discuss. Faraday Soc., 49 (1970) 98.

[54] A. Heintz, Ber. Bunsenges. J. Phys., 89 (1985) 172.

[55] H. Funke, M. Wetzel, A. Heintz, J . Pure. Appl. Chem., 61 (1989) 1429.

[56] A. Heintz, D. Papaioannou, Thermochimica. Acta., 310 (1998) 69.

[57] A. Heintz, P. K. Naicker, S. P. Verevkin, R. Pfestrof, B. Bunsenges, Phys. Chem., 102 (1998) 953.

[58] S. Villa, N. Riesco, I. Garcia de la Fuente, J. A. Gonzalz, J. C. Cobos, Fluid Phase Equilibr., 216 (2004) 123.

[59] S. L. Oswal, Thermochimica. Acta., 425 (2005) 59.

[60] H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold, New York, Chapter 8, (1943).

[61] C. Tanford, *Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley-Interscience, New York, 2nd ed., (1980).

[62] E. Vikingstad, *Aggregation Process in Solutions*, Eds. E. Wyn-Jones and J. Gormally, Elsevier, Amsterdam, 100 (1983)

[63] J. E. Desnoyers, M. Arel, H. Perron, C. Jolicoenn, J. Phys. Chem., 73 (1969) 3347.

[64] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, Chapter 2, (1973).

[65] D. K. Hazra, B. Das, J. Chem. Eng. Data., 36 (1991) 403.

[66] D. O. Masson, Phil. Mag., 8 (1929) 218.

[67] O. Redlich, D. M. Meyer, Chem. Rev., 64 (1964),221.

[68] B. B. Owen, S. R. Brinkley, J. Ann. N. Y. Acad. Sci., 51 (1949) 753.

[69] F. J. Millero, *In Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Ed. R.A. Horne, Wiley-Interscience, New York, (1972).

[70] R. Gopal, M. A. Siddiqi, J. Phys. Chem., 73 (1969) 3390.

[71] J. Padova, I. Abrahmen, J. Phys. Chem., 71 (1967) 2112.

[72] R. Gopal, D. K. Agarwal, R. Kumar, Bull. Chem. Soc. Jpn., 46 (1973) 1973.

[73] R. Gopal, P. P. Rastogi, Z. Phys. Chem. (N.F.), 69 (1970) 1.

[74] B. Das, D. K. Hazra, J. Chem. Eng. Data., 36 (1991) 403.

[75] L. G. Hepler, Can. J. Chem., 47 (1969) 4617.

[76] L. G. Hepler, J. M. Stokes, R. H. Stokes. Trans. Faraday Soc., 61 (1965) 20.

[77] F. H. Spedding, M. J. Pikal, B. O. Ayres. J. Phys. Chem., 70 (1966) 2440.

[78] L. A. Dunn, Trans. Faraday Soc., 64 (1968) 2951.

[79] R. Pogue, G. Atkinson, J. Chem. Eng. Data., 33 (1988) 370.

[80] B. E. Conway, R. E. Verral, J. E. Desnoyers. Trans. Faraday Soc., 62 (1966) 2738.

[81] K. Uosaki, Y. Koudo, N. Tokura, Bull. Chem. Soc. Jpn., 45 (1972) 871.

[82] B. S. Krumgalz, J. Chem. Soc. Faraday Trans. I., 76 (1980) 1887.

[83] A. W. Quin, D. F. Hoffmann, P. Munk, J. Chem. Eng. Data., 37 (1992) 55.

[84] Z. Atik, J. Soln Chem., 33 (2004) 1447.

[85] R. H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Great Britain, (1965).

[86] F. Vaslow, *Water and Aqueous Solutions*, Ed. R.A. Horne, Wiley-Interscience, Chapter 12 (1972).

[87] Gruneisen, Wiss, Abhaudl, Physik-tech. Reich-austatt, 4 (1905) 239.

[88] G. Jones, M. Dole, J. Am. Chem. Soc., 51 (1929) 2950.

[89] P. Debye, E. Hückel, Z. Phys. Chem., 24 (1923) 185.

[90] H. Falkenhagen, M. Dole, Phys. Z. 30 (1929) 611.

[91] H. Falkenhagen, E. L. Vernon, Phys. Z. 33 (1932) 140.

[92] H. Falkenhagen, E. L. Vernon, Phil. Mag. 14 (1983) 537.

[93] M. Kaminsky, Discuss. Faraday Soc., 24 (1957) 171.

[94] D. Feakins, D. J. Freemantle, K. G. Lawrence, J. Chem. Soc. Faraday Trans 1., 70 (1974) 795.

[95] 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.

[96] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, pp. 43 (1973).

[97] H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 3rd ed, (1958).

[98] M. Kaminsky, Z. Phys. Chem. (Frankfurt)., 12 (1957) 206.

[99] J. Desnoyers, G. Perron, J. Soln. Chem., 1,(1972) 199.

[100] R. J. M. Bicknell, K. G. Lawrence, D. Feakins, J. Chem. Soc. Faraday I, 76 (1980) 637.

[101] R. L. Kay, T. Vituccio, C. Zawoyski, D. F. Evans, J. Phys. Chem., 70 (1966) 2336.

[102] N. P. Yao, D. N. Bennion, J. Phys. Chem., 75 (1971) 1727.

[103] M. Kaminsky, Discussions Faraday Soc., 24 (1957) 171.

[104] D. Feakins, K. G. Lawrence, J. Chem. Soc., A (1966) 212.

[105] Andrade, Phil. Mag., 17 (1934) 698.

[106] V. Vand, J. Phys. Chem., 52 (1948) 277.

[107] D. G. Thomas, J. Colloid Sci., 20 (1965) 267.

[108] S. P. Moulik, J. Ind. Chem. Soc., 49 (1972) 483.

[109] D. England, G. Pilling, J. Phys. Chem., 76 (1972) 1902.

[110] D. E. Goldsack, R. C. Franchetto, Can. J. Chem., 55 (1977) 1062.

[111] D. E. Goldsack, R. C. Franchetto, Can. J. Chem., 56 (1978) 1442.

[112] C. A. Angell, J. Phys. Chem., 70 (1966) 2793.

[113] C. A. Angell, J. Chem. Phys., 46 (1967) 4673.

[114] K. Roy Chowdhury, D. K. Majumdar, Electrochim. Acta., 28 (1983) 23.

[115] K. Roy Chowdhury, D. K. Majumdar, Electrochim. Acta., 28 (1983) 597.

[116] K. Roy Chowdhury, D. K. Majumdar, Electrochim. Acta.,29 (1984) 1371.

[117] P. P. Rastogi, Bull. Chem. Soc. Japan., 43 (1970) 2442.

[118] R. Gopal, P. P. Rostogi, Z. Phys. Chem. (N.F.), 69 (1970)1.

[119] C. M. Criss, M. J. Mostroianni, J. Phys. Chem., 75(1971) 2532.

[120] K. Tamaski, Y. Ohara, Y. Isomura, Bull. Chem. Soc. Japan., 46 (1973) 951.

[121] P. P. Deluca, T. V. Rabagay, J. Phys. Chem., 79 (1975) 2493.

[122] B. N. Prasad, N. P. Singh, M. M. Singh, Ind. J. Chem., 14A (1976) 322.

[123] B. N. Prasad, M. M. Agarwal, Ind. J. Chem., 14A (1976) 343.

[124] R. T. M. Bicknell, K. G. Lawrence, M. A. Scelay, D. Feakins, L. Werblan, J. Chem. Soc. Faraday I., 72 (1976) 307.

[125] J. M. Mcdowall, N. Martinus, C. A. Vincent, J. Chem. Soc. Faraday I., 72 (1976) 654.

[126] A. Sacco, G. Petrella, M. Castagnola, J. Phys. Chem., 80 (1976) 749.

[127] R. L. Blokhra, Y. P. Segal, Ind. J. Chem., 15A (1977) 36.

[128] N. C. Das, P. B. Das, Ind. J. Chem., 15A (1977) 826.

[129] A. Sacco, G. Petrella, M. Della Monica, M. Castagnola, J. Chem. Soc. Faraday I., 73 (1977)1936.

[130] P. K. Mandal, B. K. Seal, A. S. Basu, Z. Phys. Chem. (Leipzig)., 258 (1977) 809.

[131] J. I. Kim, J. Phys. Chem., 82 (1978) 191.

[132] S. K. Vijaylakshamna, Ind. J. Chem., 17A (1979) 511.

[133] A. Sacco, G. Petrella, M. D. Monica, J. Chem. Soc. Faraday I., 75 (1979) 2325.

[134] P. T. Thomson, M. Durbana, J. L. Turner, R. H. Wood, J. Soln. Chem., 9 (1980) 955.

[135] K. Kurotaki, S. Kawamura, J. Chem. Soc. Faraday I., 77 (1981) 217.

[136] N. Martinus, C. A. Vincent, J. Chem. Soc. Faraday Trans I., 77 (1981) 141.

[137] A. Sacco, A. D. Giglio, A. D. Atti, J. Chem. Soc. Faraday I., 77 (1981) 2693.

[138] D. S. Gill, A.N. Sharma, J. Chem. Soc. Faraday I., 78 (1982) 78475.

[139] A. Sacco, G. Petrella, A. D. Atti, M. Castagnolo, J. Chem. Soc. Faraday I., 78 (1982) 1507.

[140] A. Sacco, A. D. Giglio, A. D. Atti, M. Castagnolo, J. Chem. Soc. Faraday I., 79 (1983) 431.

[141] K. G. Lawrence, A. Sacco, J. Chem. Soc. Faraday I., 79 (1983) 615.

[142] K. Miyajima, M. Sawada, M. Nakagaki, Bull. Chem. Soc. Jpn., 56 (1983) 827.

[143] J. Domenech, S. Rivera, J. Chem. Soc. Faraday I., 80 (1984) 1249.

[144] D. Dasgupta, S. Das, D. K. Hazra, Bull. Chem. Soc. Jpn., 62 (1989) 1246.

[145] S. Taniewska-Osinska, M. Jozwaik, J. Chem. Soc. Faraday Trans I., 85 (1989) 2147.

[146] D. Nandi, D. K. Hazra, J. Chem. Soc. Faraday Trans I., 85 (1989) 4227.

[147] I. Ibulci, M. Nakahara, J. Phys. Chem., 94 (1990) 8370.

[148] W. M. Cox, J. H. Wolfenden, Proc. Roy. Soc. London., 145A (1934) 475.

[149] R. W. Gurney, *Ionic Processes in Solution*, McGraw Hill, New York, (1953).

[150] E. R. Nightingale, J. Phys. Chem., 63 (1959) 1381.

[151] A. Einstein, Ann. Phys., 19 (1906) 289.

[152] G. S. Benson, A. R. Gordon, J. Chem. Phys., 13 (1945) 473.

[153] D. F. T. Tuan, R. M. Fuoss, J. Phys. Chem., 67 (1963) 1343.

[154] C. H. Springer, J. F. Coetzee, R. L. Key, J. Phys. Chem., 78 (1969) 471.

[155] G. Petrella, A. Sacco, J. Chem. Soc. Faraday I., 74 (1978) 2070.

[156] B. S. Krumgalz, J. Chem. Soc. Faraday I., 76 (1980) 1275.

[157] B. S. Krumgalz, Russ. J. Phys. Chem., 46 (1972) 858.

[158] B. S. Krumgalz, Russ. J. Phys. Chem., 47 (1973) 956.

[159] B. S. Krumgalz, Russ. J. Phys. Chem., 48 (1974) 1163.

[160] B. S. Krumgalz, Russ. J. Phys. Chem., 45 (1971) 1448.

[161] H. D. B. Jenkins, M. S. F. Pritcheit, J. Chem. Soc. Faraday I., 80 (1984) 721.

[162] K. Fajan, Naturwissenschaften., 9 (1921) 729.

[163] D. F. C. Morris, Struct. Bonding., 6 (1969) 157.

[164] R. W. Gurney, *Ionic Processes in Solutions*, Doves, New York, (1962).

[165] H.S. Frank, W. Y. Wen, Disc. Farad. Soc., 24 (1957) 133.

[166] Asmus, Z. Naturforsch., 4A (1949) 589.

[167] M. H. Abraham, J. Liszi, E. Papp, J. Chem. Soc. Faraday I., 78 (1982) 197.

[168] M. H. Abraham, J. Liszi, L. Meszaros, J. Chem. Phys., 70 (1979) 249.

[169] M. H. Abraham, J. Liszi, J. Chem. Soc. Faraday I., 76 (1980) 1219.

[170] S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, pp. 477 (1941).

[171] E. R. Nightingale, R. F. Benck, J. Phys. Chem., 63 (1959) 1777.

[172] D. Feakins, D. J. Freemantle, K. G. Lawrence, J. Chem. Soc. Faraday I., 70 (1974) 795.

[173] R. Simha, J. Phys. Chem., 44 (1940) 25.

[174] D. Feakins, K. G. Lawrence, J. Chem. Soc., A (1966) 212.

[175] S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, pp. 514 (1941).

[176] D. S. Gill, T. S. Kaur, H. Kaur, I. M. Joshi, J. Singh, J. Chem. Soc. Faraday Trans., 89 (1993) 1737.

[177] J. G. Mathieson, B. E. Conway, J. Soln. Chem., 3 (1974) 455.

[178] S. Bhowmik, R. K. Mohanty, Ind. J. Chem., 25A (1986) 416.

[179] M. V. Kaulgud, K. S. Mohan Rao, Ind. J. Chem., 27A (1988) 12.

[180] K. J. Patil, A. B. Wazalwar, G. R. Mehta, Ind. J. Chem., 27A (1988) 799.

[181] M. Iqbal, R. E. Verral, Can. J. Chem., 67 (1989) 727.

[182] M. Kikuchi, M. Sakurai, K. Nitta, J. Chem. Eng. Data., 41 (1996) 1439.

[183] B. E. Conway, R. E. Verral, J. Phys. Chem., 70 (1966) 3952.

[184] K. Gekko, H. Noguchi, J. Phys. Chem., 83 (1979) 2706.

[185] W. L. Masterson, J. Chem. Phys., 22 (1954) 1830.

[186] L. G. Hepler, Can. J. Chem., 47 (1969) 4613.

[187] M. V. Kaulgud, K. J. Patil, J. Phys. Chem., 80 (1976) 138.

[188] K. J. Patil, G. R. Mehta, R.K. Chandewar, Ind. J. Chem., 25A (1986) 1147.

[189] C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, Int. J. Thermophys., 25 (2004)1735.

[190] G. Douheret, A. Pal, M. I. Davis, J. Chem. Thermodyn., 22 (1990) 99.

[191] I. Gascon, S. Martin, P. Cea, M. C. Lopez, F. M. Royo, J. Soln. Chem., 31 (2002) 905.

[192] R. C. Reid, J. M. Prausnitz, B. E. Poling, *The properties of Gases and Liquids*, 4th ed, McGraw-Hill International, (1987).

[193] J. B. Irving, *Viscosities of Liquid Mixtures*, NEL Report No 630 and 631, National Engineering Laboratory, East Kilbride, Glassgow, (1977).

[194] L. Grunberg, A. H. Nissan, Nature, 164 (1949) 799.

[195] R. J. Fort, W. R. Moore, Trans. Faraday Soc., 62 (1966) 1112.

[196] M. Tamura, M. Kurata, Bull. Chem. Soc. Jpn., 25 (1952) 32.

[197] R. K. Hind, E. McLaughlin, A. R. Ubbelohde, Trans. Faraday. Soc., 56 (1960) 328.

[198] S. L. Oswal, H. S. Desai, Fluid Phase Equilibr., 186 (2001) 81.

[199] O. Redlich, A.J. Kister, Ind. Eng. Chem., 40 (1948) 345.

[200] D. W. Marquardt, J. Soc. Ind. Appl. Math., 11 (1963) 431.

[201] D. F. Evans, Sister Marry, A. Matesich, *Electro Chemistry*, Ed. E. Yeager, A. J. Salkind, John-Wiley and Sons, Vol-2, Chapter 1, (1973).

[202] R. Fernandez-Prini, *Physical Chemistry of Organic Solvent Systems*, Ed. A. K. Covington, T. Dickinson, Plenum Press, New York, Chapter 5, (1973).

[203] D. A. McInnes, *The Principles of Electro Chemistry*, Reinhold, New York, (1961).

[204] S. Glasstone, *An Introduction to Electrochemistry*, Van Nostrand, New York, (1942).

[205] T. Shedlovsky, *In Techniques of Organic Chemistry*, Vol. 1, part 4, Ed. A, Weissberger, Wiley, New York, 3rd ed, 3011 (1959).

[206] R. M. Fuoss, F. Accascina, *Electrolyte Conductance*, Wiley, New York, (1959).

[207] R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 2nd ed, (1959).

[208] D. L. Goldfarb, H. R. Corti, J. Phys. Chem-B, 108 (2004) 3358.

[209] P. Haldar, B. Das, Z. Phys. Chem, 218 (2004) 1129.

[210] E. J. King, *Acid-base Equilibria*, Pergamon, Great Britain, (1965).

[211] V. K. Syal, S. Chauhan, P. K. Gupta, J. Indian. Chem. Soc., 79 (2002) 860.

[212] P. J. Victor, B. Das, D. K. Hazra, J. Phys. Chem-A., 105 (2001) 5960.

[213] Y. Marcus, *Ion Properties*, Dekker, New York (1997).

[214] Y. Marcus, Y. Migron, J. Phys. Chem., 95 (1991) 400.

[215] L. Onsager, Z. Phys. Chem., 28 (1927) 277.

[216] R. M. Fuoss, Rev. Pure Appl. Chem., 18 (1968) 125.

[217] E. Pitts, Proc. Roy. Soc., 217A (1953) 43.

[218] R. M. Fuoss, L. Onsager, J. Phys. Chem., 61 (1957) 668.

[219] R. M. Fuoss, *Chemical Physics of Ionic Solutions*, Eds. B.E. Conway, R. G. Barradas, Wiley, New York, 462 (1966).

[220] E. Pitts, R. E. Tabor, J. Daly, Trans. Faraday Soc., 65 (1969) 849.

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

[222] R. Fernandez-Prini, J. E. Prue. Z. Phys. Chem. (Leipzig), 228 (1965) 373.

[223] R. Fernandez-Prini, J. E. Prue. Z. Phys. Chem. (Leipzig), 228 (1965) 473.

[224] D. F. Evans, R. L. Kay, J. Phys. Chem., 70 (1966) 366.

[225] D. F. Arrington, E. Griswold, J. Phys. Chem., 74 (1970) 123.

[226] R. M. Fuoss, C. A. Kraus. J. Am. Chem. Soc., 55 (1933) 476.

[227] T. Shedlovsky, J. Franklin, Instt., 225 (1938) 739.

[228] (a) J. C. Justice, J. Chem. Phys., 65 (1968) 353.
(b) J. C. Justice, R. Bury, C. Treiner, J. Chem. Phys., 65 (1968) 1708.

[229] R. M. Fuoss, F. Accascina, *Electrolytic Conductance*, Wiley, New York, 207 (1959).

[230] N. Bjerrum, K. Dan. Vidensk. Selek., 7 (1926) 9.

[231] M. Tissier, G. Douheret, J. Soln. Chem., 7 (1978) 87.

[232] R. Fernandez-Prini, J. Prue, Trans. Faraday Soc., 62 (1966) 1257.

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

[234] (a) R. M. Fuoss, J. Phys. Chem., 49 (1975) 525.
(b) R. M. Fuoss, J. Phys. Chem., 82 (1978) 2427.

[235] J. Padova, *Water and Aqueous Solutions*, Ed. R. A. Horne, Wiley Interscience, Chapter 4 (1972).

[236] M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Ed. A. K. Covington, T. Dickinson, Plenum, New York, Vol-2, Chapter 5, (1973).

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

[238] P. Walden, H. Ulich, D. Bush, Z. Phys. Chem., 123 (1926) 429.

[239] R. M. Fuoss, E. Hirsch, J. Am. Chem. Soc., 82 (1960) 1018.

[240] S. Takezawa, Y. Kondo, N. Tokura, J. Phys. Chem., 77 (1973) 2133.

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

[242] M. A. Coplan, R. M. Fuoss, J. Phys. Chem., 68 (1964) 1177.

[243] J. F. Coetzee, G. P. Cunningham, J. Am. Chem. Soc., 87 (1965) 2529.

[244] R. H. Stokes, R. A. Robinson, Trans. Faraday Soc., 53 (1957) 301.

[245] M. Born, Z. Phys. Chem., 1 (1920) 221.

[246] R. H. Boyd, J. Chem. Phys., 35 (1961) 1281.

[247] R. Zwanzig, J. Chem. Phys., 38 (1963) 1603.

[248] E. J. Passeron, J. Phys. Chem., 68 (1964) 2728.

[249] (a) P. Walden, Z. Phys. Chem., 55 (1906) 207.
(b) P. Walden, Z. Phys. Chem., 78 (1912) 257.

[250] R. Gopal, M. M. Hussain, J. Ind. Chem. Soc., 40 (1963) 981.

[251] L. G. Longsworth, J. Phys. Chem., 67 (1963) 689.

[252] M. Della Monica, U. Lamauna, L. Seutatore, J. Phys. Chem., 72 (1968) 2124.

[253] S. Brocus, J. Chem. Phys., 28 (1958) 1158.

[254] D. G. Miller, J. Phys. Chem., 64 (1960) 1598.

[255] G. J. Hills, *Chemical Physics of Ionic Solutions*, Ed. B.E. Conway, R.G. Barradas, Wiley, New York, 571 (1966).

[256] R. H. Stokes, I.A. Weeks, Aust. J. Chem., 17 (1964) 304.

[257] R. H. Stokes, *The Structure of Electrolytic Solutions*, Ed. W.J. Hamer, Wiley, New York, (1959).

[258] R. M. Fuoss, Proc. Nati. Acad. Sci. (U.S.A.), 45 (1959) 807.

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

[260] G. Atkinson, S. K. Koz, J. Phys. Chem., 69 (1965) 128.

[261] R. L. Kay, G. P. Cunningham, D. F. Evans, *Hydrogen bonded Solvent Systems*, Ed. A. K. Covington, P. Jones, Taylor and Francis, London, 249 (1968).

[262] R. L. Kay, B. J. Hales, G. P. Cunningham, J. Phys. Chem., 71 (1967) 3925.

[263] R. L. Kay, C. Zawoyski, D. F. Evans, J. Phys. Chem., 69 (1965) 4208.

[264] D. F. Evans, J. L. Broadwater, J. Phys. Chem., 72 (1968) 1037.

[265] M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Ed. A. K. Covington, T. Dickinson, Plenum, New York, 3, Chapter 5, (1973).

[266] R. Fernandez-Prini, G. Atkinson, J. Phys. Chem., 75 (1971) 239.

[267] L. Bahadur, M. V. Ramanamurti, J. Chem. Soc. Faraday I., 76 (1980) 1409.

[268] L. Bahadur, M. V. Ramanamurti, J. Electrochem. Soc., 128 (1981) 339.

[269] L. Bahadur, M. V. Ramanamurti, Can. J. Chem., 62 (1984) 1051.

[270] J. L. Broadwater, R. L. Kay, J. Phys. Chem., 74 (1970) 3803.

[271] S. Das, D. K. Hazra, Ind. J. Chem., 274 (1988) 1073.

[272] S. Das, D. K. Hazra, J. Ind. Chem. Soc., LXV (1988) 100.

[273] (a) R. L. Kay, J. L. Broadwater, Electrochim. Acta., 16 (1971) 667.
(b) R. L. Kay, J. L. Broadwater, J. Solution Chem., 5 (1976) 57.

[274] A. D. Aprano, R. M. Fuoss, J. Phys. Chem., 67 (1963) 1704.

[275] P. Hemmes, J. Phys. Chem., 78 (1974) 907.

[276] J. Hubbard, L. Onsager, J. Chem. Phys., 53 (1977) 4850.

[277] N. Islam, M. R. Islam, M. Ahmed, Z. Phys. Chem. (Leipzig), 262 (1981) 129.

[278] D. S. Gill, A. N. Sharma, H. Schneider, J. Chem. Soc. Faraday. I., 78 (1982) 465.

[279] C. J. Cramer, D. G. Truhlar, J. Am. Chem. Soc., 113 (1991) 8305.

[280] D.J. Giesen, J.W. Stores, C.J. Cramer, D.G. Truhlar, J. Am. Chem. Soc., 117 (1995) 1057.

[281] (a) C. J. Cramer, D. G. Truhlar, J. Org. Chem., 61 (1996) 8720.
(b) C. J. Cramer, D. G. Truhlar, Erratum., 101 (1999) 309.

[282] G. D. Hawkins, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B., 101 (1997) 7147.

[283] G. D. Hawkins, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B., 102 (1998) 3257.

[284] A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, A.N. Burgess, J. Chem. Phys., 106 (1997) 4168.

[285] A. Galindo, L. A. Davies, A. Gil-Villegas, G. Jackson, Mol. Phys., 93 (1998) 241.

[286] M. Roses, C. Rafols, J. Ortega, E. Bosch, J. Chem. Soc. Perkin Trans 2, (1995) 1607.

[287] O. Bernard, W. Kunz, P. Turq, L. Blum, J. Phys. Chem., 96 (1992) 3833.

[288] S. Durand-Vidal, P. Turq, O. Bernard, J. Phys. Chem., 100 (1996) 17345.

[289] H. L. Bianchi, I. Dujovne, R. Fernandez-Prini, J. Soln. Chem., 29 (2000) 237.

[290] A. Chandra, B. Bagchi, J. Phys. Chem. B., 104 (2000) 9067.

CHAPTER III

3.1. Source and Purification of the Chemicals used

3.1.1. Solvents

1,4-Dioxane ($C_4H_8O_2$, M.W. 88.11), Merck, India, was kept several days over potassium hydroxide (KOH), followed by refluxing over excess of sodium for 12 hours.[1, 2] Finally, it was distilled from sodium. The pure liquid had a boiling point of 375 K/760 mm, a density of 1026.5 kg.m^{-3} and a coefficient of viscosity of 1.196 mPa.s at 298.15 K.

1,3-Dioxolane ($C_3H_6O_2$, M.W. 74.08), Merck, India, 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.[2, 3] The solvent obtained after purification had a boiling point of 348 K / 760 mm, a density of 1057.1 kg.m^{-3} and a coefficient of viscosity of 0.531 mPa.s at 298.15 K.

Tetrahydrofuran (C_4H_8O, M.W. 72.11), Merck, India was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over $LiAlH_4$.[1] The purified solvent had boiling point of 339 K/760 mm, a density of 880.7 kg.m^{-3} and a coefficient of viscosity 0.463 mPa.s at 298.15 K.

N, N-Dimethylformamide (C_3H_7NO, M.W. 73.10), Merck, India, was mixed with 10% (by volume) benzene, and the azeotrope was distilled off under atmospheric pressure at about 353 K. The product was dried over silica gel and distilled at reduced pressure, with the middle fraction being collected. The purified solvents was stored over P_2O_5 in a desiccator before use.[4] The solvent had boiling point of 426 K/760 mm and 349 K/39 mm, a density of 944.2 kg.m^{-3} and a coefficient of viscosity 0.8016 mPa.s at 298.15 K.

n-Hexane (C_6H_{14}, M.W. 86.20), Merck, India, was washed with fuming H_2SO_4, dried and distilled from sodium hydride. The pure compound had a boiling point of 342 K/760 mm, a density of 660.0 kg.m^{-3} and a co-efficient of viscosity of 0.2814 mPa.s at 298.15 K.

Benzene (C_6H_6, M.W. 78.10), Merck, India, was at first washed with conc. H_2SO_4 and then with aqueous NaOH. After drying with P_2O_5 it was distilled. The solvent had a boiling point of 353 K/760 mm, a density of 872.2 kg.m^{-3} and a co-efficient of viscosity of 0.5881 mPa.s at 298.15 K.

The Alcohols used for the experimental purposes i.e. methanol (MeOH, CH_3OH, M.W. 32.04), ethanol (EtOH, C_2H_5OH, M.W. 46.07), 1-propanol (1-PrOH, C_3H_7OH, M.W. 60.10), 2-propanol (2-PrOH, C_3H_7OH, M.W. 60.10), 1-butanol (1-BuOH, C_4H_9OH, M.W. 74.12), 2-butanol (2-BuOH, C_4H_9OH, M.W. 74.12), t-butanol (t-BuOH, C_4H_9OH, M.W. 74.12) and i-amyl alcohol (i-AmOH, $C_5H_{11}OH$, M.W. 88.15), (Merck, India, Urasol grade) were dried over 4Å molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled.

Water was first deionized and then distilled in an all glass distilling set along with alkaline $KMnO_4$ solution to remove any organic matter^5 therein. The doubly distilled water was 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} S.cm^{-1}.

Densities and viscosities of the purified solvents were in good agreement with the literature values.$^{2-8}$ and are listed in the respective chapters. The purity of most of the solvents finally obtained was better than 99.5 %.

The research work has been carried out with binary or ternary solvent systems with 1, 4-dioxane and 1, 3- dioxolane or tetrahydrofuran as primary solvents with some polar, weakly polar and non-polar solvents as well as with some solutes.

3.1.2. Mixed solvents

The mixed solvents containing 10, 20, 30, 40, 60, 80 mass % of 1,4-dioxane + H_2O mixtures 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.

Besides these solvent mixtures, other solvent mixtures includes 1,3-dioxolane + monoalkanols; THF + methanol + benzene; isopropanol + benzene + n-hexane; THF + H_2O, + monoalkanols; THF + H_2O + 1,4-dioxane;

1,4-dioxane/1,3-dioxolane + butyl acetate, + butyric acid, + butylamine, + 2-butanone and butylamine/DMF + alkyl acetates etc. have been used for my research studies. The physical properties of different pure and mixed solvents have been presented in the respective chapters.

3.1.3. Solutes

Tetraalkylammonium salts viz. tetramethylammonium chloride (Me_4NCl, M.W. 109.60), tetraethylammonium bromide (Et_4NBr, M.W. 210.16), tetrapropylammonium bromide (Pr_4NBr, M.W. 266.27), tetrabutylammonium bromide (Bu_4NBr, M.W. 322.37), and tetrabutylammonium iodide (Bu_4NI, M.W. 369.38) were of A. R. grade (Aldrich) and purified by dissolving in mixed alcohol medium and recrystallised from solvent ether medium. After filtration, the salts were dried in an oven for few hours. The bromide salts of higher tetraalkyl homologues were recrystallised second time to ensure highest purity. The crystallised salts were dried in vacuum. The salts were stored in glass bottles in darkened desiccator over fused $CaCl_2$.

Ammonium fluoride (NH_4F, M.W. 37.04), ammonium chloride (NH_4Cl, M.W. 53.50), and ammonium bromide (NH_4Br, M.W. 97.95) were of A. R. grade (SD fine chemicals) and were dried at about 80-100^0 C in a vacuum oven for 48 hours before use.

Sodium molybdate ($Na_2MoO_4.2H_2O$, M. W. 241.95) was of A. R. grade (NICE, India) and purified by recrystallising twice from conductivity water and was dried in a vacuum desiccator over P_2O_5 for 24 hours before use.

Resorcinol ($C_6H_6O_2$, M.W. 110.10) of A.R. grade (SD fine chemicals) was crystallized from benzene/ethyl ether.[9] The compound was dried and stored in a vacuum desiccator.

The purity of the solutes finally obtained was better than 99.0 % as checked by melting point determination.

3.2. Experimental Methods

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.[10, 11] The pycnometer filled with air bubble free experimental liquid was kept vertically in a thermostatic water bath maintained at ± 0.01 K 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}. Figure 1 shows an Ostwald-Sprengel type pycnometer (Single arm) used in our works.

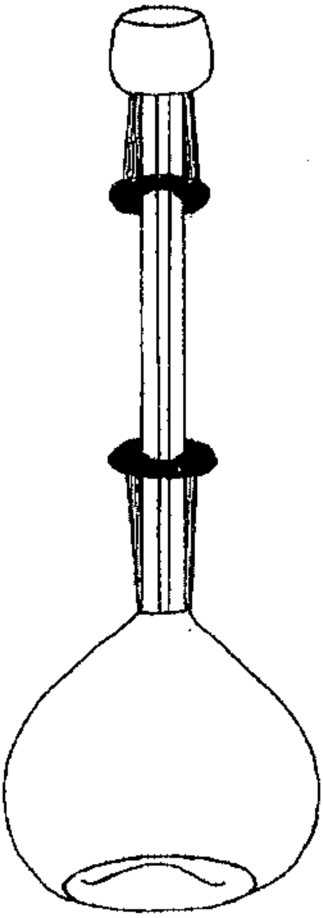

Figure 1. An Ostwald- Sprengel type pycnometer.

The temperature of the thermostatic water bath was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.[12] 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.[1, 13-16]

3.2.2. Measurement of Viscosity

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[17] 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 1.9602×10^{-3} and 4.2019 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 2 shows a suspended-level Ubbelohde viscometer used in our works.

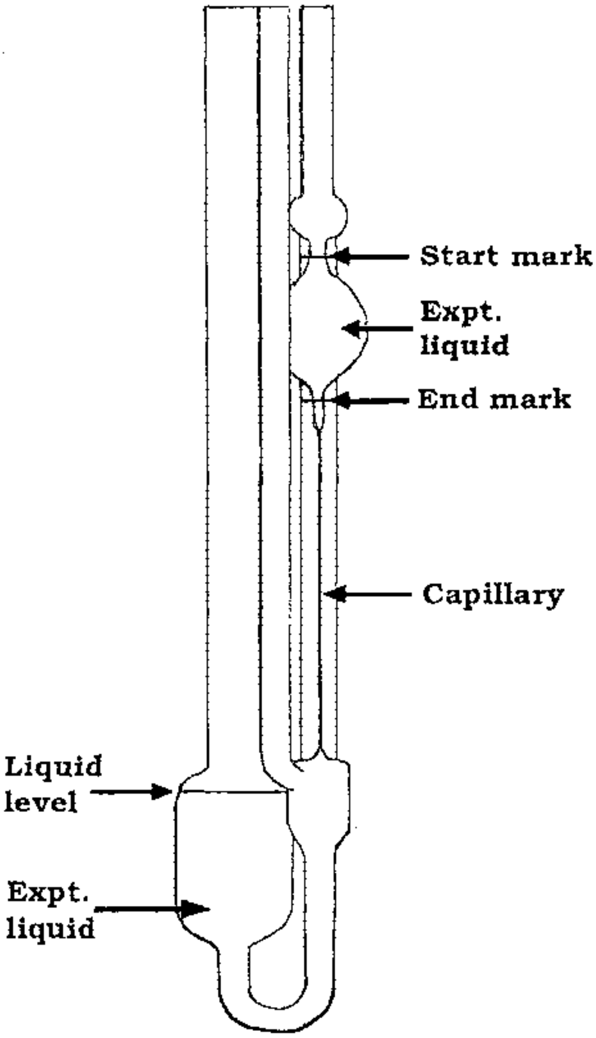

Figure 2. A suspended-level Ubbelohde viscometer.

3.2.3. Measurement of Ultrasonic Speed

Ultrasonic speeds were measured, with an accuracy of 0.3 %, using a single-crystal variable-path ultrasonic interferometer[18] (Model M-81, Mittal Enterprise, New Delhi) operating at 2 MHz, which was calibrated with water, methanol and benzene at the experimental temperature. The temperature stability was maintained within ± 0.01 K of the desired temperature by circulating thermostatic water around the cell with the aid of a circulating pump.

Experimental Section

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.

In figure 3- (A) Cross-section of the measuring cell of a Multi-frequency Ultrasonic Interferometer and (B) Position of reflector vs. crystal current are depicted.

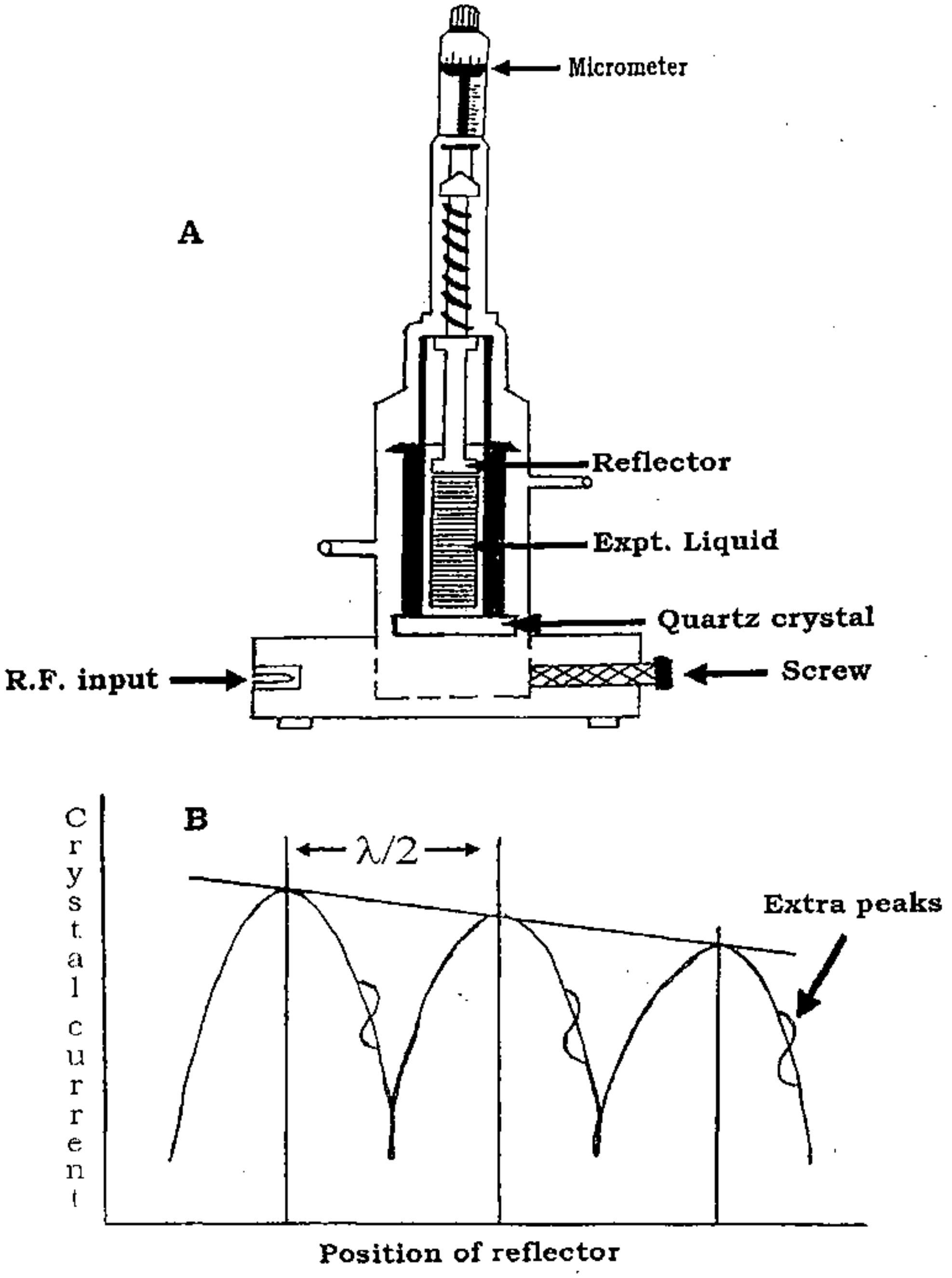

Figure 3. (A) Cross-section of the measuring cell of A Multi-frequency Ultrasonic Interferometer, (B) Position of reflector vs. crystal current.

However, the extra peaks (Figure 3B) in between minima and maxima occurs due to a number of reasons, but these do not effect the value of $\lambda/2$.

3.2.4. Measurement of Conductance

Systronic 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.[19] The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of ± 0.01 K.

Several solutions were prepared by mass accurate to ± 0.01 mg with the aid of a Mettler electronic analytical balance (AG 285, Switzerland) 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 4 shows the Systronic Conductivity meter- 306 i.e. (a) Isometric view and (b) Block diagram of the instrument.

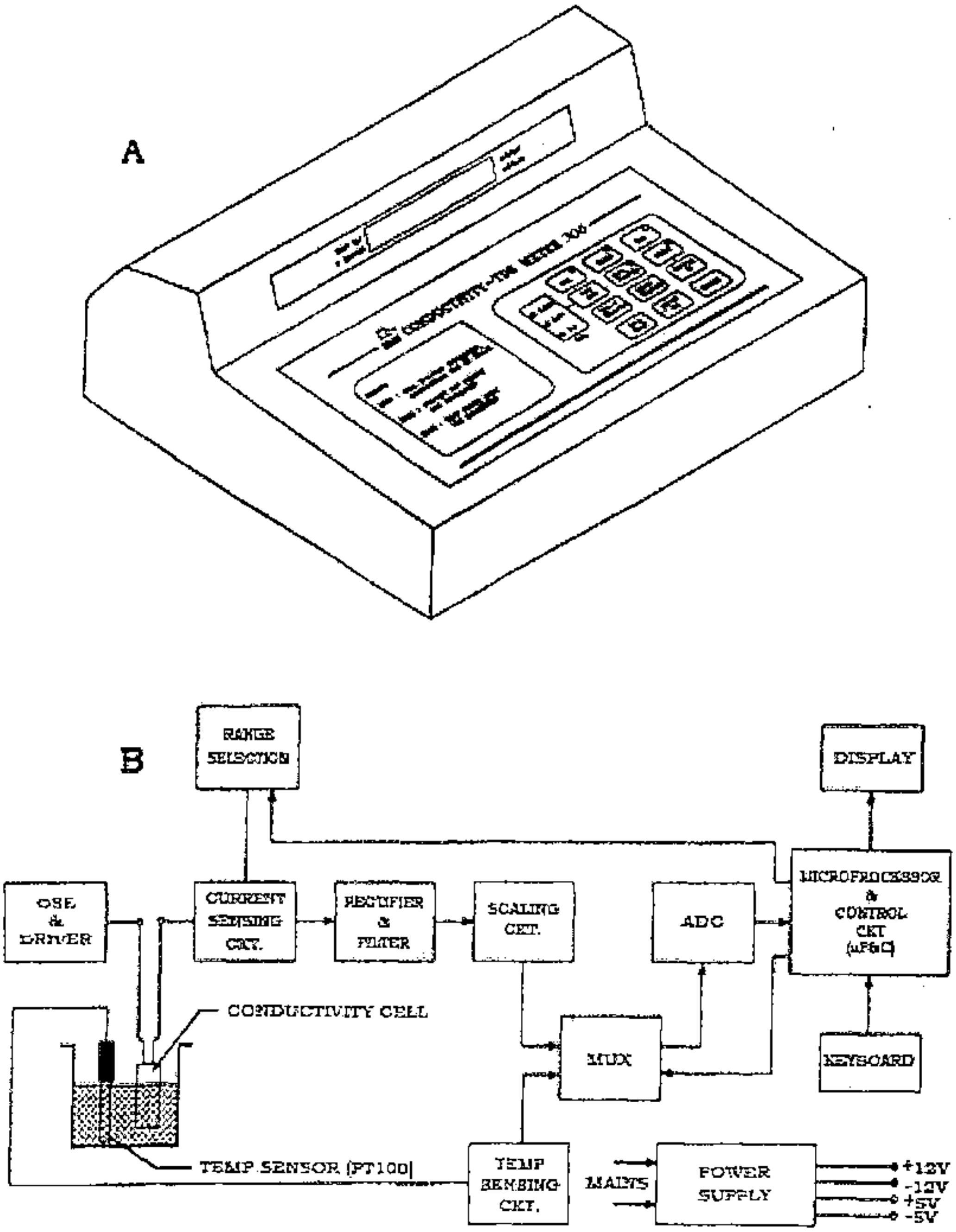

Figure 4. The Systronic Conductivity meter 306- (A) Isometric view and (B) Block diagram of the instrument.

References

[1] B. Das, M.N. Roy, D.K.Hazra, Ind. J. Chem. Tech., 1 (1994) 93.

[2] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).

[3] J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, Wiley, New York, (1986).

[4] Y. Zhao, J. Wang, X. Xuan, J. Lu, J. Chem. Eng. Data., 45 (2000) 440.

[5] Z. Yan, J. Wang, J. Lu, J. Chem. Eng. Data., 1 (2001) 217.

[6] T. Timmermans, *Physico Chemical Constants of Pure organic Compounds*, Elsevier, Amsterdam, 1, (1950).

[7] J. V. Herraez, R. Belda, J. Soln. Chem., 33 (2004) 117.

[8] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1327.

[9] S. K. Ghosh, D. K. Hazra. Ind. J. Chem., 29A (1990) 656.

[10] K. N. Marsh, "*Recommended Reference Materials for the Realisation of Physicochemical Properties*", Blackwell Scientific Publications, Oxford, U. K., (1987).

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

[12] D. Dasgupta, S. Das, D. K. Hazra. J. Chem. Soc. Faraday Trans I., 84 (1988) 1057.

[13] P. S. Nikam, M. Hosan, J. Chem. Eng. Data., 33 (1988) 165.

[14] R. D. Peralta, R. Infante, G. Cortez, G. Cadenas, J. Wisniak, Int. J. Thermophys., 24 (2003) 1061.

[15] S. Martin Contreras, J. Chem. Eng. Data., 46 (2001) 1149.

[16] R. Francesconi, F. Comelli, J. Chem. Eng. Data., 40 (1995) 31.

[17] J. R. Suindells, J. R. Coe Jr., T. B. Godfray. J. Res. Natd. Bus. Stand., 48 (1952) 1.

[18] M. N. Roy, A. Jha, A. Choudhury, J. Chem. Eng. Data., 49 (2004) 291.

[19] J. E. Lind Jr., J. J. Zwolenik, R. M. Fuoss, J. Chem. Soc. Faraday Trans I., 81 (1959) 1557.

CHAPTER IV

Viscous Synergy and Isentropic Compressibility of Some Monoalkanols and Cyclic Ethers in Water at 298.15 K*

4.1. Introduction

The increasing use of cyclic ether, monoalkanols and their aqueous mixtures in many industrial processes such as pharmaceutical and cosmetics has greatly stimulated the need for extensive information on their properties. 1,4-dioxane (DO), tetrahydrofuran (THF) and their aqueous mixtures are very important solvents that are widely used in various industries. They figure prominently in the high-energy battery technology and have also found application in organic synthesis as manifested from the physico-chemical studies in these media.[1-7]

The thermodynamic properties of various alkanols have been studied in numerous solvents.[8-14] Pure or aqueous alcohols are most widely used in industry, including in the manufacture of pharmaceuticals and cosmetic products. However, in the case of insolubility of some solutes in water, non-water solvents may be used possessing the common characteristic of being soluble in water; as a result, such solvents may be used with different purposes, such as increasing water solubility, or modifying the viscosity or absorption of the dissolved substance. In our systematic study of the thermodynamic properties, we have reported densities, viscosities and speeds of sound of different solvents and their mixtures in the previous papers[15-22] from our laboratory. In this chapter we extend our studies to the aqueous mixtures of 1,4-dioxane (DO) and tetrahydrofuran (THF) with some monoalkanols; where water is represented as A; cyclic ether (DO or THF), represented as B; and monoalkanol, represented as C. The monoalkanols include methanol (MeOH), ethanol (EtOH), 1- propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH) and 2-butanol (2-BuOH). The density and viscosity data have been analyzed using the equation developed by Kaletunc-Gencer and Peleg.

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4.2. Experimental section

4.2.1. Chemicals

1, 4-dioxane and tetrahydrofuran (Merck, India) were purified as described earlier.[16, 23] The source and purification of pure alcohols (Merck, India) methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol have been described earlier.[16, 24] Triply distilled water was used for the experiment. The chemicals after purification were 99.9% pure and their purity was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature[12, 15, 25-26] as listed in Table 1.

4.2.2. Measurements

Densities were measured with an Ostwald –Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostated bath controlled to ± 0.01K. The weighings were done on a Mettler AG-285 electronic balance with a precision of ± 0.01mg. The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm^{-3}.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. 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 details of the methods and techniques had been described earlier.[4, 16]

Speeds of sound were determined by a multi-frequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 2 MHz, which was calibrated with water, methanol and benzene at 298.15 K. The precision of the speed measurements was ± 0.2 m s^{-1}. The details of the methods and techniques had been described earlier.[16] The mixtures 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. Adequate precautions were taken to minimize evaporation loses during the actual measurements.

4.3. Results and discussion

4.3.1. Viscous synergy

The measurements made yielded the viscosity values, η_{exp}, for the different mixtures at different concentrations (*w/w*), are listed in Table 2 along with the viscosity values, η_{mix} in the absence of interaction. The method most widely used to analyze the antagonic and synergic behaviour of various solvent-mixtures is that developed by Kaletunc-Gencer and Peleg[27] allowing quantification of the synergic and antagonic interactions taking place in mixtures involving variable proportions of the constituent components. Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component in the system. In contraposition to viscous synergism, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component in the system. If the total viscosity of the system is equal to the sum of the viscosities of each component, the system is said to lack interaction.[28]

The viscosity in the absence of interaction, η_{mix}, is defined by the simple mixing rule:

$$\eta_{mix} = w_A\eta_A + w_B\eta_B + w_C\eta_C \tag{1}$$

where w_A, w_B and w_C are the fractions by weight and η_A, η_B and η_C are the viscosities, measured experimentally, of the components A, B and C respectively. Viscous synergy exists when, $\eta_{exp} > \eta_{mix}$. The procedure is valid for Newtonian fluids, since in non-Newtonian systems shear rate must be taken into account and consequently, other synergy indices have been defined.[29]

The values in Table 2 are graphically represented in Figures 1 and 2, where the viscosity is seen to increase non-linearly for all the mixtures, reaching maximum values (saturation point) at different concentrations in each case and thereafter decreases.

Maximum viscosity is found in the mixtures when the molecules are in the following ratios:

H_2O : THF = 1 : 0.17
H_2O : THF : MeOH = 1 : 0.08 : 0.19
H_2O : THF : EtOH = 1 : 0.10 : 0.16
H_2O : THF : 1-PrOH = 1 : 0.10 : 0.16
H_2O : THF : 2-PrOH = 1 : 0.11 : 0.13
H_2O : THF : 1-BuOH = 1 : 0.19 : 0.18
H_2O : THF : 2-BuOH = 1 : 0.54 : 0.51
H_2O : DO = 1 : 0.38
H_2O : DO : MeOH = 1 : 0.10 : 0.28
H_2O : DO : EtOH = 1 : 0.10 : 0.20
H_2O : DO : 1-PrOH = 1 : 0.10 : 0.15
H_2O : DO : 2-PrOH = 1 : 0.10 : 0.15
H_2O : DO : 1-BuOH = 1 : 0.15 : 0.18
H_2O : DO : 2-BuOH = 1 : 0.41 : 0.49
H_2O : THF : DO = 1 : 0.08 : 0.07

The explanation of this type of behavior is based on the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture - producing an increase in size of the resulting molecular package, which logically implies a rise in viscosity and density. After reaching the maximum viscosity, the subsequent addition of more water induces a decrease in mixture viscosity, as the latter tends to approach the viscosity of water as concentration approaches zero.

Such characteristics in the viscosity versus composition curve is a manifestation of specific interaction[30] between the unlike molecules, predominated by hydrogen bonding interaction.

Table 2 shows that at the point of specific interaction (Saturation point) the molar ratio of tetrahydrofuran (THF), 1,4-dioxane (DO), water and the various monoalkanols in the mixtures is as follows:

THF : H_2O : MeOH : EtOH : 1-PrOH : 2-PrOH : 1-BuOH : 2-BuOH

= 1: 5.88 : 2.37 : 1.6 : 1.6 : 1.18 : 0.95 : 0.94

DO : H_2O : MeOH : EtOH : 1-PrOH : 2-PrOH : 1-BuOH : 2-BuOH

= 1: 2.63 : 2.8 : 2 : 1.5 : 1.5 : 1.2 : 1.19

It can be concluded that the affinity of monoalkanol molecules towards tetrahydrofuran (THF) and 1,4 dioxane (DO) molecules in presence of water is enhanced by the following orders, respectively:

MeOH > EtOH = 1-PrOH > 2-PrOH > 1-BuOH > 2-BuOH

MeOH > EtOH > 1-PrOH = 2-PrOH > 1-BuOH > 2-BuOH

The monoalkanols with hydroxyl group positioned at the second carbon atom accept more tetrahydrofuran and 1,4-dioxane than those with the terminal hydroxyl group. Similar results were also reported earlier by Herraez et al.[12] Also, the maximum viscosity logically increases with the number of carbon atoms contained in the alkanol molecules, as shown in Figure 3.

4.3.2. Synergy index and Enhancement index

Table 3 represents the corresponding pure state viscosity, η_0; the maximum viscosity reached on addition of water, η_{max}; the viscosity of the mixture at the concentration where the maximum viscosity is reached in the event no interaction occurs in the mixture, η_{mix}; the corresponding viscosity increment given by $\Delta\eta = \eta_{exp} - \eta_{mix}$; the synergy indices, I_η, introduced by Howell[29] and the enhancement indices, E_η; calculated by the following equations:

$$I_\eta = \frac{\eta_{exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \qquad (2)$$

$$E_\eta = \frac{\eta_{max}}{\eta_0} \qquad (3)$$

The values recorded in Table 3 allow us to plot the graphic representations shown in Figures 3-5. The figure 3 jointly presents the viscosities, η_{max} and η_0, as a function of the number of carbon atoms, for the alkanols with terminal hydroxyl group and shows that the values η_0 increases almost linearly with the number of carbon atoms, while the η_{max} values, expected to be greater than η_0, also increase in a similar fashion. For the monoalkanols with the hydroxyl group at the second carbon atom of the molecular chain, Figure 3b provides a graphic illustration to the same scale as in Figure 3a.

Figure 4 shows the viscous synergy index, I_η, as a function of the number of carbon atoms corresponding to the monoalkanols with the hydroxyl group at the end of the molecular chain and the second carbon atom. This figure reflects a decreasing tendency with the exception of ethanol. This figure also shows that the synergy indices of the monoalkanols with the hydroxyl group at the second carbon atom of the molecular chain are greater than those of the monoalkanols with terminal hydroxyl group. Similar results were reported earlier by Herraez et al.[12]

Figure 5 depicts the enhancement index, E_η, as a function of the number of carbon atoms in the monoalkanol structure and shows a linear, sharp gradient decrease for the monoalkanols.

4.3.3. Synergy in density

The increase in density was analyzed by carrying out a procedure analogous to that used for mixture viscosity based on the following equation:

$$\rho_{mix} = w_A \rho_A + w_B \rho_B + w_C \cdot \rho_C \qquad (4)$$

where w_A, w_B and w_C are the fractions by weight and ρ_A, ρ_B and ρ_C are the densities, measured experimentally, of the components A, B and C respectively. Accordingly, when $\rho_{exp} > \rho_{mix}$, volume contraction occurs. A perusal of Table 4 shows that the values of the density determined experimentally, ρ_{exp} for various liquid mixtures are higher than those of its theoretical values, ρ_{mix}. This fact can be explained in terms of electrostriction as a consequence solvent molecules are accommodated in the void space left in the packing of dispersed solvent molecules. Similar results were reported by some authors earlier.[12, 26]

4.3.4. Deviation in isentropic compressibility

Isentropic compressibility, K_S and deviation in isentropic compressibility, K_S^E were calculated using the following relations:

$$K_S = (u^2 \rho_{exp})^{-1} \qquad (5)$$

$$K_S^E = K_S - \sum_{i=1}^{j} x_i K_{s,i} \qquad (6)$$

where u and K_S are the speed of sound, isentropic compressibility of the mixture and $K_{S,i}$ the isentropic compressibility of ith component in the mixture, respectively. The experimental speed of sound, isentropic compressibility and deviation in isentropic compressibility are listed in Table 5 and are graphically represented in Figures 6a and 6b as a function of mole fraction of the monoalkanols.

Experimental speeds of sound, estimated isentropic compressibility and deviation in isentropic compressibility are listed in Table 5. Figures 6a and 6b show that K_S^E values are negative for all the mixtures under investigation and they increase as the length of the molecular chain of the monoalkanols increase. The donor-acceptor interactions between the mixing components play a pivotal role to yield negative K_S^E values, which are more negative for the lower monoalkanols. However, the branched isomers have lower K_S^E values than their terminal counter part, as they can fit well into the structure of the cyclic ethers and water. Similar results were reported by some author earlier.[23, 31, 32]

4.4. Conclusion

In summary, monoalkanols containing up to three carbon atoms mix with water in any proportion and the higher monoalkanols mix with water in limited proportion. The monoalkanols with the hydroxyl group positioned at the second carbon atom accept more water than those with the terminal hydroxyl group and their $\eta_{\max}$, I_η, and E_η values are, therefore, considerably higher. Also, the monoalkanols with hydroxyl group positioned at the second carbon atom accept more tetrahydrofuran and 1,4-dioxane than those with the terminal hydroxyl group.

List of symbols

A	water
B	cyclic ether
C	monoalkanol
w_A	weight fraction of water
w_B	weight fraction of cyclic ether
w_C	weight fraction of monoalkanol
x_A	mole fraction of water
x_B	mole fraction of cyclic ether
x_C	mole fraction of monoalkanol
u	speed of sound
I_η	synergy index
E_η	enhancement index
K_S	isentropic compressibility
K_S^E	deviation in isentropic compressibility
η	viscosity
η_o	pure state viscosity
η_A	viscosity of component A
η_B	viscosity of component B
η_C	viscosity of component C
η_{exp}	experimental viscosity of mixture
η_{mix}	theoretical viscosity of mixture
η_{max}	maximum viscosity of mixture
ρ	density
ρ_A	density of component A
ρ_B	density of component B
ρ_C	density of component C
ρ_{exp}	experimental density of mixture
ρ_{mix}	theoretical density of mixture

References

[1] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001)1247.

[2] C. G. Janz, R. P. T Tomkins, *Non-aqueous Electrolytes Handbook,* Vol. 2, Academic Press, New York, (1973).

[3] R. Jasinki, *High Energy Batteries*, Plenum Press, New York, (1967).

[4] M. N. Roy, D. K. Hazra, Indian J. Chem. Technol., 1 (1994) 93.

[5] A. Sacco, M. D. Monika, A. D. Giglio, J. Chem. Soc. Faraday Trans I., 79 (1983) 2631.

[6] F. J. Millero, *Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, New York, (1972).

[7] M. L. Parmar, V. N. Rao, S. K. Bhardwaj, J. Indian Chem. Soc., 67 (1990) 591.

[8] S. L. Oswal, H.S. Desai, Fluid Phase Equilibr., 161 (1999) 191.

[9] S. L. Oswal, H. S. Desai, Fluid Phase Equilibr., 186 (2001) 81.

[10] P. Dimitrios, P. Constantinos, J. Chem. Eng. Data., 40 (1995) 202.

[11] G. Czechowski, B. Zywucki, J. Jadzyn, J. Chem. Eng. Data., 33 (1998) 55.

[12] J. V. Herraez, R. Belda, J. Soln. Chem., 33 (2004) 117.

[13] R. Belda, J. V. Herraez, O. Diez, Physics and Chemistry of Liquids., 42 (2004) 467.

[14] R. Belda, J. V. Herraez, O. Diez, Physics and Chemistry of Liquids., 43 (2005) 91.

[15] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1327.

[16] M. N. Roy, A. Sinha, B. Sinha, J. Soln. Chem., 34 (2005) 1319.

[17] M. N. Roy, S. R. Choudhury, A. Jha, J. Ind. Chem. Soc., 79 (2002) 623.

[18] M. N. Roy, A. Jha, A. Choudhury, J. Chem. Eng. Data., 49 (2004) 291.

[19] M. N. Roy, B. B. Gurung, A. Choudhury, J. Ind. Chem. Soc., 81 (2004) 1.

[20] M. N. Roy, B. Sinha, V. K. Dakua, J. Chem. Eng. Data., 51 (2006) 590.

[21] B. Sinha, A. Sinha, A. Jha, M. N. Roy, J. Ind. Chem. Soc., 82 (2005) 814.

[22] M. N. Roy, B. Sinha, R. Dey, A. Sinha, Int. J. Thermophys., 26 (2005) 1549.

[23] M. N. Roy, A. Sinha, Fluid Phase Equilibr., 243 (2006) 133.

[24] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Great Britain, (1988).

[25] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).

[26] A. Choudhury, A. Sinha, M. N. Roy, J. Tech. Res., 11 (2004)12.

[27] G. Kalentunc-Gencer, M. Peleg, J. Texture Studies., 17 (1986) 61.

[28] J. Pellicer, *Sinergia viscose. Ponencia en el curso: Fundamentos de reologia. Matetiales viscoelasticos. Aplicaciones a las industrias alimentarias y quimico- farmaceuticas*, U. I. M. P., Valencia, (1997).

[29] N. K. Howell, *Elucidation of protein-protien interactions in gels and foums*. Proceedings of the 7th Intern. Conf, Wales, (1993).

[30] R. J. Fort, W. R. Moore, Trans. Faraday. Soc., 61 (1965) 2102.

[31] C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, Int. J. Thermophys., 25 (2004) 1735.

[32] I. Gascon, S. Martin, P. Cea, M. C. Lopez, F. M. Royo, J. Soln. Chem., 31 (2002) 905.

Table 1.

Comparison of density, $\rho \times 10^3$/kg.m^{-3} and viscosity, η of the pure liquids with literature data at 298.15 K.

Solvent	**$\rho \times 10^3$/kg.m^{-3}**		**η/mPa.s**	
	Expt.	**Lit.**	**Expt.**	**Lit.**
Water	0.9971	0.9971 [25]	0.8904	0.8904 [25]
Tetrahydrofuran	0.8807	0.8807 [15]	0.4630	0.4630 [15]
1,4-Dioxane	1.0305	1.0305 [26]	1.2000	1.2000 [26]
Methanol	0.7869	0.7869 [12]	0.5470	0.5470 [12]
Ethanol	0.7850	0.7850 [12]	1.0760	1.0760 [12]
1-Propanol	0.8025	0.8025 [12]	1.9460	1.9460 [12]
2-Propanol	0.7825	0.7825 [12]	2.0314	2.0314 [12]
1-Butanol	0.8060	0.8060 [12]	2.5420	2.5420 [12]
2-Butanol	0.8035	0.8035 [12]	2.8230	2.8230 [12]

Table 2.
Comparison of the theoretical and experimental viscosities for the indicated water- soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols as a function of (*w*/*w*) concentration.

Mass% of H_2O	Pure THF		THF + MeOH (w/w = 1:1)		THF + EtOH (w/w = 1:1)		THF + 1-PrOH (w/w = 1:1)	
	η_{mix}/mPa.s	η_{exp}/mPa.s	η_{mix}/mPa.s	η_{exp}/mPa.s	η_{mix}/mPa.s	η_{exp}/mPa.s	η_{mix}/mPa.s	η_{exp}/mPa.s
0	0.4630	0.4630	0.5050	0.4761	0.7695	0.6728	1.2045	0.7603
10	0.5057	0.6564	0.5435	0.7377	0.7816	1.0009	1.1731	1.1857
20	0.5485	0.9237	0.5821	1.0404	0.7937	1.3311	1.1417	1.5186
30	0.5912	1.2238	0.6206	1.3114	0.8058	1.6325	1.1103	1.8789
35	0.6126	1.3994	0.6399	1.4428	0.8118	1.7806	1.0946	1.9117
40	0.6340	1.4904	0.6596	1.5381	0.8179	1.8862	1.0789	2.0208
45	0.6553	1.5817	0.6784	1.6474	0.8239	1.9729	1.0632	2.0917
50	0.6767	1.6776	0.6977	1.7686	0.8299	2.0332	1.0475	2.1581
55	0.6981	1.7013	0.7169	1.7698	0.8360	2.0907	1.0317	2.2296
60	0.7199	1.7321	0.7362	1.7852	0.8420	2.0152	1.0160	2.1679
70	0.7622	1.6798	0.7748	1.7787	0.8541	1.8765	0.9846	2.0124
80	0.8049	1.4900	0.8133	1.5651	0.8662	1.6345	0.9532	1.6478
90	0.8477	1.2015	0.8519	1.2485	0.8783	1.2372	0.9218	1.2592
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Mass% of H_2O	THF + 2-PrOH (w/w = 1:1)		THF + 1-BuOH (w/w = 1:1)		THF + 2-BuOH (w/w = 1:1)	
	η_{mix}/mPa.s	η_{exp}/mPa.s	η_{mix}/mPa.s	η_{exp}/mPa.s	η_{mix}/mPa.s	η_{exp}/mPa.s
0	1.2472	0.6917	1.5025	0.8514	1.6430	0.8021
10	1.2115	1.1171	1.4413	1.2586	1.5677	1.2436
20	1.1758	1.4952	1.3801	1.6069	1.4925	1.6700
30	1.1402	1.8652	1.3189	1.9206		
35	1.1223	2.0303	1.2883	2.1404		
40	1.1045	2.1759	1.2577	2.1910		
45	1.0866	2.2524				

Contd...

50	1.0688	2.2905				
55	1.0509	2.3370				
60	1.0331	2.2876				
70	0.9974	2.1204			1.1162	2.0884
80	0.9618	1.7880			1.0409	1.7427
90	0.9261	1.3276	0.9516	1.3354	0.9657	1.3178
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Mass% of H_2O	Pure DO		DO + MeOH (*w/w* = 1:1)		DO + EtOH (*w/w* = 1:1)		DO + 1-PrOH (*w/w* = 1:1)	
	η_{mix}/**mPa.s**	η_{exp}/**mPa.s**	η_{mix}/**mPa.s**	η_{exp}/**mPa.s**	η_{mix}/**mPa.s**	η_{exp}/**mPa.s**	η_{mix}/**mPa.s**	η_{exp}/**mPa.s**
0	1.2000	1.2000	0.8735	0.6148	1.1380	0.9243	1.5730	1.1309
10	1.1690	1.4419	0.8752	0.9069	1.1132	1.3182	1.5047	1.6458
20	1.1381	1.7859	0.8769	1.2053	1.0885	1.7779	1.4365	2.0743
30	1.1071	1.9762	0.8786	1.4429	1.0637	2.0719	1.3682	2.3439
35	1.0916	2.0230	0.8794	1.5471	1.0513	2.1364	1.3341	2.3963
40	1.0762	1.9871	0.8803	1.6171	1.0389	2.1975	1.2999	2.4199
45	1.0607	1.9577	0.8811	1.6712	1.0266	2.2388	1.2658	2.4286
50	1.0452	1.9139	0.8819	1.7057	1.0142	2.2636	1.2317	2.4468
55	1.0297	1.8346	0.8828	1.6971	1.0018	2.2029	1.1976	2.3527
60	1.0142	1.6970	0.8836	1.6349	0.9894	2.1110	1.1634	2.2553
70	0.9833	1.5181	0.8853	1.5233	0.9647	1.8947	1.0952	2.0141
80	0.9523	1.2967	0.8870	1.3352	0.9399	1.5610	1.0269	1.6868
90	0.9214	1.0949	0.8887	1.1766	0.9153	1.2005	0.9587	1.2584
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Mass% of H_2O	DO + 2-PrOH (*w/w* = 1:1)		DO + 1-BuOH (*w/w* = 1:1)		Do + 2-BuOH (*w/w* = 1:1)		DO + THF (*w/w* = 1:1)	
0	1.6157	1.0778	1.8710	1.2715	2.0115	1.1333	0.8315	0.6797
10	1.5432	1.6710	1.7729	1.7840	1.8994	1.8135	0.8374	0.9285
20	1.4706	2.2000	1.6749	2.1742	1.7873	3.0482	0.8433	1.2432
30	1.3981	2.5134	1.5768	2.2031			0.8492	1.5476
35	1.3618	2.5920	1.5278	2.2643			0.8521	1.6815
40	1.3256	2.6547	1.4788	2.4169			0.8551	1.7972

Contd...

45	1.2893	2.6967					0.8580	1.8754
50	1.2530	2.6892					0.8609	1.8939
55	1.2168	2.6212					0.8639	1.9094
60	1.1805	2.5276					0.8663	1.9166
70	1.1080	2.1706			1.2267	2.0546	0.8727	1.7124
80	1.0355	1.7344			1.1146	1.7101	0.8786	1.4701
90	0.9629	1.3143	0.9885	1.2371	1.0025	1.2626	0.8845	1.1930
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Table 3.
Pure-state viscosity, η_0; maximum viscosity, η_{max}; viscosity of the mixture without interaction, η_{mix}; viscosity increment, $\Delta\eta$; synergy indices, I_η; enhancement indices, E_η for the indicated water- soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols.

Solvent	η_0	η_{max}	η_{mix}	$\Delta\eta$	I_η	E_η
THF	0.4630	1.7321	0.7194	1.0127	1.4076	3.7146
THF + MeOH	0.4761	1.7852	0.7362	1.0489	1.4247	3.7443
THF + EtOH	0.6728	2.0907	0.8360	1.2547	1.5008	3.1074
THF + 1-PrOH	0.7603	2.2296	1.0317	1.1978	1.1609	2.9323
THF + 2-PrOH	0.6917	2.3370	1.0510	1.2860	1.2237	3.3787
THF + 1-BuOH	0.8514	2.1910	1.2577	0.9334	0.7421	2.5733
THF + 2-BuOH	0.8021	2.0884	1.1162	0.9722	0.8710	2.6038
DO	1.2000	2.0230	1.0916	0.9313	0.8531	1.6858
DO + MeOH	0.6148	1.7057	0.8819	0.8237	0.9340	2.7742
DO + EtOH	0.9243	2.2636	1.0142	1.2494	1.2319	2.4489
DO + 1-PrOH	1.1309	2.4468	1.2317	1.2151	0.9865	2.1636
DO + 2-PrOH	1.0776	2.6967	1.2893	1.4074	1.0915	2.5026
DO + 1-BuOH	1.2715	2.4169	1.4788	0.9382	0.6344	1.9008
DO + 2-BuOH	1.1333	3.0482	1.7873	1.2609	0.7055	2.6896
THF + DO	0.6797	1.9166	0.8663	1.0502	1.2122	2.8198

Table 4.
Comparison of the theoretical, ρ_{mix}/kg.m^{-3}, and experimental, ρ_{exp}/kg.m^{-3}, densities for the indicated water- soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols as a function of (*w*/*w*) concentration.

Mass% of H_2O	**Pure THF**		**THF + MeOH (*w*/*w* = 1:1)**		**THF + EtOH (*w*/*w* = 1:1)**		**THF + 1-PrOH (*w*/*w* = 1:1)**	
	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**
0	880.7	880.7	833.8	830.6	832.9	842.1	841.6	843.3
10	892.4	898.5	850.1	861.6	849.3	862.4	857.2	864.4
20	904.0	915.9	866.5	884.4	865.7	884.7	872.7	884.7
30	915.6	930.2	882.8	904.7	882.1	904.3	888.2	903.4
35	921.4	940.7	891.0	914.0	890.3	912.4	896.0	911.8
40	927.3	946.0	899.1	924.4	898.5	921.1	903.8	918.7
45	933.1	952.5	907.3	923.3	906.7	930.1	911.6	927.5
50	938.9	959.0	915.4	941.6	914.9	939.1	919.3	936.3
55	944.7	963.8	923.6	949.3	923.2	947.8	927.1	944.8
60	950.5	966.4	931.8	956.5	931.4	954.7	934.9	951.8
70	962.2	978.3	948.1	969.9	947.8	968.2	950.4	966.9
80	973.8	986.7	964.4	979.5	964.2	979.1	966.0	979.8
90	985.4	990.0	980.7	989.5	980.6	989.7	981.5	983.5
100	997.1	997.1	997.1	997.1	997.1	997.1	997.1	997.1

Mass%of H_2O	**THF + 2-PrOH (*w*/*w* = 1:1)**		**THF + 1-BuOH (*w*/*w* = 1:1)**		**THF + 2-BuOH (*w*/*w* = 1:1)**	
	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**
0	831.6	830.5	843.4	847.1	842.1	840.6
10	848.2	856.0	858.7	867.1	857.6	862.9
20	864.7	877.1	874.1	883.5	873.1	887.1
30	881.2	897.2	889.5	902.5		
35	889.5	906.4	897.2	909.9		
40	897.8	916.9	904.8	918.2		
45	906.1	925.1				
50	914.3	933.6				

Contd...

55	922.6	943.9				
60	930.9	949.9				
70	947.4	966.3			950.6	965.9
80	964.0	979.3			966.1	981.6
90	980.5	987.9	981.7	988.8	981.6	991.0
100	997.1	997.1	997.1	997.1	997.1	997.1

Mass% of H_2O	**Pure DO**		**DO + MeOH (w/w = 1:1)**		**DO + EtOH (w/w = 1:1)**		**DO + 1-PrOH (w/w = 1:1)**	
	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**	ρ_{mix}/**kg.m^{-3}**	ρ_{exp}/**kg.m^{-3}**
0	1030.5	1030.5	908.7	899.6	907.8	901.1	916.5	900.2
10	1027.2	1036.8	917.6	917.8	916.7	919.0	924.6	924.7
20	1023.8	1040.5	926.4	934.2	925.6	936.0	932.6	933.8
30	1020.5	1040.8	935.2	950.9	934.5	951.2	940.7	949.7
35	1018.8	1043.0	939.6	955.5	939.0	958.3	944.7	953.5
40	1017.1	1040.1	944.1	962.6	943.5	963.9	948.7	961.0
45	1015.5	1037.5	948.5	968.8	947.9	969.1	952.8	966.3
50	1013.8	1035.6	952.9	972.2	952.4	974.0	956.8	971.1
55	1012.1	1033.6	957.3	977.3	956.9	978.5	960.8	975.6
60	1010.4	1031.3	961.7	981.7	961.3	983.6	964.8	980.9
70	1007.1	1022.1	970.6	987.0	970.3	987.7	972.9	987.5
80	1003.8	1016.1	979.4	990.5	979.2	991.5	981.0	993.2
90	1000.4	1009.0	988.2	993.3	988.1	996.2	989.0	996.5
100	997.1	997.1	997.1	997.1	997.1	997.1	997.1	997.1
Mass% of H_2O	**DO + 2-PrOH (w/w = 1:1)**		**DO + 1-BuOH (w/w = 1:1)**		**DO + 2-BuOH (w/w = 1:1)**		**DO + THF (w/w = 1:1)**	
0	906.5	887.3	918.3	906.2	971.0	901.2	955.6	951.8
10	915.6	915.8	926.1	926.3	925.0	926.8	959.8	965.5
20	924.6	928.9	934.0	935.6	933.0	938.4	963.9	979.0
30	933.7	944.1	941.9	946.2			968.1	987.5
35	938.2	951.0	945.8	953.0			970.1	992.6
40	942.7	958.5	949.8	958.6			972.2	996.1

Contd...

45	947.3	964.6					974.3	998.1
50	951.8	970.7					976.3	1000.8
55	956.3	975.1					978.4	1003.5
60	960.8	981.7					980.5	1005.9
70	969.9	989.1			973.0	989.3	984.6	1005.1
80	979.0	992.9			981.1	994.8	988.8	1003.8
90	988.0	995.3	989.2	995.1	989.1	995.9	992.9	1002.2
100	997.1	997.1	997.1	997.1	997.1	997.1	997.1	997.1

Table 5.

Experimental densities (ρ_{exp}), speeds of sound (u), isentropic compressibilities (K_S) and deviations in isentropic compressibility (K_S^E) for the indicated water- soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols as a function of mole fractions of water (x_A) and the monoalkanols (x_C).

x_A	x_B [a]	ρ_{exp}/kg.m^{-3}	u /(m.s^{-1})	K_S x 10^{12} /(Pa^{-1})	K_S^E x10^{12} /(Pa^{-1})	x_A	x_C	ρ_{exp}/kg.m^{-3}	u /(m.s^{-1})	K_S x 10^{12} /(Pa^{-1})	K_S^E x10^{12} /(Pa^{-1})
		H_2O + THF						H_2O + THF + MeOH			
0	1	880.7	1283.2	689.6	0	0	0.6924	830.6	1150.4	909.7	-25.7
0.3078	0.6922	898.5	1351.1	609.6	-5.5	0.2149	0.5436	861.6	1202.3	803.0	-27.6
0.5002	0.4998	915.9	1395.7	560.5	-8.1	0.3811	0.4285	884.4	1256.3	716.4	-33.1
0.6317	0.3683	930.2	1435.3	521.8	-15.0	0.5135	0.3368	904.7	1309.4	644.7	-40.3
0.6831	0.3169	940.7	1449.6	505.9	-18.5	0.5701	0.2976	914.0	1339.9	609.4	-48.0
0.7274	0.2726	946.0	1467.8	490.7	-23.0	0.6215	0.2620	924.4	1368.5	577.6	-54.7
0.7661	0.2339	952.5	1487.0	474.8	-29.5	0.6683	0.2297	933.3	1396.4	549.5	-60.0
0.8001	0.1999	959.0	1504.6	460.6	-35.5	0.7112	0.2000	941.6	1422.8	524.6	-64.0
0.8303	0.1697	963.8	1519.3	449.5	-39.3	0.7506	0.1727	949.3	1446.6	503.4	-66.0
0.8572	0.1428	966.4	1529.6	442.3	-40.0	0.7870	0.1475	956.5	1467.9	485.2	-66.4
0.9033	0.0967	978.3	1528.4	437.6	-33.6	0.8518	0.1026	970.0	1490.4	464.1	-55.9
0.9412	0.0588	986.7	1523.6	436.6	-25.4	0.9078	0.0638	979.5	1496.4	455.9	-36.8
0.9730	0.0270	990.0	1515.3	439.9	-14.4	0.9568	0.0299	989.5	1493.9	452.8	-16.0
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
		H_2O + THF + EtOH						H_2O + THF + 1-PrOH			
0	0.6101	832.1	1193.3	843.9	-18.0	0	0.5454	841.3	1239.4	773.8	-6.6
0.2575	0.4530	862.4	1258.3	732.3	-22.9	0.2879	0.3884	864.4	1312.2	671.9	-12.8
0.4383	0.3427	884.7	1315.6	653.1	-27.3	0.4764	0.2856	884.7	1368.9	603.2	-18.8
0.5722	0.2610	904.3	1370.9	588.4	-36.5	0.6093	0.2131	903.4	1415.0	552.8	-24.9
0.6269	0.2277	912.4	1401.1	558.3	-44.0	0.6621	0.1843	911.8	1438.3	530.2	-30.0
0.6754	0.1980	921.1	1433.0	528.7	-53.5	0.7081	0.1592	918.7	1461.1	509.9	-35.0
0.7186	0.1717	930.1	1457.2	506.3	-58.0	0.7486	0.1371	927.5	1489.1	486.2	-45.2
0.7573	0.1481	939.1	1478.1	487.4	-60.9	0.7844	0.1176	936.3	1512.1	467.1	-52.4

Contd...

0.7923	0.1267	947.8	1496.6	471.1	-62.7
0.8240	0.1074	954.8	1507.7	460.7	-59.9
0.8793	0.0736	968.2	1504.8	456.1	-41.6
0.9258	0.0453	979.1	1496.0	456.4	-22.1
0.9656	0.0210	989.7	1490.6	454.7	-7.3
1	0	997.1	1496.6	447.8	0
		H_2O + THF + 2-PrOH			
0	0.5454	830.5	1213.4	817.7	-10.0
0.2879	0.3884	856.0	1291.1	700.8	-17.5
0.4764	0.2856	877.1	1352.3	623.4	-23.3
0.6093	0.2131	897.2	1405.5	564.2	-32.0
0.6621	0.1843	906.4	1432.2	537.9	-38.3
0.7081	0.1592	916.9	1458.0	513.1	-45.6
0.7486	0.1371	925.1	1484.7	490.4	-52.9
0.7844	0.1176	933.6	1505.8	472.4	-57.3
0.8164	0.1002	943.9	1517.2	460.2	-57.3
0.8452	0.0844	949.9	1517.6	457.1	-49.5
0.8946	0.0575	966.3	1512.4	452.4	-35.4
0.9357	0.0351	979.3	1508.9	448.5	-23.7
0.9704	0.0161	987.9	1500.6	449.5	-9.5
1	0	997.1	1496.6	447.8	0
		H_2O + THF + 2-BuOH			
0	0.4931	840.6	1249.5	762.0	-2.7
0.3108	0.3398	862.9	1329.8	655.3	-10.9
0.5036	0.2448	887.1	1381.2	590.9	-14.2

0.8164	0.1002	944.8	1519.1	458.6	-50.2
0.8452	0.0844	951.8	1520.6	454.4	-44.9
0.8946	0.0575	966.9	1518.2	448.7	-34.1
0.9357	0.0351	979.8	1513.7	445.5	-23.7
0.9704	0.0161	983.5	1504.6	449.1	-8.5
1	0	997.1	1496.6	447.8	0
		H_2O + THF + 1-BuOH			
0	0.4931	842.7	1261.1	746.1	-0.3
0.3108	0.3398	867.1	1338.1	644.1	-9.5
0.5036	0.2448	883.5	1391.2	584.8	-11.2
0.6349	0.1800	902.5	1432.9	539.7	-17.1
0.6860	0.1548	909.9	1454.2	519.7	-21.8
0.7301	0.1331	918.2	1483.4	494.9	-33.4
0.9733	0.0132	988.8	1498.6	450.3	-5.4
1	0	997.1	1496.6	447.8	0
		H_2O + DO			
0		1030.5	1345.8	535.8	0
0.3521		1036.8	1405.0	488.6	-16.2
0.5501		1040.5	1436.4	465.8	-21.5
0.6770		1040.8	1458.2	451.8	-24.3
0.7248		1043.0	1483.8	435.5	-36.5
0.7653		1040.1	1550.9	399.7	-68.7
0.8001		1037.5	1577.0	387.6	-77.8
0.8302		1035.6	1590.0	382.0	-80.7
0.8567		1033.6	1593.0	381.3	-79.1
0.8800		1031.3	1588.2	384.4	-73.9

Contd...

0.9045	0.0471	965.9	1508.2	455.1	-22.9	0.9194		1022.1	1558.4	402.9	-52.0
0.9420	0.0286	981.6	1501.7	451.7	-14.4	0.9514		1016.1	1540.4	414.8	-37.3
0.9733	0.0132	991.0	1497.1	450.2	-6.0	0.9778		1009.0	1509.0	435.2	-14.5
1	0	997.1	1496.6	447.8	0	1		997.1	1496.6	447.8	0
		H_2O + DO + MeOH						H_2O + DO + EtOH			
0	0.7333	899.6	1197.0	775.8	-133.0	0	0.6566	901.1	1236.9	725.4	-96.8
0.2247	0.5686	917.8	1249.1	698.3	-107.0	0.2718	0.4781	919.0	1297.9	645.9	-74.5
0.3947	0.4439	934.2	1304.6	628.9	-97.9	0.4564	0.3569	936.0	1353.7	583.0	-68.3
0.5278	0.3463	950.9	1379.3	552.8	-112.7	0.5901	0.2691	951.2	1418.7	522.3	-78.9
0.5841	0.3050	955.5	1423.6	516.4	-123.1	0.6439	0.2338	958.3	1452.4	494.7	-86.4
0.6349	0.2677	962.6	1463.9	484.8	-131.3	0.6913	0.2027	963.9	1487.7	468.7	-94.6
0.6809	0.2340	968.8	1503.0	456.9	-138.0	0.7332	0.1752	969.1	1523.8	444.4	-103.0
0.7229	0.2032	972.2	1537.0	435.4	-140.1	0.7706	0.1506	974.0	1549.2	427.8	-105.9
0.7612	0.1751	977.4	1555.0	423.1	-134.7	0.8041	0.1286	978.5	1556.0	422.1	-99.0
0.7964	0.1493	981.7	1565.5	415.6	-126.0	0.8344	0.1087	983.6	1566.2	414.5	-95.3
0.8589	0.1035	987.0	1576.1	407.8	-105.0	0.8868	0.0743	987.7	1572.9	409.2	-80.9
0.9125	0.0642	990.5	1568.2	410.5	-77.6	0.9307	0.0455	991.5	1562.6	413.1	-60.6
0.9591	0.0300	993.3	1553.8	417.0	-49.6	0.968	0.0210	996.2	1547.1	419.4	-40.3
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
		H_2O + DO + 1-PrOH						H_2O + DO + 2-PrOH			
0	0.5945	900.2	1248.6	712.5	-13.7	0	0.5945	887.3	1247.4	724.3	-53.5
0.3059	0.4126	924.7	1335.1	606.7	-34.4	0.3059	0.4126	915.8	1320.6	626.1	-50.7
0.4979	0.2985	933.8	1385.8	557.6	-30.0	0.4979	0.2985	928.9	1373.2	570.9	-42.6
0.6296	0.2202	949.7	1429.2	515.5	-35.4	0.6296	0.2202	944.1	1419.3	525.8	-44.2
0.6811	0.1896	953.5	1453.0	496.7	-39.8	0.6811	0.1896	951.0	1443.0	505.0	-48.0
0.7256	0.1631	961.0	1477.4	476.7	-47.4	0.7256	0.1631	958.5	1468.7	483.7	-54.6
0.7644	0.1401	966.3	1502.7	458.3	-55.1	0.7644	0.1401	964.6	1494.3	464.3	-61.2
0.7986	0.1197	971.1	1526.2	442.1	-61.7	0.7986	0.1197	970.7	1521.9	444.8	-69.4
0.8290	0.1017	975.6	1543.3	430.4	-65.0	0.8290	0.1017	975.1	1540.6	432.1	-72.1
0.8561	0.0856	980.9	1545.8	426.6	-61.2	0.8561	0.0856	981.7	1541.6	428.6	-66.6
0.9025	0.0580	987.5	1541.8	426.0	-48.9	0.9025	0.0580	989.1	1542.7	424.8	-55.1
0.9407	0.0353	993.2	1541.1	424.0	-40.3	0.9407	0.0353	992.9	1543.7	422.6	-44.7

Contd...

0.9727	0.0162	996.5	1531.4	427.9	-27.4	0.9727	0.0162	995.3	1527.5	430.6	-26.1
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
		H_2O + DO + 1-BuOH						H_2O + DO + 2-BuOH			
0	0.5431	906.2	1268.6	685.7	3.8	0	0.5431	901.2	1263.9	694.6	-7.4
0.3318	0.3629	926.3	1364.6	579.7	-24.5	0.3318	0.3629	926.8	1356.4	586.5	-31.2
0.5277	0.2565	935.6	1411.2	536.7	-21.6	0.5277	0.2565	938.4	1401.2	542.8	-25.1
0.6570	0.1863	946.2	1457.1	497.8	-30.3						
0.7064	0.1595	953.0	1480.8	478.5	-38.0						
0.7487	0.1365	958.6	1508.2	458.6	-48.0						
						0.9125	0.0475	994.8	1539.7	426.4	-43.6
						0.9470	0.0288	995.9	1535.4	426.4	-34.8
0.9757	0.0132	995.1	1523.7	432.8	-20.6	0.9757	0.0132	997.1	1516.5	436.6	-17.3
1	0	997.1	1496.6	447.8	0	1	0	994.8	1496.6	447.8	0
x_A	x_B[b]	ρ_{exp}/kg.m^{-3}	u /(m.s^{-1})	K_S x 10^{12} /(Pa^{-1})	K_S^E x10^{12} /(Pa^{-1})	x_A	x_B[b]	ρ_{exp}/kg.m^{-3}	u /(m.s^{-1})	K_S x 10^{12} /(Pa^{-1})	K_S^E x10^{12} /(Pa^{-1})
		H_2O + THF + DO						H_2O + THF + DO			
0	0.4501	951.8	1289.0	632.4	12	0.8149	0.0833	1000.8	1520.1	432.4	-47.3
0.3285	0.3022	965.5	1377.6	545.8	-17.9	0.8433	0.0705	1003.5	1539.8	420.3	-54.5
0.5239	0.2143	979.0	1417.0	508.7	-21.2	0.8685	0.0592	1005.9	1552.9	412.2	-58.2
0.6536	0.1559	987.5	1444.8	485.1	-22.4	0.9113	0.0399	1005.1	1557.6	410.1	-53.0
0.7033	0.1335	992.6	1457.2	474.4	-24.5	0.9463	0.0242	1003.8	1542.8	418.5	-38.5
0.7459	0.1144	996.1	1474.4	461.8	-29.8	0.9754	0.0111	1002.2	1523.4	429.9	-22.0
0.7827	0.0978	998.1	1494.0	448.9	-36.4	1	0	997.1	1496.6	447.8	0

[a] mole fraction of THF, [b] mole fraction of DO.

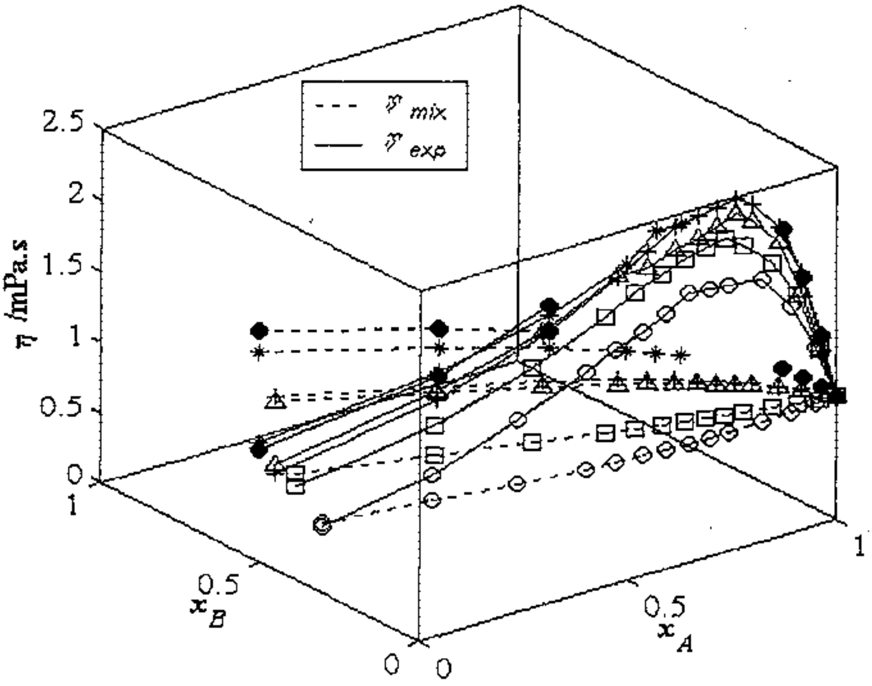

Figure1a. Experimental viscosity, η_{exp}/mPa.s, and theoretical viscosity, η_{mix}/mPa.s, of water-soluble alkanols as a function of mole fractions of water (x_A) and tetrahydrofuran (x_B). Methanol (o), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (•)

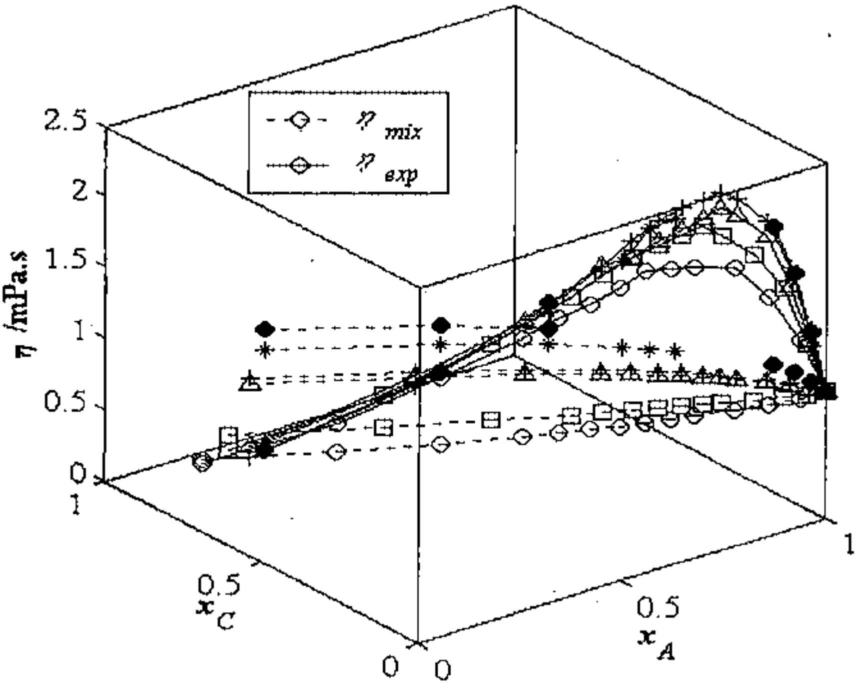

Figure 1b. Experimental viscosity, η_{exp}/mPa.s, and theoretical viscosity, η_{mix}/mPa.s, of water-soluble alkanols as a function of mole fractions of water (x_A) and alkanol (x_C). Methanol (o), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (•)

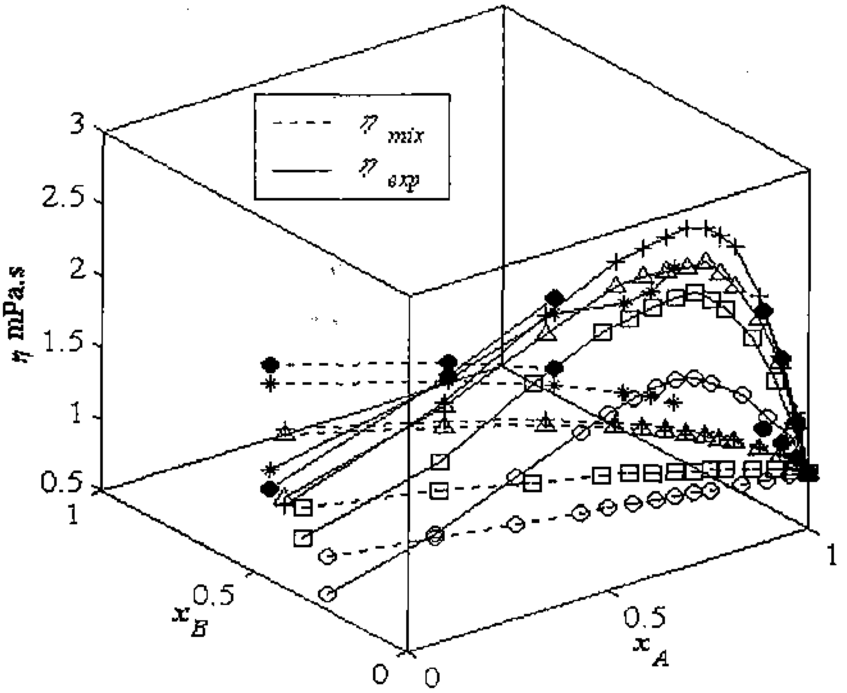

Figure 2a. Experimental viscosity, η_{exp}/mPa.s, and theoretical viscosity, η_{mix}/mPa.s, of water-soluble alkanols as a function of mole fractions of water (x_A) and 1,4-dioxane (x_B). Methanol (o), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (•)

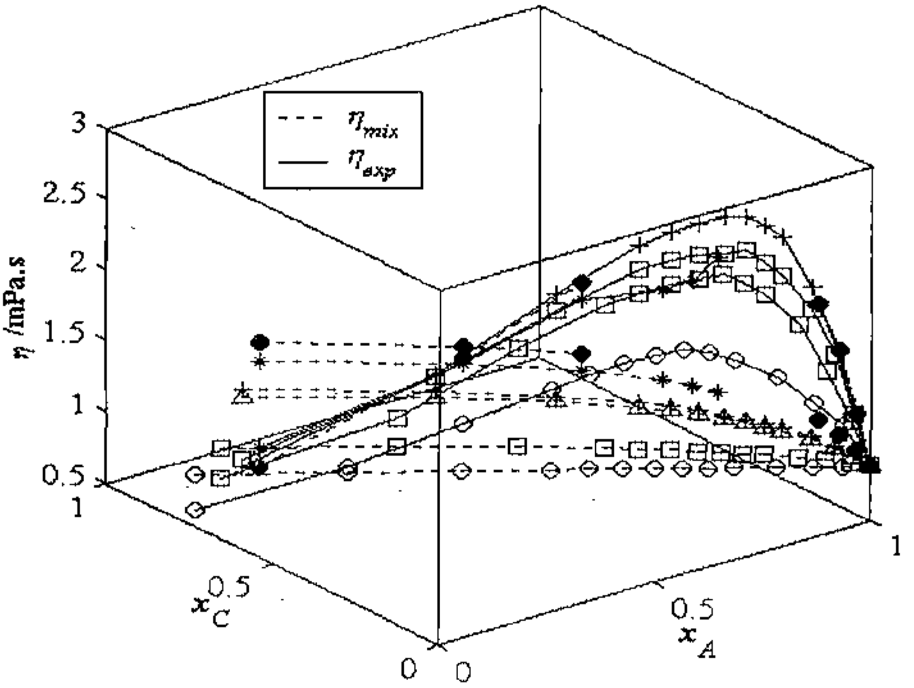

Figure 2b. Experimental viscosity, η_{exp}/mPa.s, and theoretical viscosity, η_{mix}/mPa.s, of water-soluble alkanols as a function of mole fractions of water (x_A) and alkanol (x_C). Methanol (o), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (•)

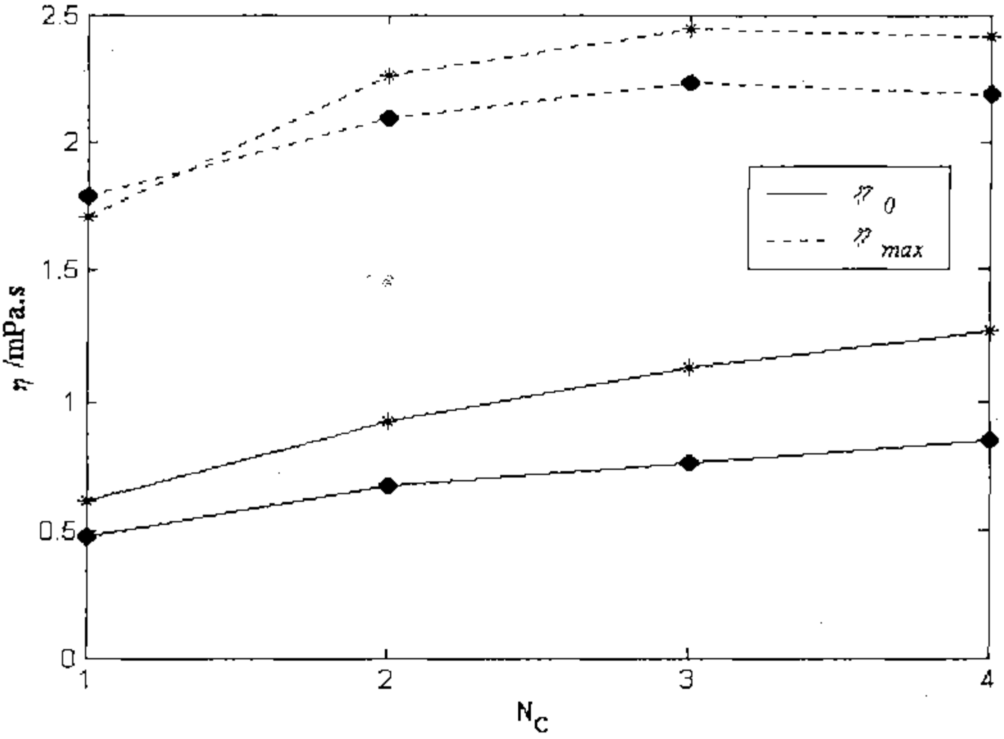

Figure 3a. Viscosity values, η_0/mPa.s, and η_{max}/mPa.s, of the monoalkanols with terminal hydroxyl group as a function of the number of carbon atoms, N_C. H_2O + THF systems (•), H_2O + DO systems (*).

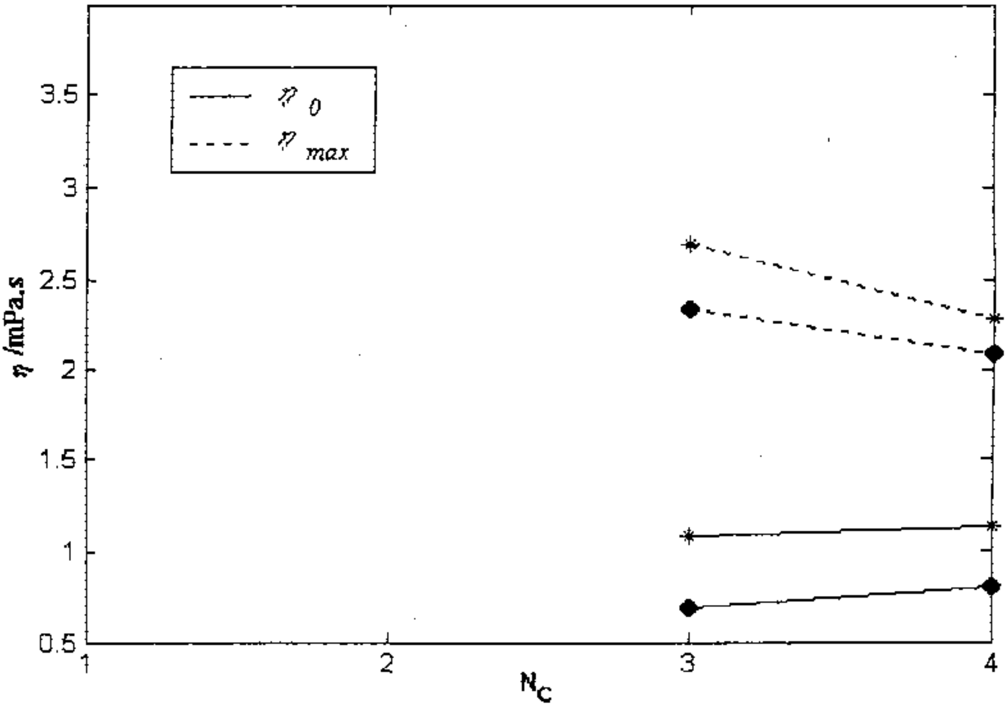

Figure 3b. Viscosity values, η_o /mPa.s, and η_{max} /mPa.s, of the monoalkanols with hydroxyl group at the second carbon atom of the molecular chain as a function of the number of carbon atoms, N_C. H_2O + THF systems (•), H_2O + DO systems (*).

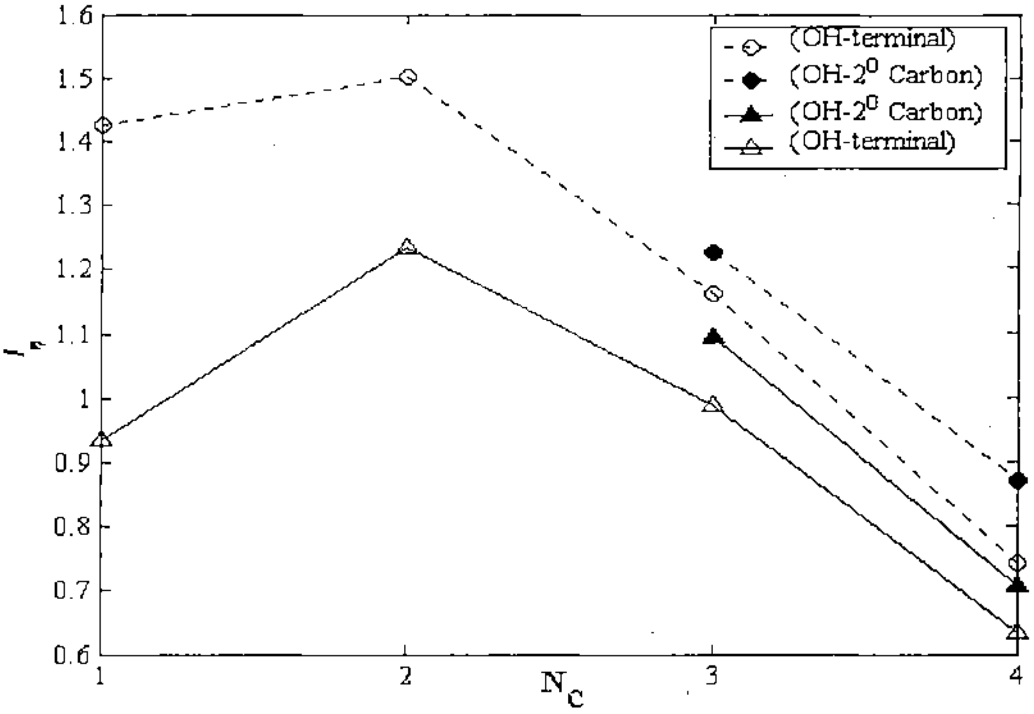

Figure 4. Viscous synergy index, I_η, of the monoalkanols as a function of the number of carbon atoms, N_C. H_2O + DO systems (—), H_2O+THF systems (---).

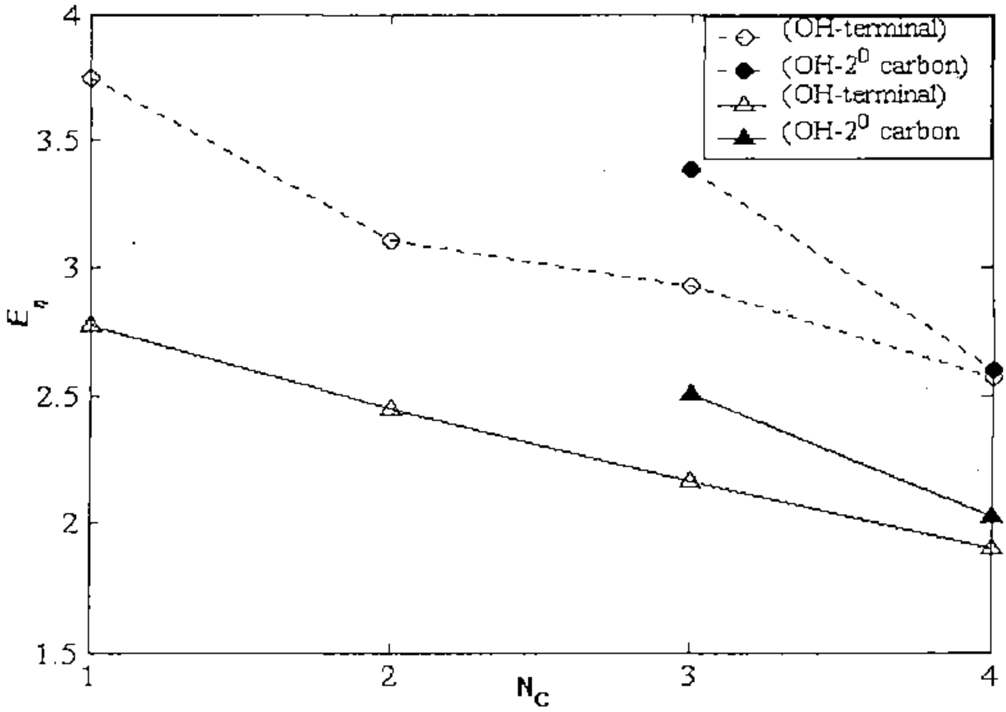

Figure 5. Enhance index, E_η, of the monoalkanols as a function of the number of carbon atoms, N_C. H_2O + DO systems (—), H_2O+THF systems (---).

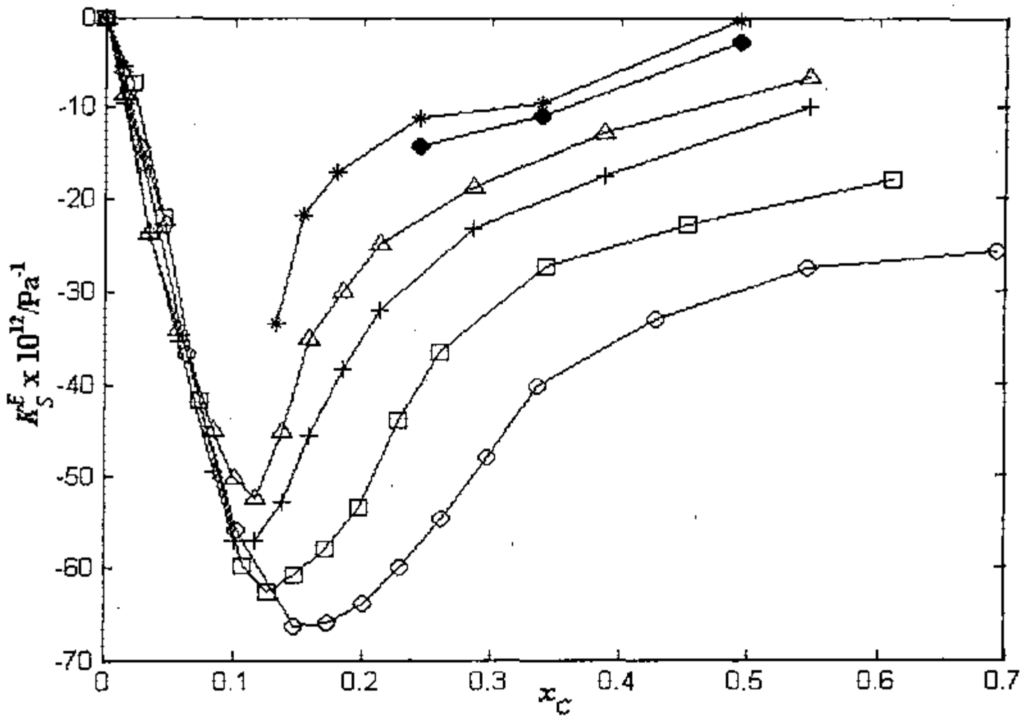

Figure 6a. Deviation in isentropic compressibility, K_S^E, of { H_2O + THF + monoalkanol } mixtures as a function of mole fraction, x_C, of monoalkanols. Methanol (o), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (•)

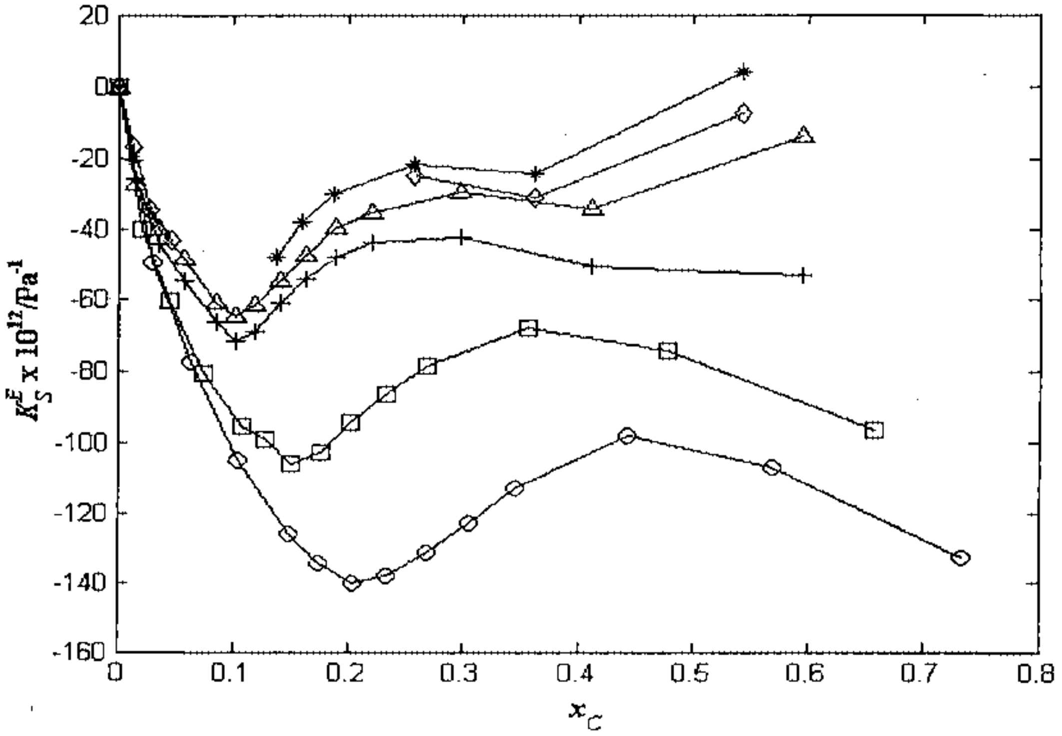

Figure 6b. Deviation in isentropic compressibility, K_S^E, of { H_2O + DO + monoalkanol } mixtures as a function of mole fraction, x_C, of monoalkanols. Methanol (o), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (•)

CHAPTER V

Solute-Solvent and Solute-Solute Interactions of Resorcinol in Mixed 1,4-Dioxane-Water Systems at Different Temperatures*

5.1. Introduction

Studies on densities, viscosities, and ultrasonic speeds of electrolyte solutions are of great use in characterizing the structure and properties of solutions. Various types of interactions exist between the ions in solutions, and these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions provide a better understanding of the nature of the solute and solvent, i.e., whether the solute modifies or distorts the structure of the solvent. 1,4-dioxane and its aqueous mixtures are very important solvents that are widely used in various industries. They figure prominently in the high-energy battery technology and have also found application in organic synthesis as manifested from the physico-chemical studies in these media.[1-8] Several workers have reported volumetric, viscometric, and ultrasonic studies of this compound in aqueous solutions,[9-13] but such studies in pure 1,4-dioxane and its aqueous mixtures are still scarce. Henceforth, in this chapter we report the densities, viscosities and ultrasonic speeds of resorcinol in 1,4-dioxane + water mixtures and in pure 1,4-dioxane at 303.15, 313.15 and 323.15 K. Apparent molar volumes (V_ϕ) and viscosity B - coefficients were obtained from these experimental data.

5.2. Experimental Section

5.2.1. Chemicals

1,4-dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 hours, and distilled over lithium aluminium hydride ($LiAlH_4$) as described earlier.[1] Resorcinol (SD fine chemicals, A. R. grade) was purified by reported procedure,[14] and the compound was dried and stored in a vacuum desiccator. Freshly distilled conductivity water was used.

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5.2.2. Measurements

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 303.15, 313.15, 323.15 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 absolute temperature was determined by a calibrated platinum resistant thermometer and 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. An average of triplicate measurements was taken into account. The total uncertainty of density is $\pm 1.0 \times 10^{-5}$ g.cm^{-3} and of the temperature is 0.01 K. Details have been described earlier.[15, 5, 16]

The viscosities were measured by means of a suspended-level Ubbelohde[17] viscometer at the desired temperature (uncertainty of ± 0.01 K). The precision of the viscosity measurement was ± 0.003 mPa.s. Details have been described earlier.[15, 5, 16]

Sound speeds were determined with an uncertainty of 0.3 % using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 2 MHz which was calibrated with water, methanol and benzene at each temperature, as described in detail elsewhere.[18, 19] The experimental values of densities (ρ_0) and viscosities (η_0) of pure 1,4-dioxane and 1,4-dioxane + water mixtures at 303.15, 313.15 and 323.15 K are reported in Table 1. The various salt solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished[20] using density values.

The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

5.3. Results and Discussion

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation:

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

where M is the molar mass of the solute, c is the molarity of the solution, ρ_0 and ρ are the densities of the solvent/solvent mixtures and solution, respectively.

The limiting apparent molar volumes (V_ϕ^0) were calculated using a least-squares treatment to the plots of V_ϕ versus $\sqrt{c}$ using the following Masson equation: [21]

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_V^* is the experimental slope. The plots of V_ϕ against square root of molar concentration ($\sqrt{c}$) were found to be linear with negative slopes. The values of V_ϕ^0 and S_V^* along with the standard errors are reported in Table 3.

As the investigated systems are characterized by hydrogen bonds, 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, V_ϕ^0 can be used and Table 3 shows that the V_ϕ^0 values are positive and increase with a rise in temperature and decrease with an increase in the amount of 1,4-dioxane in the mixtures. This indicates the presence of strong solute -solvent interactions, and these interactions are strengthened with a rise in temperature and weakened with an increase in the amount of 1,4-dioxane in the mixed solvent under investigation, suggesting larger electrostriction at higher temperature and lower amount of 1,4-dioxane in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous DMF[22] and aqueous THF.[1]

It is evident from Table 3 that the S_V^* values are negative for all temperatures for aqueous mixtures of 1,4-dioxane, but positive for pure 1,4-dioxane. Since S_V^* is a measure of solute-solute interactions, the results indicate the presence of weak solute- solute interactions. These interactions, however, decrease with a rise in temperature, which is attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of solute-solute interactions.[7] The S_V^* values increase with an increase in the amount of 1,4-dioxane in the mixture which results in a decrease in solvation of ions, i.e., more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the addition of 1,4-dioxane to the mixture.

The variation of V_ϕ^0 with temperature of resorcinol in solvent mixtures follows the polynomial,

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{3}$$

over the temperature range under investigation, where T is the temperature in Kelvin.

Values of coefficients of the above equation for resorcinol for compositions of 1,4-dioxane + water mixtures are reported in Table 4.

From the values of coefficients the following equations are obtained:

<u>10 mass% 1,4-dioxane + Water mixture</u>

$$V_\phi^0 = -1123.39/\text{cm}^3.\text{mol}^{-1} + 7.23T/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-1} - 0.010T^2/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-2} \tag{4}$$

<u>20 mass% 1,4-dioxane + Water mixture</u>

$$V_\phi^0 = -74.86/\text{cm}^3.\text{mol}^{-1} + 1.02T/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-1} - 0.001T^2/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-2} \tag{5}$$

<u>30 mass% 1,4-dioxane + Water mixture</u>

$$V_\phi^0 = -216.27/\text{cm}^3.\text{mol}^{-1} + 1.89T/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-1} - 0.002T^2/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-2} \tag{6}$$

<u>Pure 1,4-dioxane</u>

$$V_\phi^0 = -500.30/\text{cm}^3.\text{mol}^{-1} + 3.30T/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-1} - 0.005T^2/\text{cm}^3.\text{mol}^{-1}.\text{K}^{-2} \tag{7}$$

The apparent molar expansibilities (Φ_E^0) can be obtained by the following equation:

$$\Phi_E^0 = (\delta V_\phi^0 / \delta T)_P = a_1 + a_2 T \tag{8}$$

The values of Φ_E^0 of the studied compounds at 303.15, 313.15, and 323.15 K are determined and reported in Table 5.

It is found from Table 5 that the values of Φ_E^0 decrease with a rise in temperature as well as with an increase in the amount of 1,4-dioxane in the mixture, which can be ascribed to the absence of caging or packing effects.[23]

During the past few years it has been emphasized by different workers have suggested that S_V^* is not the sole criterion for determining the structure-making or breaking nature of any solute. Hepler[24] developed a technique of examining the sign of $(\delta V_\phi^0/\delta T)_P$ for the solute in terms of long-range structure-making and breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$(\delta C_P/\delta P)_T = -(\delta^2 V_\phi^0/\delta T^2)_P \tag{9}$$

On the basis of this expression, it has been deduced that the structure-making solutes should have positive values, whereas structure-breaking solutes negative values. In our present investigation, it is evident from Table 5 that $(\delta^2 V_\phi^0/\delta T^2)_P$ values are negative for resorcinol and for all 1,4-dioxane + water mixtures investigated here, suggesting thereby that resorcinol acts as a structure breaker in these solvent mixtures.

The viscosity data of solutions for resorcinol in 10, 20, 30 mass% of 1,4-dioxane + water mixtures and pure 1,4-dioxane have been analyzed using the Jones-Dole[25] equation;

$$\eta/\eta_0 = 1 + A\sqrt{c} + B \tag{10}$$

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \text{ where } \eta = (Kt - L/t)\rho$$

where η_0 and η are the viscosities of solvent/solvent mixtures and solution, respectively. K and L are the constants for a particular viscometer and t is the flow time of the solvent/solution in seconds. A and B are the constants which are estimated by a least- squares method and reported in Table 6.

A perusal of Table 6 shows that the values of the A- coefficient are negative for 10 and 20 mass% of 1, 4-dioxane and positive for 30 and 100 mass% of 1,4-dioxane for all temperatures. These results indicate the presence of weak solute-solute interactions, and these interactions increase with an increase of 1, 4-dioxane to the mixture.

It is also observed from Table 6 that the values of the B-coefficient of resorcinol in the studied solvent systems are positive thereby suggesting the presence of strong solute-solvent interactions, and these type of interactions are strengthened with a rise in temperature and weakened with increase of 1,4-dioxane in the mixture. These conclusions are in excellent agreement with those drawn from V_ϕ^0 values discussed earlier.

It has been reported in a number of studies[26, 27] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 6 that the values of B-coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of resorcinol in the solvent systems. A similar result was reported in a study[28] for the case of viscosity of some salts in propionic acid + ethanol mixtures.

The adiabatic compressibility (β) was calculated from the following relation:

$$\beta = 1/(u^2\rho) \tag{11}$$

where ρ is the solution density and u is the sound speed in the solution. The apparent molal adiabatic compressibility (Φ_K) of the liquid solutions was determined from the relation,

$$\Phi_K = M\beta/\rho_0 + 1000(\beta\rho_0 - \beta_0\rho)/(m\rho\rho_0) \tag{12}$$

The limiting apparent molal adiabatic 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 a least-squares method.

$$\Phi_K = \Phi_K^0 + S_K^\bullet\sqrt{m} \tag{13}$$

where $S_K^\bullet$ is the experimental slope.

The values of u, β, Φ_K, Φ_K^0 and $S_K^\bullet$, are reported in Table 7.

A perusal of Table 7 shows that the Φ_K^0 values increase whereas $S_K^\bullet$ values decrease with an increase of 1,4-dioxane in the mixtures for the compound studied here. Since the values of Φ_K^0 and $S_K^\bullet$ are measures of the solute-solvent and solute-solute interactions, respectively, the results are in good agreement with those drawn from the conclusion based on the values of V_ϕ^0 and S_V^* explained here earlier. The same result was obtained by us in studies[29] on the sound speeds of some salts in different tetrahydrofuran (THF) + water mixtures.

5.4. Conclusion

In summary, resorcinol seemed to act as a structure breaker in pure and aqueous 1,4-dioxane mixtures. Also these systems were characterized by the presence of strong solute-solvent and weak solute-solute interactions. However, more extensive studies are required to have a better say in this regard.

References

[1] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1247.

[2] C. G. Janz, R. P. T Tomkins, *Non-aqueous Electrolytes Handbook,* Academic Press, New York, Vol. 2, (1973).

[3] R. Jasinki, *High Energy Batteries,* Plenum Press, New York, (1967).

[4] M. N. Roy, J. Teach.and Res., 7 (2000) 17.

[5] M. N. Roy, D. K. Hazra, Indian J. Chem. Technol., 1 (1994) 93.

[6] A. Sacco, M. D. Monika, A. D. Giglio, *J.* Chem. Soc. Faraday Trans I., 79 (1983) 2631.

[7] F. J. Millero, *Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, New York, (1972).

[8] M. L. Parmar, V. N. Rao, S. K. Bhardwaj, J. Indian Chem. Soc., 67 (1990) 591.

[9] K. Masayuki, N. Kastutoshi, J. Chem. Eng. Data., 40 (1995) 935.

[10] T. V. Chalikian, A. P. Sarvasyan, K. J. Breslauer, J. Phys. Chem., 97 (1993) 1301.

[11] T. S. Banipal, P. Kapoor, J. Indian Chem. Soc., 76 (1999) 341.

[12] D. P. Kharakoz, Biophys. Chem., 34 (1989) 115.

[13] M. N. Roy, D. Nandi, D. K. Hazra, J. Indian Chem. Soc., 70 (1993) 1123.

[14] P. Franzosini, F. W. Falgar, J. Chem. Thermodyn., 16 (1984) 81.

[15] P. S. Nikam, M. Hosan, J. Chem. Eng. Data., 33 (1988) 165.

[16] R. D. Peralta, R. Infante, G. Cortez, G. Cadenas, J. Wisniak, Int. J. Thermophys., 24 (2003) 1061.

[17] J. R. Suindels, T. B. Goodfray, J. Res. Natd. Bur. Stand., 48 (1952) 1.

[18] K. Tamura, K. Ohomura, S.Murakami, J. Chem. Thermodyn., 15 (1983) 859.

[19] M. N. Roy, A. Jha, A. Choudhury, J. Indian Chem. Soc., 80 (2003) 1.

[20] D. P. Shoemaker, C. W. S. Garland, *Experiments in Physical Chemistry*, McGraw Hill, New York, pp.131, (1967).

[21] D. O. Masson, Phil. Mag., 8 (1929) 218.

[22] E. Garland-Paneda, C. Yanes, J. J. Calventa, J. Chem. Soc. Faraday Trans., 94 (1994) 573.

[23] P. R. Misra, B. Das, Indian J. Chem., 16 (1978) 348.

[24] L. G. Hepler, Can. J. Chem., 47 (1969) 4617.

[25] G. Jones, M. Dole, J. Am. Chem. Soc., 51 (1929) 2950.

[26] R. Gopal, M. A. Siddique, J. Phy. Chem., 72 (1969) 1814.

[27] N. Saha, B. Das, J. Chem. Eng. Data., 42 (1997) 277.

[28] M. L. Parmer, M. K. Chouhan, Indian J. Chem., 34A (1995) 434.

[29] M. N. Roy, D. K. Hazra, N. B. Univ. Rev. (Sci. and Technol), 8 (1997) 54.

[30] S. Martin Contreras, J. Chem. Eng. Data., 46 (2001) 1149.

[31] A. Choudhury, A. Sinha, M. N. Roy, J. Teach. Res. Chem, 11 (2004) 12.

Table 1.

Physical Properties of Pure 1,4-Dioxane and 1,4-Dioxane + Water Mixtures at Different Temperatures

Composition of 1,4-dioxane (Mass%)	**ρ_0 /g.cm^{-3}**						**η_0 /mPa.s**					
	303.15 K		**313.15 K**		**323.15 K**		**303.15 K**		**313.15 K**		**323.15 K**	
	Expt.	**Lit.**	**Expt.**	**Lit.**	**Expt.**	**Lit.**	**Expt.**	**Lit.**	**Expt.**	**Lit.**	**Expt.**	**Lit.**
10	1.0058	-	1.0068	-	0.9973	-	1.0321	-	1.0014	-	0.6895	-
20	1.0148	-	1.0100	-	1.0033	-	1.2014	-	1.0186	-	0.8787	-
30	1.0202	-	1.0162	-	1.0103	-	1.3977	-	1.2493	-	1.0755	-
100 (Pure)	1.0199	1.0222 [30]	1.0144	1.0143 [31]	1.0027	1.0032 [31]	1.0886	1.0937 [30]	0.9785	0.9783 [31]	0.8441	0.8443 [31]

Table 2.
Concentration (c), Density (ρ), Viscosity (η), Apparent Molar Volume (V_ϕ), and $(\eta/\eta_0-1)/\sqrt{c}$ of Resorcinol in Pure 1,4-Dioxane and 1,4-Dioxane + Water Mixture at Different Temperatures.

c /mol. dm^{-3}	ρ /g.cm^{-3}	η /mPa.s	V_ϕ /cm^3.mol^{-1}	$(\eta/\eta_0-1)/\sqrt{c}$
10 mass% of 1,4-dioxane + Water				
T = 303.15 K				
0.00696	1.00769	1.03758	115.98421	-0.14432
0.04872	1.00758	1.02551	112.58358	-0.10662
0.09048	1.00824	1.03581	103.84121	-0.04564
0.13224	1.00912	1.05069	98.94112	0.00123
0.17400	1.01037	1.07889	94.29936	0.06542
0.21575	1.01186	1.10903	90.34211	0.12054
T = 313.15 K				
0.00694	1.00125	0.94077	123.54652	-1.00021
0.04851	1.00093	0.83336	118.51121	-0.85342
0.09014	1.00109	0.82462	112.78923	-0.65441
0.13168	1.00186	0.83508	106.02315	-0.51338
0.17331	1.00302	0.86198	100.31120	-0.38453
0.21502	1.00501	0.92907	92.90543	-0.20423
T = 323.15 K				
0.00689	0.99751	0.68339	130.02543	-0.72798
0.04818	0.99706	0.69393	122.54321	-0.20922
0.08946	0.99722	0.76091	115.12037	0.15437
0.13074	0.99787	0.89312	108.67535	0.63042
0.17242	0.99911	1.07930	101.87342	1.16540
20 mass% of 1,4-dioxane + Water				
T = 303.15 K				
0.00712	1.01637	1.22046	114.98541	-0.05432
0.04981	1.01629	1.21797	110.88871	-0.02961
0.09251	1.01647	1.22654	107.78321	0.00124
0.13519	1.01717	1.23913	102.87120	0.02897
0.17789	1.01868	1.25629	95.80971	0.05843
0.22059	1.02075	1.26989	89.00087	0.07609
T = 313.15 K				
0.00707	1.00995	0.94893	118.05435	0.00113
0.04951	1.00981	0.96814	112.98431	0.09142
0.09186	1.01005	0.99395	108.56321	0.15689
0.13432	1.01065	1.02309	104.28711	0.21354
0.17679	1.01185	1.06479	98.73584	0.29065
0.21967	1.01416	1.11135	90.33200	0.36543
T = 323.15 K				
0.00703	1.00354	0.85946	121.00652	-0.51652
0.04932	1.00342	0.81889	113.89012	-0.39836
0.09122	1.00359	0.81979	109.99872	-0.28966
0.13396	1.00412	0.85545	106.00067	-0.13055
0.17589	1.00541	0.90459	99.57092	0.01651
0.21793	1.00749	0.94864	91.99642	0.11985
30 mass% of 1,4-dioxane + Water				
T = 303.15 K				
0.00702	1.02019	1.43758	103.65571	0.10065

Contd...

0.04913	1.02078	1.46349	95.56437	0.12001
0.91246	1.02177	1.48054	90.58478	0.12766
0.13336	1.02291	1.49722	87.67532	0.13765
0.17548	1.02415	1.51775	85.62294	0.15437
0.21758	1.02666	1.53258	78.65435	0.16094
		T = 313.15 K		
0.00698	1.01628	1.28547	105.09876	0.10154
0.04895	1.01679	1.30914	97.68765	0.12226
0.09097	1.01769	1.32596	92.89043	0.13343
0.13284	1.01888	1.34016	88.98760	0.14098
0.17481	1.02024	1.36022	85.94978	0.16054
0.21672	1.02258	1.37875	79.65439	0.17542
		T = 323.15 K		
0.00693	1.01063	1.10758	106.51690	0.10171
0.04859	1.01107	1.12788	99.60034	0.12224
0.09025	1.011886	1.14450	95.00654	0.14007
0.13184	1.013185	1.16071	89.65432	0.15654
0.17359	1.01431	1.17628	87.89543	0.17045
0.21493	1.01669	1.18991	80.99765	0.17995
		Pure 1,4-dioxane		
		T = 303.15 K		
0.00694	1.02031	1.11085	47.45322	0.25399
0.04850	1.02259	1.15145	53.00011	0.26554
0.09025	1.02452	1.17821	57.55432	0.27654
0.13189	1.02608	1.20005	61.87762	0.28405
0.17356	1.02784	1.22222	62.98762	0.29654
0.21521	1.02921	1.24614	65.44322	0.31369
		T = 313.15 K		
0.00691	1.01468	0.99899	49.49872	0.25445
0.04800	1.01689	1.03616	54.76542	0.26999
0.08939	1.01863	1.05918	60.47652	0.27654
0.13078	1.02019	1.08088	63.87651	0.28998
0.17206	1.02187	1.10407	64.99980	0.30996
0.21337	1.02334	1.12243	66.62787	0.31898
		T = 323.15 K		
0.00682	1.00365	0.86213	50.65425	0.25506
0.04752	1.00581	0.89419	55.97865	0.27087
0.08839	1.00749	0.91465	61.88796	0.28007
0.12929	1.00908	0.93471	64.78313	0.29765
0.17021	1.01075	0.95499	65.81603	0.31765
0.21105	1.01219	0.97384	67.53009	0.33387

Table 3.

Limiting Apparent Molar Volume (V_ϕ^0) and Experimental Slope (S_V^*) for Resorcinol in Different 1,4-Dioxane + Water Mixtures at Different Temperatures. Standard errors are given in parenthesis.

Composition of 1,4-dioxane (Mass%)	**V_ϕ^0 / cm^3.mol^{-1}**			**S_V^* / cm^2.dm$^{1/2}$.mol$^{-3/2}$**		
	303.15 K	**313.15 K**	**323.15 K**	**303.15 K**	**313.15 K**	**323.15 K**
10	124.5 (± 0.05)	133.5 (± 0.02)	140.5 (± 0.04)	-70.8 (± 0.02)	-79.6 (± 0.01)	-92.2 (± 0.04)
20	123.8 (± 0.01)	126.6 (± 0.03)	129.1 (± 0.02)	-64.8 (± 0.04)	-67.8 (± 0.03)	-71.2 (± 0.02)
30	109.1 (± 0.01)	111.3 (± 0.05)	113.0 (± 0.02)	-60.6 (± 0.03)	-63.4 (± 0.01)	-64.1 (± 0.02)
100	43.1 (± 0.01)	45.5 (± 0.02)	46.8 (± 0.01)	48.5 (± 0.02)	47.5 (± 0.04)	46.7 (± 0.01)

Table 4.

Values of Various Coefficients for Resorcinol in Different 1,4-Dioxane + Water mixtures.

Composition of 1,4-dioxane (Mass%)	a_0 / **cm^3.mol^{-1}**	a_1 / **cm^3.mol^{-1}. K^{-1}**	a_2 / **cm^3.mol^{-1}.K^{-2}**
10	-1123.39	7.23	-0.010
20	-74.86	1.02	-0.001
30	-216.27	1.89	-0.002
100	-500.30	3.30	-0.005

Table 5.

Limiting Apparent Molar Expansibilities (Φ_K^0) for Resorcinol in Various 1,4-Dioxane + Water Mixtures at Different Temperatures.

Composition of 1,4-dioxane (Mass%)	Φ_K^0 / **cm^3.mol^{-1}.K^{-1}**			$(\delta \Phi_E^0/\delta T)_P$
	303.15 K	**313.15 K**	**323.15 K**	
10	1.004	0.798	0.593	Negative
20	0.292	0.268	0.244	Negative
30	0.248	0.194	0.140	Negative
100(Pure)	0.287	0.187	0.088	Negative

Table 6.

Values of *A* and *B* Parameters for Resorcinol in Different 1,4-dioxane + Water Mixtures at Different Temperatures. Standard errors are given in parenthesis.

Composition of 1,4-dioxane (Mass%)	***A* / cm$^{3/2}$.mol$^{-1/2}$**			***B* / cm^3.mol^{-1}**		
	303.15 K	**313.15 K**	**323.15 K**	**303.15 K**	**313.15 K**	**323.15 K**
10	-0.23 (± 0.01)	-1.24 (± 0.02)	-1.41 (± 0.01)	0.70 (± 0.01)	2.08 (± 0.02)	5.95 (± 0.02)
20	-0.09 (± 0.01)	-0.10 (± 0.02)	-0.73 (± 0.02)	0.35 (± 0.01)	0.92 (± 0.02)	1.70 (± 0.01)
30	0.08 (± 0.01)	0.08 (± 0.01)	0.07 (± 0.02)	0.16 (± 0.01)	0.18 (± 0.02)	0.21 (± 0.02)
100	0.24 (± 0.02)	0.23 (± 0.01)	0.23 (± 0.01)	0.15 (± 0.02)	0.17 (± 0.02)	0.21 (± 0.01)

Table 7.

Molality (m), Density (ρ), Sound Speed (u), Adiabatic Compressibility (β), Apparent Molal Adiabatic Compressibility (Φ_K), Limiting Apparent Adiabatic Compressibility (Φ_K^0), and Experimental Slope (S_K^*) of Resorcinol in Different 1,4-Dioxane + Water Mixtures at 303.15 K. Standard errors are given in parenthesis.

Composition of 1,4-dioxane (Mass%)	m **/ mol.kg^{-1}**	ρ **x 10^{-3} / kg.m^{-3}**	u **/ m.s^{-1}**	β **x 10^{10} / Pa^{-1}**	Φ_K **x 10^{10} / m^3.mol^{-1}.Pa^{-1}**	Φ_K^0 **x 10^{10} / m^3.mol^{-1}.Pa^{-1}**	S_K^* **x 10^{10} / m^3.mol$^{-3/2}$.Pa^{-1}.kg$^{1/2}$**
10	0.00691	1.00769	1576.73	3.99168	1.050	1.31 (± 0.02)	-2.02 (± 0.04)
	0.04861	1.00758	1572.70	4.01262	0.963		
	0.09064	1.00824	1570.36	4.02194	0.794		
	0.13296	1.00912	1573.30	4.00343	0.515		
	0.17555	1.01037	1573.09	3.99957	0.446		
	0.21835	1.01186	1575.75	3.98003	0.327		

Contd...

20	0.00701	1.01637	1590.39	3.88993	1.440	1.81 (± 0.03)	-3.58 (± 0.05)
	0.04928	1.01629	1584.30	3.92019	1.180		
	0.09193	1.01647	1586.07	3.91075	0.720		
	0.13488	1.01717	1590.98	3.88397	0.408		
	0.17805	1.01868	1593.76	3.86472	0.271		
	0.22137	1.02075	1596.57	3.84330	0.168		
30	0.00687	1.02019	1590.07	3.87045	2.850	3.47 (± 0.02)	-7.63 (± 0.03)
	0.04839	1.02078	1580.33	3.92260	1.910		
	0.09019	1.02178	1583.03	3.90540	0.991		
	0.13227	1.02291	1584.14	3.89559	0.704		
	0.17463	1.02415	1595.59	3.83525	0.265		
	0.21699	1.02666	1605.11	3.78063	0.001		

CHAPTER VI

Electrical Conductances of Some Ammonium and Tetraalkylammonium Halides in Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K*

6.1. Introduction

Studies on ionic solvation of ammonium and tetraalkylammonium salts in solvents of low permitivity are very few. Such studies have major importance because of their applications in modern technology.[1]

1, 4-dioxane and its aqueous binary mixtures are very important solvents widely used in various industries. It is a good industrial solvent and figures prominantly in the high-energy battery technology[1] and has also found its application in the organic syntheses as manifested from the physico-chemical studies in these media.[2-5] With a system of varying dielectric constant, in the mixed solvents there is scope of variation of solvent-solvent interaction since composition of the solvents in a binary mixture is varied. Thus, studies in mixed solvents may provide information regarding both the specific and non-specific solvent effects on the ion-association phenomena.

In the present chapter, an attempt has been made to ascertain the complete nature of ion-solvent, solvent-solvent interactions of ammonium and tetraalkylammonium halides measured in different mass% of 1,4-dioxane + water mixtures (20%, 40%, 60% and 80%) at 298.15 K. The limiting molar conductivity (Λ_0), the association constant (K_A) and association distance (R) in the solvent mixtures have been evaluated using Fuoss conductance equation (1978).

6.2. Experimental Section

6.2.1. Chemicals

1,4-dioxane (Merck, India) was kept several days over KOH, refluxed for 24 hours and distilled over $LiAlH_4$, as described earlier.[2] The purified solvent has a density of 1.03052 g.cm^{-3} and a co-efficient of viscosity of 1.20011 cp at 298.15 K compared well with literature values.[6]

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The salts Me_4NCl, Et_4NBr, Pr_4NBr, Bu_4NBr and Bu_4NI of A.R grade (Aldrich) were purified by dissolving in mixed alcohol medium and re-crystallized from solvent ether medium. After filtration, the salts were dried in an oven for few hours. The salts NH_4F, NH_4Br and NH_4Cl were dried at about 80-100°C in a vacuum oven for 48 hours before use.[7]

6.2.2. Measurements

A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The values of dielectric constant (ε) were taken from the literature[6] and the densities (ρ_0) and viscosities (η_0) of the solvent mixtures were measured by an Ostwald-Sprengel type pycnometer and suspended-level Ubbelohde type viscometer respectively, as described in detail earlier.[2] The conductance measurements were carried out in a systronic 306 conductivity bridge (accuracy ± 0.1%) using a dip-type immersion conductivity cell, CD-10 having cell constant 1.0 ± 10%. Measurements were made in a water bath maintained within 298.15 ± 0.01 K.

6.3. Results and Discussion

The solvent properties of the different aqueous binary mixtures of 1,4-dioxane are given in Table 1, where ε is the dielectric constant, ρ_0 the density (g.cm^{-3}), η_0 the viscosity (cp), x_1 the mole fraction of 1,4-dioxane. Molar conductances (Λ) of the electrolyte solutions as a function of molar concentration (c) are given in Table 2 for the different solvent mixtures at 298.15 K.

The analysis of conductance data in terms of limiting molar conductance, Λ_0 and ion-association constant, K_A of the electrolytes have been carried out iteratively according to Shedlovsky equation using least square treatment for the reasons described earlier.[8] Shedlovsky method involves the linear extrapolation using equation,[9]

$$1/\Lambda S(z) = 1/\Lambda_0 + [K_A/\Lambda_0^2]c\Lambda f_\pm^2 S(z) \qquad (1)$$

where Λ is the equivalent conductance at a concentration c (mol.lit^{-1}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are given by,

$$S(z) = [(z/2) + \sqrt{(1 + (z/2)^2)}]^2, z = [(\alpha \Lambda_0 + \beta)/\Lambda_0^{3/2}](c\Lambda)^{1/2}$$

$$\alpha = 0.8204 \times 10^6/(\varepsilon T)^{3/2}; \beta = 82.0501/\eta(\varepsilon T)^{1/2} \quad (2)$$

where ε is the dielectric constant and η is the viscosity of the medium. The degree of dissociation (τ) is related to $S(z)$ by,

$$\tau = \Lambda S(z)/\Lambda_0$$

$f_{\pm}$, the mean activity co-efficient of the free ions was calculated by the following equation-

$$-\log f_{\pm} = A(\tau c)^{1/2}/[1 + BR(\tau c)^{1/2}] \quad (3)$$

where $A = 1.8246 \times 10^6/(\varepsilon T)^{3/2}$; $B = 0.5029 \times 10^{10}/(\varepsilon T)^{1/2}$ and R = association distance.

The initial Λ_0 values for the iteration procedure were, thus obtained from Shedlovsky extrapolation of the data.[10]

The conductance data was analyzed using Fuoss conductance equation,[11] which has been programmed in a computer. So with a given set of conductivity values (c_j, Λ_j; j=1,...., n), three adjustable parameters, i.e. Λ_j, K_A and R were derived from the Fuoss equation. Here R is the association distance, i.e. the maximum centre-to-centre distance between the ions in the solvent separated ion-pairs. There is no precise method for determining the R-value[12] but in order to treat the data in our system, R-value is assumed to be, $R = a + d$; where a is the sum of the crystallographic radii of ions, which varies from 2 to 7Å and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d(Å) is given by,[11]

$$d = 1.183(M/\rho_0)^{1/3} \quad (4)$$

where M is the molecular weight and ρ_0 is the density of the solvent. For mixed solvents, M is replaced by the mole fraction average molecular weight (M_{AV}), which is given by,

$$M_{AV} = M_1 M_2/[W_1 M_2 + W_2 M_1] \quad (5)$$

where W_1 is the weight fraction of the first component of molecular weight M_1 and W_2 is the weight fraction of the second component of molecular weight M_2. Though, this is an over simplification which ignores possible selective solvation, it at least provides a self-consistent way to obtain an acceptable value for the parameters when a broad range of R-values fit the data.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = p[\Lambda_0(1+R_X)+E_L] \tag{6}$$

$$p = 1-\alpha(1-\gamma) \tag{7}$$

$$\gamma = 1-K_A c\gamma^2 f^2 \tag{8}$$

$$-\ln f = \beta\kappa/2(1+K_R) \tag{9}$$

$$\beta = e^2/\varepsilon K_B T \tag{10}$$

$$K_A = K_R/(1-\alpha) = K_R(1+K_S) \tag{11}$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current constant, κ^{-1} is the radius of the ionic atmosphere, ε is the relative permittivity of the solvent, e is the electric charge, K_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, β is twice the Bjerrum distance, K_R describes the formation and separation of solvent separated pairs by diffusion in and out of sphere of diameter R around cations and K_S is a constant describing the short-range process by which contact pairs forms and dissociates.

We input for the program the number of data, n; followed by dielectric constant of the solvent mixture, ε; initial Λ_0 values, T, ρ, molecular weight of the solvents along with c_j, Λ_j values where j=1, 2,....., n and an instruction to cover pre-selected range of R-values.

In practice calculations, were performed by finding the values of Λ_0 and σ, which minimized the standard deviation (σ),

$$\sigma^2 = \sum_{j=1}^{n} \frac{[\Lambda_j(calc) - \Lambda_j(obs)]^2}{(n-2)} \tag{12}$$

for a sequence of R-values and then plotting σ against R.

The best-fit R corresponds to the minimum of the σ versus R curve. First, approximate run over a fairly wide range of R-values were made to locate the minimum, and then a fine scan around the minimum was made. Thus, the corresponding Λ_0 and K_A values were noted. The Λ_0, K_A, R and Walden products ($\Lambda_0\eta_0$) for the ammonium and tetraalkylammonium halides in different aqueous binary mixtures of 1,4-dioxane were thus reported in Table 3.

The association constant, K_A recorded in Table 3 indicates that all the electrolytes are highly associated in these solvent mixtures. This is quite expected due to the low dielectric constant (2.209) of 1,4-dioxane. The most outstanding feature is that the electrolytes containing smaller cations show almost considerable amount of association. Here, values of K_A decrease as the size of the cation increases with the exception of Bu_4N^+ ion whereas Λ_0 increases. The possible explanation may be due to the larger size of the cations, which are less solvated than the smaller one. Similar results were reported earlier by some workers[13] in the conductance study of 1-ethyl-4-cyano pyridinium iodide in aqueous binary mixtures of 1,4-dioxane.

The K_A values of various tetraalkylammonium halides in these solvent mixtures follow the order:

$$Me_4N^+ > Bu_4N^+ > Et_4N^+ > Pr_4N^+$$

However, in case of ammonium halides the value of Λ_0 is enhanced by the order:

$$F^- < Cl^- < Br^-$$

This trend of variation indicates the relative actual sizes of these anions having common ammonium ion as they exist in the solution. Thus the sizes of these anions as they exist in these solutions follow the order:

$$F^- > Cl^- > Br^-$$

This shows that F^- is the most solvated and Br^- is the least solvated one in any mole fraction of 1,4-dioxane. Roy et al[14] found similar trends for many of the alkali metal halides in THF + H_2O mixtures. In case of Bu_4NI, the value of K_A is grater than that of Bu_4NBr. This may be expected owing to the larger size of I^- as compared to Br^-.

From Table 3 it is observed that K_A values are found to increase whereas Λ_0 values are found to decrease in aqueous binary mixtures of 1,4-dioxane with the increase of the mole fraction of 1,4-dioxane.

This indicates that association of ions increase with the addition of 1,4-dioxane to the mixture rendering to the decrease of the mobility of ions in the mixture. The significantly large values of K_A and exothermic ion-pair formation in the solvent mixtures indicates the presence of specific short-range interaction within the ion-pair.

The variation of Walden product, $\Lambda_0\eta_0$ with x_1, the mole fraction of 1,4-dioxane for the electrolytes studied at 298.15 K are shown in figure 1. The values of Walden product pass through a maximum at about x_1 = 0.11996 mole fraction of 1,4-dioxane whereas the maximum viscosity of the aqueous binary mixtures at 298.15 K is observed at about x_1 = 0.23472 mole fraction of 1,4-dioxane. It is known that the variation of Walden product indicates the change of solvation.[12] The increase of Walden products indicates weak solvation of ions, which attains a maximum value at a particular solvent composition (x_1 = 0.11996). Such results have been interpreted in terms of microheterogeneity[15] in the mixtures.

On water rich side, there exists a region where the water structure remains more or less intact as the 1,4-dioxane molecules are added into the cavities in this structure. The cluster of water molecule has lower ability to donate a hydrogen atom to the solvation of ions. This may cause hydrophobic dehydration of cations[13] or may reduce the ability of hydrophobic ions to promote the structure in water rich region resulting in excess mobility, which in turn results an increase in Walden products to attain a maximum. As the percentage of 1,4-dioxane in the mixture increases the self-associated structure gradually breaks at an increased mole fraction of 1,4-dioxane and there is preferential solvation[16] due to specific ion-solvent interaction leading to a decrease of Walden product. However, this decrease in large part may be due to the Zwanzig[17] solvent relaxation effect also.

6.4. Conclusion

The study revealed that all the electrolytes under investigation are highly associated in these solvent mixtures. Smaller cations are relatively more solvated that the larger ones. The same trend was observed for the anions too. Also the variation of Walden product indicated preferential salvation at higher mole fraction of 1,4-dioxane justifying specific ion-solvent interactions in these media.

References

[1] R. Jasinki, *High Energy Batteries*. Plenum Press, New York, USA, (1967).

[2] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1247.

[3] M. N. Roy, *J. Teach. Res.*, 7 (2002) 17.

[4] M. N. Roy, D. K. Hazra, Indian. J. Chem. Technol., 1 (1994) 93.

[5] C. G. Janz, *Non-aqueous Electrolytes Handbook*, Vol. 2, Academic Press, New York, USA, (1973).

[6] A. K. Covington, T. Dickinson, (Eds.), *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, USA, (1973).

[7] D. D. Perrin, W. L. F. Armarego, (Eds.), *Purification of Laboratory Chemicals*. Pergamon, Great Britain. 3rd ed., (1988).

[8] D. S. Gill, M. S. Chauhan, Z. Phys. Chem. Neue Folge., 140 (1984)139.

[9] G. C. Bag, N. M. Singh, N. R. Singh, J. Ind. Chem. Soc., 77 (2000)146.

[10] M. N. Roy, D. Nandi, D. K. Hazra, J. Indian. Chem. Soc., 70 (1993) 305.

[11] R. M. Fuoss, J. Phys. Chem., 82 (1978) 2427.

[12] H. Doe, H. Ohe, H. Matoba, A. Ichimura, T. Kitagawa, Bull. Chem. Soc. Jpn. 63 (1990) 2785.

[13] A. Mukhopadhyay, M. Pal, Indian. J. Chem., 41A (2002) 1120.

[14] M. N. Roy, D. Nandi, D. K. Hazra, J. Indian. Chem. Soc., 70 (1993) 121.

[15] Y. Marcus, Y. Migron, J. Phys. Chem. 95 (1991) 400.

[16] S. Taniewska-Osinska, A. Piekarska, A. Bald, A. Szejgis, J. Chem. Soc., Faraday Trans I., 85 (1989) 3709.

[17] B. Das, D. K. Hazra, J. Phys. Chem., 99 (1995) 269.

Table 1.

Physical properties of 1, 4-dioxane + water mixtures at 298.15 K.

x_1	ε	ρ_0/g.cm^{-3}		η_0/ cp	
		Expt.	Lit.	Expt.	Lit.
0	78.3	0.99707	0.9971[6]	0.89041	0.8903 [6]
0.04863	63.5	1.01612	1.0143 [6]	1.29671	1.30 [6]
0.11996	44.4	1.03127	1.0284 [6]	1.69701	1.74 [6]
0.23472	27.5	1.04011	1.0360 [6]	1.98712	1.98 [6]
0.44991	12.1	1.04053	1.0350 [6]	1.78589	1.73 [6]
1	2.209	1.03052	1.0269 [6]	1.20011	1.196 [6]

Table 2.
Molar Conductances (Λ) and Corresponding Molarities (c) of Some Tetraalkylammonium Halides and Ammonium Halides in Different Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K.

$c \times 10^4$ /mol.lit^{-1}	**Λ /S.cm^2.mol^{-1}**	**$c \times 10^4$ /mol.lit^{-1}**	**Λ /S.cm^2.mol^{-1}**	**$c \times 10^4$ /mol.lit^{-1}**	**Λ /S.cm^2.mol^{-1}**	**$c \times 10^4$ /mol.lit^{-1}**	**Λ /S.cm^2.mol^{-1}**
$x_1 = 0.04863$							
NH_4F		NH_4Cl		NH_4Br		Me_4NCl	
42.7	49.26	48.1	71.93	48.5	81.44	46.2	55.63
55.9	48.65	61.9	71.24	62.4	80.77	56.5	54.69
68.6	48.00	74.8	70.59	75.4	80.24	65.2	54.45
80.8	47.82	86.9	70.20	87.6	79.79	72.6	53.86
92.6	47.55	98.2	69.55	99.0	79.19	79.0	53.67
104.0	47.31	108.8	69.39	109.7	78.85	84.6	53.31
125.7	46.61	118.8	69.02	119.8	78.71	89.6	53.01
136.0	46.40	128.2	68.49	129.3	78.50	94.0	52.66
Et_4NBr		Pr_4NBr		Bu_4NBr		Bu_4NI	
44.8	66.96	45.6	78.24	51.7	87.62	47.1	60.65
57.6	65.97	54.2	77.47	67.8	86.92	61.6	59.64
69.6	65.09	69.1	76.52	75.2	86.51	66.1	59.33
80.8	64.36	75.6	74.04	82.1	86.25	74.7	58.78
91.3	63.86	81.6	75.76	88.6	86.07	78.8	58.53
101.2	63.34	92.2	75.28	94.8	85.91	82.8	58.48
110.5	62.81	96.9	74.99	97.8	85.82	97.6	57.62
119.3	62.45	101.3	74.91	100.7	85.67	104.4	57.24
$x_1 = 0.11996$							
NH_4F		NH_4Cl		NH_4Br		Me_4NCl	
25.6	45.31	22.5	59.11	20.2	72.65	17.8	47.49
34.8	43.97	25.8	58.02	26.0	71.08	21.2	46.45

Contd...

38.4	43.75	33.8	57.24	29.8	70.89	26.6	45.63
43.7	43.25	38.5	57.15	39.1	69.84	37.0	44.35
55.5	42.34	48.9	55.51	48.1	68.67	43.9	43.34
71.4	41.18	56.1	55.18	73.6	65.31	48.7	42.69
79.0	40.76	69.7	53.68	89.3	63.92	57.8	41.79
93.4	39.83	82.4	52.80	104.2	62.66	66.4	41.04
Et_4NBr		Pr_4NBr		Bu_4NBr		Bu_4NI	
17.9	59.74	24.5	72.68	19.4	82.62	16.8	53.88
21.1	59.58	29.6	71.86	23.2	82.26	31.8	52.06
24.2	58.97	34.4	71.24	26.7	81.66	36.5	51.22
30.1	57.76	36.7	70.76	28.4	81.37	45.3	50.24
32.9	57.34	43.1	70.10	35.8	80.75	49.5	49.87
35.6	56.91	50.8	69.63	37.1	80.73	53.5	49.36
43.1	55.77	54.3	69.40	38.4	80.49	61.2	48.75
47.8	55.29	57.6	69.06	40.8	80.38	68.4	48.18
x_1 = 0.23472							
NH_4F		NH_4Cl		NH_4Br		Me_4NCl	
9.7	23.09	3.7	35.07	5.4	40.37	3.7	37.45
11.4	22.81	10.9	33.39	7.2	39.58	6.1	36.52
13.1	22.44	14.5	32.76	9.0	39.33	7.8	35.82
16.3	21.90	18.1	31.99	12.6	37.62	9.4	35.55
19.3	21.45	23.3	31.33	16.2	36.98	13.5	34.74
24.7	20.69	28.4	30.99	23.2	35.78	16.4	34.34
27.1	20.48	31.8	30.50	28.3	35.69	17.8	34.18
34.6	19.94	35.2	29.83	33.4	34.73	19.2	33.94
Et_4NBr		Pr_4NBr		Bu_4NBr		Bu_4NI	
3.7	48.56	5.2	51.69	4.1	56.76	4.3	43.88
6.1	47.62	6.7	51.49	5.9	56.32	6.2	43.19

Condt...

7.1	46.97	10.3	51.08	6.4	56.22	7.1	42.94
8.8	46.14	11.2	51.00	7.4	56.02	10.5	41.76
10.3	45.87	13.9	50.81	8.4	55.93	11.3	41.48
11.8	45.59	15.2	50.68	10.3	55.45	14.1	41.13
16.1	44.50	18.8	50.56	11.1	55.38	15.4	40.88
21.3	43.74	22.1	50.39	11.9	55.24	16.6	40.75
x_1 = 0.44991							
NH_4F		NH_4Cl		NH_4Br		Me_4NCl	
1.9	2.12	0.3	5.88	0.5	5.98	0.6	23.12
3.2	1.85	0.7	5.51	0.7	5.80	0.9	22.30
3.7	1.79	1.4	5.08	1.2	5.51	1.0	21.40
4.9	1.65	1.7	4.78	1.7	5.32	1.2	20.90
6.8	1.50	2.1	4.55	2.2	5.07	1.9	18.80
7.9	1.46	2.9	4.51	2.5	4.94	2.4	17.33
9.5	1.41	3.3	4.27	3.2	4.69	2.7	17.11
9.9	1.39	3.9	4.36	3.5	4.54	2.8	16.82
Et_4NBr		Pr_4NBr		Bu_4NBr		Bu_4NI	
0.4	33.40	0.7	39.71	1.2	41.50	0.7	31.60
0.6	31.50	1.5	34.93	1.7	40.32	0.9	31.22
1.2	27.83	1.7	34.53	2.0	39.90	1.2	29.50
1.5	26.80	2.0	33.85	2.5	39.12	1.4	28.50
1.8	25.44	2.2	33.68	2.8	38.86	1.6	27.63
2.3	24.78	2.5	32.88	3.3	38.24	1.9	26.32
2.7	23.80	3.2	32.13	3.6	37.89	2.0	26.25
3.1	21.60	3.5	31.57	4.1	37.37	2.2	25.68

Table 3.
Values of Λ_0, K_A, $\Lambda_0\eta_0$, R and σ for Some Ammonium and Tetraalkylammonium Halides in Different Aqueous Binary Mixtures of 1, 4-Dioxane at 298.15 K.

x_1	Λ_0 /S.cm^2.mol^{-1}	K_A /dm^3.mol^{-1}	R /Å	$\Lambda_0\eta_0$	σ
NH_4F					
0.04863	51.53 ± 0.12	8.42	6.18	66.82	0.12
0.11996	49.36 ± 0.11	36.45	6.41	78.89	0.11
0.23472	26.27 ± 0.08	149.62	6.71	52.20	0.08
0.44991	3.14 ± 0.02	4535.07	7.21	5.61	0.02
NH_4Cl					
0.04863	75.58 ± 0.10	8.03	6.66	98.01	0.10
0.11996	63.67 ± 0.26	32.92	6.88	108.05	0.26
0.23472	37.76 ± 0.30	107.84	7.19	75.03	0.30
0.44991	6.36 ± 0.11	2500.04	7.68	11.36	0.11
NH_4Br					
0.04863	84.87 ± 0.11	5.85	6.69	110.05	0.11
0.11996	78.14 ± 0.28	33.76	7.02	132.60	0.28
0.23472	42.96 ± 0.36	100.72	7.33	85.37	0.36
0.44991	6.72 ± 0.06	2247.41	7.82	12.00	0.06
Me_4NCl					
0.04863	59.98 ± 0.12	16.78	8.65	77.78	0.12
0.11996	52.12 ± 0.15	59.64	8.67	88.45	0.15
0.23472	39.07 ± 0.16	90.51	9.17	77.64	0.16
0.44991	29.94 ± 0.28	6215.89	9.67	53.47	0.28
Et_4NBr					
0.04863	71.59 ± 0.07	14.79	9.32	92.83	0.07
0.11996	65.19 ± 0.16	47.24	9.53	110.63	0.16
0.23472	50.77 ± 0.24	94.19	9.85	100.89	0.24
0.44991	39.69 ± 0.49	5682.46	10.34	70.88	0.49
Pr_4NBr					
0.04863	82.65 ± 0.11	11.19	9.84	107.17	0.11
0.11996	77.21 ± 0.19	22.65	10.06	131.03	0.19
0.23472	53.10 ± 0.01	73.70	10.37	105.52	0.01
0.44991	44.74 ± 0.59	2253.78	10.86	79.90	0.59
Bu_4NBr					
0.04863	91.13 ± 0.06	5.56	10.26	118.17	0.06
0.11996	86.37 ± 0.11	16.39	10.48	146.57	0.11
0.23472	58.63 ± 0.01	30.94	10.79	116.50	0.01
0.44991	45.68 ± 0.08	659.09	11.28	81.58	0.08
Bu_4NI					
0.04863	65.18 ± 0.01	15.63	10.47	84.52	0.01
0.11996	57.80 ± 0.11	39.08	10.69	98.09	0.11
0.23472	46.17 ± 0.16	91.24	11.01	91.75	0.16
0.44991	40.57 ± 0.31	5107.55	11.49	72.45	0.31

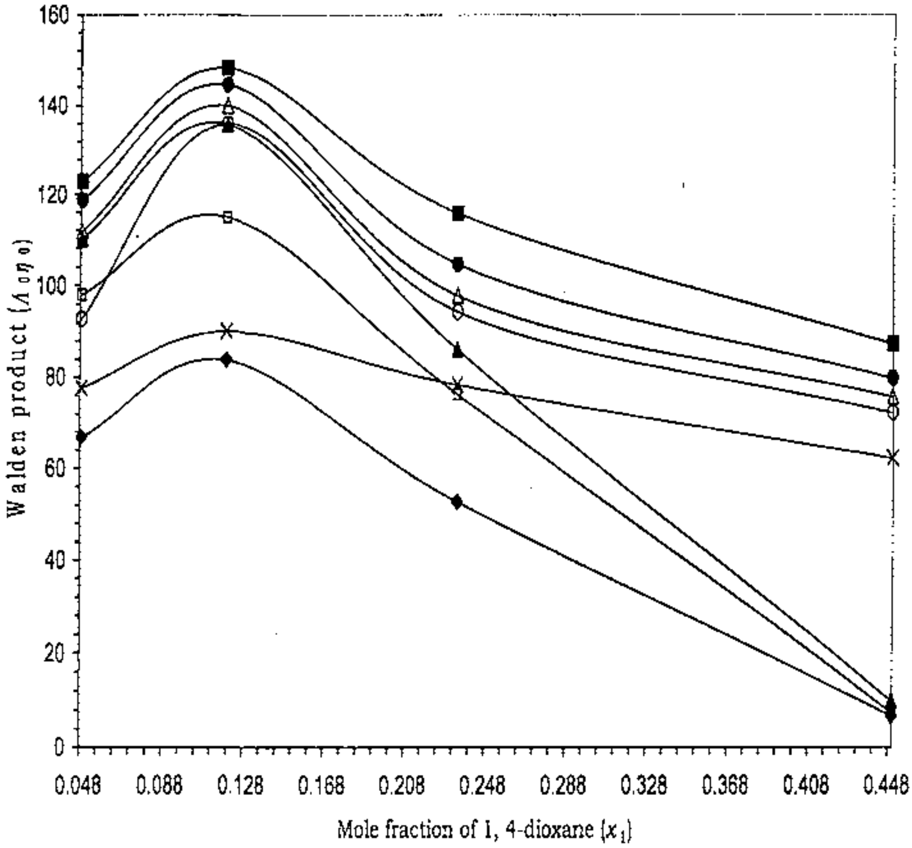

Figure 1. Plots of mole fraction of 1,4-dioxane (x_1) versus walden products ($\Lambda_0\eta_0$) for NH_4F (◆), NH_4Cl (□), NH_4Br (▲), Me_4NCl (×), Et_4NBr (O), Pr_4NBr (●), Bu_4NBr (▪) and Bu_4NI (Δ) at 298.15K

CHAPTER VII

Investigation on Viscous Antagonism of Ternary Liquid Mixtures and Its Relation to Concentration*

7.1. Introduction

Rheology is the branch of science that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products[1-9] and to establish their stability and even bioavailability- since it has been firmly established that viscosity influences drug absorption rate in the body.[10, 11]

Tetrahydrofuran (THF) is a good industrial solvent. It figures prominently in the high energy battery industry and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium.[12,13] Alcohols are very widely used in industry, including the manufacture of pharmaceuticals and cosmetic products, in enology and as an energy source. A knowledge of the physico-chemical properties of mixed solvent systems are increasingly important for their wide applications such as in chromatography, solvent extraction, in the elucidation of reaction mechanism, etc.

The present chapter quantifies the viscous antagonism established in two ternary mixtures consisting of tetrahydrofuran + methanol + benzene and isopropanol + benzene + n-hexane at 303.15, 313.15 and 323.15 K over the entire composition range. The experimental data have been analyzed using the equation developed by Kaletune-Gencer and Peleg. Since these systems exhibit volume contraction, an analysis has also been made of the density of the mixtures at various temperatures.

7.2. Experimental Section

7.2.1. Chemicals

Tetrahydrofuran, methanol, isopropanol, n-hexane and benzene were purified as described earlier.[14] The values of densities and viscosities of these solvents at various temperatures are in good agreement with the literature data.[15-19]

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Various mixtures of solutions with *W/W* concentrations of 0%, 5%, 10%, 15%, 20%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 90%, 100% were prepared at 303.15, 313.15 and 323.15 K. Each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. The ternary liquid solutions were made by mass.

7.2.2. Measurements

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 303.15, 313.15 and 323.15 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 temperatures 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 in an electronic balance. The balance used here is Mettler Toledo AG-285, made in Switzerland. 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.[20]

The viscosity of these mixtures was determined by means of a suspended-level Ubbelohde[21] viscometer at the desired temperatures (303.15, 313.15 and 323.15 K). The precision of the viscosity measurements was 0.05%. Details have been described earlier.[14]

7.3. Results and Discussion

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products. Viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately.

In contraposition to viscous antagonism, viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component considered separately.

In turn, if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction.[22, 23]

The method most widely used to analyze the antagonic and synergic behaviour of various solvent-mixtures is that developed by Kaletunc-Gencer and Peleg[24] allowing quantification of the antagonic interactions taking place in mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, $\eta_{\exp}$, with the viscosity expected in the absence of interaction, η_{mix}, defined as[25]:

$$\eta_{mix} = \sum_{i=1}^{n} x_i \eta_i \tag{1}$$

where x_i, and η_i are the fraction by weight and viscosity measured experimentally, of the ith component respèctively.

This procedure is used when Newtonian fluids are involved, since in Non-Newtonian systems shear rate must be taken into account, and other antagonism indices are defined in consequence.[26]

In order to secure more comparable viscous antagonism results, the so-called antagonic index (I_η), introduced by Howell,[27] is also taken into account:

$$I_\eta = (\eta_{mix} - \eta_{\exp})/\eta_{mix} = \Delta\eta/\eta_{mix} \tag{2}$$

The method used to analyze volume contraction and dilatation is similar to that applied to viscosity, *i.e.*, density of the mixture is determined experimentally, $\rho_{\exp}$ and a calculation is made of its theoretical value, ρ_{mix} in the supposition that volume contraction exists, based on the following expression[25]:

$$\rho_{mix} = \sum_{i=1}^{n} x_i \rho_i \tag{3}$$

where ρ_i denotes the density, measured experimentally of ith component. Accordingly, when $\rho_{\exp} > \rho_{mix}$, volume contraction occurs.

The physical properties of various pure solvents (tetrahydrofuran, isopropanol, methanol, benzene and n-hexane) along with their literature values at various temperatures are recorded in Table 1.

The measurements made yielded the viscosity values determined experimentally, η_{exp} and the viscosity values expected in the absence of interaction, η_{mix} along with antagonic interaction index (I_η) of various ternary liquid mixtures studied here at different temperatures are recorded in Table 2.

From Table 2 in case of mixture tetrahydrofuran + methanol + benzene it is observed that the antagonic interaction in the mixture is maximum where maximum amount of benzene (80 mass%) is present in the mixture whereas it is minimum where the mixture does not contain benzene for all temperatures studied here.

The explanation of this behavior is based on the known phenomenon of molecular dissociation, as a consequence of weakening the hydrogen bonds formed between the molecules of the components of the mixture due to presence of benzene – producing a decrease in size of the molecular package which logically implies an increase in antagonic interaction index (I_η). Some result was reported earlier[25] in the density and viscosity measurements of the ternary mixtures.

Further Table 2 in case of mixture isopropanol + n-hexane + benzene shows that the value of antagonic interaction index (I_η) is maximum when maximum amount of isopropanol is present in the mixture and it is minimum when the mixture contains no isopropanol. The possible explanation of this behavior is that the maximum addition of isopropanol to the mixture either destroys or complicates the establishment of molecular interaction formed between the molecules of the components of the mixture resulting a maximum value of antagonic interaction index (I_η).

The density of the mixture is determined experimentally, ρ_{exp} and a calculation is made of theoretical value, ρ_{mix} for two ternary liquid mixtures at 303.15, 313.15 and 323.15 K are presented in Table 3.

A perusal of Table 3 shows that the values of density determined experimentally, ρ_{exp} for both mixtures for various mass % and various temperatures are higher than those of its theoretical values, ρ_{mix} in the supposition that volume contraction exists, based on the equation (3). This type of behavior can be explained on the basis of known phenomenon of electrostriction as a consequence solvent molecules are accommodated in the void space left in the packing of dispersed solvent molecules. Same results are reported for 2:2 electrolytes in aqueous mixtures of THF.[28]

7.4. Conclusion

In summary, benzene seemed to produce a decrease in the size of the molecular package for (tetrahydrofuran + methanol + benzene) mixture. Similar role was played by isopropanol for (isopropanol + n-hexane + benzene) mixture. However, more extensive studies are required to have a better say in this regard.

References

[1] J. Ferguson, Z. Kemblonski, *Applied Fluid Rheology*, Elsevier Science Publishers Ltd., University Press, Cambridge, (1991).

[2] H. A. Barnes, J. F. Hutton, K.Walters, *An Introduction to Rheology*, Elsevier Science Publishers BV, Amsterdam, (1993).

[3] C. W. Macosko, *Rheology. Principles, measurements and applications*, VCH Publishers Inc, New York, (1994).

[4] R. Shukla, M. Cheryan, J. Membrane Science., 198 (2002) 104.

[5] J. M. Resa, C. Gonzalez, J. Lanz, J. Food Engineering., 51 (2002) 113.

[6] M. J Assael, N. K Dalaouti, I. Metaxa, Fluid Phase Equilibr., 199, (2002) 237.

[7] A. Das, *Teenologia Farmaceutica*, Ed. Acribia S.A., Zaragoza, (1979).

[8] R. Voight, *Tratado de tecnologia farmaceutica*, Ed. Acribia S.A., Zaragoza, (1982).

[9] C. K. Zeberg-Mikkelsen, Fluid Phase Equilibr., 194 (2002) 1191.

[10] C. Fauli-Trillo, *Tratado de Farmacia Galenica*, Ed. Lujan S.A., Madrid, (1993).

[11] J. Swarbrik, J. C Boyland, *Encyclopaedia of pharmaceutical technology*, Marcel Dekker Inc. New York, (1993).

[12] C. G. Janz and R. P. T Tomkins, *Non-aqueous electrolytes Handbook*, Academic Press, New York, Vol. 2 (1973).

[13] R. Jasinki, *High Energy Batteries*, Plenum Press, New York, (1967).

[14] M. N. Roy, D. K. Hazra, Indian J. Chem. Technol., 1 (1994) 93.

[15] A. Jha, S. R. Choudhury, A. Choudhury, M. N. Roy, J. Teach. Res. Chem., 10 (2003) 1.

[16] S. Martin Contreras, J. Chem. Eng. Data., 2001, 46 (2001) 1149.

[17] Changsheng Yang, Piesheng Ma, Qing Zhou, J. Chem. Eng. Data., 49 (2004) 881.

[18] P. S. Nikam , J. K. Sanjeevan, J. Chem. Eng. Data., 48 (2003) 1202.

[19] Changsheng Yang, Wei Xu, Piesheng Ma, J. Chem. Eng. Data., 49 (2004) 802.

[20] P. S. Nikam, M. Hosan, J. Chem. Eng. Data., 33 (1988)165.

[21] J. R. Suindells, T. B. Godfray, J. Res. Natd. Bur. Stand., 48 (1952).

[22] J. Pellicer, *Sinergia viscosa. Fundamentos de reologia. Los materiales viscoelasticos. Aplicaciones a las industrias alimentarias y quimico-farmaceuticas*, Universidad Internacional Menendez Pelayo, Valencia (Spain), October (1997).

[23] G. Copetti, R. Lapasin, E. R. *Morris et al.*: Proceeding of the 4th European Rheology Conference. Seville (Spain), 215 (1994).

[24] G. Kalentunc-Gencer, M. Peleg, J. Texture Studies., 17 (1986) 61.

[25] J. V. Herraez, R. Belda, J. Soln. Chem., 33 (2004)117.

[26] D. D Christianson, *Hydrocolloid interactions with starches. In: Food Carbohydrates*, D. R. Linebak, G. E. Inglett (Ed.s), Avi. Pub. Wesport. Conn, 399 (1982).

[27] N. K. Howell, *Proceedings of the 7th Internacional Conference*, Wales (1993), G. O. Phillips, P. A. Williams, D. J. Wdlock, Oxford University Press, New York, 77 (1994).

[28] S. Roy Choudhury, A. Jha, M. N. Roy, J. Indian Chem. Soc., 79 (2002) 623.

Table 1.
Physical properties of various pure solvents at different temperatures

T/K	ρ_0 /g.cm^{-3}									
	Tetrahydrofuran (THF)		Isopropanol		Methanol		Benzene		n-hexane	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
303.15	0.8757	0.8734[15]	0.7854	0.7766[16]	0.7846	0.7846[15]	0.8637	0.8682[17]	0.6497	0.6529[19]
313.15	0.8673	0.8661[15]	0.7704	0.7681[16]	0.7772	0.7772[15]	0.8604	0.8574[18]	0.6428	0.6435[19]
323.15	0.8583	0.8582[15]	0.7651	-	0.7675	0.7675[15]	0.8517	0.8466[17]	0.6332	0.6341[19]

T/K	η_0 /cp									
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
303.15	0.4452	0.4451[15]	1.7686	1.792[16]	0.4086	0.4089[15]	0.5637	0.5612[17]	0.2643	0.2774[19]
313.15	0.4088	0.4088[15]	1.3611	1.352[16]	0.3847	0.3848[15]	0.5029	0.5000[18]	0.2487	0.2504[19]
323.15	0.3716	0.3745[15]	1.2713	-	0.3308	0.3311[15]	0.4381	0.4362[17]	0.2307	0.2333[19]

Table 2.

Viscosities of the ternary liquid mixtures without interaction (η_{mix}) and with interaction (η_{exp}) along with antagonic interaction index (I_η) at various temperatures

1. Tetrahydrofuran (THF) + Methanol (MeOH) + Benzene (C_6H_6)

Mass% of THF	Mass % of MeOH	Mass % of C_6H_6	η_{mix}			η_{exp}/cp			I_η		
			303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
10	10	80	0.5363	0.4817	0.4207	0.4190	0.3962	0.3710	0.2188	0.1774	0.1182
20	15	65	0.5167	0.4663	0.4087	0.4517	0.4213	0.3748	0.1259	0.0966	0.0829
30	30	40	0.4816	0.4392	0.3859	0.4060	0.3839	0.3674	0.1570	0.1259	0.0481
35	35	30	0.4679	0.4286	0.3773	0.4629	0.3823	0.3713	0.0108	0.1080	0.0158
40	40	20	0.4543	0.4180	0.3686	0.3981	0.3972	0.3659	0.1236	0.0497	0.0073
45	45	10	0.4406	0.4074	0.3598	0.4337	0.3825	0.3618	0.0156	0.0610	-0.0053
50	50	00	0.4269	0.3967	0.3512	0.4482	0.4075	0.4297	-0.0498	-0.0271	-0.2235
55	40	05	0.4365	0.4039	0.3586	0.3897	0.3777	0.3801	0.1072	0.0648	-0.0599
60	30	10	0.4461	0.4109	0.3660	0.4063	0.3719	0.4296	0.0892	0.0951	-0.1737
65	20	15	0.4556	0.4181	0.3734	0.3882	0.3659	0.3685	0.1480	0.1248	0.0132
70	10	20	0.4652	0.4252	0.3808	0.4456	0.3789	0.3713	0.0422	0.1089	0.0249
75	00	25	0.4748	0.4323	0.3882	0.4050	0.3996	0.4009	0.1470	0.0757	-0.0326
80	00	20	0.4689	0.4276	0.3849	0.3954	0.3811	0.4007	0.1567	0.1088	-0.0410
90	00	10	0.4570	0.4182	0.3782	0.3948	0.3760	0.3863	0.1362	0.1009	-0.0213

2. Isopropanol (Me_2CHOH) + n-Hexane (C_6H_{14}) + Benzene (C_6H_6)

Mass% of Me_2CHOH	Mass% of C_6H_{14}	Mass% of C_6H_6	η_{mix}			η_{exp}/cp			I_η		
			303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
00	65	35	0.3691	0.3377	0.3033	1.1240	0.4077	0.3936	-2.0453	-0.2074	-0.2978
05	80	15	0.3844	0.3424	0.3138	0.3808	0.3207	0.2600	0.0094	0.0635	0.1715
10	10	80	0.6542	0.5633	0.5007	0.4413	0.4126	0.4092	0.3255	0.2675	0.1827
20	15	65	0.7598	0.6364	0.5736	0.4682	0.4354	0.4118	0.3838	0.3158	0.2821
30	25	45	0.8503	0.6968	0.6362	0.5654	0.5082	0.4632	0.3351	0.2707	0.2719
40	35	25	0.9409	0.7572	0.6988	0.6739	0.6475	0.5600	0.2837	0.1449	0.1986
50	45	05	1.0314	0.8176	0.7614	0.7315	0.6858	0.6509	0.2908	0.1612	0.1451
60	40	00	1.1669	0.9161	0.8551	0.9803	0.6940	0.6526	0.1599	0.2425	0.2368
70	20	10	1.3472	1.0528	0.9799	0.9100	0.6983	0.6239	0.3245	0.3367	0.3633
80	00	20	1.5276	1.1895	1.1046	1.0656	0.8413	0.7631	0.3024	0.2927	0.3092
90	05	05	1.6331	1.2626	1.1776	0.9609	0.8137	0.7238	0.4116	0.3555	0.3854

Table 3.

Densities of the ternary liquid mixtures calculated theoretically (ρ_{mix}) and determined experimentally (ρ_{exp}) at various temperatures

1: Tetrahydrofuran (THF) + Methanol (MeOH) + Benzene (C_6H_6)

Mass % of THF	Mass % of MeOH	Mass % of C_6H_6	ρ_{mix}/g. cm^{-3}			ρ_{exp}/g. cm^{-3}		
			303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
10	10	80	0.8569	0.8528	0.8439	0.8599	0.8545	0.8496
20	15	65	0.8542	0.8493	0.8404	0.8570	0.8523	0.8459
30	30	40	0.8436	0.8375	0.8284	0.8452	0.8404	0.8349
35	35	30	0.8402	0.8337	0.8245	0.8415	0.8361	0.8296
40	40	20	0.8367	0.8299	0.8207	0.8390	0.8336	0.8257
45	45	10	0.8335	0.8261	0.8168	0.8352	0.8310	0.8230
50	50	00	0.8301	0.8222	0.8129	0.8306	0.8263	0.8166
55	40	05	0.8387	0.8309	0.8216	0.8375	0.8353	0.8269
60	30	10	0.8472	0.8396	0.8304	0.8491	0.8397	0.8345
65	20	15	0.8557	0.8482	0.8391	0.8576	0.8504	0.8430
70	10	20	0.8642	0.8569	0.8479	0.8658	0.8610	0.8527
75	00	25	0.8727	0.8656	0.8566	0.8752	0.8670	0.8634
80	00	20	0.8733	0.8659	0.8569	0.8743	0.8667	0.8596
90	00	10	0.8745	0.8666	0.8576	0.8743	0.8664	0.8607

2: Isopropanol (Me_2CHOH) + n-Hexane (C_6H_{14}) + Benzene (C_6H_6)

Mass % of Me_2CHOH	Mass % of C_6H_{14}	Mass % of C_6H_6	ρ_{mix}/g. cm^{-3}			ρ_{exp}/g. cm^{-3}		
			303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
00	65	35	0.7246	0.7190	0.7097	0.8798	0.8715	0.8686
05	80	15	0.6886	0.6818	0.6726	0.8950	0.8843	0.8813
10	10	80	0.8345	0.8296	0.8212	0.8585	0.8494	0.8430
20	15	65	0.8159	0.8098	0.8016	0.8517	0.8437	0.8390
30	25	45	0.7867	0.7790	0.7711	0.8552	0.8488	0.8427
40	35	25	0.7575	0.7482	0.7406	0.8637	0.8543	0.8496
50	45	05	0.7282	0.7175	0.7101	0.8688	0.8584	0.8556
60	40	00	0.7311	0.7194	0.7123	0.8565	0.8460	0.8397
70	20	10	0.7661	0.7539	0.7474	0.8257	0.8164	0.8114
80	00	20	0.8011	0.7884	0.7824	0.8128	0.8029	0.7988
90	05	05	0.7825	0.7685	0.7628	0.7946	0.7847	0.7408

CHAPTER VIII

Excess Molar Volumes, Viscosity Deviations and Isentropic Compressibility of Binary Mixtures Containing 1,3-Dioxolane and Monoalcohols at 303.15 K*

8.1. Introduction

The increasing use of the cyclic diethers and monoalcohols in many industrial processes such as pharmaceutical and cosmetics have greatly stimulated the need for an extensive information on the thermodynamic, acoustic and transport properties of cyclic diethers, monoalcohols and their mixtures.[1-6] 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.[7, 8] Thermodynamic properties of various alcohols have been studied in numerous solvents. In our systematic investigation of the properties, we have reported viscosities, densities, speeds of sound, isentropic compressibilities and excess molar volumes for many binary systems in earlier works.[1-4] There has been a recent upsurge of interest[9,10] in the study of thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on intermolecular interactions and stereo chemical effects in these systems.[3] In this chapter we extend our studies to the binary mixtures formed from 1,3-dioxolane, represented as (1) with eight monoalcohols, represented as (2), including methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), t-butanol (t-BuOH), i-amyl alcohol (i-AmOH).

The various thermodynamic properties such as excess molar volume (V^E) and viscosity deviations ($\Delta\eta$) obtained from experimental observations have been rationalized.[4] Besides this, speed of sound and calculated isentropic compressibility as well as deviation in isentropic compressibility (ΔK_S)[7,11] of 1,3-dioxolane (1) with the monoalchols (2) mixtures are presented at 303.15

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K. The cyclic diether 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. [12] In addition, this work also provides a test of various empirical equations to correlate viscosity and ultrasonic sound data of binary mixtures containing both polar components.

8.2. Experimental Section

8.2.1. Apparatus and Procedures

Densities (ρ) at 303.15 K were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The measurements were done in a thermostated bath controlled to ± 0.01 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer.[13] Calibration was done at 303.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. Speeds of sound were determined by a multifrequency ultrasonic interferometer (M-81, Mittal enterprise, New Delhi) working at 2 MHz calibrated with purified water, methanol and benzene at 303.15 K. The details of the methods and techniques had been described earlier.[14, 15] The mixtures were prepared by mixing known volume of pure liquids in air-tight stoppered bottles. The weights were taken on a Mettler electronic analytical balance (Mettler, AG 285, Switzerland) accurate to 0.01 mg. The precisions of the speed of sound, density and viscosity measurements are ± 0.2 m s^{-1}, $\pm 3 \times 10^{-5}$ g cm^{-3} and $\pm 2 \times 10^{-5}$ cP respectively.

8.2.2. Chemicals

The source and purification of pure alcohols (Merck, India) methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, t-butanol, and i-amyl alcohol have been described in other papers.[5,16,17] 1,3-dioxolane (Merck, India) was purified by standard methods. It was refluxed with PbO_2, then it was fractionally distilled after addition of xylene.[18] The solvents finally obtained after purification were 99.9% pure as checked by gas chromatography. The purity of the liquids, as checked by measuring their densities and viscosities at 303.15 K, was in good agreement with the literature values[6, 18-21] and are listed in Table 1.

8.3. Results

The measured density (ρ) and viscosity (η) data for mixtures of 1,3-dioxolane (1) and monoalcohols (2) such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, t-Butanol, iso-amyl alcohol were used to calculate the excess molar volume (V^E), viscosity deviations ($\Delta\eta$), Gibbs excess free energy of activation for viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1) and the results are presented in Table 2.

The excess molar volume (V^E) was calculated using the equation, [8, 22]

$$V^E = (M_1x_1 + M_2x_2)/\rho_{mix} - M_1x_1/\rho_1 - M_2x_2/\rho_2 \tag{1}$$

where, ρ_{mix} is the density of the mixture and M_1, M_2, x_1, x_2 and ρ_1, ρ_2 are the molecular weights, mole fractions and densities of pure components 1 and 2 respectively.

Quantitatively, as per the absolute reaction rates theory[4,23] the deviation of viscosities, $\Delta\eta$ from the ideal mixture values and the Gibbs excess free energy of activation, G^{*E} for viscous flow are calculated as,[24]

$$\Delta\eta = \eta_{mix} - [x_1\eta_1 + x_2\eta_2] \tag{2}$$

$$G^{*E} = RT[\ln(\eta_{mix}V_{mix}) - \{x_1\ln(\eta_1V_1) + x_1\ln(\eta_2V_2)\}] \tag{3}$$

where η_{mix}, V_{mix} are the viscosity, molar volume of the mixture; η_1, η_2 and V_1, V_2 are the viscosities and molar volumes of pure components (1) and (2) respectively.

Isentropic compressibility, K_S and deviation in isentropic compressibility, ΔK_S are calculated from experimental densities, ρ and speeds of sound, u using the following equations, [7, 11, 25-27]

$$K_S = 1/u^2\rho \tag{4}$$

$$\Delta K_S = K_S - x_1K_{S,1} - x_2K_{S,2} \tag{5}$$

where K_S, $K_{S,1}$, $K_{S,2}$ are the isentropic compressibility of the mixture, pure component 1 and pure component 2 respectively.

Experimental speeds of sound and estimated isentropic compressibility as well as deviation in isentropic compressibility are compiled in Table 3.

The viscosity values were further used to determine the Grunberg-Nissan parameter (d^1)[28] as:

$$\ln\eta_{mix} = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1 x_2 d^1 \tag{6}$$

where d^1 is proportional to the interchange energy. The d^1 values for the mixtures are reported in Table 2.

Again, the V^E, $\Delta\eta$, G^{*E} and ΔK_S values have been fitted to a Redlich-Kister[29] equation by the method of least squares using the Marquardt algorithm[30] to derive the binary coefficients, A_J,

$$Y^E = x_1 x_2 \sum_{J=1}^{k} A_J (x_1 - x_2)^{J-1} \tag{7}$$

Here, Y^E denotes V^E, $\Delta\eta$, G^{*E} and ΔK_S. In each case, the optimum number of coefficients, A_J is ascertained from an examination of the variation of the standard deviation, σ, with

$$\sigma = [(Y^E_{exp} - Y^E_{cal})^2/(n-m)]^{1/2} \tag{8}$$

where n represents the number of measurements and m the number of coefficients. The estimated values of A_J and σ for V^E, $\Delta\eta$, G^{*E} and ΔK_S are summarized for all mixtures in Table 4.

8.4. Discussion

We have calculated $\Delta\eta$, V^E and G^{*E} at 303.15 K for the binary mixtures of 1,3-dioxolane (1) with monoalcohols (2). The variation of the excess properties over the entire range of composition for the binary mixtures has been depicted in figures 1-3.

The value of the excess molar volume (V^E) was found to be negative for 1, 3-dioxolane and methanol mixture but the magnitude of negative value decreases and positive value increases with increasing chain length of the alcohols in the series (Figure 1). The trend it followed is:

MeOH < EtOH< 1-PrOH < 2-PrOH < 1-BuOH < i-AmOH < 2-BuOH < t-BuOH

The negative V^E values indicate the presence of strong molecular interaction between the components of the mixture.

Several effects may contribute to the value of V^E, such as, [31-33] a) dipolar interaction, b) interstitial accommodation of one component into the other, c) possible hydrogen bond interactions between unlike molecules. The actual volume change, therefore, depends on the relative strength of these three effects. It is known fact that as the C-atoms of the alkyl group increases, the electron releasing ability (+I effect) increases, thereby decreasing the polarity of the O---H bond of the monoalcohols. So MeOH with the highest polarity gains the most favorable intermolecular H-bonded interactions with the cyclic diether molecules. Moreover, its simple structure and smaller size leads to interstitial accommodation with 1, 3-dioxolane molecules more easily compared to the higher monoalcohols which have greater complexity in struture. Similar results have been reported earlier.[34, 35]

It is further observed that in the case of branched monoalcohols, the V^E values are higher than the respective normal alcohols. This may be attributed primarily due to the steric factors arising from a change in the proportion of different structural forms of the alcohol molecules with a change in its mole fraction. This also explains the expected behavior of i-AmOH in this chapter. Similar types of work have been reported in the literature. [36, 37]

Figure 2 shows that $\Delta\eta$ values are positive for 1, 3-dioxolane and methanol systems but with the increase in the chain length in alcohols, the magnitude of positive deviation decreases. The order it followed is:

MeOH > EtOH > 1-PrOH > 2-PrOH > i-AmOH > 1-BuOH > 2-BuOH > t-BuOH

A correlation between signs of $\Delta\eta$ and V^E have been observed for a number of binary solvent systems[38, 39] i.e. $\Delta\eta$ is positive when V^E is negative and vice-versa. 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 $\Delta\eta$ values.[40]

In figure 3, the value of Gibbs excess free energy for activation of viscous flow i.e. G^{*E} is observed to be positive for (1) and methanol mixture and negative for (1) and ethanol mixture onwards. G^{*E} values for the systems under study suggested the following order:

MeOH > AmOH > EtOH > PrOH > BuOH

It have been reported[41, 42] that G^{*E} parameter may be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. The magnitude of the positive value is an excellent indication of the strength of specific interaction.

Here it is observed that the magnitude of negative values increases with increasing chain length of alcohols. Alcohol molecules self associate[43] very strongly (OH---OH interaction) while the cyclic diether; 1, 3-dioxolane molecules self associate rather marginally, this causes a dramatic influence on the thermo-physical properties studied. The positive value for (1) and MeOH mixture indicates favorable inter molecular complex through H-bonding, i.e. O-O------H-O. This interaction may be considered as the H-bonded interaction between alcohols as a Lewis acid and the cyclic diether as a Lewis base.[31, 46]

Fort and Moore[44] and Ramamoorthy[45] reported in their works that for any binary liquid mixture, the positive value of d^{l} indicates the presence of strong interactions and the negative value of d^{l} indicates the presence of weak interactions between the components. On this basis, positive d^{l} values for (1) and MeOH system confirm the presence of strong interactions between the component molecules, whereas for higher monoalcohols this affinity for bonding decreases. These conclusions are in excellent agreement with that reported by Subha et al.[31, 46, 47]

In Table 3, deviation in isentropic compressibility, ΔK_S are reported for the 1,3-dioxolane + monoalcohol mixtures. From figure 4, 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 order it followed is:

MeOH < EtOH < PrOH < BuOH < AmOH

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.[48] Interactions between the molecules of cyclic diether or monoalcohols are broken in the mixing process; the breaking of strong dipole-dipole interactions in 1, 3-dioxolane, which can be considered as a polar fluid,[49] leads to positive ΔK_S values for the mixture containing greater chain length of alcohols as compared to the lower alcohols. The donor-acceptor interaction between the oxygen and hydrogen atom of the cyclic diether and the alcohols play an important part for the mixtures containing lower alcohols like MeOH, EtOH where there is strong specific interaction between the component molecules leading to negative value of ΔK_S.

Also it is observed that for isomeric monoalcohols, i.e. 1-PrOH and 2-PrOH, the ΔK_S values are less negative for linear 1-PrOH as compared to branched 2-PrOH. The same trend is observed between butanol isomers, whereby ΔK_S values are positive for linear 1-BuOH, partially negative for 2-BuOH and totally negative for the branched isomer t-BuOH.

This type of trend has been observed and reported earlier in the literature.[7,25] This type of behavior can be explained by the concept of interstitial accommodation and changes in free volume as described in the literature.[26,35] The branched isomers fit into the structure of cyclic diether more easily compared to the linear isomers, thereby possessing more negative ΔK_S. Thus, it can also be explained that due to extensive branching and chain length, iso-amyl alcohol have exhibited exceptional behavior in many cases.

In the eight binary mixtures of the cyclic diether and the monoalcohols, it is really interesting to note that V^E, $\Delta\eta$, G^{*E} and ΔK_S have maximum in the mole fraction range $x_1 = 0.3$ to 0.5. This is a manifestation of strong specific interaction[50] between the cyclic diether and monoalcohol molecules through by H-bonded interaction. The maximum points are clear indication of the highest point of interaction between the component molecules for the above-mentioned binary mixtures studied.

8.5. Conclusion

In summary, the study provided us some idea about the type and nature of molecular interactions between the mixed components. The lower monoalcohols were found to associate more strongly with cyclic diethers as compared to the higher ones. However, the branched isomers differed from the linear ones in behavior toward the cyclic diethers. Self-association between the alcohol molecules was found to increase with an increase in chain length. The study of excess or deviation properties along with the speeds of sound has been found to be very useful in understanding the nature of interactions in the binaries, though more extensive studies are needed to have a better say in this regard.

References

[1] M. N. Roy, A. Choudhury, A. Sinha, J. Teach. Res. Chem., 11 (2004) 12.

[2] D. K. Hazra, M. N. Roy, B. Das, Ind. J. Chem. Technol., 1 (1994) 93(1994).

[3] M. N. Roy, A. Choudhury, J. Teach. Res. Chem., 1 (2000) 17.

[4] M. N. Roy, B. B. Gurung, A. Choudhury, J. Indian. Chem. Soc., 81 (2004) 1.

[5] S. L. Oswal, H. S. Desai, Fluid Phase Equilibr., 161 (1999) 191.

[6] S. L. Oswal, H. S. Desai, Fluid Phase Equilibr., 186 (2001) 81.

[7] C. Lafuente, B. Giner, A. Villares, I. Gascon P. Cea, Int. J. Thermophys., 25 (2004) 1735.

[8] P. S. Nikam, L. N. S Shirsat, M. Hasan, J. Indian. Chem. Soc., 77 (2000) 244.

[9] E. Perez, M. Cardoso, A. M. Mainar, J. I. Pardo, J. S. Urieta, J. Chem. Eng. Data., 48 (2003) 1306.

[10] J. N. Nayak, T. M. Aminabhavi, M. I. Aralaguppi, J. Chem. Eng. Data., 48 (2003)1152.

[11] G. Douheret, A. Pal, M. I. Davis, J. Chem. Thermodyn., 22 (1990) 1.

[12] S. L. Oswal, K. D. Prajapati, J. Chem. Eng. Data., 43 (1998) 367.

[13] R. Suindells, T. B. Godfray, J. Res. Natd. Bur. Stand., 48 (1952) 1.

[14] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1247.

[15] M. N. Roy, A. Jha, A. Choudhury, J. Chem. Eng. Data., 49 (2004) 291.

[16] S. L. Oswal, H. S. Desai, Fluid Phase Equilibr., 149 (1998) 359.

[17] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory chemicals*, 3rd ed., Pergamon, Great Britain, (1988).

[18] J. Riddick, W. B. Bunger, T. K Sakano, *Organic solvents: physical properties and methods of purification*, Wiley, New York, (1986).

[19] J. N. Gurtu, R. Kapoor, *Advanced Experimental Chemistry*, 1, 338, 346 (1987).

[20] J. Timmermans, *Physico chemical constants of pure organic compounds*, Elsevier, Amsterdam, 1 (1950), 2 (1965).

[21] A. K. Covington, T. Dickinson, *Physical Chemistry of Organic solvent systems*, Plenum, New York, (1973).

[22] A. W. Quin, D. F. Hoffmann, P. Munk, J. Chem. Eng. Data., 37 (1992) 55.

[23] S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw-Hill, New York, pp-514 (1941).

[24] D. S. Gill, T. S. Kaur, H. Kaur, I. M. Joshi, J. Singh, J. Chem. Soc. Faraday Trans., 89 (1993) 1737.

[25] H. Artigas, C. Lafuente, M. C. Lopez, F. M. Royo, J. S. Urieta, Z. Phys. Chem., 215 (2001) 933.

[26] I. Gascon, S. Martin, P. Cea, M. C. Lopez, F. M. Royo, J. Soln. Chem., 31 (2002) 905.

[27] F. Kimura, A. Treszczanowicz, C. Halpin, G. Benson, J. Chem. Thermodyn., 15 (1983) 503.

[28] L. Grunberg, A. H. Nissan, Nature., 164 (1949) 799.

[29] O. Redlich, A. J. Kister, Ind. Eng. Chem., 40 (1948) 345.

[30] D. W. Marquardt, J. Soc. Ind. Appl. Math., 11 (1963) 431.

[31] M. C. S. Subha, K. C. Rao, J. Phys. Chem. Liq., 18 (1988) 185.

[32] A. Assarsson, F. R. Eirich, J. Phys. Chem., 72 (1968) 2710.

[33] E. A. Muller, J. Chem. Eng. Data., 36 (1991)214.

[34] P. Brocos, E. Calvo, R. Bravo et al., J. Chem. Eng. Data., 44 (1999) 1341.

[35] A. Amigo, R. Bravo, M. Pintos, J. Chem. Eng. Data., 38 (1993) 141.

[36] D. Papaioannou, M. Bridakis, C. Panayiotou, J. Chem. Eng. Data., 38 (1993) 616.

[37] A. Krishnaiah, P. R. Naidu, Acta Chem. Acad. Sci. Hung., 104 (1986) 295.

[38] D. S. Gill, T. S. Cheema, Z. Phys. Chem (N.F)., 134 (1983) 205.

[39] Y. Marcus, *Ion Solvation*, Wiley, New York, (1985).

[40] M. G. Prolongo, R. M. Masegosa, H. I. Fuentes, A. Horta, J. Phy. Chem., 88 (1984) 2163.

[41] T. M. Reed, T. E. Taylor, J. Phys. Chem., 63 (1959) 58.

[42] R. Meyer, M. Meyer, J. Metzer, A. Peneloux. Chem. Phys., 62 (1971) 406.

[43] A. J. Treszczanowicz, T. Treszczanowicz, T. Pawlowski, T. K. Guttman, J. Soln. Chem, 33 (2004) 1049.

[44] R. J. Fort, W. R. Moore, Trans. Faraday. Soc., 62 (1966)1112.

[45] K. Ramamoorthy, J. Pure. App. Phys., 11 (1973) 554.

[46] P. S. Nikam, M. Hasan, J. Chem. Eng. Data., 33 (1988) 165.

[47] B. V. K. Naidu, K. C. Rao, M. C. S. Subha, J. Indian. Chem. Soc., 78 (2001) 259.

[48] R. J. Fort, W. R. Moore, Trans. Faraday. Soc., 61 (1965) 2102.

[49] T. Takizawa, K. Tamura, J. Therm. Anal. Calorim., 69 (2002) 1075.

[50] L. Pikkarainen, J. Chem. Eng. Data., 33 (1988) 299.

Table 1.

Physical Properties of Pure Components at 303.15 K.

	ρ (g.cm^{-3})		η (cP)		
Components	Obs.	Lit.	Obs.	Lit.	u (m. s^{-1})
1,3-Dioxolane	1.05184	1.04940 [18]	0.54866	0.54355[18]	1288.5
Methanol	0.78242	0.78297 [19]	0.50409	0.51000 [19]	1088.5
Ethanol	0.78435	0.78069 [6]	0.96749	0.99301 [6]	1144.3
1-Propanol	0.79584	0.79581 [6]	1.66262	1.78433 [6]	1182.6
2-Propanol	0.77731	0.77786 [20]	1.61419	1.77321 [20]	1126.6
1-Butanol	0.80207	0.80194 [6]	2.53963	2.28530 [6]	1196.6
2-Butanol	0.79923	0.79589 [18]	2.33939	2.41700 [18]	1168.9
t-Butanol	0.77506	0.77622 [21]	3.09856	3.32109 [21]	1078.8
iso-Amyl alcohol	0.80319	–	3.11110	–	1197.0

Table2.
Experimental results for the binary liquid mixtures of 1,3-dioxolane (1) + monoalcohols (2) at 303.15K.

ole fraction of ,3-dioxolane (x_1)	ρ x 10^{-3} ($kg.m^{-3}$)	η x 10^3 ($kg.m^{-1}.s^{-1}$)	$\Delta\eta$ x 10^3 ($kg.m^{-1}.s^{-1}$)	V^E x 10^3 ($m^3.mol^{-1}$)	G^{*E} x 10^{-3} ($J.mol^{-1}$)	d^1
1,3-dioxolane + methanol						
0.00000	0.78242	0.50409	0.00000	0.00000	0.00000	-
0.04585	0.80385	0.50565	-0.00048	-0.04543	0.01448	-0.01817
0.09758	0.82641	0.50884	0.00040	-0.09238	0.03523	0.01262
0.15637	0.85072	0.51595	0.00489	-0.16997	0.07095	0.07586
0.22381	0.87556	0.52719	0.01312	-0.20763	0.12473	0.14877
0.30192	0.90216	0.53818	0.02063	-0.26618	0.17006	0.18911
0.39348	0.92962	0.55157	0.02994	-0.28935	0.21978	0.23749
0.50228	0.95845	0.56418	0.03770	-0.29641	0.25465	0.28026
0.63370	0.98828	0.54544	0.01311	-0.25413	0.13379	0.10834
0.79561	1.01936	0.54465	0.00509	-0.16004	0.07283	0.06138
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + ethanol						
0.00000	0.78435	0.96749	0.00000	0.00000	0.00000	-
0.06463	0.80501	0.89803	-0.04239	-0.01432	-0.09335	-0.62597
0.13455	0.82672	0.83803	-0.07311	-0.02483	-0.16571	-0.57821
0.21044	0.84953	0.76911	-0.11024	-0.02875	-0.27159	-0.66266
0.29308	0.87359	0.68516	-0.15958	-0.03001	-0.44315	-0.86305
0.38344	0.89912	0.63329	-0.17360	-0.03570	-0.51148	-0.87254
0.48263	0.92601	0.61205	-0.15330	-0.02995	-0.45496	-0.73741
0.59202	0.95457	0.59099	-0.12854	-0.02422	-0.38705	-0.65042
0.71327	0.98493	0.58855	-0.08020	-0.01712	-0.22544	-0.45208
0.84842	1.01723	0.56902	-0.04313	-0.00503	-0.11996	-0.38524
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + 1- propanol						
0.00000	0.79584	1.66262	0.00000	0.00000	0.00000	-
0.08269	0.81516	1.25778	-0.31273	0.04909	-0.47023	-2.47020
0.16862	0.83574	1.06683	-0.40795	0.07303	-0.64392	-1.83154
0.25799	0.85742	0.93446	-0.44077	0.09519	-0.72703	-1.51572
0.35101	0.88035	0.82076	-0.45085	0.11086	-0.79334	-1.39053
0.44791	0.90452	0.73389	-0.42978	0.12845	-0.80375	-1.29892
0.54893	0.93008	0.64538	-0.40575	0.14471	-0.84483	-1.36397
0.65434	0.95773	0.59197	-0.34174	0.11624	-0.76907	-1.35842
0.76444	0.98721	0.56844	-0.24262	0.07633	-0.56526	-1.25362
0.87954	1.01856	0.55642	-0.12643	0.03507	-0.29936	-1.12795
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + 2-propanol						
0.00000	0.77731	1.61419	0.00000	0.00000	0.00000	-
0.08269	0.79735	1.21247	-0.31361	0.07625	-0.49315	-2.59639
0.16862	0.81849	0.97764	-0.45688	0.15165	-0.79886	-2.27901
0.25799	0.84127	0.83857	-0.50072	0.18617	-0.94080	-1.96672
0.35101	0.86537	0.74771	-0.49247	0.22121	-0.97525	-1.71550
0.44791	0.89113	0.66451	-0.47242	0.23696	-1.00817	-1.63452
0.54893	0.91900	0.60823	-0.42106	0.21107	-0.95724	-1.54956
0.65434	0.94875	0.60327	-0.31370	0.17812	-0.69243	-1.22964
0.76444	0.98069	0.58560	-0.21406	0.12895	-0.47001	-1.04979

Contd...

0.87954	1.01482	0.56368	-0.11333	0.08009	-0.25558	-0.97199
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + 1-butanol						
0.00000	0.80207	2.53963	0.00000	0.00000	0.00000	-
0.10005	0.82064	1.73995	-0.60048	0.10328	-0.55615	-2.49729
0.20009	0.84032	1.37339	-0.76787	0.18245	-0.75747	-1.92522
0.30011	0.86111	1.11332	-0.82880	0.24712	-0.89359	-1.73685
0.40013	0.88368	0.95874	-0.78424	0.24314	-0.88094	-1.50416
0.50013	0.90754	0.84187	-0.70202	0.23225	-0.82118	-1.35121
0.60013	0.93281	0.73054	-0.61425	0.21418	-0.79337	-1.36020
0.70011	0.95972	0.65818	-0.48755	0.18020	-0.67348	-1.32180
0.80009	0.98832	0.61924	-0.32743	0.14009	-0.44671	-1.15856
0.90005	1.01882	0.58733	-0.16033	0.08933	-0.20229	-0.94536
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + 2-butanol						
0.00000	0.79923	2.33939	0.00000	0.00000	0.00000	-
0.10005	0.81699	1.51615	-0.64408	0.21125	-0.71372	-3.20554
0.20009	0.83605	1.18133	-0.79975	0.37022	-0.96592	-2.45596
0.30011	0.85714	0.93545	-0.86652	0.41589	-1.18211	-2.29194
0.40013	0.87988	0.81197	-0.81089	0.40842	-1.17009	-1.99115
0.50013	0.90408	0.70718	-0.73661	0.38031	-1.15202	-1.88435
0.60013	0.92976	0.65889	-0.60583	0.34322	-0.96612	-1.65351
0.70011	0.95708	0.61199	-0.47369	0.29514	-0.79056	-1.55106
0.80009	0.98619	0.58939	-0.31725	0.23646	-0.52623	-1.36480
0.90005	1.01762	0.55877	-0.16887	0.14236	-0.30518	-1.40824
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + t-butanol						
0.00000	0.77506	3.09856	0.00000	0.00000	0.00000	-
0.10005	0.79409	1.96702	-0.87642	0.22469	-0.69302	-3.12317
0.20009	0.81487	1.46803	-1.12032	0.36090	-0.98214	-2.50302
0.30011	0.83733	1.10228	-1.23103	0.43729	-1.25951	-2.44712
0.40013	0.86138	0.87929	-1.19898	0.48229	-1.38717	-2.36169
0.50013	0.88759	0.76572	-1.05756	0.45732	-1.29797	-2.12818
0.60013	0.91549	0.67551	-0.89278	0.42926	-1.17859	-2.01802
0.70011	0.94566	0.60671	-0.70664	0.36261	-1.01782	-1.99376
0.80009	0.97824	0.57312	-0.48529	0.26885	-0.73349	-1.89108
0.90005	1.01327	0.56596	-0.23756	0.16555	-0.34069	-1.57837
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-
1,3-dioxolane + iso-amyl alcohol						
0.00000	0.80319	3.11110	0.00000	0.00000	0.00000	-
0.11678	0.82142	2.29991	-0.51195	0.15588	-0.22415	-0.96433
0.22928	0.84113	1.80646	-0.71712	0.22984	-0.32135	-0.82479
0.33774	0.86196	1.45757	-0.78809	0.28423	-0.37398	-0.76962
0.44236	0.88396	1.16673	-0.81085	0.32478	-0.46884	-0.86414
0.54336	0.90791	0.99491	-0.72386	0.28621	-0.42717	-0.79483
0.64092	0.93313	0.88176	-0.58702	0.25432	-0.30807	-0.64592
0.73520	0.95989	0.78122	-0.44597	0.21604	-0.20933	-0.54508
0.82638	0.98836	0.71042	-0.28313	0.16819	-0.06358	-0.29898
0.91459	1.01899	0.62119	-0.14633	0.09110	-0.03559	-0.30788
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	-

Table3.

Speeds of sound (u), Isentropic Compressibility (K_S) and Deviation in Isentropic Compressibility (ΔK_S) of binary mixtures of various compositions (in mole fraction) at 303.15 K.

Mole fraction of 1,3-dioxolane (x_1)	u /m.s^{-1}	$K_S \times 10^{12}$ /Pa^{-1}	$\Delta K_S \times 10^{12}$ (Pa^{-1})	Mole fraction of 1,3-dioxolane (x_1)	u /m.s^{-1}	$K_S \times 10^{12}$ /Pa^{-1}	$\Delta K_S \times 10^{12}$ /Pa^{-1}
1,3-dioxolane + methanol				1,3-dioxolane + ethanol			
0.00000	1088.5	1078.7	0.0	0.00000	1144.3	973.7	0.0
0.04585	1122.2	987.9	-67.6	0.06463	1159.1	924.7	-23.1
0.09758	1135.7	938.1	-91.2	0.13455	1171.1	881.9	-37.8
0.15637	1145.7	895.5	-104.1	0.21044	1183.4	840.6	-48.7
0.22381	1157.9	851.9	-113.5	0.29308	1197.8	797.8	-58.3
0.30192	1174.8	803.2	-122.7	0.38344	1215.0	753.4	-66.5
0.39348	1198.8	748.5	-131.1	0.48263	1225.3	719.3	-60.8
0.50228	1230.7	688.8	-135.7	0.59202	1238.7	682.7	-53.5
0.63370	1255.6	641.8	-116.2	0.71327	1255.9	643.6	-44.0
0.79561	1281.4	597.5	-78.5	0.84842	1275.5	604.3	-29.1
1.00000	1288.5	572.6	0.0	1.00000	1288.5	572.6	0.0
1,3-dioxolane + 1-propanol				1,3-dioxolane + 2-propanol			
0.00000	1182.6	898.5	0.0	0.00000	1126.6	1013.6	0.0
0.08269	1185.5	872.9	1.3	0.08269	1136.9	970.2	-6.9
0.16862	1195.3	837.5	-6.0	0.16862	1151.2	921.9	-17.3
0.25799	1208.8	798.1	-16.3	0.25799	1166.3	873.8	-26.0
0.35101	1211.1	774.4	-9.7	0.35101	1182.5	826.4	-32.4
0.44791	1215.2	748.7	-3.8	0.44791	1199.2	780.3	-35.8
0.54893	1218.6	724.0	4.4	0.54893	1208.4	745.1	-26.4

Contd...

0.65434	1236.8	682.6	-2.7	0.65434	1221.8	706.1	-18.9
0.76444	1255.7	642.5	-6.9	0.76444	1239.9	663.2	-13.3
0.87954	1271.4	607.4	-4.5	0.87954	1260.9	619.7	-6.0
1.00000	1288.5	572.6	0.0	1.00000	1288.5	572.6	0.0
1,3-dioxolane + 1-butanol				1,3-dioxolane + 2-butanol			
0.00000	1196.6	870.7	0.0	0.00000	1168.9	915.7	0.0
0.10005	1200.8	845.1	4.2	0.10005	1173.1	889.4	8.0
0.20009	1205.3	819.1	8.0	0.20009	1177.5	862.6	15.6
0.30011	1208.4	795.3	14.1	0.30011	1182.8	833.9	21.2
0.40013	1218.8	761.8	10.4	0.40013	1193.2	798.3	19.9
0.50013	1229.6	728.8	7.2	0.50013	1212.5	752.4	8.3
0.60013	1240.9	696.1	4.3	0.60013	1234.4	705.9	-3.9
0.70011	1251.9	664.8	2.8	0.70011	1253.6	664.9	-10.6
0.80009	1263.1	634.2	2.0	0.80009	1267.5	631.2	-9.9
0.90005	1275.2	603.6	1.2	0.90005	1274.8	604.7	-2.2
1.00000	1288.5	572.6	0.0	1.0000	1288.5	572.6	0.0
1,3-dioxolane + t-butanol				1,3-dioxolane + iso-amyl alcohol			
0.00000	1078.8	1108.6	0.0	0.00000	1197.0	868.9	0.0
0.10005	1098.7	1042.9	-12.0	0.11678	1199.8	845.7	11.4
0.20009	1121.1	976.4	-24.9	0.22928	1203.8	820.4	19.4
0.30011	1144.7	911.4	-36.3	0.33774	1208.5	794.3	25.5
0.40013	1169.0	849.5	-44.6	0.44236	1215.8	765.3	27.5
0.50013	1184.7	802.7	-37.8	0.54336	1230.3	727.7	19.8
0.60013	1201.2	757.0	-29.9	0.64092	1242.7	693.9	14.9
0.70011	1221.4	708.8	-24.5	0.73520	1255.7	660.7	9.6
0.80009	1243.2	661.5	-18.3	0.82638	1266.1	631.2	7.2
0.90005	1266.5	615.3	-10.9	0.91459	1276.6	602.2	4.3
1.00000	1288.5	572.6	0.0	1.00000	1288.5	572.6	0.0

Table 4.
Estimated parameters of equation (7) for excess or deviation properties for the binary mixtures of 1,3-dioxolane (1) + monoalcohols (2) at 303.15K.

Excess function	A_0	A_1	A_2	σ
1,3-dioxolane + methanol				
V^E x 10^3 /$m^3.mol^{-1}$	-1.18037	0.29341	0.21420	0.00648
$\Delta\eta$ x 10^3 /$kg.m^{-1}.s^{-1}$	0.12407	-0.05029	-0.24601	0.00411
G^{*E} x 10^{-3} /$J.mol^{-1}$	0.90054	-0.28662	-1.11756	0.01869
ΔK_S x 10^{12} /Pa^{-1}	-542.5	-65.4	-355.9	0.1
1,3-dioxolane + ethanol				
V^E x 10^3 /$m^3.mol^{-1}$	-0.11914	0.10135	-	0.00179
$\Delta\eta$ x 10^3 /$kg.m^{-1}.s^{-1}$	-0.59825	0.42012	-0.86330	0.00029
G^{*E} x 10^{-3} /$J.mol^{-1}$	-1.77518	1.23789	-3.14322	0.01421
ΔK_S x 10^{12} /Pa^{-1}	-242.8	146.7	-44.9	1.1
1,3-dioxolane + 1-propanol				
V^E x 10^3 /$m^3.mol^{-1}$	0.55476	0.16595	-0.55390	0.00357
$\Delta\eta$ x 10^3 /$kg.m^{-1}.s^{-1}$	-1.67833	0.61688	-0.86578	0.00313
G^{*E} x 10^{-3} /$J.mol^{-1}$	-3.35532	-0.22204	-0.29213	0.01290
ΔK_S x 10^{12} /Pa^{-1}	3.6	85.6	-373.2	1.9
1,3-dioxolane + 2-propanol				
V^E x 10^3 /$m^3.mol^{-1}$	0.88575	-0.25715	-	0.00628
$\Delta\eta$ x 10^3 /$kg.m^{-1}.s^{-1}$	-1.81023	1.00486	0.88281	0.00265
G^{*E} x 10^{-3} /$J.mol^{-1}$	-4.02077	0.91517	5.47182	0.01367
ΔK_S x 10^{12} /Pa^{-1}	-123.4	105.4	72.8	1.5
1,3-dioxolane + 1-butanol				
V^E x 10^3 /$m^3.mol^{-1}$	0.93948	-0.42461	0.40040	0.00583

Contd...

$\Delta\eta \times 10^3$ /kg.m^{-1}.s^{-1}	-2.80851	1.64517	-2.91633	0.00201
$G^{*E} \times 10^{-3}$ /J.mol^{-1}	-3.41517	0.83967	-1.24054	0.02121
$\Delta K_S \times 10^{12}$ /Pa^{-1}	32.9	-42.8	-	1.7
		1,3-dioxolane + 2-butanol		
$V^E \times 10^3$ /m^3.mol^{-1}	1.52385	-0.65650	0.96778	0.00052
$\Delta\eta \times 10^3$ /kg.m^{-1}.s^{-1}	-2.94697	2.02543	0.74317	0.00035
$G^{*E} \times 10^{-3}$ /J.mol^{-1}	-4.55415	2.05980	0.49414	0.02744
$\Delta K_S \times 10^{12}$ /Pa^{-1}	28.8	-147.2	-	4.1
		1,3-dioxolane + t-butanol		
$V^E \times 10^3$ /m^3.mol^{-1}	1.85435	-0.46020	0.39839	0.00639
$\Delta\eta \times 10^3$ /kg.m^{-1}.s^{-1}	-4.23108	3.23501	-3.59752	0.00123
$G^{*E} \times 10^{-3}$ /J.mol^{-1}	-5.28143	1.27430	-0.54361	0.03782
$\Delta K_S \times 10^{12}$ /Pa^{-1}	-154.1	111.2	48.3	1.7
		1,3-dioxolane + iso- amyl alcohol		
$V^E \times 10^3$ /m^3.mol^{-1}	1.19788	-0.22010	0.15846	0.01055
$\Delta\eta \times 10^3$ /kg.m^{-1}.s^{-1}	-3.06573	1.53808	0.46358	0.00804
$G^{*E} \times 10^{-3}$ /J.mol^{-1}	-1.79697	0.58402	2.77346	0.01795
$\Delta K_S \times 10^{12}$ /Pa^{-1}	95.2	-118.3	-88.9	0.8

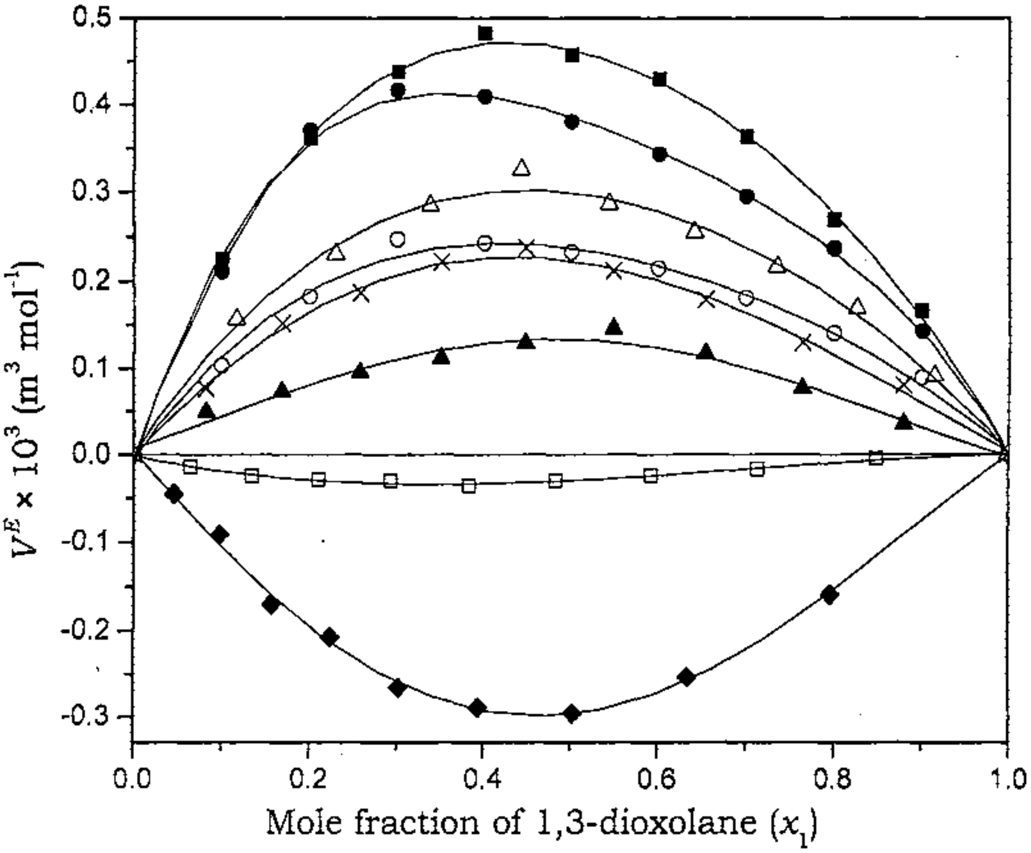

Figure 1.

Plots of excess molar volume (V^E) versus mole fraction of 1,3-dioxolane (x_1) at 303.15K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (O), 2-butanol (●), t-butanol (■) and i-amyl alcohol (Δ).

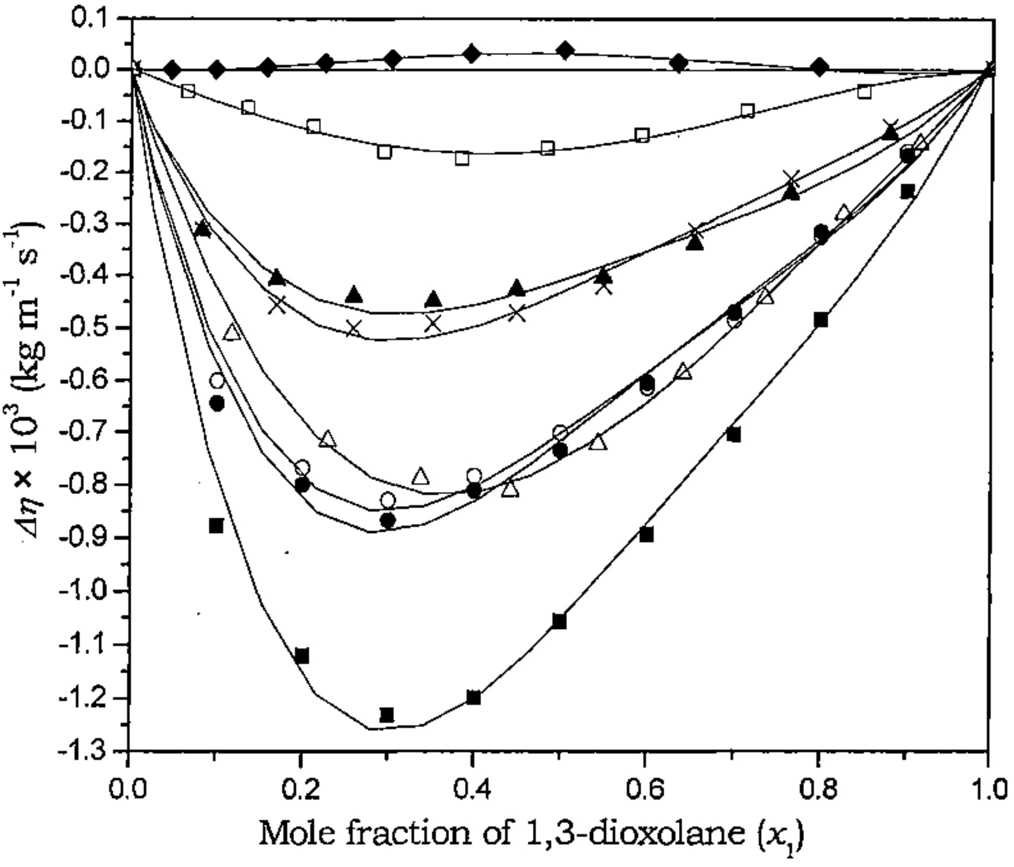

Figure 2.

Plots of viscosity deviations ($\Delta\eta$) versus mole fraction of 1,3-dioxolane (x_1) at 303.15K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (O), 2-butanol (●), t-butanol (■) and i-amyl alcohol (Δ).

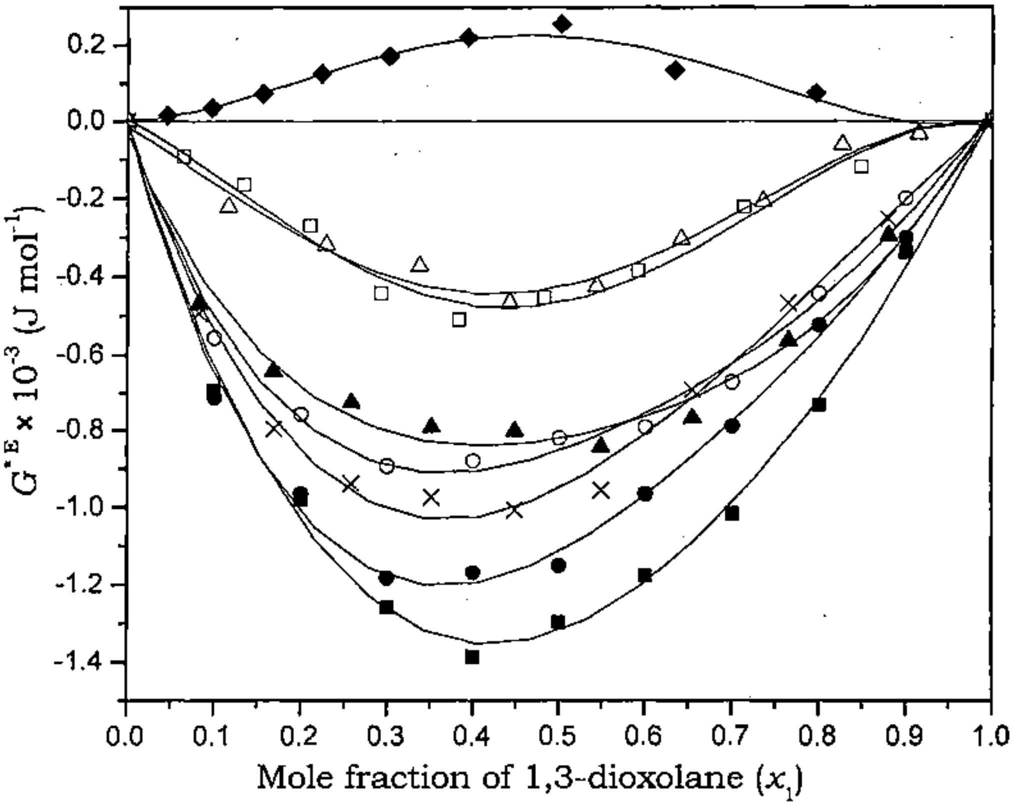

Figure 3.

Plots of Gibbs excess free energy of activation for viscous flow (G^{*E}) versus mole fraction of 1,3-dioxolane (x_1) at 303.15K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (X), 1-butanol (O), 2-butanol (●), t-butanol (■) and i-amyl alcohol (Δ).

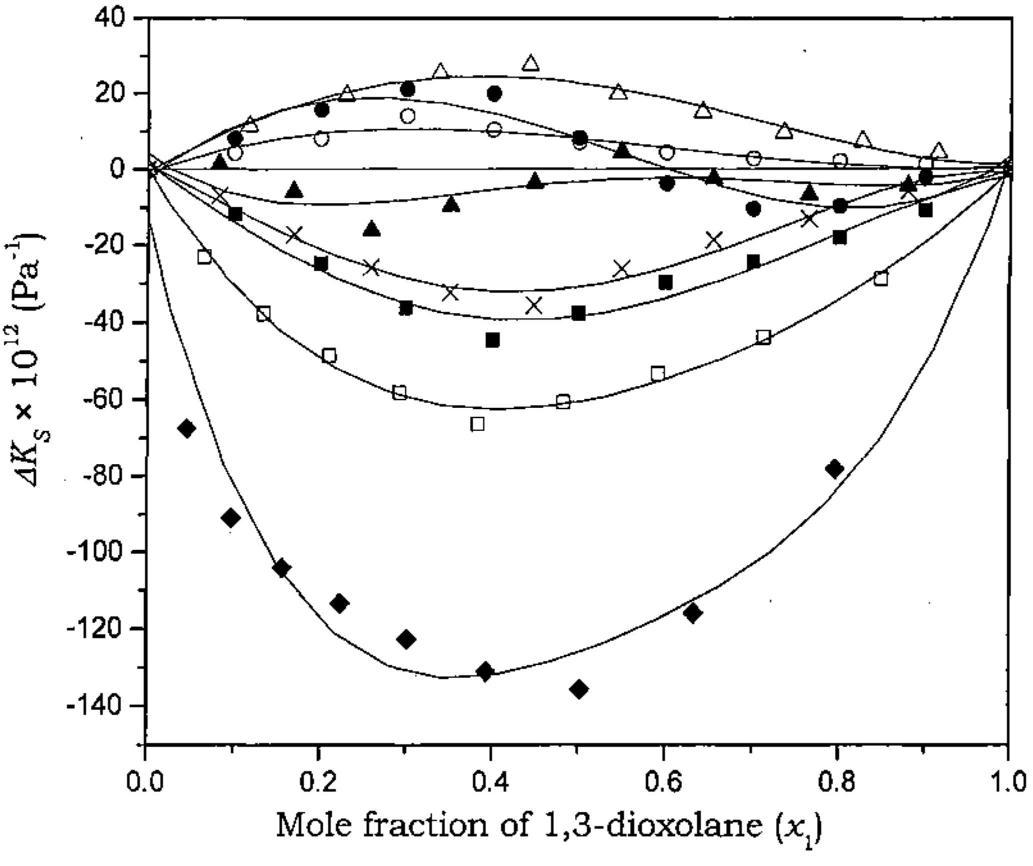

Figure 4.

Plots of Excess Isentropic compressibility (ΔK_S) versus mole fraction of 1,3-dioxolane (x_1) at 303.15K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (O), 2-butanol (●), t-butanol (■) and i-amyl alcohol (Δ).

CHAPTER IX

Ion-Solvent and Ion-Ion interactions of Sodium Molybdate in Aqueous Binary Mixtures of 1,4-Dioxane at Different Temperatures*

9.1. Introduction

Partial molar volumes of electrolytes at infinite dilution provide valuable information about ion-ion, ion-solvent and solvent-solvent interactions.[1-3] This information is of fundamental importance for a proper understanding of the behaviour of electrolytes in solution. Measurement of ultrasonic speeds of the solutions also helps in this regard. Recently, we have undertaken a comprehensive program to study the solvation and association behaviour of some electrolytes[3, 4] in different aqueous and non-aqueous solvent media from the measurement of various transport and thermodynamic properties. Aqueous 1,4-dioxane is an important mixed solvent for a number of separation processes and solution studies,[5] because of its wide-ranging relative permittivity (2.2 to 78.3 at 298.15 K). In this chapter, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of sodium molybdate in aqueous 1,4-dioxane mixtures from volumetric, viscometric and acoustic measurements at 303.15, 313.15 and 323.15 K and at various electrolyte concentrations. Partial molar volumes (ΔV_{ϕ}^{0}) and viscosity B-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane mixtures were determined and are discussed in terms of ion-solvent interactions. Partial molar volumes at infinite dilution have been fitted to a second order polynomial equation in terms of temperature and the structure-making or breaking capacity of the electrolyte has been inferred from the sign of $(\delta^{2}V_{\phi}^{0}/\delta T^{2})_{p}$. Also, adiabatic compressibility of different solutions has been determined from the measurement of ultrasonic speeds of sound at 303.15 K.

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9.2. Experimental Section

9.2.1 *Materials*

1,4-dioxane (Merck, India) was held for several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminium hydride ($LiAlH_4$). Details have been described earlier.[8] Doubly distilled, degassed and deionised water with a specific conductance of 1×10^{-6} ohm^{-1} cm^{-1} was used. Sodium molybdate ($Na_2MoO_4.2H_2O$), NICE, India was purified by recrystallizing twice from conductivity water and was dried in a vacuum desiccator over P_2O_5 for 24 hours before use. Experimental density (ρ_0) and viscosity (η_0) values of pure 1,4-dioxane and different aqueous 1,4-dioxane mixtures at 303.15 K, 313.15 K and 323.15 K are reported in Table 1 and are compared with earlier literature values.[3, 5, 6]

9.2.2 *Apparatus and procedures*

Densities were measured using an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal capillary diameter of ca. 0.1 cm. The pycnometer was calibrated at 303.15 K, 313.15 K and 323.15 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 temperatures. 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 total uncertainty of density is ± 0.0001 g cm^{-3} and that of the temperature is ± 0.01 K.

Viscosity was measured by means of a suspended Ubbelohde type viscometer, which was calibrated at 303.15 K, 313.15 K and 323.15 K with triply-distilled water and purified methanol using density and viscosity values from the literature. Flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was within ± 0.03% of the reported value. Ultrasonic speeds of sound for the solutions were determined at 298.15 K by a multi-frequency ultrasonic interferometer working at 2 MHz with an uncertainty of ± 0.2

m s^{-1}, as described earlier.[9] Details of the methods and techniques of density and viscosity measurements have been described earlier.[8, 9]

The electrolyte solutions studied here were prepared by mass and the conversion of molality to molarity was accomplished[3] using experimental density values. Experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

9.3. Results and discussion

Apparent molar volumes (V_ϕ) were determined from solution densities using the following equation:[3]

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

where M is the molar mass of the solute, c the molarity of the solution, ρ_0 and ρ the densities of the solvent and solution, respectively. The limiting apparent molar volumes or partial molar volumes (V_ϕ^0) at infinite dilution were calculated using a least-squares treatment of plots of V_ϕ versus $\sqrt{c}$ together with the Masson equation:[6]

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_V^* the experimental slope. Values of V_ϕ^0 and S_V^* along with their standard errors are reported in Table 3. Table 3 shows that V_ϕ^0 values are generally positive and increase with a rise in both temperature and amount of 1,4-dioxane in the ternary mixtures. This indicates the presence of strong ion-solvent interactions and these interactions are further strengthened at higher temperatures and higher mass% of 1,4-dioxane in the mixtures, suggesting larger electrostriction at higher temperatures and increased amount of cyclic diether. However, in the case of water, V_ϕ^0 values are positive and decrease with increase in temperature. This may be attributed to a slow desolvation[7,10] and thermal agitation at higher temperature. A perusal of Table 3 also reveals that S_V^* values are negative for all the solutions and at all experimental temperatures and S_V^* values decrease as the temperature of the solutions and amount of 1,4-dioxane in the mixtures increases. Since S_V^* is a measure of ion-ion interactions, the results indicate the presence of weak ion-ion interactions in the solutions at all experimental temperatures and these interactions further decrease with a rise in temperature and mass% of 1,4-dioxane in the solutions. This is probably due to more violent thermal agitation at higher temperatures and lower dielectric constants of the aqueous 1,4-dioxane mixtures, resulting in a diminishing force of ion-ion interactions (ionic dissociation).[11] However, these interactions increase in water at higher temperatures, which results in a decrease in hydration of ions, i.e. more and more solute in accommodated in the void space left in the packing of water molecules.[11]

Partial molar volumes (V_ϕ^0) at infinite dilution were fitted to a second order polynomial in terms of absolute temperature (T):

$$V_\phi^0 = a_0 + a_1T + a_2T^2 \tag{3}$$

Values of the coefficients a_0, a_1, and a_2 for different sodium molybdate solutions along with their standard errors (σ) are reported in table 4. From the values of coefficients the following equations were obtained:

For 10 mass% 1,4-dioxane + 90% water solutions

$$V_\phi^0 = -30891.740/\text{cm}^3\ \text{mol}^{-1} + 194.809T/\text{cm}^3\ \text{mol}^{-1} - 0.305T^2/\text{cm}^3\ \text{mol}^{-1} \tag{4}$$

For 20 mass% 1,4-dioxane + 80% water solutions

$$V_\phi^0 = -13694.068/\text{cm}^3\ \text{mol}^{-1} + 86.613T/\text{cm}^3\ \text{mol}^{-1} + 0.134T^2/\text{cm}^3\ \text{mol}^{-1} \tag{5}$$

For 30 mass% 1,4-dioxane + 70% water solutions

$$V_\phi^0 = 6943.536/\text{cm}^3\ \text{mol}^{-1} - 46.374T/\text{cm}^3\ \text{mol}^{-1} + 0.080T^2/\text{cm}^3\ \text{mol}^{-1} \tag{6}$$

For 100 mass% water solutions

$$V_\phi^0 = -3372.559/\text{cm}^3\ \text{mol}^{-1} + 28.544T/\text{cm}^3\ \text{mol}^{-1} - 0.055T^2/\text{cm}^3\ \text{mol}^{-1} \tag{7}$$

The partial molar expansibilities (ϕ_E^0) at infinite dilution can be obtained by differentiating equation (3) with respect to temperature:

$$\phi_E^0 = \left(\delta V_\phi^0 / \delta T\right)_P = a_1 + 2a_2 T \tag{8}$$

Values of ϕ_E^0 for different solutions of the studied electrolyte at 303.15 K, 313.15 K and 323.15 K are reported in Table 5. It is found from Table 5 that the values of ϕ_E^0 decrease with a rise in temperature as well as an increase in the amount of 1,4-dioxane in the mixtures up to 20 mass% of 1,4-dioxane, however, for 30 mass% of 1,4-dioxane mixtures, the solutions behave in an opposite manner. For aqueous solutions of sodium molybdate, the same trend as observed for the 10 mass% and 20 mass% of 1,4-dioxane solutions was observed. This can be ascribed to the absence of caging or packing effect.[11,12] According to Hepler,[13] the sign of $(\delta^2 V_\phi^0 / \delta T^2)_P$ is a better criterion than S_V^* in characterizing the long-range structure-making and breaking capacity of electrolytes in solution. The general thermodynamic expression used is:

$$\left(\delta C_P / \delta P\right)_T = -\left(\delta^2 V_\phi^0 / \delta T^2\right)_P \tag{9}$$

If the sign of $(\delta^2 V_\phi^0 / \delta T^2)_P$ is positive, the electrolyte is a structure-maker and when the sign of $(\delta^2 V_\phi^0 / \delta T^2)_P$ is negative, it is a structure-breaker. As is evident from Table 5, the electrolyte under investigation is a structure-breaker in all the experimental solvent mixtures except 30 mass% 1,4-dioxane solutions.

Viscosity data of solutions of sodium molybdate in 10 mass%, 20 mass% and 30 mass% 1,4-dioxane + water mixtures as well as pure water have been analyzed using the Jones-Dole[14] equation;

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \tag{10}$$

$$\frac{(\eta/\eta_0 - 1)}{\sqrt{c}} = A + B\sqrt{c} \tag{11}$$

where η_0 and η are the viscosities of solvent/solvent mixtures and solution, respectively. The coefficients A and B were estimated by a least-squares method and are reported in Table 6. A perusal of Table 6 shows that value of the A-coefficients are negative for all the solutions under investigation at all temperatures. These results indicate the presence of weak ion-ion interactions, and these interactions decrease with an increase in the amount of 1, 4-dioxane to the mixture.

The B-coefficient[15] reflects the effects of ion-solvent interactions on solution viscosity. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the near environment of solute molecules or ions. Table 6 indicates that values of the B-coefficient of sodium molybdate in the studied solvent systems are positive thereby suggesting the presence of strong ion-solvent interactions, and these types of interactions are strengthened with a rise in both temperature and mass% of 1,4-dioxane in the solutions. Similar results were reported earlier by us for resorcinol in aqueous 1, 4-dioxane mixtures[3] as described in chapter V.

A number of studies[16, 17] report that dB/dT is a better criterion for determining the structure-making/ breaking nature of any solute rather than the B-coefficient. Table 6 indicates that values of the B-coefficients increase with a rise in temperature (positive dB/dT), suggesting the structure-breaking tendency of sodium molybdate in the studied solvent systems. A similar result has been reported in a study[18] of the viscosity of various salts in propionic acid + ethanol mixtures.

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = u^{-2}\rho^{-1} \qquad (12)$$

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

The apparent molal adiabatic compressibility (ϕ_K) of the solutions was determined from the relation,

$$\phi_K = \frac{M\beta}{\rho_0} + \frac{1000(\beta\rho_0 - \beta_0\rho)}{m\rho\rho_0} \qquad (13)$$

where β_0, β are the adiabatic compressibility of the solvent and solution, respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were obtained by fitting ϕ_K against the square root of molality of the electrolyte ($\sqrt{m}$) using the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m} \tag{14}$$

Values of m, u, β, ϕ_K, ϕ_K^0 and S_K^* are presented in Table 7. A perusal of Table 7 shows that ϕ_K^0 values are positive and S_K^* values are negative for all the ternary solutions. Since the values of ϕ_K^0 and S_K^* are measures of ion-solvent and ion-ion interactions, respectively, the results are in good agreement with those drawn from the values of V_ϕ^0 and S_V^* discussed earlier.

Partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane solutions have been determined using the relations[19, 20].

$$\Delta V_\phi^0 = V_\phi^0(\text{Aqueous 1,4-dioxane solution}) - V_\phi^0(\text{Water}) \tag{15}$$

$$\Delta B = B\ (\text{Aqueous 1,4-dioxane solution}) - B\ (\text{Water}) \tag{16}$$

The value of ΔV_ϕ^0 is by definition free from ion-ion interactions and therefore provides information regarding ion-solvent interactions.[19] As can be seen from figure 1, the value of ΔV_ϕ^0 is negative at 303.15 K for 10 mass% of 1,4-dioxane solution but becomes positive at higher temperatures. ΔV_ϕ^0 is positive and increases monotonically with mass% of 1,4-dioxane in the remaining mixtures. These results further confirm the presence strong ion-solvent interactions in the chosen solvent mixtures for sodium molybdate. ΔB values[20] shown in Table 8 and figure 1 also support the results obtained from ΔV_ϕ^0 values.

9.4. Conclusion

In summary, the values of V_ϕ^0 and viscosity B - coefficients obtained for the solutions indicate the presence of strong ion-solvent and weak ion-ion interactions. Furthermore, sodium molybdate was found to be a structure breaker in all the aqueous 1,4-dioxane mixtures except aqueous 30 mass% 1,4-dioxane mixture.

References

[1] J. M. McDowali, C. A. Vincent, J. Chem. Soc. Faraday Trans., 1 (1974) 1862.

[2] M. R. J. Deck, K. J. Bird, A. J. Parker, Aust. J. Chem., 28 (1975) 955.

[3] M. N. Roy, B. Sinha, R. Dey, A. Sinha, Int. J. Thermophys., 26 (2005)1549.

[4] M. N. Roy, B. Sinha, V. K. Dakua, A. Sinha, Pak. J. Sci. Ind. Res., 49 (3) (2006) 153.

[5] D. P. Shoemaker, C. W. S. Garland, *Experiments in Physical Chemistry*, McGraw Hill., New York, pp131, (1967).

[6] D. O. Masson, Phil. Mag., 8 (1929) 218.

[7] E. Havega, D. G. Leaist, J. Chem. Soc. Faraday Trans., 94 (1988) 3353.

[8] M. N. Roy, B. Sinha, V. K. Dakua, J. Chem. Eng. Data., 51 (2006) 590.

[9] M. N. Roy, A. Sinha, B. Sinha, J. Soln. Chem., 34 (2005) 1311.

[10] C. Guha, J. M. Chakraborty, S. Karanjai, B. Das, J. Phys. Chem. B., 107 (2003) 12814.

[11] F. J. Millero. *Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, New York, (1972).

[12] M. L. Parmar, D. S. Banyal, Indian J. Chem., 44A (2005) 1582.

[13] L. G. Hepler, Can. J. Chem., 47 (1969) 4617.

[14] G. Jones, M. Dole, J. Am. Chem. Soc., 51 (1929) 2950.

[15] F. J. Millero, A. L. Surdo, C. Shin, J. Phys. Chem., 82 (1978) 784.

[16] R. Gopal, M. A. Siddique, J. Phys. Chem., 72 (1969) 1814.

[17] N. Saha, B. Das, J. Chem. Eng. Data., 42 (1997) 277.

[18] S. Martin Contreras, J. Chem. Eng. Data., 46 (2001) 149.

[19] K. Belibagli, E. Agranci, J. Soln. Chem., 19 (1990) 867.

[20] C. Zhao, P. Ma, J. Li, J. Chem. Thermodyn., 37 (2005) 37.

Table 1.

Physical properties of pure 1,4-dioxane and 1,4-dioxane + water mixtures at different temperatures.

Temperature (K)	ρ /g.cm^{-3}		η /mPa.s	
	This work	Literature	This work	Literature
10 mass% of 1,4-dioxane + water				
303.15	1.0058	1.0058 [3]	1.0320	1.0321 [3]
313.15	1.0041	1.0048 [3]	1.0015	1.0014 [3]
323.15	0.9973	0.9973 [3]	0.6895	0.6895 [3]
20 mass% of 1,4-dioxane + water				
303.15	1.0148	1.0148 [3]	1.2014	1.2014 [3]
313.15	1.0100	1.0100 [3]	1.0186	1.0186 [3]
323.15	1.0033	1.0033 [3]	0.8787	0.8787 [3]
30 mass% of 1,4-dioxane + water				
303.15	1.0202	1.0202 [3]	1.3977	1.3977 [3]
313.15	1.0162	1.0162 [3]	1.2493	1.2493 [3]
323.15	1.0103	1.0103 [3]	1.0755	1.0755 [3]
Pure 1,4-dioxane				
303.15	1.0199	1.0222 [5]	1.0886	1.0937 [5]
313.15	1.0144	1.0143 [6]	0.9785	0.9783 [6]
323.15	1.0027	1.0032 [6]	0.8441	0.8443 [6]

Table 2.
Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_ϕ), and $(\eta/\eta_0-1)/\sqrt{c}$ of sodium molybdate in water and aqueous 1,4-dioxane mixture at different temperatures.

c /mol .dm^{-3}	ρ /g .cm^{-3}	η /mPa.s	V_ϕ /cm^3 .mol^{-1}	$\frac{(\eta/\eta_0-1)}{\sqrt{c}}$
10 mass% of 1,4-dioxane + Water				
T = 303.15 K				
0.0241	1.0086	1.0336	125.042	0.0103
0.0321	1.0099	1.0356	113.565	0.0195
0.0561	1.0140	1.0433	95.230	0.0464
0.0723	1.0170	1.0491	86.538	0.0617
0.0883	1.0197	1.0555	84.045	0.0767
0.1003	1.0218	1.0606	81.953	0.0875
T = 313.15 K				
0.0240	1.0057	1.0041	174.568	0.0168
0.0319	1.0066	1.0073	162.912	0.0325
0.0559	1.0096	1.0172	142.974	0.0664
0.0719	1.0123	1.0244	127.380	0.0854
0.0878	1.0148	1.0320	119.592	0.1029
0.0998	1.017	1.0382	112.231	0.1159
T = 323.15 K				
0.0238	0.9990	0.6986	170.983	0.0856
0.0318	1.0000	0.7036	157.469	0.1144
0.0556	1.0035	0.7193	130.792	0.1836
0.0716	1.0065	0.7301	113.765	0.2201
0.0874	1.0094	0.7413	103.786	0.2544
0.0993	1.0119	0.7498	95.178	0.2774
20 mass% of 1,4-dioxane + Water				
T = 303.15 K				
0.0244	1.0168	1.2032	157.650	0.0096
0.0326	1.0177	1.2090	150.762	0.0349
0.0570	1.0212	1.2257	127.778	0.0846
0.0733	1.0238	1.2379	117.429	0.1123
0.0896	1.0268	1.2523	106.446	0.1416
0.1018	1.0293	1.2625	98.062	0.1595
T = 313.15 K				
0.0243	1.0115	1.0226	178.437	0.0250
0.0325	1.0125	1.0282	163.393	0.0521
0.0567	1.0160	1.0440	134.782	0.1046
0.0729	1.0187	1.0553	121.394	0.1333
0.0891	1.0219	1.0679	107.319	0.1621
0.1013	1.0247	1.0778	95.878	0.1825
T = 323.15 K				
0.0242	1.0047	0.8831	183.493	0.0321
0.0323	1.0057	0.8881	167.095	0.0595
0.0564	1.0094	0.9064	133.354	0.1326

Contd...

0.0724	1.0122	0.9189	118.630	0.1698
0.0886	1.0156	0.9325	102.785	0.2056
0.1006	1.0179	0.9435	96.502	0.2324
30 mass% of 1,4-dioxane + Water				
T = 303.15 K				
0.0228	1.0222	1.4013	151.177	0.0172
0.0304	1.0233	1.4079	137.205	0.0419
0.0532	1.0271	1.4304	110.028	0.1015
0.0684	1.0306	1.4465	88.123	0.1334
0.0835	1.0340	1.4639	75.162	0.1640
0.0950	1.0366	1.4781	67.946	0.1866
T = 313.15 K				
0.0227	1.0176	1.2553	177.402	0.0321
0.0303	1.0184	1.2622	166.643	0.0595
0.0530	1.0217	1.2874	135.974	0.1326
0.0680	1.0246	1.3046	116.533	0.1698
0.0830	1.0276	1.3233	102.933	0.2056
0.0944	1.0301	1.3385	93.194	0.2324
T = 323.15 K				
0.0225	1.0113	1.0790	195.492	0.0220
0.0301	1.0122	1.0859	177.004	0.0559
0.0527	1.0158	1.1087	136.183	0.1346
0.0677	1.0190	1.1254	112.285	0.1783
0.0826	1.0227	1.1421	90.893	0.2154
0.0939	1.0253	1.1582	81.367	0.2510
Pure water				
T = 303.15 K				
0.0241	0.9990	0.8028	105.474	0.0444
0.0322	1.0006	0.8083	90.164	0.0769
0.0563	1.0063	0.8262	53.905	0.1530
0.0723	1.0105	0.8395	37.408	0.1967
0.0884	1.0150	0.8542	23.726	0.2401
0.1004	1.0189	0.8654	10.921	0.2695
T = 313.15 K				
0.0240	0.9956	0.6577	101.072	0.0465
0.0321	0.9970	0.6625	93.144	0.0815
0.0561	1.0014	0.6781	78.570	0.1625
0.0720	1.0044	0.6878	73.075	0.1986
0.0879	1.0078	0.6988	64.982	0.2368
0.0963	1.0096	0.7059	61.746	0.2613
T = 323.15 K				
0.0239	0.9923	0.5547	67.015	0.0931
0.0319	0.9937	0.5586	67.201	0.1209
0.0558	0.9980	0.5704	65.308	0.1829
0.0717	1.0009	0.5793	64.192	0.2222
0.0876	1.0038	0.5873	63.482	0.2500
0.0959	1.0053	0.5920	63.350	0.2667

Table 3.

Limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_V^*) for sodium molybdate in different aqueous1,4-dioxane mixtures at different temperatures. Standard errors are given in parenthesis.

Mass % of 1,4-dioxane	V_ϕ^0 /cm^3.mol^{-1}			S_V^* /cm^2.dm$^{1/2}$.mol$^{-3/2}$		
	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0 (Water)	193.96 (± 0.013)	138.28 (± 0.013)	71.53 (± 0.011)	-578.82 (± 0.022)	-246.92 (± 0.015)	-26.77 (± 0.013)
10	162.66 (± 0.014)	232.88 (± 0.012)	242.16 (± 0.013)	-267.93 (± 0.011)	-384.50 (± 0.021)	-470.70 (± 0.014)
20	215.91 (± 0.012)	254.04 (± 0.013)	265.30 (± 0.012)	-366.91 (± 0.014)	-498.57 (± 0.013)	-542.25 (± 0.011)
30	231.96 (± 0.011)	260.93 (± 0.015)	305.89 (± 0.012)	-538.69 (± 0.013)	-547.73 (± 0.014)	-740.63 (± 0.012)

Table 4.

Values of the coefficients of equation (3) for sodium molybdate in different aqueous 1,4-dioxane mixtures.

Mass% of 1,4-dioxane	a_0 /cm^3.mol^{-1}	a_1 /cm^3.mol^{-1}	a_2 /cm^3.mol^{-1}
0 (water)	-3372.559	28.544	-0.055
10	-30891.740	194.809	-0.305
20	-13694.068	86.613	-0.134
30	6943.536	-46.374	0.080

Table 5.

Limiting partial molar expansibilities (ϕ_E^0) for sodium molybdate in various aqueous 1,4-dioxane mixtures at different temperatures.

Mass% of 1,4-dioxane	ϕ_E^0 / cm^3.mol^{-1}.K^{-1}			$\left(\frac{\delta\phi_E^0}{\delta T}\right)_p$
	303.15 *K*	313.15 *K*	323.15 *K*	
0 (Water)	-4.802	-5.902	-7.002	Negative
10	9.887	3.787	-2.312	Negative
20	5.187	2.501	-0.185	Negative
30	2.069	3.667	5.265	Positive

Table 6.

Values of *A* and *B* coefficients for sodium molybdate in different aqueous 1,4-dioxane mixtures at different temperatures. Standard errors are given in parenthesis.

Mass% of 1,4-dioxane	*A* / cm$^{3/2}$ .mol$^{-1/2}$			*B* / cm^3 .mol^{-1}		
	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0 (Water)	-0.172 (± 0.011)	-0.162 (± 0.012)	-0.079 (± 0.021)	1.384 (± 0.012)	1.356 (± 0.013)	1.116 (± 0.011)
10	-0.065 (± 0.011)	-0.077 (± 0.013)	-0.098 (± 0.012)	0.478 (± 0.011)	0.608 (± 0.012)	1.192 (± 0.014)
20	-0.132 (± 0.011)	-0.122 (± 0.023)	-0.0161 (± 0.012)	0.909 (± 0.011)	0.953 (± 0.012)	1.236 (± 0.021)
30	-0.145 (± 0.011)	-0.162 (± 0.014)	-0.195 (± 0.013)	1.071 (± 0.015)	1.278 (± 0.022)	1.439 (± 0.011)

Table 7.

Molality (*m*), density (*ρ*), sound speed (*u*), adiabatic compressibility (*β*), partial molal adiabatic compressibility (ϕ_K), Limiting partial adiabatic compressibility (ϕ_K^0), and experimental slope (S_K^*) of sodium molybdate in different aqueous 1,4-dioxane mixtures at 303.15 *K*. Standard errors are given in parenthesis.

m (mol kg-1)	*u* (m s-1)	$\beta \times 10^{10}$ (Pa-1)	$\phi_K \times 10^{10}$ (m3 mol-1 Pa-1)	$\phi_K^0 \times 10^{10}$ (m3 mol-1 Pa-1)	$S_K^* \times 10^{10}$ (m3 mol-3/2 Pa-1 kg1/2)
10 mass% of 1,4-dioxane + Water					
0.0240	1530.1	4.2349	-1.134		
0.0320	1532.5	4.2160	-1.353		
0.0561	1541.5	4.1504	-1.807	0.051	-7.770
0.0724	1548.5	4.1006	-2.034	(± 0.012)	(± 0.024)
0.0884	1557.2	4.0442	-2.224		
0.1005	1564.9	3.9963	-2.416		
20 mass% of 1,4-dioxane + Water					
0.0242	1572.2	3.979	0.390		
0.0323	1573.2	3.970	1.650		
0.0567	1577.0	3.977	-3.080	1.599	-7.901
0.0729	1580.3	3.911	-5.240	(± 0.011)	(± 0.013)
0.0891	1584.5	3.879	-7.450		
0.1013	1588.6	3.850	-9.200		
30 mass% of 1,4-dioxane + Water					
0.0224	1579.9	3.919	0.400		
0.0299	1580.4	3.913	0.182		
0.0524	1584.1	3.880	-0.380	1.756	-9.159
0.0674	1586.4	3.855	-0.640	(± 0.024)	(± 0.011)
0.0824	1590.0	3.826	-0.864		
0.0937	1593.4	3.799	-1.030		
Pure Water					
0.0243	1510.2	4.389	-2.960		
0.0324	1515.0	4.354	-3.250		
0.0567	1529.9	4.246	-3.770	-1.454	-9.829
0.0729	1542.7	4.158	-4.150	(± 0.012)	(± 0.011)
0.0891	1555.8	4.070	-4.410		
0.1012	1564.9	4.008	-4.540		

Table 8.

Partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to different aqueous 1,4-dioxane mixtures for sodium molybdate at different temperatures.

Mass% of 1,4-dioxane	V_ϕ^0	ΔV_ϕ^0	B	ΔB
		303.15 K		
0 (Water)	193.96 (± 0.013)	0.00	1.384 (± 0.012)	0.00
10	162.66 (± 0.014)	-31.30	0.478 (± 0.011)	-0.906
20	215.91 (± 0.012)	21.95	0.909 (± 0.011)	-0.475
30	231.96 (± 0.011)	38.00	1.071 (± 0.015)	-0.313
		313.15 K		
0 (Water)	138.28 (± 0.013)	0.00	1.356 (± 0.013)	0.00
10	232.88 (± 0.012)	94.60	0.608 (± 0.012)	-0.748
20	254.04 (± 0.013)	115.76	0.953 (± 0.012)	-0.403
30	260.93 (± 0.015)	122.65	1.278 (± 0.022)	-0.078
		323.15 K		
0 (Water)	71.53 (± 0.011)	0.00	1.116 (± 0.011)	0.00
10	242.16 (± 0.013)	170.63	1.192 (± 0.014)	0.076
20	265.30 (± 0.012)	193.77	1.236 (± 0.021)	0.120
30	305.89 (± 0.012)	234.36	1.439 (± 0.011)	0.323

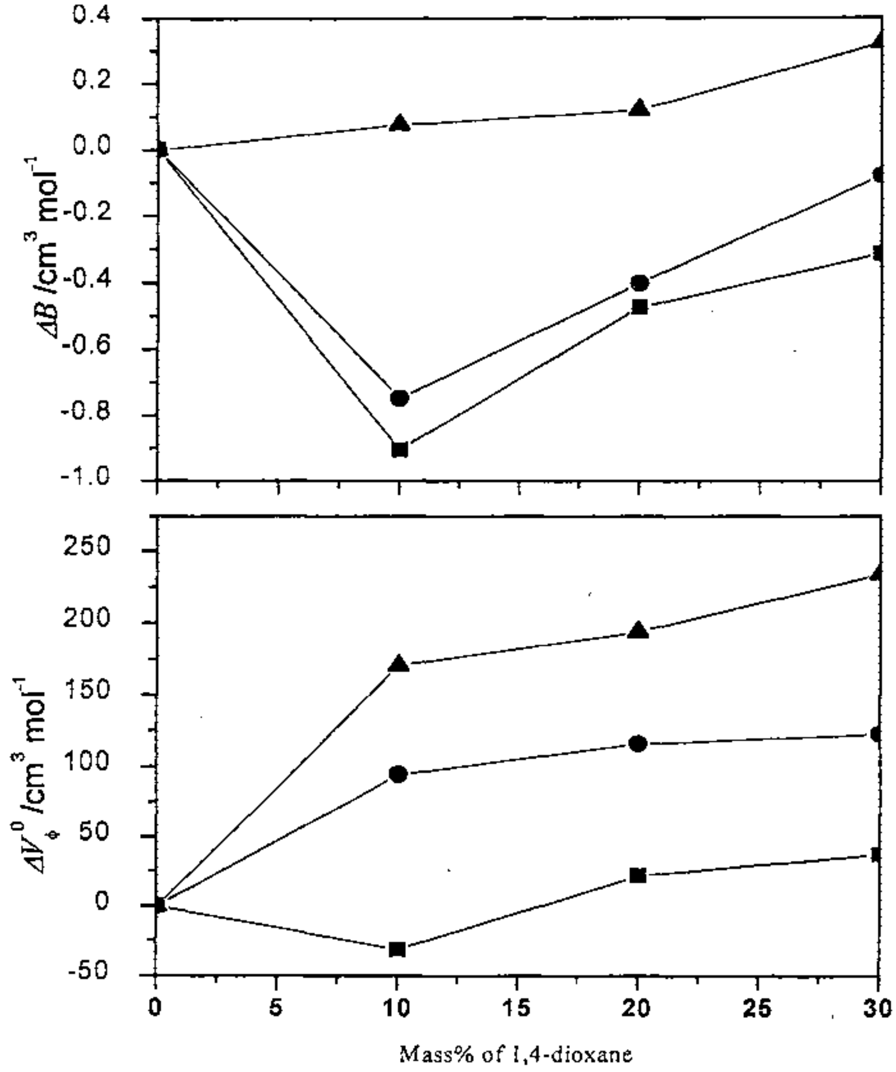

Figure 1.
Plots of partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to different aqueous 1,4-dioxane mixtures against mass% of 1,4-dioxane in the mixtures at different temperatures. 303.15 K (■); 313.15 K (●); 323.15 K (▲)

CHAPTER X

Studies on Excess Molar Volumes and Viscosity Deviations of Binary Mixtures of Butylamine and N, N-dimethylformamide with Some Alkyl Acetates at 298.15 K*

10.1. Introduction

Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. These properties are extremely useful for designing many types of transport and process equipment in chemical industries. There has been a recent upsurge of interest[1, 2] in the study of thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on intermolecular interactions and stereo chemical effects in these systems. BA and DMF are versatile solvents used in the separation of saturated and unsaturated hydrocarbons and in pharmaceutical synthesis, and serve as solvents for many polymers.[3] In this chapter we report experimental data for density (ρ) and viscosity (η) of the following mixtures at 298.15 K: butylamine (BA) or N, N- dimethylformamide (DMF) + methyl acetate (MA), ethyl acetate (EA), butyl acetate (BUA), and iso-amyl acetate (AA). Using these data, excess molar volume (V^E), viscosity deviation ($\Delta\eta$), Grunberg- Nissan (d_{12}), Tamura- Kurata (T_{12}), and Hind (H_{12}) interaction parameters have been calculated. These results have been fitted to Redlich-Kister type polynomial equations to estimate the binary coefficients and standard errors between the experimental and calculated values.

10.2. Experimental Section

10.2.1 *Materials*

Butylamine (S. D. Fine Chem, minimum assay GLC, 98%) was stored over sodium hydroxide pellets for several days and fractionally distilled twice.[4] N, N- dimethylformamide (S. D. Fine Chemicals, AR, purity>99%) was purified by the method described by Y. Zhao et al.[5] Methyl, ethyl, butyl and iso-amyl acetates (S. D. Fine Chemicals, AR, purity>99%) were used. Methyl acetate was washed with saturated solution of NaCl, dried with

Published in Indian Journal of Chemistry, Sec-A anhydrous $MgCl_2$, and then distilled. Ethyl acetate was dried over K_2CO_3, filtered, and distilled, and the first and the last portions of the distillate were discarded. The entire middle fraction was then distilled over P_2O_5. Butyl acetate and iso-amyl acetate were purified by drying over $CaCO_3$ overnight, filtered, and freshly distilled. The densities and viscosities of the solvents at 298.15 K were in good agreement with the literature values [5-8] as given in Table 1 and the purity of the solvents used in the present study is expected to be about 99.5%.

10.2.2 *Apparatus and procedures*

Densities (ρ) at 298.15 K were measured with an Ostwald –Sprengel type pycnometer having a bulb volume of about 25 cm^3 and the capillary of internal diameter of about 1 mm. The measurements were done in a thermostated bath controlled to ± 0.1 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. 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 details of the methods and techniques have been described earlier.[9-11] 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 mass measurements accurate to ± 0.01mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm^{-3}.

10.3. Results and discussion

10.3.1. Excess Molar Volume

The experimental viscosities, densities, excess volumes (V^E), viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 298.15 K are presented in Table 2. The excess molar volumes (V^E) were calculated using the equation,

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

where ρ is the density of the mixture and M_i, x_i and ρ_i are the molecular weight, mole fraction and density of i^{th} component in the mixture, respectively. The estimated uncertainty for excess molar volumes (V^E) is ± 0.005 $cm^3.mol^{-1}$. From Table 2, it is observed that excess molar volumes (V^E) for all the BA systems, except for that involving MA, are positive over the entire range of composition. The positive values of excess volumes (V^E) for the three systems follow the order:

BA + AA > BA + BUA > BA + EA

The excess molar volumes (V^E) for all the DMF systems are negative and their negative values follow the order:

DMF + MA > DMF + EA> DMF + BUA > DMF + AA

The negative values of excess molar volume (V^E) suggest specific interactions[12, 13] between the unlike molecules in the systems while its positive values suggest dominance of dispersion forces[12, 13] between them. Treszczanowicz et al.[14] suggested that V^E is the result of contributions from several opposing effects. These may be divided arbitrary into three types, namely, physical, chemical, and structural. Physical contributions contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change, therefore, depends on the relative strength of these effects. The negative values of excess molar volume (V^E) for all the mixtures studied may be attributed to dipole-induced dipole interactions between the unlike molecules in the binary mixtures through hydrogen bonding. The plots of excess molar volume (V^E) versus mole fraction (x_1) of BA or DMF for the binary mixtures are presented in figures 1 and 2. It is evident from the values of V^E that for both the binary systems, the degree of specific intermolecular interactions between unlike molecules in the binary mixtures decreases as the chain length of the alkyl acetate increases. The excess enthalpy values determined by Venkatesu et al.[15] for DMF + EA and DMF + BUA mixtures also report similar results.

10.3.2. Viscosity Deviation

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

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

where η is the dynamic viscosities 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 viscosity deviation ($\Delta\eta$) is ± 0.004 mPa.s. A perusal of Table 2 shows that the values of viscosity deviation ($\Delta\eta$) are negative over the entire composition range for all the binary mixtures studied and the negative values increase as the chain length of the alkyl acetates increases. It is observed in many systems that there is no simple correlation between the strength of the interactions and the observed properties. Rastogi et al.[16] therefore, suggested that the observed excess property is a combination of an interaction and a non-interaction part. The non-interaction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. In general, the negative values imply the presence of dispersion forces[17] in these mixtures; while positive values may be attributed to the presence of specific interactions.[17] The plots of viscosity deviation ($\Delta\eta$) versus mole fraction (x_1) for the different binary mixtures of BA and DMF have been presented in figures 3 and 4, respectively. The $\Delta\eta$ values for all the binary mixtures studied supported the results obtained from the values of V^E discussed earlier.

10.3.3. Correlation Equations

Several semiempirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data.[18, 19] Some of these that we examined are as follows:

Grunberg and Nissan[20] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp\left[\sum_{i=1}^{j}(x_i \ln\eta_i) + d_{12}\prod_{i=1}^{j} x_i\right] \tag{3}$$

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.

Tamura-Kurata[21] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \tag{4}$$

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

Molecular interactions may also be interpreted by the following viscosity model of Hind et al:[22]

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \tag{5}$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[23] The values of Grunberg-Nissan interaction parameter (d_{12}), the values of interaction parameters T_{12} and H_{12} have been calculated as a function of the composition of the binary mixtures of BA and DMF with MA, EA, BUA and AA, and were presented in Table 3.

From Table 3, it is seen that the values of d_{12} are negative for all the binary systems studied, except for the mixtures of DMF + MA. The negative values of d_{12} indicate the presence of dispersion forces[17] or weak specific interaction while its positive values indicate the presence of strong specific interactions[17] between the unlike molecules in the binary mixtures. Also for a given binary mixture, it has been observed that the values of 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[17] in regard to the nature of parameter T_{12} and H_{12}.

The excess properties (V^E and $\Delta\eta$) were fitted to the Redlich-Kister polynomial equation,

$$Y^E = x_1 x_2 \sum_{i=1}^{k} a_i (x_1 - x_2)^i \tag{6}$$

where Y^E refers to excess properties and x_1 and x_2 are the mole fraction BA or DMF and other component, respectively. The coefficients, a_i, were obtained by fitting equation (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 calculated values of a_i along with the tabulated standard deviations (σ) are listed in Table 4. The standard deviation (σ) was calculated using,

$$\sigma = [(Y^E_{\exp} - Y^E_{cal})^2/(n-m)]^{1/2} \tag{7}$$

where n is the number of data points and m is the number of coefficients. From Table 4, it is observed that the fits were good as presented by the small values of standard deviation (σ).

In the eight binary mixtures studied, it is really interesting to note that V^E and $\Delta\eta$ have maxima/minima in the mole fraction range x_1 = 0.5 to 0.7 (Table 2). This indicates that specific interaction between the component molecules is predominated by hydrogen bonding. The maximum/minimum points are clear indication of the highest point of interaction between the component molecules in the binary mixtures.

10.4. Conclusion

In summary, the V^E and $\Delta\eta$ values for the eight binary mixtures studied indicate that the degree of specific interactions between the mixing components decreases as the chain length of the alkyl acetates increases. This is in line with the concept of +I-effect of the alkyl groups of the alkyl acetates.

References

[1] E. Perez, M. Cardoso, A. M. Mainar, J. I. Pardo, J. S. Urieta, J. Chem. Eng. Data., 48 (2003) 1306.

[2] J. N. Nayak, T. M. Aminabhavi, M. I. Aralaguppi, J. Chem. Eng. Data., 48 (2003) 1152.

[3] P. S. Nikam, S. J. Kharat, J. Chem. Eng. Data., 50 (2005) 455.

[4] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory chemicals*, 3rd ed., Pergamon, Great Britain, (1988).

[5] Y. Zhao, J. Wang, X. Xuan, J. Lu, J. Chem. Eng. Data., 45 (2000) 440.

[6] C. M. Kinart, W. J. Kinart, D. Checinska-Majak, J. Chem. Eng. Data., 48 (2003) 1037.

[7] A. Pal, R. K. Bhardwaj, Z. Phys. Chem., 216 (2002) 1033.

[8] N. V. Sastry, M. C. Patel, J. Chem. Eng. Data., 48 (2003) 1019.

[9] M. N. Roy, D. K. Hazra, Indian. J. Chem. Technol., 1 (1994) 93.

[10] P. J. Victor, B. Das, D. K. Hazra, J. Phys. Chem. A., 105 (2001) 5960.

[11] P. K. Muhuri, D. K. Hazra, J. Chem. Eng. Data., 40 (1995) 582.

[12] R. C. Reid, J. M. Prausnitz, B. E. Poling, *The properties of Gases and Liquids*, 4th ed., McGraw-Hill International, New York, (1987).

[13] J. B. Irving, *Viscosities of Liquid Mixtures*, NEL Report No 630 and 631, National Engineering Laboratory, Glassgow, (1977).

[14] L. Grunberg, A. H. Nissan, Nature, 164 (1949) 799.

[15] M. Tamura, M. Kurata, Bull. Chem. Soc. Japan., 25 (1952) 32.

[16] R. K. Hind, E. McLaughlin, A. R. Ubbelohde, Trans. Faraday. Soc., 56 (1960) 328.

[17] S. L. Oswal, D. B. Gheewala, K. D. Prajapati, R. L. Gardas, N. Y. Ghael, S. P. Ijardar, Thermochim. Acta., 426 (2005) 141.

[18] K. Hsu-Chen, T. Chein-Hsiun, J. Chem. Eng. Data., 50 (2005) 608.

[19] M. N. Roy, A. Sinha, B. Sinha, J. Soln. Chem., 34 (2005) 1311 .

[20] P. S. Nikam, S. J. Kharat, J. Chem. Eng. Data., 50 (2005) 455.

[21] P. Venkatesu, R. S. Ramadevi, M. V. P. Rao, D. H. L. Prasad, J. Chem. Eng. Data., 45 (2000) 515.

[22] S. Viswanathan, M. A. Rao, J. Chem. Eng. Data., 45 (2000) 764.

[23] M. N. Roy, B. Sinha, V. Dakua, J. Chem. Eng. Data., 51 (2006), 590.

Table 1.
Comparison of experimental density and viscosity of pure liquids with literature values at 298.15 K.

Pure liquids	$\rho \times 10^{-3}$ (kg.m^{-3})		η (mPa.s)	
	Exp.	Lit.	Exp.	Lit.
Butylamine	0.7319	0.7331 [6]	0.4934	0.496 [7]
N, N- Dimethylformamide	0.9442	0.9440 [5]	0.8016	0.802 [5]
Methyl Acetate	0.9261	0.9268 [8]	0.3798	0.384 [8]
Ethyl Acetate	0.8941	0.894 [8]	0.4233	0.428 [8]
Butyl Acetate	0.8744	0.8762 [8]	0.6684	0.674 [8]
Iso- amyl Acetate	0.8660	0.8662 [8]	0.7822	0.781 [8]

Table2.

Values of density (ρ), viscosity (η), excess molar volume (V^E), viscosity deviation ($\Delta\eta$) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K.

Mole fraction (x_1)	ρ x 10^{-3} (kg. m^{-3})	η (mPa.s)	V^E x 10^6 (m^3. mol^{-1})	$\Delta\eta$ (mPa.s)
		BA (1) + MA (2)		
0	0.9261	0.3798	0	0
0.1011	0.9032	0.3847	-0.090	-0.007
0.2020	0.8827	0.3889	-0.308	-0.014
0.3027	0.8653	0.3942	-0.740	-0.020
0.4031	0.8501	0.4024	-1.330	-0.023
0.5032	0.8352	0.4109	-1.894	-0.026
0.6031	0.8191	0.4211	-2.270	-0.027
0.7027	0.7998	0.4359	-2.200	-0.024
0.8020	0.7776	0.4516	-1.685	-0.019
0.9011	0.7535	0.4701	-0.770	-0.012
1	0.7319	0.4934	0	0
		BA (1) + EA (2)		
0	0.8941	0.4233	0	0
0.1180	0.8741	0.4059	0.070	-0.026
0.2315	0.8546	0.3973	0.181	-0.042
0.3405	0.8364	0.3923	0.240	-0.055
0.4454	0.8188	0.3929	0.300	-0.062
0.5464	0.8015	0.3967	0.431	-0.065
0.6437	0.7860	0.4071	0.403	-0.061
0.7376	0.7720	0.4192	0.259	-0.056
0.8281	0.7588	0.4353	0.091	-0.046
0.9156	0.7454	0.4591	0.010	-0.028
1	0.7319	0.4934	0	0
		BA (1) + BUA (2)		
0	0.8744	0.6684	0	0
0.1500	0.8570	0.6056	0.101	-0.036
0.2842	0.8398	0.5618	0.269	-0.057
0.4050	0.8235	0.5299	0.389	-0.068
0.5143	0.8080	0.5081	0.469	-0.070
0.6136	0.7931	0.4887	0.530	-0.072
0.7043	0.7802	0.4786	0.391	-0.066
0.7875	0.7680	0.4715	0.211	-0.059
0.8640	0.7558	0.4714	0.100	-0.046
0.9346	0.7439	0.4753	0.020	-0.029
1	0.7319	0.4934	0	0
		BA (1) + AA (2)		
0	0.8660	0.7822	0	0
0.1651	0.8493	0.6901	0.181	-0.044
0.3080	0.8329	0.6290	0.400	-0.064
0.4327	0.8171	0.5855	0.590	-0.072
0.5427	0.8024	0.5512	0.680	-0.074

Contd...

0.6403	0.7885	0.5200	0.730	-0.077
0.7275	0.7766	0.5003	0.539	-0.072
0.8059	0.7650	0.4865	0.371	-0.063
0.8768	0.7538	0.4778	0.210	-0.051
0.9412	0.7428	0.4780	0.090	-0.032
1	0.7319	0.4934	0	0
DMF (1) + MA (2)				
0	0.9261	0.3798	0	0
0.1012	0.9292	0.4148	-0.112	-0.008
0.2022	0.9320	0.4504	-0.193	-0.015
0.3028	0.9347	0.4858	-0.275	-0.022
0.4032	0.9372	0.5236	-0.331	-0.026
0.5034	0.9393	0.5636	-0.349	-0.028
0.6032	0.9412	0.6045	-0.357	-0.030
0.7028	0.9425	0.6504	-0.312	-0.026
0.8021	0.9435	0.6976	-0.242	-0.020
0.9012	0.9438	0.7482	-0.117	-0.012
1	0.9442	0.8016	0	0
DMF (1) + EA (2)				
0	0.8941	0.4233	0	0
0.1181	0.8998	0.4567	-0.100	-0.011
0.2316	0.9056	0.4896	-0.198	-0.021
0.3406	0.9113	0.5232	-0.267	-0.029
0.4456	0.9168	0.5591	-0.315	-0.033
0.5466	0.9220	0.5955	-0.330	-0.035
0.6439	0.9269	0.6339	-0.308	-0.033
0.7377	0.9316	0.6737	-0.264	-0.029
0.8282	0.9359	0.7153	-0.183	-0.021
0.9156	0.9400	0.7573	-0.086	-0.012
1	0.9442	0.8016	0	0
DMF (1)+ BUA (2)				
0	0.8744	0.6684	0	0
0.1501	0.8816	0.6705	-0.091	-0.018
0.2843	0.8891	0.6761	-0.206	-0.030
0.4051	0.8963	0.6849	-0.258	-0.037
0.5144	0.9035	0.6955	-0.282	-0.041
0.6138	0.9107	0.7082	-0.296	-0.042
0.7045	0.9177	0.7247	-0.272	-0.037
0.7876	0.9243	0.7431	-0.213	-0.030
0.8641	0.9311	0.7612	-0.156	-0.022
0.9346	0.9375	0.7797	-0.070	-0.013
1	0.9442	0.8016	0	0
DMF (1)+ BUA (2)				
0	0.8660	0.7822	0	0
0.1652	0.8738	0.7649	-0.086	-0.020
0.3081	0.8819	0.7531	-0.192	-0.035
0.4329	0.8898	0.7483	-0.233	-0.042
0.5429	0.8977	0.7469	-0.247	-0.046
0.6404	0.9054	0.7481	-0.228	-0.046

Contd...

0.7277	0.9133	0.7548	-0.213	-0.041
0.8061	0.9210	0.7648	-0.172	-0.033
0.8769	0.9287	0.7750	-0.118	-0.024
0.9413	0.9363	0.7869	-0.046	-0.014
1	0.9442	0.8016	0	0

Table 3.
Grunberg-Nissan interaction parameter (d_{12}), Tamura- Kurata parameter (T_{12}), and Hind parameter (H_{12}) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K.

x_1	d_{12}	T_{12}	H_{12}
BA (1) + MA (2)			
0.1011	-0.1503	0.3997	0.4003
0.2020	-0.1803	0.3927	0.3938
0.3027	-0.1992	0.3874	0.3892
0.4031	-0.1983	0.3855	0.3884
0.5032	-0.2113	0.3806	0.3846
0.6031	-0.2274	0.3746	0.3799
0.7027	-0.2204	0.3733	0.3799
0.8020	-0.2311	0.3677	0.3758
0.9011	-0.2511	0.3591	0.3692
BA (1) + EA (2)			
0.1180	-0.5774	0.3354	0.3349
0.2315	-0.5554	0.3399	0.3397
0.3405	-0.5715	0.3361	0.3361
0.4454	-0.5778	0.3335	0.3336
0.5464	-0.5996	0.3271	0.3274
0.6437	-0.6001	0.3242	0.3247
0.7376	-0.6343	0.3135	0.3142
0.8281	-0.6945	0.2957	0.2967
0.9156	-0.7623	0.2740	0.2753
BA (1) + BUA (2)			
0.1500	-0.4148	0.4158	0.4381
0.2842	-0.4302	0.4244	0.4410
0.4050	-0.4532	0.4288	0.4406
0.5143	-0.4726	0.4327	0.4402
0.6136	-0.5349	0.4252	0.4284
0.7043	-0.5768	0.4223	0.4212
0.7875	-0.6569	0.4104	0.4043
0.8640	-0.7395	0.3977	0.3860
0.9346	-0.9348	0.3605	0.3396
BA (1) + AA (2)			
0.1651	-0.3566	0.4349	0.4768
0.3080	-0.3572	0.4555	0.4869
0.4327	-0.3674	0.4683	0.4918
0.5427	-0.4026	0.4713	0.4882
0.6403	-0.4918	0.4598	0.4700

Contd...

0.7275	-0.5633	0.4535	0.4567
0.8059	-0.6612	0.4414	0.4367
0.8768	-0.8218	0.4165	0.4012
0.9412	-1.0605	0.3763	0.3457
DMF (1) + MA (2)			
0.1012	0.1379	0.5514	0.5484
0.2022	0.1204	0.5482	0.5451
0.3028	0.0949	0.5425	0.5393
0.4032	0.0825	0.5394	0.5361
0.5034	0.0749	0.5372	0.5337
0.6032	0.0595	0.5324	0.5286
0.7028	0.0617	0.5327	0.5287
0.8021	0.0560	0.5303	0.5261
0.9012	0.0551	0.5294	0.5250
DMF (1) + EA (2)			
0.1181	0.0046	0.5802	0.5582
0.2316	-0.0133	0.5756	0.5526
0.3406	-0.0254	0.5723	0.5479
0.4456	-0.0257	0.5721	0.5461
0.5466	-0.0313	0.5703	0.5427
0.6439	-0.0321	0.5698	0.5405
0.7377	-0.0330	0.5694	0.5383
0.8282	-0.0295	0.5704	0.5376
0.9156	-0.0388	0.5671	0.5322
DMF (1) + BUA (2)			
0.1501	-0.1893	0.6940	0.6648
0.2843	-0.1978	0.6945	0.6608
0.4051	-0.2045	0.6955	0.6572
0.5144	-0.2150	0.6949	0.6521
0.6138	-0.2268	0.6938	0.6464
0.7045	-0.2262	0.6969	0.6449
0.7876	-0.2222	0.7008	0.6447
0.8641	-0.2300	0.7007	0.6401
0.9346	-0.2591	0.6938	0.6270
DMF (1) + AA (2)			
0.1652	-0.1914	0.7440	0.7176
0.3081	-0.2134	0.7416	0.7096
0.4329	-0.2237	0.7444	0.7058
0.5429	-0.2395	0.7445	0.6996
0.6404	-0.2616	0.7422	0.6909
0.7277	-0.2697	0.7448	0.6872
0.8061	-0.2699	0.7496	0.6864
0.8769	-0.2846	0.7494	0.6798
0.9413	-0.3097	0.7460	0.6689

Table 4.

Values of coefficients a_i of equation (6) and their standard deviations (σ) for the excess properties (V^E and $\Delta\eta$) of the binary mixtures of BA or DMF (1) + some alkyl acetates (2) at 298.15 K.

Binary mixture	Excess property	a_0	a_1	a_2	a_3	σ
BA + MA	$V^E \times 10^6$	-7.536	-10.229	2.901	8.387	0.011
	$\Delta\eta$	-0.104	-0.031	-	-	0.000
BA + EA	$V^E \times 10^6$	1.535	1.144	-1.694	-2.644	0.034
	$\Delta\eta$	-0.255	-0.041	-0.017	-0.043	0.001
BA + BUA	$V^E \times 10^6$	1.940	1.047	-2.131	-1.934	0.030
	$\Delta\eta$	-0.283	-0.035	-0.109	-0.084	0.001
BA + AA	$V^E \times 10^6$	2.685	1.678	-1.981	-2.086	0.029
	$\Delta\eta$	-0.297	-0.044	-0.184	-0.095	0.002
DMF + MA	$V^E \times 10^6$	-1.425	-0.335	0.199	0.355	0.007
	$\Delta\eta$	-0.116	-0.030	-0.014	-	0.000
DMF + EA	$V^E \times 10^6$	-1.301	-0.275	0.163	0.203	0.002
	$\Delta\eta$	-0.136	-0.027	-0.263	-	0.000
DMF + BUA	$V^E \times 10^6$	-1.162	-0.376	0.264	-	0.009
	$\Delta\eta$	-0.164	-0.037	-0.069	-0.081	0.001
DMF + AA	$V^E \times 10^6$	-0.984	-0.268	0.245	-	0.009
	$\Delta\eta$	-0.182	-0.054	-	-	0.001

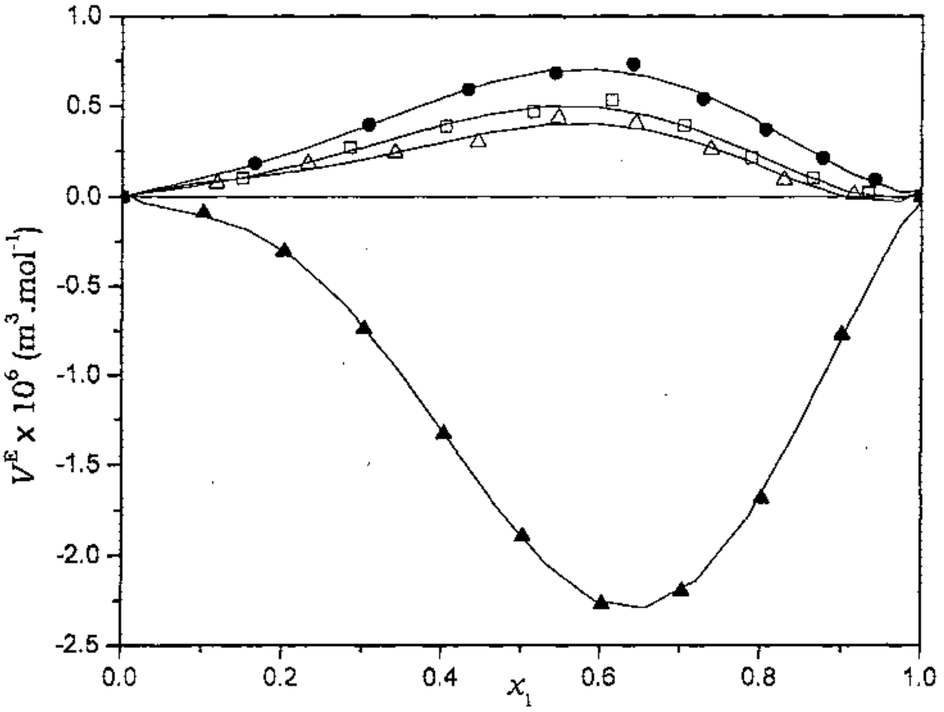

Figure 1.

Plots of excess molar volume (V^E) versus mole fraction of BA (x_1) at 298.15K for binary mixtures of BA with MA (▲), EA (△), BUA (□), AA (●).

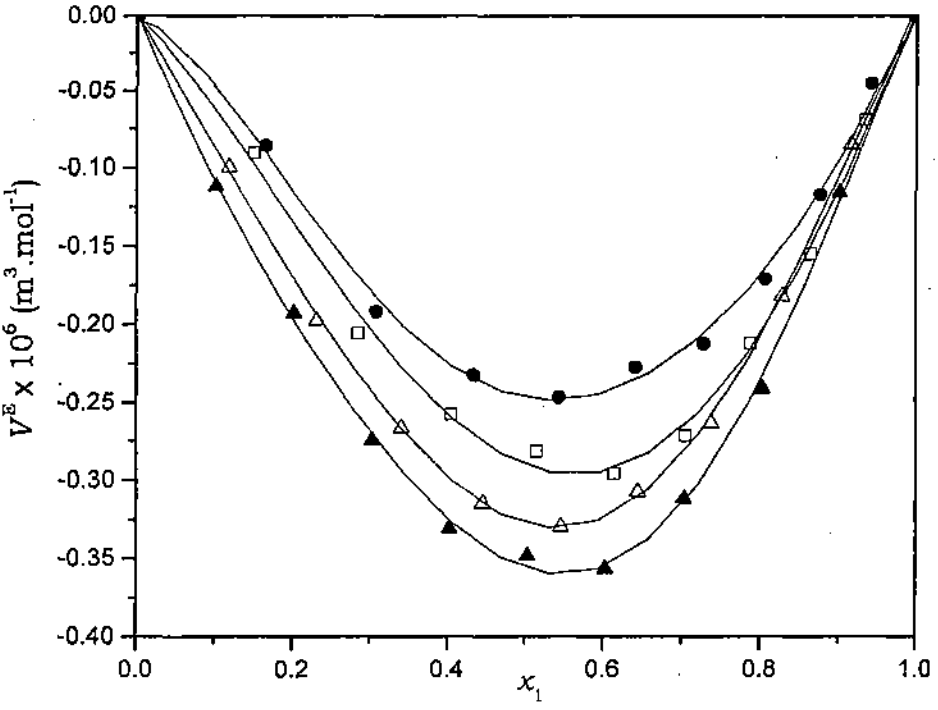

Figure 2.

Plots of excess molar volume (V^E) versus mole fraction of DMF (x_1) at 298.15K for binary mixtures of DMF with MA (▲), EA (Δ), BUA (□), AA (●).

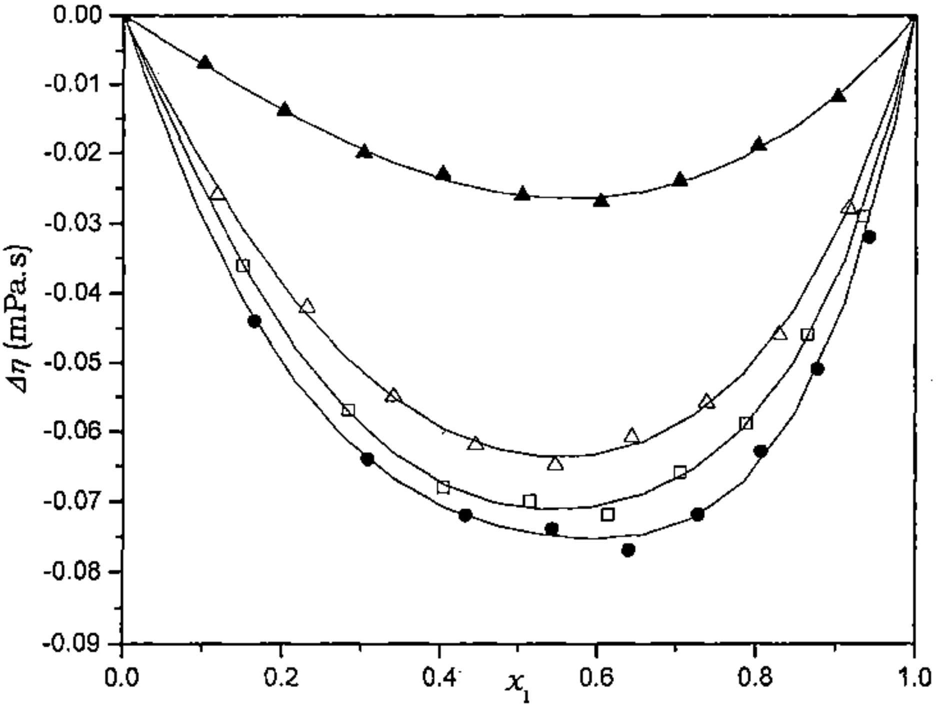

Figure 3.

Plots of viscosity deviation ($\Delta\eta$) versus mole fraction of BA (x_1) at 298.15 K for binary mixtures of BA with MA (▲), EA (Δ), BUA (□), AA (●).

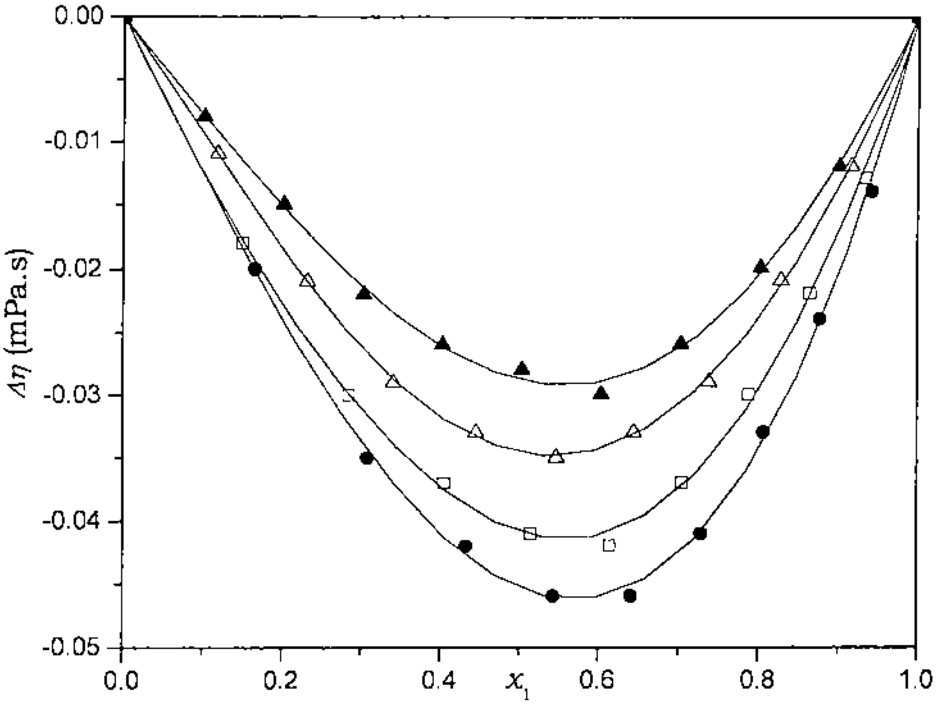

Figure 4. Plots of viscosity deviation ($\Delta\eta$) versus mole fraction of DMF (x_1) at 298.15K for binary mixtures of DMF with 1, MA (▲), 2, EA (△), 3, BUA (□), 4, AA (●).

CHAPTER XI

Excess Molar Volume and Viscosity Deviations of Binary Liquid Mixtures of 1,3-Dioxolane and 1,4-Dioxane with Butyl acetate, Butyric Acid, Butylamine and 2-Butanol at 298.15 K*

11.1. Introduction

Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. Properties of the mixtures are useful for the designing many types of transport and process equipment in chemical industries.[1-5] 1,4-dioxane, 1,3-dioxolane and their binary liquid mixtures are important solvents widely used in various industries. 1,4-dioxane and 1,3-dioxolane are cyclic diethers differing in one methylene group, thus they differs in quadrupolar and dipolar order.[6]

In this chapter we report density and viscosity for {1,4-dioxane or 1,3-dioxolane + butyl acetate, butyric acid, butylamine, 2-butanone} mixtures at 298.15 K. From density and viscosity data, the values of excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) have been determined. These results were fitted to Redlich–Kister type polynomial equations. The density and viscosity data have been analyzed for in term of some semi empirical viscosity models.

11.2. Experimental Section

11.2.1. Materials

1,4-dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminium hydride ($LiAlH_4$). Details have been described earlier.[1] 1,3-dioxolane (Merck, India) was purified by standard methods.[7] It was refluxed with PbO_2, fractionally distilled after addition of xylene. Butyl acetate, butyric acid, butylamine, 2-butanone (SD Fine Chemicals, Analytical Reagent, Purity > 99%) were used without further purification. 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 [8-13] as listed in Table 1.

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11.2.2. Apparatus and procedures

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 298.15 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 absolute temperature was determined by a calibrated platinum resistant thermometer and 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. An average of triplicate measurements was 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 ± 0.0002 units. The mass measurements accurate to ± 0.01mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty of density is ± 0.0001 g.cm^{-3} and that of the 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 triply distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was within ± 0.03% of the reported value. Details of the methods and techniques of density and viscosity measurements have been described earlier.[4, 14]

11.3. Results and Discussion

The experimental viscosities, densities, excess volumes (V^E) and viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 298.15 K are listed in Table 2.

11.3.1. Excess molar volume (V^E)

The excess molar volumes (V^E) were calculated using the equation,

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

where ρ is the density of the mixture and M_i, x_i and ρ_i are the molecular weight, mole fraction and density of ith component in the mixture, respectively. The values of excess molar volume (V^E) have been presented in Table 2. The estimated uncertainty for excess molar volumes (V^E) is ± 0.005 $cm^3.mol^{-1}$.

The excess molar volumes (V^E) for all the 1,3-dioxolane systems, except for the system involving butylamine, are negative over the entire range of composition. The negative values of excess volumes (V^E) for the three systems are in the order:

1,3-dioxolane + Butyric acid > 1,3-dioxolane + 2-Butanone > 1,3-dioxolane + Butyl acetate

The excess molar volumes (V^E) for the two 1,4-dioxane systems involving butylamine and butyl acetate are positive, while for the other two 1,4-dioxane systems involving 2-butanone and butyric acid are negative. The order V^E values for the 1,4-dioxane systems irrespective of their sign is as follows:

1,4-dioxane + Butylamine > 1,4-dioxane + Butyl acetate > 1,4-dioxane + 2-butabnone > 1,4-dioxane + Butyric acid

The negative values of excess molar volume (V^E) suggest specific interactions[15] between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces [16,13] between them. The negative V^E values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. The negative V^E values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.[15] The negative V^E values for all the systems studied may be attributed to dipole-induced dipole interactions between the components liquids of the mixtures resulting in the formation of electron donor-acceptor complexes.[17] The plots of excess molar volume (V^E) versus mole fraction (x_1) of 1,3-dioxolane or 1,4-dioxane are presented in Figures 1 and 2.

11.3.2. Viscosity deviation ($\Delta\eta$)

The deviation in viscosities ($\Delta\eta$) was computed using the relationship,[18]

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

where η is the dynamic viscosities of the mixture and x_i, η_i are the mole fraction and viscosity of ith component in the mixture, respectively.

A perusal of Table 2 shows that the values of viscosity deviation ($\Delta\eta$) are negative over the entire composition range for all the binary liquid mixtures studied except for the mixtures involving butyric acid. The estimated uncertainty for viscosity deviation ($\Delta\eta$) is ± 0.004 mPa.s. The negative values imply the presence of dispersion forces[18] between the mixing components in these mixtures, while positive values may be attributed to the presence of specific interactions[18] between them. The plots of viscosity deviation ($\Delta\eta$) versus mole fraction (x_1) for the different binary mixtures have been presented in Figures 3 and 4.

11.3.3. Viscosity models and Interaction parameters

Several semi-empirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data.[19, 20] Some of them we examined are as follows:

a) Grunberg and Nissan[21] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp[\sum_{i=1}^{j}(x_i \ln\eta_i) + d_{12}\prod_{i=1}^{j}x_i] \qquad (3)$$

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 as a function of the composition of the binary liquid mixtures of 1,3-dioxolane and 1,4-dioxane with butyl acetate, butyric acid, butylamine and 2-butanone were listed in Table 2.

It has been found that the values of d_{12} are negative for all the binary systems studied, except the systems involving butyric acid. The negative values of d_{12} indicate the presence of dispersion forces[18] between the mixing components in the mixtures while its positive values indicate the presence of specific interactions[18] between them.

b) Tamura-Kurata [22] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \tag{4}$$

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

c) Molecular interactions may also be interpreted by the following viscosity model of Hind et al:[23]

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \tag{5}$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[24] In the present study, the values of interaction parameter T_{12} and H_{12} have been calculated from equation (4) and (5), respectively and were listed in Table 2. 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[18] in regard to the nature of parameter T_{12} and H_{12}. It is also significant to note that the values of T_{12} and H_{12} are larger for the binary mixtures of butyric acid with both the cyclic ethers, which involve specific molecular interactions as revealed by the positive values of $\Delta\eta$ and d_{12}.[25]

11.3.4. Redlich-Kister polynomial equation

The excess properties (V^E and $\Delta\eta$) were fitted to the Redlich-Kister polynomial equation,[26]

$$Y^E = x_1 x_2 \sum_{i=1}^{k} a_i (x_1 - x_2)^i \tag{6}$$

where Y^E refers to excess properties and x_1 and x_2 are the mole fraction 1,3-dioxolane or 1,4-dioxane and other component, respectively. The coefficients a_i were obtained by fitting equation (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 calculated values of a$_i$ along with the tabulated standard deviations (σ) are listed in Table 3. The standard deviation (σ) was calculated using,

$$\sigma = [(Y^E_{\exp} - Y^E_{cal})^2 / (n - m)]^{1/2} \qquad (7)$$

where n is the number of data points and m is the number of coefficients. The σ values lie between 0.013 m^3.mol^{-1} and 0.001 m^3.mol^{-1} for V^E and between 0.006 mPa.s and 0.001 mPa.s for $\Delta\eta$, respectively. The largest σ values corresponds to the 1,3-dioxolane + 2-butanone system for V^E and the 1,4-dioxane + butyric acid for $\Delta\eta$, respectively. In the present study both V^E and $\Delta\eta$ are quite systematic and functions of the composition of the binary mixtures.

11.4. Conclusion

In general, for both the cyclic diether binary systems the order of specific or chemical interaction has been found to be: Butyric acid > 2-Butanone > Butyl acetate > Butylamine. More extensive studies are, however, required to arrive at a concrete conclusion about the above order and nature of solvent-solvent interactions.

References

[1] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1247.

[2] C. G. Janz, R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook*, Academic Press, New York, Vol. 2 (1973).

[3] R. Jasinki, *High Energy Batteries*, Plenum Press, New York, (1967).

[4] M. N. Roy, D. K. Hazra, Indian J. Chem. Technol., 1 (1994) 93.

[5] F. J. Millero, *Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, New York, (1972).

[6] P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo, J. Chem. Eng. Data., 48 (1999) 1341.

[7] J. Riddick, W. B. Bunger, T. K. Sakano, *Organic solvents. Physical Properties and Methods of Purification*, 4th ed., Wiley, New York, Vol-2 (1986).

[8] S. Martin Contreras, J. Chem. Eng. Data., 46 (2001) 1149.

[9] R. Francesconi, F. Comelli, J. Chem. Eng. Data., 40 (1995) 31.

[10] N. V. Sastry, M. C. Patel, J. Chem. Eng. Data., 48 (2003) 1019.

[11] C. M. Kinart, W. J. Kinart, D. Checinska-Majak, J. Chem. Eng. Data., 48 (2003) 1037.

[12] A. Pal, R. K. Bhardwaj, Z. Phys. Chem., 216 (2002) 1033.

[13] K. Hsu-Chen, T. Chein-Hsiun, J. Chem. Eng. Data., 50 (2005) 608.

[14] P. S. Nikam, M. Hosan, J. Chem. Eng. Data., 33 (1988) 165.

[15] J. N. Nayak, M. I. Aralaguppi, T. M. Aminabhavi, J. Chem. Eng. Data., 48 (2003) 1489.

[16] M. N. Roy, A. Sinha, B. Sinha, J. Soln . Chem., 34 (2005) 1311.

[17] P. Jain, M. Singh, J. Chem. Eng. Data., 49 (2004)1214.

[18] R. J. Fort, W. R. Moore, Trans. Faraday. Soc., 62 (1966) 1112.

[19] R. C. Reid, J. M. Prausnitz, B. E. Poling, *The properties of Gases and Liquids*, 4th ed., McGraw-Hill International, (1987).

[20] J. B. Irving, *Viscosities of Liquid Mixtures*, NEL Report No 630 and 631, National Engineering Laboratory, East Kilbride, Glassgow, (1977).

[21] L. Grunberg, A. H. Nissan, Nature., 164 (1949) 799.

[22] M. Tamura, M. Kurata, Bull. Chem. Soc. Jpn., 25 (1952) 32.

[23] R. K. Hind, E. McLaughlin, A. R. Ubbelohde, Trans. Faraday. Soc., 56 (1960) 328.

[24] S. L. Oswal, H. S. Desai, Fluid Phase Equilibr., 186 (2001) 81.

[25] P. Jain, M. Singh, J. Indian. Chem. Soc., 82 (2005) 225.

[26] O. Redlich, A. T. Kister, Ind. Eng. Chem., 40 (1948) 345.

Table 1.

Comparison of density (ρ), viscosity (η) of the Pure Liquids with Literature Data at 298.15 K.

Pure Liquid	ρ / (g.cm^{-3})		η / (mPa.s)	
	Expt.	Lit.	Expt.	Lit.
1,4-Dioxane	1.0265	1.0278 [8]	1.1956	1.196 [8]
1,3-Dioxolane	1.0571	1.0587 [9]	0.5307	-
Butyl acetate	0.8744	0.8761 [10]	0.6684	0.674 [10]
Butyric acid	0.9528	-	1.3962	-
Butylamine	0.7319	0.7331 [11]	0.4934	0.496 [12]
2-Butanone	0.7981	0.7996 [13]	0.3728	0.378 [13]

Table 2.
Values of density (ρ), viscosity (η), excess molar volume (V^E), viscosity deviation ($\Delta\eta$) and different interaction parameters for the binary mixtures of 1,4-dioxane or 1,3-dioxolane at 298.15 K.

x_1	ρ /(g.cm^{-3})	η /(mPa.s)	$V^E \times 10^6$ /(m^3.mol^{-1})	$\Delta\eta$ /(mPa.s)	d_{12}	T_{12}	H_{12}
1,3-dioxolane (1) + 2-Butanone (2)							
0	0.7981	0.3728	0	0	-	-	-
0.0976	0.8189	0.3843	-0.084	-0.004	-0.0479	0.4405	0.4293
0.1957	0.8405	0.3972	-0.133	-0.006	-0.0368	0.4430	0.4311
0.2944	0.8631	0.4113	-0.164	-0.008	-0.0276	0.4451	0.4325
0.3935	0.8868	0.4258	-0.185	-0.009	-0.0260	0.4455	0.4325
0.4933	0.9118	0.4408	-0.201	-0.010	-0.0273	0.4454	0.4319
0.5935	0.9381	0.4564	-0.207	-0.010	-0.0311	0.4447	0.4306
0.6943	0.9655	0.4731	-0.173	-0.009	-0.0330	0.4444	0.4297
0.7956	0.9942	0.4910	-0.113	-0.007	-0.0352	0.4440	0.4298
0.8975	1.0245	0.5102	-0.045	-0.004	-0.0366	0.4438	0.4279
1	1.0571	0.5307	0	0	-	-	-
1,3-dioxolane (1) + Butyric acid (2)							
0	0.9528	1.3962	0	0	-	-	-
0.1167	0.9631	1.2966	-0.067	0.001	0.3771	0.9201	0.9703
0.2292	0.9737	1.2017	-0.150	0.004	0.4054	0.9243	0.9743
0.3376	0.9843	1.1107	-0.209	0.007	0.4372	0.9283	0.9784
0.4422	0.9953	1.0231	-0.276	0.010	0.4735	0.9325	0.9829
0.5432	1.0061	0.9379	-0.302	0.012	0.5140	0.9363	0.9873
0.6408	1.0169	0.8541	-0.317	0.012	0.5576	0.9389	0.9906
0.7351	1.0272	0.7702	-0.270	0.010	0.5965	0.9373	0.9897
0.8263	1.0374	0.6882	-0.206	0.007	0.6393	0.9353	0.9882
0.9146	1.0473	0.6077	-0.113	0.003	0.6751	0.9297	0.9827
1	1.0571	0.5307	0	0	-	-	-
1,3-dioxolane (1) + Butyl acetate (2)							
0	0.8744	0.6684	0	0	-	-	-
0.1484	0.8907	0.6213	-0.128	-0.027	-0.3078	0.4728	0.4939
0.2816	0.9069	0.5986	-0.149	-0.031	-0.2239	0.5167	0.5230
0.4019	0.9233	0.5876	-0.129	-0.025	-0.1506	0.5490	0.5465
0.5111	0.9403	0.5828	-0.103	-0.015	-0.0771	0.5761	0.5690
0.6106	0.9578	0.5774	-0.072	-0.007	-0.0230	0.5939	0.5851
0.7017	0.9761	0.5712	-0.050	-0.001	0.0224	0.6068	0.5981
0.7853	0.9952	0.5651	-0.034	0.005	0.0783	0.6204	0.6138
0.8625	1.0150	0.5558	-0.023	0.006	0.1211	0.6291	0.6253
0.9338	1.0356	0.5442	-0.012	0.004	0.1568	0.6349	0.6344
1	1.0571	0.5307	0	0	-	-	-
1,3-dioxolane (1)+ Butylamine (2)							
0	0.7319	0.4934	0	0	-	-	-
0.1001	0.7551	0.4767	0.013	-0.020	=0.4626	0.3922	0.3988
0.2001	0.7796	0.4629	0.038	-0.038	-0.0489	0.3907	0.3937
0.3002	0.8058	0.4576	0.065	-0.047	-0.4628	0.4022	0.4001
0.4002	0.8338	0.4546	0.082	-0.054	-0.4630	0.4062	0.4002
0.5002	0.8641	0.4561	0.085	-0.056	-0.4606	0.4103	0.4003
0.6002	0.8968	0.464	0.077	-0.052	-0.4384	0.4185	0.4041
0.7002	0.9321	0.4784	0.058	-0.041	-0.3899	0.4319	0.4142

Contd...

0.8001	0.9703	0.4963	0.039	-0.027	-0.3285	0.4478	0.4277
0.9001	1.0118	0.5135	0.021	-0.013	-0.2860	0.4590	0.4370
1	1.0571	0.5307	0	0	-	-	-
1,4-Dioxane (1) +2-Butanone (2)							
0	0.7981	0.3728	0	0	-	-	-
0.0833	0.8170	0.3915	-0.077	-0.050	-0.632	0.4613	0.4576
0.1698	0.8365	0.4109	-0.124	-0.102	-0.7139	0.4283	0.4237
0.2597	0.8568	0.4364	-0.160	-0.150	-0.7555	0.3997	0.3938
0.3530	0.8779	0.4636	-0.186	-0.200	-0.8467	0.3545	0.3472
0.4501	0.9001	0.5124	-0.202	-0.231	-0.8346	0.3275	0.3180
0.5511	0.9233	0.5763	-0.205	-0.250	-0.8356	0.2909	0.2789
0.6563	0.9472	0.6497	-0.167	-0.263	-0.9285	0.2162	0.2009
0.7660	0.9722	0.7514	-0.111	-0.252	-1.0713	0.1022	0.0821
0.8805	0.9985	0.9006	-0.044	-0.197	-1.3692	-0.1215	-0.1502
1	1.0265	1.1956	0	0	-	-	-
1,4-Dioxane (1) + Butyric acid (2)							
0	0.9528	1.3962	0	0	-	-	-
0.1000	0.9617	1.5042	-0.183	0.128	0.9998	2.0259	2.0071
0.2000	0.9703	1.5699	-0.332	0.214	0.9268	1.9767	1.9642
0.3000	0.9784	1.5872	-0.420	0.251	0.8320	1.9004	1.8939
0.4000	0.9861	1.5722	-0.467	0.256	0.7531	1.8312	1.8297
0.5000	0.9934	1.5073	-0.456	0.211	0.6163	1.7161	1.7186
0.6000	1.0002	1.4428	-0.395	0.167	0.5245	1.6385	1.6437
0.7000	1.0068	1.3617	-0.307	0.106	0.3978	1.5416	1.5481
0.8000	1.0131	1.2926	-0.184	0.057	0.2938	1.4670	1.4737
0.9000	1.0194	1.2415	-0.065	0.026	0.2459	1.4322	1.4392
1	1.0265	1.1956	0	0	-	-	-
1,4-Dioxane (1) + Butyl acetate (2)							
0	0.8744	0.6684	0	0	-	-	-
0.1278	0.8875	0.6821	0.005	-0.054	-0.4852	0.7261	0.6911
0.2479	0.9010	0.6918	0.014	-0.107	-0.5890	0.6856	0.6441
0.3610	0.9149	0.7076	0.023	-0.151	-0.6628	0.6570	0.6045
0.4678	0.9292	0.7394	0.032	-0.176	-0.6871	0.6462	0.5794
0.5687	0.9441	0.7788	0.036	-0.189	-0.7249	0.6287	0.5459
0.6641	0.9594	0.8222	0.036	-0.196	-0.8028	0.5936	0.4920
0.7547	0.9753	0.8657	0.032	-0.201	-0.9734	0.5184	0.3903
0.8406	0.9918	0.9394	0.022	-0.172	-1.1077	0.4510	0.2898
0.9223	1.0089	1.0355	0.011	-0.119	-1.3746	0.3162	0.1013
1	1.0265	1.1956	0	0	-	-	-
1,4-Dioxane (1) + Butylamine (2)							
0	0.7319	0.4933	0	0	-	-	-
0.0855	0.7534	0.5087	0.020	-0.045	-0.5766	0.5699	0.5586
0.1738	0.7761	0.5242	0.052	-0.091	-0.6484	0.5408	0.5271
0.2650	0.8001	0.5408	0.089	-0.139	-0.7327	0.5055	0.4886
0.3594	0.8258	0.5601	0.117	-0.186	-0.8304	0.4626	0.4414
0.4569	0.8533	0.5901	0.141	-0.224	-0.9088	0.4199	0.3927
0.5579	0.8828	0.6369	0.147	-0.248	-0.9672	0.3762	0.3411
0.6625	0.9147	0.6994	0.127	-0.259	-1.0620	0.3105	0.2648
0.7709	0.9492	0.7919	0.080	-0.243	-1.1845	0.2176	0.1570
0.8834	0.9864	0.9412	0.039	-0.172	-1.3201	0.0898	0.0074
1	1.0265	1.1956	0	0	-	-	-

Table 3.
Values of coefficients a_i of equation 6 and standard deviations σ for excess properties of the binary mixtures of 1,3-dioxolane (1) or 1,4-dioxane (1) studied at 298.15 K.

Binary mixture	Excess property	a_0	a_1	a_2	a_3	a_4	σ
1,3-dioxolane + 2-Butanone	$V^E \times 10^6$ /(m^3.mol^{-1})	-0.798	0.084	-	-	-	0.013
	$\Delta\eta$ /(mPa.s)	-0.040	-0.009	-0.009	0.129	-	0.001
1,3-dioxolane + Butyric acid	$V^E \times 10^6$ /(m^3.mol^{-1})	-1.184	-0.640	0.215	0.253	-	0.006
	$\Delta\eta$ /(mPa.s)	0.044	0.040	-0.027	-0.037	-	0.001
1,3-dioxolane + Butyl acetate	$V^E \times 10^6$ /(m^3.mol^{-1})	-0.414	0.580	-0.371	-	-	0.001
	$\Delta\eta$ /(mPa.s)	-0.068	0.183	-0.029	-	-	0.001
1,3-dioxolane + Butylamine	$V^E \times 10^6$ /(m^3.mol^{-1})	0.342	-0.070	-0.321	0.200	0.123	0.001
	$\Delta\eta$ /(mPa.s)	-0.222	0.031	0.056	0.040	-	0.001
1,4-Dioxane +2-Butanone	$V^E \times 10^6$ /(m^3.mol^{-1})	-0.824	0.063	0.442	0.486	-0.337	0.003
	$\Delta\eta$ /(mPa.s)	-0.972	-0.422	-0.315	-0.623	-0.353	0.002
1,4-Dioxane + Butyric acid	$V^E \times 10^6$ /(m^3.mol^{-1})	-1.816	0.673	0.454	0.234	0.343	0.004
	$\Delta\eta$ /(mPa.s)	0.859	-0.819	-	-	-	0.006
1,4-Dioxane + Butyl acetate	$V^E \times 10^6$ /(m^3.mol^{-1})	0.135	0.112	-0.055	-0.063	-	0.001
	$\Delta\eta$ /(mPa.s)	-0.720	-0.319	-0.408	-0.582	-	0.003
1,4-Dioxane + Butylamine	$V^E \times 10^6$ /(m^3.mol^{-1})	0.579	0.093	-0.443	-0.105	-	0.003
	$\Delta\eta$ /(mPa.s)	-0.944	-0.527	-0.247	-0.469	-0.122	0.001

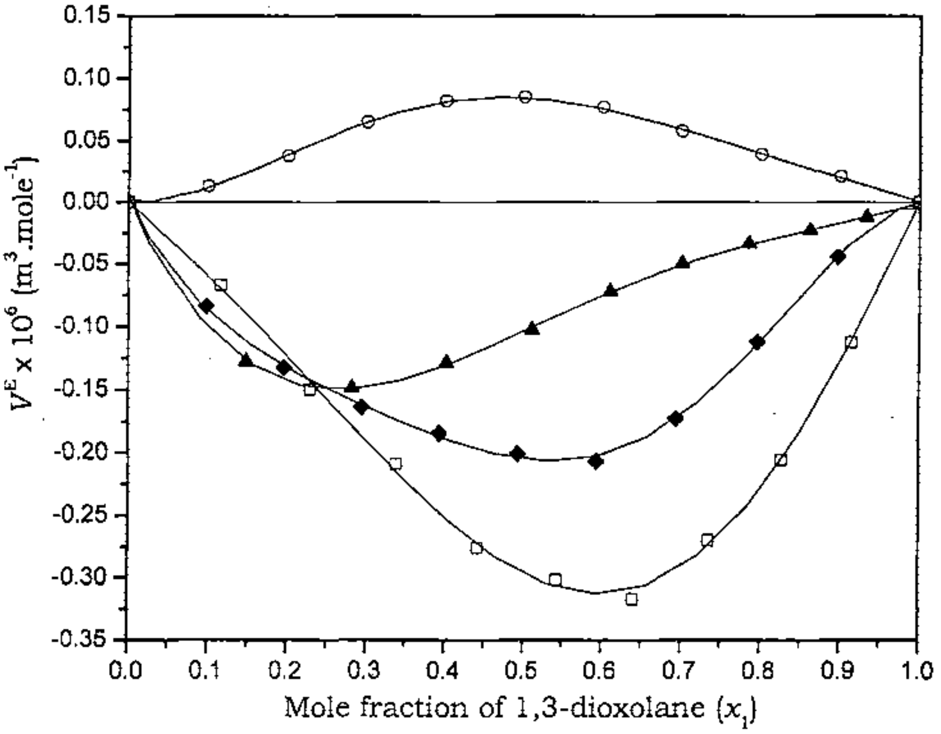

Figure 1. Excess molar volumes (V^E) at 298.15 K for binary mixtures of 1,3-dioxolane (1) with Butyric acid (□), 2-Butanone(◆), butyl acetate (▲) and butylamine (O).

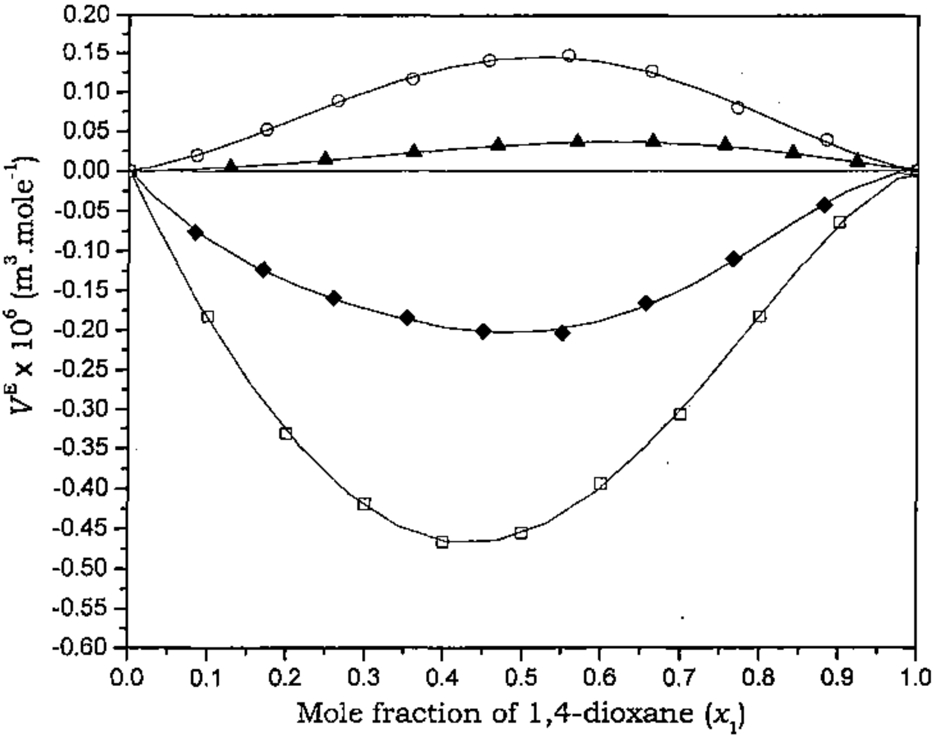

Figure 2.

Excess molar volumes (V^E) at 298.15 K for binary mixtures of 1,4-dioxane (1) with Butyric acid (□), 2-Butanone(◆), butyl acetate (▲) and butylamine (O).

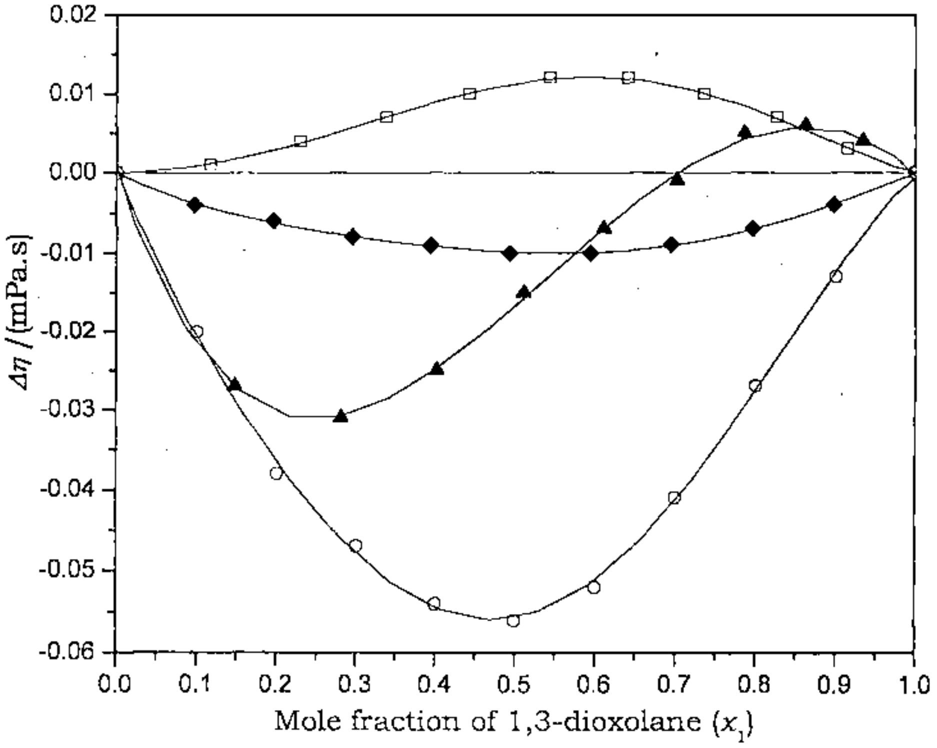

Figure 3.
Viscosity deviations ($\Delta\eta$) at 298.15 K for binary mixtures of 1,3-dioxolane (1) with Butyric acid (□), 2-Butanone(◆), butyl acetate (▲) and butylamine (O).

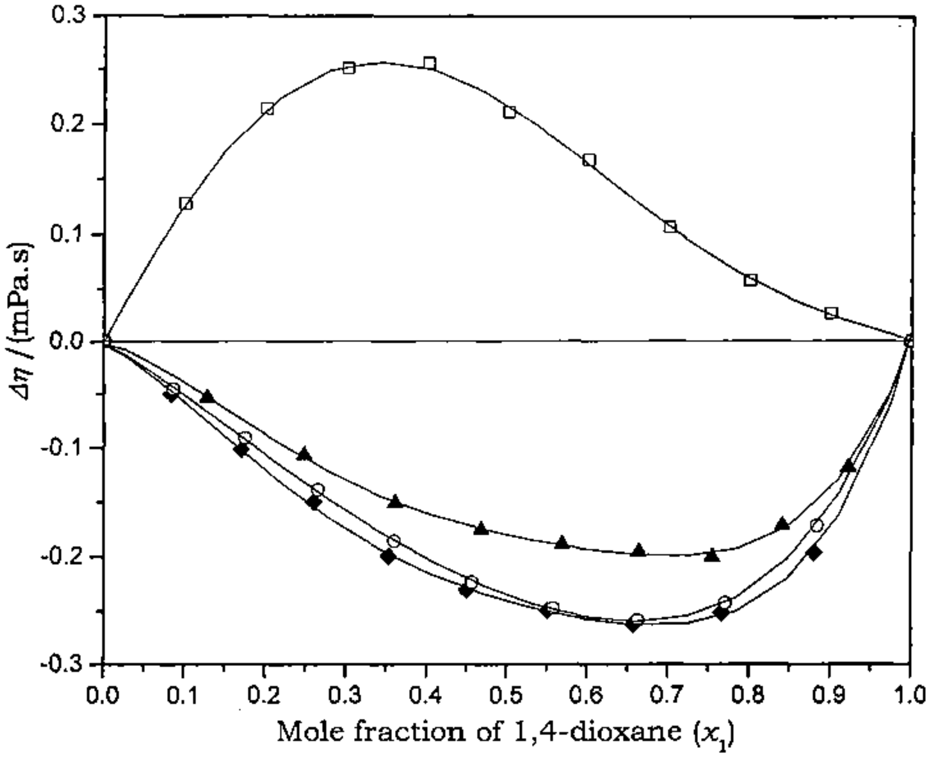

Figure 4. Viscosity deviations ($\Delta\eta$) at 298.15 K for binary mixtures of 1,4-dioxane (1) with Butyric acid (□), 2-Butanone(◆), butyl acetate (▲) and butylamine (O).

CHAPTER XII

Concluding Remarks

The aim of the works embodied in this thesis was to investigate the viscous synergy and antagonism of some liquid mixtures along with the physico-chemical properties of some solute-solvent and solvent-solvent systems.

The study of synergy and isentropic compressibility in the aqueous mixtures of 1,4-dioxane (DO) and tetrahydrofuran (THF) with some monoalkanols lead to the conclusion that lower monoalkanols have greater affinity for 1,4-dioxane (DO) or tertahydrofuran (THF) and among the isomers, the monoalkanols with hydroxyl group positioned at the second carbon atom accept more 1,4-dioxane (DO) and tetrahydrofuran (THF) than those with the terminal hydroxyl group.

Also, monoalkanols containing up to three carbon atoms mix with water in any proportion and the higher monoalkanols mix with water in limited proportion. The monoalkanols with the hydroxyl group positioned at the second carbon atom accept more water than those with the terminal hydroxyl group and their $\eta_{\max}$, I_η, and E_η values are, therefore, considerably higher.

The behavior of resorcinol in different mass % of aqueous 1,4-dioxane mixtures and pure 1,4-dioxane was observed at different temperatures. The study indicates the presence of strong solute-solvent interactions that strengthens further with a rise in temperature and weakens with an increase in the amount of 1,4-dioxane in the mixed solvents. However, the mixtures are characterized by the presence of weak solute-solute interactions that decreases with a rise in temperature and increased amount of 1,4-dioxane. Further, resorcinol acts as a structure breaker in these solvent media. The compressibilities obtained from the data supplemented with the ultrasonic speeds indicate electrostriction of the solvent molecules around resorcinol molecules.

The conductance study of some ammonium and tetraalkylammonium halides in aqueous binary mixtures of 1,4-dioxane (DO) at 298.15 reveals that all the electrolytes mentioned above are highly associated in these media. Also for an electrolyte, the association constant (K_A) increases with an increase in the amount of 1,4-dioxane (DO) in the solvent mixtures due to preferential salvation and thus leading to a decrease in Walden product. It is, however, interesting to note that electrolytes with smaller cation/anion are more solvated than those with smaller cation/anion and this is in accordance with the electrostatic theory of the simple dependence upon ionic sizes.

The volumetric and viscometric study of liquid mixtures-tetrahydrofuran + methanol, tetrahydrofuran + benzene, n-hexane + benzene, i-propanol + n-hexane, i-propanol + benzene, tetrahydrofuran + methanol + benzene, i-propanol + benzene + n-hexane at 303.15, 313.15 and 323.15 K reveals that the mixtures are characterized by the presence of viscous antagonism and volume contraction due to molecular dissociation and electrostriction. Also a decrease in the antagonic interaction index (I_A) with a rise in temperature implies a gradual increase in molecular package.

The studies of excess properties of the binary mixtures of 1,3-dioxolane with a series of monoalcohols lead to some interesting conclusions. For example, MeOH having the highest polarity achieves the most favorable intermolecular H-bonded interactions with the cyclic diether molecules. Moreover, its simple structure and smaller size leads to interstitial accommodation with 1,3-dioxolane molecules more easily compared to the higher monoalcohols with greater structural complexity.

We have studied the ion-ion and ion-solvent interactions of sodium molybdate in aqueous binary mixtures of 1,4-dioxane at different temperatures. The study reveals the presence of strong ion-solvent and weak ion-ion interactions. Also, the ion-solvent interactions are further strengthened at higher temperature and increased amount of the cyclic diether, suggesting larger electrostriction and absence of 'caging/packing' effect. Sodium molybdate behaves as a structure breaker in lower mass% of 1,4-dioxane but behaves as a structure maker at 30 mass% of the same.

The study of the molecular interactions between butylamine and N, N-dimethyformamide (DMF) with some alkyl acetates indicated that the specific interaction between the unlike molecules is predominated by hydrogen bonding and the degree of specific intermolecular interactions decreases as the chain length of the alkyl group increases.

The excess properties of the binary mixtures of 1,3-dioxolane and 1,4-dioxane with butyl acetate, butyric acid, butylamine and 2-butanone studied at 298.15 K reveals that the cyclic diethers behave differently towards the other mixing component. This may be due to their structural difference (One methylene group short in 1,3-dioxolane) and dipolar and quadrupolar order subject to the difference in the position of the –O- groups in their respective structures.

The selection of 1,4-dioxane as one of the primary solvents stems out from the fact that it is a non-hydrogen bonded cyclic diether, miscible with water in all proportion and has a boiling point (101.3°C) close to that of water. Moreover, its dipole moment is close to zero (0.45D) and has a dielectric constant of 2.209. Thus the aqueous 1,4-dioxane mixtures enabled us to study the effects of wide variation of dielectric constants and solvent characteristics on the salvation, dissociation, specific solute-solvent interactions and other structural effects associated with solution chemistry. 1,4-dioxane has been found to differ from the alcohols in their behavior towards water. While alcohols are usually structure makers, 1,4-dioxane is a net structure breaker. 1,4-dioxane can be considered as a non-polar fluid in contrast with 1,3-dioxolane, considered as a polar fluid. Also 1,3-dioxolane has more structure making character than 1,4-dioxane. The reason is probably the lower quadrupolar order and smaller electron donor strength of 1,3-dioxolane with respect to those of 1,4-dioxane.

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. It, however, is necessary to remember that molecular interactions are very complex in nature and quite difficult to explore and interpret. Numerous forces may operate between the molecules in a solvent mixture and it is really hard to separate and assign them all. Nevertheless, if careful experimental technique and methodology is used, valid conclusions may be drawn related to nature of structure and order of the systems in solution phase.

Concluding Remarks

To conclude it may be stated that extensive studies of the different physico-chemical, biological or pharmaceutical activity between different components of a given mixture will be of immense help in understanding the nature of the different interactions prevailing in mixed systems. The proper understanding of the ion-ion and ion-solvent interactions may form the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry.

APPENDIX

List of Publications

[1] Investigation on Viscous Antagonism of Ternary Liquid Mixtures and its Relation to Concentration, ***Journal of the Indian Chemical Society***, 82 (2005) 814-818.

[2] Solute-Solvent and Solute-Solute Interactions of Resorcinol in Mixed 1,4-Dioxane-Water Systems at Different Temperatures, ***International Journal of Thermophysics***, 26 (2005) 1549-1563.

[3] Excess Molar Volumes, Viscosity Deviations and Isentropic Compressibility of Binary Mixtures Containing 1,3-Dioxolane and Monoalcohols at 303.15 K, ***Journal of Solution Chemistry***, 34 (2005) 1311-1325.

[4] Electrical Conductances of Some Ammonium and Tetraalkylammonium Halides in Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K, ***Pakistan Journal of Scientific and Industrial Research***, 26 (2005) 1549-1563.

[5] Excess Molar Volumes and Viscosity Deviations of Binary Liquid Mixtures of 1,3-Dioxolane and 1,4-Dioxane with Butyl acetate, Butyric acid, Butylamine and 2-Butanone at 298.15 K, ***Journal of Chemical Engineering & Data***, 51 (2006) 590-594.

[6] Studies on Excess Molar Volumes and Viscosity Deviations of Binary Mixtures of Butylamine and N, N-dimethylamine with Some Alkyl Acetates at 298.15 K, ***Indian Journal of Chemistry***, 45A (2006) 1381-1389.

[7] Viscous Synergy and Isentropic Compressibility of Some Monoalkanols and Cyclic Ethers in Water at 298.15 k, ***Journal of Molecular Liquids***, 133 (2007) 89-99.

[8] Ion-solvent and Ion-ion Interactions of Sodium Molybdate Salt in Aqueous Binary Mixtures of 1,4-Dioxane at Different Temperatures, ***Physics and Chemistry of Liquids***, (2007) In Press.

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.

[2] 43rd Annual Convention of Chemists 2006, Aurangabad, December 23-27, 2006 organized by Indian Chemical Society and hosted by the Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, India.

REPRINTS OF THE PUBLISHED PAPERS

J. Indian Chem. Soc.,
Vol. 82, September 2005, pp. 814-818

Investigation on viscous antagonism of ternary liquid mixtures and its relation to concentration

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The densities and viscosities of ternary mixtures of tetrahydrofuran + methanol + benzene and isopropanol + benzene + *n*-hexane have been measured at 303.15, 313.15 and 323.15 K over the entire composition range. The data have been analyzed using the equation developed by Kaletunc-Gencer and Peleg. The experimental results have been discussed and explained in terms of molecular package and electrostriction.

Tetrahydrofuran (THF) is a good industrial solvent. It figures prominently in the high energy battery industry and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium[1,2]. Alcohols are very widely used in industry, including the manufacture of pharmaceuticals and cosmetic products, in enology and as an energy source. Rheology is the branch of science that studies material deformation and flow, and is increasingly applied to analyze the viscous behaviour of many pharmaceutical products[3–11] and to establish their stability and even bioavailability – since it has been firmly established that viscosity influences drug absorption rate in the body[12,13].

The present investigation quantifies the viscous antagonism established in two ternary mixtures studied here at different temperatures. Since these systems exhibit volume contraction, an analysis has also been made of the density of the mixtures at various temperatures.

Results and discussion

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products. Viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. In contraposition to viscous antagonism, viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component considered separately. In turn, if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction[14,15].

The method most widely used to analyze the antagonic and synergic behaviour of various solvent-mixtures is that developed by Kaletunc-Gencer and Peleg[16] allowing quantification of the antagonic interactions taking place in mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp}, with the viscosity expected in the absence of interaction, η_{mix}, defined as[17],

$$\eta_{mix} = \sum_{i}^{n} X_i \eta_i \qquad (1)$$

where X_i, and η_i are the fraction by weight and viscosity measured experimentally, of the *i*-th component respectively.

This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other antagonism indices are defined in consequence[18].

In order to secure more comparable viscous antagonism results, the so-called antagonic index (I_η), introduced by Howell[19], is also taken into account,

$$I_\eta = (\eta_{mix} - \eta_{exp})/\eta_{mix} = \Delta\eta/\eta_{mix} \qquad (2)$$

The method used to analyze volume contraction and dilatation is similar to that applied to viscosity. i.e. density of the mixture is determined experimentally, ρ_{exp} and a calculation is made of its theoretical value ρ_{mix}, in the supposition that volume contraction exists, based on the following expression[17],

$$\rho_{\text{mix}} = \sum_{i}^{n} X_i \eta_i \qquad (3)$$

where ρ_i denotes the density, measured experimentally of i-th component. Accordingly, when $\rho_{\text{exp}} > \rho_{\text{mix}}$, volume contraction occurs.

The physical properties of various pure solvents (tetrahydrofuran, isopropanol, methanol, benzene and *n*-hexane) along with their literature values at various temperatures are recorded in Table 1.

The measurements made yielded the viscosity values determined experimentally, ρ_{exp} and the viscosity values expected in the absence of interaction, η_{mix} along with antagonic interaction index (I_η) of various ternary liquid mixtures studied here at different temperatures are recorded in Table 2. From Table 2 in case of mixture tetrahydrofuran + methanol + benzene it is observed that the antagonic interaction in the mixture is maximum where maximum amount of benzene (80 mass%) is present in the mixture whereas it is minimum where the mixture does not contain benzene for all temperatures studied here. The explanation of this behaviour is based on the known phenomenon of molecular dissociation, as a consequence of weakening the hydrogen bonds formed between the

Table 1. Physical properties of various pure solvents at different temperatures

T/K	Tetrahydrofuran (THF)		Isopropanol		Methanol		Benzene		*n*-Hexane	
	This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.
					ρ_0/g cm^{-3}					
303.15	0.8757	0.8734[a]	0.7854	0.7766[b]	0.7846	0.7846[a]	0.8637	0.8682[c]	0.6497	0.6529[e]
313.15	0.8673	0.8661[a]	0.7704	0.7681[b]	0.7772	0.7772[a]	0.8604	0.8574[d]	0.6428	0.6435[e]
323.15	0.8583	0.8582[a]	0.7651	–	0.7675	0.7675[a]	0.8517	0.8466[c]	0.6332	0.6341[e]
					η_0/cp					
303.15	0.4452	0.4451[a]	1.7686	1.792[b]	0.4086	0.4089[a]	0.5637	0.5612[c]	0.2643	0.2774[e]
313.15	0.4088	0.4088[a]	1.3611	1.352[b]	0.3847	0.3848[a]	0.5029	0.5000[d]	0.2487	0.2504[e]
323.15	0.3716	0.3745[a]	1.2713	–	0.3308	0.3311[a]	0.4381	0.4362[c]	0.2307	0.2333[e]

[a]Ref. = 24, [b]Ref. = 25, [c]Ref. = 26, [d]Ref. = 27, [e]Ref. = 28.

Table 2. Viscosities of the ternary liquid mixtures without interaction (η_{mix}) and with interaction (η_{exp}) with antagonic interaction index (I_η) at various temperatures

(1) Tetrahydrofuran (THF) + methanol (MeOH) + benzene (C_6H_6)

Mass% of THF	Mass% of MeOH	Mass% of C_6H_6	η_{mix} 303.15 K	η_{mix} 313.15 K	η_{mix} 323.15 K	η_{exp}/cp 303.15 K	η_{exp}/cp 313.15 K	η_{exp}/cp 323.15 K	I_η 303.15 K	I_η 313.15 K	I_η 323.15 K
10	10	80	0.5363	0.4817	0.4207	0.4190	0.3962	0.3710	0.2188	0.1774	0.1182
20	15	65	0.5167	0.4663	0.4087	0.4517	0.4213	0.3748	0.1259	0.0966	0.0829
30	30	40	0.4816	0.4392	0.3859	0.4060	0.3839	0.3674	0.1570	0.1259	0.0481
35	35	30	0.4679	0.4286	0.3773	0.4629	0.3823	0.3713	0.0108	0.1080	0.0158
40	40	20	0.4543	0.4180	0.3686	0.3981	0.3972	0.3659	0.1236	0.0497	0.0073
45	45	10	0.4406	0.4074	0.3598	0.4337	0.3825	0.3618	0.0156	0.0610	–0.0053
50	50	00	0.4269	0.3967	0.3512	0.4482	0.4075	0.4297	–0.0498	–0.0271	–0.2235
55	40	05	0.4365	0.4039	0.3586	0.3897	0.3777	0.3801	0.1072	0.0648	–0.0599
60	30	10	0.4461	0.4109	0.3660	0.4063	0.3719	0.4296	0.0892	0.0951	–0.1737
65	20	15	0.4556	0.4181	0.3734	0.3882	0.3659	0.3685	0.1480	0.1248	0.0132
70	10	20	0.4652	0.4252	0.3808	0.4456	0.3789	0.3713	0.0422	0.1089	0.0249
75	00	25	0.4748	0.4323	0.3882	0.4050	0.3996	0.4009	0.1470	0.0757	–0.0326
80	00	20	0.4689	0.4276	0.3849	0.3954	0.3811	0.4007	0.1567	0.1088	–0.0410
90	00	10	0.4570	0.4182	0.3782	0.3948	0.3760	0.3863	0.1362	0.1009	–0.0213

Table-2 (contd.)

(2) Isopropanol (Me_2CHOH) + *n*-hexane (C_6H_{14}) + benzene (C_6H_6)

Mass% of Me_2CHOH	Mass% of C_6H_{14}	Mass % of C_6H_6									
00	65	35	0.3691	0.3377	0.3033	1.1240	0.4077	0.3936	–2.0453	–0.2074	–0.2978
05	80	15	0.3844	0.3424	0.3138	0.3808	0.3207	0.2600	0.0094	0.0635	0.1715
10	10	80	0.6542	0.5633	0.5007	0.4413	0.4126	0.4092	0.3255	0.2675	0.1827
20	15	65	0.7598	0.6364	0.5736	0.4682	0.4354	0.4118	0.3838	0.3158	0.2821
30	25	45	0.8503	0.6968	0.6362	0.5654	0.5082	0.4632	0.3351	0.2707	0.2719
40	35	25	0.9409	0.7572	0.6988	0.6739	0.6475	0.5600	0.2837	0.1449	0.1986
50	45	05	1.0314	0.8176	0.7614	0.7315	0.6858	0.6509	0.2908	0.1612	0.1451
60	40	00	1.1669	0.9161	0.8551	0.9803	0.6940	0.6526	0.1599	0.2425	0.2368
70	20	10	1.3472	1.0528	0.9799	0.9100	0.6983	0.6239	0.3245	0.3367	0.3633
80	00	20	1.5276	1.1895	1.1046	1.0656	0.8413	0.7631	0.3024	0.2927	0.3092
90	05	05	1.6331	1.2626	1.1776	0.9609	0.8137	0.7238	0.4116	0.3555	0.3854

molecules of the components of the mixture due to presence of benzene – producing a decrease in size of the molecular package which logically implies an increase in antagonic interaction index (I_η). Some result was reported earlier[17] in the density and viscosity measurements of the ternary mixtures. Further Table 2 in case of mixture isopropanol + *n*-hexane + benzene shows that the value of antagonic interaction index (I_η) is maximum when maximum amount of isopropanol is present in the mixture and it is minimum when the mixture contains no isopropanol. The possible explanation of this behaviour is that the maximum addition of isopropanol to the mixture either destroys or complicates the establishment of molecular interaction formed between the molecules of the components of the mixture resulting a maximum value of antagonic interaction index (I_η).

The density of the mixture is determined experimentally, ρ_{exp} and a calculation is made of theoretical value, ρ_{mix} for two ternary liquid mixtures at 303.15, 313.15 and 323.15 K are presented in Table 3. A perusal of Table 3 shows that the values of density determined experimentally, ρ_{exp} for both mixtures for various mass% and various temperatures are higher than those of its theoretical values, ρ_{mix} in the supposition that volume contraction exists, based on the eq. (3). This type of behaviour

Table 3. Densities of the ternary liquid mixtures calculated theoretically (ρ_{mix}) and determined experimentally (ρ_{exp}) at various temperatures

(1) Tetrahydrofuran (THF) + methanol (MeOH) + benzene (C_6H_6)

Mass% of THF	Mass% of MeOH	Mass% of C_6H_6	ρ_{mix}/g cm^{-3}			ρ_{exp}/g cm^{-3}		
			303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
10	10	80	0.8569	0.8528	0.8439	0.8599	0.8545	0.8496
20	15	65	0.8542	0.8493	0.8404	0.8570	0.8523	0.8459
30	30	40	0.8436	0.8375	0.8284	0.8452	0.8404	0.8349
35	35	30	0.8402	0.8337	0.8245	0.8415	0.8361	0.8296
40	40	20	0.8367	0.8299	0.8207	0.8390	0.8336	0.8257
45	45	10	0.8335	0.8261	0.8168	0.8352	0.8310	0.8230
50	50	00	0.8301	0.8222	0.8129	0.8306	0.8263	0.8166
55	40	05	0.8387	0.8309	0.8216	0.8375	0.8353	0.8269
60	30	10	0.8472	0.8396	0.8304	0.8491	0.8397	0.8345
65	20	15	0.8557	0.8482	0.8391	0.8576	0.8504	0.8430
70	10	20	0.8642	0.8569	0.8479	0.8658	0.8610	0.8527
75	00	25	0.8727	0.8656	0.8566	0.8752	0.8670	0.8634
80	00	20	0.8733	0.8659	0.8569	0.8743	0.8667	0.8596
90	00	10	0.8745	0.8666	0.8576	0.8743	0.8664	0.8607

Table-3 (contd.)

(2) Isopropanol (Me_2CHOH) + *n*-hexane (C_6H_{14}) + benzene (C_6H_6)

Mass% of Me_2CHOH	Mass% of C_6H_{14}	Mass % of C_6H_6						
00	65	35	0.7246	0.7190	0.7097	0.8798	0.8715	0.8686
05	80	15	0.6886	0.6818	0.6726	0.8950	0.8843	0.8813
10	10	80	0.8345	0.8296	0.8212	0.8585	0.8494	0.8430
20	15	65	0.8159	0.8098	0.8016	0.8517	0.8437	0.8390
30	25	45	0.7867	0.7790	0.7711	0.8552	0.8488	0.8427
40	35	25	0.7575	0.7482	0.7406	0.8637	0.8543	0.8496
50	45	05	0.7282	0.7175	0.7101	0.8688	0.8584	0.8556
60	40	00	0.7311	0.7194	0.7123	0.8565	0.8460	0.8397
70	20	10	0.7661	0.7539	0.7474	0.8257	0.8164	0.8114
80	00	20	0.8011	0.7884	0.7824	0.8128	0.8029	0.7988
90	05	05	0.7825	0.7685	0.7628	0.7946	0.7847	0.7408

can be explained on the basis of known phenomenon of electrostriction as a consequence solvent molecules are accommodated in the void space left in the packing of dispersed solvent molecules. Same results are reported for 2 : 2 electrolytes in aqueous mixtures of THF[20].

Experimental

Tetrahydrofuran, methanol, isopropanol, *n*-hexane and benzene were purified as described earlier[21]. The values of densities and viscosities of these solvents at various temperatures are in good agreement with the literature data[24-28].

Various mixtures of solutions with w/w concentrations of 0, 5, 10, 15, 20, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 90 and 100% were prepared at 303.15, 313.15 and 323.15 K. Each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. The ternary liquid solutions were made by mass.

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 0.1 cm. The pycnometer was calibrated at 303.15, 313.15 and 323.15 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 temperatures 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 in an electronic balance. The balance used here is Mettler Toledo AG-285, made in Switzerland. 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 viscosity of these mixtures was determined by means of a suspended-level Ubbelohde[23] viscometer at the desired temperatures (303.15, 313.15 and 323.15 K). The precision of the viscosity measurements were 0.05%. Details have been described earlier[21].

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References

1. C. G. Janz and R. P. T. Tomkins, "Non-aqueous Electrolytes Handbook", Academic Press, New York, 1973, Vol. 2.
2. R. Jasinki, "High Energy Batteries", Plenum Press, New York, 1967.
3. J. Ferguson and Z. Kemblonski, "Applied Fluid Rheology", Elsevier Science Publishers Ltd., University Press, Cambridge, 1991.
4. H. A. Barnes, J. F. Hutton and K. Walters, "An Introduction to Rheology", Elsevier Science Publishers BV, Amsterdam, 1993.
5. C. W. Macosko, "Rheology. Principles, Measurements and Applications", VCH Publishers Inc, New York, 1994.
6. R. Shukla and M. Cheryan, *J. Membrane Science*, 2002, **198**, 104.

7. J. M. Resa, C. Gonzalez and J. Lanz, *J. Food Engineering*, 2002, **51**, 113.

8. M. J. Assael, N. K Dalaouti and I. Metaxa, *Fluid Phase Equilibria*, 2002, **199**, 237.

9. A. Das, "Teenologia Farmaceutica", ed. S. A. Acribia, Zaragoza. 1979.

10. R. Voight, "Tratado de Tecnologia Farmaceutica", ed. S. A. Acribia, Zaragoza, 1982.

11. C. K. Zeberg-Mikkelsen, *Fluid Phase Equilibria*, 2002, **194**, 1191.

12. C. Fauli-Trillo, "Tratado de Farmacia Galenica", ed. S. A. Lujan, Madrid, 1993.

13. J. Swarbrik and J. C Eoyland, "Encyclopaedia of Pharmaceutical Technology", Marcel Dekker Inc., New York. 1993.

14. J. Pellicer, "Sinergia viscosa. Fundamentos de reologia. Los materiales viscoelasticos. Aplicaciones a las industrias alimentarias y quimico-farmaceuticas", Universidad Internacional Menendez Pelayo, Valencia (Spain), October 1997.

15. G. Copetti, R. Lapasin, E. R. Morris *et al.*, Proceeding of the 4th European Rheology Conference, Seville (Spain), 1994, 215.

16. G. Kalentunc-Gencer and M. Peleg, *J. Texture Studies*, 1986, **17**, 61.

17. J. V. Herraez and R. Belda, *J. Solution. Chem.*, 2004, **33**, 117.

18. D. D. Christianson, "Hydrocolloid Interactions with Starches", in : 'Food Carbohydrates', eds. D. R. Linebak and G. E. Inglett, Avi. Pub. Wesport. Conn, 1982, 399.

19. N. K. Howell, Proceedings of the 7th International Conference, Wales 1993. G. O. Phillips. P. A. Williams, D. J. Wdlock, Oxford University Press, New York, 1994, 77.

20. S. Roy Choudhury, A. Jha and M. N. Roy, *J. Indian Chem. Soc.*, 2002, **79**, 623.

21. M. N. Roy and D. K. Hazra, *Indian J. Chem. Technol.*, 1994, **1**, 93.

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

23. J. R. Suindells and T. B. Godfray, *J. Res. Natd. Bur. Stand.*, 1952, **48**, 1.

24. A. Jha, S. R. Choudhury, A. Choudhury and M. N. Roy, *J. T. R. Chem.*, 2003, **10**, 1.

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

26. Changsheng Yang, Piesheng Ma and Qing Zhou, *J. Chem. Eng. Data*, 2004, **49**, 881.

27. P. S. Nikam and J. K. Sanjeevan, *J. Chem. Eng. Data*, 2003, **48**, 1202.

28. Changsheng Yang, Wei Xu and Piesheng Ma, *J. Chem. Eng. Data*, 2004, **49**, 1802.

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Solute–Solvent and Solute–Solute Interactions of Resorcinol in Mixed 1,4-Dioxane–Water Systems at Different Temperatures

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The densities, viscosities, and ultrasonic speeds of resorcinol in 1,4-dioxane + water mixtures and in pure 1,4-dioxane have been measured at 303.15, 313.15, and 323.15 K. Apparent molar volumes (V_ϕ) and viscosity B-coefficients are obtained from these data supplemented with 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 the Jones–Dole equation, and the derived parameters B and A have also been interpreted in terms of solute–solvent and solute–solute interactions, respectively. The structure making/breaking capacities of resorcinol in the studied solvent systems have been discussed. The compressibilities obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent molecules around the ions.

KEY WORDS: density; electrostriction; mixed aqueous mixtures; resorcinol; solute-solvent and solute–solute interactions; structure maker and breaker; ultrasonic speed; viscosity.

1. INTRODUCTION

Studies on densities, viscosities, and ultrasonic speeds of electrolyte solutions are of great use in characterizing the structure and properties of solutions. Various types of interactions exist between the solutes in solutions, and these solute–solute and solute–solvent interactions are of current interest in all

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branches of chemistry. These interactions provide a better understanding of the nature of the solute and solvent, i.e., whether the solute modifies or distorts the structure of the solvent.

1,4-dioxane and its aqueous mixtures are very important solvents that are widely used in various industries. They figure prominently in the high-energy battery technology and have also found application in organic synthesis as manifested from the physicochemical studies in these media [1–8]. In the present work, an attempt has been made to provide an interpretation of solute–solvent and solute–solute interactions prevailing in the studied electrolyte solutions. Several workers have reported volumetric, viscometric, and ultrasonic studies of this compound in aqueous solutions [9–13], but such studies in pure 1,4-dioxane and its aqueous mixtures are still scarce.

2. EXPERIMENTAL

1,4-dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminium hydride ($LiAlH_4$) as described earlier [1]. Resorcinol (A.R.) was purified by a reported procedure [14], and the compound was dried and stored in a vacuum desiccator. Freshly distilled conductivity water was used.

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 303, 313, and 323 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 absolute temperature was determined by a calibrated platinum resistant thermometer and 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. An average of triplicate measurements was taken into account. The total uncertainty of density is $\pm 1.0 \times 10^{-5}\,g \cdot cm^{-3}$ and of the temperature is 0.01 K. Details have been described earlier [5, 15, 16].

The viscosities were measured by means of a suspended-level Ubbelohde [17] viscometer at the desired temperature (uncertainty of ±0.01 K). The precision of the viscosity measurement was ±0.003 mPa · s. Details have been described earlier [5,15,16].

Sound speeds were determined with an uncertainty of 0.3% using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 4 MHz which was calibrated with water, methanol, and benzene at each temperature, as described in detail elsewhere [18, 19]. The experimental values of densities (ρ_0) and viscosities

(η_0) of pure 1,4-dioxane and 1,4-dioxane + water mixtures at 303, 313, and 323 K are reported in Table I. The various salt solutions studied here were prepared by mass, and the conversion of molality to molarity was accomplished [20] using density values.

The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table II.

3. DISCUSSION

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation:

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

where M is the molar mass of the solute, c is the molarity of the solution, and ρ_0 and ρ are the densities of the solvent/solvent mixtures and solution, respectively.

The limiting apparent molar volumes (V_ϕ^0) were calculated using a least-squares treatment to the plots of V_ϕ versus $c^{1/2}$ using the following Masson equation [21]:

$$V_\phi = V_\phi^0 + S_v^* \sqrt{c} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_v^* is the experimental slope. The plots of V_ϕ against the square root of the molar concentration ($c^{1/2}$) were found to be linear with negative slopes. The values of V_ϕ^0 and S_v^* along with the standard errors are reported in Table III.

As the investigated systems are characterized by hydrogen bonds, 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, V_ϕ^0 can be used. Table III shows that the V_ϕ^0 values are positive and increase with a rise in temperature and decrease with an increase in the amount of 1,4-dioxane in the mixtures. This indicates the presence of strong solute–solvent interactions, and these interactions are strengthened with a rise in temperature and weakened with an increase in the amount of 1,4-dioxane in the mixed solvent under investigation, suggesting larger electrostriction at higher temperature and lower amount of 1,4-dioxane in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous DMF [22] and aqueous THF [1].

Table I. Physical Properties of Pure 1,4-Dioxane and 1,4-Dioxane + Water Mixtures at Different Temperatures

Composition of 1,4-dioxane (mass%)	ρ_0 (g · cm^{-3})						η_0 (mPa · s)					
	303.15 K		313.15 K		323.15 K		303.15 K		313.15 K		323.15 K	
	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit
10	1.0058	-	1.0068	–	0.9973	–	1.0321	–	1.0014	–	0.6895	–
20	1.0148	–	1.0100	–	1.0033	–	1.2014	–	1.0186	–	0.8787	–
30	1.0202	–	1.0162	–	1.0103	–	1.3977	–	1.2493	–	1.0755	–
100 (Pure)	1.0199	1.0222 [20]	1.0144	1.0143 [21]	1.0027	1.0032 [21]	1.0886	1.0937 [20]	0.9785	0.9783 [21]	0.8441	0.8443 [21]

Table II. Concentration (c), Density (ρ), Viscosity (η), Apparent Molar Volume (V_ϕ), and $(\eta/\eta_0 - 1)/\sqrt{c}$ of Resorcinol in Pure 1,4-Dioxane and 1,4-Dioxane + Water Mixtures at Different Temperatures

c (mol·dm^{-3})	ρ (g·cm^{-3})	η (mPa·s)	V_ϕ (cm^3·mol^{-1})	$(\eta/\eta_0 - 1)/\sqrt{c}$
10 mass% of 1,4-dioxane + water				
$T = 303.15$ K				
0.0070	1.0077	1.0376	115.9842	−0.1443
0.0487	1.0076	1.0255	112.5836	−0.1066
0.0905	1.0082	1.0358	103.8412	−0.0456
0.1322	1.0091	1.0507	98.9411	0.0012
0.1740	1.0104	1.0789	94.2994	0.0654
0.2157	1.0119	1.1090	90.3421	0.1205
$T = 313.15$ K				
0.0070	1.0012	0.9408	123.5465	−1.0002
0.0485	1.0009	0.8334	118.5112	−0.8534
0.0901	1.0010	0.8246	112.7892	−0.6544
0.1317	1.0019	0.8351	106.0231	−0.5134
0.1733	1.0030	0.8620	100.3112	−0.3845
0.2150	1.0050	0.9291	92.9054	−0.2042
$T = 323.15$ K				
0.0069	0.9975	0.6834	130.0254	−0.7280
0.0482	0.9971	0.6939	122.5432	−0.2092
0.0895	0.9972	0.7609	115.1204	0.1544
0.1307	0.9979	0.8931	108.6753	0.6304
0.1724	0.9991	1.0793	101.8734	1.1654
0.2140	1.0009	1.2354	94.8752	1.5102
20 mass% of 1,4-dioxane + Water				
$T = 303.15$ K				
0.0071	1.0164	1.2205	114.9854	−0.0543
0.0498	1.0163	1.2180	110.8887	−0.0296
0.0925	1.0165	1.2265	107.7832	0.0012
0.1352	1.0172	1.2391	102.8712	0.0290
0.1779	1.0187	1.2563	95.8097	0.0584
0.2206	1.0207	1.2699	89.0009	0.0761
$T = 313.15$ K				
0.0071	1.0099	0.9489	118.0543	0.0011
0.0495	1.0098	0.9681	112.9843	0.0914
0.0919	1.0100	0.9939	108.5632	0.1569
0.1343	1.0106	1.0231	104.2871	0.2135
0.1768	1.0118	1.0648	98.7358	0.2906
0.2197	1.0142	1.1113	90.3320	0.3654

Table II. *(Continued)*

c (mol · dm^{-3})	ρ (g · cm^{-3})	η (mPa · s)	V_ϕ (cm^3 · mol^{-1})	$(\eta/\eta_0 - 1)/\sqrt{c}$
$T = 323.15$ K				
0.0070	1.0035	0.8595	121.0065	−0.5165
0.0493	1.0034	0.8189	113.8901	−0.3984
0.0912	1.0036	0.8198	109.9987	−0.2897
0.1340	1.0041	0.8554	106.0007	−0.1305
0.1759	1.0054	0.9046	99.5709	0.0165
0.2179	1.0075	0.9486	91.9964	0.1198
30 mass % of 1,4-dioxane + Water				
$T = 303.15$ K				
0.0070	1.0202	1.4376	103.6557	0.1006
0.0491	1.0208	1.4635	95.5644	0.1200
0.9125	1.0218	1.4805	90.5848	0.1277
0.1334	1.0229	1.4972	87.6753	0.1376
0.1755	1.0241	1.5177	85.6229	0.1544
0.2176	1.0267	1.5326	78.6543	0.1609
$T = 313.15$ K				
0.0070	1.0163	1.2855	105.0988	0.1015
0.0489	1.0168	1.3091	97.6876	0.1223
0.0910	1.0177	1.3260	92.8904	0.1334
0.1328	1.0189	1.3402	88.9876	0.1410
0.1748	1.0202	1.3602	85.9498	0.1605
0.2167	1.0226	1.3787	79.6544	0.1754
$T = 323.15$ K				
0.0070	1.0106	1.1076	106.5169	0.1017
0.0486	1.0111	1.1279	99.6003	0.1222
0.0902	1.01189	1.1445	95.0065	0.1401
0.1318	1.01318	1.1607	89.6543	0.1565
0.1736	1.0143	1.1763	87.8954	0.1704
0.2149	1.0167	1.1899	80.9976	0.1799
Pure 1,4-dioxane				
$T = 303.15$ K				
0.0069	1.0203	1.1108	47.4532	0.2540
0.0485	1.0226	1.1514	53.0001	0.2655
0.0902	1.0245	1.1782	57.5543	0.2765
0.1319	1.0261	1.2001	61.8776	0.2841
0.1736	1.0278	1.2222	62.9876	0.2965
0.2152	1.0292	1.2461	65.4432	0.3137

Table II. *(Continued)*

c (mol · dm^{-3})	ρ (g · cm^{-3})	η (mPa · s)	V_ϕ (cm^3 · mol^{-1})	$(\eta/\eta_0 - 1)/\sqrt{c}$
$T = 313.15$ K				
0.0069	1.0147	0.9990	49.4987	0.2544
0.0480	1.0169	1.0362	54.7654	0.2701
0.0894	1.0186	1.0592	60.4765	0.2765
0.1308	1.0202	1.0809	63.8765	0.2901
0.1721	1.0219	1.1041	64.9998	0.3100
0.2134	1.0233	1.1224	66.6279	0.3190
$T = 323.15$ K				
0.0068	1.0036	0.8621	50.6542	0.2551
0.0475	1.0058	0.8942	55.9786	0.2709
0.0884	1.0075	0.9146	61.8881	0.2801
0.1293	1.0091	0.9347	64.7831	0.2976
0.1702	1.0107	0.9551	65.8160	0.3176
0.2110	1.0122	0.9738	67.5301	0.3339

It is evident from Table III that the S_V^* values are negative for all temperatures for aqueous mixtures of 1,4-dioxane, but positive for pure 1,4-dioxane. Since S_V^* is a measure of solute–solute interactions, the results indicate the presence of weak solute–solute interactions. These interactions, however, decrease with a rise in temperature, which is attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of solute–solute interactions (ionic dissociation) [7]. The S_V^* values increase with an increase in the amount of 1,4-dioxane in the mixture which results in a decrease in solvation of ions, i.e., more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the addition of 1,4-dioxane to the mixture.

The variation of V_ϕ^0 with temperature of resorcinol in solvent mixtures follows the polynomial,

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{3}$$

over the temperature range under investigation where T is the temperature in K.

Values of coefficients of the above equation for resorcinol for compositions of 1,4-dioxane + water mixtures are reported in Table IV.

From the values of coefficients the following equations are obtained: 10 mass% 1,4-dioxane + water mixture

Table III. Limiting Apparent Molar Volume (V_ϕ^0) and Experimental Slope (S_v^*) for Resorcinol in Different 1,4-Dioxane + Water Mixtures at Different Temperatures

	V_ϕ^0 ($cm^3 \cdot mol^{-1}$)			S_v^* ($cm^2 \cdot dm^{1/2} \cdot mol^{-3/2}$)		
Composition of 1,4-dioxane (mass%)	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
10	124.5 (±0.05)	133.5 (±0.02)	140.5 (±0.04)	−70.8 (±0.02)	−79.6 (±0.01)	−92.2 (±0.04)
20	123.8 (±0.01)	126.6 (±0.03)	129.1 (±0.02)	−64.8 (±0.04)	−67.8 (±0.03)	−71.2 (±0.02)
30	109.1 (±0.01)	111.3 (±0.05)	113.0 (±0.02)	−60.6 (±0.03)	−63.4 (±0.01)	−64.1 (±0.02)
100	43.1 (±0.01)	45.5 (±0.02)	46.8 (±0.01)	48.5 (±0.02)	47.5 (±0.04)	46.7 (±0.01)

Standard errors are given in parentheses.

$$V_\phi^0 = -1123.39/\text{cm}^3\cdot\text{mol}^{-1} + 7.23T/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1} - 0.010T^2/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-2} \tag{4}$$

20 mass % 1,4-dioxane + water mixture

$$V_\phi^0 = -74.86/\text{cm}^3\cdot\text{mol}^{-1} + 1.02T/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1} - 0.001T^2/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-2} \tag{5}$$

30 mass % 1,4-dioxane + water mixture

$$V_\phi^0 = -216.27/\text{cm}^3\cdot\text{mol}^{-1} + 1.89T/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1} - 0.002T^2/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-2} \tag{6}$$

Pure 1,4-dioxane

$$V_\phi^0 = -500.30/\text{cm}^3\cdot\text{mol}^{-1} + 3.30T/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1} - 0.005T^2/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-2} \tag{7}$$

The apparent molar expansibilities (Φ_E^0) can be obtained by the following equation:

$$\Phi_\text{E}^0 = (\delta V_\phi^0/\delta T)_\text{P} = a_0 + 2a_2T \tag{8}$$

The values of Φ_E^0 of the studied compounds at 303.15, 313.15, and 323.15 K are determined and reported in Table V.

Table IV. Values of Various Coefficients for Resorcinol in Different 1,4-Dioxane + Water Mixtures

Composition of 1,4-dioxane (mass %)	a_0 (cm$^3\cdot$mol^{-1})	a_1 (cm$^3\cdot$mol$^{-1}\cdot$K^{-1})	a_2 (cm$^3\cdot$mol$^{-1}\cdot$K^{-2})
10	−1123.39	7.23	−0.010
20	−74.86	1.02	−0.001
30	−216.27	1.89	−0.002
100	−500.30	3.30	−0.005

It is found from Table V that the values of Φ_E^0 decrease with a rise in temperature as well as with an increase in the amount of 1,4-dioxane in the mixture, which can be ascribed to the absence of caging or packing effects [23].

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 breaking nature of any solute. Hepler [24] developed a technique of examining the sign of $(\delta^2 V_\phi^0/\delta T^2)_P$ for the solute in terms of long-range structure-making and breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$(\delta c_P/\delta P)_T = -(\delta^2 V_\phi^0/\delta T^2)_P \tag{9}$$

On the basis of this expression, it has been deduced that the structure-making solutes should have positive values, whereas structure-breaking solutes should have negative values. In our present investigation, it is evident from Table V that $(\delta^2 V_\phi^0/\delta T^2)_P$ values are negative for resorcinol and for all 1,4-dioxane + water mixtures investigated here, suggesting thereby that resorcinol acts as a structure breaker in these solvent mixtures.

The viscosity data of solutions for resorcinol in 10, 20, and 30 mass% of 1,4-dioxane + water mixtures and pure 1,4-dioxane have been analyzed using the Jones–Dole [25] equation:

$$\begin{aligned} \eta/\eta_0 &= 1 + Ac^{1/2} + Bc \\ (\eta/\eta_0 - 1)/c^{1/2} &= A + Bc^{1/2}, \quad \text{where } \eta = (kt - L/t)\rho, \end{aligned} \tag{10}$$

and η_0 and η are the viscosities of solvent/solvent mixtures and solution, respectively. k and L are the constants for a particular viscometer, and t is

Table V. Limiting Apparent Molar Expansibilities (Φ_E^0) for Resorcinol in Various 1, 4-Dioxane + Water Mixtures at Different Temperatures

	Φ_E^0 (cm^3·mol^{-1}·K^{-1})			
Composition of 1,4-dioxane (mass%)	303.15 K	313.15 K	323.15 K	$(\delta\Phi_E^0/\delta T)_P$
10	1.01	0.81	0.59	Negative
20	0.29	0.27	0.24	Negative
30	0.25	0.19	0.14	Negative
100 (Pure)	0.29	0.19	0.09	Negative

the flow time of the solvent/solution in seconds. A and B are the constants which are estimated by a least-squares method and reported in Table VI.

A perusal of Table VI shows that the values of the A coefficient are negative for 10 and 20 mass% of 1,4-dioxane and positive for 30 and 100 mass% of 1,4-dioxane for all temperatures. These results indicate the presence of weak solute–solute interactions, and these interactions increase with an increase of 1,4-dioxane to the mixture.

It is also observed from Table VI that the values of the B-coefficient of resorcinol in the studied solvent systems are positive, thereby suggesting the presence of strong solute–solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of 1,4-dioxane in the mixture. These conclusions are in excellent agreement with those drawn from V_{ϕ}^{0} values discussed earlier.

It has been reported in a number of studies [26, 27] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table VI that the values of the B-coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of resorcinol in the solvent systems. A similar result was reported in a study [30] for the case of the viscosity of some salts in propionic acid + ethanol mixtures.

The adiabatic compressibility (β) was calculated from the following relation:

$$\beta = 1/(u^2\rho) \tag{11}$$

where ρ is the solution density and u is the sound speed in the solution. The apparent molal adiabatic compressibility (Φ_K) of the liquid solutions was determined from the relation,

$$\Phi_{\mathrm{K}} = M\beta/\rho_0 + 1000(\beta\rho_0 - \beta_0\rho)/(m\rho\rho_0) \tag{12}$$

The limiting apparent molal adiabatic 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 a least-squares method.

$$\Phi_{\mathrm{K}} = \Phi_{\mathrm{K}}^{0} + S_{\mathrm{K}}^{*} m^{1/2} \tag{13}$$

where S_{K}^{*} is the experimental slope.

Table VI. Values of A and B Parameters for Resorcinol in Different 1,4-dioxane + Water Mixtures at Different Temperatures

	A ($cm^{3/2} \cdot mol^{-1/2}$)			B ($cm^3 \cdot mol^{-1}$)		
Composition of 1,4-dioxane (mass%)	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
10	−0.23 (±0.01)	−1.24 (±0.02)	−1.41 (±0.01)	0.70 (±0.01)	2.08 (±0.02)	5.95 (±0.02)
20	−0.09 (±0.01)	−0.10 (±0.02)	−0.73 (±0.02)	0.35 (±0.01)	0.92 (±0.02)	1.70 (±0.01)
30	0.08 (±0.01)	0.08 (±0.01)	0.07 (±0.02)	0.16 (±0.01)	0.18 (±0.02)	0.21 (±0.02)
100	0.24 (±0.02)	0.23 (±0.01)	0.23 (±0.01)	0.15 (±0.02)	0.17 (±0.02)	0.21 (±0.01)

Standard errors are given in parentheses.

Table VII. Molality (m), Density (ρ), Sound Speed (u), Adiabatic Compressibility (β), Apparent Molal Adiabatic Compressibility (ϕ_K), Limiting Apparent Adiabatic Compressibility (ϕ_K^0), and Experimental Slope (S_K^*) of Resorcinol in Different 1,4-Dioxane + Water Mixtures at 303.15 K

Composition of 1,4-dioxane (mass%)	m (mol · kg^{-1})	$\rho \times 10^{-3}$ (kg · m^{-3})	u (m · s^{-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$^{1/2}$)
10	0.00691	1.00769	1576.73	3.99168	1.050		
	0.04861	1.00758	1572.70	4.01262	0.963		
	0.09064	1.00824	1570.36	4.02194	0.794	1.31 (±0.02)	−2.02(±0.04)
	0.13296	1.00912	1573.30	4.00343	0.515		
	0.17555	1.01037	1573.09	3.99957	0.446		
	0.21835	1.01186	1575.75	3.98003	0.327		
20	0.00701	1.01637	1590.39	3.88993	1.440		
	0.04928	1.01629	1584.30	3.92019	1.180		
	0.09193	1.01647	1586.07	3.91075	0.720		
	0.13488	1.01717	1590.98	3.88397	0.408	1.81 (±0.03)	−3.58(±0.05)
	0.17805	1.01868	1593.76	3.86472	0.271		
	0.22137	1.02075	1596.57	3.84330	0.168		
30	0.00687	1.02019	1590.07	3.87045	2.850	3.47 (±0.02)	−7.63(±0.03)
	0.04839	1.02078	1580.33	3.92260	1.910		
	0.09019	1.02178	1583.03	3.90540	0.991		
	0.13227	1.02291	1584.14	3.89559	0.704		
	0.17463	1.02415	1595.59	3.83525	0.265		
	0.21699	1.02666	1605.11	3.78063	0.001		

Standard errors are given in parentheses.

The values of α, β, Φ_K, Φ_K^0, and S_K^* are reported in Table VII.

A perusal of Table VII shows that the Φ_K^0 values increase whereas S_K^* values decrease with an increase of 1,4-dioxane in the mixtures for the compounds studied here. Since the values of Φ_K^0 and S_K^* are measures of the solute–solvent and solute–solute interactions, respectively, the results are in good agreement with those drawn from the conclusion based on the values of Φ_K^0 and S_K^* explained here earlier. The same result was obtained by us [29] in studies on the sound speeds of some salts in different tetrahydrofuran (THF) + water mixtures.

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REFERENCES

1. M. N. Roy, A. Jha, and R. Dey, *J. Chem. Eng. Data* **46**:1247 (2001).
2. C. G. Janz and R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook* (Academic Press, New York, 1973), Vol. **2**
3. R. Jasinki, *High Energy Batteries* (Plenum Press, New York, 1967).
4. M. N. Roy, *J. Teach. Res.* **7**:17(2000).
5. M. N. Roy and D. K. Hazra, *Indian J. Chem. Technol.* **1**:93 (1994).
6. A. Sacco, M. D. Monika, and A. D. Giglio, *J. Chem. Soc. Faraday Trans. I* **79**:631 (1983).
7. F. J. Millero, in *Structure and Transport Process in Water and Aqueous Solutions* (R. A. Horne, New York, 1972).
8. M. L. Parmar, V. N. Rao, and S. K. Bhardwaj, *J. Indian Chem. Soc.* **67**:591 (1990).
9. K. Masayuki and N. Kastutoshi, *J. Chem. Eng. Data.* **40**:935 (1995).
10. T. V. Chalikian, A. P. Sarvasyan, and K. J. Breslauer, *J. Phys. Chem.* **97**:1301 (1993).
11. T. S. Banipal and P. Kapoor, *J. Indian Chem. Soc.* **76**:341 (1999).
12. D. P. Kharakoz, *Biophys. Chem.* **34**:115 (1989).
13. M. N. Roy, D. Nandi, and D. K. Hazra, *J. Indian Chem. Soc.* **70**:1123 (1993).
14. P. Franzosini and F. W. Falgar, *J. Chem. Thermodyn.* **16**:81 (1984).
15. P. S. Nikam and M. Hosan, *J. Chem. Eng. Data.* **33**:165 (1988).
16. R. D. Peralta, R. Infante, G. Cortez, G. Cadenas, and J. Wisniak, *Int. J. Thermophys.* **24**:1061 (2003).
17. J. R. Suindels and T. B. Goodfray, *J. Res. Natl. Bur. Stand.* **48**:1 (1952).
18. K. Tamura, K. Ohomura, and S. Murakami, *J. Chem. Thermodyn.* **15**:859 (1983).
19. M. N. Roy, A. Jha, and A. Choudhury, *J. Indian Chem. Soc.* **80**:1 (2003).
20. D. P. Shoemaker and C. W. S. Garland, *Experiments in Physical Chemistry* (McGraw Hill, New York, 1967), p. 131.
21. D. O. Masson, *Phil. Mag.* **8**:218 (1929).
22. E. Garland-Paneda, C. Yanes, and J. J. Calventa, *J. Chem. Soc. Faraday Trans.* **94**:573 (1994).
23. P. R. Misra and B. Das, *Indian J. Chem.* **16**:348 (1978).

24. L. G. Hepler, *Can. J. Chem.* **47**:4617 (1969).
25. G. Jones and M. Dole, *J. Am. Chem. Soc.* **51**:2950 (1929).
26. R. Gopal and M. A. Siddique, *J. Phys. Chem.* **72**:1814 (1969).
27. N. Saha and B. Das, *J. Chem. Eng. Data* **42**:277 (1997).
28. M. L. Parmer and M. K. Chouhan, *Indian J. Chem.* **34A**:434 (1995).
29. M. N. Roy and D. K. Hazra; *N. B. Univ. Rev. (Sci. and Technol.)* **8**:54 (1997).
30. S. Martin Contreras, *J. Chem. Eng. Data* **46**:1149 (2001).
31. A. Choudhury, A. Sinha, and M. N. Roy, *J. Teach. Res.* **11**:12 (2004).

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Excess Molar Volumes, Viscosity Deviations and Isentropic Compressibility of Binary Mixtures Containing 1,3-Dioxolane and Monoalcohols at 303.15 K

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The excess molar volume (V^E), viscosity deviations ($\Delta\eta$) and Gibbs excess energy of activation for viscous flow (G^{*E}) have been investigated from density (ρ) and viscosity (η) measurements of eight binary mixtures of 1,3-dioxolane with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *t*-butanol, and *i*-amyl alcohol over the entire range of mole fractions at 303.15 K. The viscosity data have been correlated with the Grunberg and Nissan equation. Furthermore, excess isentropic compressibilities (K_S^E) have been calculated from ultrasonic speed measurements of these binary mixtures at 303.15 K. The deviations have been fitted by 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 the liquid mixtures. The systems studied exhibit very strong cross association through hydrogen bonding.

KEY WORDS: Excess molar volumes; viscosity deviations; Gibbs excess energy of activation; isentropic compressibility; density and viscosity measurements; speed of sound; cyclic diether; monoalcohols; molecular interactions; dipole–dipole interaction; interstitial accommodation.

1. INTRODUCTION

The increasing use of cyclic diethers and monoalcohols in many industrial processes such as pharmaceutical and cosmetics have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of cyclic diethers, monoalcohols and their mixtures.$^{(1-6)}$ The viscosities and densities of binary liquid mixtures are used extensively to understand molecular interactions between the components of the mixture to develop new theoretical

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models and also for engineering applications.(7,8) The thermodynamic properties of various alcohols have been studied in numerous solvents. In our systematic investigation of these properties, we have reported the viscosities, densities, speeds of sound, isentropic compressibilities and excess molar volumes of many binary systems in previous papers.(1–4) There has been a recent upsurge of interest(9,10) in the study of thermodynamic properties of binary liquid mixtures, which have been used extensively to obtain information on intermolecular interactions and stereochemical effects in these systems.(3) In this paper we extend our studies to binary mixtures formed from 1,3-dioxolane, represented as (1) with eight monoalcohols, represented as (2) with methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), *t*-butanol (*t*-BuOH), and *i*-amyl alcohol (*i*-AmOH).

The various thermodynamic properties, such as excess molar volume (V^E) and viscosity deviations ($\Delta\eta$), obtained from experimental observations have been rationalized.(4) Besides this, speed of sound measurements and calculated isentropic compressibilities, as well as excess isentropic compressibilities (K_S^E)(7,11) of 1,3-dioxolane (1) with the monoalchols (2) mixtures are presented at 303.15 K.

The cyclic diether 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 the pure state in addition to mutual association in their binaries.(12) In addition, this work also provides a test of various empirical equations to correlate viscosity and ultrasonic sound data of binary mixtures containing both polar components.

2. EXPERIMENTAL

2.1. Apparatus and Procedures

Densities (ρ) at 303.15 K were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The measurements were done in a thermostatted bath controlled to ±0.01 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer.(13) Calibration was done at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. 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 details of the methods and techniques have been described previously.(14,15) The mixtures were prepared by mixing known volumes of the pure liquids in air-tight stoppered bottles. The weights were taken on a Mettler electronic analytical balance (AG 285) accurate to 0.01 mg. The precisions of the speed of sound, density and viscosity measurements are ± 0.2 m-s^{-1}, $\pm 3 \times 10^{-5}$ g-cm^{-3} and $\pm 2 \times 10^{-5}$ cP, respectively.

Table I. Physical Properties of Pure Components at 303.15 K

	ρ (g-cm^{-3})		η (cP)		
Components	Observed	Literature	Observed	Literature	u (m-s^{-1})
1,3-Dioxolane	1.05184	1.04940 [18]	0.54866	0.54355 [18]	1288.5
Methanol	0.78242	0.78297 [19]	0.50409	0.51000 [19]	1088.5
Ethanol	0.78435	0.78069 [6]	0.96749	0.99301 [6]	1144.3
1-Propanol	0.79584	0.79581 [6]	1.66262	1.78433 [6]	1182.6
2-Propanol	0.77731	0.77786 [20]	1.61419	1.77321 [20]	1126.6
1-Butanol	0.80207	0.80194 [6]	2.53963	2.28530 [6]	1196.6
2-Butanol	0.79923	0.79589 [18]	2.33939	2.41700 [18]	1168.9
t-Butanol	0.77506	0.77622 [21]	3.09856	3.32109 [21]	1078.8
i-Amyl alcohol	0.80319	—	3.11110	—	1197.0

2.2. Chemicals

The source and purification of the pure alcohols, (Merck) methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *t*-butanol and *i*-amyl alcohol, have been described in other papers.(5,16,17) 1,3-dioxolane (LR) was purified by standard methods; it was refluxed with PbO_2, then fractionally distilled after addition of xylene.(18) The solvents finally obtained after purification were 99.9% pure as checked by gas chromatography. The purity of the liquids was also checked by measuring their densities and viscosities at 303.15 K and were in reasonable agreement with the literature values(6,18–21) as depicted in Table I.

3. RESULTS

The measured density (ρ) and viscosity (η) data for mixtures of 1,3-dioxolane (1) and the monoalcohols (2), methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *t*-butanol, and *i*-amyl alcohol, were used to calculate the excess molar volume (V^E), viscosity deviations ($\Delta\eta$), Gibbs excess energy of activation for viscous flow (G^{*E}) and the Grunberg–Nissan interaction parameter (d^1). The results are presented in Table II.

The excess molar volume (V^E) is calculated using the equation(8,22)

$$V^E = (M_1x_1 + M_2x_2)/\rho_{mix} - M_1x_1/\rho_1 - M_2x_2/\rho_2 \qquad (1)$$

where ρ_{mix} is the density of the mixture and M_1, M_2, x_1, x_2, ρ_1, and ρ_2 are the molecular weights, mole fractions and densities of pure components 1 and 2, respectively.

Quantitatively, as per the absolute reaction rates theory,(4,23) the deviation of the viscosities, $\Delta\eta$, from the ideal mixture values and the Gibbs excess energies

Table II. Experimental Results for the Binary Liquid Mixtures of 1,3-Dioxolane (1) + Monoalcohols (2) at 303.15 K

Mole fraction 1,3-dioxolane (x_1)	$\rho \times 10^{-3}$ (kg-m^{-3})	$\eta \times 10^3$ (kg-m^{-1}-s^{-1})	$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	$V^E \times 10^3$ (m^3-mol^{-1})	$G^{*E} \times 10^{-3}$ (J-mol^{-1})	d^1
		1,3-Dioxolane + methanol				
0.00000	0.78242	0.50409	0.00000	0.00000	0.00000	—
0.04585	0.80385	0.50565	−0.00048	−0.04543	0.01448	−0.01817
0.09758	0.82641	0.50884	0.00040	−0.09238	0.03523	0.01262
0.15637	0.85072	0.51595	0.00489	−0.16997	0.07095	0.07586
0.22381	0.87556	0.52719	0.01312	−0.20763	0.12473	0.14877
0.30192	0.90216	0.53818	0.02063	−0.26618	0.17006	0.18911
0.39348	0.92962	0.55157	0.02994	−0.28935	0.21978	0.23749
0.50228	0.95845	0.56418	0.03770	−0.29641	0.25465	0.28026
0.63370	0.98828	0.54544	0.01311	−0.25413	0.13379	0.10834
0.79561	1.01936	0.54465	0.00509	−0.16004	0.07283	0.06138
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—
		1,3-Dioxolane + ethanol				
0.00000	0.78435	0.96749	0.00000	0.00000	0.00000	—
0.06463	0.80501	0.89803	−0.04239	−0.01432	−0.09335	−0.62597
0.13455	0.82672	0.83803	−0.07311	−0.02483	−0.16571	−0.57821
0.21044	0.84953	0.76911	−0.11024	−0.02875	−0.27159	−0.66266
0.29308	0.87359	0.68516	−0.15958	−0.03001	−0.44315	−0.86305
0.38344	0.89912	0.63329	−0.17360	−0.03570	−0.51148	−0.87254
0.48263	0.92601	0.61205	−0.15330	−0.02995	−0.45496	−0.73741
0.59202	0.95457	0.59099	−0.12854	−0.02422	−0.38705	−0.65042
0.71327	0.98493	0.58855	−0.08020	−0.01712	−0.22544	−0.45208
0.84842	1.01723	0.56902	−0.04313	−0.00503	−0.11996	−0.38524
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—
		1,3-Dioxolane + 1-propanol				
0.00000	0.79584	1.66262	0.00000	0.00000	0.00000	—
0.08269	0.81516	1.25778	−0.31273	0.04909	−0.47023	−2.47020
0.16862	0.83574	1.06683	−0.40795	0.07303	−0.64392	−1.83154
0.25799	0.85742	0.93446	−0.44077	0.09519	−0.72703	−1.51572
0.35101	0.88035	0.82076	−0.45085	0.11086	−0.79334	−1.39053
0.44791	0.90452	0.73389	−0.42978	0.12845	−0.80375	−1.29892
0.54893	0.93008	0.64538	−0.40575	0.14471	−0.84483	−1.36397
0.65434	0.95773	0.59197	−0.34174	0.11624	−0.76907	−1.35842
0.76444	0.98721	0.56844	−0.24262	0.07633	−0.56526	−1.25362
0.87954	1.01856	0.55642	−0.12643	0.03507	−0.29936	−1.12795
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—
		1,3-Dioxolane + 2-propanol				
0.00000	0.77731	1.61419	0.00000	0.00000	0.00000	—
0.08269	0.79735	1.21247	−0.31361	0.07625	−0.49315	−2.59639
0.16862	0.81849	0.97764	−0.45688	0.15165	−0.79886	−2.27901
0.25799	0.84127	0.83857	−0.50072	0.18617	−0.94080	−1.96672
0.35101	0.86537	0.74771	−0.49247	0.22121	−0.97525	−1.71550
0.44791	0.89113	0.66451	−0.47242	0.23696	−1.00817	−1.63452
0.54893	0.91900	0.60823	−0.42106	0.21107	−0.95724	−1.54956
0.65434	0.94875	0.60327	−0.31370	0.17812	−0.69243	−1.22964
0.76444	0.98069	0.58560	−0.21406	0.12895	−0.47001	−1.04979
0.87954	1.01482	0.56368	−0.11333	0.08009	−0.25558	−0.97199
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—

Table II. Continued

Mole fraction 1,3-dioxolane (x_1)	$\rho \times 10^{-3}$ (kg-m^{-3})	$\eta \times 10^3$ (kg-m^{-1}-s^{-1})	$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	$V^E \times 10^3$ (m^3-mol^{-1})	$G^{*E} \times 10^{-3}$ (J-mol^{-1})	d^1
1,3-Dioxolane + 1-butanol						
0.00000	0.80207	2.53963	0.00000	0.00000	0.00000	—
0.10005	0.82064	1.73995	−0.60048	0.10328	−0.55615	−2.49729
0.20009	0.84032	1.37339	−0.76787	0.18245	−0.75747	−1.92522
0.30011	0.86111	1.11332	−0.82880	0.24712	−0.89359	−1.73685
0.40013	0.88368	0.95874	−0.78424	0.24314	−0.88094	−1.50416
0.50013	0.90754	0.84187	−0.70202	0.23225	−0.82118	−1.35121
0.60013	0.93281	0.73054	−0.61425	0.21418	−0.79337	−1.36020
0.70011	0.95972	0.65818	−0.48755	0.18020	−0.67348	−1.32180
0.80009	0.98832	0.61924	−0.32743	0.14009	−0.44671	−1.15856
0.90005	1.01882	0.58733	−0.16033	0.08933	−0.20229	−0.94536
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—
1,3-Dioxolane + 2-butanol						
0.00000	0.79923	2.33939	0.00000	0.00000	0.00000	—
0.10005	0.81699	1.51615	−0.64408	0.21125	−0.71372	−3.20554
0.20009	0.83605	1.18133	−0.79975	0.37022	−0.96592	−2.45596
0.30011	0.85714	0.93545	−0.86652	0.41589	−1.18211	−2.29194
0.40013	0.87988	0.81197	−0.81089	0.40842	−1.17009	−1.99115
0.50013	0.90408	0.70718	−0.73661	0.38031	−1.15202	−1.88435
0.60013	0.92976	0.65889	−0.60583	0.34322	−0.96612	−1.65351
0.70011	0.95708	0.61199	−0.47369	0.29514	−0.79056	−1.55106
0.80009	0.98619	0.58939	−0.31725	0.23646	−0.52623	−1.36480
0.90005	1.01762	0.55877	−0.16887	0.14236	−0.30518	−1.40824
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—
1,3-Dioxolane + *t*-butanol						
0.00000	0.77506	3.09856	0.00000	0.00000	0.00000	—
0.10005	0.79409	1.96702	−0.87642	0.22469	−0.69302	−3.12317
0.20009	0.81487	1.46803	−1.12032	0.36090	−0.98214	−2.50302
0.30011	0.83733	1.10228	−1.23103	0.43729	−1.25951	−2.44712
0.40013	0.86138	0.87929	−1.19898	0.48229	−1.38717	−2.36169
0.50013	0.88759	0.76572	−1.05756	0.45732	−1.29797	−2.12818
0.60013	0.91549	0.67551	−0.89278	0.42926	−1.17859	−2.01802
0.70011	0.94566	0.60671	−0.70664	0.36261	−1.01782	−1.99376
0.80009	0.97824	0.57312	−0.48529	0.26885	−0.73349	−1.89108
0.90005	1.01327	0.56596	−0.23756	0.16555	−0.34069	−1.57837
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—
1,3-Dioxolane + *i*-amyl alcohol						
0.00000	0.80319	3.11110	0.00000	0.00000	0.00000	—
0.11678	0.82142	2.29991	−0.51195	0.15588	−0.22415	−0.96433
0.22928	0.84113	1.80646	−0.71712	0.22984	−0.32135	−0.82479
0.33774	0.86196	1.45757	−0.78809	0.28423	−0.37398	−0.76962
0.44236	0.88396	1.16673	−0.81085	0.32478	−0.46884	−0.86414
0.54336	0.90791	0.99491	−0.72386	0.28621	−0.42717	−0.79483
0.64092	0.93313	0.88176	−0.58702	0.25432	−0.30807	−0.64592
0.73520	0.95989	0.78122	−0.44597	0.21604	−0.20933	−0.54508
0.82638	0.98836	0.71042	−0.28313	0.16819	−0.06358	−0.29898
0.91459	1.01899	0.62119	−0.14633	0.09110	−0.03559	−0.30788
1.00000	1.05184	0.54866	0.00000	0.00000	0.00000	—

Note: Density, ρ; viscosity, η; viscosity deviation, ($\Delta\eta$); excess molar volume, (V^E); Gibbs excess energy of activation for viscous flow, (G^{*E}), and Grunberg–Nissan interaction parameter, (d^1).

of activation, G^{*E}, for viscous flow are calculated as[24]

$$\Delta\eta = \eta_{\mathrm{mix}} - [x_1\eta_1 + x_2\eta_2] \tag{2}$$

$$G^{*E} = \mathrm{RT}[\ln \eta_{\mathrm{mix}} V_{\mathrm{mix}} - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \tag{3}$$

where η_{mix} and V_{mix} are the viscosity and molar volume of the mixture; η_1, η_2, V_1, and V_2 are the viscosities and molar volumes of pure components (1) and (2), respectively.

Isentropic compressibilities, K_S, and excess isentropic compressibilities, K_S^E, are calculated from the experimental densities, ρ, and speeds of sound, u, using the following equations[7,11,25–27]

$$K_S = 1/u^2\rho \tag{4}$$

$$\Delta K_S = K_S - x_1 K_{S,1} - x_2 K_{S,2}, \tag{5}$$

where K_S, $K_{S,1}$, and $K_{S,2}$ are the isentropic compressibilities of the mixture, pure component 1 and pure component 2, respectively.

Experimental speeds of sound and estimated isentropic compressibilities, as well as the excess isentropic compressibilities, are compiled in Table III.

3.1. Correlating Equations

The viscosity values are further used to determine the Grunberg–Nissan parameter[28] d^1 as

$$\ln \eta_{\mathrm{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d^1 \tag{6}$$

where d^1 is proportional to the interchange energy. The d^1 values for the mixtures are reported in Table II.

Again, V^E, $\Delta\eta$, G^{*E}, and K_S^E values were fitted by the Redlich–Kister equation[29] using the method of least squares involving the Marquardt algorithm[30] to derive the binary coefficient, A_J:

$$Y^E = x_1 x_2 \sum_{J=1}^{k} A_{J-1}(x_1 - x_2)^{J-1} \tag{7}$$

Here, Y^E denotes V^E, $\Delta\eta$, G^{*E}, and K_S^E. In each case, the optimum number of coefficients, A_J is ascertained from an examination of the variation of the standard deviation, σ, with

$$\sigma = \left[\left(Y_{\mathrm{exp}}^E - Y_{\mathrm{cal}}^E\right)^2/(n-m)\right]^{1/2} \tag{8}$$

where n represents the number of measurements and m the number of coefficients.

The estimated values of A_J and σ for V^E, $\Delta\eta$, G^{*E}, and K_S^E are summarized for all studied mixtures in Table IV.

Table III. Speeds of Sound (u), Isentropic Compressibilities (K_S) and Excess Isentropic Compressibility (K_S^E) of Binary Mixtures of Various Compositions (Mole Fraction) at 303.15 K

Mole fraction 1,3-dioxolane (x_1)	u (m-s^{-1})	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})	Mole fraction 1,3-dioxolane (x_1)	u (m-s^{-1})	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})
	1,3-Dioxolane + methanol				1,3-Dioxolane + ethanol		
0.00000	1088.5	1078.7	0.0	0.00000	1144.3	973.7	0.0
0.04585	1122.2	987.9	−67.6	0.06463	1159.1	924.7	−23.1
0.09758	1135.7	938.1	−91.2	0.13455	1171.1	881.9	−37.8
0.15637	1145.7	895.5	−104.1	0.21044	1183.4	840.6	−48.7
0.22381	1157.9	851.9	−113.5	0.29308	1197.8	797.8	−58.3
0.30192	1174.8	803.2	−122.7	0.38344	1215.0	753.4	−66.5
0.39348	1198.8	748.5	−131.1	0.48263	1225.3	719.3	−60.8
0.50228	1230.7	688.8	−135.7	0.59202	1238.7	682.7	−53.5
0.63370	1255.6	641.8	−116.2	0.71327	1255.9	643.6	−44.0
0.79561	1281.4	597.5	−78.5	0.84842	1275.5	604.3	−29.1
1.00000	1288.5	572.6	0.0	1.00000	1288.5	572.6	0.0
	1,3-Dioxolane + 1-propanol				1,3-Dioxolane + 2-propanol		
0.00000	1182.6	898.5	0.0	0.00000	1126.6	1013.6	0.0
0.08269	1185.5	872.9	1.3	0.08269	1136.9	970.2	−6.9
0.16862	1195.3	837.5	−6.0	0.16862	1151.2	921.9	−17.3
0.25799	1208.8	798.1	−16.3	0.25799	1166.3	873.8	−26.0
0.35101	1211.1	774.4	−9.7	0.35101	1182.5	826.4	−32.4
0.44791	1215.2	748.7	−3.8	0.44791	1199.2	780.3	−35.8
0.54893	1218.6	724.0	4.4	0.54893	1208.4	745.1	−26.4
0.65434	1236.8	682.6	−2.7	0.65434	1221.8	706.1	−18.9
0.76444	1255.7	642.5	−6.9	0.76444	1239.9	663.2	−13.3
0.87954	1271.4	607.4	−4.5	0.87954	1260.9	619.7	−6.0
1.00000	1288.5	572.6	0.0	1.00000	1288.5	572.6	0.0
	1,3-Dioxolane + 1-butanol				1,3-Dioxolane + 2-butanol		
0.00000	1196.6	870.7	0.0	0.00000	1168.9	915.7	0.0
0.10005	1200.8	845.1	4.2	0.10005	1173.1	889.4	8.0
0.20009	1205.3	819.1	8.0	0.20009	1177.5	862.6	15.6
0.30011	1208.4	795.3	14.1	0.30011	1182.8	833.9	21.2
0.40013	1218.8	761.8	10.4	0.40013	1193.2	798.3	19.9
0.50013	1229.6	728.8	7.2	0.50013	1212.5	752.4	8.3
0.60013	1240.9	696.1	4.3	0.60013	1234.4	705.9	−3.9
0.70011	1251.9	664.8	2.8	0.70011	1253.6	664.9	−10.6
0.80009	1263.1	634.2	2.0	0.80009	1267.5	631.2	−9.9
0.90005	1275.2	603.6	1.2	0.90005	1274.8	604.7	−2.2
1.00000	1288.5	572.6	0.0	1.0000	1288.5	572.6	0.0
	1,3-Dioxolane + *t*-butanol				1,3-Dioxolane + *i*-amyl alcohol		
0.00000	1078.8	1108.6	0.0	0.00000	1197.0	868.9	0.0
0.10005	1098.7	1042.9	−12.0	0.11678	1199.8	845.7	11.4
0.20009	1121.1	976.4	−24.9	0.22928	1203.8	820.4	19.4
0.30011	1144.7	911.4	−36.3	0.33774	1208.5	794.3	25.5
0.40013	1169.0	849.5	−44.6	0.44236	1215.8	765.3	27.5
0.50013	1184.7	802.7	−37.8	0.54336	1230.3	727.7	19.8
0.60013	1201.2	757.0	−29.9	0.64092	1242.7	693.9	14.9
0.70011	1221.4	708.8	−24.5	0.73520	1255.7	660.7	9.6
0.80009	1243.2	661.5	−18.3	0.82638	1266.1	631.2	7.2
0.90005	1266.5	615.3	−10.9	0.91459	1276.6	602.2	4.3
1.00000	1288.5	572.6	0.0	1.00000	1288.5	572.6	0.0

Table IV. Estimated Parameters of Eq. (7) for Excess Functions for the Binary Mixtures of 1,3-Dioxolane (1) + Monoalcohols (2) at 303.15 K

Function	A_0	A_1	A_2	σ
1,3-Dioxolane + methanol				
$V^E \times 10^3$ (m^3-mol^{-1})	−1.18037	0.29341	0.21420	0.00648
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	0.12407	−0.05029	−0.24601	0.00411
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	0.90054	−0.28662	−1.11756	0.01869
$K_S^E \times 10^{12}$ (Pa^{-1})	−542.5	−65.4	−355.9	0.1
1,3-Dioxolane + ethanol				
$V^E \times 10^3$ (m^3-mol^{-1})	−0.11914	0.10135	—	0.00179
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−0.59825	0.42012	−0.86330	0.00029
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−1.77518	1.23789	−3.14322	0.01421
$K_S^E \times 10^{12}$ (Pa^{-1})	−242.8	146.7	−44.9	1.1
1,3-Dioxolane + 1-propanol				
$V^E \times 10^3$ (m^3-mol^{-1})	0.55476	0.16595	−0.55390	0.00357
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−1.67833	0.61688	−0.86578	0.00313
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−3.35532	−0.22204	−0.29213	0.01290
$K_S^E \times 10^{12}$ (Pa^{-1})	3.6	85.6	−373.2	1.9
1,3-Dioxolane + 2-propanol				
$V^E \times 10^3$ (m^3-mol^{-1})	0.88575	−0.25715	—	0.00628
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−1.81023	1.00486	0.88281	0.00265
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−4.02077	0.91517	5.47182	0.01367
$K_S^E \times 10^{12}$ (Pa^{-1})	−123.4	105.4	72.8	1.5
1,3-Dioxolane + 1-butanol				
$V^E \times 10^3$ (m^3-mol^{-1})	0.93948	−0.42461	0.40040	0.00583
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−2.80851	1.64517	−2.91633	0.00201
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−3.41517	0.83967	−1.24054	0.02121
$K_S^E \times 10^{12}$ (Pa^{-1})	32.9	−42.8	—	1.7
1,3-Dioxolane + 2-butanol				
$V^E \times 10^3$ (m^3-mol^{-1})	1.52385	−0.65650	0.96778	0.00052
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−2.94697	2.02543	0.74317	0.00035
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−4.55415	2.05980	0.49414	0.02744
$K_S^E \times 10^{12}$ (Pa^{-1})	28.8	−147.2	—	4.1
1,3-Dioxolane + *t*-butanol				
$V^E \times 10^3$ (m^3-mol^{-1})	1.85435	−0.46020	0.39839	0.00639
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−4.23108	3.23501	−3.59752	0.00123
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−5.28143	1.27430	−0.54361	0.03782
$K_S^E \times 10^{12}$ (Pa^{-1})	−154.1	111.2	48.3	1.7
1,3-Dioxolane + *i*-amyl alcohol				
$V^E \times 10^3$ (m^3-mol^{-1})	1.19788	−0.22010	0.15846	0.01055
$\Delta\eta \times 10^3$ (kg-m^{-1}-s^{-1})	−3.06573	1.53808	0.46358	0.00804
$G^{*E} \times 10^{-3}$ (J-mol^{-1})	−1.79697	0.58402	2.77346	0.01795
$K_S^E \times 10^{12}$ (Pa^{-1})	95.2	−118.3	−88.9	0.8

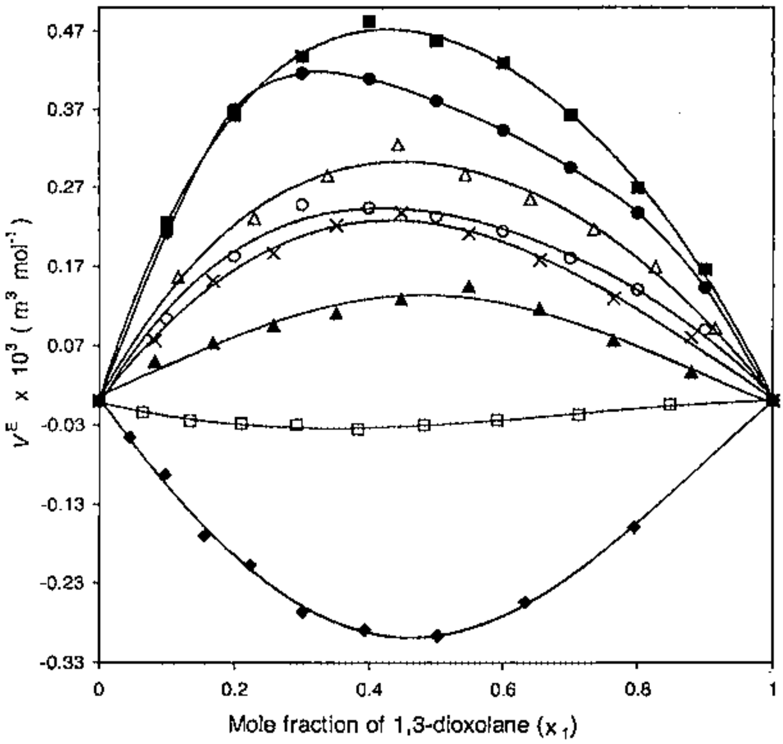

Fig. 1. Plots of excess molar volume (V^E) *versus* mole fraction of 1,3-dioxolane (x_1) at 303.15 K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (○), 2-butanol (●), *t*-butanol (■), and *i*-amyl alcohol (△).

4. DISCUSSION

We have calculated $\Delta\eta$, V^E and G^{*E} at 303.15 K for the binary mixtures of 1,3-dioxolane (1) with the monoalcohols (2). The variations of the excess properties over the entire range of compositions for the binary mixtures are depicted in Figs. 1–3.

The value of the excess molar volume was found to be negative for the 1,3-dioxolane and methanol mixture, but the magnitude of negative value decreases and the positive value increases with increasing chain length of the alcohols in the series (Fig. 1). The trend it follows is

$$\text{MeOH} < \text{EtOH} < \text{1-PrOH} < \text{2-PrOH} < \text{1-BuOH} < i\text{-AmOH}$$
$$< \text{2-BuOH} < t\text{-BuOH}$$

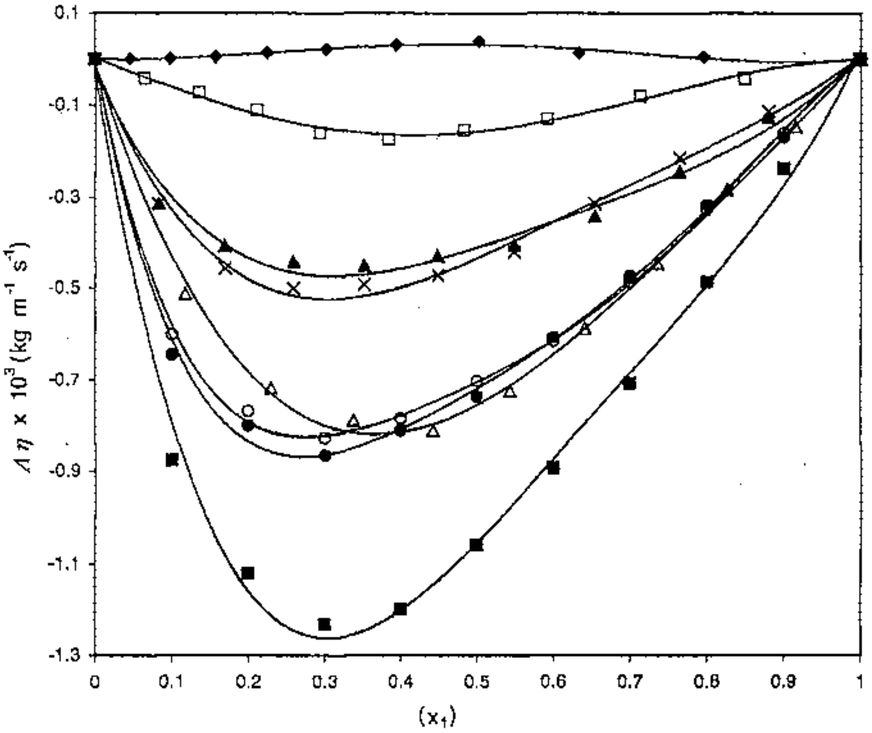

Fig. 2. Plots of viscosity deviations ($\Delta\eta$) *versus* mole fraction of 1,3-dioxolane (x_1) at 303.15 K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (○), 2-butanol (●), *t*-butanol (■), and *i*-amyl alcohol (Δ).

The negative V^E values indicate the presence of strong molecular interactions between the components of the mixture.

Several effects may contribute to the value of V^E, such as(31–33) (a) dipolar interactions, (b) interstitial accommodation of one component into the other and (c) possible hydrogen-bond interactions between unlike molecules. The actual volume change, therefore, depends on the relative strength of these three effects. It is known fact that as the number of C-atoms of the alkyl group increases, the electron releasing ability (+I effect) increases, thereby decreasing the polarity of the O—H bond of the monoalcohols. Consequently, MeOH having the highest polarity achieves the most favorable intermolecular H-bonded interactions with the cyclic diether molecules. Moreover, its simple structure and smaller size leads to interstitial accommodation with 1, 3-dioxolane molecules more easily compared to the higher monoalcohols that have greater structural complexity. Similar results have been reported earlier.(34,35)

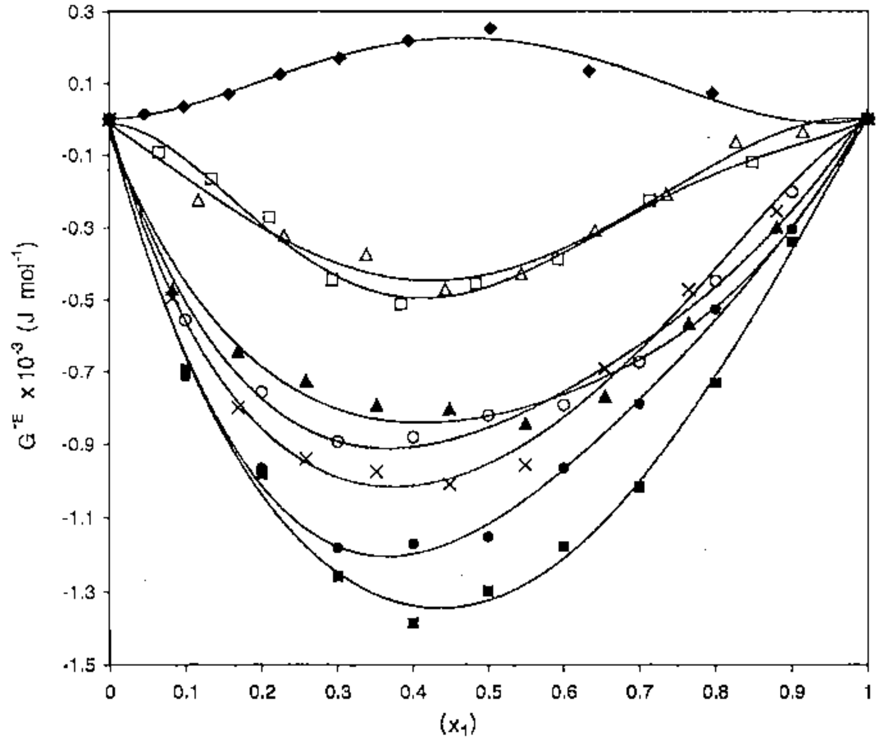

Fig. 3. Plots of Gibbs excess energy of activation for viscous flow (G^{*E}) *versus* mole fraction of 1,3-dioxolane (x_1) at 303.15 K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (○), 2-butanol (●), *t*-butanol (■), and *i*-amyl alcohol (△).

It is further observed that in the case of branched monoalcohols, V^E values are higher than the respective normal alcohols. This may be attributed primarily to steric factors arising from a change in the proportion of different structural forms of the alcohol molecules with a change in its mole fraction. This also explains the expected behavior of *i*-AmOH in this paper. Similar types of work have been reported in other papers.(36,37)

Figure 2 shows that $\Delta\eta$ values are positive for 1,3-dioxolane and methanol systems, but with the increase in the chain length in alcohols, the magnitude of the negative deviation increases. The order it follows is:

$$\text{MeOH} > \text{EtOH} > \text{1-PrOH} > \text{2-PrOH} > i\text{-AmOH}$$
$$> \text{1-BuOH} > \text{2-BuOH} > t\text{-BuOH}$$

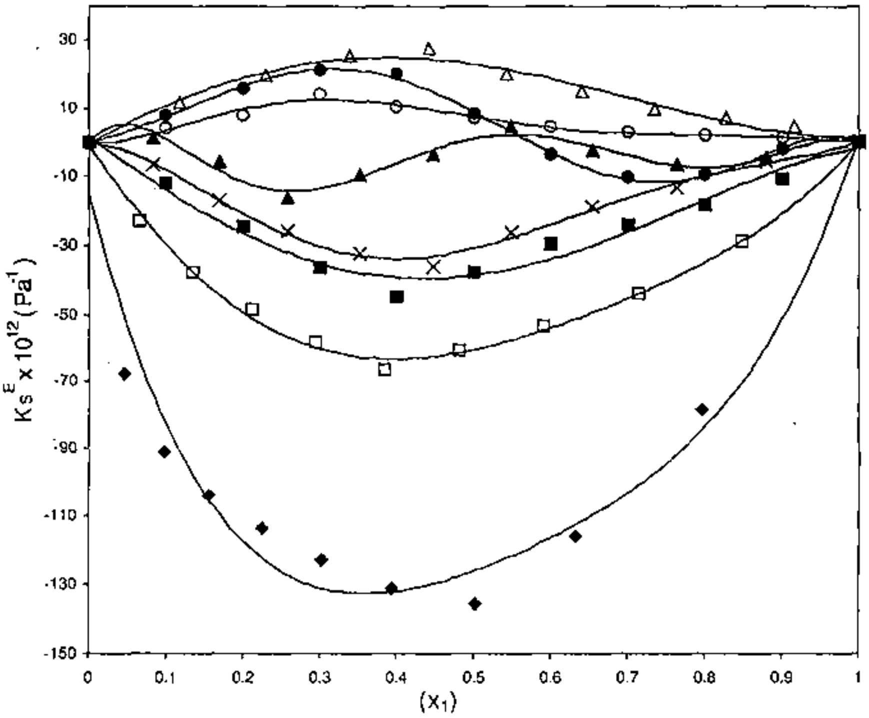

Fig. 4. Plots of excess isentropic compressibility (K_S^E) *versus* mole fraction of 1,3-dioxolane (x_1) at 303.15 K for binary mixtures of 1,3-dioxolane with methanol (◆), ethanol (□), 1-propanol (▲), 2-propanol (x), 1-butanol (○), 2-butanol (●), *t*-butanol (■), and *i*-amyl alcohol (△).

A correlation between the signs of $\Delta\eta$ and V^E have been observed for a number of binary solvent systems,(38,39) *i.e.*, $\Delta\eta$ is positive when V^E is negative and *vice-versa*. 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 $\Delta\eta$ values.(40)

In Fig. 3, the value of Gibbs excess energy of activation of viscous flow, *i.e.*, G^{*E} is observed to be positive for the (1) and methanol mixture, and negative for the (1) and ethanol mixture onwards. G^{*E} values for the systems under study suggest the following order:

$$\text{MeOH} > \text{AmOH} > \text{EtOH} > \text{PrOH} > \text{BuOH}$$

It has been reported(41,42) that the G^{*E} parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules.

The magnitude of the positive value is an excellent indication of the strength of a specific interaction.

Here it is observed that the magnitude of negative values increases with increasing chain length of the alcohols. Alcohol molecules self-associate(43) very strongly (OH—OH interaction), whereas the cyclic diether, 1,3-dioxolane, molecules self-associate rather marginally. This has a dramatic influence on the thermo-physical properties studied. The positive value for the (1) and MeOH mixture indicates favorable intermolecular complexation through H-bonding, *i.e.*, O—O—H—O. This interaction can be considered as the H-bond formation between the alcohols as Lewis acids and the cyclic diether as a Lewis base.(31,46)

Fort and Moore,(44) and Ramamoorthy(45) reported that for any binary liquid mixture, a positive value of d^1 indicates the presence of strong interactions and a negative value of d^1 indicates the presence of weak interactions between the components. On this basis, positive d^1 values for the (1) and MeOH system confirm the presence of strong interactions between the component molecules, whereas for higher monoalcohols this affinity for bonding decreases. These conclusions are in excellent agreement with that reported by Subha *et al.*(31,46,47)

In Table III, the excess isentropic compressibilities, K_S^E, are reported for the 1,3-dioxolane + monoalcohol mixtures. From Fig. 4, it is evident that the K_S^E values are negative for lower monoalcohols, but the magnitude of the negative values diminishes and the positive values increase with increasing chain length of the alcohols. The order it follows is:

$$\text{MeOH} < \text{EtOH} < \text{PrOH} < \text{BuOH} < \text{AmOH}$$

These results can be explained in terms of molecular interactions and structural effects. Positive K_S^E values are due to the breaking of interactions and the corresponding disruption of molecular order in the pure components.(48) Interactions between the molecules of cyclic diether and monoalcohols are broken in the mixing process; the breaking of strong dipole–dipole interactions in 1,3-dioxolane, which can be considered as a polar fluid,(49) leads to positive K_S^E values for the mixtures containing the longer chain length of alcohols as compared to the lower alcohols. The donor–acceptor interaction between the oxygen and hydrogen atoms of the cyclic diether and the alcohols play an important part for the mixtures containing lower alcohols, like MeOH and EtOH, where there is a strong specific interaction between the component molecules leading to negative value of K_S^E.

Also, it is observed that for isomeric monoalcohols, *i.e.*, 1-PrOH and 2-PrOH, the K_S^E values are less negative for linear 1-PrOH as compared to the branched 2-PrOH. The same trend is observed between butanol isomers, whereby K_S^E values are positive for linear 1-BuOH, partially negative for 2-BuOH and totally negative for the branched isomer *t*-BuOH. This type of trend has been observed and reported in earlier papers.(7,25) This type of behavior is explained by the interstitial accommodation and changes in free volume as explained in other papers.(26,35) The branched isomers fit into the structure of cyclic diether more easily compared to the linear isomers, thereby producing more negative K_S^E values. Thus, it can also be explained that due to extensive branching and longer chain length, *i*-amyl alcohol exhibited exceptional behavior in many cases.

In the eight binary mixtures of the cyclic diether and the monoalcohols, it is really interesting to note that V^E, $\Delta\eta$, G^{*E}, and K_S^E have maxima in the mole fraction range $x_1 = 0.3$ to 0.5. This is a manifestation of strong specific interactions(50) between the cyclic diether and monoalcohol molecules predominated by H-bonded interactions. These maximum values are a clear indication of the highest interaction between the component molecules for the above-mentioned binary mixtures.

5. CONCLUSION

After a thorough study of the behavior of monoalcohols and the cyclic diether, we get a clear idea about the type and amount of molecular interactions between the components. The lower monoalcohols are found to associate more strongly with cyclic diether molecules as compared to the higher ones. Further, the branched isomers exhibited a different behavior than the linear forms. Self-association between the alcohol molecules was found to increase with increasing chain length. The study of excess properties along with the speeds of sound has been found to be very useful in understanding the nature of the interactions within binary liquid mixtures. The parameters obtained from the correlating equations have also provided us with valuable information.

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REFERENCES

1. M. N. Roy, A. Choudhury, and A. Sinha, *J. Teach. Res. Chem.* **11**, 12 (2004).
2. D. K. Hazra, M. N. Roy, and B. Das, *Indian J. Chem. Techno.* **1**, 93 (1994).
3. M. N. Roy and A. Choudhury, *J. Teach. Res. Chem.* **1**, 17 (2000).
4. M. N. Roy, B. B. Gurung, and A. Choudhury, *J. Indian Chem. Soc.* **81**, 1 (2004).
5. S. L. Oswal and H. S. Desai, *Fluid Phase Equilib.* **161**, 191 (1999).
6. S. L. Oswal and H. S. Desai, *Fluid Phase Equilib.* **186**, 81 (2001).
7. C. Lafuente, B. Giner, A. Villares, I. Gascon, and P. Cea, *Int. J. Thermophys.* **25**, 1735 (2004).
8. P. S. Nikam, L. N. Shirsat, and M. Hasan, *J. Indian Chem. Soc.* **77**, 244 (2000).

9. E. Perez, M. Cardoso, A. M. Mainar, J. I. Pardo, and J. S. Urieta, *J. Chem. Eng. Data* **48**, 1306 (2003).
10. J. N. Nayak, T. M. Aminabhavi, and M. I. Aralaguppi, *J. Chem. Eng. Data* **48**, 1152 (2003).
11. G. Douheret, A. Pal, and M. I. Davis, *J. Chem. Thermodyn.* **22**, 1 (1990).
12. S. L. Oswal and K. D. Prajapati, *J. Chem. Eng. Data.* **43**, 367 (1998).
13. J. R. Suindells and T. B. Godfray, *J. Res. Natd. Bur. Stand.* **48**, 1 (1952).
14. M. N. Roy, A. Jha, and R. Dey, *J. Chem. Eng. Data* **46**, 1247 (2001).
15. M. N. Roy, A. Jha, and A. Choudhury, *J. Chem. Eng. Data* **49**, 291 (2004).
16. S. L. Oswal and H. S. Desai, *Fluid Phase Equilib.* **149**, 359(1998).
17. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. (Pergamon, Great Britain, 1988).
18. J. Riddick, W. B. Bunger, and T. K Sakano, *Organic Solvents: Physical Properties and Methods of Purification* (Wiley, New York, 1986).
19. J. N. Gurtu and R. Kapoor, *Adv. Exp. Chem.* **1**, 338, 346 (1987).
20. J. Timmermans, *Physico Chemical Constants of Pure Organic Compounds* (Elsevier, Amsterdam, 1950, 1; 1965, 2).
21. A. K. Covington and T. Dickinson, *Physical Chemistry of Organic Solvent Systems* (Plenum, New York, 1973).
22. A. W. Quin, D. F. Hoffmann, and P. Munk, *J. Chem. Eng. Data* **37**, 55 (1992).
23. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Process* (McGraw-Hill, New York, 1941, p. 514).
24. D. S. Gill, T. S. Kaur, H. Kaur, I. M. Joshi, and J. Singh, *J. Chem. Soc., Faraday Trans.* **89**, 1737 (1993).
25. H. Artigas, C. Lafuente, M. C. Lopez, F. M. Royo, and J. S. Urieta, *Zeit. Phys. Chem.* **215**, 933 (2001).
26. I. Gascon, S. Martin, P. Cea, M. C. Lopez, and F. M. Royo, *J. Solution Chem.* **31**, 905 (2002).
27. F. Kimura, A. Treszczanowicz, C. Halpin, and G. Benson, *J. Chem. Thermodyn.* **15**, 503 (1983).
28. L. Grunberg and A. H. Nissan, *Nature* **164**, 799(1949).
29. O. Redlich and A. J. Kister, *Ind. Eng. Chem.* **40**, 345 (1948).
30. D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
31. M. C. S. Subha and K. C. Rao, *J. Phys. Chem. Liq.* **18**, 185 (1988).
32. A. Assarsson and F. R. Eirich, *J. Phys. Chem.* **72**, 2710 (1968).
33. E. A. Muller, *J. Chem. Eng. Data* **36**, 214 (1991).
34. P. Brocos, E. Calvo, A. Pineiro, R. Bravo, and A. Amigo, *J. Chem. Eng. Data* **44**, 1341 (1999).
35. A. Amigo, R. Bravo, and M. Pintos, *J. Chem. Eng. Data* **38**, 141 (1993).
36. D. Papaioannou, M. Bridakis, and C. Panayiotou, *J. Chem. Eng. Data* **38**, 616 (1993).
37. A. Krishnaiah and P. R. Naidu, *Acta Chem. Acad. Sci. Hung.* **104**, 295 (1986).
38. D. S. Gill and T. S. Cheema, *Z. Phys. Chem* (*N.F*). **134**, 205 (1983).
39. Y. Marcus, *Ion Solvation* (Wiley, New York, 1985).
40. M. G. Prolongo, R. M. Masegosa, H. I. Fuentes, and A. Horta, *J. Phys. Chem.* **88**, 2163 (1984).
41. T. M. Reed and T. E. Taylor, *J. Phys. Chem.* **63**, 58 (1959).
42. R. Meyer, M. Meyer, and J. Metzer, *A. Peneloux. Chem. Phys.* **62**, 406 (1971).
43. A. J. Treszczanowicz, T. Treszczanowicz, T. Pawlowski, and T. K. Guttman, *J. Solution Chem.* **33**, 1049 (2004)..
44. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.* **62**, 1112 (1966).
45. K. Ramamoorthy, *J. Pure. Appl. Phys.* **11**, 554 (1973).
46. P. S. Nikam and M. Hasan, *J. Chem. Eng. Data* **33**, 165 (1988).
47. B. V. K. Naidu, K. C. Rao, and M. C. S. Subha, *J. Indian Chem. Soc.* **78**, 259 (2001).
48. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.* **61**, 2102 (1965).
49. T. Takizawa and K. Tamura, *J. Therm. Anal. Calorim.* **69**, 1075 (2002).
50. L. Pikkarainen, *J. Chem. Eng. Data* **33**, 299 (1988).

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Electrical Conductances of Some Ammonium and Tetraalkylammonium Halides in Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K

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Abstract. Electrical conductances of some ammonium and tetraalkylammonium halides have been measured in different mass (20-80%) of 1,4-dioxane + water mixtures at 298.15 K. The limiting molar conductivity (Λ_0), the association constant (K_A), and association distance (R) in the solvent mixtures have been evaluated using Fuoss conductance equation (Fuoss, 1978). 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 been also discussed. The results have been considered in terms of ion-solvent and ion-ion interactions and the structural changes in the mixed solvent systems.

Keywords: 1,4-dioxane, ammonium and tetraalkylammonium halides, limiting molar conductivity, association constant, solvation, Walden product, ion-solvent and ion-ion interactions, Fuoss conductance equation

Introduction

Studies on ionic solvation of ammonium and tetraalkylammonium salts in solvents of low permitivity are very few. Such studies have significant importance because of their applications in modern technology (Jasinki, 1967). 1,4-dioxane and its aqueous binary mixtures are very important solvents, widely used in various industries. These solvents figure prominantly in the high-energy battery technology, having also found application in organic syntheses as manifested from the numerous physicochemical studies in these media (Roy *et al.*, 2001; Roy, 2000; Roy and Hazra, 1994; Janz, 1973). With a system of varying dielectric constant in the mixed solvents, there exists scope of variation of solvent-solvent interactions since composition of the solvents in a binary mixture is varied. Thus, studies in mixed solvents may provide information regarding both the specific and non-specific solvent effects on the ion-association phenomena.

In the present work, an attempt has been made to ascertain the complete nature of ion-solvent and solvent-solvent interactions of ammonium and tetraalkylammonium salts in aqueous binary mixtures of 1,4-dioxane at 298.15 K.

Materials and Methods

1,4-dioxane (Merck, India) was kept several days over KOH, refluxed for 24 h and distilled over $LiAlH_4$, as described earlier (Roy *et al.*, 2001). The purified solvent had a density of 1.03052 g.cm^{-3} and viscosity co-efficient of 1.20011 cp at 298.15 K, which compared well with the values reported in literature (Covington and Dickinson, 1973). Five salts, namely, Me_4NCl, Et_4NBr, Pr_4NBr, Bu_4NBr and Bu_4NI (A.R. grade), were purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium. After filtration, the salts were dried in an oven for few hours. The ammonium halide salts, NH_4F, NH_4Br and NH_4Cl, were dried at about 80-100 °C in a vacuum oven for 48 h before use (Perrin and Armarego, 1988). Stock solutions of each salt were prepared by mass, and the working solutions were obtained by mass dilution. The values of dielectric constant (ε) were taken from those reported in the literature (Covington and Dickinson, 1973), whereas the densities (ρ_0) and viscosities (η_0) of the solvent mixtures were measured by an Ostwald-Sprengel type pycnometer and suspended-level Ubbelohde type viscometer, respectively, as described in detail earlier (Roy *et al.*, 2001). The conductance measurements were carried out in a systronic 306 conductivity bridge (accuracy ± 0.1%), using a dip-type immersion conductivity cell, CD-10 having cell constant 1.0 ± 10%. Measurements were made in a waterbath maintained within 298.15 ± 0.01 K.

Results and Discussion

The solvent properties of the different aqueous binary mixtures of 1,4-dioxane are given in Table 1, where ε is the dielectric constant, ρ_0 the density (g.cm^{-3}), η_0 the viscosity (cp), and x_1 the mole fraction of 1,4-dioxane. Molar conductances (Λ) of the electrolyte solutions, as a function of molar concentration (c), are given in Table 2 for the different solvent mixtures at 298.15 K.

The analysis of conductance data in terms of limiting molar conductance (Λ_0) and ion-association constant (K_A) of the electrolytes have been carried out iteratively according to

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Shedlovsky equation using least square treatment for the reasons described earlier (Gill and Chauhan, 1984). Shedlovsky method involves the linear extrapolation using the following equation (Bag *et al.*, 2000):

$$1/\Lambda S(z) = 1/\Lambda_0 + [K_A/\Lambda_0^2]c\Lambda f_{\pm}^2 S(z) \qquad (1)$$

where:

Λ = the equivalent conductance at the concentration c
c = molar concentration (mol.lit^{-1})
Λ_0 = the limiting equivalent conductance
K_A = the observed association constant

The other symbols are given by:

$$S(z) = [(z/2) + \sqrt{(1 + (z/2)^2)}]^2$$
$$z = [(\alpha\Lambda_0 + \beta)/\Lambda_0^{3/2}](c\Lambda)^{1/2}$$
$$\alpha = 0.8204 \times 10^6/(\varepsilon T)^{3/2}\ ;\ \beta = 82.501/\eta(\varepsilon T)^{1/2} \qquad (2)$$

where:

ε = the dielectric constant
η = the viscosity of the medium
T = absolute temperature

The degree of dissociation (τ) is related to S(z) by:

$$\tau = \Lambda S(z)/\Lambda_0$$

$f_{\pm}$ = the mean activity co-efficient of the free ions, which was calculated by the following equation:

$$-\log f_{\pm} = \Lambda(\tau c)^{1/2}/[1 + BR(\tau c)^{1/2}] \qquad (3)$$

where:

$\Lambda = 1.8246 \times 10^6/(\varepsilon T)^{3/2}$
$B = 0.5029 \times 10^{10}/(\varepsilon T)^{1/2}$
R = association distance

The initial Λ_0 values for the iteration procedure were, thus, obtained from Shedlovsky extrapolation of the data (Roy *et al.*, 1993a).

The conductance data were analyzed using Fuoss conductance equation (Fuoss, 1978), which was programmed in a computer. So, with a given set of conductivity values (c_j, Λ_j; j = 1,........ n), three adjustable parameters, i.e., Λ_j, K_A and R were derived from the Fuoss equation. Here, R is the association distance, i.e., the maximum centre-to-centre distance between the ions in the solvent separated ion-pairs. There is no precise method for determining the R-value (Doe *et al.*, 1990), but in order to treat the data in our system, R-value was assumed to be:

$$R = a + d$$

where:

a = the sum of the crystallographic radii of ions, which varies from 2 to 7Å
d = the average distance corresponding to the side of a cell occupied by a solvent molecule

The distance d(Å) is given by (Fuoss, 1978):

$$d = 1.183(M/\rho_0)^{1/3} \qquad (4)$$

where:

M = the molecular weight
ρ_0 = the density of the solvent

For mixed solvents, M is replaced by the mole fraction average molecular weight (M_{AV}), which is given by:

$$M_{AV} = M_1M_2/[W_1M_2 + W_2M_1] \qquad (5)$$

where:

W_1 = the weight fraction of the first component of molecular weight, M_1
W_2 = the weight fraction of the second component of molecular weight, M_2

Though, this is an over-simplification, which ignores the possible selective solvation, it at least provides a self-consistent approach to obtain an acceptable value for the parameters when a broad range of R-values fit the data.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = \rho[\Lambda_0(1+R_X) + E_L] \qquad (6)$$

$$\rho = 1 - \alpha(1-\gamma) \qquad (7)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \qquad (8)$$

$$-\ln f = \beta\kappa/2(1+K_R) \qquad (9)$$

$$\beta = e^2/\varepsilon k_B T \qquad (10)$$

$$K_A = K_R/(1-\alpha) = K_R(1+K_S) \qquad (11)$$

where:

R_X = the relaxation field effect
E_L = the electrophoretic counter current constant
κ^{-1} = the radius of the ionic atmosphere
ε = the relative permittivity of the solvent
e = the electric charge
k_B = the Boltzmann constant
γ = the fraction of solute present as unpaired ion

c = the molarity of the solution

f = the activity coefficient

T = the temperature in absolute scale

β = twice the Bjerrum distance

K_R = formation and separation of the solvent-separated pairs by diffusion in and out of the sphere of dia R around cations

K_S = a constant describing the short-range process by which contact pairs form and dissociate

We input into the programme the number of data, n; followed by dielectric constant of the solvent mixture, ε; initial Λ_0 values, T, ρ; molecular weight of the solvents along with c_j, Λ_j values (where j = 1, 2,....., n); and an instruction to cover preselected range of R-values.

In practice, calculations were performed by finding the values of Λ_0 and σ, which minimized the standard deviation (σ), for a sequence of R-values and then plotting σ against R:

$$\sigma^2 = \sum_{j=1}^{n} \frac{[\Lambda_j[(\text{calc}) - \Lambda_j\,(\text{obs})]^2}{(n-2)} \qquad (12)$$

The best-fit R corresponds to the minimum of the σ versus R curve. First, approximate runs over a fairly wide range of R-values were made to locate the minimum, and then a fine scan around the minimum was made. Thus, the corresponding Λ_0 and K_A values were noted. The Λ_0, K_A, R, and Walden products ($\Lambda_0\eta_0$) for the ammonium and tetraalkylammonium halides in different aqueous binary mixtures of 1,4-dioxane were thus reported in Table 3.

The association constants, K_A recorded in Table 3 indicate that all the electrolytes were highly associated in these solvent mixtures. This was quite expected due to the low dielectric constant of 1,4-dioxane (2.209). The most outstanding feature was that the electrolytes containing smaller cations showed considerable amount of association. Here, values of K_A decreased as the size of the cation increased with the exception of Bu_4N^+ ion, whereas Λ_0 increased. The possible explanation is that it may be due to the larger size of the cations, which are less solvated than the smaller ones. Similar results have been reported earlier by some workers (Mukhopadhyay and Pal, 2002) during the conductance study of 1-ethyl-4-cyanopyridinium iodide in aqueous binary mixtures of 1,4-dioxane.

The K_A values of various tetraalkylammonium halides in these solvent mixtures follow the order:

$Me_4N^+ > Bu_4N^+ > Et_4N^+ > Pr_4N^+$

However, in the case of ammonium halides, the value of Λ_0 enhanced in the order:

$F^- < Cl^- < Br^-$

This trend of variation indicates the relative actual sizes of these anions, having common ammonium ion as they existed in the solution. Thus, the sizes of these anions as they existed in these solutions followed the order:

$F^- > Cl^- > Br^-$

This shows that F^- was the most solvated and Br^- was the least solvated in any mole fraction of 1,4-dioxane. Roy *et al.* (1993b) found similar trends for many of the alkali metal halides in tetrahydrofuran (THF) + H_2O mixtures. In the case of Bu_4NI, the value of K_A was greater than that of Bu_4NBr. This was expected owing to the larger size of I^- anion as compared to Br^- anion.

From Table 3 it may be observed that K_A values were noted to increase, whereas Λ_0 values decreased in aqueous binary mixtures of 1,4-dioxane with the increase of the mole fraction of 1,4-dioxane. This indicates that association of ions increased with the addition of 1,4-dioxane to the mixture rendering decreased mobility of ions in the mixture. The significantly large values of K_A and exothermic ion-pair formation in the solvent

Table 1. Physical properties of 1,4-dioxane + water mixtures at 298.15 K; ρ_0= density; η_0= viscosity; ε = dielectric constant; x_1 = mole fraction of 1,4-dioxane

x_1	ε	ρ_0/(g.cm^{-3}) present work	ρ_0/(g.cm^{-3}) literature[a]	η_0/(cp) present work	η_0/(cp) literature[b]
0	78.3	0.99707	0.9971	0.89041	0.8903
0.04863	63.5	1.01612	1.0143	1.29671	1.30
0.11996	44.4	1.03127	1.0284	1.69701	1.74
0.23472	27.5	1.04011	1.0360	1.98712	1.98
0.44991	12.1	1.04053	1.0350	1.78589	1.73
1	2.209	1.03052	1.0269	1.20011	1.196

a = ρ_0; b = η_0 (Covington and Dickinson, 1973)

Table 2. Molar conductances (Λ) and corresponding molarities (c) of some tetraalkylammonium halides and ammonium halides in different aqueous binary mixtures of 1,4-dioxane at 298.15 K (x_1 = mole fraction of 1,4-dioxane)

$c \times 10^4$ (mol.lit^{-1})	Λ (S.cm^2.mol^{-1})	$c \times 10^4$ (mol.lit^{-1})	Λ (S.cm^2.mol^{-1})	$c \times 10^4$ (mol.lit^{-1})	Λ (S.cm^2.mol^{-1})	$c \times 10^4$ (mol.lit^{-1})	Λ (S.cm^2.mol^{-1})
x_1 = 0.04863							
NH$_4$F		NH$_4$Cl		NH$_4$Br		Me$_4$NCl	
42.7	49.26	48.1	71.93	48.5	81.44	46.2	55.63
55.9	48.65	61.9	71.24	62.4	80.77	56.5	54.69
68.6	48.00	74.8	70.59	75.4	80.24	65.2	54.45
60.8	47.82	86.9	70.20	87.6	79.79	72.6	53.86
92.6	47.55	98.2	69.55	99.0	79.19	79.0	53.67
104.0	47.31	108.8	69.39	109.7	78.85	84.6	53.31
125.7	46.61	118.8	69.02	119.8	78.71	89.6	53.01
136.0	46.40	128.2	68.49	129.3	78.50	94.0	52.66
Et$_4$NBr		Pr$_4$NBr		Bu$_4$NBr		Bu$_4$NI	
44.8	66.96	45.6	78.24	51.7	87.62	47.1	60.65
57.6	65.97	54.2	77.47	67.8	86.92	61.6	59.64
69.6	65.09	69.1	76.52	75.2	86.51	66.1	59.33
80.8	64.36	75.6	74.04	82.1	86.25	74.7	58.78
91.3	63.86	81.6	75.76	88.6	86.07	78.8	58.53
101.2	63.34	92.2	75.28	94.8	85.91	82.8	58.48
110.5	62.81	96.9	74.99	97.8	85.82	97.6	57.62
119.3	62.45	101.3	74.91	100.7	85.67	104.4	57.24
x_1 = 0.11996							
NH$_4$F		NH$_4$Cl		NH$_4$Br		Me$_4$NCl	
25.6	45.31	22.5	59.11	20.2	72.65	17.8	47.49
34.8	43.97	25.8	58.02	26.0	71.08	21.2	46.45
38.4	43.75	33.8	57.24	29.8	70.89	26.6	45.63
43.7	43.25	38.5	57.15	39.1	69.84	37.0	44.35
55.5	42.34	48.9	55.51	48.1	68.67	43.9	43.34
71.4	41.18	56.1	55.18	73.6	65.31	48.7	42.69
79.0	40.76	69.7	53.68	89.3	63.92	57.8	41.79
93.4	39.83	82.4	52.80	104.2	62.66	66.4	41.04
Et$_4$NBr		Pr$_4$NBr		Bu$_4$NBr		Bu$_4$NI	
17.9	59.74	24.5	72.68	19.4	82.62	16.8	53.88
21.1	59.58	29.6	71.86	23.2	82.26	31.8	52.06
24.2	58.97	34.4	71.24	26.7	81.66	36.5	51.22
30.1	57.76	36.7	70.76	28.4	81.37	45.3	50.24
32.9	57.34	43.1	70.10	35.8	80.75	49.5	49.87
35.6	56.91	50.8	69.63	37.1	80.73	53.5	49.36
43.1	55.77	54.3	69.40	38.4	80.49	61.2	48.75
47.8	55.29	57.6	69.06	40.8	80.38	68.4	48.18
x_1 = 0.23472							
NH$_4$F		NH$_4$Cl		NH$_4$Br		Me$_4$NCl	
9.7	23.09	3.7	35.07	5.4	40.37	3.7	37.45
11.4	22.81	10.9	33.39	7.2	39.58	6.1	36.52
13.1	22.44	14.5	32.76	9.0	39.33	7.8	35.82
16.3	21.90	18.1	31.99	12.6	37.62	9.4	35.55
19.3	21.45	23.3	31.33	16.2	36.98	13.5	34.74
24.7	20.69	28.4	30.99	23.2	35.78	16.4	34.34
27.1	20.48	31.8	30.50	28.3	35.69	17.8	34.18
34.6	19.94	35.2	29.83	33.4	34.73	19.2	33.94
Et$_4$NBr		Pr$_4$NBr		Bu$_4$NBr		Bu$_4$NI	
3.7	48.56	5.2	51.69	4.1	56.76	4.3	43.88
6.1	47.62	6.7	51.49	5.9	56.32	6.2	43.19
7.1	46.97	10.3	51.08	6.4	56.22	7.1	42.94
8.8	46.14	11.2	51.00	7.4	56.02	10.5	41.76
10.3	45.87	13.9	50.81	8.4	55.93	11.3	41.48
11.8	45.59	15.2	50.68	10.3	55.45	14.1	41.13
16.1	44.50	18.8	50.56	11.1	55.38	15.4	40.88
21.3	43.74	22.1	50.39	11.9	55.24	16.6	40.75
x_1 = 0.44991							
NH$_4$F		NH$_4$Cl		NH$_4$Br		Me$_4$NCl	
1.9	2.12	0.3	5.88	0.5	5.98	0.6	23.12
3.2	1.85	0.7	5.51	0.7	5.80	0.9	22.30
3.7	1.79	1.4	5.08	1.2	5.51	1.0	21.40
4.9	1.65	1.7	4.78	1.7	5.32	1.2	20.90
6.8	1.50	2.1	4.55	2.2	5.07	1.9	18.80
7.9	1.46	2.9	4.51	2.5	4.94	2.4	17.33
9.5	1.41	3.3	4.27	3.2	4.69	2.7	17.11
9.9	1.39	3.9	4.36	3.5	4.54	2.8	16.82
Et$_4$NBr		Pr$_4$NBr		Bu$_4$NBr		Bu$_4$NI	
0.4	33.40	0.7	39.71	1.2	41.50	0.7	31.60
0.6	31.50	1.5	34.93	1.7	40.32	0.9	31.22
1.2	27.83	1.7	34.53	2.0	39.90	1.2	29.50
1.5	26.80	2.0	33.85	2.5	39.12	1.4	28.50
1.8	25.44	2.2	33.68	2.8	38.86	1.6	27.63
2.3	24.78	2.5	32.88	3.3	38.24	1.9	26.32
2.7	23.80	3.2	32.13	3.6	37.89	2.0	26.25
3.1	21.60	3.5	31.57	4.1	37.37	2.2	25.68

Table 3. Values of Λ_0, K_A, $\Lambda_0\eta_0$, R and σ for some ammonium and tetraalkylammonium halides in different aqueous binary mixtures of 1, 4-dioxane at 298.15 K

x_1	Λ_0 ($S.cm^2.mol^{-1}$)	K_A ($dm^3.mol^{-1}$)	R (Å)	$\Lambda_0\eta_0$	σ
NH_4F					
0.04863	51.53 ± 0.12	8.42	6.18	66.82	0.12
0.11996	49.36 ± 0.11	36.45	6.41	78.89	0.11
0.23472	26.27 ± 0.08	149.62	6.71	52.20	0.08
0.44991	3.14 ± 0.02	4535.07	7.21	5.61	0.02
NH_4Cl					
0.04863	75.58 ± 0.10	8.03	6.66	98.01	0.10
0.11996	63.67 ± 0.26	32.92	6.88	108.05	0.26
0.23472	37.76 ± 0.30	107.84	7.19	75.03	0.30
0.44991	6.36 ± 0.11	2500.04	7.68	11.36	0.11
NH_4Br					
0.04863	84.87 ± 0.11	5.85	6.69	110.05	0.11
0.11996	78.14 ± 0.28	33.76	7.02	132.60	0.28
0.23472	42.96 ± 0.36	100.72	7.33	85.37	0.36
0.44991	6.72 ± 0.06	2247.41	7.82	12.00	0.06
Me_4NCl					
0.04863	59.98 ± 0.12	16.78	8.65	77.78	0.12
0.11996	52.12 ± 0.15	59.64	8.67	88.45	0.15
0.23472	39.07 ± 0.16	90.51	9.17	77.64	0.16
0.44991	29.94 ± 0.28	6215.89	9.67	53.47	0.28
Et_4NBr					
0.04863	71.59 ± 0.07	14.79	9.32	92.83	0.07
0.11996	65.19 ± 0.16	47.24	9.53	110.63	0.16
0.23472	50.77 ± 0.24	94.19	9.85	100.89	0.24
0.44991	39.69 ± 0.49	5682.46	10.34	70.88	0.49
Pr_4NBr					
0.04863	82.65 ± 0.11	11.19	9.84	107.17	0.11
0.11996	77.21 ± 0.19	22.65	10.06	131.03	0.19
0.23472	53.10 ± 0.01	73.70	10.37	105.52	0.01
0.44991	44.74 ± 0.59	2253.78	10.86	79.90	0.59
Bu_4NBr					
0.04863	91.13 ± 0.06	5.56	10.26	118.17	0.06
0.11996	86.37 ± 0.11	16.39	10.48	146.57	0.11
0.23472	58.63 ± 0.01	30.94	10.79	116.50	0.01
0.44991	45.68 ± 0.08	659.09	11.28	81.58	0.08
Bu_4NI					
0.04863	65.18 ± 0.01	15.63	10.47	84.52	0.01
0.11996	57.80 ± 0.11	39.08	10.69	98.09	0.11
0.23472	46.17 ± 0.16	91.24	11.01	91.75	0.16
0.44991	40.57 ± 0.31	5107.55	11.49	72.45	0.31

x_1 = mole fraction of 1,4-dioxane; Λ_0 = limiting molar conductance; K_A = observed association constant; $\Lambda_0\eta_0$ = Walden product; R = association distance between ions; σ = standard deviation mixtures indicated the presence of specific short-range interaction within the ion-pair.

The variation of Walden product, $\Lambda_0\eta_0$ with x_1, the mole fraction of 1,4-dioxane for the electrolytes studied at 298.15 K, are shown in Fig. 1. The values of Walden product pass through a maximum at about $x_1 = 0.11996$ mole fraction of 1,4-dioxane, whereas the maximum viscosity of the aqueous binary mixtures at 298.15 K was observed at about $x_1 = 0.23472$ mole fraction of 1,4-dioxane. It is known that the variation of Walden product indicates the change of solvation (Doe *et al.*, 1990). The increase of Walden products indicates weak solvation of ions, which attains a maximum value at a particular solvent composition ($x_1 = 0.11996$). Such results have been interpretted in terms of microheterogeneity in the mixtures (Marcus and Migron, 1991).

On the water-rich side, there exists a region where the water structure remains more or less intact as the 1,4-dioxane molecules are added into the cavities in this structure. The cluster of water molecule has lower ability to donate a hydrogen atom to the solvation of ions. This may cause hydrophobic dehydration of cations (Mukhopadhyay and Pal, 2002), or may reduce the ability of hydrophobic ions to promote the structure in the water-rich region resulting in excess mobility, which in turn results an increase in Walden products to attain a maximum. As the percentage of 1,4-dioxane in the mixture increases, the self-associated structure gradually breaks at an increased mole fraction of 1,4-dioxane and thus preferential solvation occurs due to specific solute-solvent interaction leading to a decrease of Walden product (Taniewska-Osinska *et al.*, 1989). However, this decrease in the Walden product in large part may be due to the Zwanzig solvent relaxation effect also (Das and Hazra, 1995).

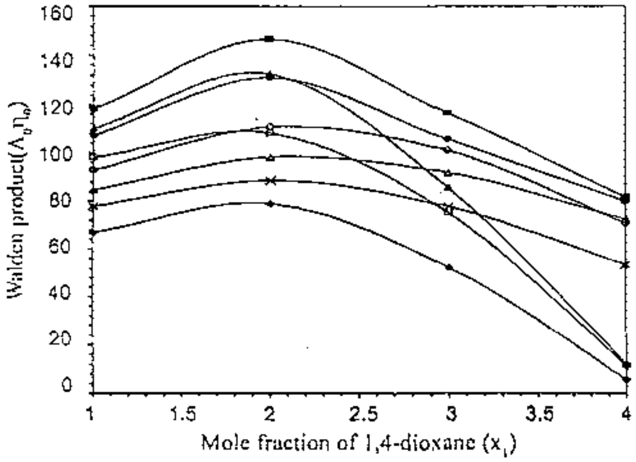

Fig. 1. Plots of mole fractions of 1,4-dioxane (x_1) versus Walden products ($\Lambda_0\eta_0$) for NH_4F (♦), NH_4Cl (□), NH_4Br (▲), Me_4NCl (x), Et_4NBr (○), Pr_4NBr (●), Bu_4NBr (■), and Bu_4NI (△) at 298.15 K.

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References

Bag, G.C., Singh, N. M., Singh, N.R. 2000. Ion association of α-alanine *bis*-biguanidecobalt(III) iodide in methanol + water mixtures at different temperatures. *J. Indian Chem. Soc.* 77: 146-151.

Covington, A.K., Dickinson, T. (eds.). 1973. *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, USA.

Das, B., Hazra, D.K. 1995. Conductometric, viscometric and spectroscopic investigations on the solvation phenomena of alkali-metal ions and ion pairs in 2-methoxyethanol. *J. Phys. Chem.* **99**: 269-273.

Doe, H., Ohe, H., Matoba, H., Ichimura, A., Kitagawa, T. 1990. Conductometric study of calcium(II), strontium(II) and barium(II) perchlorates in methanol-ethyleneglycol mixtures. *Bull. Chem. Soc. Japan* **63**: 2785-2789.

Fuoss, R.M. 1978. Conductance-concentration function for the paired-ion model. *J. Phys. Chem.* **82**: 2427-2440.

Gill, D.S., Chauhan, M.S. 1984. Preferential solvation of ions in mixed solvents. V. Preferential solvation of Li^+, Na^+, K^+, Cu^+, Ag^+, Cs^+, Br^-, I^-, NO_3^- and ClO_4^- ions in acetonitrile + methanol mixtures using conductance measurements. *Z. Phys. Chem. Neue Folge.* **140**: 139-148.

Janz, C.G. 1973. *Non-aqueous Electrolytes Handbook*, vol. **2**, Academic Press, New York, USA.

Jasinki, R. 1967. *High Energy Batteries*, Plenum Press, New York, USA.

Marcus, Y., Migron, Y. 1991. Polarity, hydrogen bonding, and structure of mixtures of water and cyanomethane. *J. Phys. Chem.* **95**: 400- 406.

Mukhopadhyay, A., Pal, M. 2002. Ion association and solvent interaction-conductance of 1-ethyl-4-cyanopyridinium iodide in aqueous-binary mixtures containing acetone and 1,4-dioxane at different temperatures. *Indian J. Chem.* **41A**: 1120-1125.

Perrin, D.D., Armarego, W.L.F. (eds.). 1988. *Purification of Laboratory Chemicals*, 3rd edition, Pergamon Publishing, London, UK.

Roy, M.N. 2000. Viscosity and density of solutions of tetraalkylammonium bromides (R_4NBr, R = butyl to heptyl) in THF at different temperatures. *J. Teach. Res.* **7:** 17-21.

Roy, M.N., Jha, A., Dey, R. 2001. A study on ion-solvent interactions of some alkali metal chlorides in tetrahydrofuran + water mixture at different temperatures. *J. Chem. Engg. Data* **46:** 1247-1252.

Roy, M.N., Hazra, D.K. 1994. Densities and viscosities of the binary aqueous mixture of tetrahydrofuran and 1,2-dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* 1: 93-97.

Roy, M.N., Nandi, D., Hazra, D.K. 1993a. Electrical conductances for tetraalkylammonium bromides, $LiBF_4$ and $LiAsF_6$ in THF at 25 °C. *J. Indian Chem. Soc.* **70:** 305-310.

Roy, M.N., Nandi, D., Hazra, D.K. 1993b. Conductance studies of alkali metal chlorides and bromides in aqueous binary mixtures of tetrahydrofuran at 25 °C. *J. Indian Chem. Soc.* **70:** 121-124.

Taniewska-Osinska, S., Piekarska, A., Bald, A., Szejgis, A. 1989. Conductivity study of NaI solutions in *n*-propanol-*n*-butanol mixtures at 298.15 K. *J. Chem. Soc. Faraday Trans.* **85:** 3709-3715.

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Excess Molar Volumes and Viscosity Deviations of Binary Liquid Mixtures of 1,3-Dioxolane and 1,4-Dioxane with Butyl Acetate, Butyric Acid, Butylamine, and 2-Butanone at 298.15 K

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Densities and viscosities were measured for the binary mixtures of 1,4-dioxane and 1,3-dioxolane with butyl acetate, butyric acid, butylamine, and 2-butanone at 298.15 K over the entire composition range. From density and viscosity data, the values of excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) have been determined. These results were fitted to Redlich−Kister type polynomial equations. The density and viscosity data have been analyzed in terms of some semiempirical viscosity models.

Introduction

Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. Properties of mixtures are useful for designing many types of transport and process equipment in the chemical industry.[1−5] 1,4-Dioxane, 1,3-dioxolane, and their binary liquid mixtures are important solvents widely used in various industries. 1,4-Dioxane and 1,3-dioxolane are cyclic diethers differing in one methylene group, thus they differ in quadrupolar and dipolar order.[6] In this work we report density and viscosity for {1,4-dioxane or 1,3-dioxolane + butyl acetate, butyric acid, butylamine, or 2-butanone} mixtures at 298.15 K.

Expermental Section

Materials. 1,4-Dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminum hydride ($LiAlH_4$). Details have been described earlier.[1] 1,3-Dioxolane (LR) was purified by standard methods.[7] It was refluxed with PbO_2 and fractionally distilled after the addition of xylene. Butyl acetate, butyric acid, butylamine, and 2-butanone (S.D. Fine Chemicals, Analytical Reagent, purity > 99 %) were used without further purification. 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[8−13] as listed in Table 1.

Apparatus and Procedure. The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 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 mercury in glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistant thermometer and 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. An average of triplicate measurements was taken into account.

Table 1. Comparison of Density ρ and Viscosity η of the Pure Liquids with Literature Data at 298.15 K

	$\rho/(g\cdot cm^{-3})$		$\eta/(mPa\cdot s)$	
pure liquid	expt.	lit.	expt.	lit.
1,4-dioxane	1.0265	1.0278[8]	1.196	1.196[8]
1,3-dioxolane	1.0571	1.0587[9]	0.531	
butyl acetate	0.8744	0.8761[10]	0.668	0.674[10]
butyric acid	0.9528		1.396	
butylamine	0.7319	0.7331[11]	0.493	0.496[12]
2-butanone	0.7981	0.7996[13]	0.373	0.378[13]

The mixtures were prepared by mixing known volume of pure liquids in airtight-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 ± 0.0001 g·cm⁻³ and that of the 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 within ± 0.03 % of the reported value. Details of the methods and techniques of density and viscosity measurements have been described earlier.[4,14]

Results and Discussion

The experimental viscosities, densities, excess volumes (V^E), and viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 298.15 K are listed in Table 2.

Excess Molar Volume. The excess molar volumes, V^E, were calculated using the equation

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

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 in the mixture, respectively. The values of excess molar volume,

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10.1021/je0504109 CCC: $33.50

Table 2. Values of Density ρ, Viscosity η, Excess Molar Volume V^E, Viscosity Deviation $\Delta\eta$, and Grunberg−Nissan Interaction Parameter d_{12} for the Binary Mixtures of 1,4-Dioxane or 1,3-Dioxolane at 298.15 K

	ρ	η	$V^E \times 10^6$	$\Delta\eta$			
x_1	$g\cdot cm^{-3}$	$mPa\cdot s$	$m^3\cdot mol^{-1}$	$mPa\cdot s$	d_{12}	T_{12}	H_{12}
1,3-Dioxolane (1) + 2-Butanone (2)							
0	0.7981	0.373	0	0			
0.0976	0.8189	0.384	−0.084	−0.004	−0.0479	0.4405	0.4293
0.1957	0.8405	0.397	−0.133	−0.006	−0.0368	0.4430	0.4311
0.2944	0.8631	0.411	−0.164	−0.008	−0.0276	0.4451	0.4325
0.3935	0.8868	0.426	−0.185	−0.009	−0.0260	0.4455	0.4325
0.4933	0.9118	0.441	−0.201	−0.010	−0.0273	0.4454	0.4319
0.5935	0.9381	0.456	−0.207	−0.010	−0.0311	0.4447	0.4306
0.6943	0.9655	0.473	−0.173	−0.009	−0.0330	0.4444	0.4297
0.7956	0.9942	0.491	−0.113	−0.007	−0.0352	0.4440	0.4298
0.8975	1.0245	0.510	−0.045	−0.004	−0.0366	0.4438	0.4279
1	1.0571	0.531	0	0			
1,3-Dioxolane (1) + Butyric acid (2)							
0	0.9528	1.396	0	0			
0.1167	0.9631	1.297	−0.067	0.001	0.3771	0.9201	0.9703
0.2292	0.9737	1.202	−0.150	0.004	0.4054	0.9243	0.9743
0.3376	0.9843	1.111	−0.209	0.007	0.4372	0.9283	0.9784
0.4422	0.9953	1.023	−0.276	0.010	0.4735	0.9325	0.9829
0.5432	1.0061	0.938	−0.302	0.012	0.5140	0.9363	0.9873
0.6408	1.0169	0.854	−0.317	0.012	0.5576	0.9389	0.9906
0.7351	1.0272	0.770	−0.270	0.010	0.5965	0.9373	0.9897
0.8263	1.0374	0.688	−0.206	0.007	0.6393	0.9353	0.9882
0.9146	1.0473	0.608	−0.113	0.003	0.6751	0.9297	0.9827
1	1.0571	0.531	0	0			
1,3-Dioxolane (1) + Butyl acetate (2)							
0	0.8744	0.668	0	0			
0.1484	0.8907	0.621	−0.128	−0.027	−0.3078	0.4728	0.4939
0.2816	0.9069	0.599	−0.149	−0.031	−0.2239	0.5167	0.5230
0.4019	0.9233	0.588	−0.129	−0.025	−0.1506	0.5490	0.5465
0.5111	0.9403	0.583	−0.103	−0.015	−0.0771	0.5761	0.5690
0.6106	0.9578	0.577	−0.072	−0.007	−0.0230	0.5939	0.5851
0.7017	0.9761	0.571	−0.050	−0.001	0.0224	0.6068	0.5981
0.7853	0.9952	0.565	−0.034	0.005	0.0783	0.6204	0.6138
0.8625	1.0150	0.556	−0.023	0.006	0.1211	0.6291	0.6253
0.9338	1.0356	0.544	−0.012	0.004	0.1568	0.6349	0.6344
1	1.0571	0.531	0	0			
1,3-Dioxolane (1) + Butylamine (2)							
0	0.7319	0.493	0	0			
0.1001	0.7551	0.477	0.013	−0.020	−0.4626	0.3922	0.3988
0.2001	0.7796	0.463	0.038	−0.038	−0.0489	0.3907	0.3937
0.3002	0.8058	0.458	0.065	−0.047	−0.4628	0.4022	0.4001
0.4002	0.8338	0.455	0.082	−0.054	−0.4630	0.4062	0.4002
0.5002	0.8641	0.456	0.085	−0.056	−0.4606	0.4103	0.4003
0.6002	0.8968	0.464	0.077	−0.052	−0.4384	0.4185	0.4041
0.7002	0.9321	0.478	0.058	−0.041	−0.3899	0.4319	0.4142
0.8001	0.9703	0.496	0.039	−0.027	−0.3285	0.4478	0.4277
0.9001	1.0118	0.513	0.021	−0.013	−0.2860	0.4590	0.4370
1	1.0571	0.531	0	0			
1,4-Dioxane (1) + 2-Butanone (2)							
0	0.7981	0.373	0	0			
0.0833	0.8170	0.391	−0.077	−0.050	−0.632	0.4613	0.4576
0.1698	0.8365	0.411	−0.124	−0.102	−0.7139	0.4283	0.4237
0.2597	0.8568	0.436	−0.160	−0.150	−0.7555	0.3997	0.3938
0.3530	0.8779	0.464	−0.186	−0.200	−0.8467	0.3545	0.3472
0.4501	0.9001	0.512	−0.202	−0.231	−0.8346	0.3275	0.3180
0.5511	0.9233	0.576	−0.205	−0.250	−0.8356	0.2909	0.2789
0.6563	0.9472	0.650	−0.167	−0.263	−0.9285	0.2162	0.2009
0.7660	0.9722	0.751	−0.111	−0.252	−1.0713	0.1022	0.0821
0.8805	0.9985	0.901	−0.044	−0.197	−1.3692	−0.1215	−0.1502
1	1.0265	1.196	0	0			
1,4-Dioxane (1) + Butyric Acid (2)							
0	0.9528	1.396	0	0			
0.1000	0.9617	1.504	−0.183	0.128	0.9998	2.0259	2.0071
0.2000	0.9703	1.570	−0.332	0.214	0.9268	1.9767	1.9642
0.3000	0.9784	1.587	−0.420	0.251	0.8320	1.9004	1.8939
0.4000	0.9861	1.572	−0.467	0.256	0.7531	1.8312	1.8297
0.5000	0.9934	1.507	−0.456	0.211	0.6163	1.7161	1.7186
0.6000	1.0002	1.443	−0.395	0.167	0.5245	1.6385	1.6437
0.7000	1.0068	1.362	−0.307	0.106	0.3978	1.5416	1.5481
0.8000	1.0131	1.293	−0.184	0.057	0.2938	1.4670	1.4737
0.9000	1.0194	1.241	−0.065	0.026	0.2459	1.4322	1.4392
1	1.0265	1.196	0	0			
1,4-Dioxane (1) + Butyl Acetate (2)							
0	0.8744	0.668	0	0			
0.1278	0.8875	0.682	0.005	−0.054	−0.4852	0.7261	0.6911
0.2479	0.9010	0.692	0.014	−0.107	−0.5890	0.6856	0.6441
0.3610	0.9149	0.708	0.023	−0.151	−0.6628	0.6570	0.6045
0.4678	0.9292	0.739	0.032	−0.176	−0.6871	0.6462	0.5794
0.5687	0.9441	0.779	0.036	−0.189	−0.7249	0.6287	0.5459
0.6641	0.9594	0.822	0.036	−0.196	−0.8028	0.5936	0.4920
0.7547	0.9753	0.866	0.032	−0.201	−0.9734	0.5184	0.3903
0.8406	0.9918	0.939	0.022	−0.172	−1.1077	0.4510	0.2898
0.9223	1.0089	1.035	0.011	−0.119	−1.3746	0.3162	0.1013
1	1.0265	1.196	0	0			
1,4-Dioxane (1) + Butylamine (2)							
0	0.7319	0.493	0	0			
0.0855	0.7534	0.509	0.020	−0.045	−0.5766	0.5699	0.5586
0.1738	0.7761	0.524	0.052	−0.091	−0.6484	0.5408	0.5271
0.2650	0.8001	0.541	0.089	−0.139	−0.7327	0.5055	0.4886
0.3594	0.8258	0.560	0.117	−0.186	−0.8304	0.4626	0.4414
0.4569	0.8533	0.590	0.141	−0.224	−0.9088	0.4199	0.3927
0.5579	0.8828	0.637	0.147	−0.248	−0.9672	0.3762	0.3411
0.6625	0.9147	0.699	0.127	−0.259	−1.0620	0.3105	0.2648
0.7709	0.9492	0.792	0.080	−0.243	−1.1845	0.2176	0.1570
0.8834	0.9864	0.941	0.039	−0.172	−1.3201	0.0898	0.0074
1	1.0265	1.196	0	0			

V^E, have been presented in Table 2. The estimated uncertainty for excess molar volumes, V^E, is ± 0.005 $cm^3\cdot mol^{-1}$.

The excess molar volumes, V^E, for all the 1,3-dioxolane systems, except for the system involving butylamine, are negative over the entire range of composition. The negative values of excess volumes for the three systems are in the order:

1,3-dioxolane + butyric acid > 1, 3-dioxolane +
2-butanone > 1,3-dioxolane + butyl acetate

The excess molar volumes for the two 1,4-dioxane systems involving butylamine and butyl acetate are positive, while the other two 1,4-dioxane systems involving 2-butanone and butyric acid are negative. The order of V^E values for the 1,4-dioxane systems irrespective of their sign is as follows:

1,4-dioxane + butylamine > 1,4-dioxane + butyl acetate >
1,4-dioxane + 2-butabnone > 1,4-dioxane + butyric acid

The negative values of excess molar volume suggest specific interactions[15] between the mixing components in the mixtures while its positive values suggest dominance of dispersion

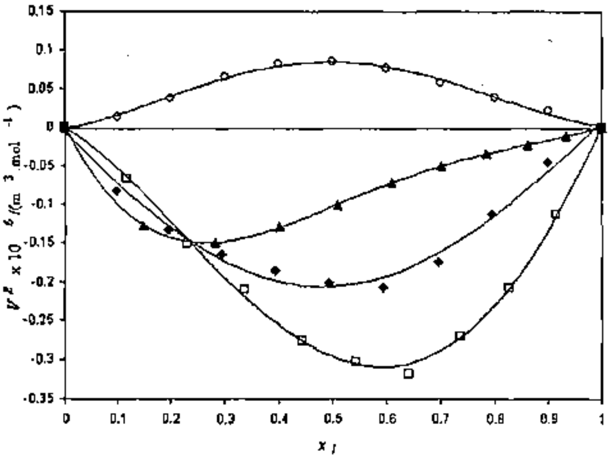

Figure 1. Excess molar volumes V^E at 298.15 K for binary mixtures of 1,3-dioxolane (1) with ◆, 2-butanone; □, butyric acid; ▲, butyl acetate; and ○, butylamine.

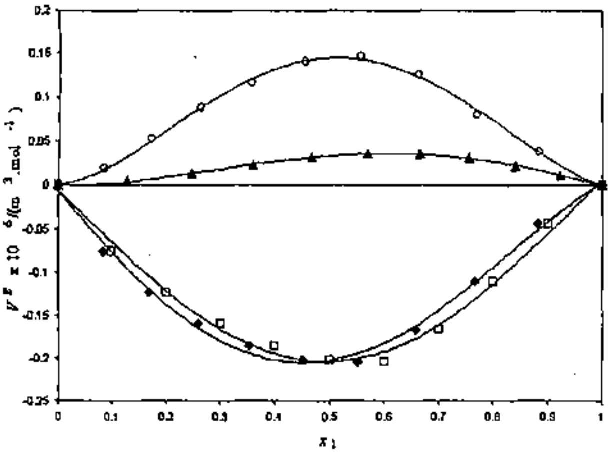

Figure 2. Excess molar volumes V^E at 298.15 K for binary mixtures of 1,4-dioxane (1) with ◆, 2-butanone; □, butyric acid; ▲, butyl acetate; and ○, butylamine.

forces[16,13] between them. The negative V^E values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. The negative V^E values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.[15] The negative V^E values for all the systems studied may be attributed to dipole−induced dipole interactions between the components liquids of the mixtures resulting in the formation of electron donor−acceptor complexes.[17] The plots of excess molar volume, V^E, versus mole fraction, x_1, of 1,3-dioxolane or 1,4-dioxane are presented in Figures 1 and 2.

Viscosity Deviation. The deviation in viscosities, $\Delta\eta$, was computed using the relationship[18]

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

where η is the dynamic viscosities of the mixture; x_i and η_i are the mole fraction and viscosity of ith component in the mixture, respectively.

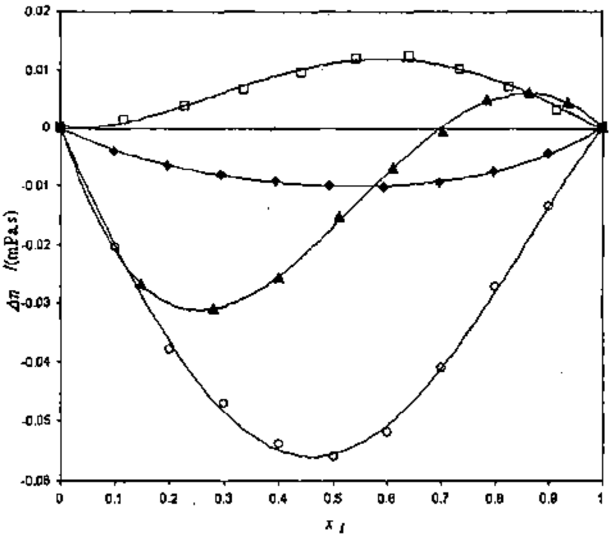

Figure 3. Viscosity deviations $\Delta\eta$ at 298.15 K for the binary mixtures of 1,3-dioxolane (1) with ◆, 2-butanone; □, butyric acid; ▲, butyl acetate; and ○, butylamine.

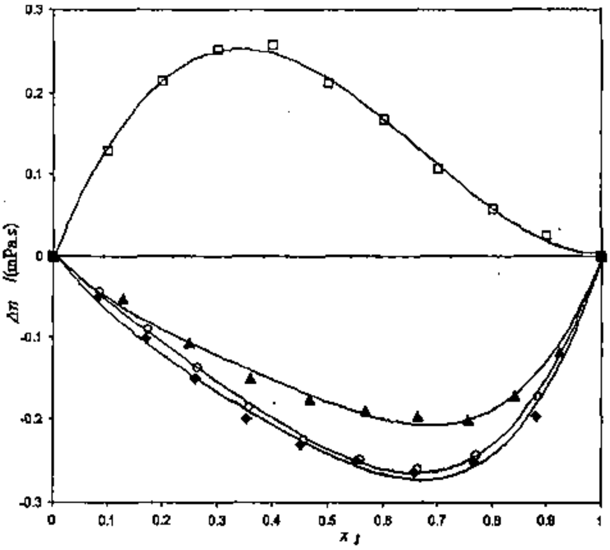

Figure 4. Viscosity deviations $\Delta\eta$ at 298.15 K for the binary mixtures of 1,4-dioxane (1) with ◆, 2-butanone; □, butyric acid; ▲, butyl acetate; and ○, butylamine.

A perusal of Table 2 shows that the values of viscosity deviation, $\Delta\eta$, are negative over the entire composition range for all the binary liquid mixtures studied except for the mixtures involving butyric acid. The estimated uncertainty for viscosity deviation, $\Delta\eta$, is ± 0.004 mPa·s. The negative values imply the presence of dispersion forces[18] between the mixing components in these mixtures, while positive values may be attributed to the presence of specific interactions[18] between them. The plots of viscosity deviation, $\Delta\eta$, versus mole fraction, x_1, for the different binary mixtures have been presented in Figures 3 and 4.

Viscosity Models and Interaction Parameters. Several semiempirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data.[19,20] Some of them we examined are as follows:

Table 3. Values of Coefficients a_i of Equation 6 and Standard Deviations σ for Excess Properties of the Binary Mixtures of 1, 3-Dioxolane (1) or 1,4-Dioxane (1) Studied at 298.15 K

binary mixture	excess property	a_0	a_1	a_2	a_3	a_4	σ
1,3-dioxolane + 2-butanone	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	−0.798	0.084				0.013
	$\Delta\eta/(mPa \cdot s)$	−0.040	−0.009	−0.009	0.129		0.001
1,3-dioxolane + butyric acid	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	−1.184	−0.640	0.215	0.253		0.006
	$\Delta\eta/(mPa \cdot s)$	0.044	0.040	−0.027	−0.037		0.001
1,3-dioxolane + butyl acetate	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	−0.414	0.580	−0.371			0.001
	$\Delta\eta/(mPa \cdot s)$	−0.068	0.183	−0.029			0.001
1,3-dioxolane + butylamine	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	0.342	−0.070	−0.321	0.200	0.123	0.001
	$\Delta\eta/(mPa \cdot s)$	−0.222	0.031	0.056	0.040	−	0.001
1,4-dioxane + 2-butanone	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	−0.824	0.063	0.442	0.486	−0.337	0.003
	$\Delta\eta/(mPa \cdot s)$	−0.972	−0.422	−0.315	−0.623	−0.353	0.002
1,4-dioxane + butyric acid	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	−1.816	0.673	0.454	0.234	0.343	0.004
	$\Delta\eta/(mPa \cdot s)$	0.859	−0.819	−	−	−	0.006
1,4-dioxane + butyl acetate	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	0.135	0.112	−0.055	−0.063	−	0.001
	$\Delta\eta/(mPa \cdot s)$	−0.720	−0.319	−0.408	−0.582	−	0.003
1,4-dioxane + butylamine	$V^E \times 10^6/(m^3 \cdot mol^{-1})$	0.579	0.093	−0.443	−0.105	−	0.003
	$\Delta\eta/(mPa \cdot s)$	−0.944	−0.527	−0.247	−0.469	−0.122	0.001

Grunberg and Nissan[21] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp\left[\sum_{i=1}^{j} (x_i \ln \eta_i) + d_{12}\prod_{i=1}^{j} x_i\right] \tag{3}$$

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 as a function of the composition of the binary liquid mixtures of 1,3-dioxolane and 1,4-dioxane with butyl acetate, butyric acid, butylamine, and 2-butanone as listed in Table 2.

It has been found that the values of d_{12} are negative for all the binary systems studied, except the systems involving butyric acid. The negative values of d_{12} indicate the presence of dispersion forces[18] between the mixing components in the mixtures while its positive values indicate the presence of specific interactions[18] between them.

Tamura and Kurata[22] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i\phi_i\eta_i + 2T_{12}\prod_{i=1}^{j}[x_i\phi_i]^{1/2} \tag{4}$$

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.:[23]

$$\eta = \sum x_i^2\eta_i + 2H_{12}\prod_{i=1}^{j} x_i \tag{5}$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[24] In the present study, the values of interaction parameter T_{12} and H_{12} have been calculated from eqs 4 and 5, respectively, and are listed in Table 2. It has been observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other, and this is in agreement with the view put forward by Fort and Moore[18] in regard to the nature of parameters T_{12} and H_{12}. It is also significant to note that the values of T_{12} and H_{12} are larger for the binary mixtures of butyric acid with both the cyclic ethers, which involve specific molecular interactions[25] as revealed by the positive values of $\Delta\eta$ and d_{12}.

Redlich−Kister Polynomial Equation. The excess properties (V^E and $\Delta\eta$) were fitted to the Redlich−Kister polynomial equation:[26]

$$Y^E = x_1x_2\sum_{i=1}^{K} a_i(x_1 - x_2)^i \tag{6}$$

where Y^E refers to excess properties; x_1 and x_2 are the mole fraction 1,3-dioxolane or 1,4-dioxane and the other component, respectively. 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 calculated values of a_i along with the tabulated standard deviations (σ) are listed in Table 3. The standard deviation (σ) was calculated using

$$\sigma = [(Y^E_{exp} - Y^E_{cal})^2/(n - m)]^{1/2} \tag{7}$$

where n is the number of data points and m is the number of coefficients. The σ values lies between 0.013 $m^3 \cdot mol^{-1}$ and 0.001 $m^3 \cdot mol^{-1}$ for V^E and between 0.006 mPa·s and 0.001 mPa·s for $\Delta\eta$, respectively. The largest σ values corresponds to the 1,3-dioxolane + 2-butanone system for V^E and the 1,4-dioxane + butyric acid for $\Delta\eta$, respectively. In the present study, V^E and $\Delta\eta$ are quite systematic and a function of the composition of the binary mixtures.

Literature Cited

(1) Roy, M. N.; Jha, A.; Dey, R. A study on ion−solvent interactions of some alkali metal chlorides in tetrahydrofuran + water mixture at different temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1247−1252.

(2) Janz, C. G.; Tomkins, R. P. T. *Non-Aqueous Electrolytes Handbook*; Academic Press: New York, 1973; Vol. 2.

(3) Jasinki, R *High Energy Batteries*; Plenum Press: New York, 1967.

(4) Roy, M. N.; Hazra, D. K. Densities and viscosities of the binary aqueous mixtures of tetrahydrofuran and 1,2-dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* **1994**, *1*, 93−97.

(5) Millero, F. J In *Structure and Transport Process in Water and Aqueous Solutions*; R. A. Horne: New York, 1972.

(6) Brocos, P.; Calvo, E.; Pineiro, A.; Bravo, R.; Amigo, A. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ether. 5. Binary systems {1,3-dioxolane + 1-alkanols}. *J. Chem. Eng. Data* **1999**, *48*, 1341−1347.

(7) Riddick, J.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986; Vol. 2.

(8) Martin Contreras, S. Densities and viscosities of binary mixtures of 1,4-dioxane with 1-propanol and 2-propanol at (25, 30, and 40) °C. *J. Chem. Eng. Data* **2001**, *46*, 1149−1152.

(9) Francesconi, R.; Comelli, F. Excess molar enthalpies and excess molar volumes of propylene carbonate + cyclic ethers. *J. Chem. Eng. Data* **1995**, *40*, 31−33.

(10) Sastry, N. V.; Patel, M. C. Densities, excess molar volume, viscosities, speeds of sound, excess isentropic compressibilities and relative permittivities for alkyl (methyl, ethyl, butyl, and isoamyl) acetates + glycols at different temperatures. *J. Chem. Eng. Data* **2003**, *48*, 1019−1027.

(11) Kinart, C. M.; Kinart, W. J.; Checinska-Majak, D. Relative permittivity, viscosity, and speed of sound for 2-methoxyethanol + butylamine mixtures. *J. Chem. Eng. Data* **2003**, *48*, 1037−1039.

(12) Pal, A.; Bhardwaj, R. K. Ultasonic speeds and volumetric properties of dipropylene glycol monomethyl ether−*n*-alkylamine mixtures at 298.15 K. *Z. Phys. Chem.* **2002**, *216*, 1033−1051.

(13) Hsu-Chen, K.; Chein-Hsiun, T. 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.

(14) Nikam, P. S.; Hosan. M. Density and viscosity studies of some metal halides in (DMSO + water) mixtures at 25 °C. *J. Chem. Eng. Data* **1988**, *33*, 165−169.

(15) Nayak, J. N.; Aralaguppi, M. I.; Aminabhavi, T. M. Density, viscosity, refractive index, and speed of sound in the binary mixtures of 1,4-dioxane + ethyl acetoacetate, + diethyl oxalate, + diethyl phthalate, or + dioctyl phthalate at 298.15, 303.15, and 308.15 K. *J. Chem. Eng. Data* **2003**, *48*, 1489−1494.

(16) Roy, M. N.; Sinha, A.; Sinha, B. Excess molar volume, viscosity deviation and isentropic compressibility of binary mixtures containing 1,3-dioxolane with monoalcohols at 303.15 K. *J. Solution. Chem.* **2005**, *34*, 1311−1325.

(17) 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.

(18) Fort, R. J.; Moore, W. R. Viscosities of binary liquid mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−1119.

(19) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(20) Irving, J. B. *Viscosities of Liquid Mixtures*; NEL Reports 630 and 631; National Engineering Laboratory: East Kilbride, Glassgow, 1977.

(21) Grunberg, L.; Nissan, A. H. Mixture law for viscosity. *Nature* **1949**, *164*, 799−800.

(22) Tamura, M.; Kurata, M. Viscosity of binary mixture of liquids. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 32−37.

(23) Hind, R. K.; McLaughlin, E.; Ubbelohde, A. R. Structure and viscosity of liquid-camphor and pyrene mixtures. *Trans. Faraday. Soc.* **1960**, *56*, 328−334.

(24) Oswal, S. L.; Desai, H. S. Studies of viscosity and excess molar volume of binary mixtures 3. 1-alkanol + di-*n*-propylamine, and + di-*n*-buylamine mixtures at 303.15 and 313.15 K. *Fluid Phase Equilib.* **2001**, *186*, 81−102.

(25) Jain, P.; Singh, M. Density and viscosity of binary mixtures of *n*-propylamine with polar and non-polar solvents vis-à-vis molecular interactions. *J. Indian Chem. Soc.* **2005**, *82*, 225−231.

(26) Redlich, O.; Kister, A. T. Algebric representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

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Studies on excess molar volumes and viscosity deviations of binary mixtures of butylamine and N, N-dimethylformamide with some alkyl acetates at 298.15 K

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Densities and viscosities have been measured for the binary mixtures of butylamine (BA) and N, N-dimethylformamide (DMF) with methyl acetate (MA), ethyl acetate (EA), butyl acetate (BUA) and *iso*-amyl acetate (AA) at 298.15 K over the entire composition range. From density and viscosity data, the values of excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) have been determined. These results have been fitted to Redlich-Kister type polynomial equations to estimate the binary coefficients and standard errors between the experimental and computed values. The density and viscosity data have been analyzed in terms of semiempirical viscosity models and the results have been 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.

Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. These properties are extremely useful for designing many types of transport and process equipment in chemical industries. There has been a recent upsurge of interest[1,2] in the study of thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on intermolecular interactions and stereochemical effects in these systems. BA and DMF are versatile solvents used in the separation of saturated and unsaturated hydrocarbons and in pharmaceutical synthesis, and serve as solvents for many polymers.[3] In this paper, we report experimental data for density (ρ) and viscosity (η) of the following mixtures at 298.15 K: butylamine (BA) or N, N-dimethylformamide (DMF) + methyl acetate (MA), ethyl acetate (EA), butyl acetate (BUA), and iso-amyl acetate (AA). Using these data, excess molar volume (V^E), viscosity deviation ($\Delta\eta$), Grunberg-Nissan (d_{12}), Tamura-Kurata (T_{12}), and Hind (H_{12}) interaction parameters have been calculated. These results have been fitted to Redlich-Kister type polynomial equations to estimate the binary coefficients and standard errors between the experimental and calculated values.

Materials and Methods

Butylamine (S. D. Fine Chem, minimum assay GLC, 98%) was stored over sodium hydroxide pellets for several days and fractionally distilled twice.[4] N, N-dimethylformamide (S. D. Fine Chemicals, AR, purity>99%) was purified by the method described by Zhao *et al.*[5] Methyl, ethyl, butyl and iso-amyl acetates (S. D. Fine Chemicals, AR, purity>99%) were used. Methyl acetate was washed with saturated solution of NaCl, dried with anhydrous $MgCl_2$, and then distilled. Ethyl acetate was dried over K_2CO_3, filtered, and distilled, and the first and the last portions of the distillate were discarded. The entire middle fraction was then distilled over P_2O_5. Butyl acetate and iso-amyl acetate were purified by drying over $CaCO_3$ overnight, filtered, and freshly distilled. The densities and viscosities of the solvents at 298.15 K were in good agreement with the literature values[5-8] as given in Table 1 and the purity of the solvents

Table 1—Comparison of experimental densities and viscosities of pure liquids with literature values at 298.15 K

Pure liquids	$\rho\times10^{-3}$ (kg.m^{-3})		η (mPa.s)	
	Exp.	Lit.	Exp.	Lit.
N, N-Dimethylformamide	0.9442	0.9440[a]	0.8016	0.802[a]
Butylamine	0.7319	0.7331[b]	0.4934	0.496[c]
Methyl acetate	0.9261	0.9268[d]	0.3798	0.384[d]
Ethyl acetate	0.8941	0.894[d]	0.4233	0.428[d]
Butyl acetate	0.8744	0.8762[d]	0.6684	0.674[d]
Iso- amyl acetate	0.8660	0.8662[d]	0.7822	0.781[d]

[a]Ref. 5; [b]Ref. 6; [c]Ref. 7 and [d]Ref. 8.

used in the present study is expected to be about 99.5%.

Densities (ρ) at 298.15 K were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and capillary of internal diameter of about 1 mm. The measurements were done in a thermostated bath controlled to ± 0.1 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. 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 details of the methods and techniques have been described earlier[9-11]. 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 mass measurements accurate to ±0.01mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The precision of density measurements was $\pm 3\times 10^{-4}$ g cm^{-3}.

Calculations

The excess molar volumes (V^E) were calculated using the equation,

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

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 i^{th} component in the mixture, respectively. The values of excess molar volume (V^E) have been presented in Table 2. The estimated uncertainty for excess molar volumes (V^E) is ± 0.005 $cm^3.mol^{-1}$.

The deviation in viscosities (Δη) can be computed using the relationship,

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

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. The estimated uncertainty for viscosity deviation (Δη) is ±0.004 mPa.s.

Several semiempirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data[12,13]. Some of these that we examined are as follows:

Grunberg and Nissan[14] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp\left[\sum_{i=1}^{j} (x_i \ln \eta_i) + d_{12} \prod_{i=1}^{j} x_i \right] \qquad \ldots (3)$$

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.

Tamura-Kurata[15] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{\frac{1}{2}} \qquad \ldots (4)$$

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.*[16]:

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \qquad \ldots (5)$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.[17]

The excess properties (V^E and Δη) were fitted to the Redlich-Kister polynomial equation,

$$Y^E = x_1 x_2 \sum_{i=1}^{K} a_i (x_1 - x_2)^i \qquad \ldots (6)$$

where Y^E refers to excess properties and x_1 and x_2 are the mole fraction BA or DMF and other component, respectively. 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 calculated values of a_i along with the tabulated standard deviations (σ) are listed in Table 3. The standard deviation (σ) was calculated using,

$$\sigma = \left[\frac{\left(Y^E_{exp} - Y^E_{cal} \right)^2}{(n-m)} \right]^{\frac{1}{2}} \qquad \ldots (7)$$

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

Table 2—Values of density (ρ), viscosity (η), excess molar volume (V^E), viscosity deviation (Δη) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K

Mole fraction (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)
		BA (1) + MA (2)		
0	0.9261	0.3798	0	0
0.1011	0.9032	0.3847	-0.090	-0.007
0.2020	0.8827	0.3889	-0.308	-0.014
0.3027	0.8653	0.3942	-0.740	-0.020
0.4031	0.8501	0.4024	-1.330	-0.023
0.5032	0.8352	0.4109	-1.894	-0.026
0.6031	0.8191	0.4211	-2.270	-0.027
0.7027	0.7998	0.4359	-2.200	-0.024
0.8020	0.7776	0.4516	-1.685	-0.019
0.9011	0.7535	0.4701	-0.770	-0.012
1	0.7319	0.4934	0	0
		BA (1) + EA (2)		
0	0.8941	0.4233	0	0
0.1180	0.8741	0.4059	0.070	-0.026
0.2315	0.8546	0.3973	0.181	-0.042
0.3405	0.8364	0.3923	0.240	-0.055
0.4454	0.8188	0.3929	0.300	-0.062
0.5464	0.8015	0.3967	0.431	-0.065
0.6437	0.7860	0.4071	0.403	-0.061
0.7376	0.7720	0.4192	0.259	-0.056
0.8281	0.7588	0.4353	0.091	-0.046
0.9156	0.7454	0.4591	0.010	-0.028
1	0.7319	0.4934	0	0
		BA (1) + BUA (2)		
0	0.8744	0.6684	0	0
0.1500	0.8570	0.6056	0.101	-0.036
0.2842	0.8398	0.5618	0.269	-0.057
0.4050	0.8235	0.5299	0.389	-0.068
0.5143	0.8080	0.5081	0.469	-0.070
0.6136	0.7931	0.4887	0.530	-0.072
0.7043	0.7802	0.4786	0.391	-0.066
0.7875	0.7680	0.4715	0.211	-0.059
0.8640	0.7558	0.4714	0.100	-0.046
0.9346	0.7439	0.4753	0.020	-0.029
1	0.7319	0.4934	0	0
		BA (1) + AA (2)		
0	0.8660	0.7822	0	0
0.1651	0.8493	0.6901	0.181	-0.044
0.3080	0.8329	0.6290	0.400	-0.064
0.4327	0.8171	0.5855	0.590	-0.072
0.5427	0.8024	0.5512	0.680	-0.074
0.6403	0.7885	0.5200	0.730	-0.077
0.7275	0.7766	0.5003	0.539	-0.072
0.8059	0.7650	0.4865	0.371	-0.063
0.8768	0.7538	0.4778	0.210	-0.051
0.9412	0.7428	0.4780	0.090	-0.032
1	0.7319	0.4934	0	0

Contd

Table 2 (Contd)—Values of density (ρ), viscosity (η), excess molar volume (V^E), viscosity deviation (Δη) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K

Mole fraction (x_1)	$\rho\times10^{-3}$ (kg. m^{-3})	η (mPa.s)	$V^E\times10^6$ (m^3. mol^{-1})	$\Delta\eta$ (mPa.s)
		DMF (1) + MA (2)		
0	0.9261	0.3798	0	0
0.1012	0.9292	0.4148	-0.112	-0.008
0.2022	0.9320	0.4504	-0.193	-0.015
0.3028	0.9347	0.4858	-0.275	-0.022
0.4032	0.9372	0.5236	-0.331	-0.026
0.5034	0.9393	0.5636	-0.349	-0.028
0.6032	0.9412	0.6045	-0.357	-0.030
0.7028	0.9425	0.6504	-0.312	-0.026
0.8021	0.9435	0.6976	-0.242	-0.020
0.9012	0.9438	0.7482	-0.117	-0.012
1	0.9442	0.8016	0	0
		DMF (1) + EA (2)		
0	0.8941	0.4233	0	0
0.1181	0.8998	0.4567	-0.100	-0.011
0.2316	0.9056	0.4896	-0.198	-0.021
0.3406	0.9113	0.5232	-0.267	-0.029
0.4456	0.9168	0.5591	-0.315	-0.033
0.5466	0.9220	0.5955	-0.330	-0.035
0.6439	0.9269	0.6339	-0.308	-0.033
0.7377	0.9316	0.6737	-0.264	-0.029
0.8282	0.9359	0.7153	-0.183	-0.021
0.9156	0.9400	0.7573	-0.086	-0.012
1	0.9442	0.8016	0	0
		DMF (1)+ BUA (2)		
0	0.8744	0.6684	0	0
0.1501	0.8816	0.6705	-0.091	-0.018
0.2843	0.8891	0.6761	-0.206	-0.030
0.4051	0.8963	0.6849	-0.258	-0.037
0.5144	0.9035	0.6955	-0.282	-0.041
0.6138	0.9107	0.7082	-0.296	-0.042
0.7045	0.9177	0.7247	-0.272	-0.037
0.7876	0.9243	0.7431	-0.213	-0.030
0.8641	0.9311	0.7612	-0.156	-0.022
0.9346	0.9375	0.7797	-0.070	-0.013
1	0.9442	0.8016	0	0
		DMF (1)+ BUA (2)		
0	0.8660	0.7822	0	0
0.1652	0.8738	0.7649	-0.086	-0.020
0.3081	0.8819	0.7531	-0.192	-0.035
0.4329	0.8898	0.7483	-0.233	-0.042
0.5429	0.8977	0.7469	-0.247	-0.046
0.6404	0.9054	0.7481	-0.228	-0.046
0.7277	0.9133	0.7548	-0.213	-0.041
0.8061	0.9210	0.7648	-0.172	-0.033
0.8769	0.9287	0.7750	-0.118	-0.024
0.9413	0.9363	0.7869	-0.046	-0.014
1	0.9442	0.8016	0	0

Table 3—Values of coefficients a_i of Eq. 6 and standard deviations (σ) for the excess properties $V^E \times 10^6$ ($m^3.mol^{-1}$) and $\Delta\eta$ (mPa s) for the binary mixtures of BA or DMF (1) + some alkyl acetates (2) at 298.15 K

Binary mixture	Excess property	a_0	a_1	a_2	a_3	σ
BA + MA	$V^E \times 10^6$	-7.536	-10.229	2.901	8.387	0.011
	$\Delta\eta$	-0.104	-0.031	-	-	0.000
BA + EA	$V^E \times 10^6$	1.535	1.144	-1.694	-2.644	0.034
	$\Delta\eta$	-0.255	-0.041	-0.017	-0.043	0.001
BA + BUA	$V^E \times 10^6$	1.940	1.047	-2.131	-1.934	0.030
	$\Delta\eta$	-0.283	-0.035	-0.109	-0.084	0.001
BA + AA	$V^E \times 10^6$	2.685	1.678	-1.981	-2.086	0.029
	$\Delta\eta$	-0.297	-0.044	-0.184	-0.095	0.002
DMF + MA	$V^E \times 10^6$	-1.425	-0.335	0.199	0.355	0.007
	$\Delta\eta$	-0.116	-0.030	-0.014	-	0.000
DMF + EA	$V^E \times 10^6$	-1.301	-0.275	0.163	0.203	0.002
	$\Delta\eta$	-0.136	-0.027	-0.263	-	0.000
DMF + BUA	$V^E \times 10^6$	-1.162	-0.376	0.264	-	0.009
	$\Delta\eta$	-0.164	-0.037	-0.069	-0.081	0.001
DMF + AA	$V^E \times 10^6$	-0.984	-0.268	0.245	-	0.009
	$\Delta\eta$	-0.182	-0.054	-	-	0.001

Results and Discussion

The experimental viscosities, densities, excess volumes (V^E), viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 298.15 K are presented in Table 2. The values of Grunberg-Nissan interaction parameter (d_{12}), the values of interaction parameters T_{12} and H_{12} have been calculated as a function of the composition of the binary mixtures of BA and DMF with MA, EA, BUA and AA, and were presented in Table 4.

From Table 2, it is observed that excess molar volumes (V^E) for all the BA systems, except for that involving MA, are positive over the entire range of composition. The positive values of excess volumes (V^E) for the three systems follow the order:

BA + AA > BA + BUA > BA + EA

The excess molar volumes (V^E) for all the DMF systems are negative and their negative values follow the order:

DMF+MA>DMF+EA>DMF + BUA>DMF + AA

The negative values of excess molar volume (V^E) suggest specific interactions[18,19] between the unlike molecules in the systems while its positive values suggest dominance of dispersion forces[18,19] between them. Treszczanowicz *et al.*[20] suggested that V^E is the result of contributions from several opposing effects. These may be divided arbitrarily into three types, namely, physical, chemical, and structural. Physical contributions contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change, therefore, depends on the relative strength of these effects. The negative values of excess molar volume (V^E) for all the mixtures studied may be attributed to dipole-induced dipole interactions between the unlike molecules in the binary mixtures through hydrogen bonding. The plots of excess molar volume (V^E) versus mole fraction (x_1) of BA or DMF for the binary mixtures are presented in Figs 1 and 2. It is evident from the values of V^E that for both the binary systems, the degree of specific intermolecular interactions between unlike molecules in the binary mixtures decreases as the chain length of the alkyl acetate increases. The excess enthalpy values determined by Venkatesu *et al.*[21] for DMF + EA and DMF + BUA mixtures report similar results.

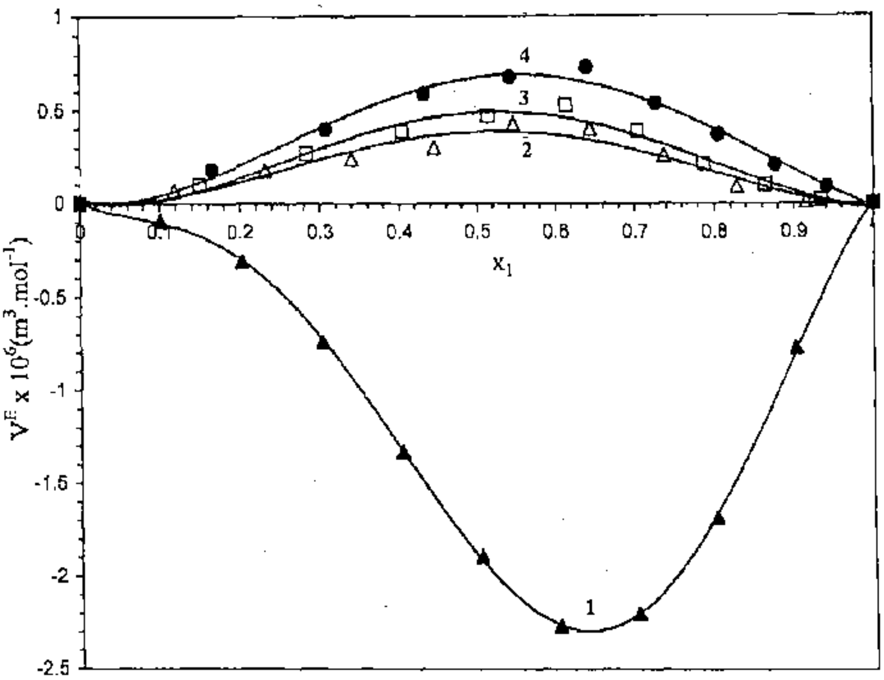

Fig. 1—Plots of excess molar volume (V^E) versus mole fraction of BA (x_1) at 298.15K for binary mixtures of BA with 1, MA (▲) 2, EA (Δ); 3, BUA (□); and 4, AA (●).

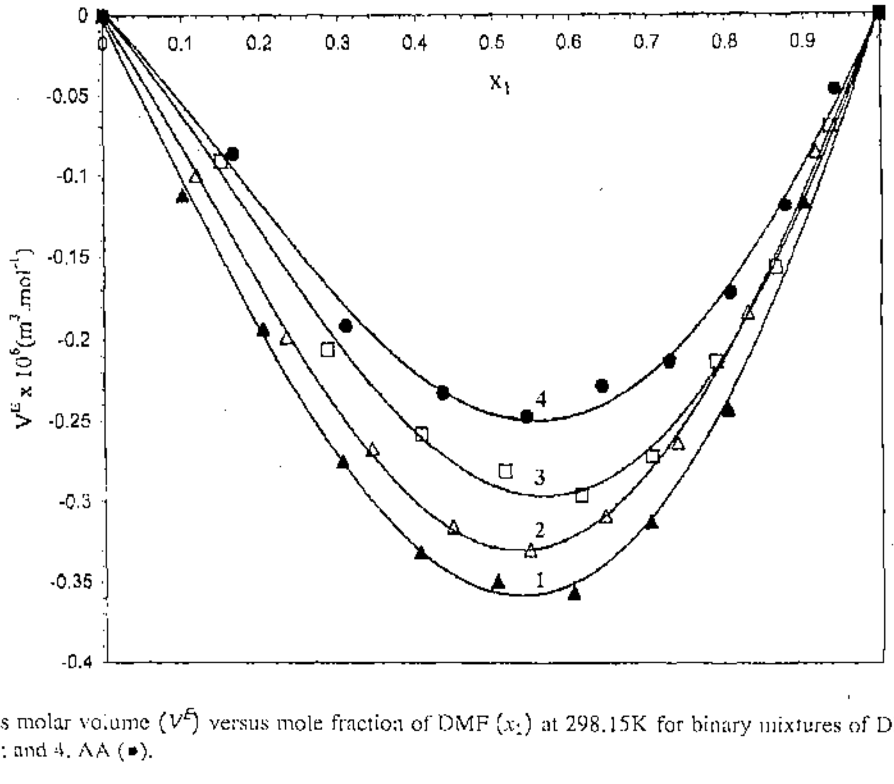

Fig. 2—Plots of excess molar volume (V^E) versus mole fraction of DMF (x_1) at 298.15K for binary mixtures of DMF with 1, MA (▲) 2, EA (Δ); 3, BUA (□); and 4, AA (●).

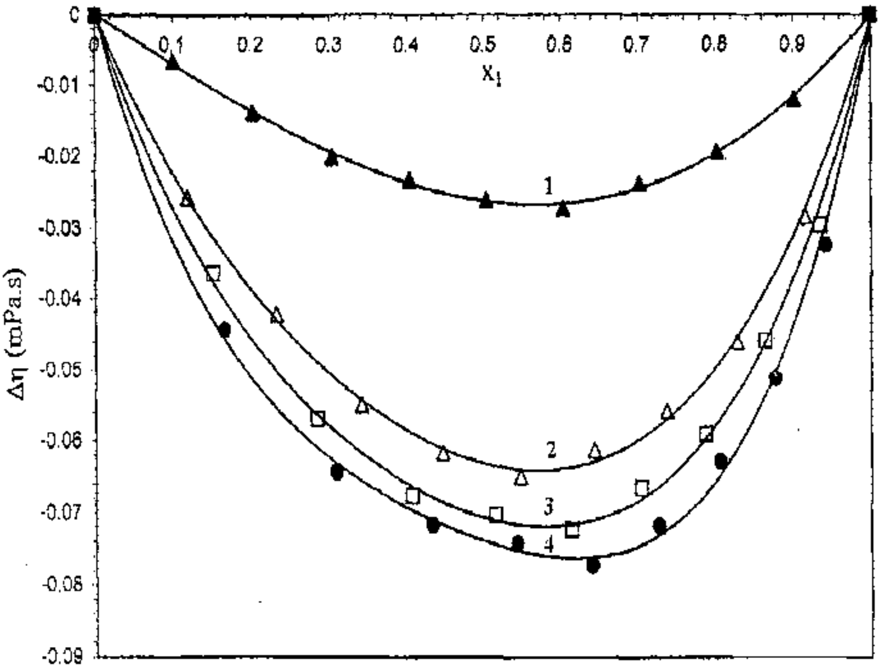

Fig. 3—Plots of viscosity deviation (Δη) versus mole fraction of BA (x_1) at 298.15 K for binary mixtures of BA with 1, MA (▲); 2, EA (Δ); 3, BUA (□); and 4, AA (●).

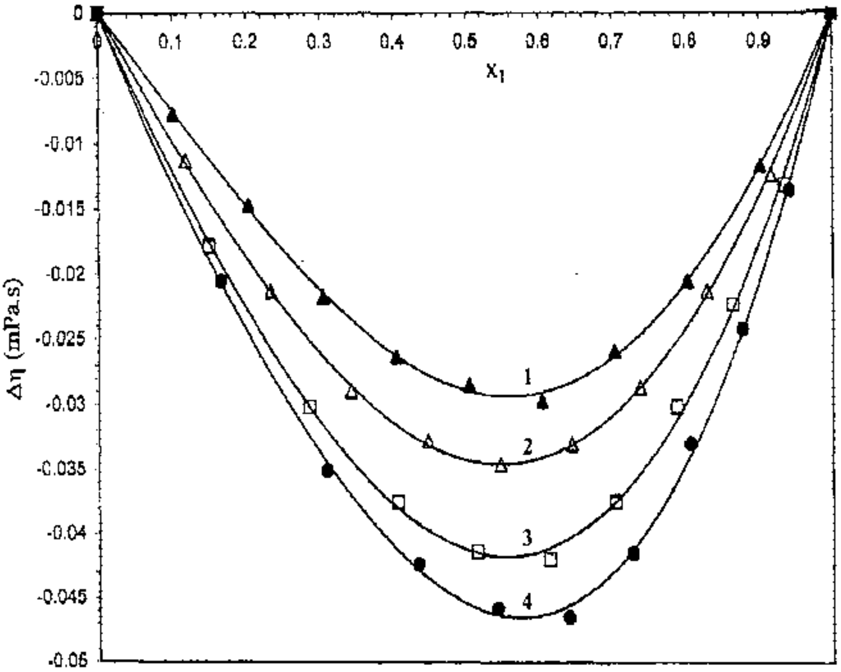

Fig. 4—Plots of viscosity deviation (Δη) versus mole fraction of DMF (x_1) at 298.15K for binary mixtures of DMF with 1, MA (▲); 2, EA (Δ); 3, BUA (□); and 4, AA (●).

Table 4—Grunberg-Nissan interaction parameter (d_{12}), Tamura-Kurata parameter (T_{12}), and Hind parameter (H_{12}) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K

x_1	d_{12}	T_{12}	H_{12}	x_1	d_{12}	T_{12}	H_{12}
	BA (1) + MA (2)				DMF (1) + MA (2)		
0.1011	-0.1503	0.3997	0.4003	0.1012	0.1379	0.5514	0.5484
0.2020	-0.1803	0.3927	0.3938	0.2022	0.1204	0.5482	0.5451
0.3027	-0.1992	0.3874	0.3892	0.3028	0.0949	0.5425	0.5393
0.4031	-0.1983	0.3855	0.3884	0.4032	0.0825	0.5394	0.5361
0.5032	-0.2113	0.3806	0.3846	0.5034	0.0749	0.5372	0.5337
0.6031	-0.2274	0.3746	0.3799	0.6032	0.0595	0.5324	0.5286
0.7027	-0.2204	0.3733	0.3799	0.7028	0.0617	0.5327	0.5287
0.8020	-0.2311	0.3677	0.3758	0.8021	0.0560	0.5303	0.5261
0.9011	-0.2511	0.3591	0.3692	0.9012	0.0551	0.5294	0.5250
	BA (1) + EA (2)				DMF (1) + EA (2)		
0.1180	-0.5774	0.3354	0.3349	0.1181	0.0046	0.5802	0.5582
0.2315	-0.5554	0.3399	0.3397	0.2316	-0.0133	0.5756	0.5526
0.3405	-0.5715	0.3361	0.3361	0.3406	-0.0254	0.5723	0.5479
0.4454	-0.5778	0.3335	0.3336	0.4456	-0.0257	0.5721	0.5461
0.5464	-0.5996	0.3271	0.3274	0.5466	-0.0313	0.5703	0.5427
0.6437	-0.6001	0.3242	0.3247	0.6439	-0.0321	0.5698	0.5405
0.7376	-0.6343	0.3135	0.3142	0.7377	-0.0330	0.5694	0.5383
0.8281	-0.6945	0.2957	0.2967	0.8282	-0.0295	0.5704	0.5376
0.9156	-0.7623	0.2740	0.2753	0.9156	-0.0388	0.5671	0.5322
	BA (1) + BUA (2)				DMF (1) + BUA (2)		
0.1500	-0.4148	0.4158	0.4381	0.1501	-0.1893	0.6940	0.6648
0.2842	-0.4302	0.4244	0.4410	0.2843	-0.1978	0.6945	0.6608
0.4050	-0.4532	0.4288	0.4406	0.4051	-0.2045	0.6955	0.6572
0.5143	-0.4726	0.4327	0.4402	0.5144	-0.2150	0.6949	0.6521
0.6136	-0.5349	0.4252	0.4284	0.6138	-0.2268	0.6938	0.6464
0.7043	-0.5768	0.4223	0.4212	0.7045	-0.2262	0.6969	0.6449
0.7875	-0.6569	0.4104	0.4043	0.7876	-0.2222	0.7008	0.6447
0.8640	-0.7395	0.3977	0.3860	0.8641	-0.2300	0.7007	0.6401
0.9346	-0.9348	0.3605	0.3396	0.9346	-0.2591	0.6938	0.6270
	BA (1) + AA (2)				DMF (1) + AA (2)		
0.1651	-0.3566	0.4349	0.4768	0.1652	-0.1914	0.7440	0.7176
0.3080	-0.3572	0.4555	0.4869	0.3081	-0.2134	0.7416	0.7096
0.4327	-0.3674	0.4683	0.4918	0.4329	-0.2237	0.7444	0.7058
0.5427	-0.4026	0.4713	0.4882	0.5429	-0.2395	0.7445	0.6996
0.6403	-0.4918	0.4598	0.4700	0.6404	-0.2616	0.7422	0.6909
0.7275	-0.5633	0.4535	0.4567	0.7277	-0.2697	0.7448	0.6872
0.8059	-0.6612	0.4414	0.4367	0.8061	-0.2699	0.7496	0.6864
0.8768	-0.8218	0.4165	0.4012	0.8769	-0.2846	0.7494	0.6798
0.9412	-1.0605	0.3763	0.3457	0.9413	-0.3097	0.7460	0.6689

A perusal of Table 2 shows that the values of viscosity deviation ($\Delta\eta$) are negative over the entire composition range for all the binary mixtures studied and the negative values increase as the chain length of the alkyl acetates increases. It is observed in many systems that there is no simple correlation between the strength of the interactions and the observed properties. Rastogi *et al.*[22] therefore, suggested that the observed excess property is a combination of an interaction and a non-interaction part. The non-interaction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. In general, the negative values imply the presence of dispersion forces[23] in these mixtures; while positive values may be attributed to the presence of specific interactions[23]. The plots of viscosity deviation ($\Delta\eta$) versus mole fraction (x_1) for the different binary mixtures of BA and DMF have been presented in Figs 3 and 4, respectively. The $\Delta\eta$ values for all the binary mixtures studied supported the results obtained from the values of V^E discussed earlier.

From Table 4, it is seen that the values of d_{12} are negative for all the binary systems studied, except for the mixtures of DMF + MA. The negative values of d_{12} indicate the presence of dispersive forces[23] or weak specific interaction while its positive values indicate the presence of strong specific interactions[23] between the unlike molecules in the binary mixtures. Also for a given binary mixture, it has been observed that the values of 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[23] in regard to the nature of parameter T_{12} and H_{12}. From Table 3, it is observed that the fits were good as presented by the small values of standard deviation (σ).

In the eight binary mixtures studied, it is really interesting to note that V^E and $\Delta\eta$ have maxima/minima in the mole fraction range x_1=0.5 to 0.7 (Table 2). This indicates that specific interaction between the component molecules is predominated by hydrogen bonding. The maximum/minimum points are clear indications of the highest point of interaction between the component molecules in the binary mixtures.

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References

1 Perez E, Cardoso M, Mainar A M, Pardo J I & Urieta J S, *J Chem Eng Data*, 48 (2003) 1306.

2 Nayak J N, Aminabhavi T M & Aralaguppi M I, *J Chem Eng Data*, 48 (2003) 1152.

3 Nikam P S & Kharat S J, *J Chem Eng Data*, 50 (2005) 455.

4 Perrin D D & Armarego W L F, *Purification of Laboratory chemicals*, 3rd Edn. (Pergamon, UK) 1988.

5 Zhao Y, Wang J, Xuan X & Lu J, *J Chem Eng Data*, 45 (2000) 440.

6 Kinart C M, Kinart W J & Checinska-Majak D, *J Chem Eng Data*, 48 (2003) 1037.

7 Pal A & Bhardwaj R K, *Z Phys Chem*, 216 (2002) 1033.

8 Sastry N V & Patel MC, *J Chem Eng Data*, 48 (2003) 1019.

9 Roy M N & Hazra D K, *Indian J Chem Technol*, 1 (1994) 93.

10 Victor P J, Das B & Hazra D K, *J Phys Chem A*, 105 (2001) 5960.

11 Muhuri P K & Hazra D K, *J Chem Eng Data*, 40 (1995) 582.

12 Reid R C, Prausnitz J M & Poling B E, *The Properties of Gases and Liquids*, 4th Edn, (McGraw-Hill International, New York) 1987.

13 Irving J B, *Viscosities of Liquid Mixtures, NEL Report No. 630 and 631*, (National Engineering Laboratory, Glassgow) 1977, pp. 19.

14 Grunberg L & Nissan A H, *Nature*, 164 (1949) 799.

15 Tamura M & Kurata M, *Bull Chem Soc Japan*, 25 (1952) 32.

16 Hind R K, McLaughlin E & Ubbelohde A R, *Trans Faraday Soc*, 56 (1960) 328.

17 Oswal S L, Gheewala D B, Prajapati K D, Gardas R L, Ghael N Y & Ijardar S P, *Thermochim Acta*, 426 (2005) 141.

18 Ku Hsu-Chen & Tu Chein-Hsiun, *J Chem Eng Data*, 50 (2005) 608.

19 Roy M N, Sinha A & Sinha B, *J Sol Chem*, 34 (2005) 1311.

20 Nikam P S & Kharat S J, *J Chem Eng Data*, 50 (2005) 455.

21 Venkatesu P, Ramadevi R S, Rao M V P & Prasad D H L, *J Chem Eng Data*, 45 (2000) 515.

22 Viswanathan S & Rao M A, *J Chem Eng Data*, 45 (2000) 764.

23 Roy M N, Sinha B & Dakua V, *J Chem Eng Data*, 51 (2006), 590.

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Viscous synergy and isentropic compressibility of some monoalkanols and cyclic ethers in water at 298.15 K

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Abstract

Pure or aqueous alcohols are most widely used in industry, including in the manufacture of pharmaceuticals and cosmetic products. However, in the case of insolubility of some solutes in water, non-water solvents may be used possessing the common characteristic of being soluble in water; as a result, such solvents may be used with different purposes, such as increasing water solubility, or modifying the viscosity or absorption of the dissolved substance. Also, the nature of intermolecular forces between the solvents brings a marked effect on the thermodynamic properties such as density, viscosity and surface tension etc. The present study investigates viscous synergy and isentropic compressibility in the systems comprising some monoalkanols (C_1–C_4) and cyclic ethers (1,4-dioxane and tetrahydrofuran) in the proportion *w*/*w* = 1:1, in water at different concentrations (*w*/*w*) at 298.15 K to determine the proportion of monoalkanol + cyclic ether + water, at which maximum synergy occurs. The density and viscosity data have been analyzed using the equation developed by Kaletunc–Gencer and Peleg. Also a correlation between the density and viscosity increment for all the systems has been attempted. The ratio between maximum viscosity reached by the mixtures and pure state viscosity is expressed by the enhancement index defined as $E_\eta = \eta_{max}/\eta_0$.

Keywords: Viscous synergy; Isentropic compressibility; 1,4-dioxane; Tetrahydrofuran

1. Introduction

The increasing use of cyclic ether, monoalkanols and their aqueous mixtures in many industrial processes such as pharmaceutical and cosmetics has greatly stimulated the need for extensive information on their properties. 1,4-dioxane (DO), tetrahydrofuran (THF) and their aqueous mixtures are very important solvents that are widely used in various industries. They figure prominently in the high-energy battery technology and have also found application in organic synthesis as manifested from the physico-chemical studies in these media [1–7]. The thermodynamic properties of various alkanols have been studied in numerous solvents [8–14]. In our systematic study of the thermodynamic properties, we have reported densities, viscosities and speeds of sound of different solvents and their mixtures in the previous papers [15–22] from our laboratory. In this paper we extend our studies to the aqueous mixtures of 1,4-dioxane (DO) and tetrahydrofuran (THF) with some monoalkanols where water is represented as A, cyclic ether (DO or THF) is represented as B, and monoalkanol, represented as C. The monoalkanols include methanol (MeOH),

Table 1
Comparison of density, $\rho \times 10^3$/kg m^{-3} and viscosity, η of the pure liquids with literature data at 298.15 K

Solvent	$\rho \times 10^3$/kg m^{-3}		η/mPa s	
	Expt.	Lit.	Expt.	Lit.
Water	0.9971	0.9971 [25]	0.8904	0.8904 [25]
Tetrahydrofuran	0.8807	0.8807 [15]	0.4630	0.4630 [15]
1,4-Dioxane	1.0305	1.0305 [26]	1.2000	1.2000 [26]
Methanol	0.7869	0.7869 [12]	0.5470	0.5470 [12]
Ethanol	0.7850	0.7850 [12]	1.0760	1.0760 [12]
1-Propanol	0.8025	0.8025 [12]	1.9460	1.9460 [12]
2-Propanol	0.7825	0.7825 [12]	2.0314	2.0314 [12]
1-Butanol	0.8060	0.8060 [12]	2.5420	2.5420 [12]
2-Butanol	0.8035	0.8035 [12]	2.8230	2.8230 [12]

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Table 2

Comparison of the theoretical and experimental viscosities for the indicated water-soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols as a function of (*w/w*) concentration

Mass % of H_2O	Pure THF		THF + MeOH (*w/w* = 1:1)		THF + EtOH (*w/w* = 1:1)		THF + 1-PrOH (*w/w* = 1:1)	
	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s
0	0.4630	0.4630	0.5050	0.4761	0.7695	0.6728	1.2045	0.7603
10	0.5057	0.6564	0.5435	0.7377	0.7816	1.0009	1.1731	1.1857
20	0.5485	0.9237	0.5821	1.0404	0.7937	1.3311	1.1417	1.5186
30	0.5912	1.2238	0.6206	1.3114	0.8058	1.6325	1.1103	1.8789
35	0.6126	1.3994	0.6399	1.4428	0.8118	1.7806	1.0946	1.9117
40	0.6340	1.4904	0.6596	1.5381	0.8179	1.8862	1.0789	2.0208
45	0.6553	1.5817	0.6784	1.6474	0.8239	1.9729	1.0632	2.0917
50	0.6767	1.6776	0.6977	1.7686	0.8299	2.0332	1.0475	2.1581
55	0.6981	1.7013	0.7169	1.7698	0.8360	2.0907	1.0317	2.2296
60	0.7199	1.7321	0.7362	1.7852	0.8420	2.0152	1.0160	2.1679
70	0.7622	1.6798	0.7748	1.7787	0.8541	1.8765	0.9846	2.0124
80	0.8049	1.4900	0.8133	1.5651	0.8662	1.6345	0.9532	1.6478
90	0.8477	1.2015	0.8519	1.2485	0.8783	1.2372	0.9218	1.2592
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Mass % of H_2O	THF + 2-PrOH (*w/w* = 1:1)		THF + 1-BuOH (*w/w* = 1:1)		THF + 2-BuOH (*w/w* = 1:1)	
	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s
0	1.2472	0.6917	1.5025	0.8514	1.6430	0.8021
10	1.2115	1.1171	1.4413	1.2586	1.5677	1.2436
20	1.1758	1.4952	1.3801	1.6069	1.4925	1.6700
30	1.1402	1.8652	1.3189	1.9206		
35	1.1223	2.0303	1.2883	2.1404		
40	1.1045	2.1759	1.2577	2.1910		
45	1.0866	2.2524				
50	1.0688	2.2905				
55	1.0509	2.3370				
60	1.0331	2.2876				
70	0.9974	2.1204			1.1162	2.0884
80	0.9618	1.7880			1.0409	1.7427
90	0.9261	1.3276	0.9516	1.3354	0.9657	1.3178
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Mass % of H_2O	Pure DO		DO + MeOH (*w/w* = 1:1)		DO + EtOH (*w/w* = 1:1)		DO + 1-PrOH (*w/w* = 1:1)	
	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s	η_{mix}/mPa s	η_{exp}/mPa s
0	1.2000	1.2000	0.8735	0.6148	1.1380	0.9243	1.5730	1.1309
10	1.1690	1.4419	0.8752	0.9069	1.1132	1.3182	1.5047	1.6458
20	1.1381	1.7859	0.8769	1.2053	1.0885	1.7779	1.4365	2.0743
30	1.1071	1.9762	0.8786	1.4429	1.0637	2.0719	1.3682	2.3439
35	1.0916	2.0230	0.8794	1.5471	1.0513	2.1364	1.3341	2.3963
40	1.0762	1.9871	0.8803	1.6171	1.0389	2.1975	1.2999	2.4199
45	1.0607	1.9577	0.8811	1.6712	1.0266	2.2388	1.2658	2.4286
50	1.0452	1.9139	0.8819	1.7057	1.0142	2.2636	1.2317	2.4468
55	1.0297	1.8346	0.8828	1.6971	1.0018	2.2029	1.1976	2.3527
60	1.0142	1.6970	0.8836	1.6349	0.9894	2.1110	1.1634	2.2553
70	0.9833	1.5181	0.8853	1.5233	0.9647	1.8947	1.0952	2.0141
80	0.9523	1.2967	0.8870	1.3352	0.9399	1.5610	1.0269	1.6868
90	0.9214	1.0949	0.8887	1.1766	0.9153	1.2005	0.9587	1.2584
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

Mass % of H_2O	DO + 2-PrOH (*w/w* = 1:1)		DO + 1-BuOH (*w/w* = 1:1)		Do + 2-BuOH (*w/w* = 1:1)		DO + THF (*w/w* = 1:1)	
0	1.6157	1.0778	1.8710	1.2715	2.0115	1.1333	0.8315	0.6797
10	1.5432	1.6710	1.7729	1.7840	1.8994	1.8135	0.8374	0.9285
20	1.4706	2.2000	1.6749	2.1742	1.7873	3.0482	0.8433	1.2432
30	1.3981	2.5134	1.5768	2.2031			0.8492	1.5476
35	1.3618	2.5920	1.5278	2.2643			0.8521	1.6815
40	1.3256	2.6547	1.4788	2.4169			0.8551	1.7972
45	1.2893	2.6967					0.8580	1.8754
50	1.2530	2.6892					0.8609	1.8939
55	1.2168	2.6212					0.8639	1.9094

Table 2 (*continued*)

Mass % of H_2O	DO+2-PrOH (*w*/*w*=1:1)		DO+1-BuOH (*w*/*w*=1:1)		Do+2-BuOH (*w*/*w*=1:1)		DO+THF (*w*/*w*=1:1)	
60	1.1805	2.5276					0.8663	1.9166
70	1.1080	2.1706			1.2267	2.0546	0.8727	1.7124
80	1.0355	1.7344			1.1146	1.7101	0.8786	1.4701
90	0.9629	1.3143	0.9885	1.2371	1.0025	1.2626	0.8845	1.1930
100	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904	0.8904

ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH) and 2-butanol (2-BuOH).

2. Experimental section

2.1. Chemicals

1, 4-dioxane and tetrahydrofuran (Merck, India) were purified as described earlier [16,23]. The source and purification of pure alcohols (Merck, India) methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol have been described earlier [16,24]. Triply distilled water was used for the experiment. The chemicals after purification were 99.9% pure and their purity was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature [12,15,25,26] as listed in Table 1.

2.2. Measurements

Densities were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostated bath controlled to ±0.01 K. The weighings were done on a Mettler AG-285 electronic balance with a

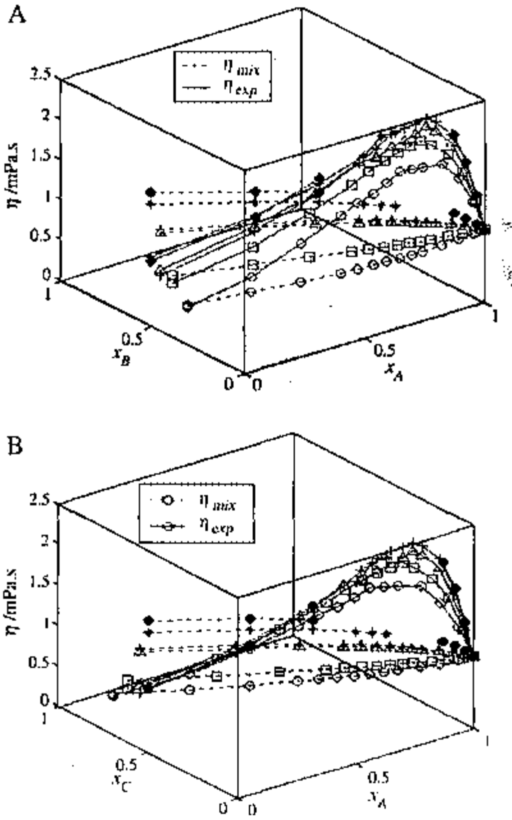

Fig. 1. A. Experimental viscosity, η_{exp}/mPa s, and theoretical viscosity, η_{mix}/mPa s, of water-soluble alkanols as a function of mole fractions of water (x_A) and tetrahydrofuran (x_B). Methanol (○), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (●). B. Experimental viscosity, η_{exp}/mPa s, and theoretical viscosity, η_{mix}/mPa s, of water-soluble alkanols as a function of mole fractions of water (x_A) and alkanol (x_C). Methanol (○), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (●).

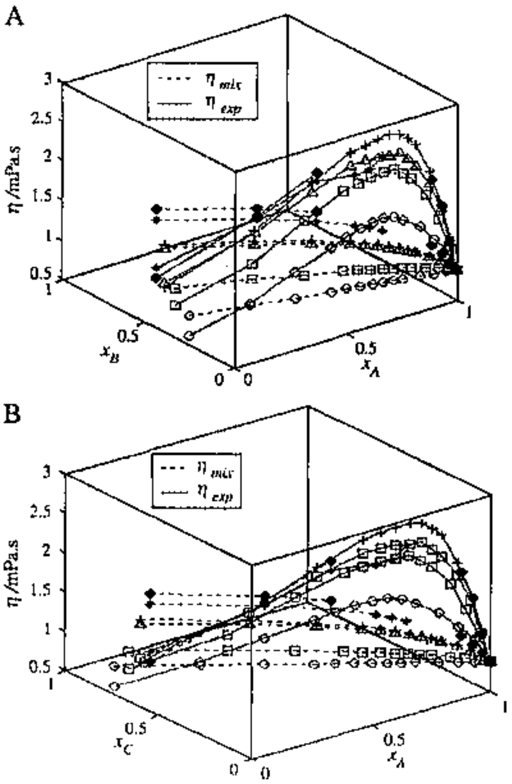

Fig. 2. A. Experimental viscosity, η_{exp}/mPa s, and theoretical viscosity, η_{mix}/mPa s, of water-soluble alkanols as a function of mole fractions of water (x_A) and 1,4-dioxane (x_B). Methanol (○), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (●). B. Experimental viscosity, η_{exp}/mPa s, and theoretical viscosity, η_{mix}/mPa s, of water-soluble alkanols as a function of mole fractions of water (x_A) and alkanol (x_C). Methanol (○), ethanol (□), 1-propanol (Δ), 2-propanol (+), 1-butanol (*), 2-butanol (●).

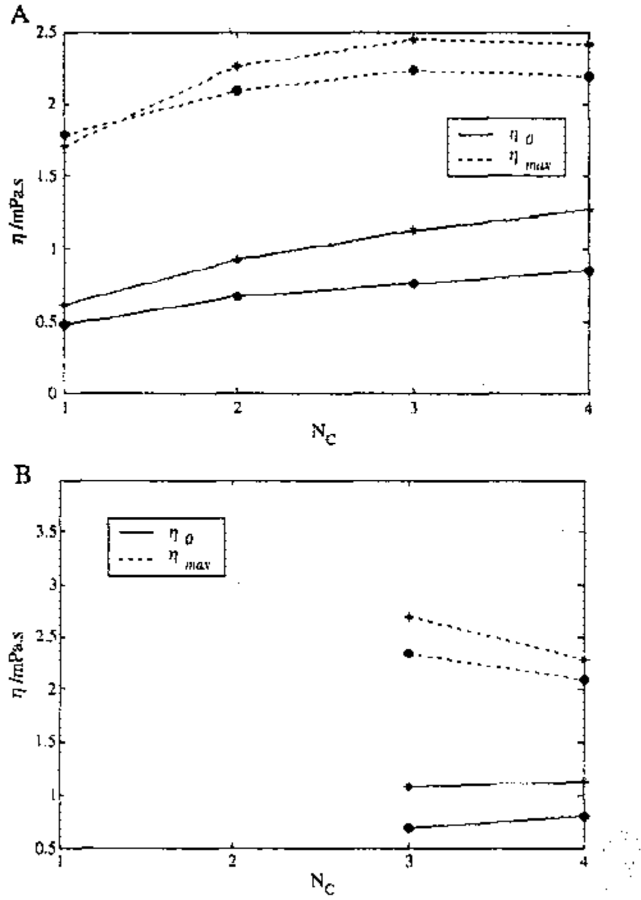

Fig. 3. A. Viscosity values, η_0/mPa s, and η_{max}/mPa s, of the monoalkanols with terminal hydroxyl group as a function of the number of carbon atoms, N_C: H_2O+THF systems (●), H_2O+DO systems (*). B. Viscosity values, η_0/mPa s, and η_{max}/mPa s, of the monoalkanols with hydroxyl group at the second carbon atom of the molecular chain as a function of the number of carbon atoms, N_C. H_2O+THF systems (●). H_2O+DO systems (*).

precision of ±0.01 mg. The precision of density measurements was $\pm 3\times 10^{-4}$ g cm^{-3}. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply 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 $\pm 2\times 10^{-4}$ mPa s. The details of the methods and techniques have been described earlier [4,16].

Speeds of sound were determined by a multi-frequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 2 MHz, which was calibrated with water, methanol and benzene at 298.15 K. The precision of the speed measurements was ±0.2 m s^{-1}. The details of the methods and techniques have been described earlier [16]. The mixtures were prepared by mixing known volumes of pure liquids in airtight-stopper bottles. Each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation losses during the actual measurements.

Table 3
Pure-state viscosity, η_0; maximum viscosity, η_{max}; viscosity of the mixture without interaction, η_{mix}; viscosity increment, $\Delta\eta$; synergy indices, I_η; enhancement indices, E_η for the indicated water-soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols

Solvent	η_0	η_{max}	η_{mix}	$\Delta\eta$	I_η	E_η
THF	0.4630	1.7321	0.7194	1.0127	1.4076	3.7146
THF+MeOH	0.4761	1.7852	0.7362	1.0489	1.4247	3.7443
THF+EtOH	0.6728	2.0907	0.8360	1.2547	1.5008	3.1074
THF+1-PrOH	0.7603	2.2296	1.0317	1.1978	1.1609	2.9323
THF+2-PrOH	0.6917	2.3370	1.0510	1.2860	1.2237	3.3787
THF+1-BuOH	0.8514	2.1910	1.2577	0.9334	0.7421	2.5733
THF+2-BuOH	0.8021	2.0884	1.1162	0.9722	0.8710	2.6038
DO	1.2000	2.0230	1.0916	0.9313	0.8531	1.6858
DO+MeOH	0.6148	1.7057	0.8819	0.8237	0.9340	2.7742
DO+EtOH	0.9243	2.2636	1.0142	1.2494	1.2319	2.4489
DO+1-PrOH	1.1309	2.4468	1.2317	1.2151	0.9865	2.1636
DO+2-PrOH	1.0776	2.6967	1.2893	1.4074	1.0915	2.5026
DO+1-BuOH	1.2715	2.4169	1.4788	0.9382	0.6344	1.9008
DO+2-BuOH	1.1333	3.0482	1.7873	1.2609	0.7055	2.6896
THF+DO	0.6797	1.9166	0.8663	1.0502	1.2122	2.8198

3. Results and discussion

3.1. Viscous synergy

The measurements yielded the viscosity values, η_{exp}, for the different mixtures at different concentrations (*w/w*), listed in Table 2 along with the viscosity values, η_{mix} in the absence of interaction. The method most widely used to analyze the antagonic and synergic behavior of various solvent–mixtures is that developed by Kaletunc–Gencer and Peleg [27] allowing quantification of the synergic and antagonic interactions taking place in mixtures involving variable proportions of the constituent components. Viscous synergy is the term applied to the interaction between the components of a system which causes the total viscosity to be greater than the sum of the viscosities of each component in the system. In contraposition to viscous synergism,

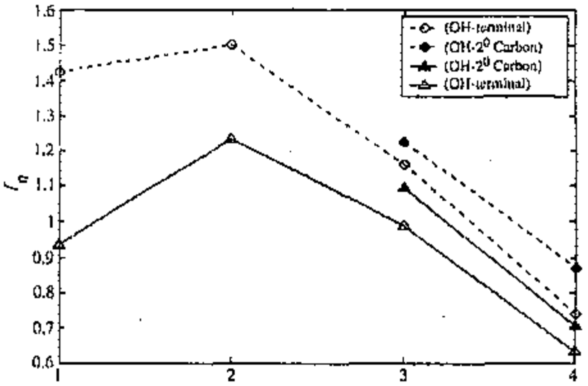

Fig. 4. Viscous synergy index, I_η, of the monoalkanols as a function of the number of carbon atoms, N_C. H_2O+DO systems (—), H_2O+THF systems (- - -).

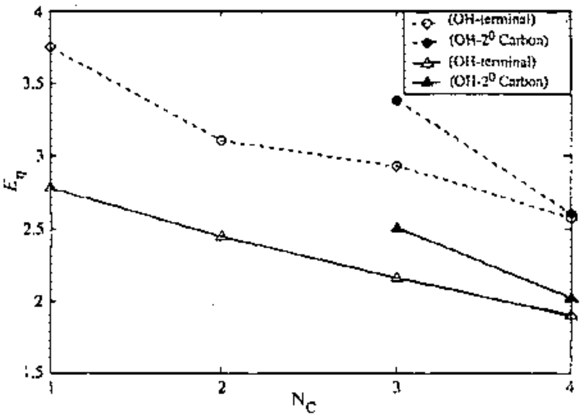

Fig. 5. Enhance index, E_η, of the monoalkanols as a function of the number of carbon atoms, N_C. H_2O+DO systems (—), H_2O+THF systems (- - -).

viscous antagonism is defined as the interaction between the components of a system causing the net viscosity to be less than the sum of the viscosities of each component in the system. If the total viscosity of the system is equal to the sum of the viscosities of each component, the system is said to lack interaction [28]. The viscosity in the absence of interaction, η_{mix}, is defined by the simple mixing rule

$$\eta_{mix} = w_A\eta_A + w_B\eta_B + w_C\eta_C \tag{1}$$

where w_A, w_B and w_C are the weight fractions and η_A, η_B and η_C are the measured viscosities, of the components A, B and C respectively. Viscous synergy exists when, $\eta_{exp} > \eta_{mix}$. The procedure is valid for Newtonian fluids, since in non-Newtonian systems shear rate must be taken into account and consequently, other synergy indices have been defined [29].

The values in Table 2 are graphically represented in Figs. 1 and 2, where the viscosity is seen to increase non-linearly for all the mixtures, reaching maximum values (saturation point) at different concentrations in each case and thereafter decreases.

Maximum viscosity is found in the mixtures when the molecules are in the following ratios

H_2O : THF = 1 : 0.17

H_2O : THF : MeOH = 1 : 0.08 : 0.19

Table 4
Comparison of the theoretical, ρ_{mix}/kg m^{-3}, and experimental, ρ_{exp}/kg m^{-3}, densities for the indicated water-soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols as a function of (w/w) concentration

Mass% of H_2O	Pure THF		THF+MeOH (w/w=1:1)		THF+EtOH (w/w=1:1)		THF+1-PrOH (w/w=1:1)	
	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}
0	880.7	880.7	833.8	830.6	832.9	842.1	841.6	843.3
10	892.4	898.5	850.1	861.6	849.3	862.4	857.2	864.4
20	904.0	915.9	866.5	884.4	865.7	884.7	872.7	884.7
30	915.6	930.2	882.8	904.7	882.1	904.3	888.2	903.4
35	921.4	940.7	891.0	914.0	890.3	912.4	896.0	911.8
40	927.3	946.0	899.1	924.4	898.5	921.1	903.8	918.7
45	933.1	952.5	907.3	923.3	906.7	930.1	911.6	927.5
50	938.9	959.0	915.4	941.6	914.9	939.1	919.3	936.3
55	944.7	963.8	923.6	949.3	923.2	947.8	927.1	944.8
60	950.5	966.4	931.8	956.5	931.4	954.7	934.9	951.8
70	962.2	978.3	948.1	969.9	947.8	968.2	950.4	966.9
80	973.8	986.7	964.4	979.5	964.2	979.1	966.0	979.8
90	985.4	990.0	980.7	989.5	980.6	989.7	981.5	983.5
100	997.1	997.1	997.1	997.1	997.1	997.1	997.1	997.1

Mass % of H_2O	THF+2-PrOH (w/w=1:1)		THF+1-BuOH (w/w=1:1)		THF+2-BuOH (w/w=1:1)	
	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}
0	831.6	830.5	843.4	847.1	842.1	840.6
10	848.2	856.0	858.7	867.1	857.6	862.9
20	864.7	877.1	874.1	883.5	873.1	887.1
30	881.2	897.2	889.5	902.5		
35	889.5	906.4	897.2	909.9		
40	897.8	916.9	904.8	918.2		
45	906.1	925.1				
50	914.3	933.6				
55	922.6	943.9				
60	930.9	949.9				
70	947.4	966.3			950.6	965.9
80	964.0	979.3			966.1	981.6
90	980.5	987.9	981.7	988.8	981.6	991.0
100	997.1	997.1	997.1	997.1	997.1	997.1

(continued on next page)

Table 4 (*continued*)

Mass% of H_2O	Pure DO		DO + MeOH (w/w = 1:1)		DO + EtOH (w/w = 1:1)		DO + 1-PrOH (w/w = 1:1)	
	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}	ρ_{mix}/kg m^{-3}	ρ_{exp}/kg m^{-3}
0	1030.5	1030.5	908.7	899.6	907.8	901.1	916.5	900.2
10	1027.2	1036.8	917.6	917.8	916.7	919.0	924.6	924.7
20	1023.8	1040.5	926.4	934.2	925.6	936.0	932.6	933.8
30	1020.5	1040.8	935.2	950.9	934.5	951.2	940.7	949.7
35	1018.8	1043.0	939.6	955.5	939.0	958.3	944.7	953.5
40	1017.1	1040.1	944.1	962.6	943.5	963.9	948.7	961.0
45	1015.5	1037.5	948.5	968.8	947.9	969.1	952.8	966.3
50	1013.8	1035.6	952.9	972.2	952.4	974.0	956.8	971.1
55	1012.1	1033.6	957.3	977.3	956.9	978.5	960.8	975.6
60	1010.4	1031.3	961.7	981.7	961.3	983.6	964.8	980.9
70	1007.1	1022.1	970.6	987.0	970.3	987.7	972.9	987.5
80	1003.8	1016.1	979.4	990.5	979.2	991.5	981.0	993.2
90	1000.4	1009.0	988.2	993.3	988.1	996.2	989.0	996.5
100	997.1	997.1	997.1	997.1	997.1	997.1	997.1	997.1

Mass% of H_2O	DO + 2-PrOH (w/w = 1:1)		DO + 1-BuOH (w/w = 1:1)		DO + 2-BuOH (w/w = 1:1)		DO + THF (w/w = 1:1)	
0	906.5	887.3	918.3	906.2	971.0	901.2	955.6	951.8
10	915.6	915.8	926.1	926.3	925.0	926.8	959.8	965.5
20	924.6	928.9	934.0	935.6	933.0	938.4	963.9	979.0
30	933.7	944.1	941.9	946.2			968.1	987.5
35	938.2	951.0	945.8	953.0			970.1	992.6
40	942.7	958.5	949.8	958.6			972.2	996.1
45	947.3	964.6					974.3	998.1
50	951.8	970.7					976.3	1000.8
55	956.3	975.1					978.4	1003.5
60	960.8	981.7					980.5	1005.9
70	969.9	989.1			973.0	989.3	984.6	1005.1
80	979.0	992.9			981.1	994.8	988.8	1003.8
90	988.0	995.3	989.2	995.1	989.1	995.9	992.9	1002.2
100	997.1	997.1	997.1	997.1	997.1	997.1	997.1	997.1

$$H_2O : THF : EtOH = 1 : 0.10 : 0.16$$

$$H_2O : THF : 1-PrOH = 1 : 0.10 : 0.16$$

$$H_2O : THF : 2-PrOH = 1 : 0.11 : 0.13$$

$$H_2O : THF : 1-BuOH = 1 : 0.19 : 0.18$$

$$H_2O : THF : 2-BuOH = 1 : 0.54 : 0.51$$

$$H_2O : DO = 1 : 0.38$$

$$H_2O : DO : MeOH = 1 : 0.10 : 0.28$$

$$H_2O : DO : EtOH = 1 : 0.10 : 0.20$$

$$H_2O : DO : 1-PrOH = 1 : 0.10 : 0.15$$

$$H_2O : DO : 2-PrOH = 1 : 0.10 : 0.15$$

$$H_2O : DO : 1-BuOH = 1 : 0.15 : 0.18$$

$$H_2O : DO : 2-BuOH = 1 : 0.41 : 0.49$$

$$H_2O : THF : DO = 1 : 0.08 : 0.07$$

The explanation of this type of behavior is based on the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture — producing an increase in size of the resulting molecular package, which logically implies a rise in viscosity and density. After reaching the maximum viscosity, the subsequent addition of more water induces a decrease in mixture viscosity, as the latter tends to approach the viscosity of water as concentration approaches zero.

Such characteristics in the viscosity versus composition curve is a manifestation of specific interaction [30] between the unlike molecules, predominated by hydrogen bonding interaction.

Table 2 shows that at the point of specific interaction (saturation point) the molar ratio of tetrahydrofuran (THF), 1,4-dioxane (DO), water and the various monoalkanols in the mixtures is as follows

$$\begin{aligned}THF &: H_2O : MeOH : EtOH : 1-PrOH : 2-PrOH\\ &: 1-BuOH : 2-BuOH = 1 : 5.88 : 2.37 : 1.6 : 1.6\\ &: 1.18 : 0.95 : 0.94\end{aligned}$$

$$\begin{aligned}DO &: H_2O : MeOH : EtOH : 1-PrOH : 2-PrOH\\ &: 1-BuOH : 2-BuOH = 1 : 2.63 : 2.8 : 2 : 1.5 : 1.5\\ &: 1.2 : 1.19\end{aligned}$$

Table 5

Experimental densities (ρ_{exp}), speeds of sound (u), isentropic compressibilities (K_S) and deviations in isentropic compressibility (K_S^E) for the indicated water-soluble mixtures of tetrahydrofuran (THF), 1,4-dioxane (DO) and different monoalkanols as a function of mole fractions of water (x_A) and the monoalkanols (x_C)

x_A	x_B^a	ρ_{exp}/kg m^{-3}	u/(m s^{-1})	$K_S \times 10^{12}$ /(Pa^{-1})	$K_S^E \times 10^{12}$ /(Pa^{-1})	x_A	x_C	ρ_{exp}/kg m^{-3}	u/(m s^{-1})	$K_S \times 10^{12}$ /(Pa^{-1})	$K_S^E \times 10^{12}$/(Pa^{-1})
H_2O + THF						H_2O + THF + MeOH					
0	1	880.7	1283.2	689.6	0	0	0.6924	830.6	1150.4	909.7	−25.7
0.3078	0.6922	898.5	1351.1	609.6	−5.5	0.2149	0.5436	861.6	1202.3	803.0	−27.6
0.5002	0.4998	915.9	1395.7	560.5	−8.1	0.3811	0.4285	884.4	1256.3	716.4	−33.1
0.6317	0.3683	930.2	1435.3	521.8	−15.0	0.5135	0.3368	904.7	1309.4	644.7	−40.3
0.6831	0.3169	940.7	1449.6	505.9	−18.5	0.5701	0.2976	914.0	1339.9	609.4	−48.0
0.7274	0.2726	946.0	1467.8	490.7	−23.0	0.6215	0.2620	924.4	1368.5	577.6	−54.7
0.7661	0.2339	952.5	1487.0	474.8	−29.5	0.6683	0.2297	933.3	1396.4	549.5	−60.0
0.8001	0.1999	959.0	1504.6	460.6	−35.5	0.7112	0.2000	941.6	1422.8	524.6	−64.0
0.8303	0.1697	963.8	1519.3	449.5	−39.3	0.7506	0.1727	949.3	1446.6	503.4	−66.0
0.8572	0.1428	966.4	1529.6	442.3	−40.0	0.7870	0.1475	956.5	1467.9	485.2	−66.4
0.9033	0.0967	978.3	1528.4	437.6	−33.6	0.8518	0.1026	970.0	1490.4	464.1	−55.9
0.9412	0.0588	986.7	1523.6	436.6	−25.4	0.9078	0.0638	979.5	1496.4	455.9	−36.8
0.9730	0.0270	990.0	1515.3	439.9	−14.4	0.9568	0.0299	989.5	1493.9	452.8	−16.0
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
H_2O + THF + EtOH						H_2O + THF + 1-PrOH					
0	0.6101	832.1	1193.3	843.9	−18.0	0	0.5454	841.3	1239.4	773.8	−6.6
0.2575	0.4530	862.4	1258.3	732.3	−22.9	0.2879	0.3884	864.4	1312.2	671.9	−12.8
0.4383	0.3427	884.7	1315.6	653.1	−27.3	0.4764	0.2856	884.7	1368.9	603.2	−18.8
0.5722	0.2610	904.3	1370.9	588.4	−36.5	0.6093	0.2131	903.4	1415.0	552.8	−24.9
0.6269	0.2277	912.4	1401.1	558.3	−44.0	0.6621	0.1843	911.8	1438.3	530.2	−30.0
0.6754	0.1980	921.1	1433.0	528.7	−53.5	0.7081	0.1592	918.7	1461.1	509.9	−35.0
0.7186	0.1717	930.1	1457.2	506.3	−58.0	0.7486	0.1371	927.5	1489.1	486.2	−45.2
0.7573	0.1481	939.1	1478.1	487.4	−60.9	0.7844	0.1176	936.3	1512.1	467.1	−52.4
0.7923	0.1267	947.8	1496.6	471.1	−62.7	0.8164	0.1002	944.8	1519.1	458.6	−50.2
0.8240	0.1074	954.8	1507.7	460.7	−59.9	0.8452	0.0844	951.8	1520.6	454.4	−44.9
0.8793	0.0736	968.2	1504.8	456.1	−41.6	0.8946	0.0575	966.9	1518.2	448.7	−34.1
0.9258	0.0453	979.1	1496.0	456.4	−22.1	0.9357	0.0351	979.8	1513.7	445.5	−23.7
0.9656	0.0210	989.7	1490.6	454.7	−7.3	0.9704	0.0161	983.5	1504.6	449.1	−8.5
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
H_2O + THF + 2-PrOH						H_2O + THF + 1-BuOH					
0	0.5454	830.5	1213.4	817.7	−10.0	0	0.4931	842.7	1261.1	746.1	−0.3
0.2879	0.3884	856.0	1291.1	700.8	−17.5	0.3108	0.3398	867.1	1338.1	644.1	−9.5
0.4764	0.2856	877.1	1352.3	623.4	−23.3	0.5036	0.2448	883.5	1391.2	584.8	−11.2
0.6093	0.2131	897.2	1405.5	564.2	−32.0	0.6349	0.1800	902.5	1432.9	539.7	−17.1
0.6621	0.1843	906.4	1432.2	537.9	−38.3	0.6860	0.1548	909.9	1454.2	519.7	−21.8
0.7081	0.1592	916.9	1458.0	513.1	−45.6	0.7301	0.1331	918.2	1483.4	494.9	−33.4
0.7486	0.1371	925.1	1484.7	490.4	−52.9						
0.7844	0.1176	933.6	1505.8	472.4	−57.3						
0.8164	0.1002	943.9	1517.2	460.2	−57.3						
0.8452	0.0844	949.9	1517.6	457.1	−49.5						
0.8946	0.0575	966.3	1512.4	452.4	−35.4						
0.9357	0.0351	979.3	1508.9	448.5	−23.7						
0.9704	0.0161	987.9	1500.6	449.5	−9.5	0.9733	0.0132	988.8	1498.6	450.3	−5.4
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
H_2O + THF + 2-BuOH						H_2O + DO					
0	0.4931	840.6	1249.5	762.0	−2.7	0		1030.5	1345.8	535.8	0
0.3108	0.3398	862.9	1329.8	655.3	−10.9	0.3521		1036.8	1405.0	488.6	−16.2
0.5036	0.2448	887.1	1381.2	590.9	−14.2	0.5501		1040.5	1436.4	465.8	−21.5
						0.6770		1040.8	1458.2	451.8	−24.3
						0.7248		1043.0	1483.8	435.5	−36.5
						0.7653		1040.1	1550.9	399.7	−68.7
						0.8001		1037.5	1577.0	387.6	−77.8
						0.8302		1035.6	1590.0	382.0	−80.7
						0.8567		1033.6	1593.0	381.3	−79.1
						0.8800		1031.3	1588.2	384.4	−73.9

(continued on next page)

Table 5 (*continued*)

x_A	x_B^a	ρ_{exp}/kg m^{-3}	u/(m s^{-1})	$K_S \times 10^{12}$ /(Pa^{-1})	$K_S^E \times 10^{12}$ /(Pa^{-1})	x_A	x_C	ρ_{exp}/kg m^{-3}	u/(m s^{-1})	$K_S \times 10^{12}$ /(Pa^{-1})	$K_S^E \times 10^{12}$/(Pa^{-1})
H_2O+THF+2-BuOH						H_2O+DO					
0.9045	0.0471	965.9	1508.2	455.1	−22.9	0.9194		1022.1	1558.4	402.9	−52.0
0.9420	0.0286	981.6	1501.7	451.7	−14.4	0.9514		1016.1	1540.4	414.8	−37.3
0.9733	0.0132	991.0	1497.1	450.2	−6.0	0.9778		1009.0	1509.0	435.2	−14.5
1	0	997.1	1496.6	447.8	0	1		997.1	1496.6	447.8	0
H_2O+DO+MeOH						H_2O+DO+EtOH					
0	0.7333	899.6	1197.0	775.8	−133.0	0	0.6566	901.1	1236.9	725.4	−96.8
0.2247	0.5686	917.8	1249.1	698.3	−107.0	0.2718	0.4781	919.0	1297.9	645.9	−74.5
0.3947	0.4439	934.2	1304.6	628.9	−97.9	0.4564	0.3569	936.0	1353.7	583.0	−68.3
0.5278	0.3463	950.9	1379.3	552.8	−112.7	0.5901	0.2691	951.2	1418.7	522.3	−78.9
0.5841	0.3050	955.5	1423.6	516.4	−123.1	0.6439	0.2338	958.3	1452.4	494.7	−86.4
0.6349	0.2677	962.6	1463.9	484.8	−131.3	0.6913	0.2027	963.9	1487.7	468.7	−94.6
0.6809	0.2340	968.8	1503.0	456.9	−138.0	0.7332	0.1752	969.1	1523.8	444.4	−103.0
0.7229	0.2032	972.2	1537.0	435.4	−140.1	0.7706	0.1506	974.0	1549.2	427.8	−105.9
0.7612	0.1751	977.4	1555.0	423.1	−134.7	0.8041	0.1286	978.5	1556.0	422.1	−99.0
0.7964	0.1493	981.7	1565.5	415.6	−126.0	0.8344	0.1087	983.6	1566.2	414.5	−95.3
0.8589	0.1035	987.0	1576.1	407.8	−105.0	0.8868	0.0743	987.7	1572.9	409.2	−80.9
0.9125	0.0642	990.5	1568.2	410.5	−77.6	0.9307	0.0455	991.5	1562.6	413.1	−60.6
0.9591	0.0300	993.3	1553.8	417.0	−49.6	0.968	0.0210	996.2	1547.1	419.4	−40.3
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
H_2O+DO+1-PrOH						H_2O+DO+2-PrOH					
0	0.5945	900.2	1248.6	712.5	−13.7	0	0.5945	887.3	1247.4	724.3	−53.5
0.3059	0.4126	924.7	1335.1	606.7	−34.4	0.3059	0.4126	915.8	1320.6	626.1	−50.7
0.4979	0.2985	933.8	1385.8	557.6	−30.0	0.4979	0.2985	928.9	1373.2	570.9	−42.6
0.6296	0.2202	949.7	1429.2	515.5	−35.4	0.6296	0.2202	944.1	1419.3	525.8	−44.2
0.6811	0.1896	953.5	1453.0	496.7	−39.8	0.6811	0.1896	951.0	1443.0	505.0	−48.0
0.7256	0.1631	961.0	1477.4	476.7	−47.4	0.7256	0.1631	958.5	1468.7	483.7	−54.6
0.7644	0.1401	966.3	1502.7	458.3	−55.1	0.7644	0.1401	964.6	1494.3	464.3	−61.2
0.7986	0.1197	971.1	1526.2	442.1	−61.7	0.7986	0.1197	970.7	1521.9	444.8	−69.4
0.8290	0.1017	975.6	1543.3	430.4	−65.0	0.8290	0.1017	975.1	1540.6	432.1	−72.1
0.8561	0.0856	980.9	1545.8	426.6	−61.2	0.8561	0.0856	981.7	1541.6	428.6	−66.6
0.9025	0.0580	987.5	1541.8	426.0	−48.9	0.9025	0.0580	989.1	1542.7	424.8	−55.1
0.9407	0.0353	993.2	1541.1	424.0	−40.3	0.9407	0.0353	992.9	1543.7	422.6	−44.7
0.9727	0.0162	996.5	1531.4	427.9	−27.4	0.9727	0.0162	995.3	1527.5	430.6	−26.1
1	0	997.1	1496.6	447.8	0	1	0	997.1	1496.6	447.8	0
3H_2O+DO+1-BuOH						H_2O+DO+2-BuOH					
0	0.5431	906.2	1268.6	685.7	3.8	0	0.5431	901.2	1263.9	694.6	−7.4
0.3318	0.3629	926.3	1364.6	579.7	−24.5	0.3318	0.3629	926.8	1356.4	586.5	−31.2
0.5277	0.2565	935.6	1411.2	536.7	−21.6	0.5277	0.2565	938.4	1401.2	542.8	−25.1
0.6570	0.1863	946.2	1457.1	497.8	−30.3						
0.7064	0.1595	953.0	1480.8	478.5	−38.0						
0.7487	0.1365	958.6	1508.2	458.6	−48.0						
						0.9125	0.0475	994.8	1539.7	426.4	−43.6
						0.9470	0.0288	995.9	1535.4	426.4	−34.8
0.9757	0.0132	995.1	1523.7	432.8	−20.6	0.9757	0.0132	997.1	1516.5	436.6	−17.3
1	0	997.1	1496.6	447.8	0	1	0	994.8	1496.6	447.8	0

x_A	x_B^b	ρ_{exp}/kg m^{-3}	u/(m s^{-1})	$K_S \times 10^{12}$/(Pa^{-1})	$K_S^E \times 10^{12}$/(Pa^{-1})
H_2O+THF+DO					
0	0.4501	951.8	1289.0	632.4	12
0.3285	0.3022	965.5	1377.6	545.8	−17.9
0.5239	0.2143	979.0	1417.0	508.7	−21.2
0.6536	0.1559	987.5	1444.8	485.1	−22.4
0.7033	0.1335	992.6	1457.2	474.4	−24.5
0.7459	0.1144	996.1	1474.4	461.8	−29.8
0.7827	0.0978	998.1	1494.0	448.9	−36.4
0.8149	0.0833	1000.8	1520.1	432.4	−47.3
0.8433	0.0705	1003.5	1539.8	420.3	−54.5
0.8685	0.0592	1005.9	1552.9	412.2	−58.2

Table 5 (*continued*)

x_A	x_B^b	ρ_{exp}/kg m^{-3}	u/(m s^{-1})	$K_S \times 10^{12}$/(Pa^{-1})	$K_S^E \times 10^{12}$/(Pa^{-1})
H_2O+THF+DO					
0.9113	0.0399	1005.1	1557.6	410.1	−53.0
0.9463	0.0242	1003.8	1542.8	418.5	−38.5
0.9754	0.0111	1002.2	1523.4	429.9	−22.0
1	0	997.1	1496.6	447.8	0

[a] Mole fraction of THF, [b] mole fraction of DO.

It can be concluded that the affinity of monoalkanol molecules towards tetrahydrofuran (THF) and 1,4 dioxane (DO) molecules in the presence of water is enhanced by the following orders

MeOH>EtOH = 1 − PrOH>2 − PrOH>1 − BuOH>2 − BuOH

MeOH>EtOH>1 − PrOH = 2 − PrOH>1 −BuOH>2 − BuOH

The monoalkanols with hydroxyl group positioned at the second carbon atom accept more tetrahydrofuran and 1,4-dioxane than those with the terminal hydroxyl group. Similar results were also reported earlier by Herraez et al. [12]. Also, the maximum viscosity logically increases with the number of carbon atoms of the alkanol molecules, as shown in Fig. 3.

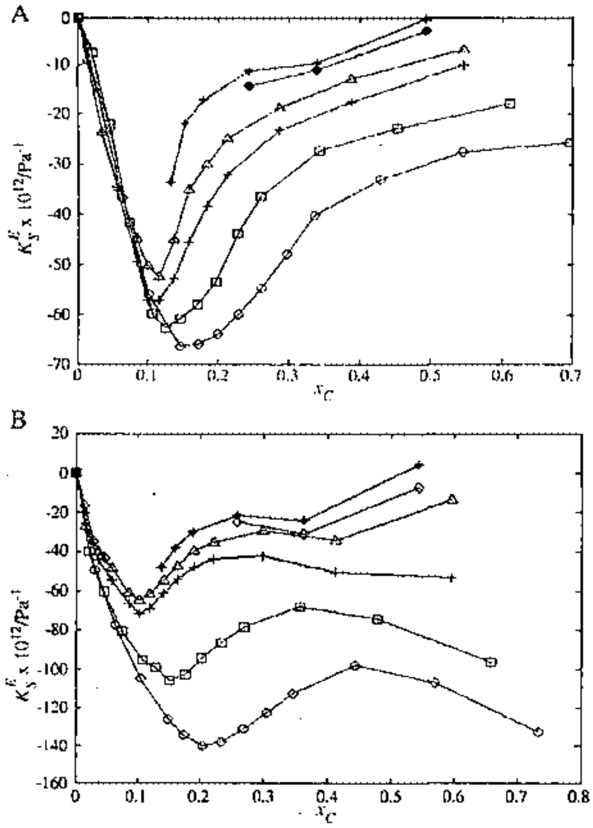

Fig. 6. A. Deviation in isentropic compressibility, K_S^E, of {H_2O+THF+ monoalkanol} mixtures as a function of mole fraction, x_C, of monoalkanols. Methanol (○), ethanol (□), 1-propanol (△), 2-propanol (+), 1-butanol (*), 2-butanol (●). B. Deviation in isentropic compressibility, K_S^E, of {H_2O+DO+monoalkanol} mixtures as a function of mole fraction, x_C, of monoalkanols. Methanol (○), ethanol (□), 1-propanol (△), 2-propanol (+), 1-butanol (*), 2-butanol (●).

3.2. *Synergy index and enhancement index*

Table 3 represents the corresponding pure state viscosity, η_0 the maximum viscosity reached on addition of water, η_{max} the viscosity of the mixture at the concentration where the maximum viscosity is reached in the event no interaction occurs in the mixture, η_{mix} the corresponding viscosity increment given by $\Delta\eta = \eta_{exp} - \eta_{mix}$ the synergy indices, I_η, introduced by Howell [29] and the enhancement indices, E_η calculated by the following equations:

$$I_\eta = \frac{\eta_{exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \tag{2}$$

$$E_\eta = \frac{\eta_{max}}{\eta_0} \tag{3}$$

The values recorded in Table 3 allow us to plot the graphic representations shown in Figs. 3–5. Fig. 3 presents the viscosities η_{max} and η_0, as a functions of the number of carbon atoms for the alkanols with terminal hydroxyl group, and shows that the values η_0 increases almost linearly with the number of carbon atoms, while the η_{max} values, expected to be greater than η_0, also increase in a similar way. For the monoalkanols with the hydroxyl group at the second carbon atom of the molecular chain, Fig. 3B provides a graphic illustration to the same scale as in Fig. 3A.

Fig. 4 shows the viscous synergy index, I_η, as a function of the number of carbon atoms corresponding to the monoalkanols with the hydroxyl group at the end of the molecular chain and the second carbon atom. This figure reflects a decreasing tendency with the exception of ethanol. This figure also shows that the synergy indices of the monoalkanols with the hydroxyl group at the second carbon atom of the molecular chain are greater than those of the monoalkanols with terminal hydroxyl group. Similar results were reported earlier by Herraez et al. [12].

Fig. 5 depicts the enhancement index, E_η, as a function of the number of carbon atoms in the monoalkanol structure and shows a linear, sharp gradient decrease for the monoalkanols.

3.3. Synergy in density

The increase in density was analyzed by carrying out a procedure analogous to that used for mixture viscosity based on the following equation

$$\rho_{\text{mix}} = w_A\rho_A + w_B\rho_B + w_C\rho_C \tag{4}$$

where w_A, w_B and w_C are the fractions by weight and ρ_A, ρ_B and ρ_C are the densities, measured experimentally, of the components A, B and C. Accordingly, when $\rho_{\text{exp}} > \rho_{\text{mix}}$, volume contraction occurs. A perusal of Table 4 shows that the values of the density determined experimentally, ρ_{exp} for various liquid mixtures are higher than its theoretical values, ρ_{mix}. This fact can be explained in terms of electrostriction, as a consequence solvent molecules are accommodated in the void space left in the packing of dispersed solvent molecules. Similar results were reported by some authors earlier [12,26].

3.4. Deviation in isentropic compressibility

Isentropic compressibility, K_S and deviation in isentropic compressibility, K_S^E were calculated using the following relations

$$K_S = (u^2\rho_{\text{exp}})^{-1} \tag{5}$$

$$K_S^E = K_S - \sum_{i=1}^{j} x_i K_{s,i} \tag{6}$$

where u and K_S are the speed of sound, isentropic compressibility of the mixture and $K_{S,i}$, the isentropic compressibility of the ith component in the mixture. The experimental speed of sound, isentropic compressibility and deviation in isentropic compressibility are listed in Table 5 and are graphically represented in Fig. 6A and B as functions of mole fraction of the monoalkanols.

Experimental speeds of sound, estimated isentropic compressibility and deviation in isentropic compressibility are listed in Table 5. Fig. 6A and B show that K_S^E values are negative for all the mixtures under investigation, and they increase as the length of the molecular chain of the monoalkanols increases. The donor–acceptor interactions between the mixing components play a pivotal role to yield negative K_S^E values, which are more negative for the lower monoalkanols. However, the branched isomers have lower K_S^E values than their terminal counter parts, as they can fit well into the structure of the cyclic ethers and water. Similar results were reported by some authors earlier [23,31,32].

4. Conclusions

In summary, monoalkanols containing up to three carbon atoms mix with water in any proportion and the higher monoalkanols mix with water in limited proportion. The monoalkanols with the hydroxyl group positioned at the second carbon atom accept more water than those with the terminal hydroxyl group and their η_{max}, I_η and E_η values are, therefore, considerably higher. Also, the monoalkanols with hydroxyl group positioned at the second carbon atom accept more tetrahydrofuran and 1,4-dioxane than those with the terminal hydroxyl group.

List of symbols

A	Water
B	Cyclic ether
C	Monoalkanol
w_A	Weight fraction of water
w_B	Weight fraction of cyclic ether
w_C	Weight fraction of monoalkanol
x_A	Mole fraction of water
x_B	Mole fraction of cyclic ether
x_C	Mole fraction of monoalkanol
u	Speed of sound
I_η	Synergy index
E_η	Enhancement index
K_S	Isentropic compressibility
K_S^E	Deviation in isentropic compressibility
η	Viscosity
η_0	Pure state viscosity
η_A	Viscosity of component A
η_B	Viscosity of component B
η_C	Viscosity of component C
η_{exp}	Experimental viscosity of mixture
η_{mix}	Theoretical viscosity of mixture
η_{max}	Maximum viscosity of mixture
ρ	Density
ρ_A	Density of component A
ρ_B	Density of component B
ρ_C	Density of component C
ρ_{exp}	Experimental density of mixture
ρ_{mix}	Theoretical density of mixture

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References

[1] M.N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data 46 (2001) 1247.

[2] C.G. Janz, R.P.T. Tomkins, Non-aqueous Electrolytes Handbook, vol. 2, Academic Press, New York, 1973.

[3] R. Jasinki, High Energy Batteries, Plenum Press, New York, 1967.

[4] M.N. Roy, D.K. Hazra, Indian J. Chem. Technol. 1 (1994) 93.

[5] A. Sacco, M.D. Monika, A.D. Giglio, J. Chem. Soc., Faraday Trans. I 79 (1983) 2631.

[6] F.J. Millero, Structure and Transport Process in Water and Aqueous Solutions, R.A. Horne, New York, 1972.

[7] M.L. Parmar, V.N. Rao, S.K. Bhardwaj, J. Indian Chem. Soc. 67 (1990) 591.

[8] S.L. Oswal, H.S. Desai, Fluid Phase Equilib. 161 (1999) 191.

[9] S.L. Oswal, H.S. Desai, Fluid Phase Equilib. 186 (2001) 81.

[10] P. Dimitrios, P. Constantinos, J. Chem. Eng. Data 40 (1995) 202.

[11] G. Czechowski, B. Zywucki, J. Jadzyn, J. Chem. Eng. Data 33 (1998) 55.

[12] J.V. Herraez, R. Belda, J. Solution Chem. 33 (2004) 117.

[13] R. Belda, J.V. Herraez, O. Diez, Phys. Chem. Liquids 42 (2004) 467.

[14] R. Belda, J.V. Herraez, O. Diez, Phys. Chem. Liquids 43 (2005) 91.

[15] M.N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data 46 (2001) 1327.
[16] M.N. Roy, A. Sinha, B. Sinha, J. Solution Chem. 34 (2005) 1319.
[17] M.N. Roy, S.R. Choudhury, A. Jha, J. Indian Chem. Soc. 79 (2002) 623.
[18] M.N. Roy, A. Jha, A. Choudhury, J. Chem. Eng. Data 49 (2004) 291.
[19] M.N. Roy, B.B. Gurung, A. Choudhury, J. Indian Chem. Soc. 81 (2004) 1.
[20] M.N. Roy, B. Sinha, V.K. Dakua, J. Chem. Eng. Data 51 (2006) 590.
[21] B. Sinha, A. Sinha, A. Jha, M.N. Roy, J. Indian Chem. Soc. 82 (2005) 814.
[22] M.N. Roy, B. Sinha, R. Dey, A. Sinha, Int. J. Thermophys. 26 (2005) 1549.
[23] M.N. Roy, A. Sinha, Fluid Phase Equilibria. 243 (2006) 133.
[24] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Oxford, 1988.
[25] A.K. Covington, T. Dickinson, Physical Chemistry of Organic Solvent Systems, Plenum, New York, 1973.
[26] A. Choudhury, A. Sinha, M.N. Roy, J. Technol. Res. 11 (2004) 12.
[27] G. Kalentunc-Gencer, M. Peleg, J. Texture Stud. 17 (1986) 61.
[28] J. Pellicer, Sinergia viscose. Ponencia en el curso: Fundamentos de reologia. Materiales viscoelasticos. Aplicaciones a las industrias alimentarias y quimico-farmaceuticas, U. I. M. P., Valencia, , 1997.
[29] N.K. Howell, Proceedings of the 7th Intern. Conf, Wales, 1993.
[30] R.J. Fort, W.R. Moore, Trans. Faraday Soc. 61 (1965) 2102.
[31] C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, Int. J. Thermophys. 25 (2004) 1735.
[32] I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, J. Solution Chem. 31 (2002) 905.

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Ion–solvent and ion–ion interactions of sodium molybdate salt in aqueous binary mixtures of 1,4-dioxane at different temperatures

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Apparent molar volumes and viscosity *B*-coefficients of sodium molybdate in aqueous binary mixtures of 1,4-dioxane have been determined from density and viscosity measurements at 303.15, 313.15 and 323.15 K and at various electrolyte concentrations. Also, adiabatic compressibilities of different solutions have been determined from measurement of ultrasonic speeds of sound at 303.15 K. Experimental density data were evaluated using the Masson equation and the derived parameters interpreted in terms of ion–solvent and ion–ion interactions. Partial molar volumes (ΔV_ϕ^0) and viscosity *B*-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane mixtures have also been calculated and discussed. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of the sign of $(\delta^2 V_\phi^0/\delta T^2)_p$.

Keywords: 1,4-Dioxane; Sodium molybdate; Partial molar volumes; Viscosity *B*-coefficients; Adiabatic compressibility; Ion–solvent and ion–ion interactions; Electrostriction

1. Introduction

Partial molar volumes of electrolytes at infinite dilution provide valuable information about ion–ion, ion–solvent and solvent–solvent interactions [1–3]. This information is of fundamental importance for a proper understanding of the behaviour of electrolytes in solution. Measurement of ultrasonic speeds of the solutions also helps in this regard. Recently, we have undertaken a comprehensive programme to study the solvation and association behaviour of some electrolytes [3,4] in different aqueous and non-aqueous solvent media from the measurement of various transport and thermodynamic properties. Aqueous 1,4-dioxane is an important mixed solvent for a number of separation processes and solution studies [5], because of its wide-ranging relative permittivity (2.2–78.3 at 298.15 K). In this article, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of sodium molybdate

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in aqueous 1,4-dioxane mixtures from volumetric, viscometric and acoustic measurements. Partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane mixtures were determined and are discussed in terms of ion–solvent interactions. Partial molar volumes at infinite dilution have been fitted to a second order polynomial equation in terms of temperature and the structure-making or breaking capacity of the electrolyte has been inferred from the sign of $(\delta^2 V_\phi^0/\delta T^2)_P$.

2. Experimental

2.1. *Materials*

1,4-Dioxane (Merck, India) was held for several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminium hydride ($LiAlH_4$). Details have been described earlier [6]. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6}\,\mathrm{ohm^{-1}\,cm^{-1}}$ was used. Sodium molybdate was purified by recrystallising twice from conductivity water and was dried in a vacuum desiccator over P_2O_5 for 24 h before use. Experimental density (ρ_0) and viscosity (η_0) values of pure 1,4-dioxane and different aqueous 1,4-dioxane mixtures at 303.15, 313.15 and 323.15 K are reported in table 1 and are compared with our earlier literature values [3,5,8].

2.2. *Apparatus and procedures*

Densities were measured using an Ostwald–Sprengel-type pycnometer having a bulb volume of 25 cm^3 and an internal capillary diameter of ca. 0.1 cm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K with doubly distilled water and benzene.

Table 1. Physical properties of pure 1,4-dioxane and 1,4-dioxane + water mixtures at different temperatures.

	ρ (g cm^{-3})		η (mPa s)	
Temperature (K)	This work	Literature	This work	Literature
10 mass% of 1,4-dioxane + water				
303.15	1.0058	1.0058 [3]	1.0320	1.0321 [3]
313.15	1.0041	1.0048 [3]	1.0015	1.0014 [3]
323.15	0.9973	0.9973 [3]	0.6895	0.6895 [3]
20 mass% of 1,4-dioxane + water				
303.15	1.0148	1.0148 [3]	1.2014	1.2014 [3]
313.15	1.0100	1.0100 [3]	1.0186	1.0186 [3]
323.15	1.0033	1.0033 [3]	0.8787	0.8787 [3]
30 mass% of 1,4-dioxane + water				
303.15	1.0202	1.0202 [3]	1.3977	1.3977 [3]
313.15	1.0162	1.0162 [3]	1.2493	1.2493 [3]
323.15	1.0103	1.0103 [3]	1.0755	1.0755 [3]
Pure 1,4-dioxane				
303.15	1.0199	1.0222 [5]	1.0886	1.0937 [5]
313.15	1.0144	1.0143 [6]	0.9785	0.9783 [6]
323.15	1.0027	1.0032 [6]	0.8441	0.8443 [6]

The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K of the desired temperatures. 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 total uncertainty of density is $\pm 0.0001\,\mathrm{g\,cm^{-3}}$ and that of the temperature is ±0.01 K.

Viscosity was measured by means of a suspended Ubbelohde-type viscometer, which was calibrated at 303.15, 313.15 and 323.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. Flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was within ±0.03% of the reported value. Ultrasonic speeds of sound for the solutions were determined at 298.15 K by a multi-frequency ultrasonic interferometer working at 2 MHz with an uncertainty of $\pm 0.2\,\mathrm{m\,s^{-1}}$, as described earlier [9]. Details of the methods and techniques of density and viscosity measurements have been described earlier [6,9].

The electrolyte solutions studied here were prepared by mass, and the conversion of molality to molarity was accomplished [3] using experimental density values. Experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in table 2.

3. Results and discussion

Apparent molar volumes (V_ϕ) were determined from solution densities using the following equation [3]:

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

where M is the molar mass of the solute, c the molarity of the solution, ρ_0 and ρ the densities of the solvent and solution, respectively. The limiting apparent molar volumes or partial molar volumes (V_ϕ^0) at infinite dilution were calculated using a least-squares treatment of plots of V_ϕ *versus* $\sqrt{c}$ together with the Masson equation [8]:

$$V_\phi = V_\phi^0 + S_V^*\sqrt{c} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_V^* the experimental slope. Values of V_ϕ^0 and S_V^* along with their standard errors are reported in table 3. Table 3 shows that V_ϕ^0 values are generally positive and increase with a rise in both temperature and amount of 1,4-dioxane in the ternary mixtures. This indicates the presence of strong ion–solvent interactions and these interactions are further strengthened at higher temperatures and higher mass% of 1,4-dioxane in the mixtures, suggesting larger electrostriction at higher temperatures and increased amount of cyclic diether. However, in the case of water, V_ϕ^0 values are positive and decrease with increase in temperature. This may be attributed to a slow desolvation [10] and thermal agitation at higher temperature. A perusal of table 3 also reveals that S_V^* values are negative for all the solutions and at all experimental temperatures and S_V^* values decrease as the

Table 2. Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_ϕ) and $(\eta/(\eta_0-1))/\sqrt{c}$ of sodium molybdate in water and aqueous 1,4-dioxane mixture at different temperatures.

c (mol dm^{-3})	ρ (g cm^{-3})	η (mPa s)	V_ϕ (cm^3 mol^{-1})	$(\eta/(\eta_0-1))/\sqrt{c}$
10 mass% of 1,4-dioxane + water				
$T=303.15$ K				
0.0241	1.0086	1.0336	125.042	0.0103
0.0321	1.0099	1.0356	113.565	0.0195
0.0561	1.0140	1.0433	95.230	0.0464
0.0723	1.0170	1.0491	86.538	0.0617
0.0883	1.0197	1.0555	84.045	0.0767
0.1003	1.0218	1.0606	81.953	0.0875
$T=313.15$ K				
0.0240	1.0057	1.0041	174.568	0.0168
0.0319	1.0066	1.0073	162.912	0.0325
0.0559	1.0096	1.0172	142.974	0.0664
0.0719	1.0123	1.0244	127.380	0.0854
0.0878	1.0148	1.0320	119.592	0.1029
0.0998	1.017	1.0382	112.231	0.1159
$T=323.15$ K				
0.0238	0.9990	0.6986	170.983	0.0856
0.0318	1.0000	0.7036	157.469	0.1144
0.0556	1.0035	0.7193	130.792	0.1836
0.0716	1.0065	0.7301	113.765	0.2201
0.0874	1.0094	0.7413	103.786	0.2544
0.0993	1.0119	0.7498	95.178	0.2774
20 mass% of 1,4-dioxane + water				
$T=303.15$ K				
0.0244	1.0168	1.2032	157.650	0.0096
0.0326	1.0177	1.2090	150.762	0.0349
0.0570	1.0212	1.2257	127.778	0.0846
0.0733	1.0238	1.2379	117.429	0.1123
0.0896	1.0268	1.2523	106.446	0.1416
0.1018	1.0293	1.2625	98.062	0.1595
$T=313.15$ K				
0.0243	1.0115	1.0226	178.437	0.0250
0.0325	1.0125	1.0282	163.393	0.0521
0.0567	1.0160	1.0440	134.782	0.1046
0.0729	1.0187	1.0553	121.394	0.1333
0.0891	1.0219	1.0679	107.319	0.1621
0.1013	1.0247	1.0778	95.878	0.1825
$T=323.15$ K				
0.0242	1.0047	0.8831	183.493	0.0321
0.0323	1.0057	0.8881	167.095	0.0595
0.0564	1.0094	0.9064	133.354	0.1326
0.0724	1.0122	0.9189	118.630	0.1698
0.0886	1.0156	0.9325	102.785	0.2056
0.1006	1.0179	0.9435	96.502	0.2324
30 mass% of 1,4-dioxane + water				
$T=303.15$ K				
0.0228	1.0222	1.4013	151.177	0.0172
0.0304	1.0233	1.4079	137.205	0.0419
0.0532	1.0271	1.4304	110.028	0.1015
0.0684	1.0306	1.4465	88.123	0.1334
0.0835	1.0340	1.4639	75.162	0.1640
0.0950	1.0366	1.4781	67.946	0.1866

(Continued)

Table 2. Continued.

c (mol dm^{-3})	ρ (g cm^{-3})	η (mPa s)	V_ϕ (cm^3 mol^{-1})	$(\eta/(\eta_0 - 1))/\sqrt{c}$
$T = 313.15$ K				
0.0227	1.0176	1.2553	177.402	0.0321
0.0303	1.0184	1.2622	166.643	0.0595
0.0530	1.0217	1.2874	135.974	0.1326
0.0680	1.0246	1.3046	116.533	0.1698
0.0830	1.0276	1.3233	102.933	0.2056
0.0944	1.0301	1.3385	93.194	0.2324
$T = 323.15$ K				
0.0225	1.0113	1.0790	195.492	0.0220
0.0301	1.0122	1.0859	177.004	0.0559
0.0527	1.0158	1.1087	136.183	0.1346
0.0677	1.0190	1.1254	112.285	0.1783
0.0826	1.0227	1.1421	90.893	0.2154
0.0939	1.0253	1.1582	81.367	0.2510
Pure water				
$T = 303.15$ K				
0.0241	0.9990	0.8028	105.474	0.0444
0.0322	1.0006	0.8083	90.164	0.0769
0.0563	1.0063	0.8262	53.905	0.1530
0.0723	1.0105	0.8395	37.408	0.1967
0.0884	1.0150	0.8542	23.726	0.2401
0.1004	1.0189	0.8654	10.921	0.2695
$T = 313.15$ K				
0.0240	0.9956	0.6577	101.072	0.0465
0.0321	0.9970	0.6625	93.144	0.0815
0.0561	1.0014	0.6781	78.570	0.1625
0.0720	1.0044	0.6878	73.075	0.1986
0.0879	1.0078	0.6988	64.982	0.2368
0.0963	1.0096	0.7059	61.746	0.2613
$T = 323.15$ K				
0.0239	0.9923	0.5547	67.015	0.0931
0.0319	0.9937	0.5586	67.201	0.1209
0.0558	0.9980	0.5704	65.308	0.1829
0.0717	1.0009	0.5793	64.192	0.2222
0.0876	1.0038	0.5873	63.482	0.2500
0.0959	1.0053	0.5920	63.350	0.2667

temperature of the solutions and amount of 1,4-dioxane in the mixtures increases. Since S_V^* is a measure of ion–ion interactions, the results indicate the presence of weak ion–ion interactions in the solutions at all experimental temperatures and these interactions further decrease with a rise in temperature and mass% of 1,4-dioxane in the solutions. This is probably due to more violent thermal agitation at higher temperatures and lower dielectric constants of the aqueous 1,4-dioxane mixtures, resulting in a diminishing force of ion–ion interactions (ionic dissociation) [11]. However, these interactions increase in water at higher temperatures, which results in a decrease in hydration of ions, i.e. more and more solute in accommodated in the void space left in the packing of water molecules [11].

Partial molar volumes (V_φ^0) at infinite dilution were fitted to a second order polynomial in terms of absolute temperature (T):

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2. \tag{3}$$

Table 3. Limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_V^*) for sodium molybdate in different aqueous 1,4-dioxane mixtures at different temperatures.

	V_ϕ^0 (cm^3 mol^{-1})			S_V^* (cm^2 dm$^{1/2}$ mol$^{-3/2}$)		
Mass% of 1,4-dioxane	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0 (water)	193.96 (±0.013)	138.28 (±0.013)	71.53 (±0.011)	−578.82 (±0.022)	−246.92 (±0.015)	−26.77 (±0.013)
10	162.66 (±0.014)	232.88 (±0.012)	242.16 (±0.013)	−267.93 (±0.011)	−384.50 (±0.021)	−470.70 (±0.014)
20	215.91 (±0.012)	254.04 (±0.013)	265.30 (±0.012)	−366.91 (±0.014)	−498.57 (±0.013)	−542.25 (±0.011)
30	231.96 (±0.011)	260.93 (±0.015)	305.89 (±0.012)	−538.69 (±0.013)	−547.73 (±0.014)	−740.63 (±0.012)

Standard errors are given in parenthesis.

Values of the coefficients a_0, a_1 and a_2 for different sodium molybdate solutions along with their standard errors (σ) are reported in table 4. From the values of coefficients the following equations were obtained:

For 10 mass% 1,4-dioxane + 90% water solutions,

$$V_\phi^0 = -30891.740\ (\mathrm{cm^3\,mol^{-1}}) + 194.809T\ (\mathrm{cm^3\,mol^{-1}}) - 0.305T^2\ (\mathrm{cm^3\,mol^{-1}}) \quad (4)$$

For 20 mass% 1,4-dioxane + 80% water solutions,

$$V_\phi^0 = -13694.068\ (\mathrm{cm^3\,mol^{-1}}) + 86.613T\ (\mathrm{cm^3\,mol^{-1}}) + 0.134T^2\ (\mathrm{cm^3\,mol^{-1}}) \quad (5)$$

For 30 mass% 1,4-dioxane + 70% water solutions,

$$V_\phi^0 = 6943.536\ (\mathrm{cm^3\,mol^{-1}}) - 46.374T\ (\mathrm{cm^3\,mol^{-1}}) + 0.080T^2\ (\mathrm{cm^3\,mol^{-1}}) \quad (6)$$

For 100 mass% water solutions,

$$V_\phi^0 = -3372.559\ (\mathrm{cm^3\,mol^{-1}}) + 28.544T\ (\mathrm{cm^3\,mol^{-1}}) - 0.055T^2\ (\mathrm{cm^3\,mol^{-1}}) \quad (7)$$

The partial molar expansibilities (ϕ_E^0) at infinite dilution can be obtained by differentiating equation (3) with respect to temperature:

$$\phi_E^0 = \left(\frac{\delta V_\phi^0}{\delta T}\right)_P = a_1 + 2a_2T. \quad (8)$$

Values of ϕ_E^0 for different solutions of the studied electrolyte at 298.15, 308.15, and 318.15 K are reported in table 5. It is found from table 5 that the values of ϕ_E^0 decrease with a rise in temperature as well as an increase in the amount of 1,4-dioxane in the mixtures up to 20 mass% of 1,4-dioxane, however, for 30 mass% of 1,4-dioxane mixtures, the solutions behave in an opposite manner. For aqueous solutions of sodium molybdate, the same trend as observed for the 10 and 20 mass% of 1,4-dioxane

Table 4. Values of the coefficients of equation (3) for sodium molybdate in different aqueous 1,4-dioxane mixtures.

Mass% of 1,4-dioxane	a_0 ($\mathrm{cm^3\,mol^{-1}}$)	a_1 ($\mathrm{cm^3\,mol^{-1}}$)	a_2 ($\mathrm{cm^3\,mol^{-1}}$)
0 (water)	−3372.559	28.544	−0.055
10	−30891.740	194.809	−0.305
20	−13694.068	86.613	−0.134
30	6943.536	−46.374	0.080

Table 5. Limiting partial molar expansibilities (ϕ_E^0) for sodium molybdate in various aqueous 1,4-dioxane mixtures at different temperatures.

	ϕ_E^0 ($\mathrm{cm^3\,mol^{-1}\,K^{-1}}$)			
Mass% of 1,4-dioxane	303.15 K	313.15 K	323.15 K	$(\delta\phi_E^0/\delta T)_P$
0 (water)	−4.802	−5.902	−7.002	Negative
10	9.887	3.787	−2.312	Negative
20	5.187	2.501	−0.185	Negative
30	2.069	3.667	5.265	Positive

solutions was observed. This can be ascribed to the absence of caging or packing effect [11,12].

According to Hepler [13], the sign of $(\delta^2 V_\phi^0/\delta T^2)_P$ is a better criterion than S_V^* in characterising the long-range structure-making and breaking capacity of electrolytes in solution. The general thermodynamic expression used is:

$$\left(\frac{\delta C_P}{\delta P}\right)_T = -\left(\frac{\delta^2 V_\phi^0}{\delta T^2}\right)_P \tag{9}$$

If the sign of $(\delta^2 V_\phi^0/\delta T^2)_p$ is positive, the electrolyte is a structure-maker and when the sign of $(\delta^2 V_\phi^0/\delta T^2)_p$ is negative, it is a structure-breaker. As is evident from table 5, the electrolyte under investigation is a structure-breaker in all the experimental solvent mixtures except 30 mass% 1,4-dioxane solutions.

Viscosity data of solutions of sodium molybdate in 10, 20 and 30 mass% 1,4-dioxane + water mixtures as well as pure water have been analysed using the Jones–Dole [14] equation;

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \tag{10}$$

$$\frac{(\eta/(\eta_0 - 1))}{\sqrt{c}} = A + B\sqrt{c} \tag{11}$$

where η_0 and η are the viscosities of solvent/solvent mixtures and solution, respectively. The coefficients A and B were estimated by a least-squares method and are reported in table 6. A perusal of table 6 shows that values of the A coefficient are negative for all the solutions under investigation at all temperatures. These results indicate the presence of weak ion-ion interactions, and these interactions decrease with an increase in the amount of 1,4-dioxane to the mixture.

The B-coefficient [15] reflects the effects of ion-solvent interactions on solution viscosity. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the near environment of solute molecules or ions. Table 6 indicates that values of the B-coefficient of sodium molybdate in the studied solvent systems are positive, thereby suggesting the presence of strong ion–solvent interactions, and these types of interactions are strengthened with a rise in both temperature and mass% of 1,4-dioxane in the solutions. Similar results were reported earlier by us for resorcinol in aqueous 1,4-dioxane mixtures [3].

A number of studies [16,17] report that $\mathrm{d}B/\mathrm{d}T$ is a better criterion for determining the structure-making/breaking nature of any solute rather than the B-coefficient. Table 6 indicates that values of the B-coefficients increase with a rise in temperature (positive $\mathrm{d}B/\mathrm{d}T$), suggesting the structure-breaking tendency of sodium molybdate in the studied solvent systems. A similar result has been reported in a study [18] of the viscosity of various salts in propionic acid + ethanol mixtures.

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = u^{-2}\rho^{-1} \tag{12}$$

Table 6. Values of *A* and *B* coefficients for sodium molybdate in different aqueous 1,4-dioxane mixtures at different temperatures.

	A ($cm^{3/2}\,mol^{-1/2}$)			B ($cm^3\,mol^{-1}$)		
Mass% of 1,4-dioxane	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0 (water)	−0.172 (±0.011)	−0.162 (±0.012)	−0.079 (±0.021)	1.384 (±0.012)	1.356 (±0.013)	1.116 (±0.011)
10	−0.065 (±0.011)	−0.077 (±0.013)	−0.098 (±0.012)	0.478 (±0.011)	0.608 (±0.012)	1.192 (±0.014)
20	−0.132 (±0.011)	−0.122 (±0.023)	-0.0161 (±0.012)	0.909 (±0.011)	0.953 (±0.012)	1.236 (±0.021)
30	−0.145 (±0.011)	−0.162 (±0.014)	−0.195 (±0.013)	1.071 (±0.015)	1.278 (±0.022)	1.439 (±0.011)

Standard errors are given in parenthesis.

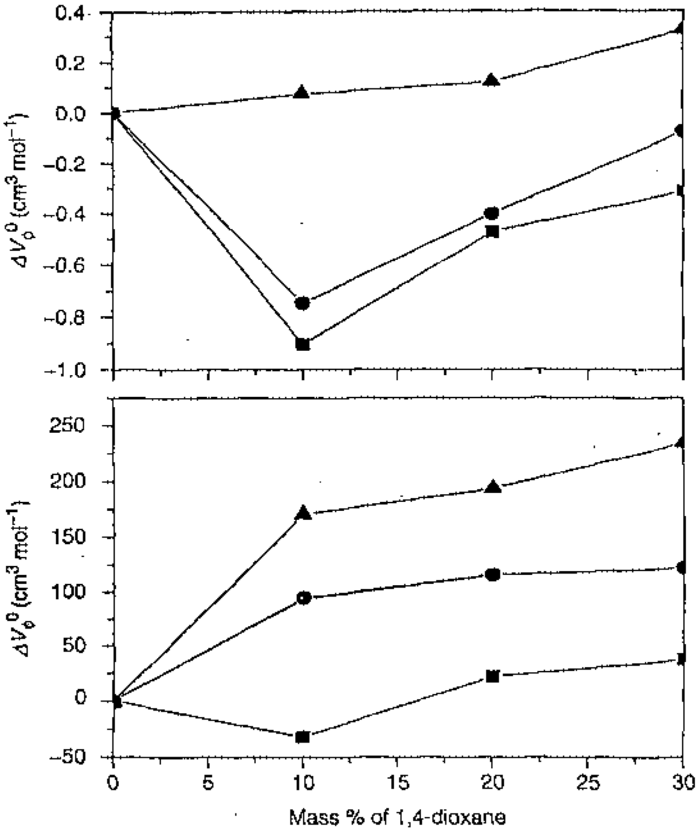

Figure 1. Plots of partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to different aqueous 1,4-dioxane mixtures against mass% of 1,4-dioxane in the mixtures at different temperatures. 303.15 K (■); 313.15 K (●); 323.15 K (▲).

where ρ is the solution density and u is the sound speed in the solution. The apparent molal adiabatic compressibility (ϕ_K) of the solutions was determined from the relation,

$$\phi_K = \frac{M\beta}{\rho_0} + \frac{1000(\beta\rho_0 - \beta_0\rho)}{m\rho\rho_0} \tag{13}$$

where β_0, β are the adiabatic compressibility of the solvent and solution, respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were obtained by fitting ϕ_K against the square root of molality of the electrolyte ($\sqrt{m}$) using the method of least squares.

$$\phi_K = \phi_K^0 + S_K^*\sqrt{m} \tag{14}$$

Values of m, u, β, ϕ_K, ϕ_K^0 and S_K^* are presented in table 7. A perusal of table 7 shows that ϕ_K^0 values are positive and S_K^* values are negative for all the ternary solutions. Since the values of ϕ_K^0 and S_K^* are measures of ion-solvent and ion-ion interactions,

Table 7. Molality (m), density (ρ), sound speed (u), adiabatic compressibility (β), partial molal adiabatic compressibility (ϕ_K), limiting partial adiabatic compressibility (ϕ_K^0), and experimental slope (S_K^*) of sodium molybdate in different aqueous 1,4-dioxane mixtures at 303.15 K.

m (mol kg^{-1})	u (m s^{-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$^{1/2}$)
10 mass% of 1,4-dioxane + water					
0.0240	1530.1	4.2349	−1.134	0.051 (±0.012)	−7.770 (±0.024)
0.0320	1532.5	4.2160	−1.353		
0.0561	1541.5	4.1504	−1.807		
0.0724	1548.5	4.1006	−2.034		
0.0884	1557.2	4.0442	−2.224		
0.1005	1564.9	3.9963	−2.416		
20 mass% of 1,4-dioxane + water					
0.0242	1572.2	3.979	0.390	1.599 (±0.011)	−7.901 (±0.013)
0.0323	1573.2	3.970	1.650		
0.0567	1577.0	3.977	−3.080		
0.0729	1580.3	3.911	−5.240		
0.0891	1584.5	3.879	−7.450		
0.1013	1588.6	3.850	−9.200		
30 mass% of 1,4-dioxane + water					
0.0224	1579.9	3.919	0.400	1.756 (±0.024)	−9.159 (±0.011)
0.0299	1580.4	3.913	0.182		
0.0524	1584.1	3.880	−0.380		
0.0674	1586.4	3.855	−0.640		
0.0824	1590.0	3.826	−0.864		
0.0937	1593.4	3.799	−1.030		
Pure water					
0.0243	1510.2	4.389	−2.960	−1.454 (±0.012)	−9.829 (±0.011)
0.0324	1515.0	4.354	−3.250		
0.0567	1529.9	4.246	−3.770		
0.0729	1542.7	4.158	−4.150		
0.0891	1555.8	4.070	−4.410		
0.1012	1564.9	4.008	−4.540		

Standard errors are given in parenthesis.

Table 8. Partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to different aqueous 1,4-dioxane mixtures for sodium molybdate at different temperatures.

Mass % of 1,4-dioxane	V_ϕ^0	ΔV_ϕ^0	B	ΔB
303.15 K				
0 (water)	193.96 (±0.013)	0.00	1.384 (±0.012)	0.00
10	162.66 (±0.014)	−31.30	0.478 (±0.011)	−0.906
20	215.91 (±0.012)	21.95	0.909 (±0.011)	−0.475
30	231.96 (±0.011)	38.00	1.071 (±0.015)	−0.313
313.15 K				
0 (water)	*138.28 (±0.013)*	*0.00*	*1.356 (±0.013)*	*0.00*
10	232.88 (±0.012)	94.60	0.608 (±0.012)	−0.748
20	254.04 (±0.013)	115.76	0.953 (±0.012)	−0.403
30	260.93 (±0.015)	122.65	1.278 (±0.022)	−0.078
323.15 K				
0 (water)	71.53 (±0.011)	0.00	1.116 (±0.011)	0.00
10	242.16 (±0.013)	170.63	1.192 (±0.014)	0.076
20	265.30 (±0.012)	193.77	1.236 (±0.021)	0.120
30	305.89 (±0.012)	234.36	1.439 (±0.011)	0.323

respectively, the results are in good agreement with those drawn from the values of V_ϕ^0 and S_V^* discussed earlier.

Partial molar volumes (ΔV_ϕ^0) and viscosity *B*-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane solutions have been determined using the relations [19,20],

$$\Delta V_\phi^0 = V_\phi^0(\text{Aqueous 1,4-dioxane solution}) - V_\phi^0(\text{Water}) \qquad (15)$$

$$\Delta B = B(\text{Aqueous 1,4-dioxane solution}) - B(\text{Water}). \qquad (16)$$

The value of ΔV_ϕ^0 is by definition free from ion–ion interactions and therefore provides information regarding ion–ion interactions [19]. As can be seen from figure 1, the value of ΔV_ϕ^0 is negative at 303.15 K for 10 mass% of 1,4-dioxane solution but becomes positive at higher temperatures. ΔV_ϕ^0 is positive and increases monotonically with mass% of 1,4-dioxane in the remaining mixtures. These results further confirm the presence strong ion–solvent interactions in the chosen solvent mixtures for sodium molybdate. ΔB values [20] shown in table 8 and figure 1 also support the results obtained from ΔV_ϕ^0 values.

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References

[1] J.M. McDowall, C.A. Vincent. *J. Chem. Soc. Faraday Trans.*, 1, 1862 (1974).
[2] M.R.J. Deck, K.J. Bird, A.J. Parker. *Aust. J. Chem.*, **28**, 955 (1975).
[3] M.N. Roy, B. Sinha, R. Dey, A. Sinha. *Int. J. Thermophys.*, **26**, 1549 (2005).
[4] M.N. Roy, B. Sinha, V.K. Dakua, A. Sinha. *Pak. J. Sci. Ind. Res.*, **49**, 153 (2006).
[5] D.P. Shoemaker, C.W.S. Garland. *Experiments in Physical Chemistry*, p. 131, McGraw Hill, New York (1967).
[6] M.N. Roy, B. Sinha, V.K. Dakua. *J. Chem. Eng. Data*, **51**, 590 (2006).
[7] E. Havega, D.G. Leaist. *J. Chem. Soc. Faraday Trans.*, **94**, 3353 (1988).
[8] D.O. Masson. *Phil. Mag.*, **8**, 218 (1929).
[9] M.N. Roy, A. Sinha, B. Sinha. *J. Sol. Chem.*, **34**, 1311 (2005).
[10] C. Guha, J.M. Chakraborty, S. Karanjai, B. Das. *J. Phys. Chem. B*, **107**, 12814 (2003).
[11] F.J. Millero. *Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, New York (1972).
[12] M.L. Parmar, D.S. Banyal. *Indian J. Chem.*, **44A**, 1582 (2005).
[13] L.G. Hepler. *Can. J. Chem.*, **47**, 4617 (1969).
[14] G. Jones, M. Dole. *J. Am. Chem. Soc.*, **51**, 2950 (1929).
[15] F.J. Millero, A.L. Surdo, C. Shin. *J. Phys. Chem.*, **82**, 784 (1978).
[16] R. Gopal, M.A. Siddique. *J. Phys. Chem.*, **72**, 1814 (1969).
[17] N. Saha, B. Das. *J. Chem. Eng. Data*, **42**, 277 (1997).
[18] S. Martin Contreras. *J. Chem. Eng. Data*, **46**, 1149 (2001).
[19] K. Belibagli, E. Agranci. *J. Sol. Chem.*, **19**, 867 (1990).
[20] C. Zhao, P. Ma, J. Li. *J. Chem. Thermodyn.*, **37**, 37 (2005).