

**“STUDY ON VISCOUS SYNERGY AND
ANTAGONISM AND VARIOUS INTERACTIONS
PREVAILING IN MONO, BINARY AND TERNARY
SOLVENT SYSTEMS”**

*Thesis submitted for the Degree of Doctor of
Philosophy in Science (Chemistry) to the
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BY

Riju Chanda (M. Sc.)

Under the Supervision and guidance of

Dr. Mahendra Nath Roy

**Department of Chemistry
University of North Bengal
Darjeeling, West Bengal
Pin: 734013
INDIA**

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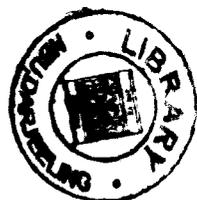
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Dedicated

To

My grand mother

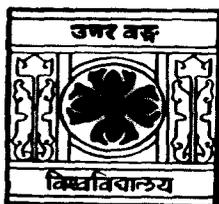
Late Bivarani Chanda.



UNIVERSITY OF NORTH BENGAL

Dr. M. N. Roy, M. Sc., Ph. D.
Reader in Chemistry

DEPARTMENT OF CHEMISTRY
E-mail: mahendraroy2002@yahoo.co.in



Mobile: 9434496154
Fax: 91 353 2699100
North Bengal University,
Darjeeling 734 013
INDIA
December 5, 2008

It gives me immense pleasure to certify that Mr. Riju Chanda, M.Sc. in Chemistry has carried out his research work embodied in the thesis entitled "Study on Viscous Synergy and Antagonism and Various Interactions Prevailing in Mono, Binary and Ternary Solvent Systems" based on his original work under my supervision and guidance. He is submitting his thesis for the award of Doctor of Philosophy (Science) degree in Chemistry according to the rules and regulations of the University of North Bengal.

I am much impressed for his keen interest and research aptitudes on such a applied and interesting field. 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.

Needless to say, he is very intelligent, alert, energetic, sincere and hard-working as he qualified 'National Eligibility Test' (NET), 'State Level Eligibility Test' (SLET) and 'Graduate Aptitude Test in Engineering' (GATE).

I wish him every success in life.



M. N. Roy
05.12.2008
Dr. Mahendra Nath Roy.

DEPARTMENT OF CHEMISTRY
University of North Bengal

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Department of Chemistry
University of North Bengal

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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 physicochemical properties of solvent-solvent¹⁻³ and solute-solvent⁴⁻⁶ systems. The physicochemical 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 mono, binary and ternary solvent systems are highly useful. 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.

Molecular behavior of a formulation^{7,8} 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} Rheology is the branch of science¹¹ 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.

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 Meck²⁰, Franks²¹, Popovych²², Bates²³, Parker²⁴, Criss and Salomon²⁵, Marcus²⁶ 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}

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, photo-electrochemical cells, electro-machining, 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.

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.^{36, 37, 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

Knowledge of ion-solvent interactions in non-aqueous solutions²⁸ 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.

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 interaction 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

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.

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 therapeutic 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:

Formamide, N,N-dimethylformamide, acetophenone, acetonitrile, dimethylsulfoxide, benzene, carbon tetrachloride, 2-butanone, monoalkanols viz. methanol, ethanol, propanol, butanol and pentanol, and some cyclic as well as acyclic ethers viz. 1,3 dioxolane, 1,4-dioxane, tetrahydrofuran, diethyl ether, di-isopropyl ether, 1,2 dimethoxy ethane, 2-methoxy ethanol, 2-ethoxy ethanol 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 25⁰C. However, its dipole moment rises with increase in temperature suggesting formation of boat form.³²

1,4-dioxane and 1,3-dioxolane are all cyclic diethers and they figure prominently in the high-energy battery technology⁴⁸ 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 differ 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 153⁰C, low vapour pressure and good solubility for a wide range of

substances. 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, 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}

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 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.

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 recipient. 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. A brief review of notable works on the behavior of viscous synergy and antagonism, 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

Study of densities, viscosities and speeds of sound have been measured for the ternary liquid mixtures of water + N,N-dimethylformamide + monoalkanols as a function of the composition at 298.15, 308.15 and 318.15 K. From the experimental measurements excess molar volumes (V^E), viscosity deviation ($\Delta\eta$), synergy index (I_s) and excess isentropic compressibilities (K_s^E) have been evaluated. The results get a clear idea about the type and amount of molecular interactions between them and also given us an idea about synergy. The lower monoalkanols are found to associate more with others molecules whereas self-association between the alcohol molecules was found to increase with increasing chain length.

Chapter V

This chapter the densities (ρ) and viscosities (η) for the ternary liquid mixtures of N,N-dimethylformamide + benzene + ethers, have been measured over the entire range of composition at 298.15 K. From the experimental measurements excess molar volumes (V^E), Viscosity deviation ($\Delta\eta$) and antagonistic index (I_A) have been evaluated. The speeds of sound have been also measured and excess isentropic compressibilities (K_s^E) are calculated at the experimental temperature. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

Chapter VI

Study of ion-solvent interactions of some tetraalkylammonium halides in THF + CCl₄ mixtures by Conductance measurements have been done in this chapter. The tendency of the ion-pair and triple-ion formation of R₄NX have been analyzed by using Fuoss and Kraus conductance equation. The various derived parameters like limiting molar conductivity (Λ_0), the association constant (K_A) and association distance (R) in the solvent mixtures have also been evaluated. The formation of ion-pair and triple-ions might be attributed to the ion sizes in solutions and bonding forces like coulombic forces and covalent interactions between the ions.

Chapter VII

Proteins are complex molecules and their behaviour in solutions is governed by a combination of many specific interactions. One approach that reduces the degree of complexity and requires less complex measurement techniques is to study the interactions in systems containing smaller biomolecules, such as amino acids and peptides. Some studies have revealed that the presence of an electrolyte drastically affects the behaviors of amino acids in solutions and this fact can be used for their separation and purification. Therefore, in this chapter an attempt has been made to unravel the various interactions prevailing in amino acid in aqueous resorcinol solutions at 298.15 K.

Chapter VIII

In this chapter conductivity study of some 1-1 electrolytes in aqueous binary mixtures of tetrahydrofuran and 1,3-dioxolane at 298.15 K has been made. The conductance data have been analyzed by the Fuoss conductance equation in terms of the limiting molar conductance (Λ^0), the association constant (K_A) and the association diameter (R). The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity value of the "reference electrolyte" Bu_4NBPh_4 . The cations are found to be substantially solvated in both solvent mixtures whereas the anions appear to have weak interactions with the solvent molecules. The results further indicate that the coulombic forces play a major role in the ion association processes.

Chapter IX

In this chapter an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of some sulphate salts in formamide + water mixtures from volumetric, viscometric, and acoustic measurements. The partial molar volumes and viscosity B -coefficients (ΔB) of transfer from water to aqueous formamide mixtures have also been calculated and discussed. The structure making or breaking capacities of the electrolyte has been inferred from the sign of $(\delta^2 V_\phi^0 / \delta T^2)_p$.

Chapter X

In this chapter electrical conductances of some tetraalkylammonium halides have been measured in THF + C_6H_6 mixtures with 10, 20, 30 and 40 mass percent of 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 and Kraus conductance equation. Based on the composition dependence of walden product ($\Lambda_0\eta_0$), the influence of the mixed solvent composition on the solvation of ions has also been discussed. The existence of triple-ions might be inferred in solutions due to coulombic interactions and covalent bonding forces between the ions ($R_4N^+ \dots X^-$).

Chapter XI

In this chapter studies on apparent molar volume, viscosity B -coefficient and adiabatic compressibility of some thiocyanate salts in aqueous binary mixtures of 1,3-dioxolane at different temperatures been made from density, viscosity and ultrasonic speed data. The structure making / breaking capacities of the electrolytes have been inferred from the sign of $(\delta^2 V_\phi^o / \delta T^2)_p$ and dB/dT . The activation parameters of viscous flow for the ternary solutions studied were also calculated and explained by the application of transition state theory.

Chapter XII

In this chapter the densities, viscosities and ultrasonic speeds have been measured for the binary mixtures of formamide with 2-Methoxyethanol, Acetophenone, Acetonitrile, 1,2-Dimethoxyethane, and Dimethylsulfoxide at Different Temperatures. 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 XIII

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

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CHAPTER II

2.1. Investigation on viscous Synergy and Antagonism

Grouping of solvents into classes is often based on the nature of the intermolecular forces because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. Rheology is the branch of science¹ that studies material deformation and flow, and is increasingly applied to analyses the viscous behaviors of many pharmaceutical products,²⁻⁷ 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.^{8,9}

The study of the viscous behaviour of pharmaceutical, 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 defined as 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.^{10,11}

In contraposition to viscous synergy, Viscous antagonism 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 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 considered separately, the system would lack interaction.

The method most widely used to analyze the synergic and antagonic behavior of various solvent mixtures studied is that developed by Kalentune-Gencer and Peleg,¹² allowing the quantification of the antagonic and synergic 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_{calcd} , defined as,¹³

$$\eta_{\text{calcd}} = \sum_{i=1}^{n=3} W_i \eta_i \quad (1)$$

Where, 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.

Accordingly, viscous synergy is exists when, $\eta_{exp} > \eta_{calcd}$ and while when, $\eta_{exp} < \eta_{calcd}$ viscous antagonism is exists. This procedure is used when Newtonian fluids are involved.
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In order to secure more comparable viscous synergy results, the so called synergy index (I_s), introduced by Howell¹³ is taken into account:

$$I_s = (\eta_{exp} - \eta_{calcd}) / \eta_{calcd} \quad (2)$$

The negative value of gives I_s antagonic interaction index I_A .

The method used to analyze volume contraction and expansion is carrying out the following equation analogous to that used for viscosity of mixture.

$$\rho_{mix} = \sum_{i=1}^{n=3} W_i \rho_i \quad (3)$$

Where, W_i and ρ_i are the fractions by weight and densities measured experimentally of the pure components respectably. Accordingly, when $\rho_{exp} > \rho_{mix}$, volume contraction occurs while, when $\rho_{exp} < \rho_{mix}$, volume expansion occurs in the system.

Besides this, power factor, F_η has also be studied which is the enhancement index of the viscosity given as

$$F_\eta = \frac{\eta_{max}}{\eta_0} \quad (4)$$

where η_{max} is the maximum viscosity attained in the mixtures, and η_0 is the experimental viscosity of the pure components. The investigations have been carried out with various binary as well as ternary mixtures

2.1. Investigation on 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 1:¹⁴

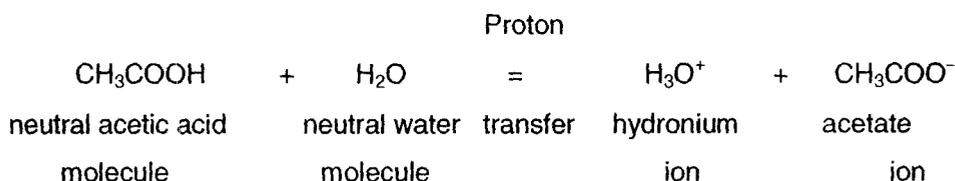


Figure 1. The chemical method of producing ionic solutions.

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 2,¹⁴ 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.

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. 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.¹⁵⁻²⁴

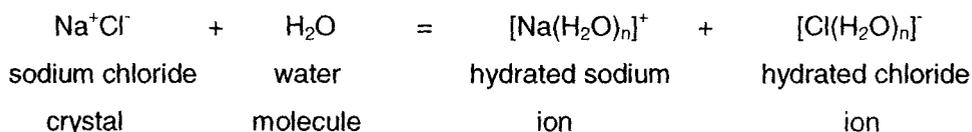


Figure 2. Dissolution of an ionic crystal by the action of a solvent.



Though water is the most abundant and versatile solvent in nature but its uniqueness as a solvent has been questioned^{25,26} 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. Non-aqueous and mixed solvents increase the range of applicability of electrochemical techniques to many organic and inorganic compounds either due to its instability or insolubility in water and many novel battery systems require their use²⁷ for important new developments.

The organic solvents have been classified based on the dielectric constants, functional group types, acid-base properties or association through hydrogen bonding,²⁴ donor-acceptor properties,²⁸⁻²⁹ hard and soft acid-base principles,³⁰ 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. 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 extent and solute structure also gets modified by the solvent molecule. Thus 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.³¹⁻³² But even qualitative or quantitative apportioning of ion-solvent interactions into the various possible factors is still an uphill 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.

2.2. 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 solvent molecules as well as also other ions. The mutual interactions between these ions constitute the essential part of 'ion-ion interactions'. The degree of these interactions affects the properties of solution.

While proton transfer reactions are particularly sensitive to the nature of the solvent, it is now clear 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.

2.3. Theory of Mixed Solvents

As the non-aqueous and mixed solvents are widely used in various field of modern science, a number of molecular theory have been developed. L. Jones and Devonshire³³ 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 Garikian³⁴ extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans³⁵ developed a two fluid version of the cell model. Treszczanowicz et al.³⁶ 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 vice-versa. This assumption is not a concrete one, as evident from some

studies.³⁷⁻³⁹ It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Based on the principle of corresponding states as suggested by Pitzer,⁴⁰ L. Huggins⁴¹ 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.⁴²⁻⁴⁴ 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.⁴⁵ Flory et al.⁴⁶⁻⁴⁹ 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. Recently, Heintz⁵⁰⁻⁵² 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 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.⁴⁶⁻⁴⁸ But Pineiro et al.⁵³ noticed that some of the mixing rules of the ERAS model have an asymmetrical form signifying that the components should be distinguishable from one another. Subsequently they introduced a new symmetrical reformulation⁵⁶ of ERAS model called 'Symmetrical-ERAS' model, which can be used to describe the excess molar enthalpies and excess molar volumes of binary mixtures containing very similar compounds like alcohol-alcohol mixtures.⁵⁷

2.4. Volumetric measurement

The volumetric information includes 'Density' as a function of composition on the bases of weight, volume and mole fraction and excess volumes of mixing. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Interpretation of fundamental macroscopic state of the system such as enthalpy, entropy and Gibbs free energy in terms of molecular

phenomena is generally difficult. The volumetric information may be of immense importance in this regard.

Various concepts regarding molecular processes in solutions like electrostriction,⁵⁸ hydrophobic hydration,⁵⁹ micellization⁶⁰ and co-sphere overlap during solute-solvent interactions⁶¹ to a large extent have been derived and interpreted from the partial molar volume data of many compounds.

2.4.1. 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 one 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. 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:⁶²

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

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, \bar{V}_2 can be obtained from the equation:⁶³

$$\bar{V}_2 = V_\phi + (1000 - cV_\phi)/(2000 + c^{3/2} \cdot \partial V_\phi / \partial \sqrt{c}) \sqrt{c} \cdot \partial V_\phi / \partial \sqrt{c} \quad (6)$$

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,⁶⁴ the Redlich-Meyer equation,⁶⁵ the Owen-Brinkley equation⁶⁶ and the Pitzer equation.⁴⁰ Masson found that the apparent molar volume of electrolyte, V_ϕ , vary with the square root of the molar concentration by the linear equation:

$$V_{\phi} = V_{\phi}^{\circ} + S_v^* \sqrt{c} \quad (7)$$

where, V_{ϕ}° is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution, \bar{V}_2°) and S_v^* is the experimental slope. The majority of V_{ϕ} data in water⁶⁷ and nearly all V_{ϕ} data in non-aqueous⁶⁸⁻⁷² solvents have been extrapolated to infinite dilution through the use of equation (7).

The temperature dependence of V_{ϕ}° for various investigated electrolytes in various solvents can be expressed by the general equation as follows:

$$V_{\phi}^{\circ} = a_0 + a_1 T + a_2 T^2 \quad (8)$$

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°) can be calculated from the general equation (9). Thus,
$$\phi_E^{\circ} = (\partial V_{\phi}^{\circ} / \partial T)_P = a_1 + 2a_2 T^2 \quad (9)$$

The limiting apparent molar expansibilities (ϕ_E°) 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. Hepler⁷³ developed a technique of examining the sign of $(\delta^2 V_{\phi}^{\circ} / \delta T^2)_P$ for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

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

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 Meyer⁶⁵ have shown that equation (11) 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:

$$V_{\phi} = V_{\phi}^{\circ} + S_v \sqrt{c} + b_v c \quad (11)$$

where,
$$S_v = K w^{3/2} \quad (12)$$

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

$$w = 0.5 \sum_i^j \gamma_i z_i^2 \quad (13)$$

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

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.

Thus for polyvalent electrolytes, the more complete Owen-Brinkley equation⁶⁶ 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:

$$V_\phi = V_\phi^0 + S_v \tau(Ka) \sqrt{c} + 0.5 w_v \theta(Ka) + 0.5 K_v c \quad (15)$$

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

2.4.2. Ionic Limiting Partial Molar Volumes

The individual partial ionic volumes provide information relevant to the general question of the structure near the ion i.e., its solvation. The calculation of the ionic limiting partial molar volumes in organic solvents is, 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 solutions⁷⁴⁻⁷⁸ to non-aqueous electrolyte solutions.

In the last few years, the method suggested by Conway et al.⁷⁸ 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,

$\bar{V}_{R_4NX}^0$ 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:

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + bM_{R_4N^+} \quad (16)$$

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

2.4.3. 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:⁷⁹⁻⁸²

$$V^E = \sum_{i=1}^j x_i M_i (1/\rho - 1/\rho_i) \quad (17)$$

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.

5. Viscometric measurement

The viscometric information includes 'Viscosity' as a function of composition on the bases of weight, volume and mole fraction, comparison of experimental viscosities with those calculated with several equations and excess Gibbs free energy of viscous flow. Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively.⁸²⁻⁸⁴ Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, \bar{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. In 1905, Grüneisen⁸⁵ 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 Dole⁸⁶ suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations, c :

$$\eta/\eta_0 = \eta_r = 1 + A\sqrt{c} + Bc \quad (18)$$

The above equation can be rearranged as:

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

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 theory⁸⁷ of inter ionic attractions in 1923.

At higher concentrations the extended Jones-Dole equation (18), involving an additional coefficient D , originally used by Kaminsky,⁸⁸ has been used by several workers^{89, 90} and is given below:

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc + Dc^2 \quad (20)$$

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.⁸⁸⁻⁹²

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.⁸⁶

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:^{93,94}

- (i) 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.
- (ii) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking or depolymeriation effect) decrease η values.
- (iii) High molal volume and low dielectric constant, which yield high B -values for similar solvents.
- (iv) 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.

2.5.1. 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:⁹⁵

$$\eta = A \exp^{b/T} \quad (21)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range⁹⁶⁻¹⁰⁰ and the equation suggested

by Angell^{101, 102} 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:
$$1/\eta = A \exp[-K_1/(N_0 - N)] \quad (22)$$

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.¹⁰³⁻¹⁰⁵ introducing the limiting condition, that is; which is the viscosity of the pure solvent. Thus, we have:

$$\ln \eta/\eta_0 = \ln \eta_{\text{Rel}} = K_1 N/N_0(N_0 - N) \quad (23)$$

The equation (23) predicts a straight line passing through the origin for the plot of $\ln \eta_{\text{Rel}}$ vs. $N / (N_0 - N)$ if a suitable choice for N_0 is made. Majumder et al. tested the equation (23) by using literature data as well as their own experimental data. The best choice for N_0 and K_1 was selected by trial and error methods. The set of K_1 and N_0 producing minimum deviations between $\eta_{\text{Rel}}^{\text{Exp}}$ and $\eta_{\text{Rel}}^{\text{theo}}$ was accepted. In dilute solutions, $N \ll N_0$ and we have:

$$\eta_{\text{Rel}} = \exp(K_1 N/N_0^2) \cong 1 + K_1 N/N_0^2 \quad (24)$$

Equation (23) 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 (23) written in the form:

$$N/\ln \eta_{\text{Rel}} = N_0^2/K_1 - (N_0/K_1)N \quad (25)$$

It closely resembles the Vand's equation¹⁰⁶ for fluidity (reciprocal for viscosity):

$$2.5c/2.3 \log \eta_{\text{Rel}} = 1/V - Qc \quad (26)$$

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.

2.5.2. Division of B -coefficient

The viscosity B -coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents.^{92,107-137} 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 –

(i) Cox and Wolfenden¹³⁸ 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 Gurney¹³⁹ and also of Kaminsky⁹³ is based on:

$$B_{K^+} = B_{Cl^-} \text{ (in water)} \quad (27)$$

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. Nightingale,¹⁴⁰ however preferred RbCl or CsCl to KCl from mobility considerations.

(ii) The method suggested by Desnoyers and Perron⁹⁴ is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation,¹⁴¹

$$B = 0.0025\bar{V}_0 \quad (28)$$

and by having an accurate value of the partial molar volume of the ion, V_0 , it is possible

to calculate the value of 0.359 for $B_{\text{Et}_4\text{N}^+}$ 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:

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{BPh}_4\text{PPh}_4} / 2 \quad (29)$$

$B_{\text{BPh}_4\text{PPh}_4}$ (Scarcely soluble in water) has been obtained by the following method:

$$B_{\text{BPh}_4\text{PPh}_4} = B_{\text{NaBPh}_4} + B_{\text{PPh}_4\text{Br}} - B_{\text{NaBr}} \quad (30)$$

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 $B_{\text{K}^+} = B_{\text{Cl}^-}$ in ethanol based on equal mobility of ions.¹⁴² They also adopted $B_{\text{Me}_4\text{N}^+}^{25} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss¹⁴³ proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer et al.¹⁴⁴

$$\lambda_{25}^0(\text{Bu}_4\text{N}^+) = 61.4 \quad \text{and} \quad \lambda_{25}^0(\text{Ph}_4\text{B}^-) = 58.3 \quad \text{in acetonitrile.}$$

$$B_{\text{Bu}_4\text{N}^+} = B_{\text{Ph}_4\text{B}^-} \quad (31)$$

(c) Gopal and Rastogi⁸⁴ resolved the B -coefficient in N-methyl propionamide solutions assumin that $B_{\text{Et}_4\text{N}^+} = B_{\text{I}^-}$ at all temperatures.

(d) In dimethyl sulphoxide, the division of B -coefficients were carried out by Yao and Beunion⁹² assuming:

$$B_{[(i-\text{pc})_2\text{BuN}^+]} = B_{\text{Ph}_4\text{B}^-} = 1/2 B_{[(i-\text{pc})_2\text{BuNPh}_4\text{B}]} \quad (32)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate¹⁴⁵ solutions.

The methods, however, have been strongly criticized by Krumgalz.¹⁴⁶ 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

$\lambda_{+}^{\circ} = \lambda_{-}^{\circ}$ in all solvents at all temperatures. Thus, though $\lambda_{K^{+}}^{\circ} = \lambda_{Cl^{-}}^{\circ}$ 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 $(i\text{-pe})_3\text{BuN}^{+}$ or $(i\text{-Am})_3\text{BuN}^{+}$ 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.

Krumgalz¹⁴⁶⁻¹⁴⁸ 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^{149, 150} in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B -values for large tetraalkylammonium ions, R_4B^{+} (where $\text{R} > \text{Bu}$) in organic solvents are proportional to their ionic dimensions. So, we have:

$$B_{\text{R}_4\text{NX}} = a + br^3\text{R}_4\text{N}^{+} \quad (33)$$

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

The extrapolation of the plot of $B_{\text{R}_4\text{NX}}$ ($\text{R} > \text{Pr}$ 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:

$$B_{\text{R}_4\text{N}^{+}} - B_{\text{R}'_4\text{N}^{+}} = B_{\text{R}_4\text{NX}} - B_{\text{R}'_4\text{NX}} \quad (34)$$

$$B_{\text{R}_4\text{N}^{+}} / B_{\text{R}'_4\text{N}^{+}} = r_{\text{R}_4\text{N}^{+}}^3 / r_{\text{R}'_4\text{N}^{+}}^3 \quad (35)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data.¹⁵¹

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^+ (5.35 Å) and Ph_4B^-

(5.45 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers.¹²⁸ They proposed the equations:

$$B_{\text{Ph}_4\text{B}^-} / B_{\text{Bu}_4\text{N}^+} = r_{\text{Ph}_4\text{B}^-}^3 / r_{\text{Bu}_4\text{N}^+}^3 = (5.35/5.00)^3 \quad (36)$$

$$B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{Ph}_4\text{B}^-} \quad (37)$$

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

$$B_{[(i-\text{Am})_3\text{BuN}^+]} = B_{\text{Ph}_4\text{B}^-} = 1/2 B_{[(i-\text{Am})_3\text{BuNPh}_4\text{B}]} \quad (38)$$

Recently, Lawrence and Sacco¹³¹ used tetrabutylammonium tetra-butylborate (Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal van der Waals volume. Thus, we have:

$$B_{\text{Bu}_4\text{N}^+} / B_{\text{Bu}_4\text{B}^-} = V_{\text{W}(\text{Bu}_4\text{N}^+)} / V_{\text{W}(\text{Bu}_4\text{B}^-)} \quad (39)$$

$$\text{or. } B_{\text{Bu}_4\text{N}^+} = B_{\text{Bu}_4\text{NBBu}_4} / [1 + V_{\text{W}(\text{Bu}_4\text{B}^-)} / V_{\text{W}(\text{Bu}_4\text{N}^+)}] \quad (40)$$

Recently, Lawrence et al. made the viscosity measurements of tetraalkyl (from Pr to Hept.) ammonium bromides in DMSO and HMPT. The B -coefficients values were $B_{\text{R}_4\text{NBr}} = B_{\text{Br}^-} + a[f_x R_4\text{N}^+]$ plotted as functions of the van der Waals volumes. The B_{Br^-} values thus obtained were compared with the accurately determined B_{Br^-} value using Bu_4NBBu_4 and Ph_4NBPh_4 as reference salts. They concluded that the 'reference electrolyte' method is the best available method for division into ionic contributions.

The principle was extended to derive absolute single ion B -coefficients for alkali metals and halides in water.¹⁵²⁻¹⁵³ They also observed that $B_{\text{Cs}^+} = B_{\text{I}^-}$ suggested by Krumgalz¹⁴⁹

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.

2.5.3. Temperature dependence of B -ion Values

Regularity in the behaviors of B_{\pm} and dB_{\pm}/dT has been observed both in aqueous and non-aqueous solvents and useful generalizations 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:

$$(i) A \text{ and } dA/dT > 0 \quad (41)$$

$$(ii) B_{ion} < 0 \text{ and } dB_{ion}/dT > 0 \quad (42)$$

Characteristic of the structure breaking ions.

$$(iii) B_{ion} > 0 \text{ and } dB_{ion}/dT < 0 \quad (43)$$

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,¹⁵⁴ A, B, C Zones of Frank and Wen¹⁵⁵ and hydrated radius of Nightingale.¹⁴⁰

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:

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta(A\sqrt{c} + Bc) \quad (44)$$

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

$$\eta^E + \eta^A + \eta^D = \eta_0 BC \quad (45)$$

B -coefficient can thus be interpreted in terms of the competitive viscosity effects. Following Stokes, Mills and Krumgalz¹⁴⁷ we can write for B_{ion} as:

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{Sr} + B_{ion}^{Reinf} \quad (46)$$

where as according to Lawrence and Sacco:

$$B_{ion} = B_w + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \quad (47)$$

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}^{Sr} 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 centrosymmetrically 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 ion (B_{ion}^{Einst} or B_{Solv} positive). At ordinary temperature,

alignment of the solvent molecules around the inner layer also cause increase in

$B_{ion}^{Orient} (\eta^A)$, $B_{ion}^{Sr} (\eta^D)$ is small for these ions. Thus, B_{ion} will be large and positive as

$B_{ion}^{Einst} + B_{ion}^{Orient} > B_{ion}^{Sr}$. However, B_{ion}^{Orient} and B_{ion}^{Einst} 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}^{Sr} 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 $B_{ion}^{Einst} + B_{ion}^{Orient} < B_{ion}^{Sr}$ 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., $B_{lon}^{Einst} + B_{lon}^{Orient} = B_{lon}^{Str}$, so that B is close to zero.

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

The increase in temperature will have no effect on B_{lon}^{Orient} . But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in B_{lon}^{Str} . B_{lon}^{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_{lon}^{Orient} , and B_{lon}^{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 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 Gurney¹⁵⁴ 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 (\bar{S}_h^0) as:

$$\bar{S}_h^0 = \bar{S}_{aq}^0 - \bar{S}_g^0 \quad (48)$$

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 ($\bar{S}_{H^+}^0$) to $-5.5 \text{ cal Mol}^{-1}\text{.deg}^{-1}$. Asmus¹⁵⁶ used the entropy of hydration to correlate ionic B -values and Nightingale¹⁴⁰ 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.¹⁵⁷ to assign single ion B -coefficients so that a plot of ΔS_e^0 ,^{158, 159} the electrostatic entropy of solvation or $\Delta S_{I,H}^0$,^{158, 159} 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_f^0 and the single ion B -coefficients.

2.5.4. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's¹⁶⁰ approach as:

$$\eta = Ae^{E_{vis}/RT} = (hN/V)e^{\Delta G^*/RT} = (hN/V)e^{(\Delta H^*/RT - \Delta S^*/R)} \quad (49)$$

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 Benck¹⁶¹ 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:

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

$$\Delta E_{\eta(Soln)}^\ddagger = \Delta E_{\eta_0(Solv)}^\ddagger + \Delta E_V^\ddagger \quad (51)$$

ΔE_v^\ddagger 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.¹⁶² have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = (\bar{V}_1^0 - \bar{V}_2^0)/1000 + \bar{V}_1^0 (\Delta\mu_2^{0\ddagger} - \Delta\mu_1^{0\ddagger})/1000RT \quad (52)$$

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

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln \eta_1 \bar{V}_1^0 / hN \quad (53)$$

2.5.5. 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 Einstein¹⁴¹ leads to the equation:

$$\eta/\eta_0 = 1 + 2.5\phi \quad (54)$$

where, ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by

- (i) Sinha¹⁶³ 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 (54):

$$2.5\phi = A\sqrt{c} + Bc \quad (55)$$

Since $A\sqrt{c}$ term can be neglected in comparison with Bc and $\phi = c\bar{V}_1$, where \bar{V}_1 is

the partial molar volume of the ion, we get:

$$2.5\bar{V}_1 = B \quad (56)$$

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

$$B_{\pm} = 2.5\bar{V}_{\pm} = 2.5 \times 4/3(\pi R_{\pm}^3 N/1000) \quad (57)$$

assuming that the ions behave like rigid spheres with a effective radii, R_{\pm} moving in a continuum. R_{\pm} , calculated using the equation (57) 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:

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$$B_{\pm} = 2.5/1000(V_i + n_b V_s) \quad (58)$$

where V_i is the molar volume of the base ion and V_s , the molar volume of the solvent. The equation (58) has been used by a number of workers to study the nature of solvation and solvation number.

2.5.6. Viscosity Deviation

Viscosity of liquid mixtures can also provide information for the elucidation of the fundamental behaviors of liquid mixtures, aid in the correlation of mixture viscosities with those of pure components, and may provide a basis for the selection of physicochemical methods of analysis.^{164, 165} Quantitatively, as per the absolute reaction rates theory,¹⁶⁶ the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^j (x_i \eta_i) \quad (59)$$

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

2.5.7. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow, G^{*E} can be calculated as:¹⁶⁶

$$G^{*E} = RT[\ln\eta V - \sum_{i=1}^j x_i \ln\eta_i V_i] \quad (60)$$

2.6. 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.

2.6.1. 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,¹⁶⁷⁻¹⁷¹ measurements in non-aqueous⁶¹⁻⁶⁴ 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 solutesolvent and solute-solute interactions. The isentropic compressibility (K_S) of a solvent/solution can be calculated from the Laplace’s equation:¹⁷²

$$K_S = 1/(u^2 \rho) \quad (61)$$

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

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

$$\phi_K = MK_S/\rho_0 + 1000(K_S\rho_0 - K_S^0\rho) \cdot m\rho\rho_0 \quad (62)$$

K_s^0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute, \sqrt{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, m to zero concentration by a least-squares method:¹⁶⁸⁻¹⁷¹

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m} \quad (63)$$

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.^{173, 174} 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.^{62, 173}

The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved.¹⁷³ However, the poor fit of the solute molecules^{175, 176} 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-electrolyte¹⁷⁶ and non-aqueous non-electrolyte¹⁷⁴ solutions.

2.6.2. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility, ΔK_s can be calculated using the following equation:¹⁷⁹⁻¹⁸¹

$$\Delta K_s = K_s - \sum_{i=1}^j X_i K_{s,i} \quad (64)$$

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

2.6.3. Acoustical parameters

In an attempt to explore the nature of the interactions occurring between the component liquids in a mixture, various acoustic parameters such as intermolecular free length,¹⁸² L_f ; specific acoustic impedance,¹⁸³ Z ; Van der Waal's constant,¹⁸⁴ b ; molecular radius,¹⁸² r ; geometrical volume,¹⁸² B ; molar surface area,¹⁸⁴ Y ; available volume,¹⁸² V_a ; molar speed of sound,¹⁸⁵ R_s ; relative association,^{185, 186} R_A and molecular association,^{185, 186} M_A of the binary mixtures have been calculated using the following equations:

$$L_f = K \sqrt{K_S} \quad (65)$$

$$Z = u \rho \quad (66)$$

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

$$r = (3b / 16 \pi N_A)^{\frac{1}{3}} \quad (68)$$

$$Y = [36 \pi N_A B^2]^{\frac{1}{3}} \quad (69)$$

$$V_a = V (1 - u / u_\infty) \quad (70)$$

$$V_0 = V - V_a \quad (71)$$

$$R_s = \overline{M} u^{\frac{1}{3}} / \rho \quad (72)$$

$$R_A = (\rho_{\text{mix}} / \rho) (u / u_{\text{mix}})^{\frac{1}{3}} \quad (73)$$

$$M_A = [(76)^2 - 1] \quad (74)$$

where K is a temperature dependent constant,¹⁸² T is the absolute temperature, R is the universal gas constant, N_A is the Avogadro's number, \overline{M} is the average molecular weight, V_0 is the volume at absolute zero, ρ_{mix} and u_{mix} are the density and speed of sound of the mixture, respectively.

2.7. 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.^{187, 188} 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:¹⁸⁹

$$\eta = \exp\left[\sum_{i=1}^j (x_i \ln \eta_i) + d_{12} \prod_{i=1}^j x_i\right] \quad (75)$$

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 forces¹⁹⁰ between the mixing components in the mixtures while its positive values indicate the presence of specific interactions¹⁹⁰ between them.

b) Tamura-Kurata¹⁹¹ put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^j x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^j [x_i \phi_i]^{1/2} \quad (76)$$

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:¹⁹²

$$\eta = \sum_{i=1}^j x_i^2 \eta_i + 2H_{12} \prod_{i=1}^j x_i \quad (77)$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.¹⁹³ 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 Moore¹⁹⁰ in regard to the nature of parameter T_{12} and H_{12} .

d) McAllister's three-body model:¹⁹⁵

$$\begin{aligned} \ln v = & x_1^3 \ln v_1 + x_2^3 \ln v_2 + 3x_1^2 x_2 \ln v_{12} + 3x_2^3 x_1 \ln v_{21} - \ln \left[x_1 + \frac{x_2 M_2}{M_1} \right] \\ & + 3x_1^2 x_2 \ln \left[\frac{2}{3} + \frac{M_2}{3M_1} \right] + 3x_2^3 x_1 \ln \left[\frac{1}{3} + \frac{2M_2}{3M_1} \right] + x_2^3 \ln \left[\frac{M_2}{M_1} \right] \end{aligned} \quad (78)$$

e) McAllister's four-body model: ¹¹⁵

$$\begin{aligned} \ln v = & x_1^4 \ln v_1 + 4x_1^3 x_2 \ln v_{1112} + 6x_1^2 x_2^2 \ln v_{1122} + 4x_1 x_2^3 \ln v_{2221} + x_2^4 \ln v_2 \\ & - \ln \left[x_1 + x_2 \left(\frac{M_2}{M_1} \right) \right] + 4x_1^3 x_2 \ln \left[\frac{3}{4} + \frac{M_2}{4M_1} \right] + 6x_1^2 x_2^2 \ln \left[\frac{1}{2} + \frac{M_2}{2M_1} \right] \\ & + 4x_1 x_2^3 \ln \left[\frac{1}{3} + \frac{3M_2}{4M_1} \right] + x_2^4 \ln \left[\frac{M_2}{M_1} \right] \end{aligned} \quad (79)$$

f) Heric-Brewer model: ¹⁹⁶

$$v = x_1 v_1 + x_2 v_2 + x_1 x_2 \left\{ a + b(x_1 - x_2) + c(x_1 - x_2)^2 \right\} \quad (80)$$

where v_1 and v_2 are kinematic viscosities of the mixture, the pure component 1 and 2, respectively. v_{12} , v_{21} , v_{1112} , v_{1122} , v_{2221} , a , b and c are model parameters and X_i and M_i are the mole fraction and molecular weight of the i^{th} pure component in the mixture, respectively.

Moreover, The excess or deviation properties (V^E , $\Delta\eta$, G^E and ΔK_s) have been fitted to Redlich-Kister¹⁹⁴ polynomial equation using the method of least squares involving the Marquardt algorithm¹⁹⁷ and the binary coefficients, a_i were determined as follows:

$$Y^E = x_1 x_2 \sum_{i=1}^J a_i (x_1 - x_2)^i \quad (81)$$

where Y^E refers to an excess or deviation property 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,

$$\sigma = [(Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2 / (n - m)]^{1/2} \quad (82)$$

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

2.8. Conductance

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte of solutions.^{198, 199} 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. Recently developed experimental techniques provide an accuracy of $\pm 0.01\%$ 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.¹⁹⁸⁻²¹¹

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 Onsager²¹² 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:

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (83)$$

$$\text{where, } S = \alpha\Lambda_0 + \beta \quad (84)$$

$$\alpha = (ze)^2 \kappa / 3(2 + \sqrt{2})\epsilon_r kT\sqrt{c} = 82.406 \times 10^4 z^3 / (\epsilon_r T)^{3/2} \quad (85a)$$

$$\beta = z^2 e F \kappa / 3\pi\eta\sqrt{c} = 82.487 z^3 / \eta\sqrt{\epsilon_r T} \quad (85b)$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution.

However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss Onsager theory differed considerably²¹³ from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned.^{199, 214-216} The original Fuoss-Onsager equation was further modified by Fuoss and Hsia²¹⁷ 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:

$$\Lambda = \Lambda_0 - \alpha\Lambda_0\sqrt{c} / (1 + \kappa a)(1 + \kappa a / \sqrt{2}) - \beta\sqrt{c} / (1 + \kappa a) + G(\kappa a) \quad (86)$$

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt[3]{c} \quad (87)$$

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.^{199, 218, 219} Further correction of the equation (87) was made by Fuoss and Accascina.²⁰³

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

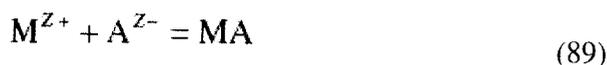
$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt[3]{c} - F\Lambda c \quad (88)$$

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.²²⁰

2.8.1. Ionic Association

The equation (83) 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_{exp}^0 is greater than Λ_{theo}^0 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 ($\Lambda_{\text{exp}}^0 < \Lambda_{\text{theo}}^0$) 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_{theo}^0 and Λ_{exp}^0 would be considerable with increasing association.²²¹

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



$$K_A = (1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 \quad (90)$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (91)$$

where γ_{\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 equation²²³ or Shedlovsky's equation:²²⁴

$$T(z)/\Lambda = 1/\Lambda_0 + K_A/\Lambda_0^2 c \gamma_{\pm}^2 \Lambda/T(z) \quad (92)$$

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

$$F(z) = 1 - z(1 - z(1 - \dots)^{-1/2})^{-1/2} \quad (93a)$$

$$\text{and } 1/T(z) \equiv S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (93b)$$

A plot of $T(z) / \Lambda$ against $c \gamma_{\pm}^2 A / T(z)$ 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 (92).

The Fuoss-Hsia²¹⁸ conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (94)$$

The equation was modified by Justice.²²⁵ The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c}) + E(\alpha c)\ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \quad (95)$$

$$(1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 = K_A \quad (96)$$

$$\ln \gamma_{\pm} = -k\sqrt{q} / (1 + kR\sqrt{\alpha c}) \quad (97)$$

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 (95) is a series expansion truncated at the $C^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much 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:²²⁶

$$K_A = (4\pi N_A a^3 / 3000) \exp(e^2 / a \epsilon kT) \quad (98)$$

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:²²⁷

$$K_A = 4\pi N_A a / 1000 \int_{r=a}^{r=q} r^2 \exp(z^2 e^2 / r \epsilon kT) dr \quad (99)$$

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.²²⁸

2.8.2. Ion size Parameter and Ionic Association

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

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec \ln c = \Lambda_0 + J_1c + J_2\sqrt[3]{c} = \Lambda_0 + J_1c \quad (100)$$

with J_2 term omitted.

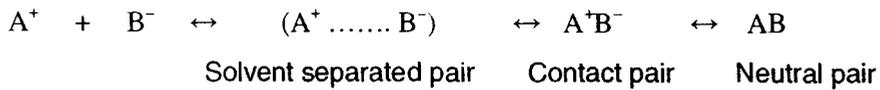
Thus, a plot of Λ_0 vs c gives a straight line with Λ_0 as intercept and J_1 as slope and 'a' values can be calculated from J_1 values. One of the reasons attributed to it is that ion-solvent interactions are not included in the continuum theory on which the conductance equations are based. The inclusion 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'²²⁹ but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J_1 .²³⁰

Fuoss²³¹ in 1978 proposed a new conductance equation. Later 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:



Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- = AB$

e.g., H_3O^+ and CH_3COO^- . Let γ be the fraction of solute present as unpaired ($r > R$) ions.

If $c\gamma$ is the concentration of unpaired ion and α is the fraction of paired ions ($r \leq R$), then the concentration of the solvent separated pair is $c(1-\alpha)(1-\gamma)$ and that of contact pair is $\alpha c(1-\gamma)$.

The equation constants for (93) are:

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 f^2 \tag{101}$$

$$K_S = \alpha/(1-\alpha) = \exp(-E_s/kT) = e^{-\epsilon} \tag{102}$$

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 shortrange ion-solvent and ion-ion interactions by which contact pairs form and dissociate. E_s is the difference in energy between a pair in the states ($r = R$) and ($r = a$); ϵ is E_s measured in units of kT .

Now, $(1-\alpha) = 1/(1+K_S)$ (103)

And the conductometric pairing constant is given by:

$$K_A = (1-\alpha)/c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \tag{104}$$

The equation determines the concentration, $c\gamma$, of active ions that produce longrange interionic effects by unpaired ions, their interaction with unpaired ions is, therefore, neglected in calculating long-range effects (activity coefficients, relaxation field ΔX and electrophoresis ΔA_e). The various patterns can be reproduced by theoretical fractions in the form:

$$\Lambda = p[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e] = p[\Lambda_0(1+R_x) + E_L] \tag{105}$$

which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_0, R, E_s)$ and $\Delta\Lambda/X$ (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:

$$p = 1 - \alpha(1 - \gamma) \quad (106)$$

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

$$\Lambda = \gamma[\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e] \quad (107)$$

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

$$K_A = (1 - \gamma)/c\gamma^2 f^2 \approx K_R K_S \quad (108)$$

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

$$\gamma = 1 - K_R c \gamma^2 f^2 / (1 - \alpha) \quad (109)$$

$$K_R = (4\pi N_A R^3 / 3000) \exp(\beta/R) \quad (110)$$

$$-\ln f = \beta_\kappa / 2(1 + \kappa R), \quad \beta = e^2 / \epsilon kT \quad (111)$$

$$\kappa^2 = 8\pi\beta\gamma n = \pi\beta N_A \gamma c / 125 \quad (112)$$

$$-\epsilon = \ln[\alpha/(1 - \alpha)] \quad (113)$$

The details of the calculations are presented in the 1978 paper.²³¹ 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).

2.8.3. 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 surrounding 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:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \quad (114)$$

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., and

$$\lambda_+^0 = t_+ \Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_- \Lambda_0 \quad (115)$$

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.²³² However, accurate transference number determinations are limited to few solvents only. Spiro²³³ and Krumgalz²³⁴ 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 Krumgalz²³⁴ and some important points are mentioned below:

(i) Walden equation,²³⁵ $(\lambda_{\pm}^0)_{\text{water}}^{25} \cdot \eta_{0, \text{water}} = (\lambda_{\pm}^0)_{\text{acetone}}^{25} \cdot \eta_{0, \text{acetone}}$ (116)

(ii)

$$\left. \begin{array}{l} \lambda_{\text{pic}^-}^0 \eta_0 = 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^0 \eta_0 = 0.296 \end{array} \right|_{\text{based on } \Lambda_{\text{Et}_4\text{N}^+\text{pic}^-}^0 = 0.563}^{231, 232} \quad (117)$$

Walden considered the products to be independent of temperature and solvent. However the $\lambda_{\text{Et}_4\text{N}_{\text{pic}}}^0$ 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.

$$(iii) \quad \lambda_{25}^0(\text{Bu}_4\text{N}^+) = \lambda_{25}^0(\text{Ph}_4\text{B}^-)^{232} \quad (118)$$

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

$$(iv) \quad \lambda_{25}^0(\text{Bu}_4\text{N}^+) = \lambda_{25}^0(\text{Bu}_4\text{B}^-)^{233} \quad (119)$$

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 Gill²³⁸ is:

$$\lambda_{25}^0(\text{R}_4\text{N}^+) = zF^2 / 6\pi N_A \eta_0 [r_i - (0.0103 \epsilon_0 + r_y)] \quad (120)$$

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.

In a paper,^{234(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.

$$(vi) \quad \lambda_{25}^0[(i - \text{Am})_3\text{BuN}^+] = \lambda_{25}^0(\text{Ph}_4\text{B}^-)^{235} \quad (121)$$

It has been found from transference number measurements that the $\lambda_{25}^0[(i - \text{Am})_3\text{BuN}^+]$

and $\lambda_{25}^0(\text{Ph}_4\text{B}^-)$ values differ from one another by 1%.

$$(vii) \quad \lambda_{25}^0(\text{Ph}_4\text{B}^-) = 1.01\lambda_{25}^0(i - \text{Am}_4\text{B}^-)^{2.36} \quad (122)$$

The value is found to be true for various organic solvents. Krumgalz²³⁴ 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:

$$r_s = \left| z \right| F^2 / A \pi \eta_0 \lambda_{\pm}^0 \quad (123)$$

where A is a coefficient varying from 4 (in the case of perfect sticking) to 6 (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:

$$\lambda_{\pm}^0 \eta_0 = \text{constant} \quad (124)$$

This relation has been verified using λ_{\pm}^0 values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^-$, Ph_4As^+ and Ph_4B^- ions and for tetraalkylammonium cations starting with Et_4N^+ . The relationship can be well utilized to determine λ_{\pm}^0 of ions in other organic solvents from the determined Λ_0 values.

2.8.4. Solvation Number

If the limiting conductance of the ion i of charge z 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:

$$V_s = (4\pi/3)(r_s^3 - r_c^3) \quad (125)$$

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

$$n_s = V_s / V_0 \quad (126)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects²⁴¹ from

$$V_s^0 = 4.35r_s^3 \quad (127)$$

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 equations²⁰⁴ and theoretical corrections²⁴²⁻²⁴⁵ have been suggested to make the general method.

2.8.5. 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:

$$\lambda_i^0 = |z_i e| \hat{e} F / 6\pi\eta_0 R_i = 0.819|z_i| / \eta_0 R_i \quad (128)$$

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:

$$\lambda_i^0 \eta_0 = 0.819|z_i| / R_i = \text{constant} \quad (129)$$

This is known as Walden's rule.²⁴⁶ 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,²⁰⁴ Nightingale¹⁴⁰ and others²⁴⁷⁻²⁴⁹ have suggested a method of correcting the radii. 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 viscosity²⁵⁰ was invoked without much success^{251, 252} but it has been found that:

$$\lambda_i^0 \eta^p = \text{constant} \quad (130)$$

where p is usually 0.7 for alkali metal or halide ions and p = 1 for the large ions.^{253, 254}

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 Fuoss²⁵⁵ 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:

$$\lambda_{i,0}^0 = F e |z_i| / 6\pi R_\infty (1 + A/\epsilon R_\infty^2) \quad (131)$$

$$\text{or, } R_i = R_\infty + A/\epsilon \quad (132)$$

where R_∞ 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.

Boyd²⁴³ gave the expression:

$$\lambda_i^0 = F e |z_i| / 6\pi \eta_0 r_i [1 + (2/27 \pi \eta_0 \cdot Z_i^2 e^2 \tau / r_i^4 \epsilon_0)] \quad (133)$$

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

Zwanzig²⁴⁴ treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda_i^0 = z_i^2 e F / \{A_V \pi \eta_0 r_i + A_D [z_i^2 e^2 (\epsilon_r^0 - \epsilon_r^\infty) \tau / \epsilon_r^0 (2\epsilon_r^0 + 1) r_i^3]\} \quad (134)$$

$\epsilon_r^0, \epsilon_r^\infty$ 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's²⁴² and Zwanzig's²⁴⁴ equations are very similar and both may be written in the form:

$$\lambda_i^0 = A r_i^3 / (r_i^4 + B) \quad (135)$$

The theory predicts²⁵⁶ that λ_i^0 pass through a maximum of $27^{1/4} A / 4 B^{1/4}$ 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 (129) can be rearranged as:²⁵⁷

$$z_i^2 e F / \lambda_i^0 \eta_0 = A_V \pi r_i + A_D z_i^2 / r_i^3 \cdot e^2 (\epsilon_r^0 - \epsilon_r^\infty) / \epsilon_r^0 (2\epsilon_r^0 + 1) \cdot \tau / \eta_0 \quad (136)$$

$$\text{or, } L^* = A_V \pi r_i + A_D z_i^2 / r_i^3 P^* \quad (137)$$

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.²⁵⁶⁻²⁷¹ 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.²³²

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,²⁵⁷ 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.²⁵⁸

(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.²⁵⁷

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 + water²⁵⁶⁻²⁶⁶ 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^{243, 244, 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,²⁷² 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 Onsager²⁷³ 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, improvements²⁷⁴⁻²⁷⁶ 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.

2.9. Solvation Models- Some Recent Trends

The advantage of models like SM 1- SM 5 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.^{282, 283} 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.²⁸³ of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

2.10. Conductance- Some Recent Trends

Recently Blum, Turq and coworkers^{284, 285} 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. 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^{286,287} 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.

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CHAPTER III

3.1. Source and Purification of the Chemicals used:

3.1.1. Solvents:

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.^{1,2} 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.

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.^{2, 3} Finally, it was distilled from sodium. The pure liquid had a boiling point of 375 K/760 mm, density of 1026.5 kg.m^{-3} and a coefficient of viscosity of 1.196 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.

Tetrahydrofuran (Merck, India) was kept for several days over KOH, refluxed for 24 h, and distilled over $LiAlH_4$.^{2,5} The boiling point (66°C), density (0.8807 g/cm^3), and viscosity ($\eta_0 = 0.4630 \text{ mPa s}$) at 298.15 K. The specific conductance of THF was $\approx 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 28.15 K. The purity of the solvent finally obtained was $>99.0 \%$.

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 (PrOH, C_3H_7 , M.W.60), 1-butanol (1-BuOH, C_4H_9OH C_4H_9OH , M.W. 74.12), Pentanol (PenOH, $C_5H_{11}OH$, M.W. 88), (Merck, India, Urasol grade) were dried over 4\AA molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled.

2-methoxy- and 2-ethoxy- ethanol (S. D. Fine Chemicals, AR, India) were purified as described in the literature.⁶

Benzene (S. D. Fine Chemicals, purity > 99%) was purified by means of a simple distillation technique with the first and last 20% of the distillate being discarded and finally the density and viscosity value compared with the literature.⁷

Extrapure grade formamide, 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane, and dimethylsulfoxide procured from S.d.fine-Chem Limited, Mumbai, India. 2-Methoxyethanol was dried with potassium carbonate and distilled twice in an all-glass distillation set immediately before use, and the middle fraction was collected.⁸ Acetophenone was dried over anhydrous potassium carbonate for 3 days, filtered, and then distilled. The middle fraction of the distillates was retained.⁶ Acetonitrile was distilled from P₂O₅ and then from CaH₂ in an all-glass distillation apparatus.⁹ The middle fraction was collected. 1,2-Dimethoxyethane was purified by double-fractional distillation over LiAlH₄ to eliminate traces of acids, peroxides, and water, and the middle portion was collected for the preparation of mixtures.¹⁰ Formamide and dimethylsulfoxide were purified according to the standard procedures.^{2,11} All solvents were stored over 3 Å molecular sieves for 3 days before use. The purity of the purified liquids was ascertained by GLC and also by comparing experimental values of densities, viscosities, and ultrasonic speeds of sound with their literature values.^{2, 8-13}

Water was first deionized and then distilled in an all glass distilling set along with alkaline KMnO₄ solution to remove any organic matter⁸ therein. The doubly distilled water was finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO₂ 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.²⁻¹⁴ and are listed in the respective chapters. The purity of most of the solvents finally obtained was better than 99.5 %.

3.1.2. Mixed solvents:

The mixed solvents containing 10, 20, 30 mass % of formamide + H₂O mixtures and 10, 20, 30 mass % of 1,3-dioxolane + H₂O mixtures were prepared accurately by mixing the requisite volume of the respective cyclic ethers and H₂O 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 formamide with 2 Methoxyethanol, Acetophenone, Acetonitrile, 1,2-Dimethoxyethane, and N,N-dimethylformamide +benzene, 1,3-dioxolane, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, di-isopropylether, diethylether, 2-methoxyethanol and 2-ethoxyethanol 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. tetrapentylammonium chloride (Pen₄NCl), tetrahexylammonium chloride (Hex₄NCl), tetraheptylammonium chloride (Hp₄NCl) and tetraoctylammonium chloride (Oct₄NCl), tetrabutylammonium bromide (Bu₄NBr), tetrapentylammonium bromide (Pen₄NBr), tetrahexylammonium bromide (Hex₄NBr) and tetraheptylammonium bromide (Hp₄NBr) were of Fluka's purum or puriss grade 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 crystallised salts were dried in vacuum. The salts were stored in glass bottles in darkened desiccator over fused CaCl₂.^{15, 16}

Ammonium thiocyanate, Sodium thiocyanate and Potassium thiocyanate (NH₄CNS, NaCNS and KCNS) salts (all A.R., B.D. H.) were purified by recrystallization twice from conductivity water. The samples were dried in vacuum and stored over P₂O₅ under vacuum.

The amino acids glycine (Analar, BDH, Purity>99%), DL-alanine (S.D. Fine Chemicals, India, Purity > 98.5%), L-valine (Loba Chemie, India, Purity > 99%), and L-leucine (Thomas Baker, India, Purity>98%) were were recrystallised from methanol-water mixture and dried at 373.15 K for 12 h in an infrared drier and then in vacuo over P₂O₅ at

room temperature. 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 cm³ 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.^{17,18} 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.

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.¹⁹ 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.^{3, 20-23}

3.2.2. Measurement of Viscosity:

The kinematics viscosities were measured by means of a suspended-level Ubbelohde²⁴ 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 ± 0.1 s. 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 were measured a number of times and the average of the readings was taken into account. The kinematics viscosity (ν) and the absolute viscosity (η) are given by the following equations.

$$\nu = Kt - Lt \quad (1)$$

$$\eta = \nu \rho \quad (2)$$

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:

$$\eta_r = \eta/\eta_0 = \rho t/\rho_0 t_0 \quad (3)$$

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 $\pm 2 \times 10^{-4}$ mPa.s.

3.2.3. Measurement of Ultrasonic Speed:

Ultrasonic speeds were measured, with an accuracy of 0.3 %, using a single crystal variable-path ultrasonic interferometer²⁵ (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.

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:

$$u = \lambda \times f \quad (4)$$

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.

$$d = n \times \lambda / 2 \quad (5)$$

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

$$K_S = 1/u^2 \rho \quad (6)$$

where ρ is the density of the experimental liquid.

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 $1.0 \pm 10\% \text{ cm}^{-1}$. The instrument was standardized using 0.1 (M) KCl solution. The cell was calibrated by the method of Lind and co-workers.²⁶ The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of $\pm 0.01 \text{ K}$.

Several solutions were prepared by mass accurate to $\pm 0.01 \text{ mg}$ 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.

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CHAPTER IV

Viscous Synergy, Excess Molar volumes, Viscosity Deviations and Isentropic Compressibility of some Primary Monoalkanols in Aqueous N, N-dimethylformamide Mixtures.

Keywords: Viscous synergy; viscosity deviations; excess molar volumes; isentropic compressibility; molecular interactions; interstitial accommodation.

4.1. Introduction

The increasing use of N,N-dimethylformamide as a versatile solvent in the separation of saturated and unsaturated hydrocarbons, as solvents for vinyl resins, polyacrylic fibres and catalyst in carbonylation reaction as well as in organic synthesis enhance the importance to obtain information on its behavior when mixed with other solvents. On the other hand monoalkanols are useful solvents in paint, varnishes and fuel industries. So we need to require extensive information on the various properties when these monoalkanols are taken with DMF as mixed solvent systems.¹⁻⁷

The determination of density, viscosity and speeds of sound is a valuable tool to learn about the liquid state^{8, 9} because of the close connection between liquid structure and macroscopic properties.

Viscosity and density of these ternary liquid mixtures are used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications.^{10,11} In our systematic investigation of the properties, we have reported viscosities, densities and speeds of sound of different solvents and their mixtures in previous papers¹²⁻¹⁸ from our laboratory. The present work contributes and extends our study of density (ρ), viscosity deviations ($\Delta\eta$), viscous syne

rgy, excess molar volumes (V^E) and isentropic compressibility (K_s^E) to the aqueous mixtures of N,N-dimethylformamide (DMF) with some monoalkanols; where water is represented as A; amide (DMF) represented as B; and monoalkanol represented as C. 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 these ternaries.

4.2. Experimental Section

4.2.1. Source and purity of samples

DMF (N,N-dimethylformamide, C_3H_7NO , FW=73.10) is obtained from Merck and LR, further purified by standard methods.¹⁹ The source and purification of pure alcohols (Merck, India) methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 1-butanol (1-BuOH), and 1-pentanol (1-PentOH) have been described earlier.¹⁹⁻²⁵ Triply distilled water was used for the experimental purpose. The purity of the liquids was ascertained by GLC and also by comparing experimental values of densities, viscosities and sound velocities with those reported in the literature^{23, 26-31} as listed in Table 1. The purity of the solvents finally obtained were >99%.

4.2.2. Apparatus and Procedure

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15, 308.15 and 318.15 K with triply distilled water and DMF. The measurements were done in a thermostated water bath controlled to ± 0.01 K.⁶ The weighings were done on a Mettler electronic balance (AG-285) with a precision of ± 0.01 mg. The viscosities (η) were measured by means of a suspended Ubbelohde type viscometer⁷ which was calibrated at the desired temperature with triply distilled water and purified methanol using density and viscosity values from the literature. The ultrasonic speeds (u) were determined using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz,³² which was calibrated with water, methanol and benzene and the temperature stability was maintained within ± 0.01 K by circulating thermostatic water around the cell with a circulating pump. The

solutions were prepared by mixing known volumes of pure liquids in airtight-stopper bottles at 298.15 K. The precisions of the speed of sound, density and viscosity measurements are $\pm 0.2 \text{ m s}^{-1}$, $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$ and $\pm 2 \times 10^{-4} \text{ m Pa s}$, respectively.

4.3. Results and discussion

The measured density (ρ), viscosity (η) and the speeds of sound (u) data for mixtures of water (A), DMF (B), and the monoalkanols (C), i.e., methanol, ethanol, propanol, butanol, pentanol, were used to calculate the excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) and excess isentropic compressibilities (K_s^E).

The method most widely used to analyze the antagonistic and synergistic behavior of various solvent mixtures studied is that developed by Kalentune-Gencer and Peleg,³³ allowing the quantification of the antagonistic and synergistic 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. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is considered as lack of interaction.³⁴ The method compares the viscosity of the system determined experimentally, η_{exp} with the viscosity expected in the absence of interaction, η_{calcd} , defined as,³⁵

$$\eta_{\text{calcd}} = \sum_{i=1}^{n=3} W_i \eta_i \quad (1)$$

Where, W_i and η_i are the fraction by weight and the viscosity measured experimentally, of the pure components respectively.

Viscous synergy exists when, $\eta_{\text{exp}} > \eta_{\text{calcd}}$. This procedure is used when Newtonian fluids are involved.³⁵ Quantitatively, as per the absolute reaction rates theory,³⁶ the deviations of viscosities from the ideal mixture values can be calculated as

$$\Delta\eta = \eta - \sum_{i=1}^{n=3} X_i \eta_i \quad (2)$$

where, η is the viscosity of the mixture and X_i , η_i are the mole fraction and viscosity of the pure components respectively.

In order to secure more comparable viscous synergy results, the so called synergy index (I_s), introduced by Howell³⁵ is taken into account

$$I_s = (\eta_{exp} - \eta_{calcd}) / \eta_{calcd} \quad (3)$$

The increase in density was analyzed by carrying out the following equation analogous to that used for viscosity of mixture.

$$\rho_{mix} = \sum_{i=1}^{n=3} W_i \rho_i \quad (4)$$

Where, W_i and ρ_i are the fractions by weight and densities measured experimentally of the pure components respectably. Accordingly, when $\rho_{exp} > \rho_{mix}$, volume contraction occurs. The excess molar volumes, V^E are calculated from density data according to the following equation:³⁷

$$V^E = \sum_{i=1}^{n=3} X_i M_i (1/\rho - 1/\rho_i) \quad (5)$$

Where, M_i , ρ_i and ρ are the molar mass, density of the pure components and density of the mixture respectively.

Table 4 contains the sound velocity (u), isentropic compressibility (K_s) and excess isentropic compressibility (K_s^E) data for the mixtures observed and calculated using the following equation [38]:

$$K_s = (u^2 \rho_{exp})^{-1} \quad (6)$$

$$K_s^E = K_s - \sum_{i=1}^{n=3} X_i K_{s,i} \quad (7)$$

where, $K_{s,i}$ gives the isentropic compressibility for the the pure components of the mixture.

In Fig.1, $\Delta\eta$ values for the ternary mixtures (A) + (B) + MeOH, EtOH, 1-PrOH, 1-BuOH, and 1-PentOH (C) have been plotted against the mole fraction of water (X_A) at 298.15 K. It is observed that $\Delta\eta$ values increases to attain a maximum and then decreases as the mole fraction of water increases. Similar curves are obtained at 308.15 and 318.15 K. This trend is observed for all the ternary mixtures examined here. The values become less positive as the temperature rises from 298.15 to 318.15 K. However, the mixtures have maximum, $\Delta\eta$ at $X_A=0.70$ for all the temperatures indicating strong specific interaction between the unlike molecules. The estimated uncertainty for, $\Delta\eta$ is ± 0.0004 poise.

Here, dispersion and dipolar interactions are operating between water, N,N-dimethylformamide and MeOH/ EtOH/ 1-PrOH/1-BuOH/ 1-PentOH molecules resulting in negative $\Delta\eta$ but with the increase in temperature and mole fraction of water (X_A), the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive $\Delta\eta$.³⁹

In Fig. 2, synergy index (I_S) values for the ternary mixtures (A) + (B) + MeOH, EtOH, 1-PrOH, 1-BuOH, and 1-PentOH (C) have been plotted against the mole fraction of water (X_A) at 298.15 K. It is found that each mixture has a maximum at $X_A =0.7$ and then it decreases as X_A increases. Furthermore, the magnitude falls as the temperature rises from 298.15 to 318.15 K. The estimated uncertainty for I_S is ± 0.002 . This may be attributed to the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture-producing an increasing in size of the resulting molecular package, which legally implies rise in viscosity. After reaching the maximum viscosity, it decreases on subsequent addition of more water, as the latter tends to approach the viscosity of water.

Such characteristics in the viscosity versus composition curve is a manifestation of specific interaction³¹ between the unlike molecules, predominated by hydrogen bonding interaction. It can be concluded that the affinity of monoalkanols molecules towards N,N-dimethylformamide (DMF) molecules in the presence of water is enhanced by the following order,



Similar results were also reported earlier.^{25,30,40,41}

In Fig. 3 $\Delta\rho$ versus mole fraction of water (X_A) behavior similar to the previous figure thus reflecting the relation between viscous synergy and volume contraction.⁶ This fact can be explained in terms of electrostriction as a consequence of solvent molecules is accommodated in the void space left in the packing of dispersed solvent molecules. Similar results were reported by some authors earlier.^{30, 40-42}

Fig. 4 represents the V^E values for the five ternary mixtures under examination. In general, V^E is found to be negative throughout all the temperatures for all the ternary mixtures. However, the values at first decreases to minima and then it increase with increasing X_A . V^E decreases systematically from 298.15 to 318.15K over the whole range of mole fractions. The five ternary mixtures shows the minima at the same point i.e. at $X_A = 0.5$. The estimated uncertainty for V^E is $\pm 0.5 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$. The trend is:



The negative V^E indicates the presence of strong molecular interaction between the components of the mixture. Several effects contribute to the value of V^E , such as:⁴³ dipolar interaction, interstitial accommodation and possible hydrogen bonded interactions between unlike molecules. The actual volume change would, therefore, depend 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 monoalkanols. Consequently, MeOH having the highest polarity achieves the most favorable intermolecular H-bonded interactions with water and DMF. Moreover, its simple structure and smaller size leads to interstitial accommodation with others molecules more easily compared to the higher monoalkanols that have greater structural complexity. Similar results have been reported earlier.^{23, 44, 45}

Fig. 5 predicts the curves for the ternary mixtures of K_s^E . The values decreases to attain a minima and then increases as the mole fraction of water increases and they also increase as the length of the molecular chain of the monoalkanols increases. However, the values

attend a minima at $X_A = 0.7$ and thereafter increases for every mixture. The estimated uncertainty for K_s^E is $\pm 0.2 \text{ Pa}^{-1}$. The K_s^E values follow the sequence:



The results can be qualitatively explained in terms (i) molecular interactions (ii) structural effects and (iii) geometrical fitting of component molecules into each other structure. Negative deviation in isentropic compressibility is an indication of strong interactions such as formation of hydrogen bonds, charge transfer complexes or strong dipole-dipole interactions between the component molecules. The more easily the molecules fit into each others structure, K_s^E values become more and more negative. Similar results have been reported by some authors earlier.^{25, 29, 41, 46, 47}

4.4. Conclusion

After a thorough study of the behavior of monoalkanols on aqueous DMF we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about synergy. The lower monoalkanols are found to associate more with others molecules whereas self-association between the alcohol molecules was found to increase with increasing chain length.

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Table 1. Comparison of experimental (I) densities (ρ), viscosities (η), and ultrasonic speeds (u) of pure liquids with literature values (II).

T (K)	$\rho \times 10^{-3}$ kg m ⁻³		η m Pa s		u m s ⁻¹	
	I	II	I	II	I	II
Water						
298.15	0.99707	0.9970 ²⁶	0.8903	0.8904 ²⁶	1496.2	1497.4 ²⁷
308.15	0.99406	0.9940 ²⁶	0.7194	0.7194 ²⁶		
318.15	0.99025	0.9902 ²⁶	0.5960	0.5960 ²⁶		
N,N-dimethylformamide						
298.15	0.9460	0.9461 ²³	0.8586	0.8586 ²³	1465.2	1465.0 ²³
308.15	0.9399	0.9399 ²³	0.7763	0.7763 ²³		
318.15	0.9316	0.9316 ²³	0.7125	0.7120 ²³		
Methanol						
298.15	0.78659	0.7866 ²⁶	0.5446	0.54230 ²⁶	1108.2	1105 ²⁶
308.15	0.77728	0.7772 ²⁶	0.4747	0.47424 ²⁶		
318.15	0.76774	0.7677 ²⁶	0.4185	0.41739 ²⁶		
Ethanol						
298.15	0.78508	0.7849 ²⁹	1.088	1.0830 ²⁹	1144.3	1144.9 ²⁶
308.15	0.77809	0.7764 ²⁹	0.897	0.8930 ²⁹		
318.15	0.76391	0.7678 ²⁹	0.767	0.76304 ²⁹		
Propanol						
298.15	0.8025	0.8025 ³⁰	1.946	1.95 ²⁸	1206.5	1207 ²⁶
308.15	0.79141	0.7915 ²⁸	1.564	1.40 ²⁸		
318.15	0.7834	0.7832 ²⁸	1.178	1.10 ²⁸		
Butanol						
298.15	0.8056	0.8057 ²⁹	2.566	2.57 ²⁹	1240.2	1240 ²⁶
308.15	0.798	0.7982 ²⁹	1.998	1.981 ²⁹		
318.15	0.7905	----	1.55	----		
Pentanol						
298.15	0.8104	0.8112 ³¹	3.510	3.5104 ³¹	1277.2	1277 ³¹
308.15	0.8029	----	2.582	----		
318.15	0.78508	----	2.106	----		

Table 2. Viscosity deviations ($\Delta\eta$) and synergic index (I_S) of water (A) + N,N-dimethylformamide (B) + methanol, ethanol, propanol, butanol and pentanol (C) at 298.15, 308.15 and 318.15 K.

X_A	X_B	T (K)					
		298.15		308.15		318.15	
		$\Delta\eta$, mPa s	I_S	$\Delta\eta$, mPa s	I_S	$\Delta\eta$, mPa s	I_S
water (A)+ N,N-dimethylformamide (B)+ methanol (C)							
0.00000	0.30447	-0.12100	-0.25997	-0.14800	-0.33089	-0.02300	-0.14233
0.21555	0.23917	0.17900	0.21188	0.15600	0.19009	0.14900	0.18912
0.38205	0.18815	0.79000	1.06366	0.46800	0.69636	0.35600	0.57038
0.51453	0.14781	1.28100	1.70355	0.66700	1.00741	0.49400	0.82248
0.62245	0.11495	1.53500	1.99946	0.75800	1.14111	0.56000	0.94354
0.71206	0.08767	1.57700	2.00925	0.76900	1.14794	0.55800	0.94346
0.78766	0.06465	1.45400	1.81179	0.69400	1.02531	0.50283	0.85021
0.85230	0.04497	1.18400	1.44368	0.57500	0.83994	0.41000	0.69209
0.90819	0.02795	0.84300	1.00604	0.38200	0.55200	0.28000	0.47130
0.95700	0.01309	0.43200	0.50501	0.21000	0.29974	0.15500	0.26017
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ ethanol(C)							
0.00000	0.38623	-0.38600	-0.36977	-0.33700	-0.38638	-0.14800	-0.19169
0.25847	0.28640	0.16800	0.18053	0.12900	0.14620	0.10300	0.11693
0.43954	0.21646	0.89600	0.93107	0.50000	0.58978	0.33200	0.42340
0.57346	0.16474	1.34200	1.40280	0.68800	0.82572	0.46500	0.61487
0.67652	0.12494	1.48800	1.56734	0.74200	0.90411	0.49700	0.67315
0.75828	0.09336	1.45400	1.54413	0.70000	0.86506	0.47100	0.65187
0.82473	0.06769	1.26600	1.35556	0.61800	0.77523	0.40000	0.56432
0.87980	0.04642	1.01400	1.09501	0.44600	0.56531	0.30600	0.43950
0.92619	0.02851	0.67769	0.73778	0.32300	0.41626	0.21300	0.31263
0.96579	0.01321	0.38500	0.42333	0.14799	0.19251	0.09000	0.13230
1.00000	0.00000	-0.00000	-0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ propanol (C)							
0.00000	0.45079	-0.70500	-0.46459	-0.55592	-0.44196	-0.28400	-0.27621
0.28918	0.32043	0.06983	0.00816	0.11800	0.05358	0.09000	0.04417
0.47790	0.23536	0.90000	0.60441	0.48100	0.34812	0.34200	0.29347
0.61077	0.17546	1.30000	0.93034	0.64500	0.50246	0.44500	0.41093
0.70938	0.13101	1.41200	1.05982	0.65400	0.53120	0.47100	0.45882
0.78547	0.09671	1.32000	1.03402	0.58100	0.48756	0.42600	0.42980
0.84597	0.06944	1.12100	0.91615	0.47000	0.40580	0.35200	0.36649
0.89521	0.04724	0.87700	0.74971	0.35500	0.31718	0.26500	0.28429
0.93608	0.02881	0.59400	0.53160	0.23900	0.22252	0.16800	0.18313
0.97055	0.01328	0.32481	0.30828	0.11800	0.11425	0.07700	0.08406

Viscous Synergy.....of some Pr. Monoalkanols in Aqueous DMF Mixtures.

1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water(A)+ N,N-dimethylformamide (B)+ butanol (C)							
0.00000	0.50306	-0.96600	-0.56720	-0.77500	-0.56139	-0.47569	-0.42277
0.31224	0.34598	0.03300	-0.08897	0.07100	-0.05551	0.06000	-0.05137
0.50532	0.24886	0.87200	0.39955	0.46000	0.20284	0.31500	0.14676
0.63651	0.18286	1.23500	0.65259	0.58600	0.30328	0.40400	0.22969
0.73147	0.13509	1.27800	0.72579	0.58100	0.32022	0.41000	0.25284
0.80338	0.09891	1.17200	0.70821	0.50700	0.28832	0.36700	0.23634
0.85973	0.07057	0.97800	0.62650	0.40000	0.22914	0.29000	0.18593
0.90507	0.04776	0.74900	0.51009	0.29700	0.17365	0.22400	0.15067
0.94234	0.02901	0.47900	0.34292	0.18100	0.10052	0.14600	0.09909
0.97353	0.01332	0.24400	0.18860	0.09200	0.05445	0.07500	0.05477
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+N,N-dimethylformamide (B)+ pentanol (C)							
0.00000	0.54624	-1.28500	-0.64442	-0.94265	-0.61112	-0.62200	-0.48710
0.33019	0.36588	-0.27000	-0.31630	-0.02100	-0.18814	0.03700	-0.14562
0.52588	0.25898	0.61000	0.06762	0.37600	0.01590	0.29800	0.00194
0.65534	0.18827	0.99000	0.27167	0.51100	0.10148	0.37800	0.05733
0.74734	0.13802	1.06000	0.34775	0.50700	0.11777	0.36400	0.06019
0.81607	0.10047	0.98000	0.35678	0.44900	0.10865	0.31000	0.04100
0.86937	0.07136	0.79000	0.30217	0.35300	0.07574	0.24700	0.02119
0.91191	0.04812	0.62000	0.26202	0.26000	0.04890	0.17200	-0.00716
0.94666	0.02914	0.40000	0.17726	0.15600	0.01184	0.11800	-0.00620
0.97557	0.01335	0.20000	0.09730	0.07100	-0.00437	0.04900	-0.02071
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table 3. Density deviation ($\Delta\rho$) and excess molar volumes (V^E) of water (A) + N,N-dimethylformamide (B) + methanol, ethanol, propanol, butanol and pentanol (C) at 298.15, 308.15 and 318.15 K.

X_A	X_B	T (K)					
		298.15		308.15		318.15	
		$\Delta\rho \times 10^{-3}$ kg m ⁻³	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\rho \times 10^{-3}$ kg m ⁻³	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\rho \times 10^{-3}$ kg m ⁻³	$V^E \times 10^6$ m ³ mol ⁻¹
water (A)+ N,N-dimethylformamide (B)+ methanol (C)							
0.00000	0.30447	-0.00450	-0.17119	-0.00048	-0.44018	-0.00012	-0.48428
0.21555	0.23917	0.00626	-0.73502	0.00662	-0.78618	0.00799	-0.88910
0.38205	0.18815	0.01399	-0.98792	0.01248	-0.96290	0.01333	-1.03718
0.51453	0.14781	0.01855	-1.03907	0.01756	-1.04015	0.01703	-1.05790
0.62245	0.11495	0.02015	-0.96488	0.01949	-0.97701	0.01903	-0.99603
0.71206	0.08767	0.02043	-0.85295	0.01991	-0.86596	0.01859	-0.85711
0.78766	0.06465	0.01904	-0.70609	0.01939	-0.73755	0.01912	-0.75457
0.85230	0.04497	0.01549	-0.52399	0.01688	-0.57310	0.01644	-0.58076
0.90819	0.02795	0.01120	-0.34705	0.01267	-0.38908	0.01259	-0.39920
0.95700	0.01309	0.00598	-0.17106	0.00764	-0.20897	0.00839	-0.22963
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ ethanol(C)							
0.00000	0.38623	-0.00811	0.04770	-0.00586	-0.17954	-0.00304	-0.41865
0.25847	0.28640	0.00195	-0.63493	0.00269	-0.70271	0.00467	-0.89594
0.43954	0.21646	0.00875	-0.91620	0.00897	-0.92963	0.00931	-1.01789
0.57346	0.16474	0.01180	-0.89188	0.01171	-0.91415	0.01170	-0.97783
0.67652	0.12494	0.01361	-0.82811	0.01370	-0.85407	0.01216	-0.85430
0.75828	0.09336	0.01320	-0.75508	0.01409	-0.74096	0.01480	-0.80936
0.82473	0.06769	0.01221	-0.56010	0.01274	-0.58993	0.01357	-0.64913
0.87980	0.04642	0.01145	-0.44703	0.01099	-0.44756	0.01019	-0.45438
0.92619	0.02851	0.00808	-0.28793	0.00789	-0.29145	0.00720	-0.29341
0.96579	0.01321	0.00407	-0.13570	0.00577	-0.17333	0.00639	-0.19431
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ propanol (C)							
0.00000	0.45079	-0.01001	0.36101	-0.00448	-0.16769	-0.00256	-0.34810
0.28918	0.32043	-0.00006	-0.45100	0.00225	-0.65920	0.00495	-0.87107
0.47790	0.23536	0.00642	-0.73899	0.00742	-0.84074	0.00884	-0.94513
0.61077	0.17546	0.00901	-0.73901	0.01064	-0.85401	0.01050	-0.87519
0.70938	0.13101	0.01034	-0.67500	0.01195	-0.77184	0.01168	-0.78662
0.78547	0.09671	0.01019	-0.56599	0.01203	-0.65515	0.01296	-0.70610
0.84597	0.06944	0.00933	-0.45100	0.01160	-0.53804	0.01136	-0.54830
0.89521	0.04724	0.00736	-0.32300	0.00905	-0.38195	0.00892	-0.39123
0.93608	0.02881	0.00457	-0.19383	0.00651	-0.24790	0.00629	-0.25125
0.97055	0.01328	0.00125	-0.07071	0.00230	-0.09696	0.00246	-0.10394
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Viscous Synergy.....of some Pr. Monoalkanols in Aqueous DMF Mixtures.

water(A)+ N,N-dimethylformamide (B)+ butanol (C)							
0.00000	0.50306	-0.01278	0.70001	-0.00590	0.01056	-0.00278	-0.30063
0.31224	0.34598	-0.00179	-0.34200	0.00124	-0.58874	0.00330	-0.76306
0.50532	0.24886	0.00392	-0.62399	0.00593	-0.76380	0.00653	-0.82100
0.63651	0.18286	0.00540	-0.59200	0.00858	-0.76193	0.00808	-0.76207
0.73147	0.13509	0.00638	-0.53400	0.00974	-0.68406	0.00932	-0.68899
0.80338	0.09891	0.00694	-0.46402	0.00972	-0.57311	0.00957	-0.58615
0.85973	0.07057	0.00547	-0.34200	0.00909	-0.45893	0.00870	-0.46248
0.90507	0.04776	0.00485	-0.25900	0.00817	-0.35248	0.00822	-0.36486
0.94234	0.02901	0.00324	-0.22900	0.00623	-0.23590	0.00604	-0.23898
0.97353	0.01332	0.00168	-0.07799	0.00343	-0.11644	0.00342	-0.11986
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+N,N-dimethylformamide (B)+ pentanol (C)							
0.00000	0.54624	-0.01387	0.91400	-0.01424	0.03700	-0.00540	-0.22595
0.33019	0.36588	-0.00327	-0.21600	-0.00961	-0.53900	-0.00093	-0.58971
0.52588	0.25898	0.00093	-0.44800	0.00513	-0.71800	0.01081	-1.14472
0.65534	0.18827	0.00188	-0.42200	0.00559	-0.71300	0.01135	-0.97022
0.74734	0.13802	0.00236	-0.37100	0.00370	-0.63800	0.01058	-0.77757
0.81607	0.10047	0.00226	-0.30200	0.00279	-0.52900	0.00691	-0.52411
0.86937	0.07136	0.00133	-0.21600	0.00249	-0.46400	0.00767	-0.45163
0.91191	0.04812	0.00096	-0.15500	0.00308	-0.29400	0.00505	-0.29651
0.94666	0.02914	-0.00074	-0.06900	0.00458	-0.21700	0.00570	-0.23871
0.97557	0.01335	-0.00065	-0.02900	0.00203	-0.08000	0.00261	-0.10667
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table 4. Experimental sound velocities (u), isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) of water (A)+ N,N-dimethylformamide (B) + methanol, ethanol, propanol, butanol and pentanol (C) at 298.15.

x_A	u $m\ s^{-1}$	$K_S \times 10^{12}$ Pa^{-1}	$K_S^E \times 10^{12}$ Pa^{-1}
water (A)+ N,N-dimethylformamide (B)+ methanol (C)			
0.00000	1364.1	623.6	43.7
0.21555	1376.6	595.8	45.0
0.38205	1458.2	518.8	-9.6
0.51453	1552.4	449.1	-61.5
0.62245	1628.0	401.9	-94.1
0.71206	1674.6	374.5	-109.4
0.78766	1679.9	367.7	-106.1
0.85230	1659.7	373.0	-92.1
0.90819	1619.9	388.0	-69.5
0.95700	1569.3	410.1	-40.8
1.00000	1496.2	448.0	0.0
water (A)+ N,N-dimethylformamide (B)+ ethanol (C)			
0.00000	1385.6	607.4	69.0
0.25847	1417.2	565.3	51.0
0.43954	1513.4	484.5	-12.9
0.57346	1604.9	423.4	-61.5
0.67652	1663.3	387.9	-87.4
0.75828	1675.6	376.3	-91.4
0.82473	1665.8	376.7	-84.8
0.87980	1635.9	385.6	-70.8
0.92619	1593.1	402.5	-49.5
0.96579	1550.8	420.8	-27.5
1.00000	1496.2	448.0	0.0
water (A)+ N,N-dimethylformamide (B)+ propanol (C)			
0.00000	1391.7	597.3	95.6
0.28918	1436.8	546.4	61
0.47790	1540.0	465.8	-8.9
0.61077	1616.9	415.7	-51.5
0.70938	1656.0	390.5	-71.1
0.78547	1655.4	385.8	-71.5
0.84597	1639.2	388.8	-65.1
0.89521	1610.8	398.3	-52.8
0.93608	1575.0	412.6	-36.2
0.97055	1547.8	423.3	-23.5
1.00000	1496.2	448.0	0.0

Viscous Synergy.....of some Pr. Monoalkanols in Aqueous DMF Mixtures.

water (A)+ N,N-dimethylformamide (B)+ butanol (C)			
0.00000	1391.2	598.6	116.6
0.31224	1442.7	542.1	71.6
0.50532	1538.9	467.1	3.7
0.63651	1596.3	427.7	-30.9
0.73147	1622.3	408.3	-46.8
0.80338	1615.4	406.2	-46.2
0.85973	1602.6	408.1	-42.2
0.90507	1580.8	414.5	-34.2
0.94234	1558.5	421.8	-25.5
0.97353	1528.3	433.9	-12.2
1.0000	1496.2	448.0	0.0
water (A)+ N,N-dimethylformamide (B)+ pentanol (C)			
0.00000	1386.1	602.2	135.9
0.33019	1447.2	538.4	79.1
0.52588	1533.7	470.9	15.7
0.65534	1584.9	434.7	-17.7
0.74734	1600.2	420.8	-29.7
0.81607	1593.4	419.0	-30.0
0.86937	1583.9	419.2	-28.7
0.91191	1565.8	423.8	-23.2
0.94666	1543.5	431.6	-14.7
0.97557	1523.7	437.5	-8.2
1.00000	1505.6	448.0	0.0

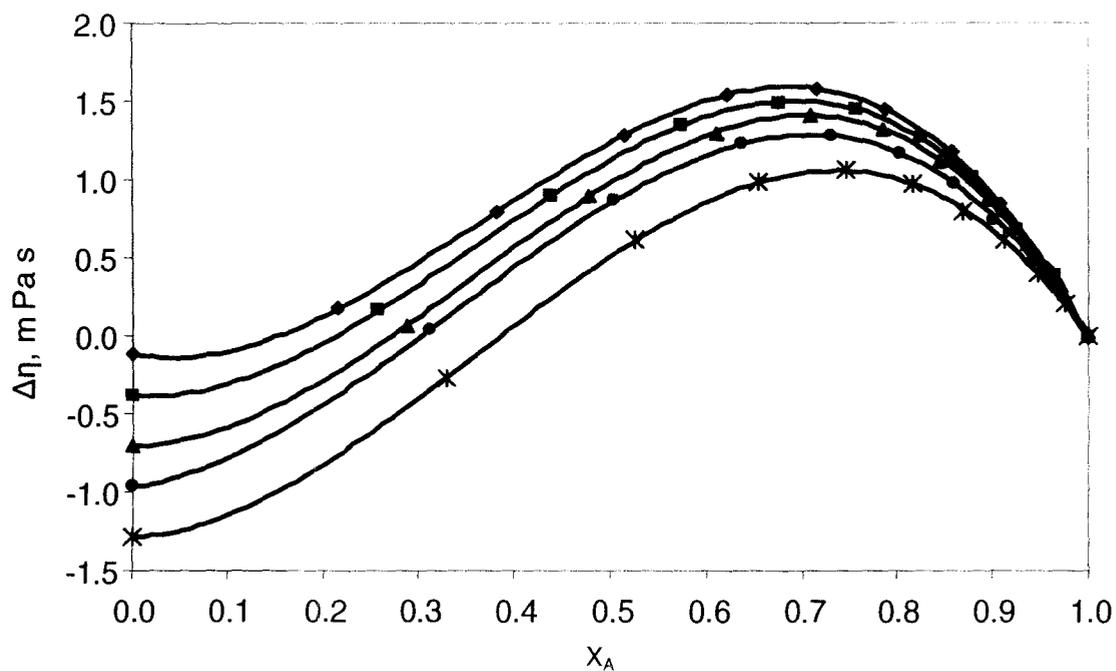


Fig. 1. Viscosity deviations ($\Delta\eta$) of: (◆), water (A)+ N,N-dimethylformamide (B) + methanol (C); (■), water (A)+ N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A) + N,N- dimethylformamide (B) + propanol (C); (●), water (A) + N,N-dimethyl formamide (B)+ butanol (C); and (⋈), water (A)+N,N-dimethylformamide (B) + pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

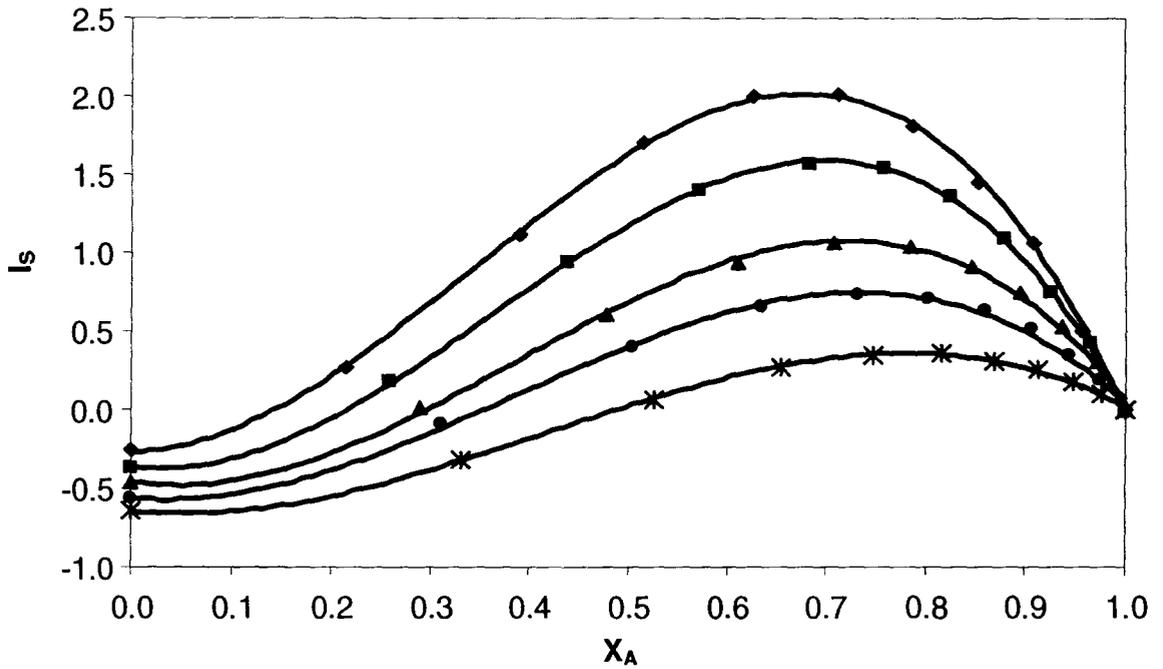


Fig. 2. Synergy Index (I_s) of: (♦), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A)+ N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A)+ N,N-dimethylformamide (B)+ propanol (C); (●), water(A)+ N,N-dimethylformamide (B)+ butanol (C); and (✱), water (A)+N,N-dimethylformamide (B)+ pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

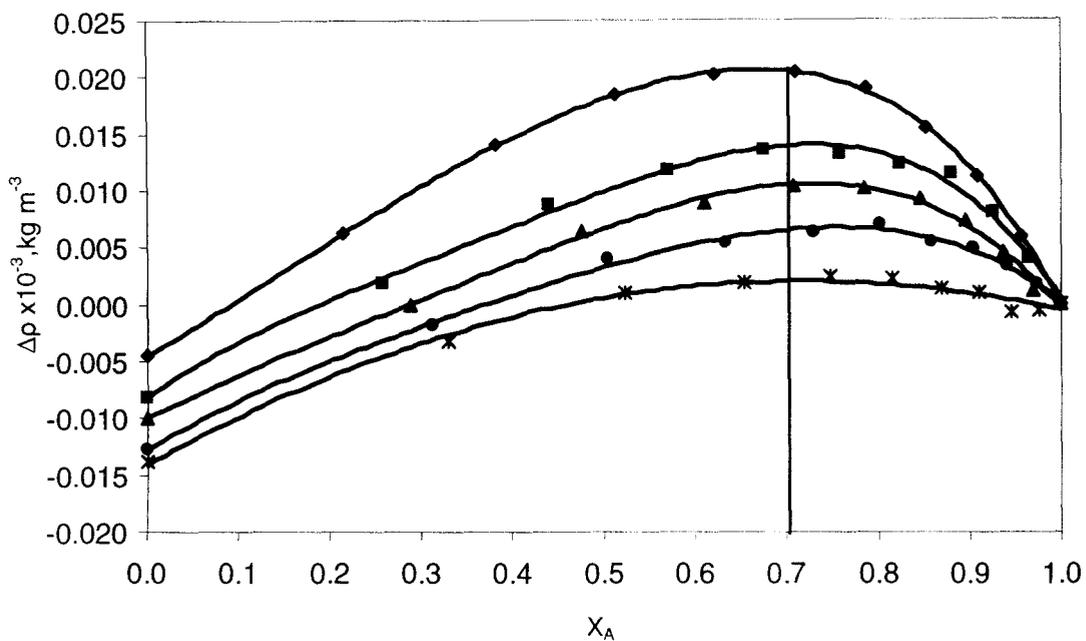


Fig. 3. Density Differences ($\Delta\rho$) of: (♦), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A) + N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A)+ N,N-dimethylformamide (B)+ propanol (C); (●),water (A)+ N,N-dimethylformamide (B)+ butanol (C); and (⋈), water (A)+N,N-dimethylformamide (B) + pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

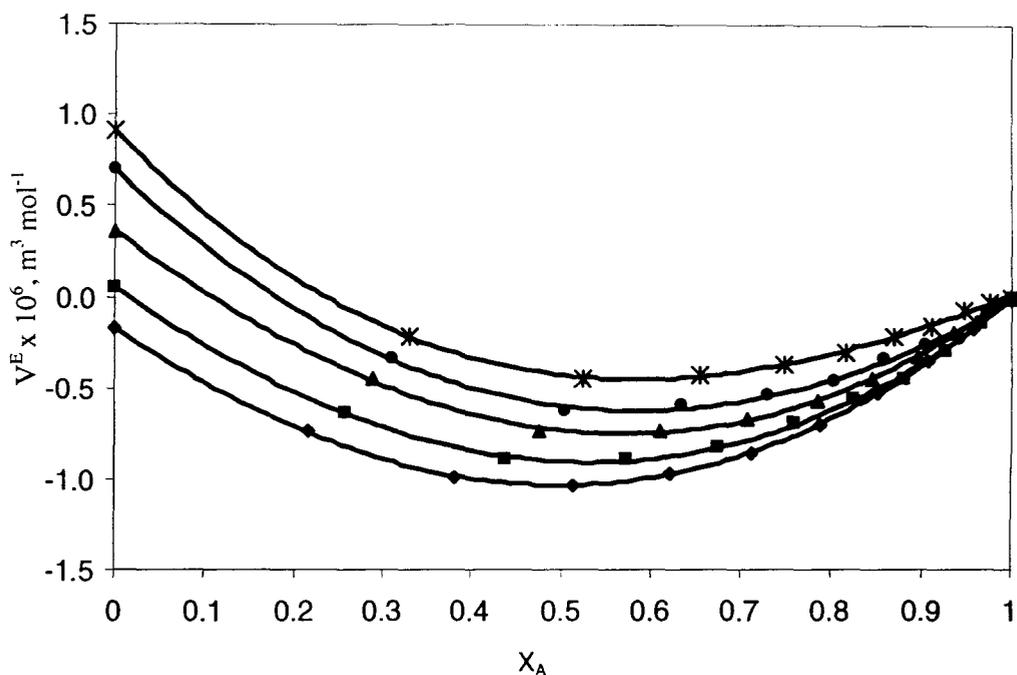


Fig. 4. Excess molar volumes (V^E) of: (\diamond), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (\blacksquare), water (A) + N,N-dimethylformamide (B)+ ethanol(C); (\blacktriangle), water(A)+ N,N-dimethylformamide (B)+ propanol (C); (\bullet), water(A)+ N,N-dimethylformamide (B)+ butanol (C); and (\times), water (A)+N,N-dimethylformamide (B)+ pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

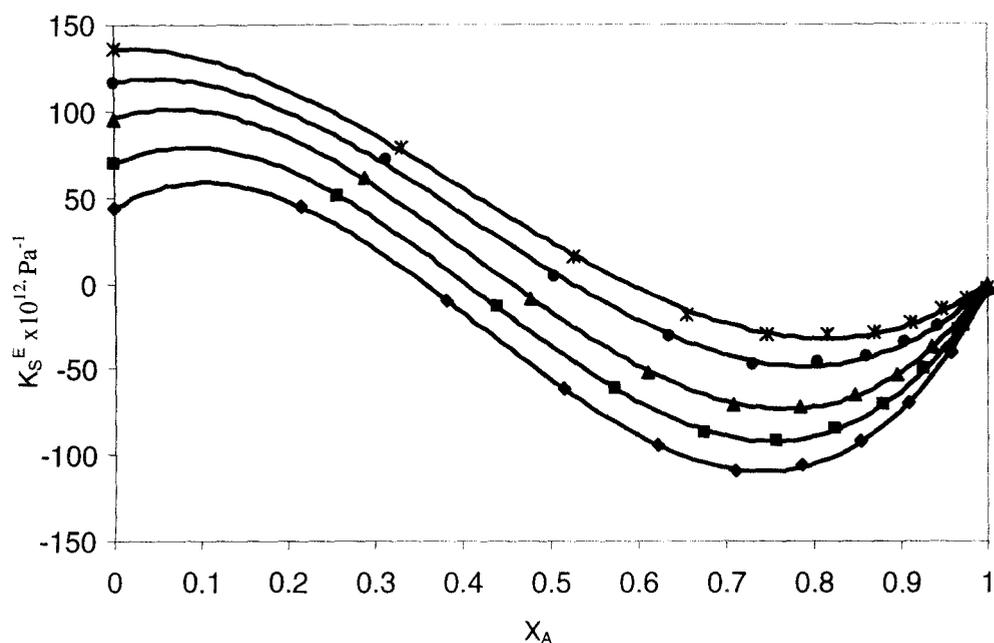


Fig. 5. Excess isentropic compressibility (K_S^E) of: (◆), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A)+ N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A)+ N,N-dimethylformamide (B)+ propanol (C); (●), water(A)+ N,N-dimethylformamide (B)+ butanol (C); and (x), water (A)+N,N-dimethylformamide (B)+ pentanol (C) mixtures with mole fraction of water(X_A) at 298.15 K.

CHAPTER V

Studies of Viscous Antagonism, Excess Molar Volumes, Viscosity Deviation and Isentropic Compressibility of Ternary Mixtures Containing N,N-dimethylformamide, Benzene and Some Ethers at 298.15 K.

Keywords: Viscous antagonism; Viscosity deviations; Excess molar volumes; Isentropic compressibility; molecular interactions.

5.1. Introduction

Grouping of solvents into classes is often based on the nature of the intermolecular forces because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. Rheology is the branch of science¹ that studies material deformation and flow, and is increasingly applied to analyse the viscous behaviour of many pharmaceutical products,² 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. The increasing use of the solvents: N,N-dimethylformamide, benzene, 1,3-dioxolane, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, di-isopropylether, diethylether, 2-methoxyethanol and 2-ethoxyethanol and their mixtures in many industrial processes such as battery, pharmaceutical and cosmetics have greatly stimulated the need for extensive information on their various properties. So present study give us extensive information on the various properties when these ethers are taken with DMF and benzene as mixed solvent systems.¹⁻⁷ The determination of density, viscosity and speeds of sound is a valuable tool to learn about the liquid state^{8,9} because of the close connection between liquid structure and macroscopic properties.

Viscosity and density of these ternary liquid mixtures are used to understand molecular interactions between the components of the mixture to develop new theoretical models

and also for engineering applications.^{10, 11} In our systematic investigation of the properties, we have reported viscosities, densities and speeds of sound of different solvents and their mixtures in previous papers¹²⁻¹⁸ from our laboratory.

The present work contributes and extends our study of density (ρ), viscosity deviations ($\Delta\eta$), viscous antagonism, excess molar volumes (V^E) and isentropic compressibility (K_s^E) to the mixture of N,N- dimethylformamide (DMF) and benzene (C_6H_6) with some ethers, where DMF is represented as A, C_6H_6 represented as B, and ethers represented as C.

5.2. Experimental Section

5.2.1. Source and purity of samples

DMF (N,N-dimethylformamide, C_3H_7NO) is obtained from Merck and LR, further purified by standard methods.¹⁹ Benzene (S. D. Fine Chemicals, purity > 99%) was further purified by means of a simple distillation technique with the first and last 20% of the distillate being discarded²⁰⁻²² and finally the density and viscosity value compared with the literature.²³

The experimental ethers namely 1,3-dioxolane (1,3-DO), 1,4-dioxane (1,4-DO), tetrahydrofuran (THF), 1,2-dimethoxyethane(1,2-DME), di-isopropylether (DIE), diethylether (DEE), 2-methoxy ethanol (2-ME) and 2-ethoxyethanol (2-EE) were obtained from Merck and LR. These were further purified by standard methods.²⁴⁻²⁷ The purity of the liquids was ascertained by GLC and also by comparing experimental values of densities, viscosities and sound velocities with those reported in the literature^{24, 27-35} as listed in Table 1. The purity of the solvents finally obtained were >99%.

5.2.2. Apparatus and Procedure

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 1 mm. The pycnometer was calibrated at the experimental temperature with triply distilled water and DMF. The measurements were done in a thermostated water bath controlled to $\pm 0.01\text{ K}$.² The weighings were done on a Mettler electronic balance (AG-285) with a precision of $\pm 0.01\text{ mg}$. The viscosities (η) were measured by means of a suspended Ubbelohde type

viscometer ⁷ which was calibrated at the desired temperature with triply distilled water and purified methanol using density and viscosity values from the literature. The ultrasonic speeds (u) were determined using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz, ^{32,36} which was calibrated with water, methanol and benzene and the temperature stability was maintained within $\pm 0.01\text{K}$ by circulating thermostatic water around the cell with a circulating pump. The solutions were prepared by mixing known volumes of pure liquids in air tight stopper bottles at 298.15 K. The precisions of the speed of sound, density and viscosity measurements are $\pm 0.2\text{m s}^{-1}$, $\pm 3 \times 10^{-4} \text{g cm}^{-3}$ and $\pm 2 \times 10^{-4} \text{mPa s}$, respectively.

5.3. Results and discussion

The measured density (ρ), viscosity (η) and the speeds of sound (u) data for mixtures of (DMF) (A), C_6H_6 (B), and the ethers (C) , i.e., 1,3-dioxolane, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, di-isopropylether, di-ethylether, 2-methoxy ethanol and 2-ethoxyethanol were used to calculate the excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) and excess isentropic compressibilities (K_s^E) .

The method most widely used to analyze the antagonistic and synergic behavior of various solvent mixtures studied is that developed by Kalentune-Gencer and Peleg, ³⁷ allowing the quantification of the antagonistic and synergic interactions taking place in mixtures involving variable proportions of the constituent components. Viscous antagonism 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 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 considered separately, the system would lack interaction.³⁸ The method compares the viscosity of the system, determined experimentally, η_{exp} with the viscosity expected in the absence of interaction, η_{calcd} , defined as,³⁹

$$\eta_{\text{calcd}} = \sum_{i=1}^{n=3} W_i \eta_i \quad (1)$$

Where, W_i and η_i are the fraction by weight and the viscosity measured experimentally, of the pure components respectively.

Viscous antagonism is exists when, $\eta_{\text{exp}} < \eta_{\text{calcd}}$. This procedure is used when Newtonian fluids are involved.³⁹ Quantitatively, as per the absolute reaction rates theory,⁴⁰ the deviations of viscosities from the ideal mixture values can be calculated as,

$$\Delta\eta = \eta - \sum_{i=1}^{n=3} X_i \eta_i \quad (2)$$

Where, η is the viscosity of the mixture and X_i , η_i are the mole fraction and viscosity of the pure components respectively.

In order to secure more comparable viscous antagonistic results, the so called antagonistic interaction index (I_A), introduced by Howell³⁹ is taken into account

$$I_A = (\eta_{\text{cal}} - \eta_{\text{exp}}) / \eta_{\text{calcd}} \quad (3)$$

The excess molar volumes, V^E are calculated from density data according to the following equation:⁴¹

$$V^E = \sum_{i=1}^{n=3} X_i M_i (1/\rho - 1/\rho_i) \quad (4)$$

Where M_i , ρ_i and ρ are the molar mass, density of the pure components and density of the mixture respectively.

On the basis of the theory of absolute reaction rates,⁴⁰ the excess Gibbs energy, ΔG^{*E} , of viscous flow was calculated from

$$\Delta G^{*E} = RT \ln(\eta M / \rho) - RT \sum_{i=1}^n x_i \ln(\eta_i M_i / \rho_i), \quad (5)$$

where n stands for the number of components of the mixture and M and M_i are the molar mass of the mixture and of the pure components i .

Table 5 contains the sound velocity (u), isentropic compressibility (K_s) and excess isentropic compressibility (K_s^E) data for the mixtures observed and calculated using the following equation: ⁴²

$$K_s = (u^2 \rho_{exp})^{-1} \quad (6)$$

$$K_s^E = K_s - \sum_{i=1}^{n=3} X_i K_{s,i} \quad (7)$$

where, $K_{s,i}$ gives the isentropic compressibility for the the pure components of the mixture.

In Fig.1, compares the viscosity of the system determined experimentally, η_{exp} with the viscosity expected in the absence of interaction, η_{calcd} and it shows that in all cases the results was the same, i.e. $\eta_{exp} < \eta_{calcd}$, viscous antagonism is exists.

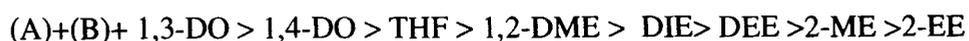
In Fig.2, $\Delta\eta$ values for the ternary mixtures (A)+(B)+ 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) have been plotted against the mole fraction of DMF (X_A) at 298.15 K. It is observed that $\Delta\eta$ values increases as the mole fraction of DMF increases. This trend is observed for all the ternary mixtures examined here. However, the mixtures have maximum, $\Delta\eta$ at $X_A=0.70$ for the experimental temperature indicating strong specific interaction between the unlike molecules. The estimated uncertainty for, $\Delta\eta$ is ± 0.0004 poise. From the value of $\Delta\eta$ as shown in table 3, it can be concluded that the affinity of ethers molecules towards benzene molecules in the presence of N,N-Dimethylformamide (DMF) is enhanced by the following order,



Here, dispersion and dipolar interactions are operating between N,N-Dimethylformamide, benzene and 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE molecules resulting in negative $\Delta\eta$ but with the increase X_A of DMF, the dipolar interactions dominate resulting less negative value of $\Delta\eta$.²⁹

In Fig. 3, antagonistic interaction index (I_A) values for the ternary mixtures (A) + (B)+ 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) have been plotted against the X_A of DMF at 298.15 K. It is found that each mixture has a maximum at $X_A = 0.0$ and then it decreases as X_A increases. The estimated uncertainty for I_A is ± 0.002 . A perusal of table 3 shows that the experimentally determined viscosities, η_{exp} for all mixtures for various mole fractions at the experimental temperature are lower than those of its calculated values, η_{calcd} which demonstrates viscous antagonism in the eight mixtures studied here. The explanation of this behavior is based on the known phenomenon of molecular dissociation, as a consequence of weakening the non-covalent bonding formed between the molecules producing a decrease in size of the molecular package which logically implies an increase in I_A .^{1,12} The maxima observed indicates strong specific interaction between the unlike molecules which is predominated by non-covalent interaction. Thus, the molecular package increases gradually with the addition of DMF to the mixtures which implies a decrease in I_A .

Fig.4 represents the V^E values for the five ternary mixtures under examination. In general, V^E is found to be negative for all the ternary mixtures at the experimental temperature. However, the values at first decreases to minima and then it increase with increasing X_A . The eight ternary mixtures shows the minima at the same point i.e. at $X_A = 0.3$. The estimated uncertainty for V^E is $\pm 0.5 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$. The trend is:

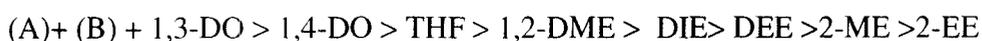


The negative V^E indicates the presence of strong molecular interaction between the components of the mixture. Volume changes for a mixed system result from changes in the free volume of the liquids, since the bond lengths and bond distances in the molecules themselves do not change. The optimum packing condition is directly related to differences in molecular sizes and intermolecular attractions, in particular when hydrogen bonding occurs between unlike molecules creating association complexes, as well as being effected by the breaking of interactions between like molecules.³² Several effects contribute to the value of V^E , such as:⁴³ dipolar interaction, interstitial accommodation and possible hydrogen bonded interactions between unlike molecules. The actual volume

change would, therefore, depend on the relative strength of these three effects. Similar results have been reported earlier.^{27, 44, 45}

Fig. 5 predicts the curves for the ternary mixtures of ΔG^{*E} . According to Reed and Taylor and Meyer et al., positive ΔG^{*E} values indicate specific interactions, while negative values indicate the dominance of dispersion forces.^{46, 47} From the ΔG^{*E} values recorded in table 4, it is seen that for all the ternary mixtures, these values are negative or positive keeping similarity with the $\Delta\eta$ values and thereby supports our conclusion drawn from V^E and $\Delta\eta$ considerations.

Fig. 6 predicts the curves for the ternary mixtures of K_s^E . The values are positive in all the cases and decreases as the mole fraction of DMF increases. There is a parallel in the qualitative behavior of K_s^E and V^E curves. The estimated uncertainty for K_s^E is $\pm 0.2 \text{ Pa}^{-1}$. The K_s^E values follow the sequence:



Positive K_s^E values are due to the breaking of interactions and the corresponding disruption of molecular order in the pure components.²⁴ The donor–acceptor interaction between the component molecule play an important part for the mixtures containing open chain ether specially having hydroxyl group, where there is strong specific interaction between the component molecules leading to lower value of K_s^E . Interactions between the molecules of DMF, benzene or ethers are broken in the mixing process; the breaking leads to positive K_s^E values for the mixture containing cyclic ethers as compared to the open chain ethers. Similar results have been reported by some authors earlier.^{24, 32}

5.4. Conclusion

After a thorough study of the behavior of ethers on DMF + C_6H_6 mixtures we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about antagonism. The similarity in the working formula of antagonistic interaction index and viscosity deviation would probably indicate that the two properties are similar but a close comparison between these two parameters has given the clear distinction.

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Table 1. Comparison of experimental (I) densities (ρ), viscosities (η), and ultrasonic speeds (u) of pure liquids with literature values (II)

Solvent	$\rho \times 10^{-3}$ kg m ⁻³		η m Pa s		u m s ⁻¹	
	I	II	I	II	I	II
N,N-dimethylformamide	0.94609	0.9461 ²⁷	0.8586	0.8586 ²⁷	1465.2	1465.0 ²⁷
Benzene	0.8735	0.8735 ²³	0.5920	0.5920 ²³	1252.7	--
1,3-dioxolane	1.0577	1.0577 ³³	0.5878	0.5878 ³³	1338.2	1338.2 ³³
1,4-dioxane	1.0287	1.0287 ³³	1.1779	1.1779 ³³	1344.4	1344.4 ³³
Tetrahydrofuran	0.8807	0.8808 ³³	0.463	0.4631 ³³	1292.2	1292.2 ³³
1,2-dimethoxy ethane	0.8615	0.8611 ³⁵	0.4089	0.4089 ³⁵	1146.2	--
Diisopropyl ether	0.7250	0.7250 ²¹	0.379	0.3791 ²¹	1050.1	--
Diethyl ether	0.7134	0.7134 ²⁵	0.224	0.22404 ²⁵	1080.8	--
2-methoxy ethanol	0.95979	0.9600 ³⁴	1.543	1.5414 ³⁴	1339.4	--
2-ethoxy ethanol	0.92497	0.9254 ³²	1.8277	1.850 ³²	1308.0	1309.0 ³²

Table 2. Experimental density (ρ_{Exp}) and Viscosity (η_{Exp}) of N,N-dimethylformamide (A) + benzene (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) at 298.15 K.

X_A	X_B	$\rho_{Exp} \times 10^{-3}$ kg m ⁻³	η mPa s	X_A	X_B	$\rho_{Exp} \times 10^{-3}$ kg m ⁻³	η mPa s
N,N-dimethylformamide (A)+ Benzene (B)+ 1,3-DO (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,4 -DO (C)			
0.0000	0.4868	0.9584	0.3650	0.0000	0.5301	0.9472	0.6569
0.1036	0.4363	0.9583	0.4296	0.1118	0.4708	0.9479	0.6990
0.2064	0.3863	0.9578	0.4859	0.2207	0.4131	0.9486	0.7290
0.3083	0.3367	0.9568	0.5393	0.3268	0.3568	0.9487	0.7539
0.4095	0.2874	0.9557	0.5862	0.4303	0.3020	0.9486	0.7750
0.5099	0.2386	0.9542	0.6320	0.5311	0.2485	0.9484	0.7900
0.6094	0.1901	0.9527	0.6775	0.6295	0.1964	0.9479	0.8027
0.7082	0.1420	0.9509	0.7235	0.7255	0.1455	0.9474	0.8180
0.8062	0.0943	0.9492	0.7682	0.8192	0.0958	0.9469	0.8329
0.9035	0.0470	0.9476	0.8148	0.9107	0.0473	0.9464	0.8483
1.0000	0.0000	0.9461	0.8586	1.0000	0.0000	0.9461	0.8586
N,N-dimethylformamide (A)+ Benzene (B)+ THF (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,2- DME (C)			
0.0000	0.4800	0.8797	0.4022	0.0000	0.5357	0.8702	0.3970
0.1023	0.4309	0.8868	0.4507	0.1128	0.4752	0.8782	0.4473
0.2041	0.3820	0.8939	0.4957	0.2225	0.4165	0.8862	0.4939
0.3054	0.3334	0.9009	0.5368	0.3291	0.3594	0.8943	0.5376
0.4061	0.2851	0.9078	0.5843	0.4329	0.3038	0.9022	0.5813
0.5064	0.2370	0.9145	0.6285	0.5338	0.2498	0.9100	0.6257
0.6061	0.1891	0.9211	0.6744	0.6320	0.1971	0.9177	0.6735
0.7053	0.1414	0.9276	0.7191	0.7276	0.1459	0.9251	0.7155
0.8041	0.0941	0.9338	0.7681	0.8208	0.0960	0.9324	0.7593
0.9023	0.0469	0.9400	0.8153	0.9115	0.0474	0.9395	0.8061
1.0000	0.0000	0.9461	0.8586	1.0000	0.0000	0.9461	0.8586
N,N-dimethylformamide (A)+ Benzene (B)+ DIE (C)				N,N-dimethylformamide (A)+ Benzene (B)+DEE (C)			
0.0000	0.5668	0.7958	0.3997	0.0000	0.4869	0.7902	0.3396
0.1186	0.4995	0.8103	0.4506	0.1036	0.4364	0.8051	0.3936
0.2324	0.4350	0.8248	0.4975	0.2064	0.3864	0.8201	0.4449
0.3417	0.3731	0.8394	0.5424	0.3084	0.3367	0.8353	0.4944
0.4467	0.3136	0.8541	0.5858	0.4096	0.2875	0.8508	0.5420
0.5478	0.2563	0.8690	0.6274	0.5099	0.2386	0.8662	0.5884
0.6450	0.2012	0.8840	0.6700	0.6095	0.1901	0.8819	0.6353
0.7386	0.1481	0.8993	0.7161	0.7083	0.1420	0.8978	0.6863

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0.8289	0.0970	0.9145	0.7608	0.8063	0.0943	0.9137	0.7364
0.9160	0.0476	0.9302	0.8069	0.9035	0.0470	0.9298	0.7947
1.0000	0.0000	0.9461	0.8586	1.0000	0.0000	0.9461	0.8586
N,N-dimethylformamide (A)+ Benzene (B)+ 2-ME(C)				N,N-dimethylformamide (A)+ Benzene (B)+ 2-EE (C)			
0.0000	0.4932	0.9229	1.0157	0.0000	0.5354	0.9066	1.1640
0.1048	0.4415	0.9269	1.0006	0.1128	0.4750	0.9139	1.1302
0.2085	0.3903	0.9306	0.9806	0.2224	0.4163	0.9202	1.0944
0.3111	0.3397	0.9343	0.9593	0.3290	0.3592	0.9252	1.0574
0.4127	0.2896	0.9375	0.9336	0.4327	0.3037	0.9297	1.0205
0.5131	0.2401	0.9402	0.9105	0.5336	0.2497	0.9331	0.9855
0.6125	0.1911	0.9427	0.8891	0.6318	0.1971	0.9361	0.9526
0.7109	0.1426	0.9444	0.8743	0.7275	0.1459	0.9390	0.9222
0.8083	0.0946	0.9457	0.8623	0.8207	0.0960	0.9414	0.8968
0.9046	0.0470	0.9462	0.8597	0.9115	0.0474	0.9437	0.8744
1.0000	0.0000	0.9461	0.8586	1.0000	0.0000	0.9461	0.8586
0.0000	0.4932	0.9229	1.0157	0.0000	0.5354	0.9066	1.1640

Table 3. Viscosity deviations ($\Delta\eta$) and antagonistic index (I_A) of N,N-dimethylformamide (A) + benzene (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) at 298.15 K.

X_A	X_B	$\Delta\eta$ mPa s	I_A	X_A	X_B	$\Delta\eta$ mPa s	I_A
N,N-dimethylformamide (A)+ Benzene (B)+ 1,3-DO (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,4-DO (C)			
0.0000	0.4868	-0.2248	0.38118	0.0000	0.5301	-0.2104	0.25767
0.1036	0.4363	-0.1881	0.30349	0.1118	0.4708	-0.1674	0.20782
0.2064	0.3863	-0.1594	0.24506	0.2207	0.4131	-0.1364	0.17129
0.3083	0.3367	-0.1334	0.19566	0.3268	0.3568	-0.1106	0.14044
0.4095	0.2874	-0.1137	0.15942	0.4303	0.3020	-0.0886	0.11372
0.5099	0.2386	-0.0949	0.12741	0.5311	0.2485	-0.0727	0.09381
0.6094	0.1901	-0.0761	0.09797	0.6295	0.1964	-0.0591	0.07641
0.7082	0.1420	-0.0567	0.07006	0.7255	0.1455	-0.0430	0.05598
0.8062	0.0943	-0.0383	0.04552	0.8192	0.0958	-0.0273	0.03588
0.9035	0.0470	-0.0179	0.02040	0.9107	0.0473	-0.0111	0.01500
1.0000	0.0000	0.0000	0.00000	1.0000	0.0000	0.0000	0.00000
N,N-dimethylformamide (A)+ Benzene (B)+ THF (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,2-DME (C)			
0.0000	0.4800	-0.1227	0.23749	0.0000	0.5357	-0.1100	0.20674
0.1023	0.4309	-0.1084	0.19612	0.1128	0.4752	-0.0994	0.16596
0.2041	0.3820	-0.0973	0.16504	0.2225	0.4165	-0.0913	0.13661
0.3054	0.3334	-0.0900	0.14359	0.3291	0.3594	-0.0851	0.11561
0.4061	0.2851	-0.0761	0.11455	0.4329	0.3038	-0.0779	0.09698
0.5064	0.2370	-0.0654	0.09315	0.5338	0.2498	-0.0690	0.07926

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0.6061	0.1891	-0.0528	0.07132	0.6320	0.1971	-0.0557	0.05849
0.7053	0.1414	-0.0412	0.05294	0.7276	0.1459	-0.0473	0.04743
0.8041	0.0941	-0.0251	0.03062	0.8208	0.0960	-0.0363	0.03519
0.9023	0.0469	-0.0107	0.01235	0.9115	0.0474	-0.0214	0.02029
1.0000	0.0000	0.0000	0.00000	1.0000	0.0000	0.0000	0.00000
N,N-dimethylformamide (A)+ Benzene (B)+ DIE (C)				N,N-dimethylformamide (A)+ Benzene (B)+DEE (C)			
0.0000	0.5668	-0.1000	0.17669	0.0000	0.4869	-0.0636	0.16770
0.1186	0.4995	-0.0917	0.13814	0.1036	0.4364	-0.0568	0.13130
0.2324	0.4350	-0.0856	0.11174	0.2064	0.3864	-0.0523	0.10686
0.3417	0.3731	-0.0800	0.09219	0.3084	0.3367	-0.0492	0.08974
0.4467	0.3136	-0.0742	0.07703	0.4096	0.2875	-0.0477	0.07860
0.5478	0.2563	-0.0689	0.06644	0.5099	0.2386	-0.0470	0.07088
0.6450	0.2012	-0.0612	0.05550	0.6095	0.1901	-0.0455	0.06354
0.7386	0.1481	-0.0487	0.04100	0.7083	0.1420	-0.0394	0.05125
0.8289	0.0970	-0.0364	0.02957	0.8063	0.0943	-0.0340	0.04178
0.9160	0.0476	-0.0215	0.01747	0.9035	0.0470	-0.0200	0.02321
1.0000	0.0000	0.0000	0.00000	1.0000	0.0000	0.0000	0.00000
N,N-dimethylformamide (A)+ Benzene (B)+ 2- ME (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 2- EE (C)			
0.0000	0.4932	-0.0583	0.04851	0.0000	0.5354	-0.0022	0.03794
0.1048	0.4415	-0.0508	0.04393	0.1128	0.4750	-0.0013	0.03793
0.2085	0.3903	-0.0485	0.04400	0.2224	0.4163	-0.0033	0.03962
0.3111	0.3397	-0.0477	0.04532	0.3290	0.3592	-0.0076	0.04265
0.4127	0.2896	-0.0515	0.05114	0.4327	0.3037	-0.0126	0.04571
0.5131	0.2401	-0.0530	0.05459	0.5336	0.2497	-0.0165	0.04707
0.6125	0.1911	-0.0530	0.05636	0.6318	0.1971	-0.0192	0.04651
0.7109	0.1426	-0.0466	0.05101	0.7275	0.1459	-0.0202	0.04333
0.8083	0.0946	-0.0376	0.04229	0.8207	0.0960	-0.0170	0.03456
0.9046	0.0470	-0.0194	0.02245	0.9115	0.0474	-0.0114	0.02160
1.0000	0.0000	0.0000	0.00000	1.0000	0.0000	0.0000	0.00000
0.0000	0.4932	-0.0583	0.04851	0.0000	0.5354	-0.0022	0.03794

Table 4. Excess molar volumes (V^E) and Gibbs energy of activation (ΔG^{*E}) of viscous flow of N,N-dimethylformamide (A) + benzene (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) at 298.15 K.

X_A	X_B	$V^E \times 10^6$ $m^3 \text{ mol}^{-1}$	ΔG^{*E} $J \text{ mol}^{-1}$	X_A	X_B	$V^E \times 10^6$ $m^3 \text{ mol}^{-1}$	ΔG^{*E} $J \text{ mol}^{-1}$
N,N-dimethylformamide (A)+ Benzene (B)+ 1,3-DO (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,4-DO (C)			
0.0000	0.4868	-0.1310	-1174.47	0.0000	0.5301	-0.2210	-548.86
0.1036	0.4363	-0.2120	-871.83	0.1118	0.4708	-0.2770	-408.52
0.2064	0.3863	-0.2630	-665.66	0.2207	0.4131	-0.3170	-317.23
0.3083	0.3367	-0.2690	-504.20	0.3268	0.3568	-0.3130	-245.96
0.4095	0.2874	-0.2600	-393.34	0.4303	0.3020	-0.2940	-189.09

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0.5099	0.2386	-0.2290	-301.30	0.5311	0.2485	-0.2540	-152.49
0.6094	0.1901	-0.1890	-222.05	0.6295	0.1964	-0.2000	-123.44
0.7082	0.1420	-0.1310	-151.39	0.7255	0.1455	-0.1430	-87.32
0.8062	0.0943	-0.0840	-94.27	0.8192	0.0958	-0.0860	-53.23
0.9035	0.0470	-0.0360	-39.35	0.9107	0.0473	-0.0380	-18.61
1.0000	0.0000	0.0000	0.00	1.0000	0.0000	0.0000	0.01
N,N-dimethylformamide (A)+ Benzene (B)+ THF (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,2- DME (C)			
0.0000	0.4800	-0.2530	-645.90	0.0000	0.5357	-0.3050	-564.64
0.1023	0.4309	-0.3150	-491.81	0.1128	0.4752	-0.3780	-418.36
0.2041	0.3820	-0.3570	-382.37	0.2225	0.4165	-0.4290	-318.28
0.3054	0.3334	-0.3840	-310.94	0.3291	0.3594	-0.4650	-250.96
0.4061	0.2851	-0.3900	-225.66	0.4329	0.3038	-0.4760	-196.86
0.5064	0.2370	-0.3790	-169.18	0.5338	0.2498	-0.4690	-150.92
0.6061	0.1891	-0.3360	-117.21	0.6320	0.1971	-0.4320	-101.41
0.7053	0.1414	-0.2860	-80.15	0.7276	0.1459	-0.3600	-81.04
0.8041	0.0941	-0.2000	-37.14	0.8208	0.0960	-0.2690	-60.68
0.9023	0.0469	-0.1090	-9.35	0.9115	0.0474	-0.1600	-36.31
1.0000	0.0000	0.0000	0.00	1.0000	0.0000	0.0000	0.00
N,N-dimethylformamide (A)+ Benzene (B)+ DIE (C)				N,N-dimethylformamide (A)+ Benzene (B)+DEE (C)			
0.0000	0.5668	-0.4880	-441.50	0.0000	0.4869	-0.5930	-149.83
0.1186	0.4995	-0.6450	-306.30	0.1036	0.4364	-0.7240	-6.68
0.2324	0.4350	-0.7330	-217.97	0.2064	0.3864	-0.8030	76.39
0.3417	0.3731	-0.7680	-157.51	0.3084	0.3367	-0.8420	118.97
0.4467	0.3136	-0.7550	-115.90	0.4096	0.2875	-0.8510	128.90
0.5478	0.2563	-0.7070	-92.30	0.5099	0.2386	-0.7940	117.13
0.6450	0.2012	-0.6140	-72.20	0.6095	0.1901	-0.7110	92.89
0.7386	0.1481	-0.5050	-47.43	0.7083	0.1420	-0.5970	71.94
0.8289	0.0970	-0.3430	-33.58	0.8063	0.0943	-0.4260	35.94
0.9160	0.0476	-0.1810	-21.97	0.9035	0.0470	-0.2290	15.69
1.0000	0.0000	0.0000	0.00	1.0000	0.0000	0.0000	0.01
N,N-dimethylformamide (A)+ Benzene (B)+ 2-ME (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 2-EE (C)			
0.0000	0.4932	-0.7550	116.78	0.0000	0.5354	-0.8320	357.25
0.1048	0.4415	-0.8290	107.22	0.1128	0.4750	-1.0870	323.16
0.2085	0.3903	-0.8770	84.83	0.2224	0.4163	-1.2200	283.41
0.3111	0.3397	-0.9170	57.87	0.3290	0.3592	-1.2330	238.98
0.4127	0.2896	-0.9120	18.99	0.4327	0.3037	-1.1800	191.86
0.5131	0.2401	-0.8690	-14.16	0.5336	0.2497	-1.0320	147.35
0.6125	0.1911	-0.8030	-43.84	0.6318	0.1971	-0.8560	104.14
0.7109	0.1426	-0.6720	-54.50	0.7275	0.1459	-0.6680	63.44
0.8083	0.0946	-0.5090	-57.14	0.8207	0.0960	-0.4490	33.23
0.9046	0.0470	-0.2770	-31.15	0.9115	0.0474	-0.2200	8.82
1.0000	0.0000	0.0000	0.00	1.0000	0.0000	0.0000	0.00

Table 5. Experimental sound velocities (u), isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) of N,N-dimethylformamide (A)+ benzene (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) at 298.15.

X_A	u $m s^{-1}$	$K_S \times 10^{12}$ Pa^{-1}	$K_S^E \times 10^{12}$ Pa^{-1}	X_A	u $m s^{-1}$	$K_S \times 10^{12}$ Pa^{-1}	$K_S^E \times 10^{12}$ Pa^{-1}
N,N-dimethylformamide (A)+ Benzene (B)+ 1,3-DO (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,4 -DO (C)			
0.0000	1302.1	615.4	340.2	0.0000	1097.5	876.5	314.0
0.1036	1326.2	593.3	301.0	0.1118	1130.9	824.9	276.0
0.2064	1336.7	584.3	275.0	0.2207	1157.7	786.6	251.0
0.3083	1339.8	582.2	256.0	0.3268	1181.8	754.7	232.0
0.4095	1339.8	583.0	240.0	0.4303	1204.9	726.1	216.0
0.5099	1338.9	584.6	225.0	0.5311	1226.6	700.8	203.0
0.6094	1344.1	581.0	205.0	0.6295	1263.5	660.8	175.0
0.7082	1359.0	569.4	177.0	0.7255	1301.5	623.1	149.0
0.8062	1387.0	547.6	139.0	0.8192	1350.9	578.7	116.0
0.9035	1444.6	505.7	81.0	0.9107	1435.8	512.6	61.0
1.0000	1465.2	440.7	0.0	1.0000	1465.2	440.7	0.0
N,N-dimethylformamide (A)+ Benzene (B)+ THF (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 1,2- DME (C)			
0.0000	1165.1	837.5	296.0	0.0000	1137.8	887.7	285.0
0.1023	1210.0	770.1	239.0	0.1128	1176.0	823.4	239.0
0.2041	1238.0	729.9	209.0	0.2225	1203.8	778.6	212.0
0.3054	1263.2	695.7	185.0	0.3291	1228.2	741.3	192.0
0.4061	1290.5	661.5	161.0	0.4329	1243.8	716.5	184.0
0.5064	1322.2	625.4	135.0	0.5338	1264.5	687.2	171.0
0.6061	1357.2	589.4	109.0	0.6320	1282.7	662.3	162.0
0.7053	1392.0	556.4	86.0	0.7276	1319.6	620.8	136.0
0.8041	1430.3	523.4	63.0	0.8208	1367.3	573.7	104.0
0.9023	1484.8	482.5	32.0	0.9115	1437.6	515.0	60.0
1.0000	1465.2	440.7	0.0	1.0000	1465.2	440.7	0.0
N,N-dimethylformamide (A)+ Benzene (B)+ DIE (C)				N,N-dimethylformamide (A)+ Benzene (B)+DEE (C)			
0.0000	1219.2	845.3	261.0	0.0000	1231.1	835.0	232.0
0.1186	1261.7	775.3	208.0	0.1036	1273.2	766.2	180.0
0.2324	1287.0	732.0	181.0	0.2064	1292.9	729.5	160.0
0.3417	1301.5	703.3	168.0	0.3084	1308.8	698.9	146.0
0.4467	1305.3	687.2	167.0	0.4096	1321.0	673.5	137.0
0.5478	1312.8	667.7	162.0	0.5099	1321.3	661.2	141.0
0.6450	1326.7	642.7	151.0	0.6095	1332.0	639.1	135.0

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0.7386	1351.0	609.2	131.0	0.7083	1347.9	613.0	125.0
0.8289	1394.5	562.3	97.0	0.8063	1377.1	577.1	105.0
0.9160	1450.8	510.8	58.0	0.9035	1433.5	523.4	67.0
1.0000	1465.2	440.7	0.0	1.0000	1465.2	440.7	0.0
N,N-dimethylformamide (A)+ Benzene (B)+ 2-ME (C)				N,N-dimethylformamide (A)+ Benzene (B)+ 2- EE (C)			
0.0000	1228.2	718.3	172.6	0.0000	1280.9	672.3	123.1
0.1048	1267.4	671.7	137.0	0.1128	1315.6	632.2	95.2
0.2085	1305.2	630.8	107.0	0.2224	1342.6	602.9	77.8
0.3111	1325.7	609.0	96.0	0.3290	1362.6	582.1	68.6
0.4127	1340.8	593.4	91.0	0.4327	1371.6	571.8	69.5
0.5131	1349.7	583.8	92.0	0.5336	1383.5	559.9	68.6
0.6125	1360.2	573.4	92.0	0.6318	1394.6	549.2	68.6
0.7109	1376.2	559.0	88.0	0.7275	1415.4	531.6	61.3
0.8083	1403.5	536.8	76.0	0.8207	1441.3	511.4	51.2
0.9046	1460.1	495.7	45.0	0.9115	1483.6	481.4	31.1
1.0000	1465.2	440.7	0.0	1.0000	1465.2	440.7	0.0

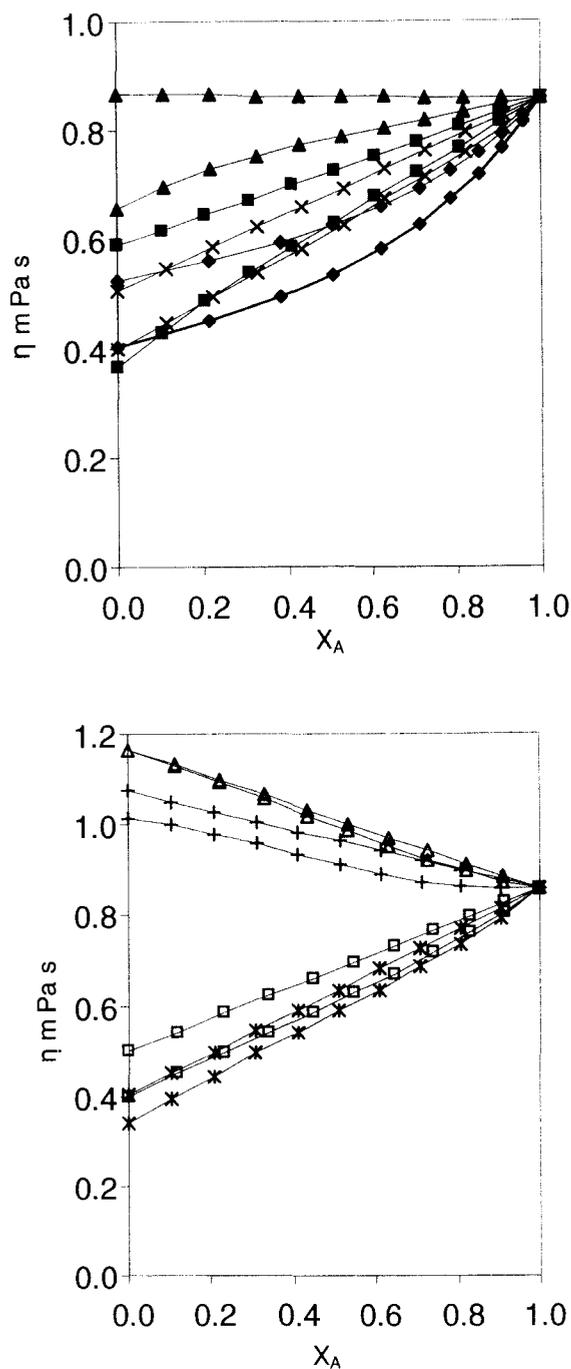


Fig.1. Calculated (....) and experimental (—) viscosity values of:(■),DMF (A)+ benzene (B)+ 1,3-DO (C); (▲),DMF (A) + benzene (B) + 1,4-DO (C); (◆),DMF (A) + benzene (B) + THF (C) ; (×), DMF(A) + benzene (B) + 1,2-DME (C); (□), DMF (A + benzene (B) + DIE (C); (ж),DMF (A) + benzene (B) + DEE (C); (+),DMF (A) + benzene (B)+ 2-ME (C) and (Δ), DMF (A)+ benz(B) + 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

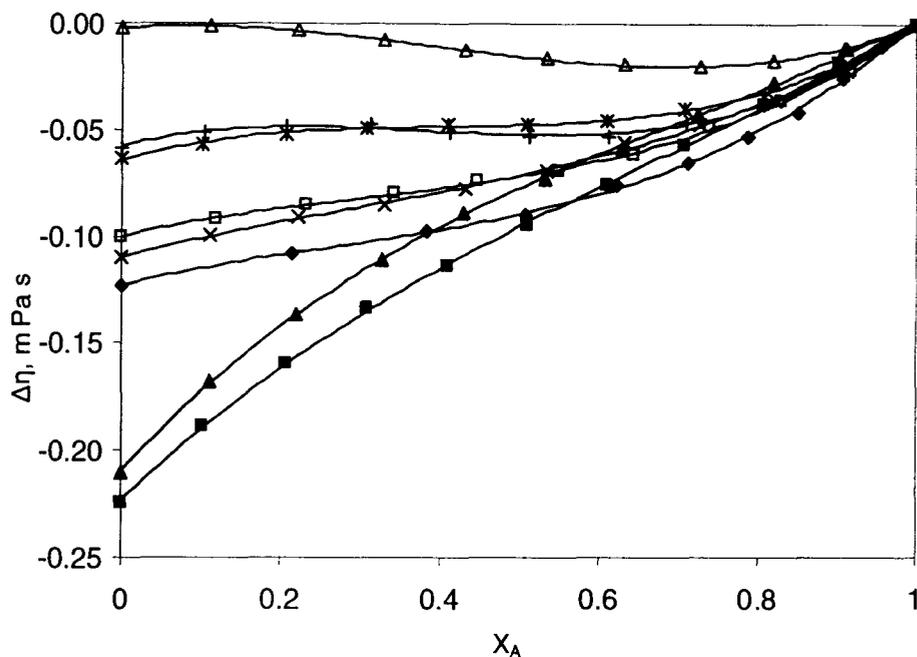


Fig. 2. Viscosity deviations ($\Delta\eta$) of: (■),DMF (A)+ benzene (B)+ 1,3-DO (C); (▲),DMF (A)+ benzene (B) + 1,4-DO (C); (◆),DMF (A) + benzene (B) + THF (C); (×),DMF (A) + benzene (B) + 1,2-DME (C); (□), DMF (A)+ benzene (B) + DIE (C); (⋈), DMF (A)+ benzene (B) + DEE (C); (+), DMF (A)+ benzene (B) + 2- ME (C) and(Δ), DMF (A)+ benzene (B)+ 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

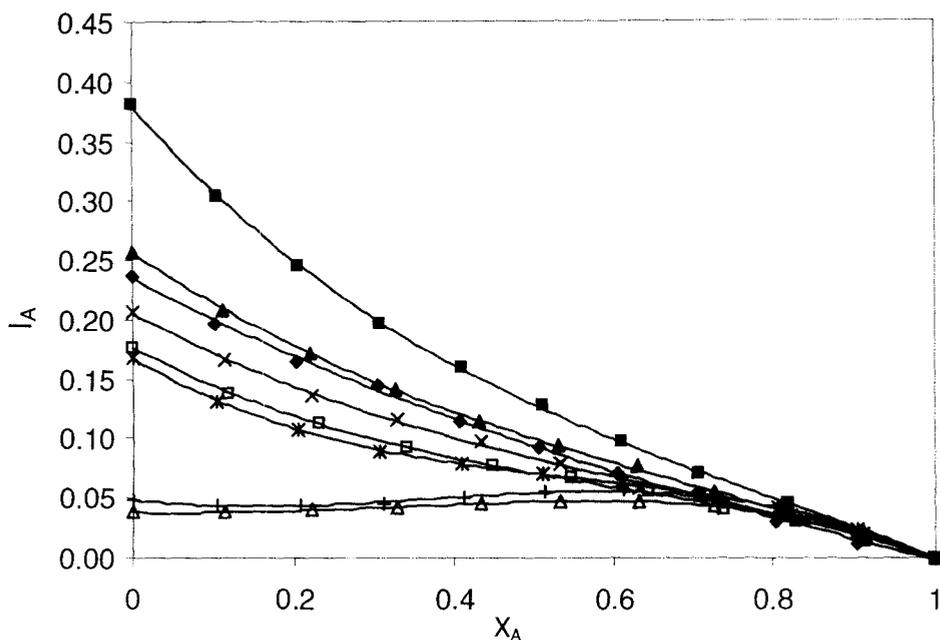


Fig. 3. Antagonistic Index (I_A) of: (■),DMF (A)+ benzene (B)+ 1,3-DO (C); (▲),DMF (A)+ benzene (B) + 1,4DO (C); (◆),DMF (A) + benzene (B) + THF (C); (×),DMF (A) + benzene (B)+ 1,2-DME (C); (□), DMF (A) benzene (B) + DIE (C); (*),DMF (A)+ benzene (B) + DEE (C); (+),DMF (A)+ benzene (B)+ 2-ME (C) and(Δ), DMF (A)+ benzene (B)+ 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

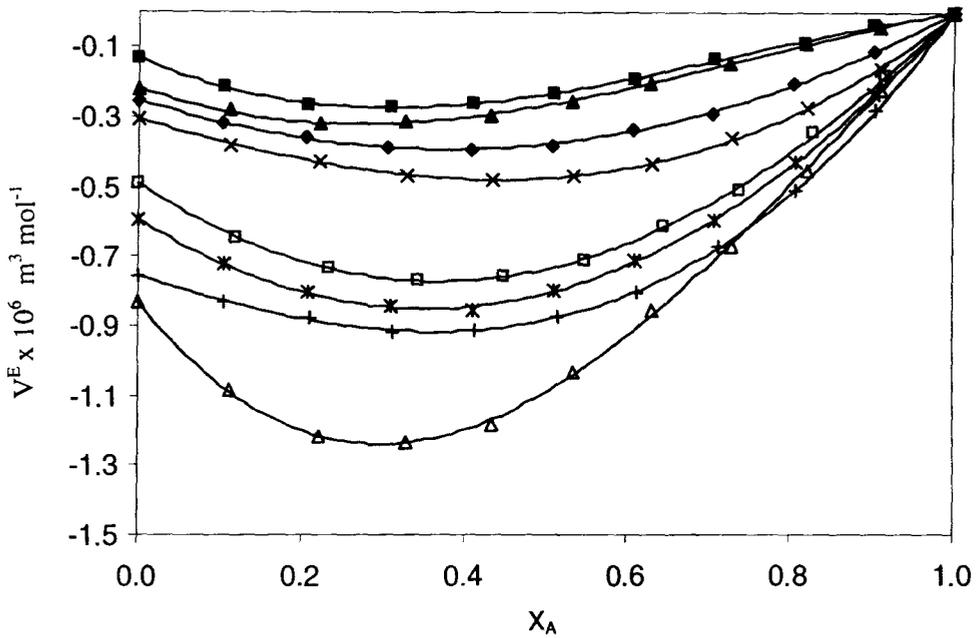


Fig. 4. Excess molar volumes (V^E) of : (■), DMF (A) + benzene (B) + 1,3- DO (C); (▲), DMF (A)+ benzene (B) + 1,4-DO (C); (◆),DMF (A) + benzene (B) + THF (C); (x), DMF (A) + benzene (B)+ 1,2-DME (C); (□), DMF (A)+benzene (B) + DIE (C); (ж),DMF (A)+ benzene (B) + DEE (C); (+), DMF (A)+ benzene (B)+ 2-ME (C) and(Δ), DMF (A)+ benzene (B)+ 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

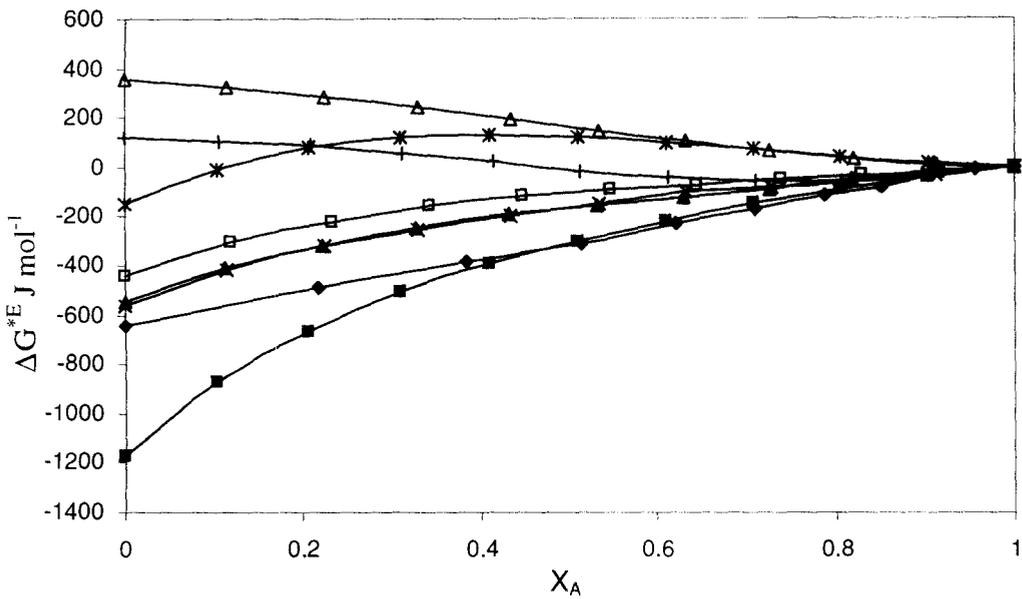


Fig. 5. Excess Gibbs energy, ΔG^{*E} of activation of viscous flow for of: (■),DMF (A)+ benzene(B)+ 1,3-DO (C); (▲),DMF (A) + benzene (B) + 1,4-DO (C); (◆),DMF (A) + benzene (B) + THF (C);(×),DMF (A) + benzene (B) + 1,2-DME (C); (□), DMF (A) benzene (B)+ DIE (C) ; (⋈), DMF (A) +benzene (B) + DEE (C); (+),DMF (A)+benzene (B)+ 2-ME (C) and (Δ),DMF (A)+ benzene (B)+ 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

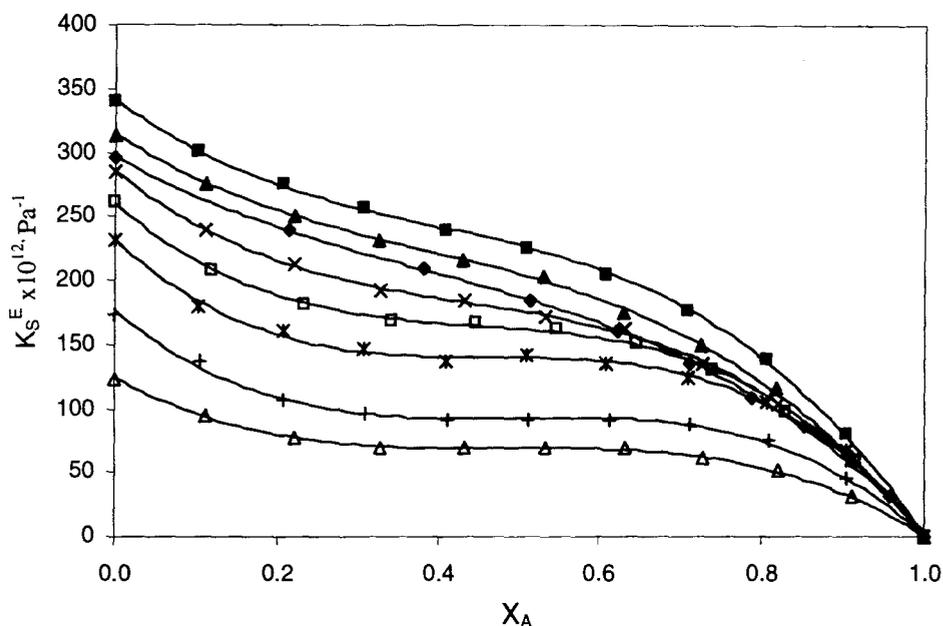


Fig.6. Excess isentropic compressibility (K_S^E) of: (■),DMF (A)+ benzene (B)+ 1,3-DO (C); (▲),DMF (A) +benzene (B) + 1,4-DO (C); (◆),DMF (A) + benzene (B) + THF (C); (×),DMF (A)+ benzene (B)+ 1,2-DME(C); (□), DMF (A) + benzene (B) + DIE (C); (ж),DMF (A) + benzene (B) + DEE (C); (+),DMF (A)+benzene (B)+ 2-ME (C) and (Δ), DMF (A)+ benzene (B)+ 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

CHAPTER VI

Study of Ion-Solvent Interactions of Some Tetraalkylammonium

Halides in THF + CCl₄ mixtures by Conductance measurements.

Keywords: Conductivity, Ion-pair, Triple-ion, Tetraalkylammonium halides, Solvation

6.1. Introduction

Studies on ionic solvation of tetraalkylammonium salts in solvents of low permittivity have assumed importance because of their applications in modern technology.¹ In media of low permittivity, salts are generally so associated that the state of the ionic species in solutions is most difficult to be elucidated. A number of conductometric² and related studies of electrolytes in non-aqueous solvents have been done in relation to the use of these types of electrolytes in high-energy batteries³ and for further understanding of organic reaction mechanisms.⁴

Further, after the classical work of Fuoss and Kraus⁵ in the thirties, there has been a renewed interest in the study of association and dimerization of electrolytes in media of low permittivity.⁶ This has been particularly of importance because knowledge of the state of association of the electrolytes along with the type and structure of the complex species in solution is essential for the optimal choice of solvents and electrolytes. The formation of triple ions in media having low permittivity⁷ ($\epsilon < 10$) have been investigated from the conductivity studies of tetraalkylammonium salts^{8,9} by fitting the Fuoss-Kraus equation. The minima observed in conductometric curves (Λ Vs \sqrt{c}) in this type of solvents were interpreted by the formation of M_2X^+ and MX_2^- triple-ion species.¹⁰

In the present study, the conductivity of tetraalkylammonium chloride, R_4NCl (R=Pentyl to Octyl) salts was examined in THF + CCl₄ mixtures with 40, 60 and 80 mass% of THF having dielectric constant (ϵ) = 4.376, 5.444 and 6.512 respectively.

6.2. Experimental Section

6.2.1. Source and purity of samples

Tetrahydrofuran (Merck, India) was kept for several days over KOH, refluxed for 24 h, and distilled over LiAlH_4 .^{7,9} The boiling point (66°C), density (0.8807 g/cm^3), and viscosity ($\eta_0 = 0.4630 \text{ mPa s}$) compared well with the literature values.⁹ The specific conductance of THF was $\approx 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 25°C . The purity of the solvent finally obtained was $>99.0\%$. The chemicals used were of analytical grade. Carbon tetrachloride ($>99.3\%$) was obtained from Merck. The organic liquids were further purified according to the procedure described in the literature¹¹⁻¹³ and the final purity was better than 99% . Tetraalkylammonium salts viz. tetrapentylammonium chloride (Pen_4NCl), tetrahexylammonium chloride (Hex_4NCl), tetraheptylammonium chloride (Hp_4NCl) and tetraoctylammonium chloride (Oct_4NCl) were of Fluka's purum or puriss grade and purified in the way given in the literature.¹⁴⁻¹⁷ Generally the salts were purified by recrystallisation. The crystallized salts were dried in vacuum. The salts were stored in glass bottles in darkened desiccators over fused CaCl_2 . The purity was determined by gas-liquid chromatography. The materials finally obtained were found to be $>99.0\%$ pure.

6.2.2. Apparatus and Procedure

Binary solvent mixtures have been prepared by mixing required volumes of tetrahydrofuran and carbon tetrachloride with earlier conversion of the required mass of each liquid into volume at 298.15 K .¹⁸ A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The value of the dielectric constant (ϵ) of the solvent mixtures was assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner.¹⁹

Densities (ρ) 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 pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The measurements were done in a thermostated water bath controlled to $\pm 0.01 \text{ K}$ of the desired temperature. The weighings were done on a Mettler electronic balance (AG-285)

with a precision of $\pm 0.01\text{mg}$. An average of triplicate measurement was taken into account. The density values were reproducible to $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature.²⁰⁻²² The accuracy of the viscosity measurements, based on our work on several pure liquids, was $\pm 0.003 \text{ mPa s}$. The details of the methods and measurement techniques had been described elsewhere.^{23, 24}

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, having cell constant 1.11 cm^{-1} . Measurements were made in a thermostatic water bath maintained at $298.15 \text{ K} \pm 0.01 \text{ K}$. The determination of the cell constant was done using a 0.1 (M) aqueous KCl solution. The cell was calibrated by the method of Lind et al.^{25, 26} All conductance data were determined at 1 KHz and were found to be $\pm 0.3 \%$ precise.

6. 3. Results and Discussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The experimental values of the molar conductances, Λ against the respective concentration, c of the tetraalkylammonium halides in different binary solvent mixtures of THF + CCl_4 mixtures at 298.15 K are presented in Table 2. Figures 1-3 give the graphical representation of Λ vs. \sqrt{c} which shows that all the salts follow the same trend, i.e. Λ decreases with increasing concentration, reaches a minimum and then increases.

The conductance data have been analyzed by the Fuoss-Kraus triple-ion theory^{5, 27} in the form as given below,

$$\Lambda \text{ g } \sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (1)$$

$$g(c) = \frac{\exp\left\{-\frac{\beta'}{\sqrt{\Lambda_0}} \sqrt{(c\Lambda)}\right\}}{\left\{1 - \frac{S}{\Lambda_0^{3/2}} \sqrt{(c\Lambda)}\right\} \sqrt{\left(1 - \frac{\Lambda}{\Lambda_0}\right)}} \quad (2)$$

$$\beta' = \frac{1.8247 \times 10^6}{(\epsilon T)^{3/2}} \quad (3)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8206 \times 10^6}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.501}{\eta_0 (\epsilon T)^{1/2}} \quad (4)$$

In the above equations, Λ_0 is the sum of the molar conductances of the simple ions at infinite dilution, Λ_0^T is the sum of the values of the two triple ions $R_4N(Cl_2)^-$ and $(R_4N)_2^+Cl$ for R_4NCl salts, K_p and K_T are the ion-pair and triple-ion formation constants respectively, S is the limiting Onsager coefficient. To make eq.1 applicable, the symmetrical approximation of the two possible formation constant of triple ions, $K_{T1} = [(R_4N)_2^+Cl] / ([R_4N^+][R_4NCl])$ and $K_{T2} = [R_4N(Cl_2)^-] / ([Cl^-][R_4NCl])$ equal to each other has been adopted, i.e. $K_{T1} = K_{T2} = K_T$.^{6,28}

The reference solvent used here is N, N-dimethylacetamide, (having a viscosity, 1.224 mPa s at 298.15 K). The limiting ionic conductances, Λ_0^+ and Λ_0^- in N, N- dimethyl acetamide taken from the work of Krumgalz²⁹ give the limiting molar conductances of the simple ions, Λ_0 , and the Walden's product, $\Lambda_0 \eta_0$ in the reference solvent. Λ_0 in THF + CCl_4 mixtures is then obtained by applying the Walden's rule³⁰ as suggested by Krumgalz. Λ_0^T is calculated by setting the triple-ion conductance equal to $2/3 \Lambda_0$.³¹ The ratio Λ_0^T / Λ_0 is equal to 0.667. The calculated values are listed in Table 3. Linear regression analysis of Eq.1 gives intercept and slope; here the values are also listed in

Table 3. The limiting molar conductances of the simple ions, Λ_0 and limiting molar conductances of the triple ions, Λ_0^T of the tetraalkylammonium salts in different binary solvent mixtures of THF + CCl₄ at 298.15 K follow the trend ,

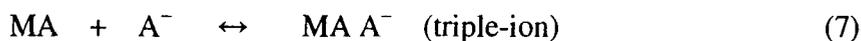
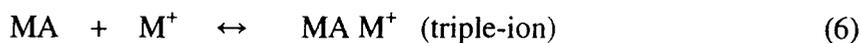


Table 3 shows that with increasing size of the tetraalkylammonium ions, both the limiting molar conductances of the simple ions, Λ_0 and that of the triple ions, Λ_0^T decrease in the different binary solvent mixtures of THF + CCl₄. Increase in Λ_0 significantly increase the mobility of ions due to lower solvation of the ions by the solvent molecules. So Pen₄N⁺ which has the smallest ionic size has the weakest solvation among the R₄N⁺ ions. Thus, the tendency of the ion-pair and triple-ion formation of R₄N⁺X⁻ depends on the size and the charge distribution of the ions. Similar type of results have been reported earlier by Roy et al.³²

Applying the Fuoss-Kraus equation, we obtain K_p , K_T , which are presented in Table 4. The K_p and K_T values predict that a major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadrupoles). Further, Oct₄NCl has the lowest K_p and highest K_T indicating that it has the highest amount of triple-ions and lowest number of ion-pairs formed in THF + CCl₄ mixtures as compared to the other salts.

The tendency of triple-ion formation can be also judged from the K_T / K_p ratios, which is highest for Oct₄NCl. The strong association between the ions may be due to the Coulombic interactions as well as to covalent bonding forces, considering the ionic sizes of the species in the solution. The results are in good agreement with the works of Hazra and Muhuri.³³

At very low permittivity of the solvent, i.e. $\epsilon < 10$, electrostatic ionic interactions are very strong. So the ion-pairs attract the free anions and cations present in the solution medium as the distance of the closest approach of the ions becomes minimum. This results in the formation of triple-ions which acquire the charge of the respective ions in the solution, i.e.^{5, 34}



The effect of ternary association³⁵ is to remove some non-conducting species MA from the solution and replace them by triple ions which contribute to the conductance. It is observed in Figs. 1-3 that Λ passes through a minimum as c increases.

Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T respectively, of the electrolyte are also calculated at the highest concentration of tetraalkylammonium halides in THF + CCl₄ mixtures using the following relations:³⁶

$$\alpha = 1 / K_P^{1/2} \cdot c^{1/2} \quad (8)$$

$$\alpha_T = (K_T / K_P^{1/2}) c^{1/2} \quad (9)$$

$$C_P = c (1 - \alpha - 3 \cdot \alpha_T) \quad (10)$$

$$C_T = (K_T / K_P^{1/2}) c^{3/2} \quad (11)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions as given in Table 5, respectively. These values show that, Pen₄NCl has the highest value of C_P and the lowest value of C_T , whereas Oct₄NCl has the highest value of C_T and the lowest value of C_P .

In Fig. 4, $\log (K_T/K_P)$ as given in Table 4 has been plotted against $\log C_{min}$, where, C_{min} is the salt concentration at the minimum conductivity of the halides in THF + CCl₄ mixtures. The graphs show an almost linear relationship. The value of $\log (K_T/K_P)$ is found to be highest in Oct₄NCl and lowest for Pen₄NCl as given in Table 4. Linear relationship holds good as long as the triple-ion formation is reasonably estimated and

assumed to form through complete electrostatic forces. The observations are in accordance with the results of Hojo and Chen.³⁷

6.4. Conclusion

An extensive study was done on the behavior of the tetraalkylammonium halides in THF + CCl₄ mixtures through conductometric measurements. It becomes clear that a major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions. The tendency of the ion-pair and triple-ion formation of R₄NX depends on the size of the ions. Further, it was found that Oct₄NCl had the highest amount of triple-ions and the lowest number of ion-pairs formed in different binary solvent mixtures of THF + CCl₄ as compared to the other electrolytes.

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Table 1. Density ρ , viscosity η , and dielectric constant ϵ , of different binary mixtures of THF and CCl₄ at 298.15 K

Solvent Mixture	$\rho \times 10^{-3} \text{ (kg m}^{-3}\text{)}$		$\eta \text{ (m Pa s)}$		ϵ
	Exp.	Lit.	Exp.	Lit.	
0 mass% of THF	1.580	1.585 ²²	0.9142	0.9128 ²²	2.240 ⁷
40 mass% of THF	1.2213	-	0.5367	-	4.376 ¹²
60 mass% of THF	1.0686	-	0.6383	-	5.444 ¹²
80 mass% of THF	0.9634	-	0.7164	-	6.512 ¹²
100mass%of THF	0.8807	0.8807 ¹¹	0.4630	0.4630 ¹¹	7.580 ⁷

Table 2. Equivalent conductances, Λ and the corresponding concentration, c for R_4NCl (R=Pentyl to Octyl) in different binary solvent mixtures of THF+CCl₄ at 298.15 K.

$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ S m ² mol ⁻¹	$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ S m ² mol ⁻¹	$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ S m ² mol ⁻¹	$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ S m ² mol ⁻¹
40 mass% of THF							
Pen₄NCl		Hex₄NCl		Hep₄NCl		Oct₄NCl	
0.1229	18.46	0.0185	108.00	0.0216	76.00	0.0219	71.76
0.1270	14.70	0.0250	95.80	0.0262	63.10	0.0270	71.69
0.1329	11.71	0.0320	85.60	0.0313	49.20	0.0304	71.68
0.1427	9.91	0.0404	77.80	0.0396	33.50	0.0354	71.74
0.1502	11.71	0.0502	72.30	0.0552	19.50	0.0386	71.78
0.1543	13.85	0.0600	71.00	0.0713	23.60	0.0434	71.87
0.1577	16.50	0.0729	74.40	0.0841	32.00	0.0466	71.94
0.1590	18.97	0.0876	82.10	0.0912	39.70	0.0512	72.04
60 mass% of THF							
0.3919	7.04	0.4186	7.20	0.1156	12.66	0.1018	11.60
0.4610	6.22	0.5535	5.74	0.1362	9.91	0.1129	10.08
0.5730	5.08	0.6512	4.88	0.1584	7.34	0.1232	8.91
0.6922	4.10	0.7586	4.15	0.1936	4.55	0.1384	7.20
0.7744	3.60	0.8427	4.20	0.2153	3.96	0.1513	6.28
0.8464	3.49	0.9216	4.40	0.2611	3.77	0.1722	5.24
0.9390	3.67	1.0000	4.75	0.3125	4.16	0.1927	5.88
1.0221	4.06	1.0858	5.22	0.3869	5.81	0.2134	7.10
80 mass% of THF							
0.9307	3.06	0.8711	3.34	0.5127	3.40	0.3606	4.75
1.0163	2.84	0.9791	3.19	0.5960	3.23	0.4109	4.55
1.1300	2.68	1.0498	3.06	0.6593	3.10	0.4581	4.37
1.2247	2.55	1.1539	2.92	0.7090	3.00	0.5041	4.23
1.3463	2.47	1.2221	2.83	0.7726	2.90	0.5521	4.11
1.4258	2.49	1.3226	2.74	0.8245	2.87	0.5960	4.03
1.5431	2.49	1.4280	2.71	0.8731	2.89	0.6464	4.00
1.6199	2.54	1.4855	2.84	0.9232	2.96	0.7039	4.05

Table 3. The calculated limiting conductance Λ_0 , slope and intercepts of eq.1 for R_4NCl (R = Pentyl to Octyl) in different binary solvent mixtures of THF+ CCl_4 at 298.15 K.

solvent mixture	$\Lambda_0 \times 10^4$ $S\ m^2\ mol^{-1}$	$\Lambda_0^T \times 10^4$ $S\ m^2\ mol^{-1}$	Slope $\times 10^3$	Intercept $\times 10^3$
40 mass% of THF	Pen ₄ NCl			
	141.34	94.22887	0.84	-0.27
	Hex ₄ NCl			
	139.95	93.30118	10.23	-0.30
	Hep ₄ NCl			
	139.18	92.78411	10.19	-1.16
	Oct ₄ NCl			
	139.08	92.72328	54.62	-1.17
60 mass% of THF	Pen ₄ NCl			
	118.85	79.23448	0.24	-0.27
	Hex ₄ NCl			
	117.68	78.45441	0.17	-0.18
	Hep ₄ NCl			
	117.03	78.01962	22.00	-15.46
	Oct ₄ NCl			
	116.95	77.96847	42.82	-19.76

Study of Ion-Solvent Interactionsby conductance measurements.

80 mass% of THF	Pen ₄ NCI			
	105.89	70.5939	1.25	-2.08
	Hex ₄ NCI			
	104.85	69.8989	1.10	-1.70
	Hex ₄ NCI			
	104.27	69.51152	15.02	-14.00
	Oct ₄ NCI			
	104.20	69.46595	24.17	-16.33

Table 4. $C_{min.}$, salt concentration at the minimum conductivity along with the ion-pair formation constant, K_P , Triple-ion formation constant, K_T , for R_4NCl (R=Pentyl to Octyl) in different binary solvent mixtures of THF+CCl₄ at 298.15 K.

Salts	$C_{min.} \times 10^4$ mol dm ⁻³	$\log C_{min.}$	$K_P \times 10^{-9}$ (mol dm ⁻³) ⁻¹	K_T (mol dm ⁻³) ⁻¹	(K_T / K_P) $\times 10^{10}$	$\log(K_T / K_P)$
40 mass% of THF						
Pen ₄ NCl	0.1427	-1.947	273.581	4.660	0.17	-10.769
Hex ₄ NCl	0.0600	-2.813	215.029	50.803	2.36	-9.627
Hep ₄ NCl	0.0552	-2.897	14.306	13.141	9.19	-9.037
Oct ₄ NCl	0.0304	-3.493	14.087	69.886	49.61	-8.304
60 mass% of THF						
Pen ₄ NCl	0.8464	-0.167	194.085	1.322	0.07	-11.167
Hex ₄ NCl	0.7586	-0.276	442.569	1.470	0.03	-11.479
Hep ₄ NCl	0.2611	-1.343	0.057	2.134	372.22	-7.429
Oct ₄ NCl	0.1722	-1.759	0.035	3.248	927.71	-7.033
80 mass% of THF						
Pen ₄ NCl	1.3463	0.297	2.591	0.900	3.47	-9.459
Hex ₄ NCl	1.4280	0.356	3.819	0.976	2.56	-9.593
Hep ₄ NCl	0.8245	-0.193	0.055	1.608	289.89	-7.538
Oct ₄ NCl	0.6464	-0.436	0.041	2.220	545.00	-7.264

Table 5. Maximum concentration c , the ion-pair fraction, α , triple-ion fraction, α_T , ion-pair concentration, C_P , triple-ion concentration, C_T for R_4NCl (R=Pentyl to Octyl) in different binary solvent mixtures of THF+CCl₄ at 298.15 K.

Salts	$C \times 10^4$ mol dm ⁻³	$\alpha \times 10^5$	$\alpha_T \times 10^5$	C_P mol dm ⁻³	$C_T \times 10^5$ mol dm ⁻³
40 mass% of THF					
Pen ₄ NCl	0.1590	0.076	0.355	0.159	0.056
Hex ₄ NCl	0.0876	0.064	3.243	0.088	0.284
Hep ₄ NCl	0.0858	0.245	3.219	0.086	0.276
Oct ₄ NCl	0.1900	0.367	25.667	0.190	4.877
60 mass% of THF					
Pen ₄ NCl	1.0221	0.229	0.303	1.022	0.310
Hex ₄ NCl	1.0858	0.157	0.230	1.086	0.250
Hep ₄ NCl	0.3869	8.215	17.530	0.387	6.782
Oct ₄ NCl	0.2134	7.807	25.362	0.213	5.413
80 mass% of THF					
Pen ₄ NCl	1.7331	2.586	2.327	1.733	4.033
Hex ₄ NCl	1.5491	2.014	1.966	1.549	3.045
Hep ₄ NCl	0.9722	13.239	21.287	0.971	20.695
Oct ₄ NCl	0.7813	13.850	30.742	0.780	24.018

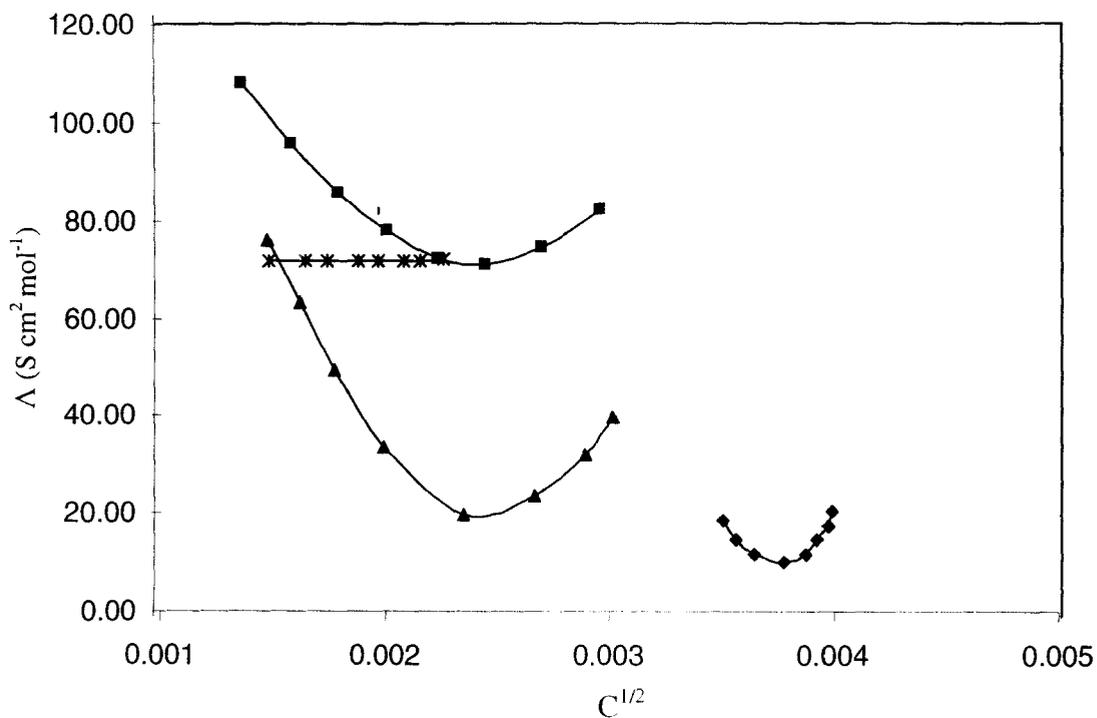


Figure 1. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at 298.15 K in 40 mass% of THF +CCl₄ solutions: (◆) Pen₄NCl; (■) Hex₄NCl; (▲) Hep₄NCl; (✱) Oct₄NCl.

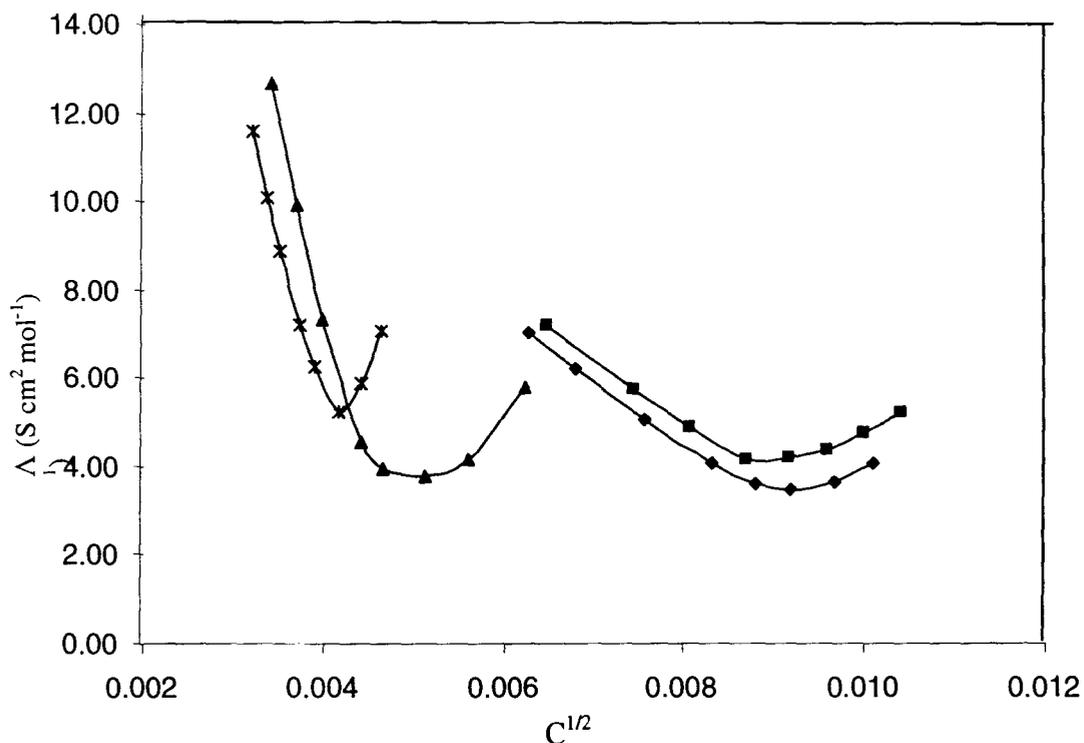


Figure 2. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at 298.15 K in 60 mass% of THF +CCl₄ solutions: (♦) Pen₄NCl; (■) Hex₄NCl; (▲) Hep₄NCl; (⋈) Oct₄NCl.

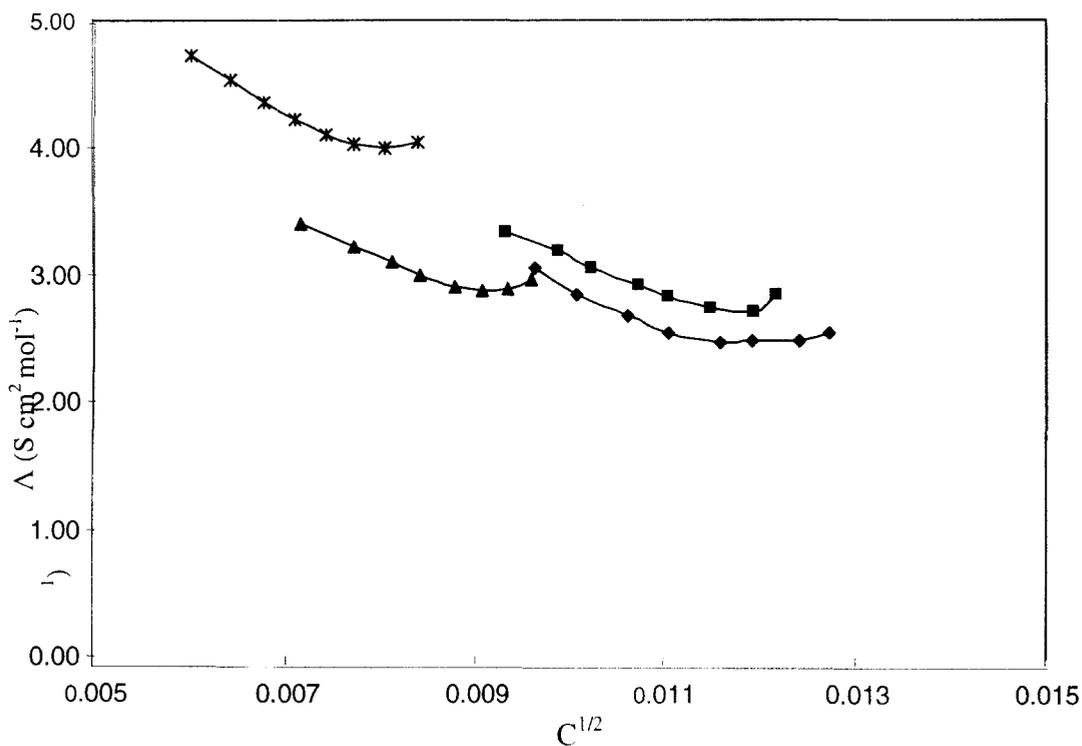


Figure 3. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at 298.15 K in 80 mass% of THF +CCl₄ solutions: (♦) Pen₄NCl; (■) Hex₄NCl; (▲) Hep₄NCl; (✱) Oct₄NCl.

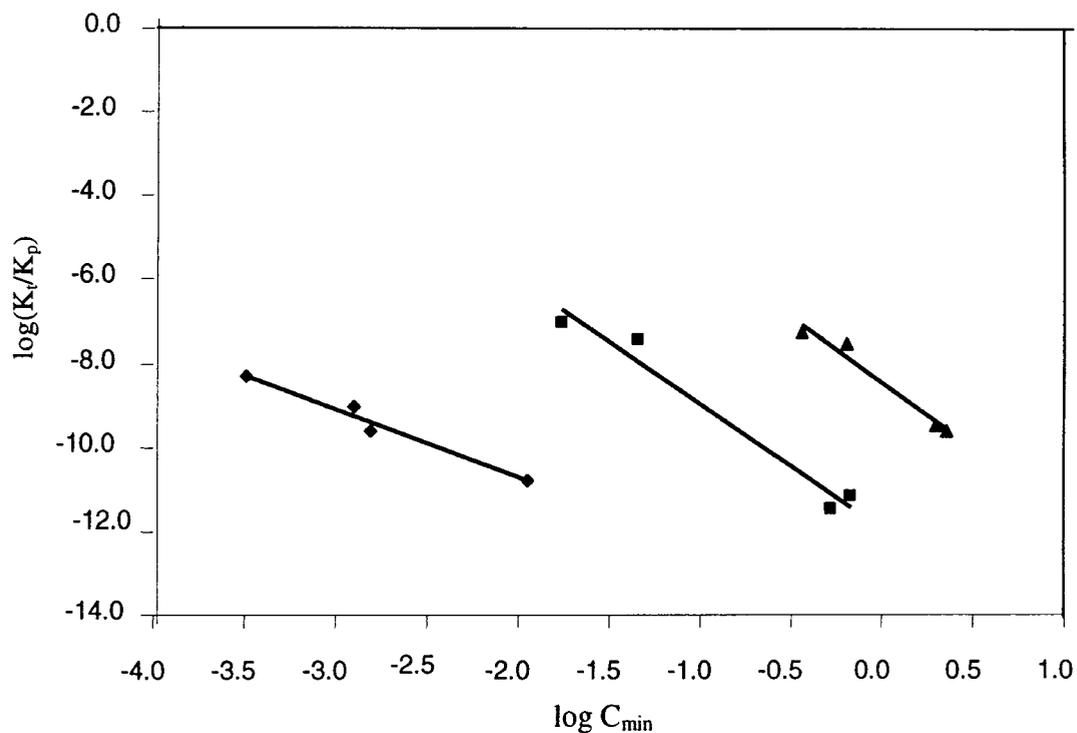


Figure 4. The plots of $\log (K_T/K_P)$ vs. $\log C_{min}$, where K_P is the ion-pair formation constant, K_T is the triple-ion formation constant and C_{min} is the salt concentration at the minimum conductivity for the salts under investigations at 298.15 K in different mass% of THF + CCl₄ mixtures: (♦) 40 mass%; (■) 60 mass%; (▲) 80 mass%.

CHAPTER VII

Partial molal volumes, viscosity *B*-coefficients and adiabatic compressibilities of some amino acids in aqueous resorcinol solutions at 298.15 K

Keywords: Partial molal volume, Viscosity *B*-coefficient, Isentropic compressibility, Amino acid.

7.1. Introduction

Globular proteins form a class of macromolecules which have well-defined physicochemical properties and functions in biological systems. They have a marginally stable native structure that results from a fine balance among various non-covalent forces: ionic and dipolar interactions, hydrogen bonding, and hydrophobic forces, etc.¹ The process of denaturation of a globular protein in aqueous solutions involves a change from the native state, in which the protein adopts its characteristic folded conformation, to the denatured state where the protein is predominantly in an extended form.^{2,3} During this process, substantial changes in protein solvation will occur, and these changes will make an important contribution to the energetics of protein denaturation. The study of these protein-solvent interactions is difficult because of the complexity of the interactions in such a large molecule. However, one useful approach, which can be of help in our understanding of these interactions, is to study simple compounds such as amino acids and peptides, which model some specific aspects of the protein structure.

The rigid nature of α helix structure of proteins and peptides are affected by alcohols via dissolution of peptide aggregates. Amino acids exist as zwitterions in aqueous solution. These dipolar ions should reflect structural interactions with water molecules as in the case of electrolytes. The properties of amino acids in aqueous alcohol solutions have been studied by some workers⁴⁻⁶ in order to understand the solute-solute interactions and the effects of various alcohols on proteins. It has been reported^{6,7} that

polyhydric alcohols increase the thermal stability of proteins or reduce the extent of their denaturation by other reagents. The properties of solutions of polyols in aqueous and mixed solutions are important in many areas of applied chemistry and are essential for understanding the chemistry of biological systems^{8,9} and act as vehicles for pharmaceuticals or cosmetics when introduced into living organisms. Resorcinol is an important organic compound, used externally as an antiseptic and disinfectant. It is also used as a chemical intermediate for the synthesis of pharmaceuticals and some organic compounds. An emerging use of resorcinol is as a template molecule in supramolecular chemistry. The -OH groups on resorcinol form hydrogen bonds to target molecules holding them in the proper orientation for a reaction. Resorcinol is readily soluble in water through hydrogen bonding.

Among the various physical parameters, the standard partial molal volume has been recognized as a quantity that is sensitive to structural changes occurring in solutions. In the present work we have studied the standard partial molal volumes of transfer of a homologous series of four amino acids in three different concentrations of aqueous Resorcinol solutions and interpreted the results in terms of possible interactions between solute and solvent molecules.

7.2. Experimental section

7.2.1 Source and purity of samples

The amino acids Glycine (Analar, >99%), DL-Alanine (S.D. fine Chemicals, >98.5%), L-valine (Loba Chemie, India, >99%), L-leucine (Loba Chemie, India, >99%). The amino acids were purified by re-crystallizing from methanol-water mixture and dried at 373.15 K for 12 h in vacuum desiccators over P₂O₅ before use. Resorcinol was purchased from Sd. Fine Chemical Limited. Resorcinol was purified by a reported procedure^{10,11} and the compound was dried and stored in a vacuum desiccator. Freshly distilled conductivity water was used for the preparation of different aqueous resorcinol solutions. The physical properties of different aqueous resorcinol solutions are listed in Table 1. Stock solutions of resorcinol in different aqueous resorcinol solutions were prepared by mass and the working solutions were prepared by mass

dilution. The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molarity of the resorcinol solutions is evaluated to $\pm 0.0001 \text{ mol dm}^{-3}$.

7.2.2. Apparatus and Procedure

Densities (ρ) 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 thermo stated bath controlled to $\pm 0.01 \text{ K}$. 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 $\pm 0.1 \text{ s}$, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was $\pm 2 \times 10^{-4} \text{ mPa s}$. 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 determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation losses during the actual measurements. The reproducibility in mole fraction was within ± 0.0002 units. The mass measurements were done on a Mettler AG-285 electronic balance with a precision of $\pm 0.01 \text{ mg}$. The precision of density measurements was $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$.

Ultrasonic speeds of sound (u) were determined by a multifrequency ultrasonic interferometer (Mittal enterprise, New Delhi, M-81) working at 2 MHz, calibrated with triply distilled and purified water, methanol and benzene at 298.15 K. The precision of ultrasonic speed measurements was $\pm 0.2 \text{ m s}^{-1}$. The details of the methods and techniques had been described elsewhere.^{12, 13}

7.3. Results and discussion

Standard partial molar volume and compressibility:

Densities of aqueous solutions of amino acids containing resorcinol determined at 298.15K are given in Table 2. These data were used to calculate the partial molar volume of the solute V_ϕ using the following equation,^{13, 14}

$$V_\phi = M/\rho - 1000(\rho - \rho_0)/m\rho_0 \quad (1)$$

where M is the molar mass of the solute in $\text{g}\cdot\text{mol}^{-1}$, m is the molality of solute in $\text{mol}\cdot\text{kg}^{-1}$ in the resorcinol-water mixture, and ρ and ρ_0 are the densities of the solution and the solvent, respectively. The partial molar volumes of the amino acids were found to be a linear function of molality over the studied concentration range. Hence, values of the standard partial molar volume, V_ϕ^0 were calculated by least-squares fitting using the following Masson equation:¹⁵

$$V_\phi = V_\phi^0 + S_v^* \sqrt{m} \quad (2)$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_v^* is the experimental slope, which is sometimes called volumetric pair wise interactions coefficient.¹⁶ The regression coefficients V_ϕ^0 and S_v^* of Eq. 2 for the amino acids in aqueous resorcinol are presented in Table 3., where values of V_ϕ^0 and S_v^* for the amino acids in pure water are adapted from the literature.^{17, 18}

The isentropic compressibility, K_ϕ , of the solution was calculated from the Laplace's equation:

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

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

The partial molar isentropic compressibility, K_ϕ , of the solutions was determined from the relation:

$$K_\phi = M K_S / \rho_0 + 1000 (K_S \rho_0 - K_S^0 \rho) / (m \rho \rho_0) \quad (4)$$

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

The standard partial molal isentropic compressibility, K_ϕ^0 , was obtained by extrapolating the plots of K_ϕ versus the square root of molal concentration of the solute, \sqrt{m} to zero concentration by a least-squares method,¹⁹

$$K_\phi = K_\phi^0 + S_K^* \sqrt{m} \quad (5)$$

where, S_K^* is the experimental slope. The regression coefficients K_ϕ^0 and S_K^* of Eq. 5 for the amino acids in aqueous resorcinol are presented in Table 4.

V_ϕ^0 and K_ϕ^0 values are by definition free from solute-solute interactions and thus provide information regarding solute- solvent interactions. Solute- solute interactions can be understood from the S_V^* and S_K^* values.

It is seen from Table 3 and Table 4 that, the S_V^* and S_K^* values for all the amino acids are positive. The positive S_V^* and S_K^* values indicate the dominance of the interaction of the charged functional groups of the zwitterionic amino acids over the pair wise interaction. With the introduction of additional methyl groups in the side chains of the amino acids, the S_V^* and S_K^* values also change indicating that, the methyl groups modulates the interaction of the charged end groups in pair wise interaction.

The values of V_ϕ^0 are positive for all the amino acids under study in aqueous resorcinol at all molalities studied. The V_ϕ^0 value increases gradually with the increase in concentration of aqueous resorcinol over the studied concentration range, except for the case of valine where V_ϕ^0 value decreases with the increase in the molality of resorcinol. From Table 4, it is observed that the value of standard partial molal isentropic compressibility K_ϕ^0 increases with the increase in concentration of resorcinol solution for all the concentration studied but all the values are negative.

At neutral pH, amino acid exist as zwitterions when dissolution in water and there is an overall decrease in the volume of water. This is due to the contraction of water near the end charged groups and termed as electrostriction. Hence the electrostricted water is much less compressible than bulk water and accounts for the partial molal compressibilities for the amino acids in mixed ternary solutions being larger than the

corresponding ones in water. It is also observed that the negative values of K_{ϕ}^0 for the studied amino acids follow the order -



Since the contribution of methylene group to the partial compressibility is negative, it implies that the ions having the larger hydrophobic group may have more negative values for the partial molal expansibilities. Hence L-leucine may have largest hydrophobic group resulting higher negative values of K_{ϕ}^0 .

Contributions of the zwitterionic end group, CH₂ groups and other alkyl chains of the α -amino acids to V_{ϕ}^0

At each molality, the V_{ϕ}^0 value varies linearly with the number of carbon atoms in the alkyl chain (R) of the amino acids. Similar correlations have been reported earlier by a number of workers,^{17, 18} and this linear variation can be represented as follows:

$$V_{\phi}^0 = V_{\phi}^0 (\text{NH}_3^+, \text{COO}^-) + N_C (\text{CH}_2) \quad (6)$$

where N_C is the number of carbon atoms in the alkyl chain of the amino acids and $V_{\phi}^0 (\text{NH}_3^+, \text{COO}^-)$ and $V_{\phi}^0 (\text{CH}_2)$ are the zwitterionic end group and methylene group contribution to V_{ϕ}^0 , respectively. The values of $V_{\phi}^0 (\text{NH}_3^+, \text{COO}^-)$ and $V_{\phi}^0 (\text{CH}_2)$, calculated by a least-square regression analysis, are listed in Table 5, where those values in pure water are also provided from the literature.¹⁹ It is well described in the literature²⁰ that $V_{\phi}^0 (\text{CH}_2)$ obtained by this scheme characterizes the mean contribution of the CH- and CH₃- groups to V_{ϕ}^0 of the amino acids. The contribution of the other alkyl chains of the amino acids has been calculated using a scheme, as suggested by Hakin et al.^{21, 22}

$$V_{\phi}^0 (\text{CH}_3) = 1.5 V_{\phi}^0 (\text{CH}_2) \quad (7)$$

$$V_{\phi}^0 (\text{CH}) = 0.5 V_{\phi}^0 (\text{CH}_2) \quad (8)$$

and are listed in Table 5. It shows that the contribution of $(\text{NH}_3^+, \text{COO}^-)$ to V_{ϕ}^0 is larger than that of the CH₂- group and increases with the increase in the concentration of the cosolute, which indicates that the interactions between the cosolute and charged

end groups (NH₃⁺,COO⁻) of amino acids are much stronger than those between the cosolute and CH₂.

Partial molal volumes of transfer of the zwitterionic end group, V_{ϕ}^0 (NH₃⁺,COO⁻), and other alkyl chain groups, V_{ϕ}^0 (R), of amino acids from water to cosolute solutions have been calculated as follows,

$$\Delta_{tr}V_{\phi}^0 (\text{NH}_3^+, \text{COO}^-) \text{ or } \Delta_{tr}V_{\phi}^0 (\text{R}) = \frac{V_{\phi}^0 (\text{NH}_3^+, \text{COO}^-) \text{ or } V_{\phi}^0 (\text{R}) [\text{in aqueous cosolute}] - V_{\phi}^0 (\text{NH}_3^+, \text{COO}^-) \text{ or } V_{\phi}^0 (\text{R}) [\text{in water}]}{1} \quad (9)$$

and are included in Table 5 and illustrated in Fig. 2. The contribution of (NH₃⁺,COO⁻) to $\Delta_{tr}V_{\phi}^0$ is positive throughout the studied concentration range of the cosolute and increases with the increase in the concentration of the cosolute. The contribution of the alkyl chain groups to $\Delta_{tr}V_{\phi}^0$ is negative for all the amino acids, and their contribution decreases with the increase in the number of carbon atoms.

The side chain contribution to the partial molar volume of the amino acids can be derived from the difference between the V_{ϕ}^0 values of each amino acid and that of glycine using the following scheme:

$$V_{\phi}^0 (\text{R}) = V_{\phi}^0 (\text{amino acid}) - V_{\phi}^0 (\text{glycine}) \quad (10)$$

where V_{ϕ}^0 (R) defines the side chain contribution to V_{ϕ}^0 of the respective amino acid relative to the H-atom of glycine. In this scheme, it is assumed that the volume contribution of the H-atom in glycine is negligible. The results are listed in Table 6.

The number of water molecule hydrated to the amino acids (N_w) in aqueous resorcinol solutions

The number of water molecules hydrated to the amino acids, N_w , calculated from the value of measured standard partial molar volume by the following manner.

The values of V_{ϕ}^0 of the studied amino acids can be expressed as,^{17, 23}

$$V_{\phi}^0 = V_{\phi}^0 (\text{int}) + V_{\phi}^0 (\text{elect}) \quad (11)$$

where V_{ϕ}^0 (int) is the intrinsic partial molar volume of the amino acid and V_{ϕ}^0 (elect) is the electrostriction partial molar volume as a result of hydration of the amino acids. The V_{ϕ}^0 (int) consists of two terms: the Vander waal volume and the volume due to packing effects. The values of V_{ϕ}^0 (int) for the amino acids were calculated from their crystal molar volume by Millero et al ¹⁷ using the following relationship,

$$V_{\phi}^0$$
 (int) = (0.7/0.634) V_{ϕ}^0 (cryst) (12)

where, 0.7 is the packing density in an organic crystal and 0.634 is the packing density of randomly packed spheres. The molar volume of crystals was calculated using the crystal densities of the amino acids represented by Berlin and Pallansch ²⁴ at 298.15 K. The values of V_{ϕ}^0 (elect) were obtained from the experimentally determined V_{ϕ}^0 values using Eq.11.

The number of water molecules hydrated to the amino acids due to electrostriction causes decrease in volume can be related to the hydration numbers,¹⁷

$$N_w = \frac{V_{\phi}^0$$
 (elect)}{V_E^0 - V_B^0} (13)

where V_E^0 is the molar volume of electrostricted water and V_B^0 is the molar volume of bulk water.

This model implies that the for every water molecules taken from the bulk phase to the surroundings of amino acid, the volume is decreased by $V_E^0 - V_B^0$, using a value of -3.0 cm³.mol⁻¹.¹⁷

The obtained N_w values are listed in Table 7, where N_w varies with the solvent composition, showing a tendency to decrease with an increase in the concentration of resorcinol for glycine and L-alanine under investigation. The observed decreasing tendency of N_w for glycine and L-alanine supports the view ²⁵ that the resorcinol has a dehydration effect on these amino acids in aqueous resorcinol solutions. In case of L-valine, a slight increase of N_w indicates that the increase in the interaction of hydrophobic groups of L-valine with those of the salt does not reduce the electrostriction of water molecules to it, but leads to a slight increase in the hydration

number, N_w . However, for L-Leucine, the N_w values remain unaltered by resorcinol concentration. This indicates that, the hydrophobic group of leucine reduces the ion-ion interaction between the amino acid and the salt.

Partial molar volume of transfer from water to aqueous resorcinol solution

The values of partial molar volume of transfer and partial molar compressibility of transfer of the amino acid¹⁸ from pure water to resorcinol are obtained from the eqns.

$$\Delta_{tr}V_{\phi}^0 \text{ (water to aqueous resorcinol)} = V_{\phi}^0 \text{ (in aqueous resorcinol)} - V_{\phi}^0 \text{ (in water)} \quad (14)$$

$$\Delta_{tr}K_{\phi}^0 \text{ (water to aqueous resorcinol)} = K_{\phi}^0 \text{ (in aqueous resorcinol)} - K_{\phi}^0 \text{ (in water)} \quad (15)$$

These results are reported in Table 8 and Table 9, graphically shown in Fig 1 and Fig 3 respectively. Since the solute-solute interactions are absent at infinite dilution, the observed transfer volume reflects the solute-solvent interactions. In general, the interactions between amino acids and resorcinol can be classified into: (i) Ion-polar group interactions between the NH_3^+ and COO^- groups of the Zwitterionic amino acid with the OH groups of the resorcinol; (ii) ion-non polar group interactions between the NH_3^+ and COO^- groups of the amino acid with the phenyl group of the resorcinol; (iii) Nonpolar- nonpolar group of interactions between the hydrophobic parts of the acids with the hydrophobic part of the resorcinol.. According to the cosphere overlap model of Gurney,²⁶ interactions of type (i) and (ii) lead to a positive $\Delta_{tr}V_{\phi}^0$ value, whereas type (iii) would lead to a negative $\Delta_{tr}V_{\phi}^0$ value because the introduction of alkyl groups provides an additional tendency for hydrophilic-hydrophobic and hydrophobic-hydrophobic group interactions leading to a reduction in the overall structure of water formed as a result of their cosphere overlap. Positive and negative values of volume transfer were observed for the studied amino acids (Table 8). The values of $\Delta_{tr}V_{\phi}^0$ for glycine, alanine increase positively with the increasing concentration of resorcinol. However for valine and leucine, the transfer value decreases.

The intrinsic volume is expressed by the following two types of terms

$$V_{intrinsic} = V_{vw} + V_{void} \quad (16)$$

Where V_{vw} is the Vanderwaal volume,²⁷ occupied by solute and V_{void} is the volume of void and empty spaces present there in.²⁸

Shahidi et al²⁹ modified the above equation to express the contribution of the solute molecules to its partial molar volume.

$$V_{\phi}^0(\text{int}) = V_{vw} + V_{void} - n \bar{\sigma}_s \quad (17)$$

Where $\bar{\sigma}_s$ is the shrinkage in the volume due to the interaction of hydrogen bonding groups present in the solute with water molecules and 'n' is the number of potential hydrogen bonding sites in the molecule.

Hence, the V_{ϕ}^0 of the amino acid can be expressed as:

$$V_{\phi}^0 = V_{vw} + V_{void} - V_{shrinkage} \quad (18)$$

Assuming the fact that V_{vw} and V_{void} remain unchanged in water as well as in aqueous resorcinol solution the positive volume transfer of the amino acid can be documented from a decrease in the volume of shrinkage in the presence of the resorcinol solute in aqueous solutions.

The observed positive values of $\Delta_{tr}V_{\phi}^0$ and $\Delta_{tr}K_{\phi}^0$ of glycine indicate that the ion-hydrophilic and hydrophilic-hydrophilic interactions mask the ion-hydrophobic and hydrophobic-hydrophobic group interactions. The ion-hydrophilic interaction takes place between OH group resorcinol and charge end groups (NH_3^+ and COO^-) reduces the electrostriction phenomenon resulting in an increase in volume.

But for DL-alanine most of the values are negative though very small implies a balance of type (i) to (iii) interactions and at higher concentration 0.15(M) the values are positive indicates the predominance of ion-hydrophilic interactions.

But in the case of L-valine owing to large hydrophobic part in the side chain leading to hydrophobic – hydrophobic group interaction, with the hydrophobic part of resorcinol resulting in a negative volume and compressibility of transfer but with the increase of

the concentration of resorcinol the negative values are lower i.e., tend to be positive indicating (i) type of interactions tends to predominant.

But in the case of L-leucine the observed values, being more and more negative, strongly indicate the large hydrophobic part reside in the side chain of leucine. Similar observation shown by Bannerjee et al³⁰ and in lit.³¹

Viscosity *B*-Coefficient.

The experimental viscosity data for the systems studied are listed in Table 2. The relative viscosity (η_r) has been analyzed using the Jones-Dole equation³²

$$\eta_r = \eta / \eta_o = 1 + A\sqrt{c} + Bc \quad (19)$$

where η and η_o are the viscosities of the ternary solutions (amino acid +resorcinol+ water) and binary solvents (resorcinol+water)and c is the molarity of the amino acids in ternary solutions. A and B are empirical constants known as viscosity A - and B -coefficients, which are specific to solute-solute and solute solvent interactions, respectively. Eq.19 can be rearranged

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

Values of A - and B -coefficients are obtained from a linear plot of the left-hand side of Eq.20 vs \sqrt{c} . The values of A - and B -coefficients are listed in Table 10. Due to the complex nature of A -coefficients, they are not discussed in the present work. Table 10 shows that B -coefficients are positive for all the amino acids and increase with the increase of the size of the side chains. The B -coefficients reflect the net structural effects of the charged groups and the hydrophobic CH_2 - groups on the amino acids. As B -coefficients vary linearly with the number of carbon atoms of the alkyl chain (N_C), these two effects can be resolved as follows

$$B = B(\text{NH}_3^+, \text{COO}^-) + N_C B(\text{CH}_2) \quad (21)$$

The regression parameters, i.e., the zwitterionic group contribution, $B(\text{NH}_3^+, \text{COO}^-)$, and the methylene group contribution, $B(\text{CH}_2)$, to B -coefficients are listed in Table 11. It shows that $B(\text{NH}_3^+, \text{COO}^-)$ values decrease while $B(\text{CH}_2)$ values increase with

increasing concentration of resorcinol in ternary solutions, indicating that the zwitterionic groups break while the CH₂-group enhances the structure of the aqueous salt solutions. The side chain contributions to *B*-coefficients, *B*(R), have also been derived using the same scheme as that of V_{ϕ}^0 (R) and are listed in Table 5, which shows that *B*(R) values are positive and follow the order: L-leucine > L-valine > DL-alanine. This order is due to the greater structure breaking tendency of L-leucine as compared to L-valine and DL-alanine, and these findings are in line with our volumetric results discussed earlier.

The viscosity data are also analyzed on the basis of transition state theory for relative Viscosity of the acetate solutions as suggested by Feakins et al.³³ using Eq 22:

$$\Delta\mu_2^{\circ*} = \Delta\mu_1^{\circ*} + (RT/V_1^{\circ})(1000B + V_2^{\circ} - V_1^{\circ}) \quad (22)$$

where $\Delta\mu_2^{\circ*}$ is the contribution per mole of the solute to free energy of activation for viscous flow of solutions and $\Delta\mu_1^{\circ*}$ is the free energy of activation per mole of solvent mixture. The values are reported in Table 12. V_1° is the partial molal volume of the solvent mixture, V_2° is the partial molal volume of the solute. $\Delta\mu_1^{\circ*}$ is calculated from

$$\Delta\mu_1^{\circ*} = \Delta G_1^{\circ*} = RT \ln (\eta_0 V_1^{\circ} / h N_A) \quad (23)$$

where *h* is Planck's constant and *N_A* is Avogadro's number. From Table 12, it is seen that $\Delta\mu_1^{\circ*}$ is almost constant at all solvent compositions. It means that $\Delta\mu_2^{\circ*}$ is dependent mainly on the values of viscosity *B*-coefficients and ($V_2^{\circ} - V_1^{\circ}$) terms. It is also evident from Table 12 that the $\Delta\mu_2^{\circ*}$ values are positive and much larger than the $\Delta\mu_1^{\circ*}$ values. This may be due to the fact that amino-acid-solvent interactions in the ground state are stronger than in the transition state. In other words, the solvation of amino acids in the transition state is unfavourable in terms of free energy. Furthermore, as $\Delta\mu_2^{\circ*} > \Delta\mu_1^{\circ*}$, for solutes having positive viscosity *B*-coefficients indicates a stronger solute-solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.³⁴ The $\Delta\mu_2^{\circ*}$ values (Table 12) of the amino acids were found to increase from Glycine to Leucine. This indicates that the solvation of the amino acids

in the transition state becomes increasingly unfavourable as the hydrophobicity (number of carbon atoms) of the side chain increases from Glycine to Leucine.

7.4. Conclusion

In summary; volume, viscosity and compressibility data have been determined for amino acids in aqueous resorcinol and the results have been used to estimate the volume and compressibility of transfer, number of hydrated water molecules and the viscosity *B*-coefficient values. The study reveals that although ion-ion or hydrophilic-hydrophilic group interactions are predominant for glycine and L-alanine, ion-hydrophobic or hydrophobic-hydrophobic group interactions are predominant for L-valine and L-leucine in aqueous resorcinol solutions. These interactions are a function of the molality of resorcinol in the ternary solutions. Also, it is evident that resorcinol has a dehydration effect on these amino acids in aqueous resorcinol solutions. The size and number of carbon atoms of the alkyl chain groups of the amino acids also play a pivotal role in determining the nature and strength of the interactions in these solvent media.

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Table 1. Experimental densities (ρ), viscosities (η), sound speed (u) of aqueous resorcinol solutions at all experimental concentration at 298.15 K

Molality of resorcinol in water mol kg ⁻¹	$\rho \times 10^{-3}$ kg.m ⁻³	η mPa.s	u ms ⁻¹
$m_s = 0.05$	0.9992	0.9013	1572.3
$m_s = 0.10$	1.0003	0.9102	1721.1
$m_s = 0.15$	1.0012	0.9208	1908.3

Table 2. Experimental molalities $m/\text{mol.kg}^{-1}$, densities $\rho \times 10^{-3}/\text{Kg.m}^{-3}$, viscosities $\eta/\text{mPa.s}$, sound speed u/ms^{-1} , partial molar volume of the solute $V\phi \times 10^6/\text{m}^3.\text{mol}^{-1}$ and partial molal isentropic compressibility $K\phi \times 10^{10}/\text{m}^3.\text{mol}^{-1}\text{Pa}^{-1}$ along with the concentration m_s of Glycine, DL-Alanine, L-Valine and L-Leucine in aqueous resorcinol solutions as a function of the molalities of Amino Acids.

m mol.kg^{-1}	$\rho \times 10^{-3}$ Kg.m^{-3}	η mPa.s	u ms^{-1}	$V\phi \times 10^6$ $\text{m}^3.\text{mol}^{-1}$	$K\phi \times 10^{10}$ $\text{m}^3.\text{mol}^{-1}\text{Pa}^{-1}$
$m_s=0.05$					
Glycine					
0.0246	1.0000	0.9066	1710.7	43.64	-25.78
0.0322	1.0002	0.9082	1757.7	43.99	-25.34
0.0566	1.0010	0.9123	1933.4	43.83	-24.41
0.0726	1.0014	0.9143	2077.0	44.01	-23.97
0.0888	1.0020	0.9169	2268.1	43.95	-23.82
0.101	1.0023	0.9191	2451.8	44.11	-23.72
DL-Alanine					
0.0258	0.9999	0.9088	1704.8	60.29	-23.66
0.0358	1.0002	0.9118	1761.6	60.35	-23.20
0.0632	1.0010	0.9185	1947.5	60.43	-22.47
0.0793	1.0015	0.9220	2081.5	60.32	-22.07
0.0978	1.0020	0.9262	2280.7	60.38	-21.85
0.1114	1.0024	0.9296	2455.5	60.44	-21.55
L-Valine					
0.0263	0.9999	0.9087	1741.2	90.43	-28.63
0.0337	1.0001	0.9119	1793.5	90.45	-28.01
0.0596	1.0008	0.9208	2029.5	90.50	-27.32
0.0762	1.0012	0.9271	2225.1	90.46	-26.74
0.0951	1.0018	0.9346	2527.6	90.48	-26.21
0.1101	1.0021	0.9405	2862.8	90.52	-25.77
L-Leucine					
0.0252	0.9998	0.9097	1762.3	106.12	-32.99
0.0360	1.0001	0.9143	1856.9	106.20	-32.01
0.0619	1.0007	0.9226	2174.1	106.18	-31.34
0.0753	1.0011	0.9282	2398.0	106.21	-30.78
0.0954	1.0016	0.9394	2923.5	106.27	-30.26
0.1091	1.0019	0.9507	3565.7	106.24	-29.97
$m_s=0.10$					
Glycine					
0.0243	1.0011	0.9149	1858.2	43.78	-19.91
0.0325	1.0013	0.9163	1902.7	43.81	-19.04
0.0573	1.0021	0.9201	2074.9	44.02	-18.51
0.0731	1.0026	0.9228	2179.0	43.90	-17.49
0.0897	1.0031	0.9247	2274.2	43.84	-16.19
0.1018	1.0034	0.9271	2366.4	44.09	-15.72
DL-Alanine					
0.0253	1.0010	0.9173	1873.2	60.46	-20.94
0.035	1.0013	0.9196	1935.4	60.49	-20.32

Contd.....

Apparent molar volumes and viscosity *B*-coefficients.....at 298.15K

0.0617	1.0021	0.9261	2149.6	60.48	-19.75
0.0768	1.0025	0.9299	2298.5	60.51	-19.41
0.0969	1.0031	0.9348	2541.6	60.52	-18.94
0.1104	1.0034	0.9371	2739.1	60.56	-18.57
L-Valine					
0.0258	1.0010	0.9163	1933.8	89.42	-27.34
0.0344	1.0013	0.9195	2007.9	89.55	-26.16
0.0621	1.0020	0.9269	2336.3	89.46	-24.95
0.0784	1.0025	0.9343	2575.3	89.34	-23.90
0.0964	1.0030	0.9420	3007.3	89.18	-23.60
0.1102	1.0034	0.9468	3428.6	89.12	-22.95
L-Leucine					
0.0248	1.0009	0.9067	1954.9	106.30	-30.74
0.0349	1.0012	0.9115	2073.4	106.36	-30.19
0.0613	1.0018	0.9220	2536.5	106.35	-29.79
0.0760	1.0022	0.9276	2934.8	106.39	-29.20
0.0941	1.0026	0.9370	3826.2	106.38	-28.65
0.1068	1.0029	0.9440	4649.0	106.40	-27.30
$m_3=0.15$					
Glycine					
0.0243	1.0020	0.9247	2027.1	43.84	-12.98
0.0326	1.0022	0.9260	2073.2	43.76	-12.98
0.0573	1.0030	0.9294	2176.9	43.98	-11.20
0.0732	1.0035	0.9323	2230.3	43.72	-10.15
0.09	1.0040	0.9348	2266.5	44.09	-8.98
0.1024	1.0044	0.9367	2252.3	43.86	-7.67
DL-Alanine					
0.0258	1.0019	0.9267	2059.8	60.72	-15.18
0.0346	1.0022	0.9294	2116.2	60.76	-14.92
0.0619	1.0029	0.9356	2310.8	60.79	-14.18
0.0792	1.0034	0.9385	2450.0	60.84	-13.70
0.0972	1.0039	0.9431	2603.0	60.76	-13.12
0.1098	1.0043	0.9469	2723.7	60.81	-12.78
L-Valine					
0.0257	1.0019	0.9260	2169.2	89.08	-24.22
0.0353	1.0022	0.9279	2291.4	89.03	-23.89
0.0627	1.0030	0.9370	2674.1	88.98	-21.52
0.0791	1.0034	0.9430	3040.2	89.01	-21.05
0.0968	1.0039	0.9495	3669.7	88.99	-20.69
0.1108	1.0043	0.9556	4098.9	88.95	-19.4
L-Leucine					
0.0246	1.0018	0.9038	2195.7	106.53	-27.36
0.0352	1.0021	0.9101	2336.7	106.55	-26.02
0.0627	1.0027	0.9196	2878.6	106.58	-24.56
0.0792	1.0031	0.9274	3321.8	106.55	-23.23
0.0975	1.0036	0.9365	4208.9	106.61	-22.36
0.1107	1.0039	0.9436	5232.3	106.58	-21.78

Table 3. Standard partial molar volumes of amino acids in aqueous resorcinol solution at 298.15 K.

Amino acids	Parameters	water	$m_s = 0.05$	$m_s = 0.10$	$m_s = 0.15$
Glycine	$\frac{V_\phi^0 \times 10^6}{m^3 \cdot \text{mol}^{-1}}$	43.14(± 0.06) ³⁴	43.28	43.59	43.72
	S_v^*	0.86	2.35	1.26	0.58
DL- Alanine	$\frac{V_\phi^0 \times 10^6}{m^3 \cdot \text{mol}^{-1}}$	60.43(± 0.73) ³⁴	60.18	60.21	60.59
	S_v^*	0.73	0.69	0.12	0.05
L-Valine	$\frac{V_\phi^0 \times 10^6}{m^3 \cdot \text{mol}^{-1}}$	90.39(± 0.14) ³⁴	90.37	89.87	89.15
	S_v^*	-	0.41	-2.12	-0.58
L-Leucine	$\frac{V_\phi^0 \times 10^6}{m^3 \cdot \text{mol}^{-1}}$	107.72(± 0.24) ₃₄	106.04	106.25	106.48
	S_v^*	-	0.65	0.47	0.33

Table 4. Standard partial isentropic compressibilities of amino acids in aqueous resorcinol solution at 298.15

Amino acids	Parameters	water	$m_s = 0.05$	$m_s = 0.10$	$m_s = 0.15$
Glycine	$\frac{K_\phi^0 \times 10^{10}}{m^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}}$	-27.00 ¹⁷	-27.70	-23.80	-18.52
	S_k^*	4.56	13.11	24.55	32.15
DL- Alanine	$\frac{K_\phi^0 \times 10^{10}}{m^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}}$	-25.26 ¹⁷	-26.32	-22.87	-17.52
	S_k^*	4.75	11.13	12.73	13.96
L-Valine	$\frac{K_\phi^0 \times 10^{10}}{m^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}}$	-30.62 ¹⁷	-31.12	-30.95	-28.71
	S_k^*	8.43	15.97	24.23	27.24
L-Leucine	$\frac{K_\phi^0 \times 10^{10}}{m^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}}$	-31.78 ¹⁷	-35.45	-33.61	-32.11
	S_k^*	13.61	16.79	17.18	31.13

Table 5. Contribution of the Zwitterionic End Group (NH₃⁺COO⁻), CH₂- Group, and Other Alkyl Chain Groups (R) to Standard Partial Molar Volume, V_{ϕ}^0 , and Transfer Volumes, $\Delta_{tr}V_{\phi}^0$ in Different Aqueous Resorcinol Solutions at 298.15 K

group	$V_{\phi}^0 \times 10^6$ $\text{m}^3 \cdot \text{mol}^{-1}$				$\Delta_{tr}V_{\phi}^0 \times 10^6$ $\text{m}^3 \cdot \text{mol}^{-1}$		
	Water	$m_s=0.05$	$m_s=0.10$	$m_s=0.15$	$m_s=0.05$	$m_s=0.10$	$m_s=0.15$
NH ₃ ⁺ COO ⁻	27.68	28.25	28.49	28.76	0.57	0.81	1.08
CH ₂	15.91	15.57	15.50	15.41	-0.34	-0.41	-0.50
CH ₃ CH	31.82	31.14	31.00	30.82	-0.68	-0.82	-1.00
(CH ₃) ₂ CHCH	63.64	62.28	61.99	61.63	-1.36	-1.65	-2.01
(CH ₃) ₂ CHCH ₂ CH	79.45	77.86	77.49	77.04	-1.60	-1.96	-2.41

Table 6. Contribution of the Alkyl Chain Group (R) to Standard Partial Molar Volume, $V_{\phi}^0(R)$, and Viscosity *B*-Coefficient *B*(R) in Different Aqueous Resorcinol Solutions at 298.15 K

group	$V_{\phi}^0(R) \times 10^6$ $\text{m}^3 \cdot \text{mol}^{-1}$			<i>B</i> (R) $\text{m}^3 \cdot \text{mol}^{-1}$		
	$m_s=0.05$	$m_s=0.10$	$m_s=0.15$	$m_s=0.05$	$m_s=0.10$	$m_s=0.15$
DL- Alanine	16.90	16.62	16.87	0.094	0.09	0.08
L-Valine	47.09	46.28	45.43	0.312	0.31	0.30
L-Leucine	62.76	62.66	62.76	0.430	0.46	0.50

Table 7. Hydration number (N_w) of amino acids in aqueous resorcinol at 298.15 K.

Amino acids	N_w		
	$m_s=0.05$	$m_s=0.10$	$m_s=0.15$
Glycine	2.9	2.8	2.7
DL-Alanine	3.9	3.8	3.7
L-Valine	4.0	4.2	4.4
L-Leucine	6.0	6.0	6.0

Table 8. Transfer volumes of amino acids ($\Delta_{tr}V_{\phi}^0 \times 10^6/\text{m}^3 \cdot \text{mol}^{-1}$) from water to aqueous resorcinol, at 298.15 K.

Amino- acids	$\Delta_{tr}V_{\phi}^0 \times 10^6/\text{m}^3 \cdot \text{mol}^{-1}$		
	$m_s=0.05$	$m_s=0.1$	$m_s=0.15$
Glycine	0.24	0.39	0.58
DL-Alanine	-0.10	-0.02	0.08
L-Valine	-0.78	-0.84	-0.93
L-Leucine	-1.02	-1.15	-1.33

Table 9 Transfer compressibilities of amino acids ($\Delta_{tr}K_{\phi}^0 \times 10^6/\text{m}^3 \cdot \text{mol}^{-1}$) from water to aqueous resorcinol, at 298.15 K

Amino- acids	$\Delta_{tr}K_{\phi}^0 \times 10^6/\text{m}^3 \cdot \text{mol}^{-1}$		
	$m_s=0.05$	$m_s=0.1$	$m_s=0.15$
Glycine	-0.70	3.20	8.48
DL-Alanine	-1.06	2.39	7.74
L-Valine	-0.50	-0.33	1.91
L-Leucine	-3.67	-1.83	-0.33

Table 10. *A*- and *B*-coefficients for the amino acids in aqueous resorcinol solutions at 298.15 K.

Amino- acids	$B/\text{m}^3 \cdot \text{mol}^{-1}$			$A/\text{m}^{3/2} \cdot \text{mol}^{-1/2}$		
	$m_s=0.05$	$m_s=0.1$	$m_s=0.15$	$m_s=0.05$	$m_s=0.1$	$m_s=0.15$
Glycine	0.140	0.148	0.165	0.020	0.013	0.003
DL-Alanine	0.234	0.241	0.247	0.016	0.011	0.002
L-Valine	0.453	0.456	0.463	-0.020	-0.031	-0.045
L-Leucine	0.571	0.604	0.660	-0.037	-0.047	-0.052

Table 11. Contributions of (NH₃⁺, COO⁻) and CH₂ groups to viscosity *B*-coefficients of the amino acids in aqueous resorcinol solutions at 298.15 K.

group	<i>B</i> /m ³ ·mol ⁻¹		
	m _s =0.05	m _s =0.10	m _s =0.15
NH ₃ ⁺ ,COO ⁻	0.026	0.024	0.022
CH ₂	0.108	0.113	0.121

Table12. Values of $(V_2^o - V_1^o) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$, free energy of activation for the solvent, $\Delta\mu_1^o / (\text{kJ} \cdot \text{mol}^{-1})$, and solute $\Delta\mu_2^o / (\text{kJ} \cdot \text{mol}^{-1})$, for the amino acids in aqueous resorcinol at 298.15 K.

Parameters	Glycine	DL-Alanine	L-Valine	L-Leucine
m _s =0.05				
$(V_2^o - V_1^o) \cdot 10^6$ m ³ ·mol ⁻¹	25.20	42.09	72.25	87.91
$\Delta\mu_1^o$ kJ·mol ⁻¹	9.20	9.20	9.20	9.20
$\Delta\mu_2^o$ kJ·mol ⁻¹	19.23	32.11	61.98	78.13
m _s =0.10				
$(V_2^o - V_1^o) \cdot 10^6$ m ³ ·mol ⁻¹	25.48	42.07	71.68	88.04
$\Delta\mu_1^o$ kJ·mol ⁻¹	9.22	9.23	9.23	9.24
$\Delta\mu_2^o$ kJ·mol ⁻¹	20.29	32.95	62.22	82.32
m _s =0.15				
$(V_2^o - V_1^o) \cdot 10^6$ m ³ ·mol ⁻¹	25.57	42.40	70.89	88.18
$\Delta\mu_1^o$ kJ·mol ⁻¹	9.26	9.26	9.27	9.28
$\Delta\mu_2^o$ kJ·mol ⁻¹	22.57	33.73	62.85	89.50

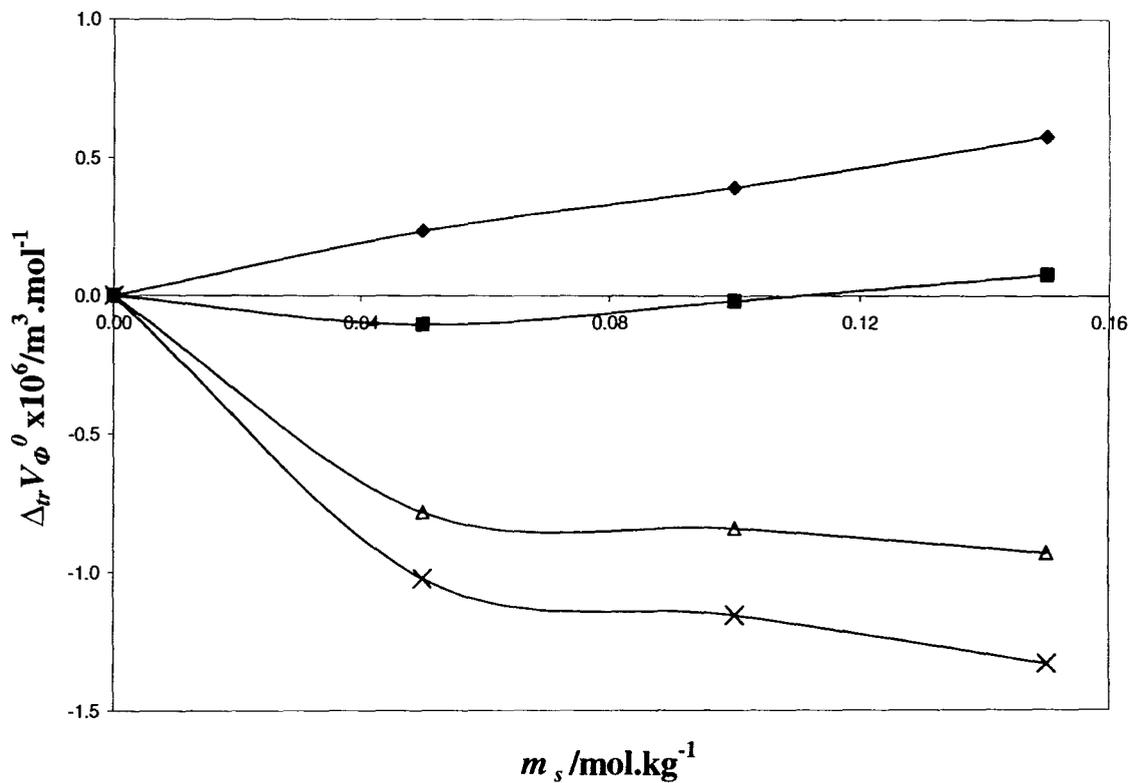


Fig. 1. The transfer volumes of Glycine(♦), DL-Alanine (■), L-Valine (Δ), L-Leucine (×), from water to aqueous resorcinol solutions plotted against the molarity m_s of the resorcinol solutions at 298.15 K.

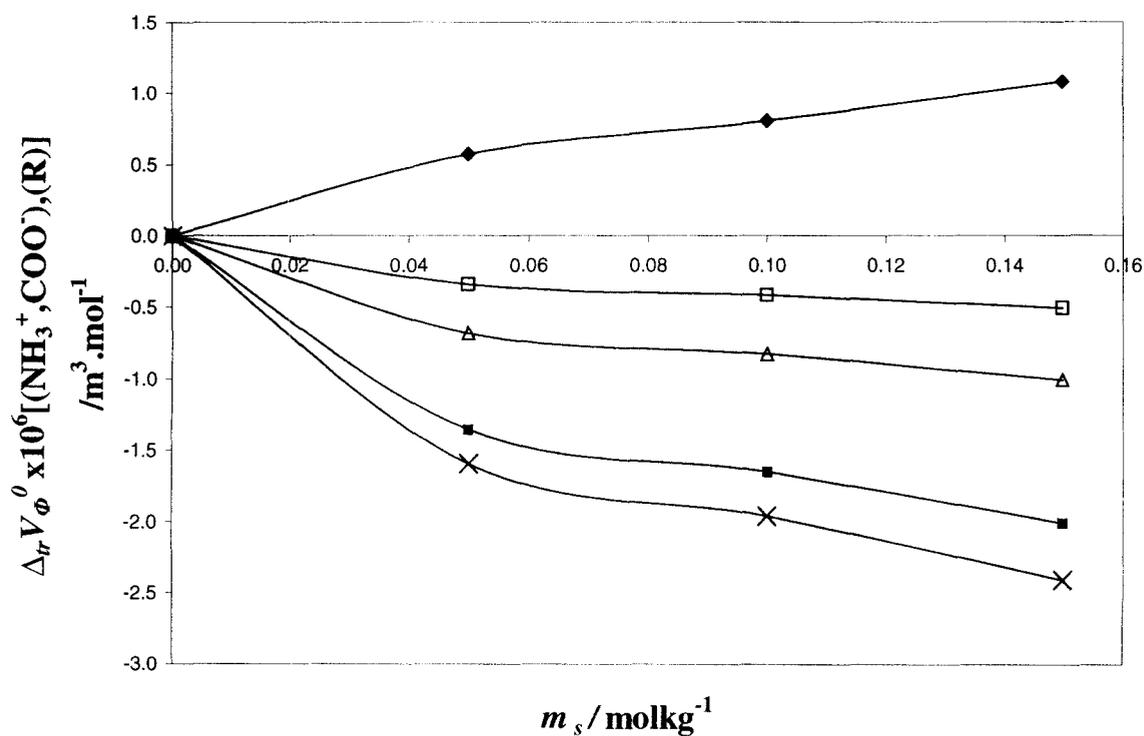


Figure 2. Contribution of $\text{NH}_3^+\text{COO}^-$ (◆) and CH_2 (□), CH_3CH (△), $(\text{CH}_3)_2\text{CHCH}$ (■), or $-(\text{CH}_3)_2\text{CHCH}_2\text{CH}$ (×) groups to standard volumes of transfer, $\Delta_{tr}V_{\phi}^0$, vs molality, m_s , at 298.15 K.

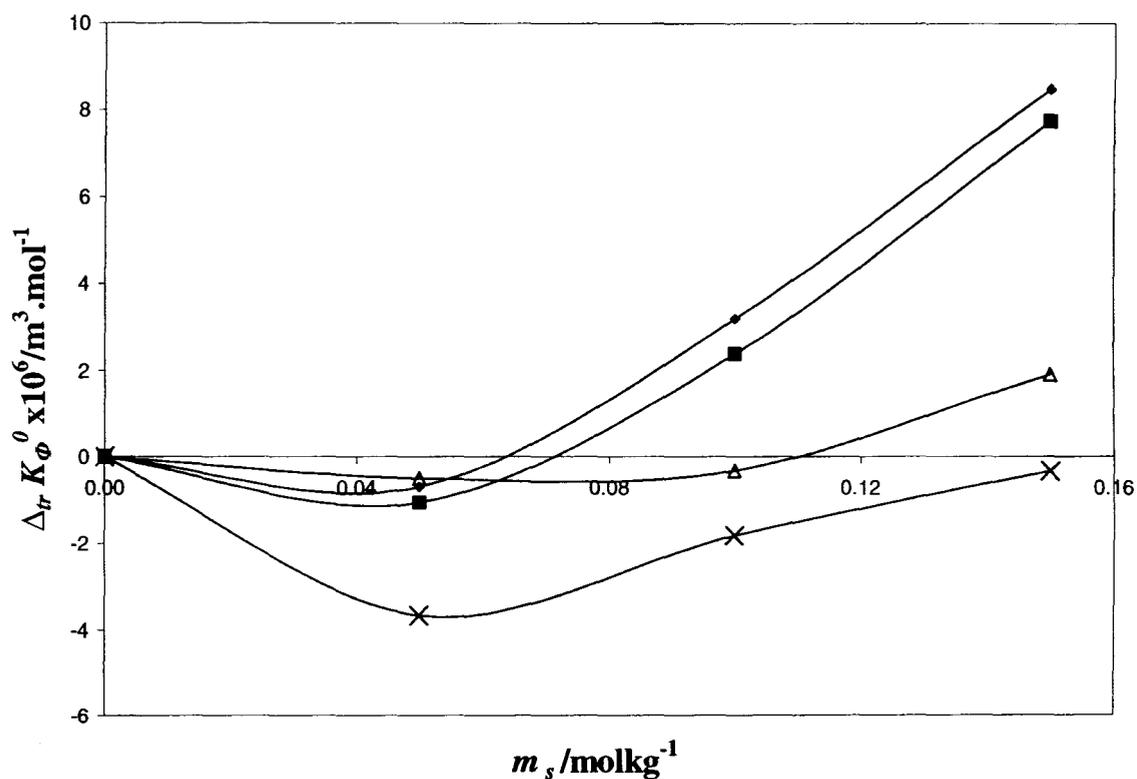


Fig. 3. The transfer compressibilities of Glycine(♦), DL-Alanine (■), L-Valine (△), L-Leucine (×), from water to aqueous resorcinol solutions plotted against the molarity, m_s , of the resorcinol solutions at 298.15 K.

CHAPTER VIII

Conductivity study of Some 1-1 Electrolytes in Aqueous Binary Mixtures of Tetrahydrofuran and 1,3-Dioxolane at 298.15 K

Keywords: Electrical conductance; reference electrolyte; Walden product; ion-pair; solvation.

8.1. Introduction

Studies of the transport properties of electrolytes in different solvent media are of considerable importance for the information they provide on the behavior of ions in solution. The conductometric method is well-suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions.¹⁻⁶

Tetrahydrofuran (THF) and 1,3-dioxolane (1,3 DO) are solvents of low permittivity which have applications in high energy batteries and organic syntheses as manifested from the physicochemical studies in these media.⁷⁻⁹ Water-THF and water-1,3 DO binary mixtures are favorite solvent systems to study association and mobility of ions, because the permittivities can be varied over a large range. Changes upon addition of these solvents to aqueous medium are due to increasing ion-ion interaction at decreasing permittivity and to changes in ion-solvent and solvent-solvent interactions.

In this paper, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of ammonium thiocyanate (NH_4CNS), sodium thiocyanate (NaCNS) and potassium thiocyanate (KCNS) in water-tetrahydrofuran and water-1,3-dioxolane binary mixtures by using precise conductivity measurements at 298.15 K.

8.1. Experimental Section

8.2.1. Source and purity of samples

Tetrahydrofuran, C_4H_8O (Merck, India) was kept for several days over KOH, refluxed for 24 h, and distilled over $LiAlH_4$.¹⁰⁻¹⁴ The boiling point (339 K), density (0.8807 g-cm^{-3}), and viscosity ($\eta_0 = 0.4630 \text{ mPa-s}$) compared well with the literature values.¹¹ The specific conductance of THF was $\approx 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 298.15 K.

1,3-Dioxolane, $C_3H_6O_2$ (Ethylene glycol formal or Ethylene glycol methylene ether, Merck) containing 0.3 % water, 0.005 % peroxides and sterilized with BHT was purified by heating under reflux with PbO_2 for 2 h., then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled.¹⁵⁻¹⁷ The solvent obtained after purification had a boiling point of $75^\circ\text{C} / 760 \text{ mm}$, a density of 1.0586 g-cm^{-3} and a coefficient of viscosity of 0.575 mPa-s at 298.15 K which was in good agreement with the literature values.¹⁷

Ammonium thiocyanate, Sodium thiocyanate and Potassium thiocyanate (NH_4CNS , $NaCNS$ and $KCNS$) salts (all A.R., B.D. H.) were purified by recrystallization twice from conductivity water. The samples were dried in vacuum and stored over P_2O_5 under vacuum.¹⁸ The purity was detected by gas-liquid chromatography. Deionizer water was used after further distillation having specific conductivity $1.99 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. The purity of the liquids was checked by measuring their densities and viscosities at 298.15 K which were in good agreement with the literature values.^{11,17,19} The materials finally obtained were found to be $> 99.5 \%$ pure.

8.2.2. Apparatus and Procedure

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, having cell constant 1.11 cm^{-1} . Measurements were made in a thermostated water bath maintained at $298.15 \pm 0.01 \text{ K}$. Solutions were prepared by weight precise to $\pm 0.02 \%$. The weights were taken on a Mettler electronic analytical balance (AG 285). Determination of cell constant was based on 0.1 (M) aqueous KCl solution. The cell was

calibrated by the method of Lind et al.^{20, 21} The entire conductance data were reported at 1 KHz and was found to be ± 0.3 % precise. Due correction was made for the specific conductance of the solvent and solvent mixtures. The relative permittivity of water, THF and 1,3 DO are 78.54, 7.58, and 7.13 respectively.

Densities (ρ) were measured at 298.15 K with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm³ and an internal diameter of the capillary of about 1 mm. Viscosities (η) were measured by means of a suspended Ubbelohde type viscometer.²²⁻²⁴ Calibration was done at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. The details of the methods and techniques for determination of the parameters were described earlier.²⁴⁻²⁶

8.3. Results and discussion

The physical properties of different solvent mixtures are given in table 1.

The experimental values of the molar conductance, Λ against the respective concentration, c for different thiocyanate salts in different binary solvent mixtures of water-THF and water-1,3 DO at 298.15 K are recorded in table 2. The conductance data is analyzed using the Fuoss conductance equation.^{27,28} So with a given set of conductivity values ($c_j, \Lambda_j, j = 1, \dots, n$), three adjustable parameters, i.e., Λ^0, K_A and R are derived from the Fuoss equation. Here, Λ^0 is the limiting molar conductance, K_A is the observed association constant and R is the association distance. In order to treat the present data, therefore, the R value was arbitrarily preset²⁸ at the center-to-center distance of the solvent-separated pair and is assumed to be, $R = a + d$, where a is the sum of the crystallographic radii of the ions 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,²⁷

$$d = 1.183 (M/\rho)^{1/3} \quad (1)$$

where M is the molecular weight and ρ 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,

$$M_{av} = M_1 M_2 / (W_1 M_2 + W_2 M_1) \quad (2)$$

where W_1 is the weight fraction of the first component of molecular weight M_1 .

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = \rho [\Lambda^0 (1 + R_X) + E_L] \quad (3)$$

$$p = 1 - \alpha (1 - \gamma) \quad (4)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (5)$$

$$-\ln f = \beta k / 2 (1 + K_R) \quad (6)$$

$$\beta = e^2 / D k_B T \quad (7)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (8)$$

where, R_X is the relaxation field effect, E_L is the electrophoretic countercurrent, k^1 is the radius of the ion atmosphere, D is the relative permittivity of the solvent or solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing constant, K_S is the association constant of contact-pairs, K_R is the association constant of solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The computations are performed on a computer using the program suggested by Fuoss. The initial Λ^0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data.^{29,30} Now, we input for the program, the no. of data, n , followed by D , η (viscosity of the solvent mixture), initial Λ^0 value, T , ρ

(density of the solvent mixture), mole fraction of the first component, molecular weights, M_1 and M_2 along with c_j , Λ_j values where $j = 1, 2, \dots, n$ and an instruction to cover preselected range of R values.

In practice, calculations are performed by finding the values of Λ^0 and α which minimize the standard deviation, σ , whereby

$$\sigma^2 = \sum [\Lambda_{j(\text{calc})} - \Lambda_{j(\text{obs})}^0]^2 / n - 2 \quad (9)$$

for a sequence of R values and then plotting σ against R , the best-fit R corresponds to the minimum in $\sigma - R$ versus R curve. So a approximate sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum but no significant minima is found in the $\sigma - R$ curves for the electrolytes studied here, thus R values is assumed to be $R = a + d$, with terms having usual significance.²⁷ Finally, the corresponding Λ^0 and K_A values are obtained which are reported in table 3 along with R and σ values for Ammonium thiocyanate, Sodium thiocyanate and Potassium thiocyanate salts in these two binary mixtures.

The Walden's product, $\Lambda^0 \eta$ ³¹ of an ion is also calculated for the various solvent compositions and the results have been depicted in figure 1.

Figure 2 predicts the nature of the curves for the Gibbs' energy of ion-pair formation, ΔG^0 for the binary mixtures studied here. ΔG^0 is given by the relationship,³²

$$\Delta G^0 = - R T \ln K_A \quad (10)$$

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting molar salt conductances into their ionic components. In the absence of accurate transference data for these systems we have used the "reference electrolyte" method. Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was used as the "reference electrolyte".^{20, 26} The Λ^0 (Bu_4NBPh_4) was obtained from the Λ^0 values of tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate (NaBPh_4), and sodium bromide (NaBr) in the appropriate solvent mixture using the relation,

$$\Lambda^{\circ}(\text{Bu}_4\text{NBPh}_4) = \Lambda^{\circ}(\text{Bu}_4\text{NBr}) + \Lambda^{\circ}(\text{Na BPh}_4) - \Lambda^{\circ}(\text{NaBr}) \quad (11)$$

The limiting molar conductances of those above electrolytes in different solvent mixtures of water-THF and water-1,3 DO were taken from our earlier work given in table 4.

Ionic divisions were accomplished through the following relationships: ^{33,34}

$$\Lambda^{\circ}(\text{Bu}_4\text{NBPh}_4) = \lambda^{\circ}(\text{Bu}_4\text{N}^+) + \lambda^{\circ}(\text{BPh}_4^-) \quad (12)$$

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{BPh}_4^-)} = \frac{r(\text{BPh}_4^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (13)$$

The r values were taken from the work of Gill et al. ^{34,35} The limiting ionic conductances for these ions investigated in these mixtures were calculated from Equation (12 and 13) and collected in table 5.

Table 2 shows that the conductance of the electrolytes is observed to be higher when water is present in higher proportion to the solvent mixtures of water-THF and water-1,3 DO considered. This is due to large D (78.54) value of water which results in greater dissociation of the electrolytes. It also shows that the limiting equivalent conductivity for thiocyanate decreases in the order, $\text{NH}_4\text{CNS} > \text{KCNS} > \text{NaCNS}$ in all the solvent mixtures studied here at the investigated temperature. This is in agreement with earlier finding in other solvent. ³⁶

All of these electrolytes are found to be slightly associated (cf., the K_A values from table 3) in all the solvent mixtures at the investigated temperature. This is expected owing to the medium relative permittivity of these solvent mixtures. These electrolytes solutions, in general, show an increase in the association constant values with an increase in mole fraction of both THF or 1,3 DO in these solvent mixtures. However, all experimental thiocyanate showed a larger association in aqueous 1,3 DO mixture than in the aqueous THF medium. This is expected as 1,3 DO has lower D (7.13) than THF ($D=7.58$).

The Walden products $\Lambda^\circ \eta$ of the ions are also included in table 5, which are usually employed to discuss the interactions of the ions with the solvent medium. From this table, we see that the Walden product of cations decrease in the order, $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+$. And, for the electrolyte taken as a whole, it follows the same sequence. This is justified as the Walden product of an ion or solute is inversely proportional to the effective radius (r) of the ion or solute in a particular solvent,³⁷

$$\Lambda^\circ \eta = 1 / 6 \Pi r T \quad (14)$$

This points out that the electrostatic ion-solvent interaction is strong in these cases, apparently due to the very high surface charge density on small ions.³⁸ Figure 1, indicates that Walden's product is higher for all thiocyanate salts (NH_4CNS , NaCNS , KCNS) in water-1,3 DO mixtures compare to water-THF mixtures. The variation of the Walden product reflects the change of solvation.^{37,38} The solvation of cations is weak in presence of THF molecules but 1,3 DO solvates the cations specifically resulting in greater ion-solvent interaction.³⁷

The starting point for most evaluations of ionic conductances is Stokes' law that states that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. In table 5, we have calculated the Stokes' radii r_s of these ions in these different solvent mixtures.

For ammonium, sodium and potassium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in these solvent mixtures. The Stokes' radius of the thiocyanate ion is, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that this ion is scarcely solvated in both solvent mixtures. This also supports our earlier contention, derived from the Walden products of those ions.

Figure 2 compares ΔG° for thiocyanate salts in the binary mixtures. The aqueous THF mixtures have higher ΔG° than aqueous 1,3 DO mixtures. This indicates greater degree of ion-pair formation and lower extent of association in presence of THF molecules, attributing to its higher D than 1,3 DO. The ΔG° curve in figure 2 along

with the other parameters mentioned above are quite in accordance with the results observed by Barthel et al.³² and Hazra et al.^{38,39}

8.4. Conclusion

It may thus be concluded that these electrolytes remain slightly associated in both solvent mixtures and that solvation of the ions is weakened as soon as the ion pair is formed. The cations are found to be substantially solvated in both solvent mixtures whereas the anions appear to have weak interactions with the solvent molecules. The results further indicate that the coulombic forces play a major role in the ion association processes.

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TABLE 1 Physical properties of different binary mixtures of THF-H₂O and 1,3 DO-H₂O at 298.15

$x_{(\text{THF}/1,3 \text{ DO})}$	D	ρ $\text{g}\cdot\text{cm}^{-3}$	η $\text{mPa}\cdot\text{s}$
THF + H ₂ O mixture			
0.143	50.16	0.9664	1.733
0.272	35.96	0.9462	1.490
0.500	21.77	0.9158	0.924
1,3 DO + H ₂ O mixture			
0.139	49.98	1.0541	1.309
0.267	35.69	1.0678	1.124
0.493	21.41	1.0724	0.836

TABLE 2 Molar conductivities Λ , and corresponding molarities c of electrolytes in different binary mixtures of THF- H₂O and 1,3 DO-H₂O at 298.15 K

$10^4 c$ mol·dm ⁻³	Λ S·cm ² ·mol ⁻¹	$10^4 c$ mol·dm ⁻³	Λ S·cm ² ·mol ⁻¹	$10^4 c$ mol·dm ⁻³	Λ S·cm ² ·mol ⁻¹
0.143 mole fraction of THF					
NH ₄ CNS		NaCNS		KCNS	
52.123	64.90	24.927	55.25	51.245	58.27
58.585	64.75	29.684	54.90	55.955	57.92
62.815	64.62	36.685	54.34	62.891	57.52
69.047	64.46	41.265	54.06	67.432	57.16
73.127	64.36	48.008	53.53	74.122	56.76
79.141	64.24	52.420	53.27	78.503	56.44
83.081	64.14	58.918	52.87	84.958	55.95
88.888	64.00	63.172	52.55	89.187	55.70
92.693	63.92	69.440	52.20	95.421	55.30
98.304	63.76	73.544	51.97	99.506	55.05
0.272 mole fraction of THF					
NH ₄ CNS		NaCNS		KCNS	
10.036	62.32	20.013	51.59	16.750	57.57
11.951	62.07	21.673	51.41	18.841	57.27
14.770	61.78	24.118	51.11	21.920	56.72
16.614	61.44	25.719	50.88	23.934	56.37
19.329	61.00	28.077	50.59	26.901	55.96
21.105	60.72	29.622	50.40	28.844	55.60
23.722	60.36	31.899	50.12	31.705	55.16
25.435	60.12	33.391	49.91	33.579	54.80
27.958	59.76	35.590	49.64	36.340	54.36
29.610	59.56	37.031	49.47	38.149	53.98
0.500 mole fraction of THF					
NH ₄ CNS		NaCNS		KCNS	
10.027	59.35	20.464	49.07	10.384	54.99
10.501	59.28	21.498	48.95	11.238	54.80
10.812	59.21	22.501	48.83	11.798	54.67
11.271	59.12	23.474	48.79	12.622	54.47
11.572	59.08	24.419	48.60	13.163	54.36
12.017	58.96	26.229	48.28	13.959	54.17
12.308	58.93	27.096	48.20	14.482	54.05
12.739	58.81	27.940	48.17	15.252	53.86
13.022	58.77	29.560	47.85	15.757	53.74
13.439	58.68	31.095	47.70	16.502	53.57

Contd.....

0.139 mole fraction of 1,3 DO					
NH ₄ CNS		NaCNS		KCNS	
49.981	91.20	24.297	85.44	47.617	90.03
54.575	90.84	28.934	84.67	51.993	89.80
61.341	90.48	35.758	83.50	58.439	89.18
65.770	90.19	40.222	82.72	62.658	88.90
72.295	89.76	46.795	81.83	68.874	88.64
76.567	89.49	51.096	81.00	72.945	88.35
82.864	89.08	57.430	80.20	78.944	87.89
86.989	88.84	61.576	79.37	82.873	87.66
93.069	88.41	67.685	78.60	88.666	87.24
97.053	88.16	71.685	78.04	92.461	86.95
0.267 mole fraction of 1,3 DO					
NH ₄ CNS		NaCNS		KCNS	
49.409	84.97	46.958	78.15	26.139	83.86
51.746	84.72	49.456	77.78	28.733	83.31
53.278	84.56	51.094	77.50	30.431	83.04
55.539	84.34	53.510	77.15	32.933	82.56
57.023	84.18	55.094	76.96	34.572	82.32
59.213	83.97	57.433	76.61	36.989	81.90
60.649	83.81	58.967	76.43	38.572	81.63
62.771	83.62	61.231	76.10	40.907	81.26
64.163	83.48	62.717	75.90	42.438	80.98
66.220	83.29	64.911	75.59	44.695	80.67
0.493 mole fraction of 1,3 DO					
NH ₄ CNS		NaCNS		KCNS	
7.695	81.43	11.620	76.92	8.970	79.25
8.024	81.25	12.026	76.82	9.597	78.90
8.510	81.05	12.293	76.65	10.008	78.73
8.828	80.88	12.687	76.51	10.613	78.36
9.298	80.65	13.328	76.25	11.010	78.26
9.606	80.51	13.949	76.00	11.596	77.90
10.060	80.30	14.553	75.78	11.980	77.69
10.358	80.17	15.139	75.51	12.547	77.44
10.797	79.97	16.261	75.07	12.918	77.25
11.086	79.80	17.321	74.60	13.466	77.00

TABLE 3 Derived conductance parameters and standard Gibbs energy changes ΔG° for the ion association process for different thiocyanate in different binary mixtures of THF-H₂O and 1,3 DO-H₂O at 298.15 K

x (THF/1,3 DO)	Λ° S·cm ² ·mol ⁻¹	K_A dm ³ ·mol ⁻¹	R Å	ΔG° J·mol ⁻¹	$\sigma\%$
THF + H ₂ O mixture					
NH ₄ SCN					
0.143	67.79 ± 0.03	3.98 ± 0.09	7.16	-3.42	0.02
0.272	65.43 ± 0.13	29.22 ± 1.34	7.49	-8.36	0.13
0.500	63.83 ± 0.09	31.15 ± 2.05	7.96	-8.52	0.03
NaSCN					
0.143	58.51 ± 0.05	18.25 ± 0.25	6.64	-7.20	0.05
0.272	56.35 ± 0.09	39.74 ± 1.06	6.97	-9.12	0.07
0.500	55.73 ± 0.24	53.92 ± 4.04	7.44	-9.88	0.10
KSCN					
0.143	64.68 ± 0.16	21.59 ± 0.59	7.01	-7.61	0.09
0.272	63.04 ± 0.20	50.41 ± 2.09	7.34	-9.71	0.16
0.500	60.30 ± 0.09	60.12 ± 2.00	7.81	-10.15	0.04
1,3-DO + H ₂ O mixture					
NH ₄ SCN					
0.139	97.34 ± 0.13	10.28 ± 0.28	7.07	-5.77	0.06
0.267	94.71 ± 0.04	21.71 ± 0.14	7.34	-7.63	0.01
0.493	88.73 ± 0.08	75.75 ± 1.78	7.76	-10.72	0.02
NaSCN					
0.139	92.81 ± 0.22	32.70 ± 0.87	6.55	-8.64	0.01
0.267	91.18 ± 0.12	41.40 ± 0.50	6.82	-9.22	0.02
0.493	86.94 ± 0.19	95.03 ± 3.37	7.24	-11.28	0.05
KSCN					
0.139	96.16 ± 0.17	11.02 ± 0.39	6.92	-5.94	0.08
0.267	92.35 ± 0.07	35.39 ± 0.39	7.19	-8.84	0.02
0.493	88.35 ± 0.15	104.62 ± 2.85	7.61	-11.52	0.04

TABLE 4 Limiting molar conductance Λ° , for different electrolytes in different binary mixtures of THF-H₂O and 1,3 DO-H₂O at 298.15 K

$x_{\text{(THF/1,3DO)}}$	Λ° S·cm ² ·mol ⁻¹		
THF + H ₂ O mixture			
	NaBr	NaBPh ₄	Bu ₄ NBr
0.143	52.82	34.62	50.84
0.272	57.70	37.82	55.54
0.500	71.62	46.94	68.93
1,3-DO + H ₂ O mixture			
0.139	74.31	48.70	71.52
0.267	84.30	55.25	81.14
0.493	109.22	71.58	105.12

TABLE 5 Limiting ionic conductances λ_{\pm}° , ionic Walden products $\eta \lambda_{\pm}^{\circ}$ and ionic Stokes radii r_s in different binary mixtures of THF- H₂O and 1,3 DO-H₂O at 298.15 K

Ion	λ_{\pm}° S·cm ² ·mol ⁻¹	$\eta \lambda_{\pm}^{\circ}$ S·cm ² ·mol ⁻¹ ·Pa·s	r_s Å
0.143 mole fraction of THF			
NH ₄ ⁺	28.13	0.049	1.68
Na ⁺	18.85	0.033	2.51
K ⁺	25.02	0.043	1.89
CNS ⁻	39.66	0.069	1.19
0.272 mole fraction of THF			
NH ₄ ⁺	29.68	0.044	1.85
Na ⁺	20.60	0.031	2.67
K ⁺	27.29	0.041	2.02
CNS ⁻	35.75	0.053	1.54
0.500 mole fraction of THF			
NH ₄ ⁺	33.66	0.031	2.64
Na ⁺	25.56	0.024	3.47
K ⁺	30.13	0.028	2.95
CNS ⁻	30.17	0.028	2.94
0.139 mole fraction of 1,3 DO			
NH ₄ ⁺	31.06	0.041	2.02
Na ⁺	26.52	0.035	2.36
K ⁺	29.87	0.039	2.10
CNS ⁻	66.29	0.087	0.94
0.267 mole fraction of 1,3 DO			
NH ₄ ⁺	33.62	0.038	2.17
Na ⁺	30.09	0.034	2.42
K ⁺	31.27	0.035	2.33
CNS ⁻	61.09	0.069	1.19
0.493 mole fraction of 1,3 DO			
NH ₄ ⁺	40.77	0.034	2.40
Na ⁺	38.99	0.033	2.51
K ⁺	40.40	0.034	2.43
CNS ⁻	47.95	0.040	2.04

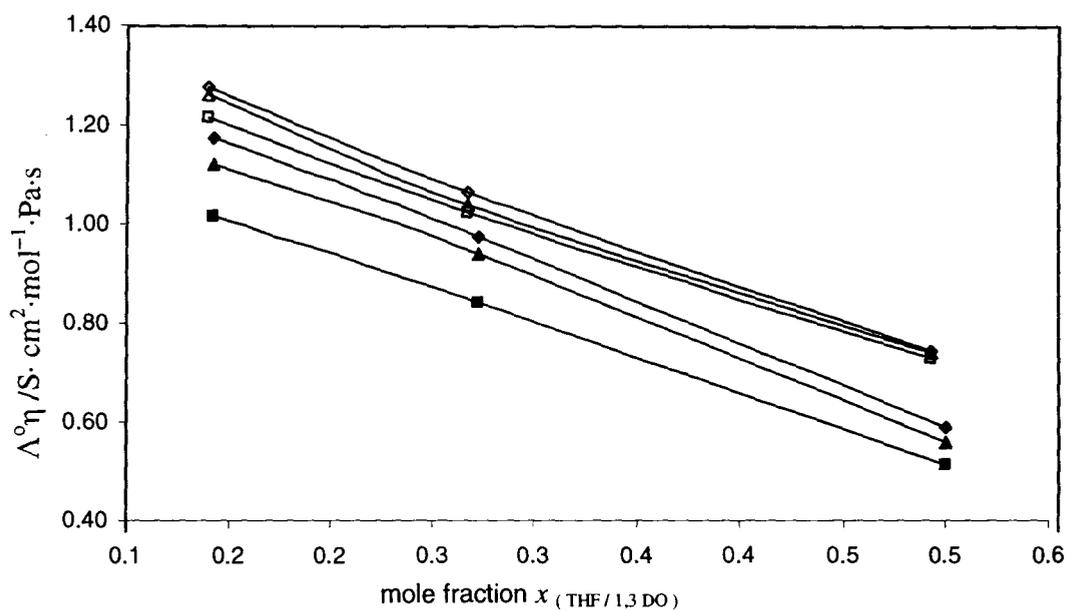


FIGURE 1. Plot of Walden product, $\Lambda^\circ\eta$ of NH_4SCN (◆), NaSCN (■) and KSCN (▲) in $\text{THF} + \text{H}_2\text{O}$ and of NH_4SCN (◇), NaSCN (□), and KSCN (△) in $1,3\text{-DO} + \text{H}_2\text{O}$ binary mixtures at 298.15 K

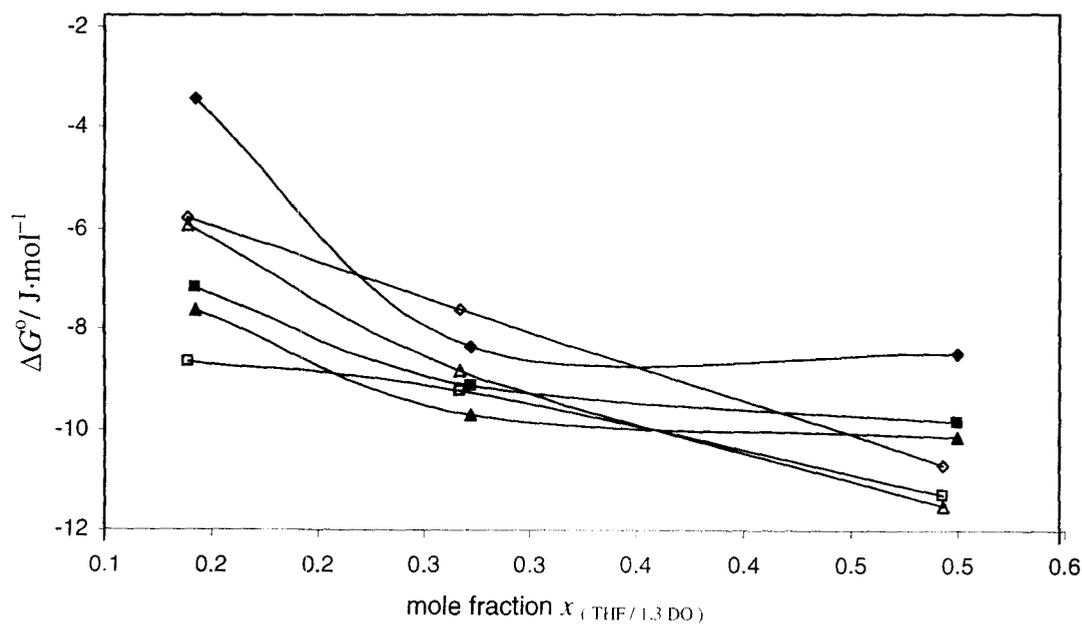


FIGURE 2. Plot of Gibbs energy of ion-pair formation, ΔG° of NH_4SCN (◆), NaSCN (■) and KSCN (▲) in $\text{THF} + \text{H}_2\text{O}$ and of NH_4SCN (◇), NaSCN (□), and KSCN (Δ) in $1,3\text{-DO} + \text{H}_2\text{O}$ binary mixtures at 298.15 K.

CHAPTER IX

APPARENT MOLAR VOLUME, VISCOSITY B-COEFFICIENT AND ADIABATIC COMPRESSIBILITY OF SOME MINERAL SULPHATES IN AQUEOUS BINARY MIXTURES OF FORMAMIDE AT T = (298.15, 308.15 AND 318.15) K

Keywords :Viscosity B-Coefficient, Adiabatic Compressibility, free energy of activation

9.1. Introduction

Studies on density, viscosity and acoustic properties of ionic solutions are of great help in characterising the structure and properties of solutions. Various types of interactions exist between the ions in the solutions and of these, ion-ion and ion-solvent interactions are of current interest. These interactions¹⁴ help in better understanding of the nature of solute and solvent, i.e. whether the added solute modifies or distorts the structure of the solvent. Recently we have undertaken a comprehensive program to study the solvation and association behaviour of some electrolytes⁴⁻⁸ in different aqueous and non-aqueous solvent media from the measurement of transport and thermodynamic properties. Formamide (FA) is chosen for the study as it is a simplest amide that contains peptide linkage, the fundamental building block of proteins,⁹ It along with some of its derivatives serves as good solvents for many organic and inorganic compounds and is also used as a plasticizer.

Hence, in the present study, we reported density, viscosity and ultrasonic speed of ammonium sulphate, sodium sulphate, potassium sulphate, magnesium sulphate, zinc sulphate, and cadmium sulphate in 10, 20 and 30 mass % formamide in water mixture at 298.15, 308.15 and 318.15 K and the derived parameters were discussed in terms of ion-ion and ion-solvent interactions.

9.2. Experimental Section

9.2.1. Source and purity of samples

Extrapure grade formamide procured from S.d.fine-Chem. Limited, India was purified by the standard procedures.¹⁰ After purification its purity was ascertained by GLC and also by

comparing experimental values of densities and viscosities with their literature values.¹⁻¹⁴ The physical properties of pure and aqueous binary mixtures of formamide at different temperatures are listed in Table 1.

All the sulphate salts (Anal R grade) were procured from E. Merck (India) Ltd, They were used after drying over P_2O_5 in a desiccator for few hours. The reagents were always placed in the desiccator over P_2O_5 to keep them in dry atmosphere. Freshly distilled conductivity water (specific conductance $< 10 \text{ ohm}^{-1} \text{ cm}^{-1}$) was used for preparing aqueous mixtures of formamide

9.2.2. Apparatus and Procedure

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 303.15 and 308.15 K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at $\pm 0.01 \text{ K}$ 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. Averages of triplicate measurements were taken into account. Mass measurements accurate to $\pm 0.01 \text{ mg}$ were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland).

The viscosities (η) were measured by means of the suspended Ubbelohde type viscometer,¹⁵ calibrated at 298.15, 303.15 and 308.15 K with triply-distilled water and purified methanol. The flow times were accurate to $\pm 0.1 \text{ s}$. The ultrasonic speeds of sound for the solutions were determined by a 2-MHz ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 2 MHz, calibrated with purified water and benzene at 298.15 K. The temperature stability was maintained within $\pm 0.01 \text{ K}$ by circulating thermostatic water around the cell with a circulating pump. The binary aqueous solutions of formamide as well as the solutions of sulphates were made by mass and conversion of molality into molarity was done [16] using experimental density values. The uncertainties in the density, viscosity and speed of sound measurements were estimated to be $\pm 0.0001 \text{ g.cm}^{-3}$, $\pm 0.003 \text{ mPa.s}$ and $\pm 0.2 \text{ m.s}^{-1}$ respectively. The details of the methods and techniques have been described elsewhere.¹⁷⁻²³

The experimental values of concentration (c), density (ρ), viscosity (η) and the derived parameters for the studied electrolytes at different temperatures are reported in Table 2.

9.3. Results and Discussion

The apparent molar volumes V_ϕ of solutions were calculated from the density data using the following standard expression,²⁴

$$V_\phi = M / \rho_o - 1000 (\rho - \rho_o) / c \rho_o \quad (1)$$

Where c is the molar concentration of the solution, M is the molecular weight of the solute and the other symbols have their usual significance.

The values of limiting apparent molar volumes V_ϕ^0 and experimental slopes S_v^* at different temperatures have been obtained by using the least-square fit to the linear plots of V_ϕ against \sqrt{c} using the Masson's equation:²⁵

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \quad (2)$$

The values of limiting apparent molar volumes (ϕ_v^0) and experimental slopes (S_v^*) are listed in Table 3. The values of ϕ_v^0 are generally small for most of the electrolytes and decrease with an increase in temperature: this indicates the presence of weak ion-solvent interaction²⁶ and such interaction decreases as the temperature of the mixtures increases. This may be due to large electrostriction at higher temperatures. The decrease in ϕ_v^0 may also be attributed to the decrease in solvation.

The slope S_v^* of equation [2] may be attributed to the measure of ion-ion interactions.²⁷⁻²⁹ A perusal of Table 3 reveals that the S_v^* values for most of the examined sulphates, are large positive at different temperatures and also increase in magnitude with a rise in temperature. This suggests that ion-ion interactions further strengthen with a rise in temperature. This may be attributed to the derivation of the electrolytes³⁰ in these systems due to more thermal agitation at higher temperatures.

Further, it is found that S_v^* increases on going from 10 to 30 mass % of formamide in the mixed solvents; thereby indicating increasing trend of ion-ion interactions. This in turn supports the behaviour of ϕ_v^0 , indicating decreased ion-solvent interactions as the content of formamide in the solutions increases.

The temperature dependence of V_ϕ^0 for various sulphate salts, studied here in these solvent mixture can be expressed by the polynomial:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Where T is the temperature in Kelvin. The values of coefficients a_0, a_1, a_2 for the studied sulphates at different temperatures in different binary mixtures of formamide are recorded in Table 4.

The apparent molar expansibilities ϕ_E^0 at infinite dilution can be obtained by differentiating eq. 3 with respect to temperature,

$$\phi_E^0 = (\delta V_\phi^0 / \delta T)_p = a_1 + 2a_2 T \quad (4)$$

The values of ϕ_E^0 along with the sign of $(\delta V_\phi^0 / \delta T)_p$ for the studied electrolytes at different temperatures in different binary mixtures of formamide are recorded in Table 5,

It is evident from Table 5 that the values of ϕ_E^0 increases as the temperature increases for all electrolytic solutions. This may be attributed to the presence of "caging or packing effect".

32,33

Hepler³⁴ has developed a technique of examining the sign of $(\delta^2 V_\phi^0 / \delta T^2)_p$ for various solutes in terms of long range structure making or breaking capacities of the solutes in mixed solvent systems using the following thermodynamic expression:³⁵

$$(\delta C_p / \delta P)_T = - (\delta^2 V_\phi^0 / \delta T^2)_P \quad (5)$$

According to this, [he left hand side of the above equation 5 should be positive for all structure breaking solutes and therefore, structure breaking solute posses negative value of $(\delta^2 V_\phi^0 / \delta T^2)_P$ On the other hand, positive value of $(\delta^2 V_\phi^0 / \delta T^2)_P$ should be associated with structure making solutes.

In the present study, Table 5 revealed that the values of $(\delta^2 V_\phi^0 / \delta T^2)_P$ for all The electrolytic solutions are positive, thereby suggesting that these electrolytes act as structure makers in these solvent mixtures.

The viscosity data of all the electrolytic solutions at different temperatures in different aqueous binary mixtures of formamide have been analyzed by Jones-Dole³⁶ equation;

$$(\eta / \eta_0 - 1) / c^{1/2} = (\eta_r - 1) / c^{1/2} = A + B c^{1/2} \quad (6)$$

$$\text{Where, } \eta = (Kt - L/t) \rho$$

Where η_0 and η are the viscosities of solvent-mixtures and solutions respectively. The values of A and B parameters have been determined from the intercept and slope linear plots of $(\eta / \eta_0 - 1) / c^{1/2}$ versus $c^{1/2}$ and recorded in Table 6.

Table 6 shows that the values of *A*-coefficients, for most of the sulphates under investigation, are positive and increase with the rise in temperature, thereby suggesting strong ion-ion interactions³⁷ and these interactions further strengthen with the increase of temperature.

Also it is found that *A*-coefficient values increase with the amount of formamide in the mixtures, suggesting the predominance of ion-ion interactions in higher amount of formamide.

A perusal of Table 6 shows that the values of *B*-coefficient are positive and decreases with a rise in both the temperatures and the amount of formamide in the mixtures. This indicates the decreasing trend in ion-solvent interactions and justifies the predominance of ion-ion interactions at higher temperatures and increased amount of formamide in the mixtures.

Also the temperature derivative of *B*, i.e., dB/dT found to be negative, indicating that these electrolytes act as Structure makers in these solvent mixtures,³⁸ These conclusions are in excellent agreement with our earlier view drawn from magnitude of $(\delta^2 V_\phi^0 / \delta T^2)_P$ illustrated earlier.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of the electrolytes as suggested by Feakings et, al³⁹ using the following equation:

$$\Delta\mu_2^{ot} = \Delta\mu_1^{ot} + RT (1000B + V_2^0 - V_1^0) / V_1^0 \quad (7)$$

where $\Delta\mu_2^{ot}$ contribution per mole of the solute to the free energy of activation of viscous (low of the solutions. V_1^0 and V_2^0 are the partial molar volumes of the solvent and solute, respectively. $\Delta\mu_2^{ot}$ of the solutions was determined from the above relation. The free energy of activation of viscous flow per mole of the pure solvent $\Delta\mu_1^{ot}$ is given by (he relation:^{39,40}

$$\Delta\mu_1^{ot} = \Delta G_1^{ot} = RT \ln (\eta_0 V_1^0 / h N_A) \quad (8)$$

where NA is the Avogadro's number, h the Planck constant, η the viscosity of the solvent, R the gas constant and T the absolute temperature. The values of the parameters $\Delta\mu_1^{ot}$ and $\Delta\mu_2^{ot}$ are reported in Table 7. Table 7 shows that $\Delta\mu_1^{ot}$ is practically constant at all the solvent compositions and temperatures, implying that $\Delta\mu_2^{ot}$ dependent mainly on the viscosity B -coefficient and $(V_2^o - V_1^o)$ terms. The $\Delta\mu_2^{ot}$ values are positive and larger than that of $\Delta\mu_1^{ot}$ at all the experimental temperatures; this suggests that the formation of the transition state is less favourable in the presence of the studied sulphate salts.

According to Feakings et al.,³⁹ $\Delta\mu_2^{ot} > \Delta\mu_1^{ot}$ electrolytes having positive B -coefficients and indicates a stronger ion-solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.³⁹ The greater the value of $\Delta\mu_2^{ot}$ the greater is the structure making tendency of the electrolyte. Table 7 also shows that the values of $\Delta\mu_2^{ot}$ decreases with the increase of temperature and this suggest that all the experimental solutes are act as structure makers.⁴¹ The entropy of activation for electrolytic solutions has been calculated using the relation:³⁹

$$\Delta S_2^{ot} = -d(\Delta\mu_2^{ot})/dT \quad (9)$$

where ΔS_2^{ot} has been obtained from the negative slope of the plots of $\Delta\mu_2^{ot}$ versus T by using a least squares Treatment,

The activation enthalpy (ΔH_2^{ot}) has been calculated using the relation:³⁹

$$\Delta H_2^{ot} = \Delta\mu_2^{ot} + T\Delta S_2^{ot} \quad (10)$$

The values of $T\Delta S_2^{ot}$ and $\Delta\mu_2^{ot}$ are reported in Table S and they are found to be

positive for all the electrolytic solutions at all the temperatures suggesting that the transition state is associated with bond breaking and decrease in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is some where in the centro-symmetric region.^{39,40}

Adiabatic compressibility ϕ_k , has been calculated at 298,15 K using the relation⁴²

$$\beta = 1 / \mu^2 \rho \quad (11)$$

where u is the ultrasonic velocity and ρ is the density of the solution.

The apparent molal adiabatic compressibility (ϕ_k) of the solution was compiled from the relation,⁴³

$$\phi_k = \beta M / \rho + 1000(\beta \rho_o - \beta_o \rho) / m \rho \rho_o \quad (12)$$

where $\phi_k, \phi_{k,0}$ are the adiabatic compressibility of solution and solvent respectively and m is the molal concentration of the solution. In equation 12 molality (m) has been used rather than concentration (c), because molality is independent of temperature and we performed acoustic calculations only at 298.15 K.

The limiting apparent molal adiabatic compressibility (ϕ_k^0) were obtained by extrapolating the plots of ϕ_k versus \sqrt{m} of the solution to zero concentration by the computerized least-squares method^{44,45}

$$\phi_k = \phi_k^0 + S_k^* \sqrt{m} \quad (13)$$

where S_k^* is the experimental slope.

The values of m , u , K_s , ϕ_k , ϕ_k^0 and S_k^* for the studied electrolytes at 29S.J5 K in different aqueous binary mixtures of formamide are determined and recorded in Table 8. A perusal of Table 8 shows that ϕ_k^0 values are negative and S_k^* values are positive 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 [46], the results are in good agreement with those drawn from the values of ϕ_v^0 and S_v^* discussed earlier.

9.4. Conclusion

In summary, the study reveals that ion-ion interactions are predominant over ion-solvent interactions for all sulphate salts in different aqueous binary mixtures of formamide at all experimental temperatures. Also, the sulphates under investigation found to act as structure makers in the solvent mixtures studied.

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Table 1. Physical properties of pure formamide (FA) and different mass% of formamide (FA) + H₂O mixtures at different temperatures.

T, K	$\rho_0 \times 10^{-3}$, kg. m ⁻³		η_0 , mPa.s		u_0 , m.s ⁻¹	
	Present work	Literature	Present Work	Literature	Present Work	Literature
10 mass% of formamide + water						
298.15	1.0116	-	0.916	-	1490.9	-
308.15	1.0073	-	0.752	-		
318.15	1.0039	-	0.609	-		
20 mass% of formamide + water						
298.15	1.0258	-	0.981	-	1507.7	-
308.15	1.0206	-	0.812	-		
318.15	1.0162	-	0.682	-		
30 mass% of formamide + water						
298.15	1.0396	-	1.062	-	1534.1	-
308.15	1.0343	-	0.877	-		
318.15	1.0284	-	0.729	-		
Pure formamide						
298.15	1.1292	1.1292 [11]	3.302	3.302 [11]	1591.3	1591.3 [12]
308.15	1.1205	1.1202 [13]	2.542	2.59 [13]		
318.15	1.1111	1.1119 [14]	2.001	2.00 [14]		

Table 2. Molar concentrations (c), densities (ρ), viscosities (η), apparent molar volumes (ϕ_v) and values of $(\eta/\eta_0 - 1) / \sqrt{c}$ of different sulphate salts in 10, 20 and 30 mass% of formamide (FA) + water mixtures at different temperatures.

$c \times 10^{-3}$, mol .L ⁻¹	$\rho \times 10^{-3}$, kg.m ⁻³	η , mPa.s	$\phi_v \times 10^6$, m ³ .mol ⁻¹	$(\eta/\eta_0 - 1) / \sqrt{c}$
(NH₄)₂SO₄ in 10 mass% of FA + H₂O				
<i>T</i> = 298.15 K				
0.0063	1.0122	0.919	45.700	0.0413
0.0252	1.0137	0.927	50.600	0.0756
0.0441	1.0151	0.932	54.300	0.0832
0.0631	1.0163	0.938	56.925	0.0956
0.0819	1.0176	0.943	58.402	0.1030
0.0996	1.0187	0.948	60.401	0.1107
<i>T</i> = 308.15 K				
0.0063	1.0079	0.756	31.800	0.0670
0.0251	1.0097	0.762	38.700	0.0839
0.0439	1.0112	0.766	43.400	0.0889
0.0628	1.0127	0.771	46.600	0.1008
0.0817	1.0140	0.775	49.697	0.1070
0.0993	1.0152	0.779	52.100	0.1139
<i>T</i> = 318.15 K				
0.0063	1.0047	0.613	22.000	0.0828
0.0250	1.0065	0.618	31.300	0.0935
0.0438	1.0081	0.622	37.400	0.1020
0.0626	1.0096	0.626	41.400	0.1116
0.0813	1.0109	0.629	46.000	0.1152
0.0989	1.0122	0.632	48.700	0.1201
(NH₄)₂SO₄ in 20 mass% of FA + H₂O				
<i>T</i> = 298.15 K				
0.0061	1.0264	0.987	35.400	0.0718
0.0242	1.0279	0.994	43.200	0.0852
0.0424	1.0293	1.001	48.200	0.0990
0.0606	1.0306	1.006	51.800	0.1035
0.0788	1.0318	1.012	55.000	0.1126
0.0969	1.0329	1.017	57.400	0.1179

T = 308.15 K

0.0060	1.0213	0.817	26.200	0.0795
0.0241	1.0229	0.823	34.500	0.0873
0.0422	1.0244	0.828	41.000	0.0959
0.0603	1.0258	0.833	45.200	0.1053
0.0784	1.0270	0.838	49.700	0.1144
0.0965	1.0282	0.842	52.700	0.1189

T = 318.15 K

0.0060	1.0169	0.687	18.500	0.0946
0.0240	1.0187	0.693	30.400	0.1041
0.0420	1.0202	0.698	36.300	0.1145
0.0601	1.0216	0.702	42.400	0.1196
0.0781	1.0228	0.706	47.000	0.1259
0.0961	1.0241	0.709	50.000	0.1277

(NH₄)₂SO₄ in 30 mass% of FA + H₂O

T = 298.15 K

0.0067	1.0403	1.070	27.701	0.0920
0.0201	1.0415	1.078	34.700	0.1063
0.0301	1.0423	1.082	39.503	0.1085
0.0535	1.0440	1.091	46.901	0.1181
0.0769	1.0456	1.099	51.868	0.1256
0.0969	1.0467	1.105	56.700	0.1301

T = 308.15 K

0.0066	1.0349	0.884	21.501	0.0982
0.0199	1.0363	0.890	30.000	0.1051
0.0299	1.0371	0.894	35.003	0.1121
0.0532	1.0389	0.901	43.201	0.1186
0.0764	1.0404	0.908	49.901	0.1279
0.0964	1.0415	0.913	54.601	0.1322

T = 318.15 K

0.0066	1.0291	0.735	16.000	0.1013
0.0198	1.0305	0.741	25.601	0.1170
0.0298	1.0314	0.744	30.600	0.1192
0.0529	1.0332	0.749	39.300	0.1193
0.0761	1.0347	0.755	46.900	0.1293
0.0959	1.0359	0.759	52.100	0.1329

Na₂SO₄ in 10 mass% of FA + H₂O

T = 298.15 K

0.0072	1.0125	0.919	27.785	0.0386
0.0289	1.0151	0.933	21.943	0.1092
0.0507	1.0179	0.947	18.149	0.1503
0.0652	1.0199	0.956	15.972	0.1710
0.0797	1.0218	0.965	14.373	0.1895
0.0942	1.0238	0.975	12.615	0.2099

$T = 308.15 \text{ K}$				
0.0072	1.0082	0.758	18.636	0.0940
0.0289	1.0108	0.771	20.643	0.1486
0.0505	1.0134	0.782	21.925	0.1775
0.0649	1.0151	0.789	22.722	0.1931
0.0794	1.0167	0.796	23.402	0.2076
0.0938	1.0184	0.803	24.067	0.2214
$T = 318.15 \text{ K}$				
0.0072	1.0049	0.619	12.610	0.1935
0.0288	1.0076	0.631	17.140	0.2129
0.0503	1.0101	0.639	19.750	0.2146
0.0647	1.0118	0.645	21.000	0.2324
0.0791	1.0134	0.649	22.400	0.2335
0.0934	1.0150	0.654	23.880	0.2418
Na_2SO_4 in 20 mass% of FA + H_2O				
$T = 298.15 \text{ K}$				
0.0059	1.0265	0.986	26.230	0.0597
0.0238	1.0286	0.998	25.377	0.1123
0.0416	1.0306	1.011	24.831	0.1499
0.0594	1.0327	1.024	24.394	0.1798
0.0772	1.0349	1.037	24.007	0.2055
0.0951	1.0370	1.049	23.660	0.2248
$T = 308.15 \text{ K}$				
0.0059	1.0214	0.819	10.200	0.1122
0.0237	1.0236	0.831	15.700	0.1520
0.0414	1.0257	0.842	19.170	0.1816
0.0591	1.0277	0.852	22.150	0.2036
0.0769	1.0296	0.861	24.540	0.2176
0.0946	1.0315	0.871	26.596	0.2362
$T = 318.15 \text{ K}$				
0.0059	1.0171	0.693	-6.000	0.2100
0.0235	1.0195	0.706	4.500	0.2296
0.0412	1.0217	0.715	10.000	0.2384
0.0589	1.0237	0.722	15.400	0.2417
0.0765	1.0256	0.729	19.600	0.2492
0.0942	1.0273	0.736	24.500	0.2580
Na_2SO_4 in 30 mass% of FA + H_2O				
$T = 298.15 \text{ K}$				
0.0028	1.0399	1.066	25.590	0.0712
0.0198	1.0418	1.081	28.330	0.1271
0.0368	1.0437	1.095	29.510	0.1620
0.0538	1.0455	1.108	30.690	0.1867
0.0707	1.0473	1.122	32.000	0.2125
0.0877	1.0490	1.136	32.750	0.2353

 $T = 308.15 \text{ K}$

0.0028	1.0347	0.884	0.200	0.1508
0.0197	1.0368	0.899	10.500	0.1787
0.0366	1.0388	0.911	16.600	0.2036
0.0535	1.0407	0.921	21.300	0.2169
0.0703	1.0424	0.931	25.400	0.2322
0.0871	1.0440	0.942	29.100	0.2511

 $T = 318.15 \text{ K}$

0.0028	1.0288	0.738	-23.199	0.2333
0.0196	1.0313	0.754	-5.699	0.2450
0.0365	1.0334	0.764	4.900	0.2513
0.0533	1.0352	0.772	12.900	0.2555
0.0701	1.0369	0.779	19.600	0.2590
0.0868	1.0383	0.786	26.300	0.2654

 K_2SO_4 in 10 mass% of FA + H_2O

 $T = 298.15 \text{ K}$

0.0060	1.0124	0.920	55.055	0.0564
0.0241	1.0146	0.928	51.603	0.0846
0.0422	1.0169	0.935	48.400	0.1010
0.0603	1.0193	0.942	46.674	0.1156
0.0784	1.0217	0.949	44.897	0.1287
0.0965	1.0242	0.955	43.409	0.1371

 $T = 308.15 \text{ K}$

0.0060	1.0081	0.757	44.147	0.0858
0.0240	1.0105	0.764	42.933	0.1030
0.0420	1.0129	0.771	42.047	0.1233
0.0601	1.0153	0.777	41.345	0.1356
0.0780	1.0177	0.782	40.837	0.1428
0.0961	1.0202	0.787	40.293	0.1501

 $T = 318.15 \text{ K}$

0.0059	1.0048	0.614	34.053	0.1069
0.0239	1.0073	0.621	34.809	0.1275
0.0419	1.0098	0.626	35.287	0.1364
0.0599	1.0123	0.631	35.718	0.1476
0.0778	1.0147	0.635	36.060	0.1531
0.0958	1.0172	0.640	36.324	0.1645

 K_2SO_4 in 20 mass% of FA + H_2O

 $T = 298.15 \text{ K}$

0.0059	1.0266	0.987	44.600	0.0796
0.0236	1.0288	0.996	45.660	0.0995
0.0413	1.0310	1.004	46.270	0.1154
0.0589	1.0332	1.011	46.750	0.1260
0.0766	1.0354	1.018	47.220	0.1363
0.0943	1.0376	1.025	47.600	0.1461

$T = 308.15 \text{ K}$				
0.0059	1.0214	0.818	33.000	0.0962
0.0235	1.0239	0.826	35.800	0.1125
0.0411	1.0262	0.833	37.400	0.1276
0.0587	1.0285	0.839	38.800	0.1372
0.0763	1.0308	0.845	39.900	0.1471
0.0939	1.0330	0.851	41.100	0.1567

$T = 318.15 \text{ K}$				
0.0058	1.0171	0.690	23.800	0.1540
0.0234	1.0196	0.699	28.000	0.1630
0.0409	1.0221	0.706	31.000	0.1740
0.0584	1.0244	0.711	33.400	0.1760
0.0759	1.0267	0.716	35.400	0.1810
0.0934	1.0289	0.721	37.500	0.1871

K_2SO_4 in 30 mass% of FA + H_2O

$T = 298.15 \text{ K}$				
0.0029	1.0400	1.067	30.800	0.0874
0.0206	1.0424	1.078	38.000	0.1050
0.0383	1.0446	1.087	42.000	0.1203
0.0559	1.0467	1.095	44.500	0.1314
0.0736	1.0488	1.103	47.100	0.1423
0.0912	1.0508	1.110	49.700	0.1497

$T = 308.15 \text{ K}$				
0.0029	1.0347	0.882	18.300	0.1059
0.0205	1.0373	0.893	27.100	0.1274
0.0381	1.0396	0.901	31.700	0.1402
0.0557	1.0419	0.908	35.800	0.1498
0.0732	1.0441	0.914	38.900	0.1559
0.0909	1.0461	0.920	42.231	0.1626

$T = 318.15 \text{ K}$				
0.0029	1.0288	0.737	10.000	0.2140
0.0204	1.0315	0.752	20.300	0.2209
0.0379	1.0339	0.761	26.400	0.2245
0.0553	1.0362	0.768	31.600	0.2269
0.0728	1.0384	0.774	35.373	0.2288
0.0904	1.0405	0.779	39.100	0.2300

MgSO_4 in 10 mass% of FA + H_2O

$T = 298.15 \text{ K}$				
0.0062	1.0122	0.918	148.300	0.0277
0.0247	1.0142	0.928	140.000	0.0834
0.0433	1.0165	0.939	133.600	0.1207
0.0619	1.0188	0.949	128.997	0.1498
0.0804	1.0211	0.961	127.583	0.1733
0.0989	1.0236	0.971	124.000	0.1909

$T = 308.15 \text{ K}$				
0.0062	1.0083	0.755	91.046	0.0507
0.0246	1.0109	0.765	102.215	0.1102
0.0431	1.0132	0.774	109.209	0.1409
0.0616	1.0154	0.783	114.801	0.1661
0.0801	1.0175	0.792	119.008	0.1879
0.0986	1.0194	0.801	123.009	0.2075
$T = 318.15 \text{ K}$				
0.0061	1.0050	0.620	74.200	0.2313
0.0245	1.0078	0.635	90.101	0.2728
0.0429	1.0102	0.646	100.800	0.2933
0.0614	1.0124	0.656	108.701	0.3115
0.0798	1.0144	0.665	115.700	0.3265
0.0982	1.0161	0.673	122.300	0.3354
MgSO₄ in 20 mass% of FA + H₂O				
$T = 298.15 \text{ K}$				
0.0059	1.0264	0.986	144.000	0.0664
0.0235	1.0282	0.997	139.000	0.1064
0.0412	1.0302	1.009	135.000	0.1406
0.0589	1.0323	1.019	132.500	0.1596
0.0765	1.0344	1.030	130.500	0.1806
0.0942	1.0367	1.041	127.400	0.1993
$T = 308.15 \text{ K}$				
0.0059	1.0215	0.818	89.000	0.0962
0.0234	1.0239	0.829	106.000	0.1369
0.0410	1.0259	0.838	116.000	0.1581
0.0586	1.0277	0.847	124.000	0.1781
0.0762	1.0292	0.856	130.800	0.1963
0.0938	1.0305	0.864	138.100	0.2091
$T = 318.15 \text{ K}$				
0.0058	1.0173	0.695	58.100	0.2503
0.0233	1.0200	0.712	81.700	0.2882
0.0408	1.0222	0.724	98.600	0.3049
0.0583	1.0240	0.735	111.400	0.3279
0.0758	1.0255	0.744	122.100	0.3302
0.0933	1.0265	0.754	133.800	0.3456
MgSO₄ in 30 mass% of FA + H₂O				
$T = 298.15 \text{ K}$				
0.0030	1.0399	1.067	141.330	0.0860
0.0210	1.0417	1.081	138.170	0.1235
0.0391	1.0437	1.094	136.050	0.1524
0.0571	1.0457	1.105	134.590	0.1694
0.0752	1.0477	1.117	133.404	0.1889
0.0932	1.0498	1.128	132.016	0.2036

$T = 308.15 \text{ K}$				
0.0059	1.0217	0.819	101.545	0.1122
0.0239	1.0248	0.832	110.003	0.1593
0.0419	1.0277	0.843	116.300	0.1865
0.0599	1.0305	0.853	120.000	0.2063
0.0778	1.0332	0.863	122.900	0.2252
0.0958	1.0358	0.872	126.700	0.2387

$T = 318.15 \text{ K}$				
0.0059	1.0174	0.692	89.900	0.1995
0.0238	1.0206	0.706	101.500	0.2281
0.0419	1.0236	0.716	108.900	0.2435
0.0596	1.0264	0.724	115.400	0.2523
0.0775	1.0291	0.733	120.000	0.2686
0.0953	1.0316	0.740	124.600	0.2755

ZnSO₄ in 30 mass% of FA + H₂O

$T = 298.15 \text{ K}$				
0.0029	1.0401	1.068	119.291	0.1049
0.0204	1.0428	1.084	125.380	0.1450
0.0379	1.0454	1.099	129.290	0.1790
0.0555	1.0479	1.114	132.160	0.2078
0.0730	1.0504	1.128	134.191	0.2300
0.0905	1.0528	1.141	136.540	0.2473

$T = 308.15 \text{ K}$				
0.0029	1.0348	0.884	99.995	0.1482
0.0203	1.0377	0.900	113.401	0.1841
0.0378	1.0404	0.912	121.900	0.2053
0.0552	1.0429	0.923	126.945	0.2232
0.0726	1.0453	0.934	131.301	0.2412
0.0900	1.0475	0.944	136.200	0.2547

$T = 318.15 \text{ K}$				
0.0029	1.0289	0.737	84.701	0.2038
0.0202	1.0321	0.754	101.300	0.2413
0.0376	1.0347	0.765	115.200	0.2547
0.0549	1.0372	0.774	123.200	0.2635
0.0722	1.0395	0.782	129.235	0.2706
0.0896	1.0416	0.791	135.400	0.2841

CdSO₄ in 10 mass% of FA + H₂O

$T = 298.15 \text{ K}$				
0.0059	1.0151	0.924	170.244	0.1137
0.0235	1.0256	0.961	170.784	0.3205
0.0410	1.0361	1.001	171.120	0.4583
0.0586	1.0466	1.041	171.423	0.5637
0.0762	1.0571	1.082	171.647	0.6565
0.0938	1.0675	1.123	171.860	0.7379

$T = 308.15 \text{ K}$				
0.0058	1.0110	0.763	141.804	0.1921
0.0234	1.0218	0.795	151.308	0.3738
0.0409	1.0323	0.828	157.309	0.4997
0.0584	1.0427	0.859	162.204	0.5888
0.0759	1.0530	0.891	166.403	0.6709
0.0935	1.0633	0.924	170.074	0.7480

$T = 318.15 \text{ K}$				
0.0058	1.0078	0.624	114.012	0.3234
0.0233	1.0188	0.652	132.064	0.4626
0.0407	1.0294	0.678	144.070	0.5616
0.0582	1.0398	0.703	153.325	0.6358
0.0756	1.0499	0.726	162.044	0.6987
0.0931	1.0598	0.749	168.785	0.7534

CdSO₄ in 20 mass% of FA + H₂O

$T = 298.15 \text{ K}$				
0.0061	1.0294	0.992	169.000	0.1436
0.0245	1.0402	1.033	177.000	0.3387
0.0428	1.0507	1.077	182.280	0.4730
0.0611	1.0612	1.121	186.360	0.5773
0.0795	1.0715	1.166	189.830	0.6688
0.0978	1.0817	1.211	193.000	0.7497

$T = 308.15 \text{ K}$				
0.0061	1.0245	0.825	138.000	0.2050
0.0243	1.0355	0.862	156.500	0.3950
0.0426	1.0461	0.898	167.000	0.5131
0.0608	1.0565	0.933	176.000	0.6043
0.0791	1.0666	0.968	185.000	0.6831
0.0974	1.0766	1.004	191.000	0.7576

$T = 318.15 \text{ K}$				
0.0061	1.0202	0.701	112.000	0.3567
0.0242	1.0315	0.735	136.000	0.4996
0.0424	1.0423	0.765	153.000	0.5910
0.0606	1.0526	0.793	165.600	0.6612
0.0787	1.0626	0.821	178.000	0.7265
0.0969	1.0724	0.847	187.000	0.7772

CdSO₄ in 30 mass% of FA + H₂O

$T = 298.15 \text{ K}$				
0.0029	1.0413	1.071	167.400	0.1574
0.0208	1.0515	1.119	187.701	0.3722
0.0387	1.0614	1.169	197.500	0.5122
0.0565	1.0710	1.216	205.200	0.6101
0.0744	1.0807	1.265	208.700	0.7008
0.0922	1.0899	1.314	215.700	0.7815

$T = 308.15 \text{ K}$				
0.0030	1.0347	0.883	82.900	0.1249
0.0209	1.0371	0.898	106.200	0.1656
0.0389	1.0390	0.909	119.700	0.1850
0.0568	1.0407	0.919	129.100	0.2009
0.0748	1.0421	0.928	136.700	0.2126
0.0927	1.0433	0.938	144.300	0.2284
$T = 318.15 \text{ K}$				
0.0029	1.0289	0.740	33.900	0.2802
0.0209	1.0319	0.762	72.000	0.3131
0.0387	1.0342	0.776	93.200	0.3277
0.0566	1.0358	0.788	111.300	0.3402
0.0746	1.0372	0.799	124.500	0.3516
0.0924	1.0379	0.808	138.896	0.3565
ZnSO₄ in 10 mass% of FA + H₂O				
$T = 298.15 \text{ K}$				
0.0062	1.0127	0.920	123.450	0.0555
0.0249	1.0157	0.931	123.625	0.1072
0.0436	1.0187	0.943	123.725	0.1412
0.0622	1.0217	0.955	123.822	0.1707
0.0809	1.0248	0.967	123.892	0.1957
0.0996	1.0278	0.978	123.965	0.2145
$T = 308.15 \text{ K}$				
0.0062	1.0085	0.757	102.802	0.0844
0.0248	1.0118	0.768	107.408	0.1351
0.0434	1.0149	0.778	110.794	0.1660
0.0620	1.0181	0.788	113.607	0.1923
0.0806	1.0211	0.798	115.517	0.2155
0.0992	1.0241	0.807	117.544	0.2322
$T = 318.15 \text{ K}$				
0.0062	1.0052	0.618	91.061	0.1877
0.0247	1.0086	0.629	100.065	0.2090
0.0432	1.0118	0.638	105.007	0.2291
0.0617	1.0149	0.646	109.161	0.2446
0.0803	1.0179	0.654	112.447	0.2608
0.0988	1.0209	0.660	115.823	0.2690
ZnSO₄ in 20 mass% of FA + H₂O				
$T = 298.15 \text{ K}$				
0.0060	1.0268	0.987	120.310	0.0790
0.0240	1.0297	1.001	123.140	0.1316
0.0421	1.0325	1.014	124.860	0.1639
0.0601	1.0353	1.027	126.170	0.1913
0.0782	1.0380	1.039	127.540	0.2114
0.0962	1.0408	1.053	128.520	0.2366

$T = 308.15 \text{ K}$				
0.0029	1.0361	0.888	131.700	0.2329
0.0207	1.0469	0.932	155.500	0.4359
0.0385	1.0571	0.972	170.900	0.5521
0.0563	1.0669	1.011	182.800	0.6439
0.0739	1.0766	1.049	190.500	0.7215
0.0917	1.0859	1.088	199.600	0.7945
$T = 318.15 \text{ K}$				
0.0029	1.0303	0.744	100.000	0.3821
0.0206	1.0413	0.784	135.900	0.5257
0.0383	1.0517	0.817	156.200	0.6168
0.0560	1.0616	0.848	171.600	0.6898
0.0737	1.0712	0.877	182.800	0.7478
0.0913	1.0802	0.905	196.101	0.7990

Table 3. Limiting apparent molar volumes (ϕ_v^0) and experimental slopes (S_v^*) of different sulphate salts in different aqueous binary mixtures of formamide (FA) at different temperatures. Standard errors are given in parenthesis.

Mass% of formamide	$\phi_v^0 \times 10^6$, $m^3 \cdot mol^{-1}$			$S_v^* \times 10^6$, $m^3 \cdot L^{1/2} \cdot mol^{-3/2}$		
	298.15 K	303.15 K	318.15 K	298.15 K	308.15 K	318.15 K
(NH₄)₂SO₄						
10	40.860 (±0.027)	25.064 (±0.064)	13.153 (±0.050)	62.383 (±0.005)	86.164 (±0.002)	114.056 (±0.003)
20	28.308 (±0.040)	17.078 (±0.056)	8.533 (±0.090)	94.818 (±0.004)	115.224 (±0.003)	136.330 (±0.005)
30	17.272 (±0.020)	9.737 (±0.062)	3.277 (±0.067)	126.326 (±0.003)	144.945 (±0.001)	157.701 (±0.001)
Na₂SO₄						
10	33.554 (±0.090)	16.515 (±0.060)	8.454 (±0.072)	-68.311 (±0.001)	24.431 (±0.002)	50.041 (±0.003)
20	27.086 (±0.007)	4.722 (±0.066)	-15.939 (±0.093)	-11.081 (±0.001)	71.325 (±0.001)	129.944 (±0.004)
30	24.046 (±0.059)	-6.171 (±0.083)	-34.113 (±0.039)	29.333 (±0.005)	119.139 (±0.001)	203.951 (±0.001)
K₂SO₄						
10	59.093 (±0.044)	45.461 (±0.036)	33.291 (±0.019)	-50.629 (±0.005)	-16.641 (±0.002)	9.854 (±0.002)
20	43.630 (±0.027)	30.363 (±0.075)	19.068 (±0.091)	12.948 (±0.002)	34.839 (±0.002)	59.555 (±0.003)
30	26.985 (±0.088)	13.182 (±0.089)	3.542 (±0.073)	74.984 (±0.004)	95.760 (±0.002)	118.231 (±0.001)
MgSO₄						
10	155.983 (±0.068)	80.697 (±0.070)	58.281 (±0.094)	-103.358 (±0.009)	135.907 (±0.003)	203.918 (±0.001)
20	149.604 (±0.088)	73.132 (±0.095)	32.344 (±0.060)	-70.855 (±0.005)	210.966 (±0.002)	328.517 (±0.003)
30	143.416 (±0.010)	70.299 (±0.059)	11.428 (±0.053)	-36.957 (±0.003)	244.964 (±0.004)	417.489 (±0.002)
ZnSO₄						
10	123.280 (±0.004)	97.731 (±0.072)	83.262 (±0.045)	2.162 (±0.002)	62.896 (±0.003)	103.883 (±0.003)
20	117.614 (±0.068)	93.560 (±0.017)	78.386 (±0.035)	35.249 (±0.002)	107.215 (±0.005)	149.948 (±0.002)
30	115.541 (±0.071)	92.541 (±0.009)	73.115 (±0.014)	69.789 (±0.002)	146.004 (±0.004)	209.983 (±0.006)
CdSO₄						
10	169.701 (±0.009)	132.434 (±0.034)	95.574 (±0.062)	7.056 (±0.001)	123.173 (±0.001)	240.327 (±0.001)
20	161.026 (±0.059)	120.519 (±0.075)	86.214 (±0.018)	102.320 (±0.001)	226.813 (±0.003)	324.289 (±0.002)
30	158.870 (±0.067)	116.857 (±0.052)	80.178 (±0.091)	189.414 (±0.009)	273.540 (±0.003)	383.534 (±0.003)

Table 4. Values of various coefficients of Eq. (3) for different sulphate salts in 10, 20 and 30 mass% of FA + H₂O mixtures.

Mass% of formamide	$a_0 \times 10^6$, $\text{m}^3 \cdot \text{mol}^{-1}$	$a_1 \times 10^6$, $\text{m}^3 \cdot \text{mol}^{-1} \text{K}^{-1}$	$a_2 \times 10^6$, $\text{m}^3 \cdot \text{mol}^{-1} \text{K}^{-2}$
(NH₄)₂SO₄			
10	2305.154	-13.414	0.019
20	1626.716	-9.457	0.014
30	781.250	-4.305	0.006
Na₂SO₄			
10	4683.603	-29.035	0.045
20	1478.222	-7.412	0.008
30	1983.849	-10.008	0.011
K₂SO₄			
10	1138.366	-5.802	0.007
20	1333.351	-7.228	0.009
30	2359.402	-14.056	0.021
MgSO₄			
10	26631.279	-167.434	0.264
20	18750.179	-115.353	0.178
30	8745.908	-49.693	0.069
ZnSO₄			
10	5978.479	-36.168	0.055
20	4938.056	-29.479	0.045
30	2447.035	-13.161	0.018
CdSO₄			
10	1479.032	-5.032	0.002
20	4244.212	-23.027	0.031
30	3850.865	-20.299	0.026

Table 5. Limiting apparent molar expansibilities (ϕ_E^0) and $(\delta^2 \phi_V^0 / \delta T^2)_P$ for various sulphate compounds in 10, 20 and 30 mass% of FA + H₂O mixtures at different temperatures.

Mass% of formamide	$\phi_E^0 \times 10^6, \text{ m}^3 \cdot \text{mol}^{-1} \text{K}^{-1}$			$(\delta^2 \phi_V^0 / \delta T^2)_P \times 10^{12},$ $\text{m}^6 \cdot \text{mol}^{-2} \text{K}^{-2}$
	T, K= 298.15	T, K= 308.15	T, K= 318.15	
(NH₄)₂SO₄				
10	-1.775	-1.384	-0.994	0.038
20	-1.265	-0.990	-0.715	0.028
30	-0.819	-0.702	-0.585	0.012
Na₂SO₄				
10	-2.158	-1.256	-0.355	0.090
20	-2.322	-2.151	-1.981	0.016
30	-3.138	-2.908	-2.678	0.022
K₂SO₄				
10	-1.437	-1.291	-1.145	0.014
20	-1.423	-1.228	-1.034	0.018
30	-1.589	-1.172	-0.753	0.042
MgSO₄				
10	-10.163	-4.888	0.387	0.528
20	-9.420	-5.867	-2.314	0.356
30	-8.012	-6.614	-5.216	0.138
ZnSO₄				
10	-3.109	-2.000	-0.891	0.110
20	-2.857	-1.964	-1.071	0.090
30	-2.478	-2.120	-1.762	0.036
CdSO₄				
10	-3.750	-3.707	-3.664	0.004
20	-4.363	-3.737	-3.111	0.062
30	-4.467	-3.936	-3.405	0.052

Table 6. Values of *A* and *B*-coefficients of different sulphate salts in different aqueous binary mixtures of formamide (FA) at different temperatures. Standard errors are given in parenthesis.

Mass% of formamide	<i>A</i> X 10 ^{3/2} , L ^{1/2} .mol ^{-1/2}			<i>B</i> X 10 ³ , L.mol ⁻¹		
	298.15 K	303.15 K	318.15 K	298.15 K	308.15 K	318.15 K
(NH₄)₂SO₄						
10	0.024 (±0.005)	0.051 (±0.002)	0.069 (±0.001)	0.282 (±0.016)	0.196 (±0.010)	0.163 (±0.008)
20	0.056 (±0.002)	0.063 (±0.003)	0.083 (±0.001)	0.200 (±0.008)	0.177 (±0.016)	0.150 (±0.010)
30	0.081 (±0.002)	0.085 (±0.001)	0.095 (±0.004)	0.161 (±0.010)	0.151 (±0.008)	0.122 (±0.030)
Na₂SO₄						
10	-0.024 (±0.003)	0.048 (±0.002)	0.175 (±0.003)	0.763 (±0.003)	0.569 (±0.004)	0.213 (±0.012)
20	0.003 (±0.002)	0.071 (±0.002)	0.197 (±0.003)	0.722 (±0.002)	0.536 (±0.003)	0.195 (±0.013)
30	0.034 (±0.002)	0.125 (±0.004)	0.227 (±0.001)	0.671 (±0.003)	0.408 (±0.010)	0.127 (±0.008)
K₂SO₄						
10	0.030 (±0.001)	0.062 (±0.003)	0.089 (±0.002)	0.349 (±0.003)	0.288 (±0.009)	0.238 (±0.008)
20	0.056 (±0.001)	0.074 (±0.002)	0.143 (±0.002)	0.289 (±0.003)	0.265 (±0.006)	0.142 (±0.012)
30	0.071 (±0.002)	0.094 (±0.001)	0.211 (±0.001)	0.257 (±0.009)	0.230 (±0.005)	0.066 (±0.010)
MgSO₄						
10	-0.026 (±0.002)	0.002 (±0.003)	0.200 (±0.003)	0.696 (±0.003)	0.658 (±0.005)	0.443 (±0.007)
20	0.021 (±0.002)	0.060 (±0.060)	0.223 (±0.003)	0.579 (±0.004)	0.491 (±0.003)	0.403 (±0.008)
30	0.058 (±0.002)	0.104 (±0.002)	0.266 (±0.003)	0.473 (±0.005)	0.405 (±0.005)	0.308 (±0.008)
ZnSO₄						
10	0.001 (±0.001)	0.035 (±0.001)	0.156 (±0.003)	0.678 (±0.002)	0.629 (±0.002)	0.358 (±0.008)
20	0.027 (±0.002)	0.073 (±0.002)	0.176 (±0.002)	0.668 (±0.003)	0.543 (±0.004)	0.326 (±0.007)
30	0.068 (±0.005)	0.123 (±0.002)	0.192 (±0.004)	0.592 (±0.009)	0.433 (±0.004)	0.309 (±0.014)
CdSO₄						
10	-0.096 (±0.001)	0.007 (±0.003)	0.178 (±0.004)	2.724 (±0.001)	2.417 (±0.001)	1.894 (±0.002)
20	-0.062 (±0.003)	0.025 (±0.003)	0.217 (±0.002)	2.590 (±0.001)	2.349 (±0.001)	1.808 (±0.001)
30	0.018 (±0.005)	0.112 (±0.001)	0.288 (±0.003)	2.502 (±0.002)	2.248 (±0.001)	1.690 (±0.002)

Table 7. Values of \bar{V}_1^0 , \bar{V}_2^0 , $\Delta\mu_1^{0*}$, $\Delta\mu_2^{0*}$, $T\Delta S_2^{0*}$ and ΔH_2^{0*} for $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 , K_2SO_4 , MgSO_4 , ZnSO_4 and CdSO_4 in different aqueous binary mixtures of formamide (FA) at different temperatures.

Parameter	10 mass% of formamide + Water		
	298.15 K	308.15 K	318.15 K
$\bar{V}_1^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	18.950	19.031	19.095
$\Delta\mu_1^{0*}, \text{kJ mol}^{-1}$	9.352	9.171	8.920
Amminium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	40.860	25.064	13.153
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	49.105	36.369	30.675
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	274.745	283.960	293.175
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	323.850	320.329	323.850
Sodium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	33.554	16.515	8.454
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	111.068	85.431	36.950
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	1104.914	1141.973	1179.032
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	1215.982	1227.404	1215.982
Potassium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	59.093	45.461	33.291
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	60.254	51.499	43.853
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	244.498	252.698	260.899
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	304.752	304.197	304.752
Magnesium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	155.983	80.697	58.281
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	118.318	106.052	75.712
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	635.149	656.452	677.755
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	753.467	762.504	753.467
Zinc Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	123.280	97.731	83.262
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	111.686	104.441	67.398
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	660.223	682.367	704.511
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	771.909	786.808	771.909
Cadmium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	169.701	132.434	95.574
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	385.390	349.813	281.869
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	1543.239	1595.000	1646.760
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	1928.629	1944.813	1928.629

Parameter	20 mass% of formamide + Water		
	298.15 K	308.15 K	318.15 K
$\bar{V}_1^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	19.955	20.057	20.144
$\Delta\mu_1^{0*}, \text{kJ mol}^{-1}$	9.650	9.502	9.360
Amminium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	28.308	17.028	8.533
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	35.531	31.724	27.532
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	119.245	123.245	127.244
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	154.776	154.969	154.776
Sodium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	27.086	4.722	-15.939
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	100.222	76.009	30.228
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	1043.436	1078.433	1113.430
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	1143.658	1154.442	1143.658
Potassium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	43.630	30.363	19.068
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	48.490	44.668	27.865
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	307.467	317.780	328.092
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	355.957	362.448	355.957
Magnesium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	149.604	73.132	32.344
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	97.678	78.999	63.881
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	503.829	520.727	537.626
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	601.507	599.726	601.507
Zinc Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	117.614	93.560	78.386
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	104.759	88.251	59.816
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	670.003	692.475	714.947
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	774.763	780.726	774.763
Cadmium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	161.026	120.519	86.214
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	348.902	322.384	255.448
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	1393.166	1439.893	1486.620
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	1742.068	1762.277	1742.068

Parameter	30 mass% of formamide + Water		
	298.15 K	308.15 K	318.15 K
$\bar{V}_1^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	21.133	21.241	21.363
$\Delta\mu_1^{0*}, \text{kJ mol}^{-1}$	9.989	9.846	9.692
Amminium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	17.272	9.737	3.277
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	28.420	26.671	22.558
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	87.388	90.319	93.250
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	115.808	116.990	115.808
Sodium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	24.046	-6.171	-34.113
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	89.035	55.749	18.548
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	1050.785	1086.028	1121.272
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	1139.820	1141.778	1139.820
Potassium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	26.985	13.182	3.542
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	40.820	36.615	15.657
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	375.117	387.699	400.280
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	415.937	424.314	415.937
Magnesium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	143.416	70.299	11.428
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	79.813	64.611	46.597
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	495.168	511.776	528.384
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	574.981	576.387	574.981
Zinc Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	115.541	92.541	73.115
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	90.501	70.671	54.359
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	538.787	556.858	574.929
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	629.288	627.529	629.288
Cadmium Sulphate			
$\bar{V}_2^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	158.870	116.857	80.178
$\Delta\mu_2^{0*}, \text{kJ mol}^{-1}$	319.618	292.513	226.222
$T\Delta S_2^{0*}, \text{kJ mol}^{-1}$	1392.301	1438.999	1485.697
$\Delta H_2^{0*}, \text{kJ mol}^{-1}$	1711.919	1731.512	1711.919

Table 8. Molal concentration (m), ultrasonic speed of sound (u), adiabatic compressibility (K_S), apparent molal adiabatic compressibility (ϕ_k), limiting apparent molal adiabatic compressibility (ϕ_k^0) and experimental slope (S_k^*) of some sulphates in different aqueous binary mixtures of formamide (FA) at 298.15 K. Standard errors are given in parenthesis.

m , (mol. kg ⁻¹)	u , (m.s ⁻¹)	$K_S \times 10^{10}$, (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} .kg ^{1/2} .Pa ⁻¹)
(NH₄)₂SO₄ in 10 mass% of FA + H₂O					
0.0062	1499.6	4.393	-8.329		
0.0249	1517.7	4.283	-6.279		
0.0438	1528.5	4.217	-4.969	-10.070	23.753
0.0626	1534.2	4.180	-3.980	(±0.058)	(±0.007)
0.0814	1537.5	4.157	-3.279		
0.0991	1539.6	4.141	-2.799		
(NH₄)₂SO₄ in 20 mass% of FA + H₂O					
0.0059	1511.5	4.264	-3.829		
0.0237	1520.8	4.206	-3.221		
0.0415	1528.7	4.157	-2.879	-4.419	7.668
0.0593	1534.9	4.119	-2.577	(±0.025)	(±0.003)
0.0772	1538.9	4.092	-2.255		
0.0951	1543.3	4.065	-2.059		
(NH₄)₂SO₄ in 30 mass% of FA + H₂O					
0.0064	1536.5	4.072	-2.259		
0.0193	1540.5	4.046	-1.929		
0.0289	1542.9	4.029	-1.752	-2.711	5.642
0.0516	1547.3	4.001	-1.431	(±0.010)	(±0.002)
0.0742	1549.7	3.982	-1.158		
0.0937	1551.6	3.969	-0.995		
Na₂SO₄ in 10 mass% of FA + H₂O					
0.0072	1499.7	4.391	-7.549		
0.0287	1520.3	4.262	-6.279		
0.0502	1534.6	4.171	-5.350	-8.906	15.759
0.0645	1542.7	4.120	-4.940	(±0.046)	(±0.003)
0.0789	1546.9	4.089	-4.419		
0.0932	1552.3	4.053	-4.119		
Na₂SO₄ in 20 mass% of FA + H₂O					
0.0058	1512.6	4.258	-5.039		
0.0232	1524.8	4.181	-4.399		
0.0406	1535.0	4.118	-3.999	-5.663	8.267
0.0580	1543.5	4.064	-3.669	(±0.011)	(±0.001)
0.0754	1550.5	4.019	-3.379		
0.0929	1556.8	3.978	-3.159		

Na₂SO₄ in 30 mass% of FA + H₂O

0.0027	1536.4	4.073	-4.820		
0.0191	1547.3	4.009	-3.819		
0.0354	1554.5	3.965	-3.199	-5.447	11.916
0.0518	1559.4	3.933	-2.740	(±0.014)	(±0.001)
0.0682	1561.9	3.914	-2.320		
0.0846	1563.1	3.901	-1.989		

K₂SO₄ in 10 mass% of FA + H₂O

0.0059	1499.5	4.393	-8.710		
0.0239	1518.2	4.276	-6.869		
0.0418	1530.2	4.199	-5.640	-10.446	23.215
0.0598	1537.1	4.152	-4.680	(±0.083)	(±0.004)
0.0777	1540.9	4.122	-3.950		
0.0957	1542.7	4.102	-3.379		

K₂SO₄ in 20 mass% of FA + H₂O

0.0057	1511.9	4.261	-4.389		
0.0230	1522.3	4.194	-3.799		
0.0403	1530.7	4.139	-3.409	-4.970	7.735
0.0576	1537.6	4.093	-3.109	(±0.007)	(±0.001)
0.0749	1543.3	4.055	-2.849		
0.0923	1548.1	4.021	-2.629		

K₂SO₄ in 30 mass% of FA + H₂O

0.0028	1536.4	4.073	-4.669		
0.0199	1546.9	4.009	-3.652		
0.0369	1553.9	3.964	-3.042	-5.299	11.774
0.0539	1558.3	3.934	-2.559	(±0.017)	(±0.001)
0.0710	1560.4	3.916	-2.138		
0.0882	1561.6	3.903	-1.819		

MgSO₄ in 10 mass% of FA + H₂O

0.0061	1498.3	4.400	-6.869		
0.0245	1512.4	4.310	-4.909		
0.0431	1519.4	4.261	-3.689	-8.367	21.588
0.0616	1522.4	4.235	-2.859	(±0.009)	(±0.010)
0.0803	1522.9	4.223	-2.219		
0.0991	1523.3	4.210	-1.839		

MgSO₄ in 20 mass% of FA + H₂O

0.0057	1509.5	4.276	-1.551		
0.0230	1514.7	4.239	-1.523		
0.0404	1519.7	4.203	-1.506	-1.578	0.364
0.0578	1524.6	4.167	-1.491	(±0.001)	(±0.001)
0.0753	1529.4	4.133	-1.478		
0.0929	1534.1	4.099	-1.468		

MgSO₄ in 30 mass% of FA + H₂O					
0.0029	1536.6	4.072	-4.390		
0.0203	1547.9	4.006	-3.300		
0.0378	1554.8	3.963	-2.620	-5.118	13.137
0.0554	1556.6	3.947	-1.909	(±0.090)	(±0.007)
0.0731	1557.7	3.934	-1.500		
0.0908	1558.7	3.921	-1.250		
ZnSO₄ in 10 mass% of FA + H₂O					
0.0061	1497.8	4.402	-6.739		
0.0247	1511.8	4.308	-5.040		
0.0433	1519.5	4.251	-3.940	-8.153	19.555
0.0620	1524.3	4.212	-3.219	(±0.028)	(±0.007)
0.0808	1525.3	4.194	-2.569		
0.0997	1525.8	4.179	-2.139		
ZnSO₄ in 20 mass% of FA + H₂O					
0.0059	1509.4	4.275	-1.781		
0.0235	1514.6	4.233	-1.761		
0.0412	1519.9	4.192	-1.749	-1.800	0.251
0.0590	1525.3	4.151	-1.739	(±0.001)	(±0.002)
0.0769	1530.8	4.111	-1.730		
0.0949	1536.5	4.069	-1.723		
ZnSO₄ in 30 mass% of FA + H₂O					
0.0028	1534.7	4.082	-1.274		
0.0197	1538.0	4.054	-1.130		
0.0367	1541.2	4.027	-1.062	-1.349	1.508
0.0538	1544.2	4.002	-0.998	(±0.007)	(±0.004)
0.0709	1546.9	3.979	-0.941		
0.0881	1549.8	3.955	-0.909		
CdSO₄ in 10 mass% of FA + H₂O					
0.0058	1498.2	4.389	-9.199		
0.0233	1511.1	4.269	-6.799		
0.0409	1515.9	4.199	-5.269	-10.836	25.822
0.0585	1516.4	4.155	-4.219	(±0.099)	(±0.015)
0.0764	1517.3	4.109	-3.669		
0.0943	1520.1	4.054	-3.419		
CdSO₄ in 20 mass% of FA + H₂O					
0.0059	1508.7	4.268	-2.699		
0.0239	1512.1	4.204	-2.682		
0.0421	1516.0	4.141	-2.671	-2.716	0.221
0.0603	1520.3	4.077	-2.662	(±0.001)	(±0.001)
0.0786	1524.9	4.013	-2.654		
0.0971	1530.0	3.949	-2.647		

CdSO₄ in 30 mass% of FA + H₂O

0.0029	1535.1	4.075	-3.520		
0.0201	1540.3	4.008	-3.039		
0.0375	1544.3	3.950	-2.735	-3.802	5.403
0.0550	1547.9	3.897	-2.529	(±0.016)	(±0.003)
0.0726	1550.2	3.850	-2.339		
0.0903	1553.0	3.804	-2.199		

CHAPTER X

Studies on Ion-pair and Triple-ion Formation of Some Tetraalkyl ammonium Salts in Binary Solvent Mixtures of Tetrahydrofuran and Benzene at 298.15 K

Keywords: Conductivity, Ion-pair, Triple-ion, Tetraalkylammonium halides, Tetrahydrofuran, Benzene, Solvation

10.1. Introduction

Studies on ionic solvation of tetraalkylammonium salts in solvents of low permittivity have assumed importance because of their applications in modern technology¹. In media of low permittivity, salts are generally so associated that the state of the ionic species in solutions is most difficult to be elucidated. A number of conductometric² and related studies of electrolytes in non-aqueous solvents have been done in relation to the use of these types of electrolytes in high-energy batteries³ and for further understanding of organic reaction mechanisms.⁴

Further, after the classical work of Fuoss and Kraus⁵ in the thirties, there has been a renewed interest in the study of association and dimerization of electrolytes in media of low permittivity.⁶ This has been particularly of importance because knowledge of the state of association of the electrolytes along with the type and structure of the complex species in solution is essential for the optimal choice of solvents and electrolytes. The formation of triple ions in media having low permittivity⁷ ($\epsilon < 10$) have been investigated from the conductivity studies of tetraalkylammonium salts^{8,9} by fitting the Fuoss-Kraus equation. The minima observed in conductometric curves (Λ Vs \sqrt{c}) in this type of solvents were interpreted by the formation of M_2X^+ and MX_2^- triple-ion species.¹⁰

In the present study, the conductivity of tetraalkylammonium bromide, R_4NBr (R=Butyl to Heptyl) salts was examined in THF + C_6H_6 mixtures with 10, 20, 30 and 40 mass% of C_6H_6 having dielectric constant (ϵ) = 7.05, 6.52, 5.99 and 5.46 respectively.

10.2. Experimental Section

10.2.1. Source and purity of samples

Tetrahydrofuran (Merck, India) was kept for several days over KOH, refluxed for 24 h, and distilled over $LiAlH_4$.^{7,9} The boiling point (66 °C), density (0.8807 g/cm^3), and viscosity ($\eta_0 = 0.4630 mPa s$) compared well with the literature values.^{9,11} The specific conductance of THF was $\approx 0.81 \times 10^{-6} \Omega^{-1} cm^{-1}$ at 25 °C. The purity of the solvent finally obtained was >99.0 %. The chemicals used were of analytical grade. Benzene (S. D. Fine Chemicals, purity > 99%) was further purified by means of a simple distillation technique with the first and last 20% of the distillate being discarded¹²⁻¹⁴ and finally the density and viscosity value compared with the literature.¹⁵

Tetraalkylammonium salts viz. tetrabutylammonium bromide (Bu_4NBr) tetrapentylammonium bromide (Pen_4NBr), tetrahexylammonium bromide (Hex_4NBr) and tetraheptylammonium bromide (Hp_4NBr) were of Fluka's purum or puriss grade and purified in the way given in the literature.¹⁶⁻¹⁹ Generally the salts were purified by recrystallisation. The crystallized salts were dried in vacuum. The salts were stored in glass bottles in darkened desiccators over fused $CaCl_2$. The purity was determined by gas-liquid chromatography. The materials finally obtained were found to be > 99.0 % pure.

10.2.2. Apparatus and Procedure

Binary solvent mixtures have been prepared by mixing required volumes of tetrahydrofuran and benzene with earlier conversion of the required mass of each liquid into volume at 298.15 K.²⁰ A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The value of the dielectric constant (ϵ) of the solvent mixtures was assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner.²¹

Densities (ρ) 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 pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The measurements were done in a thermostated water bath controlled to $\pm 0.01\text{K}$ of the desired temperature. The weighings were done on a Mettler electronic balance (AG-285) with a precision of $\pm 0.01\text{mg}$. An average of triplicate measurement was taken into account. The density values were reproducible to $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature.²²⁻²⁴ The accuracy of the viscosity measurements, based on our work on several pure liquids, was $\pm 0.003 \text{ mPa s}$. The details of the methods and measurement techniques had been described elsewhere.^{25, 26}

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, having cell constant 1.11 cm^{-1} . Measurements were made in a thermostatic water bath maintained at $298.15 \text{ K} \pm 0.01 \text{ K}$. The determination of the cell constant was done using a 0.1 (M) aqueous KCl solution. The cell was calibrated by the method of Lind et al.^{27, 28} All conductance data were determined at 1 KHz and were found to be $\pm 0.3\%$ precise.

10.3. Results and discussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in table 1. The experimental values of the molar conductances, Λ against the respective concentration, c of the tetraalkylammonium halides in different binary solvent mixtures of THF + C_6H_6 mixtures at 298.15 K are presented in table 2. Figures 1-2 gives a representative plot for Λ vs. \sqrt{c} . All the salts follow the same trend in all solvent composition, i.e. Λ decreases with increasing concentration, reaches a minimum and then increases.

The conductance data have been analyzed by the Fuoss-Kraus triple-ion theory^{5,29} in the form as given below,

$$\Lambda g \sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (1)$$

$$g(c) = \frac{\beta' \exp\left\{-\frac{\beta'}{\sqrt{\Lambda_0}} \sqrt{c \Lambda}\right\}}{S \frac{\Lambda}{\Lambda_0^{3/2}} \sqrt{c \Lambda} \sqrt{1 - \frac{\Lambda}{\Lambda_0}}} \quad (2)$$

$$\beta' = \frac{1.8247 \times 10^6}{(\epsilon T)^{3/2}} \quad (3)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8206 \times 10^6}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.501}{\eta_0 (\epsilon T)^{1/2}} \quad (4)$$

In the above equations, Λ_0 is the sum of the molar conductances of the simple ions at infinite dilution, Λ_0^T is the sum of the values of the two triple ions $R_4N(Br_2)^-$ and $(R_4N)_2^+Br$ for R_4NBr salts, K_p and K_T are the ion-pair and triple-ion formation constants respectively, S is the limiting Onsager coefficient. To make equation (1) applicable, the symmetrical approximation of the two possible formation

constant of triple ions, $K_{T1} = [(R_4N)_2^+Br] / ([R_4N^+] [R_4NBr])$ and $K_{T2} = [R_4N(Br_2)^-] / ([Br^-][R_4NBr])$ equal to each other has been adopted, i.e. $K_{T1} = K_{T2} = K_T$.^{6,30}

Λ_0 values of all the salts in different binary solvent mixtures of THF + C₆H₆ at 298.15 K have been calculated by applying the Walden's rule³¹ as suggested by Krumgalz.³² Λ_0^T is calculated by setting the triple-ion conductance equal to 2/3 Λ_0 .³³ The ratio Λ_0^T / Λ_0 is equal to 0.667. The calculated values are listed in table 3. Linear regression analysis of equation (1) gives intercept and slope, here the values are also listed in table 3. The limiting molar conductances of the simple ions, Λ_0 and limiting molar conductances of the triple ions, Λ_0^T of the tetraalkylammonium salts in different binary solvent mixtures of THF + C₆H₆ at 298.15 K follow the trend ,

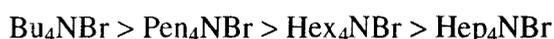


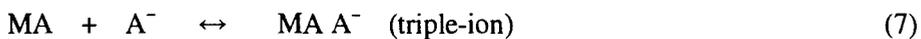
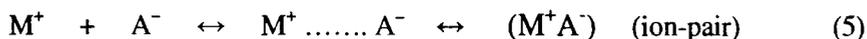
Table 3 shows that with increasing size of the tetraalkylammonium ions, both the limiting molar conductances of the simple ions, Λ_0 and that of the triple ions, Λ_0^T decrease in the different binary solvent mixtures of THF + C₆H₆. Increase in Λ_0 significantly increases the mobility of ions due to lower solvation of the ions by the solvent molecules. So Bu₄N⁺ which has the smallest ionic size has the weakest solvation among the R₄N⁺ ions. Thus, the tendency of the ion-pair and triple-ion formation of R₄N⁺X⁻ depends on the size and the charge distribution of the ions. Similar type of results have been reported earlier by Roy et al.³⁴

Applying the Fuoss-Kraus equation, we obtain K_p, K_T, which are presented in table 4. The K_p and K_T values predict that a major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadrupoles). Figures 3 show the tendency of triple-ion formation of salts in different binary solvent mixtures of THF + C₆H₆. Values predict that Hep₄NBr has the highest amount of triple-ions and lowest number of ion-pairs formed in different binary solvent mixtures of THF + C₆H₆ as compared to the other salts.

The tendency of triple-ion formation can be also judged from the K_T / K_p ratios. The ratio is highest for Hep₄NBr in all composition range studied here. The large association between the ions may be due to the Coulombic interactions as well as to covalent

bonding forces, considering the ionic sizes of the species in the solution. The results are in good agreement with the works of Hazra and Muhuri.³⁵

At very low permittivity of the solvent, i.e. $\epsilon < 10$, electrostatic ionic interactions are very strong. So the ion-pairs attract the free anions and cations present in the solution medium as the distance of the closest approach of the ions becomes minimum. This results in the formation of triple-ions which acquire the charge of the respective ions in the solution, i.e.^{5,36}



The effect of ternary association³⁷ is to remove some non-conducting species MA from the solution and replace them by triple ions which contribute to the conductance. It is observed (figure 1-2) that Λ passes through a minimum as c increases.

Furthermore, the ion-pair and triple-ion concentrations, C_p and C_T respectively, of the electrolyte are also calculated at the highest concentration of tetraalkylammonium halides in different THF + C₆H₆ mixtures using the following relations:³⁸

$$\alpha = 1 / K_p^{1/2} \cdot c^{1/2} \quad (8)$$

$$\alpha_T = (K_T / K_p^{1/2}) c^{1/2} \quad (9)$$

$$C_p = c (1 - \alpha - 3 \cdot \alpha_T) \quad (10)$$

$$C_T = (K_T / K_p^{1/2}) c^{3/2} \quad (11)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions as given in table 5, respectively. These values of C_P is maximum for Bu_4NBr and minimum for Hep_4NBr and the values of C_T is found to be highest for Hep_4NBr and lowest for Bu_4NBr . However, the ion-pair formation, α triple-ion formation, α_T ion-pair concentration, C_P triple-ion concentration C_T have been also calculated over the whole concentration range of the tetraalkylammonium halides in different binary solvent mixtures of THF + C_6H_6 and the data are provided in table 6. A representative plot for C_T vs. c is shown in figures 4 shows the variation of C_T with the concentration of the salts. It is observed for all the salts in all solvent composition that the amount of triple-ions in the solution mixture increases with the increase in concentration of the salt as well as increase in the amount of benzene the solvent mixture.³⁹

In figure 5 $\log (K_T/K_P)$ as given in table 4 has been plotted against $\log C_{min}$, where, C_{min} is the salt concentration at the minimum conductivity of the halides in THF + C_6H_6 mixtures. The graphs show an almost linear relationship. The value of $\log (K_T /K_P)$ is found to be highest in Hep_4NBr and lowest for Bu_4NBr as given in table 4. The linear relationship holds good as long as the triple-ion formation is reasonably estimated and assumed to form through complete electrostatic forces. The observations are in accordance with the results of Hojo and Chen.⁴⁰

10.4. Conclusion

An extensive study was done on the behavior of the tetraalkylammonium bromide in different THF + C_6H_6 mixtures through conductometric measurements. It becomes clear that a major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions. The tendency of the ion-pair and triple-ion formation of R_4NX depends on the size of the ions. Further, it was found that Hep_4NBr had the highest amount of triple-ions and the lowest number of ion-pairs formed in different binary solvent mixtures of THF + C_6H_6 as compared to the other electrolytes.

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Table 1. Physical properties of pure solvents and different binary mixtures of THF and C₆H₆ at 298.15 K

Solvent Mixture	$\rho \times 10^{-3} (\text{kg m}^{-3})$		$\eta \times 10^2 (\text{Poise})$		ϵ
	Exp.	Lit.	Exp.	Lit.	
0 mass% of C ₆ H ₆	0.8807	0.8807[11]	0.4630	0.4632[11]	7.58
10 mass% of C ₆ H ₆	0.8816	-	0.4771	-	7.05
20 mass% of C ₆ H ₆	0.8813	-	0.4879	-	6.52
30 mass% of C ₆ H ₆	0.8811	-	0.5041	-	5.99
40 mass% of C ₆ H ₆	0.8801	-	0.5160	-	5.46
100 mass% of C ₆ H ₆	0.8736	0.8735[15]	0.6010	0.5920[15]	2.28

Table 2 Molar conductances, Λ and the corresponding concentration, c for R_4NBr (R =Butyl to Heptyl) in different binary solvent mixtures of THF+ C_6H_6 at 298.15 K.

$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ Sm ² mol ^l	$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ Sm ² mol ^l	$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ Sm ² mol ^l	$c \times 10^4$ mol dm ⁻³	$\Lambda \times 10^4$ Sm ² mol ^l
10 mass% of C_6H_6							
Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr		Hep ₄ NBr	
0.1826	40.40	0.2060	35.10	0.2012	37.20	0.1853	39.96
0.1958	37.62	0.2169	32.90	0.2178	33.49	0.2037	36.72
0.2152	34.20	0.2331	29.65	0.2286	31.30	0.2157	34.80
0.2279	31.58	0.2437	27.80	0.2446	28.59	0.2334	32.12
0.2420	28.81	0.2592	25.40	0.2551	27.41	0.2451	30.70
0.2589	26.03	0.2695	24.20	0.2705	25.61	0.2622	29.40
0.2770	23.39	0.2845	23.10	0.2806	25.10	0.2734	28.65
0.2889	23.10	0.2944	24.00	0.2956	25.81	0.2900	28.75
0.3063	25.90	0.3090	26.20	0.3053	27.22	0.3008	29.11
0.3178	29.11	0.3185	28.40	0.3198	30.01	0.3140	29.37
20 mass% of C_6H_6							
0.2244	26.93	0.2184	26.90	0.1601	32.62	0.1742	20.14
0.2328	25.74	0.2316	24.00	0.1852	26.80	0.2032	18.50
0.2452	24.65	0.2403	22.60	0.2056	22.60	0.2286	17.10
0.2533	23.76	0.2500	21.32	0.2246	20.01	0.2511	16.18
0.2653	22.57	0.2615	20.87	0.2340	19.02	0.2710	16.23
0.2732	21.78	0.2738	20.59	0.2416	18.30	0.2888	16.43
0.2848	21.09	0.2819	20.55	0.2669	17.80	0.3049	16.67
0.2924	21.19	0.2939	20.69	0.2960	20.70	0.3194	16.91
0.3036	21.39	0.3018	21.00	0.3221	24.63	0.3326	17.05
0.3110	21.68	0.3134	21.29	0.3456	28.59	0.3446	17.25
30 mass% of C_6H_6							
0.2005	15.35	0.1788	13.32	0.1685	13.80	0.1838	13.42
0.2146	14.16	0.1913	12.59	0.1802	13.13	0.1936	13.29
0.2237	13.34	0.1995	12.18	0.1879	12.73	0.2000	13.23
0.2373	12.34	0.2115	11.78	0.1993	12.04	0.2094	13.11
0.2462	11.79	0.2194	11.45	0.2068	11.67	0.2156	13.04
0.2593	11.20	0.2311	11.13	0.2167	11.22	0.2248	12.99
0.2678	11.42	0.2388	10.96	0.2250	11.06	0.2308	13.01
0.2805	11.51	0.2501	10.88	0.2356	10.86	0.2397	13.07
0.2888	11.70	0.2575	10.80	0.2426	10.98	0.2455	13.12
0.3011	11.79	0.2684	10.93	0.2529	11.47	0.2541	13.22
40 mass% of C_6H_6							
0.1279	17.40	0.1136	15.79	0.1207	14.00	0.0965	16.04
0.1352	15.84	0.1193	15.20	0.1289	12.20	0.1013	15.03
0.1459	14.21	0.1276	14.02	0.1342	11.21	0.1084	13.91
0.1530	12.72	0.1331	13.21	0.1421	9.89	0.1130	13.05
0.1633	11.39	0.1411	12.20	0.1473	8.97	0.1198	12.00
0.1701	10.64	0.1464	11.71	0.1550	8.38	0.1243	11.49
0.1802	10.60	0.1542	11.14	0.1600	8.88	0.1309	11.17
0.1867	10.94	0.1593	10.84	0.1674	10.35	0.1353	11.44
0.1964	12.20	0.1669	11.41	0.1722	11.58	0.1417	12.13
0.2028	13.17	0.1718	12.32	0.1794	13.36	0.1459	12.69

Table 3 The calculated limiting molar conductance, Λ_0 limiting molar conductance of the triple-ions, Λ_o^T slope and intercepts of equation 1 for R_4NBr (R=Butyl to Heptyl) in different binary solvent mixtures of THF+ C_6H_6 at 298.15 K.

Salts	$\Lambda_0 \times 10^4$ $S\ m^2\ mol^{-1}$	$\Lambda^T \times 10^4$ $S\ m^2\ mol^{-1}$	Slope $\times 10^2$	Intercept $\times 10^2$
10 mass % of C_6H_6				
Bu ₄ NBr	177.78	118.52	0.80	-0.51
Pen ₄ NBr	159.90	106.60	0.87	-0.37
Hex ₄ NBr	158.33	105.55	1.02	-0.37
Hep ₄ NBr	157.46	104.97	1.13	-0.35
20 mass % of C_6H_6				
Bu ₄ NBr	173.82	115.88	0.99	-0.39
Pen ₄ NBr	156.33	104.22	1.03	-0.36
Hex ₄ NBr	154.80	103.20	1.88	-0.63
Hep ₄ NBr	153.95	102.63	7.12	-2.15
30 mass % of C_6H_6				
Bu ₄ NBr	168.25	112.16	4.90	-1.87
Pen ₄ NBr	151.32	100.88	11.61	-3.39
Hex ₄ NBr	149.84	99.89	12.14	-3.48
Hep ₄ NBr	149.01	99.34	13.46	-3.30
40 mass % of C_6H_6				
Bu ₄ NBr	164.38	109.59	8.02	-3.03
Pen ₄ NBr	147.84	98.56	8.21	-2.23
Hex ₄ NBr	146.39	97.60	18.77	-4.83
Hep ₄ NBr	145.59	97.06	27.25	-5.37

Table 4 Salt concentration at the minimum conductivity, C_{min} , along with the ion-pair formation constant, K_P Triple-ion formation constant, K_T for R_4NBr (R= Butyl to Heptyl) in different binary solvent mixtures of THF+ C_6H_6 at 298.15 K.

Salts	$C_{min} \times 10^4$ mol dm ⁻³	$\log C_{min}$	$K_P \times 10^{-8}$ (mol dm ⁻³) ⁻¹	K_T (mol dm ⁻³) ⁻¹	(K_T / K_P) $\times 10^8$	$\log(K_T / K_P)$
10 mass% of C_6H_6						
Bu ₄ NBr	0.2889	-1.242	11.959	2.334	0.195	-8.710
Pen ₄ NBr	0.2845	-1.257	18.619	3.504	0.188	-8.725
Hex ₄ NBr	0.2806	-1.271	17.863	4.079	0.228	-8.641
Hep ₄ NBr	0.2734	-1.297	20.536	4.871	0.237	-8.625
20 mass% of C_6H_6						
Bu ₄ NBr	0.2848	-1.256	19.671	3.804	0.193	-8.714
Pen ₄ NBr	0.2819	-1.266	19.313	4.353	0.225	-8.647
Hex ₄ NBr	0.2669	-1.321	5.992	4.459	0.744	-8.128
Hep ₄ NBr	0.2511	-1.382	0.511	4.959	9.698	-7.013
30 mass% of C_6H_6						
Bu ₄ NBr	0.2593	-1.350	0.806	3.917	4.862	-7.313
Pen ₄ NBr	0.2575	-1.357	0.199	5.135	25.746	-6.589
Hex ₄ NBr	0.2356	-1.446	0.185	5.226	28.234	-6.549
Hep ₄ NBr	0.2248	-1.493	0.204	6.112	29.986	-6.523

40 mass% of C ₆ H ₆						
Bu ₄ NBr	0.1802	-1.714	0.295	3.972	13.467	-6.871
Pen ₄ NBr	0.1593	-1.837	0.439	5.520	12.571	-6.901
Hex ₄ NBr	0.1550	-1.864	0.091	5.831	64.060	-6.193
Hep ₄ NBr	0.1309	-2.033	0.073	7.608	103.526	-5.985

Table 5. Maximum concentration, c the ion-pair fraction, α triple-ion fraction, α_T ion-pair concentration, C_P triple-ion concentration, C_T for R₄NBr (R=Butyl to Heptyl) in different binary solvent mixtures of THF+ C₆H₆ at 298.15 K.

Salts	$C \times 10^4$ mol dm ⁻³	$\alpha \times 10^2$	$\alpha_T \times 10^5$	$C_P \times 10^4$ mol dm ⁻³	$C_T \times 10^9$ mol dm ⁻³
10 mass% of C ₆ H ₆					
Bu ₄ NBr	0.3178	0.513	0.038	0.316	0.012
Pen ₄ NBr	0.3185	0.411	0.046	0.317	0.015
Hex ₄ NBr	0.3198	0.418	0.055	0.318	0.017
Hep ₄ NBr	0.3140	0.394	0.060	0.313	0.019
20 mass% of C ₆ H ₆					
Bu ₄ NBr	0.3110	0.404	0.048	0.310	0.015
Pen ₄ NBr	0.3134	0.406	0.055	0.312	0.017
Hex ₄ NBr	0.3456	0.695	0.107	0.343	0.037
Hep ₄ NBr	0.3446	2.382	0.407	0.336	0.140

30 mass% of C ₆ H ₆					
Bu ₄ NBr	0.3011	2.030	0.239	0.295	0.072
Pen ₄ NBr	0.2684	4.322	0.596	0.257	0.160
Hex ₄ NBr	0.2529	4.622	0.611	0.241	0.154
Hep ₄ NBr	0.2541	4.394	0.682	0.243	0.173
40 mass% of C ₆ H ₆					
Bu ₄ NBr	0.2028	4.089	0.329	0.195	0.067
Pen ₄ NBr	0.1718	3.641	0.345	0.166	0.059
Hex ₄ NBr	0.1794	7.825	0.819	0.165	0.147
Hep ₄ NBr	0.1459	9.657	1.072	0.132	0.156

Table 6. The ion-pair fraction, α triple-ion fraction, α_T ion-pair concentration, C_P triple-ion concentration, C_T along with the concentration, C for R₄NBr (R=Butyl to Heptyl) in different binary solvent mixtures of THF+ C₆H₆ at 298.15 K.

$C \times 10^4$ mol dm ⁻³	α x10 ²	α_T x10 ⁶	$C_P \times 10^4$ mol dm ⁻³	$C_T \times 10^{10}$ mol dm ⁻³	$C \times 10^4$ mol dm ⁻³	α x10 ²	α_T x10 ⁶	$C_P \times 10^4$ mol dm ⁻³	$C_T \times 10^{10}$ mol dm ⁻³
10 mass% of C ₆ H ₆									
Bu ₄ NBr					Pen ₄ NBr				
0.1826	0.677	0.288	0.181	0.053	0.2060	0.511	0.369	0.205	0.076
0.1958	0.654	0.299	0.195	0.058	0.2169	0.498	0.378	0.216	0.082
0.2152	0.623	0.313	0.214	0.067	0.2331	0.480	0.392	0.232	0.091
0.2279	0.606	0.322	0.227	0.073	0.2437	0.470	0.401	0.243	0.098
0.2420	0.588	0.332	0.241	0.080	0.2592	0.455	0.413	0.258	0.107
0.2589	0.568	0.343	0.257	0.089	0.2695	0.446	0.422	0.268	0.114
0.2770	0.549	0.355	0.275	0.098	0.2845	0.434	0.433	0.283	0.123
0.2889	0.538	0.363	0.287	0.105	0.2944	0.427	0.441	0.293	0.130
0.3063	0.522	0.373	0.305	0.114	0.3090	0.417	0.451	0.308	0.139
0.3178	0.513	0.380	0.316	0.121	0.3185	0.411	0.458	0.317	0.146
Hex ₄ NBr					Hep ₄ NBr				
0.2012	0.527	0.433	0.200	0.087	0.1853	0.513	0.463	0.184	0.086
0.2178	0.507	0.450	0.217	0.098	0.2037	0.489	0.485	0.203	0.099
0.2286	0.495	0.461	0.227	0.106	0.2157	0.475	0.499	0.215	0.108
0.2446	0.478	0.477	0.243	0.117	0.2334	0.457	0.519	0.232	0.121
0.2551	0.468	0.487	0.254	0.124	0.2451	0.446	0.532	0.244	0.130
0.2705	0.455	0.502	0.269	0.136	0.2622	0.431	0.550	0.261	0.144

0.2806	0.447	0.511	0.279	0.143	0.2734	0.422	0.562	0.272	0.154
0.2956	0.435	0.525	0.294	0.155	0.2900	0.410	0.579	0.289	0.168
0.3053	0.428	0.533	0.304	0.163	0.3008	0.402	0.590	0.300	0.177
0.3198	0.418	0.546	0.318	0.175	0.3140	0.394	0.602	0.313	0.189
20 mass% of C ₆ H ₆									
		Bu ₄ NBr					Pen ₄ NBr		
0.2244	0.476	0.406	0.223	0.091	0.2184	0.487	0.463	0.217	0.101
0.2328	0.467	0.414	0.232	0.096	0.2316	0.473	0.477	0.231	0.110
0.2452	0.455	0.425	0.244	0.104	0.2403	0.464	0.486	0.239	0.117
0.2533	0.448	0.432	0.252	0.109	0.2500	0.455	0.495	0.249	0.124
0.2653	0.438	0.442	0.264	0.117	0.2615	0.445	0.506	0.260	0.132
0.2732	0.431	0.448	0.272	0.122	0.2738	0.435	0.518	0.273	0.142
0.2848	0.423	0.458	0.284	0.130	0.2819	0.429	0.526	0.281	0.148
0.2924	0.417	0.464	0.291	0.136	0.2939	0.420	0.537	0.293	0.158
0.3036	0.409	0.473	0.302	0.143	0.3018	0.414	0.544	0.301	0.164
0.3110	0.404	0.478	0.310	0.149	0.3134	0.407	0.554	0.312	0.174
		Hex ₄ NBr					Hep ₄ NBr		
0.1601	1.021	0.729	0.158	0.117	0.1742	3.350	2.895	0.168	0.504
0.1852	0.949	0.784	0.183	0.145	0.2032	3.102	3.126	0.197	0.635
0.2056	0.901	0.826	0.204	0.170	0.2286	2.924	3.316	0.222	0.758
0.2246	0.862	0.863	0.223	0.194	0.2511	2.791	3.475	0.244	0.872
0.2340	0.844	0.881	0.232	0.206	0.2710	2.686	3.610	0.264	0.978
0.2416	0.831	0.895	0.240	0.216	0.2888	2.602	3.727	0.281	1.076
0.2669	0.791	0.941	0.265	0.251	0.3049	2.533	3.829	0.297	1.167
0.2960	0.751	0.991	0.294	0.293	0.3194	2.474	3.919	0.311	1.252
0.3221	0.720	1.034	0.320	0.333	0.3326	2.425	3.999	0.324	1.330
0.3456	0.695	1.071	0.343	0.370	0.3446	2.382	4.071	0.336	1.403

30 mass% of C ₆ H ₆									
		Bu ₄ NBr					Pen ₄ NBr		
0.2005	2.488	1.954	0.196	0.392	0.1788	5.296	4.862	0.169	0.869
0.2146	2.405	2.021	0.209	0.434	0.1913	5.120	5.029	0.181	0.962
0.2237	2.356	2.064	0.218	0.462	0.1995	5.014	5.135	0.189	1.024
0.2373	2.287	2.126	0.232	0.504	0.2115	4.868	5.288	0.201	1.119
0.2462	2.246	2.165	0.241	0.533	0.2194	4.780	5.386	0.209	1.182
0.2593	2.188	2.222	0.254	0.576	0.2311	4.658	5.528	0.220	1.278
0.2678	2.153	2.259	0.262	0.605	0.2388	4.582	5.619	0.228	1.342
0.2805	2.103	2.311	0.275	0.648	0.2501	4.478	5.750	0.239	1.438
0.2888	2.073	2.345	0.283	0.677	0.2575	4.413	5.834	0.246	1.502
0.3011	2.031	2.395	0.295	0.721	0.2684	4.322	5.957	0.257	1.599
		Hex ₄ NBr					Hep ₄ NBr		
0.1685	5.663	4.986	0.159	0.840	0.1838	5.166	5.804	0.174	1.067
0.1802	5.475	5.157	0.170	0.929	0.1936	5.034	5.956	0.184	1.153
0.1879	5.361	5.266	0.178	0.990	0.2000	4.953	6.054	0.190	1.211
0.1993	5.206	5.423	0.189	1.081	0.2094	4.840	6.196	0.199	1.298
0.2068	5.111	5.524	0.196	1.142	0.2156	4.770	6.287	0.205	1.356
0.2167	4.993	5.655	0.206	1.225	0.2248	4.672	6.419	0.214	1.443
0.2250	4.900	5.762	0.214	1.296	0.2308	4.610	6.504	0.220	1.501
0.2356	4.788	5.897	0.224	1.389	0.2397	4.524	6.628	0.229	1.588
0.2426	4.719	5.983	0.231	1.452	0.2455	4.470	6.708	0.235	1.647
0.2529	4.622	6.109	0.241	1.545	0.2541	4.394	6.824	0.243	1.734

40 mass% of C ₆ H ₆									
Bu ₄ NBr					Pen ₄ NBr				
0.1279	5.149	2.616	0.121	0.335	0.1136	4.477	2.808	0.109	0.319
0.1352	5.008	2.689	0.128	0.364	0.1193	4.369	2.877	0.114	0.343
0.1459	4.820	2.794	0.139	0.408	0.1276	4.224	2.976	0.122	0.380
0.1530	4.708	2.861	0.146	0.438	0.1331	4.137	3.039	0.128	0.404
0.1633	4.556	2.956	0.156	0.483	0.1411	4.017	3.129	0.135	0.442
0.1701	4.464	3.017	0.163	0.513	0.1464	3.944	3.187	0.141	0.467
0.1802	4.338	3.104	0.172	0.559	0.1542	3.843	3.271	0.148	0.504
0.1867	4.261	3.161	0.179	0.590	0.1593	3.781	3.325	0.153	0.530
0.1964	4.155	3.242	0.188	0.637	0.1669	3.694	3.403	0.161	0.568
0.2028	4.089	3.294	0.194	0.668	0.1718	3.641	3.453	0.166	0.593
Hex ₄ NBr					Hep ₄ NBr				
0.1207	9.541	6.714	0.109	0.810	0.0965	11.876	8.717	0.085	0.841
0.1289	9.233	6.938	0.117	0.894	0.1013	11.591	8.932	0.090	0.905
0.1342	9.047	7.081	0.122	0.950	0.1084	11.206	9.238	0.096	1.001
0.1421	8.792	7.286	0.130	1.036	0.1130	10.974	9.434	0.101	1.066
0.1473	8.636	7.418	0.135	1.093	0.1198	10.656	9.715	0.107	1.164
0.1550	8.420	7.608	0.142	1.179	0.1243	10.462	9.895	0.111	1.230
0.1600	8.287	7.730	0.147	1.237	0.1309	10.194	10.155	0.118	1.330
0.1674	8.102	7.907	0.154	1.323	0.1353	10.030	10.322	0.122	1.396
0.1722	7.987	8.021	0.158	1.381	0.1417	9.801	10.563	0.128	1.496
0.1794	7.826	8.186	0.165	1.468	0.1459	9.659	10.718	0.132	1.563

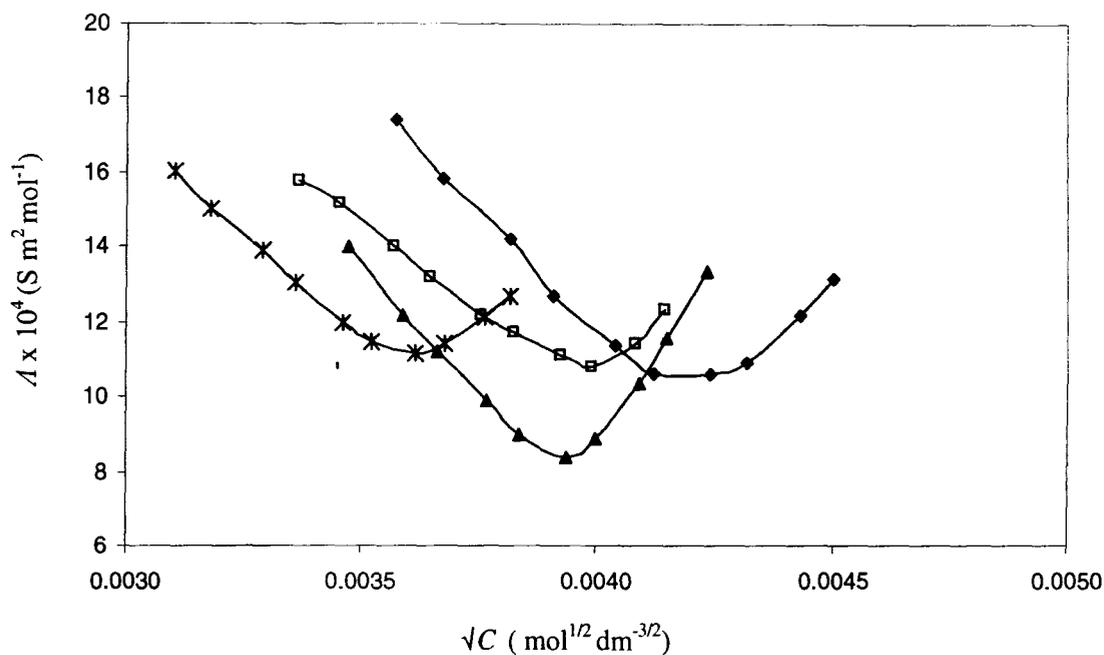


Figure 1. The plots of equivalent conductance (Λ) versus square root of salt concentration (\sqrt{C}) for the salts under investigations at 298.15 K of 40 mass% of C_6H_6 in THF + C_6H_6 mixture: (\blacklozenge) Bu_4NBr ; (\square) Pen_4NBr ; (\blacktriangle) Hex_4NBr ; (\times) Hep_4NBr .

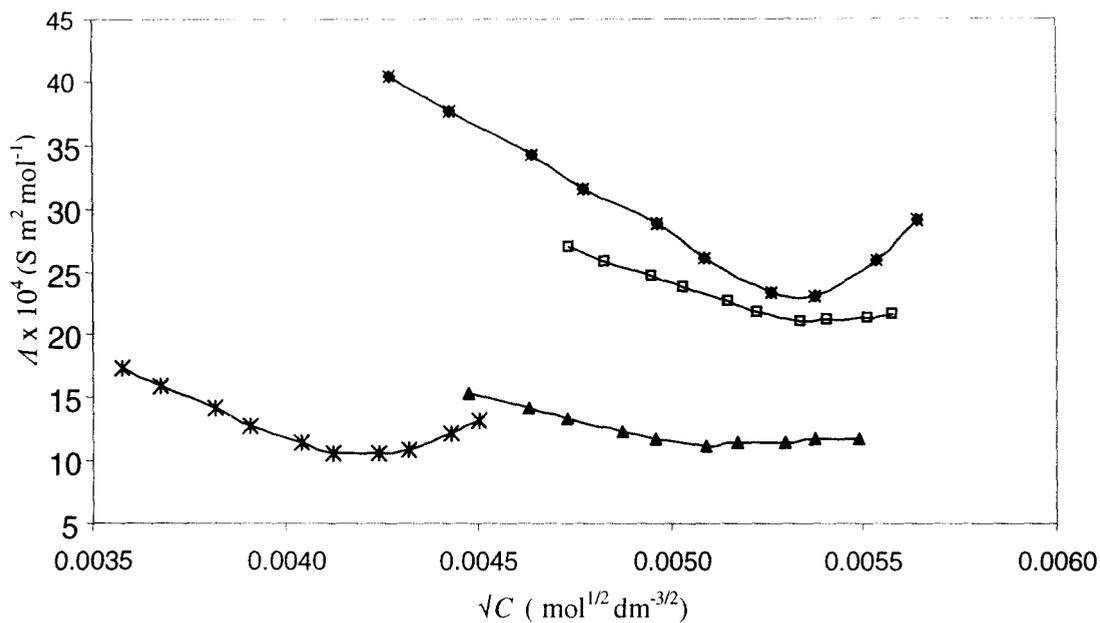


Figure 2. The plots of equivalent conductance (Λ) versus square root of salt concentration (\sqrt{C}) for the salt Bu_4NBr in different mass% of THF + C_6H_6 mixtures at 298.15 K: (◆) 10% of C_6H_6 ; (□) 20% of C_6H_6 ; (▲) 30% of C_6H_6 ; (✱) 40% of C_6H_6 .

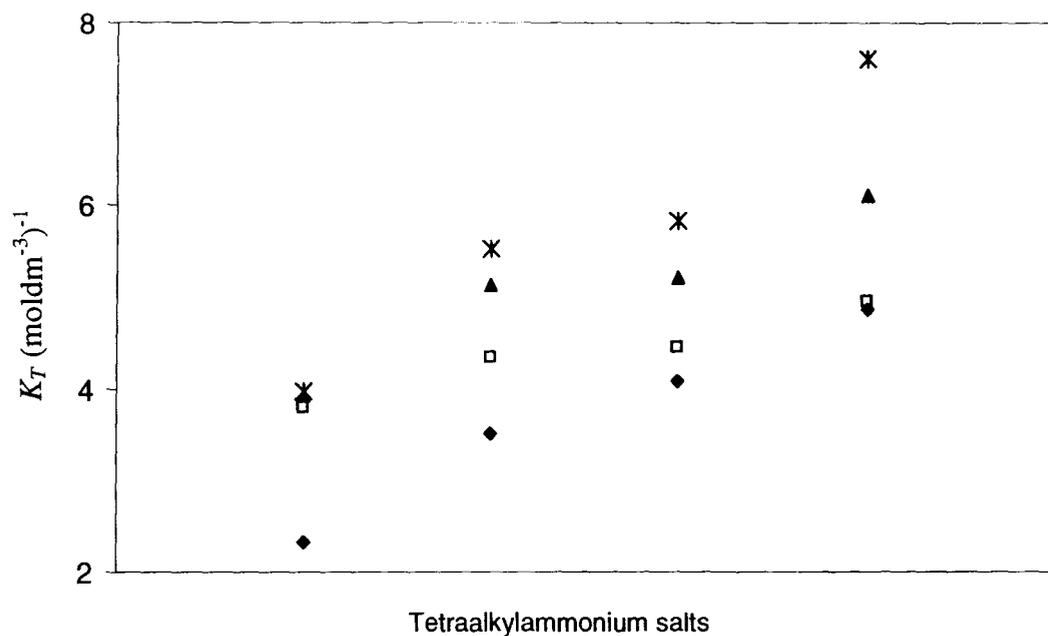


Figure 3. The plots of triple-ion formation constant, K_T of tetraalkylammonium salts in different mass% of THF + C₆H₆ solutions at 298.15 K: (◆) 10% of C₆H₆ ; (□) 20% of C₆H₆ ; (▲) 30% of C₆H₆ ; (✱) 40% of C₆H₆.

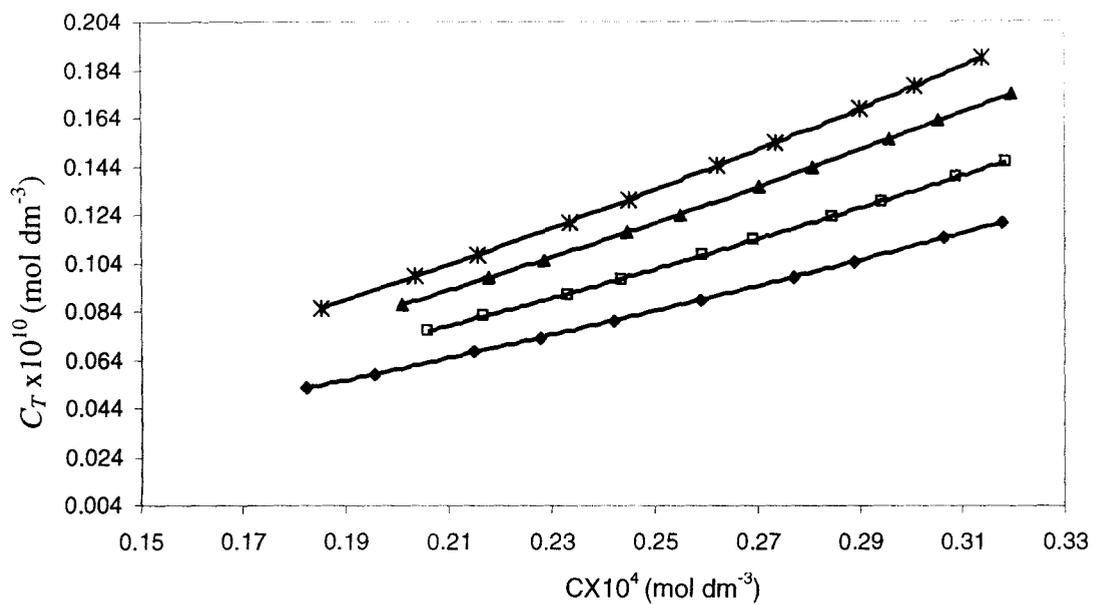


Figure 4. The plots of triple-ion constant, C_T versus salt concentration C for the salts under investigations at 298.15 K of 10 mass% of C_6H_6 in $C_6H_6 + THF$ mixture: (◆) Bu_4NBr ; (□) Pen_4NBr ; (▲) Hex_4NBr ; (✱) Hep_4NBr .

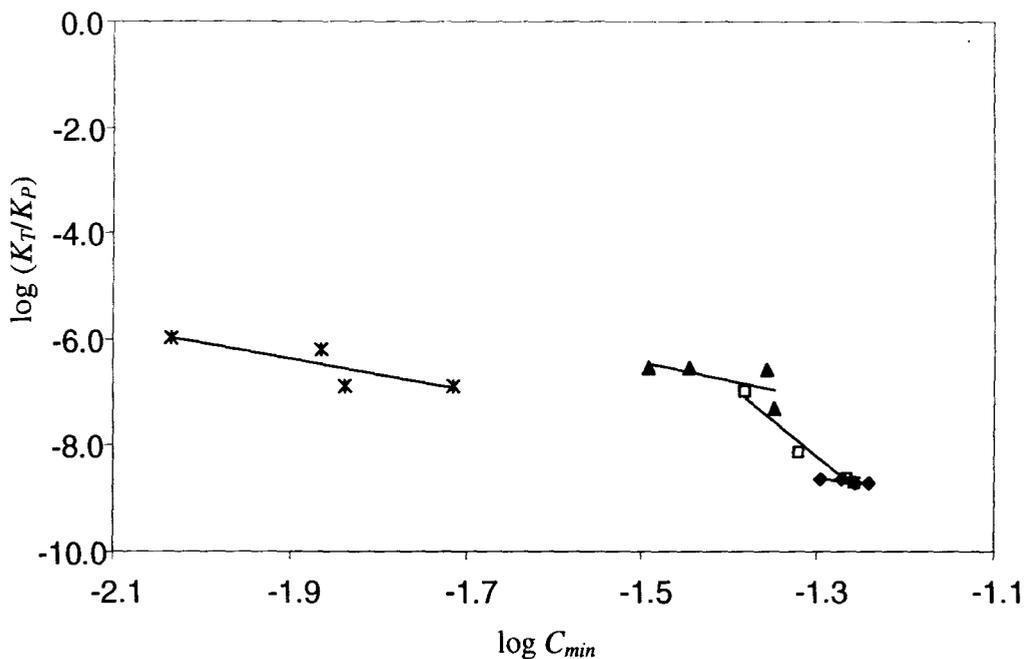


Figure 5. The plots of $\log (K_T/K_P)$ vs. $\log C_{min}$, where K_P is the ion-pair formation constant, K_T is the triple-ion formation constant and C_{min} is the salt concentration at the minimum conductivity for the salts under investigations at 298.15 K in different mass% of THF + C_6H_6 mixtures: (\blacklozenge) 10% of C_6H_6 ; (\square) 20% of C_6H_6 ; (\blacktriangle) 30% of C_6H_6 ; (\ast) 40% of C_6H_6 .

CHAPTER XI

Studies on Apparent Molar Volume, Viscosity *B*-coefficient and Adiabatic Compressibility of some Thiocyanate salts in Aqueous Binary mixtures of 1,3-dioxolane at different Temperatures.

.Keywords: Density, Viscosity, Partial molar volume, Viscosity *B*-coefficient, Enthalpy of activation, 1,3-dioxolane.

11.1. Introduction

It is well known that the reaction medium plays an important role in determining reactivity reflected in thermodynamic, transport and spectral properties.^{1,2} Gaining insights into the mechanism of such interactions, thermodynamic and transport studies involving one or more solutes in mixed solvent systems are highly useful. Studies on the apparent molar volumes of electrolytes and dependence of viscosity in connection of solutes and temperature of solutions have been employed as a function of studying ion-ion and ion-solvent interactions.³ The finding of a number of workers⁴⁻⁷ is that the addition of electrolyte could break or make the structure of a liquid. The addition of organic solvent to an aqueous solution of electrolyte brings about a change in ion's solvation and often results in a large change in the reactivity of dissolved electrolytes. The viscosity being a property of the liquid depending upon the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

1,3-dioxolane is a good industrial solvent. It figures prominently in the high energy battery industry and finds application in the organic synthesis as manifested from the physico-chemical studies in this medium.⁸ In the present study we have performed density, viscosity and ultrasonic velocity measurements in 10, 20 and 30 mass % of 1,3-dioxolane + water

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mixture of ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate as a function of temperatures in order to unravel the nature of various types of interactions prevailing in these electrolyte solutions.

11.2. Experimental Section

11.2.1. Source and purity of samples

1,3-Dioxolane, $C_3H_6O_2$ (Ethylene glycol formal or Ethylene glycol methylene ether) Merck, containing 0.3 % water, 0.005 % peroxides and sterilized with BHT was purified by heating under reflux with PbO_2 for 2 hrs., then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled.^{9, 10} The solvent obtained after purification had a boiling point of 348 K at $p = 0.1$ MPa, a density of $1058.6 \text{ kg}\cdot\text{m}^{-3}$ and a coefficient of viscosity of $0.5750 \text{ m Pa}\cdot\text{s}$ at 298.15 K which was in good agreement with the literature values.^{10, 11} The purity of the solvent finally obtained was $>99.0 \%$.

Ammonium thiocyanate, Sodium thiocyanate and Potassium thiocyanate (NH_4CNS , $NaCNS$ and $KCNS$) salts (all A.R., B.D. H.) were purified by recrystallization twice from conductivity water. The samples were dried in vacuum and stored over P_2O_5 under vacuum.

11.2.2. Apparatus and Procedure

The binary aqueous solution of 1,3-Dioxolane as well as the solutions of thiocyanate were made by weight, and conversion of molality into molarity was done¹² using density values. Adequate precautions were made to reduce evaporation losses during mixing.

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 the experimental temperatures 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 thermo-regulator and the temperature was determined by a calibrated 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 three measurements was taken into account. The density values are reproducible to $\pm 3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$.

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The viscosity was measured by means of suspended-level Ubbelohde¹³ viscometer at the desired temperature (accuracy ± 0.01 K). The precision of the viscosity measurements was 0.05 %. Details have been described earlier.⁸ Ultrasonic velocities were determined with an accuracy of 0.3 % using a single crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 2 MHz, which was calibrated with purified water and methanol at 298.15 K. The temperature stability was maintained within ± 0.01 K by circulating thermo stated water around the cell by a circulating pump.

11.3. Results and Discussion

The experimental values of densities ρ_o and viscosities η_o of pure¹⁴ 1,3-DO and 10, 20 and 30 mass % of 1,3-DO + H₂O mixtures at T= (298.15, 308.15 and 318.15) K and $p = 0.1$ mPa are reported in Table 1.

In the present investigation we have determined the ρ and η values and the values of different parameters such as V_ϕ , V_ϕ^o , S_v^* , A, B, ϕ_k , ϕ_k^o and S_k^* have been measured at different temperatures using the appropriate equations and graphical diagrams.

The experimental values of concentration c , densities ρ , viscosities η and the derived parameters for the studied electrolytes in 10, 20 and 30 mass % of 1,3-Dioxolane + water mixture at T = (298.15, 308.15 and 318.15) K and $p = 0.1$ mPa are reported in Table 2.

The apparent molar volumes V_ϕ of solutions were calculated from the density data using the following standard expression,

$$V_\phi = M / \rho_o - 1000 (\rho - \rho_o) / c \rho_o \quad (1)$$

Where c is the molar concentration of the solution, M is the molecular weight of the solute and the other symbols have their usual significance.

The values of limiting apparent molar volumes V_ϕ^o and experimental slopes S_v^* at different temperatures have been obtained by using the least-square fit to the linear plots of V_ϕ against \sqrt{c} using the Masson's equation:¹⁵

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$$V_{\phi} = V_{\phi}^{\circ} + S_{v}^{*} \sqrt{c} \quad (2)$$

Where S_{v}^{*} is a constant dependent on charge and salt type and can be related to ion-ion interactions and V_{ϕ}° is the limiting apparent molar volume which is related to ion-solvent interactions. The V_{ϕ}° values along with the experimental slopes S_{v}^{*} are listed in Table 3.

The plots of V_{ϕ} against the square root of the molar concentration \sqrt{c} were found to be linear with negative slopes. Table 3 shows that limiting apparent molar volume V_{ϕ}° for all the studied thiocyanate salts in the solvent mixture are positive and increase with rise in temperature but decrease with an increase in the amount of 1,3-dioxolane in the mixtures.

This indicates the presence of strong ion-solvent interactions, and these interactions are further strengthened with a rise in temperature and weakened with an increase in the amount of 1,3-dioxolane in the mixed solvent under investigation, suggesting larger electrostriction at higher temperature and lower amount of 1,3-dioxolane in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous DMF¹⁶ and aqueous THF.¹⁷

It is evident from Table 3 that the values of S_{v}^{*} for all the studied thiocyanate salts in the solvent mixtures are negative for all temperatures. Since S_{v}^{*} is a measure of ion-ion interactions, the results indicate the presence of weak ion-ion 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 ion-ion interactions (ionic dissociation).^{18,19} The S_{v}^{*} values increase with an increase in the amount of 1,3-dioxolane 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 1,3-dioxolane to the mixture. The same results are observed for some metal sulfates in water.^{19,20}

The temperature dependence of V_{ϕ}° for various thiocyanate salts, studied here in the solvent mixture can be expressed by the polynomial:

$$V_{\phi}^{\circ} = a_0 + a_1 T + a_2 T^2 \quad (3)$$

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Where T is the temperature in Kelvin. The values of coefficients a_0 , a_1 and a_2 for the studied thiocyanate salts for different composition of 1,3-Dioxolane + water mixture are reported in Table 4.

The apparent molar expansibilities ϕ_E° at infinite dilution can be obtained by differentiating eq. 3 with respect to temperature,

$$\phi_E^\circ = (\delta V_\phi^\circ / \delta T)_p = a_1 + 2a_2 T \quad (4)$$

The values of ϕ_E° along with the sign of magnitude of $(\delta^2 V_\phi^\circ / \delta T^2)_p$ for the studied electrolytes at T=(298.15, 308.15, and 318.15) K in different composition of 1,3-Dioxolane + water mixture are reported in Table 5.

During the past few years, it has been emphasized by a number of workers that S_v^* is not the sole criterion for determining the structure making or breaking nature of any solute. Hepler²¹ has developed a technique of examining the sign of $(\delta^2 V_\phi^\circ / \delta T^2)_p$ for various solutes in terms of long range structure making or breaking capacities of the solutes in mixed solvent systems using the following thermodynamic expression,

$$(\delta C_p / \delta P)_T = - (\delta^2 V_\phi^\circ / \delta T^2)_p \quad (5)$$

On the basis of eq. 5, it has been deduced that the structure breaker solutes should have small positive or negative values, otherwise it is structure maker. In the present study it is observed from Table 5, that the electrolyte (viz. NH_4SCN , $NaSCN$ and $KSCN$) under investigation is predominantly a structure breaker in all the experimental solvent mixtures. This may be ascribed to the absence of caging or packing effects.^{17, 22.}

The viscosity data of solutions for various electrolytes, viz. NH_4SCN , $NaSCN$ and $KSCN$ in 10, 20 and 30 mass % 1,3-Dioxolane + water mixture have been analyzed by Jones-Dole²³ equation,

$$(\eta / \eta_0 - 1) / c^{1/2} = (\eta_r - 1) / c^{1/2} = A + B c^{1/2} \quad (6)$$

$$\text{Where, } \eta = (Kt - L/t) \rho$$

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Where $\eta_r = \eta / \eta_0$, and η are the viscosities of solvent and solution respectively, c is the molar concentration of a solution, ρ is the density of the solution and K and L are constants for a particular viscometer. The values of A and B have been determined from the intercept and slope of linear plots of $(\eta / \eta_0 - 1) / \sqrt{c}$ versus \sqrt{c} and recorded in Table 6.

It is evident from the Table 6 that in all the cases small positive values of A -coefficients continuously decrease with rise in temperature, but increase with an increase in the amount of 1,3-dioxolane in the mixtures, thereby suggesting that ion-ion interactions are weakened with increase of temperature, but strengthened with the increase of 1,3-Dioxolane.

The B -coefficient is a measure of effective solvodynamic volume of solvated ions and is governed by size and shape effect of an ion and structural effect induced by ion-solvent interaction. It is observed from Table 6 that the values of the B -coefficient of different thiocyanate salts in different composition of 1,3-Dioxolane + water mixture are positive, thereby suggesting the presence of strong ion-solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of 1,3-dioxolane in the mixture. These conclusions are in excellent agreement with those drawn from V_ϕ° values discussed earlier.

It has been reported in a number of studies^{24, 25} 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 the B -coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of all studied thiocyanate salts (viz. NH_4SCN , NaSCN and KSCN) in different composition of 1,3-Dioxolane + water mixture. A similar result was reported in a study²⁶ for the case of the viscosity of some salts in propionic acid + ethanol mixtures. These conclusions are also excellent agreement with that drawn from magnitude of $(\delta^2 V_\phi^\circ / \delta T^2)_P$ illustrated earlier.

The viscosity data have also been analyzed on the basis of transition state theory for relative viscosity of the solutions as suggested by Feakings et al.²⁷ using eq 7 ,

$$\Delta\mu_2^{\text{ot}} = \Delta\mu_1^{\text{ot}} + RT (1000B + V_2^\circ - V_1^\circ) / V_1^\circ \quad (7)$$

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Where $\Delta\mu_2^{ot}$ is the contribution per mole of the solute to free energy of activation for viscous flow of solutions and $\Delta\mu_1^{ot}$ is the free energy of activation per mole of solvent mixture. The values are reported in Table 7. V_1^o is the partial molar volume of the solvent mixture, V_2^o is the partial molar volume of the solute. $\Delta\mu_1^{ot}$ is calculated from

$$\Delta\mu_1^{ot} = \Delta G_1^{ot} = RT \ln (\eta_0 V_1^o / h N_A) \quad (8)$$

Where h is Planck's constant and N_A is Avogadro's number. From Table 7, it is seen that $\Delta\mu_1^{ot}$ is almost constant at all temperatures and solvent compositions. It means that $\Delta\mu_2^{ot}$ is dependent mainly on the values of viscosity B -coefficients and $(V_2^o - V_1^o)$ terms. $\Delta\mu_2^{ot}$ values were positive at all experimental condition, suggests that with the rise in temperature and lower in concentration of 1,3-Dioxolane in the mixture, process of viscous flow of solutions becomes difficult. So the formation of the transition state becomes less favorable.²⁷ According to Feakings et al.,²⁷ $\Delta\mu_2^{ot} > \Delta\mu_1^{ot}$ for solutes having positive viscosity B -coefficients indicates a stronger solute-solvent interactions, suggesting the formation of transition state which is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.²⁷ Eq 9 has been used to calculate the entropy of activation ΔS_2^{ot} for solutions .

$$\Delta S_2^{ot} = -d(\Delta\mu_2^{ot})/dT \quad (9)$$

ΔS_2^{ot} has been calculated from the slope of the plots of $\Delta\mu_2^{ot}$ versus T by using a least square treatment. The enthalpy of activation has been determined by using the following relation,²⁷

$$\Delta H_2^{ot} = \Delta\mu_2^{ot} + T\Delta S_2^{ot} \quad (10)$$

The values of ΔS_2^{ot} and ΔH_2^{ot} are reported in Table 7. They are negative for all thiocyanate salts at all experimental temperatures and composition of 1,3-Dioxolane + water mixtures. Which suggest that the transition state is associated with bond formation and increase in order.

Coefficient of adiabatic compressibility β has been calculated using the relation,

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$$\beta = 1 / \mu^2 \rho \quad (11)$$

Where μ is the ultrasonic velocity and ρ is the density of the solution.

The apparent molal adiabatic compressibility ϕ_k of the solution was computed from the relation,

$$\phi_k = \beta M / \rho + 1000(\beta \rho_o - \beta_o \rho) / m \rho \rho_o \quad (12)$$

Where β , β_o are the adiabatic compressibility of solution and solvent respectively and m is the molal concentration of the solution.

The limiting apparent molal adiabatic compressibilities ϕ_k^o were obtained by extrapolating the plots of ϕ_k versus \sqrt{m} of the solution to zero concentration by the computerized least-squares method,

$$\phi_k = \phi_k^o + S_k^* \sqrt{m} \quad (13)$$

Where S_k^* is the experimental slope.

The values of m , μ , β , ϕ_k , ϕ_k^o and S_k^* for the studied electrolytes at 298.15 K in 10, 20 and 30 mass % of 1,3-Dioxolane + water mixture are determined and reported in Table 8.

It is evident from Table 8 that all the thiocyanate salts investigated here have negative apparent molar adiabatic compressibility ϕ_k^o and positive limiting experimental slopes S_k^* . These results can be interpreted in terms of the loss of compressibility of 1,3-Dioxolane + water mixture due to electrostrictive forces in the vicinity of the ions. The same conclusion was obtained in the case of studies on sound velocities of some alkali metal halides in THF + H₂O mixtures.^{20, 28}

11.4. Conclusion

In summary, V_ϕ^o and viscosity B -coefficient values for different thiocyanate indicate the presence of strong ion–solvent interactions and these interactions are further strengthened with rise in temperature and with decrease in the amount of 1,3-dioxolane in the mixtures. It also indicate that all studied thiocyanate salts in different composition of 1,3-Dioxolane + water mixture acts as a structure breaker.

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Table 1. Physical properties of pure 1,3-dioxolane and 1,3-dioxolane +water mixture at different temperatures

Temperature	$\rho \times 10^{-3}$ kg m ⁻³		η mPa's	
	This work	Literature	This work	Literature
10 mass % of 1,3-dioxolane + water				
298.15 K	1013.40	---	0.9970	---
308.15 K	1007.40	---	0.8350	---
318.15 K	1003.90	---	0.7452	---
20 mass % of 1,3-dioxolane + water				
298.15 K	1024.70	---	1.1240	---
308.15 K	1018.70	---	0.9652	---
318.15 K	1013.80	---	0.8548	---
30 mass % of 1,3-dioxolane + water				
298.15 K	1034.20	---	1.2460	---
308.15 K	1027.80	---	1.0618	---
318.15 K	1021.30	---	0.9373	---
Pure 1,3-dioxolane				
298.15 K	1058.6	1058.62 ¹⁴	0.5886	0.5889 ¹⁴
308.15 K	1045.8	---	0.5235	---
318.15 K	1035.6	---	0.4584	---

Table 2. Concentration c , density ρ , viscosity η , apparent molar volumes V_ϕ , and $(\eta_r - 1)/c^{1/2}$ for ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate indifferent aqueous 1,3-dioxolane solutions at different temperatures

c mol·dm ⁻³	$\rho \times 10^{-3}$ kg·m ⁻³	η mPa·s	$V_\phi \times 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/c^{1/2}$
Ammonium thiocyanate				
10 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00198	1013.50	1.0046	26.000	0.1720
0.01388	1014.14	1.0212	22.799	0.2060
0.02578	1014.83	1.0333	20.402	0.2270
0.03767	1015.57	1.0438	18.401	0.2420
0.04957	1016.30	1.0540	17.300	0.2570
0.06147	1017.05	1.0630	16.501	0.2670
T=308.15 K				
0.00197	1007.48	0.8399	37.399	0.1330
0.01379	1007.99	0.8522	32.995	0.1750
0.02561	1008.57	0.8613	30.290	0.1970
0.03742	1009.20	0.8699	27.784	0.2160
0.04923	1009.82	0.8782	26.677	0.2330
0.06104	1010.52	0.8855	24.772	0.2450
T=318.15 K				
0.00196	1003.95	0.7485	51.500	0.1003
0.01374	1004.31	0.7580	46.199	0.1460
0.02551	1004.74	0.7654	43.197	0.1700
0.03728	1005.22	0.7727	40.496	0.1910
0.04903	1005.74	0.7795	38.494	0.2080
0.06078	1006.33	0.7867	35.993	0.2260
20 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00199	1024.80	1.1343	24.800	0.2060
0.01391	1025.45	1.1551	21.600	0.2350
0.02583	1026.15	1.1692	19.500	0.2500
0.03775	1026.87	1.1821	18.100	0.2660
0.04967	1027.61	1.1939	17.200	0.2790
0.06158	1028.39	1.2038	15.800	0.2860

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T=308.15 K				
0.00198	1018.78	0.9721	32.799	0.1600
0.01382	1019.34	0.9876	28.995	0.1970
0.02566	1019.95	0.9989	26.989	0.2180
0.03750	1020.59	1.0089	25.183	0.2340
0.04933	1021.28	1.0179	23.378	0.2460
0.06116	1021.97	1.0277	22.172	0.2620
T=318.15 K				
0.00197	1013.86	0.8591	44.678	0.1130
0.01375	1014.29	0.8708	39.609	0.1600
0.02553	1014.80	0.8801	36.563	0.1850
0.03731	1015.33	0.8886	34.529	0.2050
0.04907	1015.93	0.8965	32.291	0.2200
0.06084	1016.55	0.9041	30.459	0.2340
30 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00206	1034.31	1.2578	23.700	0.2090
0.01406	1034.96	1.2809	21.501	0.2360
0.02636	1035.68	1.2968	19.401	0.2510
0.03809	1036.38	1.3100	18.200	0.2630
0.04980	1037.07	1.3225	17.800	0.2750
0.06205	1037.86	1.3341	16.502	0.2840
T=308.15 K				
0.00205	1027.90	1.0697	28.700	0.1650
0.01397	1028.49	1.0862	25.797	0.1942
0.02619	1029.16	1.0982	23.493	0.2120
0.03783	1029.82	1.1089	21.990	0.2280
0.04945	1030.50	1.1180	20.985	0.2380
0.06161	1031.24	1.1269	19.781	0.2470
T=318.15 K				
0.00204	1021.37	0.9428	41.004	0.1290
0.01388	1021.84	0.9545	36.515	0.1560
0.02602	1022.38	0.9636	34.010	0.1740
0.03758	1022.93	0.9718	32.188	0.1900
0.04912	1023.50	0.9799	30.589	0.2050
0.06119	1024.17	0.9881	28.669	0.2190
Sodium thiocyanate				
10 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00199	1013.50	1.0047	28.001	0.1730
0.01390	1014.19	1.0216	24.000	0.2090
0.02581	1014.92	1.0343	21.800	0.2330
0.03773	1015.69	1.0446	20.000	0.2460
0.04964	1016.49	1.0554	18.599	0.2630
0.06156	1017.31	1.0655	17.300	0.2770
T=308.15 K				
0.00197	1007.47	0.8400	43.300	0.1350
0.01381	1008.00	0.8523	37.600	0.1760
0.02565	1008.61	0.8619	33.700	0.2010

Studies on Apparent molar volume, Adiabatic Compressibility.....at different temperatures.

0.03749	1009.25	0.8711	31.398	0.2230
0.04932	1009.91	0.8799	29.998	0.2420
0.06115	1010.64	0.8879	27.803	0.2560
T=318.15 K				
0.00197	1003.95	0.7487	56.800	0.1050
0.01376	1004.31	0.7577	50.901	0.1430
0.02556	1004.78	0.7659	46.501	0.1740
0.03734	1005.29	0.7740	43.802	0.2000
0.04912	1005.85	0.7814	41.305	0.2190
0.06090	1006.46	0.7884	38.808	0.2350
20 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00201	1024.81	1.1344	26.900	0.2055
0.01409	1025.50	1.1558	23.500	0.2380
0.02617	1026.26	1.1708	21.100	0.2572
0.03825	1027.03	1.1835	19.700	0.2706
0.05033	1027.85	1.1956	18.000	0.2840
0.06240	1028.67	1.2066	17.100	0.2940
T=308.15 K				
0.00200	1018.78	0.9722	39.200	0.1617
0.01401	1019.35	0.9877	33.901	0.1970
0.02601	1019.99	0.9998	30.703	0.2220
0.03800	1020.68	1.0105	28.502	0.2407
0.05000	1021.39	1.0207	26.704	0.2572
0.06199	1022.16	1.0300	24.806	0.2695
T=318.15 K				
0.00199	1013.86	0.8592	49.100	0.1152
0.01394	1014.35	0.8709	40.803	0.1600
0.02588	1014.86	0.8806	39.703	0.1880
0.03781	1015.44	0.8900	37.105	0.2119
0.04974	1016.08	0.8994	34.707	0.2340
0.06167	1016.73	0.9076	33.108	0.2490
30 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00215	1034.32	1.2579	24.899	0.2060
0.01497	1035.09	1.2818	21.200	0.2350
0.02780	1035.89	1.2984	19.499	0.2520
0.04051	1036.72	1.3125	18.201	0.2650
0.05182	1037.47	1.3246	17.300	0.2770
0.06662	1038.50	1.3383	16.000	0.2870
T=308.15 K				
0.00213	1027.91	1.0699	30.302	0.1650
0.01487	1028.60	1.0869	26.396	0.1940
0.02762	1029.37	1.1003	23.576	0.2180
0.04024	1030.16	1.1112	21.800	0.2320
0.05148	1030.90	1.1206	20.249	0.2440
0.06617	1031.89	1.1328	18.711	0.2600
T=318.15 K				
0.00212	1021.38	0.9429	44.001	0.1290
0.01478	1021.90	0.9553	39.401	0.1580
0.02744	1022.50	0.9652	36.381	0.1800
0.03997	1023.15	0.9753	33.962	0.2030
0.05112	1023.75	0.9833	32.459	0.2170
0.06570	1024.58	0.9926	30.427	0.2300

Studies on Apparent molar volume, Adiabatic Compressibility.....at different temperatures.

Potassium thiocyanate				
10 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00199	1013.53	1.0048	33.001	0.1750
0.01391	1014.37	1.0242	26.900	0.2310
0.02583	1015.25	1.0393	25.101	0.2640
0.03776	1016.19	1.0528	23.000	0.2880
0.04968	1017.15	1.0659	21.501	0.3100
0.06160	1018.18	1.0782	19.400	0.3280
T=308.15 K				
0.00197	1007.50	0.8401	48.490	0.1380
0.01382	1008.17	0.8540	41.500	0.1940
0.02566	1008.89	0.8652	38.799	0.2260
0.03752	1009.69	0.8758	35.999	0.2520
0.04939	1010.53	0.8866	33.499	0.2780
0.06127	1011.40	0.8958	31.699	0.2940
T=318.15 K				
0.00197	1003.96	0.7487	64.294	0.1060
0.01377	1004.46	0.7591	56.400	0.1590
0.02556	1005.04	0.7680	52.399	0.1910
0.03737	1005.69	0.7772	49.199	0.2220
0.04919	1006.39	0.7855	46.299	0.2440
0.06101	1007.15	0.7949	43.798	0.2700
20 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00209	1024.84	1.1345	30.333	0.2039
0.01465	1025.73	1.1562	26.022	0.2370
0.02721	1026.68	1.1722	23.723	0.2600
0.03977	1027.67	1.1863	21.999	0.2780
0.05234	1028.69	1.1988	20.466	0.2910
0.06490	1029.75	1.2113	18.933	0.3050
T=308.15 K				
0.00208	1018.81	0.9724	44.625	0.1630
0.01457	1019.54	0.9880	38.939	0.1960
0.02705	1020.34	1.0001	35.910	0.2200
0.03952	1021.20	1.0111	33.396	0.2390
0.05200	1022.10	1.0222	31.203	0.2590
0.06447	1023.03	1.0328	29.449	0.2760
T=318.15 K				
0.00207	1013.88	0.8593	55.461	0.1160
0.01449	1014.49	0.8712	49.128	0.1590
0.02691	1015.19	0.8810	44.749	0.1870
0.03932	1015.96	0.8909	41.560	0.2130
0.05173	1016.79	0.9008	38.887	0.2364
0.06413	1017.66	0.9098	36.560	0.2540
30 mass % of 1,3-dioxolane + water				
T=298.15 K				
0.00215	1034.35	1.2581	28.485	0.2100
0.01497	1035.27	1.2818	24.582	0.2350
0.02780	1036.29	1.2996	21.375	0.2580
0.04051	1037.28	1.3160	20.408	0.2790

Studies on Apparent molar volume, Adiabatic Compressibility.....at different temperatures.

0.05182	1038.30	1.3288	17.515	0.2920
0.06662	1039.41	1.3444	18.311	0.3060
T=308.15 K				
0.00213	1027.92	1.0700	39.958	0.1680
0.01487	1028.71	1.0874	34.883	0.1980
0.02762	1029.59	1.1006	31.452	0.2200
0.04024	1030.48	1.1125	29.799	0.2380
0.05148	1031.42	1.1227	26.222	0.2530
0.06617	1032.43	1.1358	26.409	0.2710
T=318.15 K				
0.00212	1021.40	0.9430	50.382	0.1320
0.01478	1022.07	0.9568	44.032	0.1710
0.02744	1022.86	0.9676	39.553	0.1950
0.03997	1023.65	0.9791	37.556	0.2230
0.05113	1024.50	0.9877	33.948	0.2380
0.06572	1025.44	0.9993	33.479	0.2580

Table 3. Limiting partial molar volume V_{ϕ}° and experimental slope S_v^* for ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate in different aqueous 1,3-dioxolane solutions at different temperatures

Mass % of 1,3- dioxolane	$V_{\phi}^{\circ} \times 10^6$ $m^3 \cdot mol^{-1}$			$S_v^* \times 10^4$ $m^2 \cdot L^{1/2} \cdot mol^{-3/2}$		
	T=298.15 K	T=308.15 K	T=318.15 K	T=298.15 K	T=308.15 K	T=318.15 K
Ammonium thiocyanate						
10	28.216	40.184	55.024	-48.497	-62.078	-75.578
20	26.708	35.211	47.804	-43.754	-52.505	-69.906
30	25.382	30.792	43.685	-35.408	-44.380	-59.913
Sodium thiocyanate						
10	30.267	46.455	60.951	-52.520	-76.063	-89.101
20	29.120	42.232	51.500	-48.659	-70.161	-75.294
30	26.557	32.948	47.102	-41.319	-55.592	-64.970
Potassium thiocyanate						
10	35.346	51.774	68.521	-63.900	-81.835	-100.370
20	32.697	47.865	59.833	-53.911	-72.830	-91.831
30	30.658	43.029	54.054	-49.746	-68.155	-84.055

Table 4. Values of various coefficients of eq. 4 for different thiocyanate in different aqueous 1,3-dioxolane solutions

Mass % of 1,3-dioxolane	$a_0 \times 10^6$ $\text{m}^3 \cdot \text{mol}^{-1}$	$a_1 \times 10^6$ $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$a_2 \times 10^6$ $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
Ammoniam thiocyanate			
10	-1329.000	7.705	-0.010
20	803.020	-6.355	0.013
30	27.389	-0.584	0.002
Sodium thiocyanate			
10	-2623.200	16.056	-0.024
20	1278.900	-9.638	0.019
30	-570.480	3.120	-0.004
Potassium thiocyanate			
10	220.740	-1.743	0.004
20	3797.400	-25.738	0.044
30	4690.500	-31.185	0.052

Table 5. Limiting partial molar expansibility ϕ_E^0 for ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate in different aqueous 1,3-dioxolane solutions at different temperatures

Mass % of 1,3-dioxolane	$\phi_E^0 \times 10^6$ $m^3 \cdot mol^{-1} \cdot K^{-1}$			$(\delta\phi_E^0/\delta T)_P \times 10^6$ $m^3 \cdot mol^{-1} \cdot K^{-2}$
	298.15 K	308.15 K	318.15 K	
Ammonium thiocyanate				
10	1.623	1.419	1.215	-0.020
20	1.278	1.534	1.790	0.026
30	0.668	0.710	0.752	0.004
Sodium thiocyanate				
10	1.983	1.511	1.039	-0.047
20	1.393	1.763	2.133	0.037
30	0.974	0.902	0.830	-0.007
Potassium thiocyanate				
10	0.881	0.969	1.057	0.009
20	0.618	1.502	2.386	0.088
30	0.001	1.047	2.093	0.105

Table 6. Values of A and B-coefficients for ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate in different aqueous 1,3-dioxolane solutions at different temperatures

Mass % of 1,3-dioxolane	$A \times 10^{-3}$ $m^{3/2} \cdot mol^{-1/2}$			$B \times 10^6$ $m^3 \cdot mol^{-1}$		
	T=298.15 K	T=308.15 K	T=318.15 K	T=298.15 K	T=308.15 K	T=318.15 K
Ammonium thiocyanate						
10	0.151	0.109	0.073	0.471	0.555	0.614
20	0.188	0.138	0.088	0.400	0.494	0.597
30	0.192	0.146	0.106	0.368	0.410	0.444
Sodium thiocyanate						
10	0.150	0.107	0.072	0.507	0.602	0.658
20	0.186	0.136	0.083	0.433	0.536	0.665
30	0.188	0.142	0.102	0.386	0.451	0.496
Potassium thiocyanate						
10	0.142	0.103	0.067	0.752	0.775	0.804
20	0.180	0.134	0.081	0.486	0.543	0.671
30	0.184	0.142	0.100	0.468	0.489	0.606

Table 7. Values of $V_2^0 - V_1^0$, $\Delta\mu_2^0$, $T\Delta S_2^0$ and ΔH_2^0 for ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate in different aqueous 1,3-dioxolane solutions at different temperatures

Parameters	T=298.15 K	T=308.15 K	T=318.15 K
Ammonium thiocyanate			
10 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	8.18	20.39	35.37
$\Delta\mu_1^0 / (\text{kJ mol}^{-1})$	9.70	9.54	9.53
$\Delta\mu_2^0 / (\text{kJ mol}^{-1})$	59.35	74.40	87.42
$T\Delta S_2^0 / (\text{kJ mol}^{-1})$	-418.46	-432.50	-446.53
$\Delta H_2^0 / (\text{kJ mol}^{-1})$	-359.11	-358.09	-359.11
20 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	4.38	13.13	25.95
$\Delta\mu_1^0 / (\text{kJ mol}^{-1})$	10.27	10.19	10.17
$\Delta\mu_2^0 / (\text{kJ mol}^{-1})$	44.94	58.92	75.45
$T\Delta S_2^0 / (\text{kJ mol}^{-1})$	-454.77	-470.03	-485.28
$\Delta H_2^0 / (\text{kJ mol}^{-1})$	-409.83	-411.11	-409.83
30 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	0.39	6.11	19.31
$\Delta\mu_1^0 / (\text{kJ mol}^{-1})$	10.80	10.72	10.71
$\Delta\mu_2^0 / (\text{kJ mol}^{-1})$	36.57	43.23	50.30
$T\Delta S_2^0 / (\text{kJ mol}^{-1})$	-204.75	-211.62	-218.48
$\Delta H_2^0 / (\text{kJ mol}^{-1})$	-168.18	-168.39	-168.18
Sodium thiocyanate			
10 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	10.20	26.62	41.26
$\Delta\mu_1^0 / (\text{kJ mol}^{-1})$	9.70	9.54	9.53
$\Delta\mu_2^0 / (\text{kJ mol}^{-1})$	63.96	81.29	93.90
$T\Delta S_2^0 / (\text{kJ mol}^{-1})$	-446.33	-461.30	-476.27
$\Delta H_2^0 / (\text{kJ mol}^{-1})$	-382.36	-380.00	-382.36
20 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	6.72	20.09	29.57
$\Delta\mu_1^0 / (\text{kJ mol}^{-1})$	10.27	10.20	10.18
$\Delta\mu_2^0 / (\text{kJ mol}^{-1})$	48.64	64.35	83.75
$T\Delta S_2^0 / (\text{kJ mol}^{-1})$	-523.30	-540.85	-558.40
$\Delta H_2^0 / (\text{kJ mol}^{-1})$	-474.65	-476.50	-474.65

30 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	1.45	8.12	22.59
$\Delta\mu_1^0 / (\text{kJ} \cdot \text{mol}^{-1})$	10.81	10.74	10.72
$\Delta\mu_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	38.17	47.44	55.97
$T\Delta S_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-265.37	-274.27	-283.17
$\Delta H_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-227.19	-226.83	-227.19
Potassium thiocyanate			
10 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	15.20	31.87	48.75
$\Delta\mu_1^0 / (\text{kJ} \cdot \text{mol}^{-1})$	9.71	9.55	9.54
$\Delta\mu_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	94.46	103.86	114.15
$T\Delta S_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-293.48	-303.32	-313.17
$\Delta H_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-199.02	-199.46	-199.02
20 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	10.10	25.34	37.71
$\Delta\mu_1^0 / (\text{kJ} \cdot \text{mol}^{-1})$	10.30	10.22	10.21
$\Delta\mu_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	54.46	65.18	84.74
$T\Delta S_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-451.46	-466.60	-481.75
$\Delta H_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-397.00	-401.42	-397.00
30 mass % of 1,3-dioxolane + water			
$(V_2^0 - V_1^0) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	5.16	17.84	29.18
$\Delta\mu_1^0 / (\text{kJ} \cdot \text{mol}^{-1})$	10.85	10.77	10.76
$\Delta\mu_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	45.98	51.51	67.52
$T\Delta S_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-320.99	-331.76	-342.52
$\Delta H_2^0 / (\text{kJ} \cdot \text{mol}^{-1})$	-275.01	-280.24	-275.01

Table 8. Molality m , sound velocity u , adiabatic compressibility β , partial molal compressibility ϕ_k , limiting partial adiabatic compressibility ϕ_k^0 , and experimental slope S_k^* of ammonium thiocyanate, sodium thiocyanate and potassium thiocyanate in different aqueous 1,3-dioxolane solutions at $T=298.15$ K

m mol kg^{-1}	u ms^{-1}	$\beta \times 10^{10}$ Pa^{-1}	$\phi_k \times 10^{10}$ $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$	$\phi_k^0 \times 10^{10}$ $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$	$S_k^* \times 10^{10}$ $\text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{Pa}^{-1}$ $\text{kg}^{1/2}$
Ammonium thiocyanate					
10 mass % of 1,3-dioxolane + water					
0.00196	1473.7	4.5432	-1.102		
0.01370	1490.9	4.4361	-0.949		
0.02545	1505.1	4.3497	-0.857		
0.03720	1513.8	4.2971	-0.734		
0.04896	1525.8	4.2265	-0.706	-1.215	2.360
0.06072	1531.2	4.1934	-0.628		
20 mass % of 1,3-dioxolane + water					
0.00194	1485.7	4.4206	-1.680		
0.01358	1510.7	4.2730	-1.320		
0.02522	1529.2	4.1674	-1.130		
0.03686	1545.8	4.0755	-1.024		
0.04851	1554.2	4.0289	-0.877	-1.865	4.511
0.06016	1558.5	4.0033	-0.754		
30 mass % of 1,3-dioxolane + water					
0.00200	1496.7	4.3161	-1.840		
0.01360	1524.6	4.1569	-1.420		
0.02551	1540.9	4.0666	-1.110		
0.03685	1557.8	3.9761	-1.012		
0.04819	1564.7	3.9384	-0.855	-2.070	5.599
0.06006	1566.5	3.9264	-0.710		
Sodium thiocyanate					
10 mass % of 1,3-dioxolane + water					
0.00196	1475.1	4.5343	-1.551		
0.01372	1499.6	4.3845	-1.320		
0.02549	1517.0	4.2818	-1.120		
0.03726	1532.7	4.1909	-1.015		
0.04903	1548.4	4.1035	-0.953	-1.717	3.593
0.06081	1552.4	4.0787	-0.814		
20 mass % of 1,3-dioxolane + water					
0.00196	1486.2	4.4175	-1.810		
0.01376	1515.6	4.2454	-1.500		
0.02555	1537.5	4.1220	-1.290		
0.03735	1550.7	4.0493	-1.080		
0.04916	1566.2	3.9664	-0.991	-2.045	4.853
0.06097	1568.4	3.9522	-0.827		
30 mass % of 1,3-dioxolane + water					
0.00208	1498.2	4.3075	-2.170		
0.01448	1531.8	4.1176	-1.600		

Studies on Apparent molar volume, Adiabatic Compressibility.....at different temperatures.

0.02689	1553.8	3.9985	-1.300	-2.463	6.957
0.03920	1569.2	3.9172	-1.100		
0.05015	1571.2	3.9043	-0.890		
0.06448	1573.4	3.8895	-0.720		
Potassium thiocyanate					
10 mass % of 1,3-dioxolane + water					
0.00196	1477.3	4.5209	-2.230		
0.01373	1508.7	4.3308	-1.710		
0.02551	1529.0	4.2130	-1.390		
0.03729	1545.7	4.1187	-1.210		
0.04908	1549.8	4.0932	-0.978	-2.522	6.892
0.06086	1554.5	4.0643	-0.842		
20 mass % of 1,3-dioxolane + water					
0.00204	1488.1	4.4064	-2.280		
0.01431	1523.1	4.2027	-1.740		
0.02658	1547.6	4.0665	-1.450		
0.03885	1559.8	3.9993	-1.170		
0.05113	1568.7	3.9501	-0.990	-2.589	7.046
0.06341	1572.6	3.9270	-0.840		
30 mass % of 1,3-dioxolane + water					
0.00208	1499.2	4.3014	-2.460		
0.01448	1537.1	4.0883	-1.800		
0.02690	1559.8	3.9665	-1.420		
0.03920	1573.3	3.8949	-1.160		
0.05015	1574.3	3.8863	-0.930	-2.805	8.243
0.06449	1578.9	3.8594	-0.770		

CHAPTER XII

Viscosity, Density, and Speed of Sound for the Binary Mixtures of Formamide with 2-Methoxyethanol, Acetophenone, Acetonitrile, 1,2-Dimethoxyethane, and Dimethylsulfoxide at Different Temperatures

.Keywords: Density, Viscosity, excess molar volumes, viscosity deviations, isentropic compressibility.

12.1. Introduction

The derived deviation or excess properties from the experimental measurements of density, viscosity, and ultrasonic speed provide valuable information that allows us to have a better understanding of the structure of liquids and intermolecular interactions in liquid mixtures.¹⁻³ Formamide and its derivatives are good solvents for many organic and inorganic compounds and are also used as a plasticizer. Acetophenone, a typical ketone, has been used in perfumery and as a hypnotic under the name “hypnone”. It is also used as a solvent for cellulose ethers. Acetonitrile is widely used for dissolving inorganic and organic compounds. 1,2-Dimethoxyethane is used in selected reactions as an alternative to diethyl ether. Dimethylsulfoxide is a powerful broad spectrum solvent for a wide variety of inorganic and organic reactants. Having low toxicity, it can be used in biology and medicine, especially for low-temperature preservation.⁴ 2-Methoxyethanol finds a wide range of applications of technological importance, namely, as solvents and solubilizing agents in organic synthesis, reaction kinetics, and electrochemical studies.⁵ Hence, we report in this paper the experimental values of densities ρ and viscosities η for the binary mixtures of formamide with 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane, and dimethylsulfoxide over the entire range of compositions at $T =$

(298.15, 308.15, and 318.15) K and $p = 0.1$ mPa. Also, the experimental values of ultrasonic speeds of sound u have been reported at $T = 298.15$ K and at the same pressure. From the experimental values of density ρ , viscosity η , and ultrasonic speed of sound u , the values of excess molar volume V_m^E , viscosity deviation $\Delta\eta$, and deviation in isentropic compressibility ΔK_S have been calculated. This work also provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

12.2. Experimental Section:

12.2.1. Source and purity of samples

Extrapure grade formamide, 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane, and dimethylsulfoxide were procured from S.d.fine-Chem Limited, Mumbai, India. 2-Methoxyethanol was dried with potassium carbonate and distilled twice in an all-glass distillation set immediately before use, and the middle fraction was collected.⁵ Acetophenone was dried over anhydrous potassium carbonate for 3 days, filtered, and then distilled. The middle fraction of the distillates was retained.⁶ Acetonitrile was distilled from P_2O_5 and then from CaH_2 in an all-glass distillation apparatus.⁷ The middle fraction was collected. 1,2-Dimethoxyethane was purified by double-fractional distillation over $LiAlH_4$ to eliminate traces of acids, peroxides, and water, and the middle portion was collected for the preparation of mixtures.⁸ Formamide and dimethylsulfoxide were purified according to the standard procedures.⁹ All solvents, pure or mixed, were stored over 3 Å molecular sieves for 3 days before use. The purity of the purified liquids was ascertained by GLC and also by comparing experimental values of densities, viscosities, and ultrasonic speeds of sound with their literature values,^{5-7, 10-17} whenever available as listed in Table 1.

12.2.2. Apparatus and Procedure

The mixtures were prepared by mixing the required volume of pure liquids in airtight stoppered bottles with adequate precautions to reduce evaporation losses during mixing. The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and a capillary of internal diameter of about 0.1 cm. The pycnometer

was calibrated at the experimental temperatures with doubly distilled water. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at (0.01 K of the desired temperature by means of a mercury-in-glass thermoregulator. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed in a digital electronic analytical balance (Mettler, AG-285, Switzerland). The mass measurements were accurate to (0.01 mg. The evaporation losses were insignificant during the time of actual measurements, and averages of triplicate measurements were taken into account.

The viscosity was measured by means of a suspended Ubbelohde-type viscometer, calibrated at the experimental temperatures with triply distilled water and purified methanol using density and viscosity values from the literature.¹⁸⁻²⁰ The flow times were accurate to ± 0.1 s.

The ultrasonic speeds of sound were determined using a multifrequency ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 2 MHz and calibrated with purified water and methanol at 298.15 K. The temperature was maintained within (0.01 K by circulating thermostated water around the cell with the aid of a circulating pump. The uncertainties in the mole fraction, density, viscosity, and ultrasonic speed of sound measurements were estimated to be ± 0.0002 , $\pm 3 \times 10^{-4}$ g.cm⁻³, ± 0.003 mPa.s, and ± 0.2 m.s⁻¹. The details of the methods and techniques of the measurements have been described earlier.^{2, 3, 21-23}

12.3. Results and Discussion

The experimental densities, viscosities, excess molar volumes, and viscosity deviations for the binary mixtures studied at (298.15, 308.15, and 318.15) K and $p = 0.1$ mPa as a function of mole fraction X_1 are listed in Table 2.

Excess Molar Volum: The excess molar volume, V_m^E , was calculated using the relation²⁴

$$V_m^E = (x_1M_1 + x_2M_2) / \rho - x_1M_1 / \rho_1 - x_2M_2 / \rho_2 \quad (1)$$

where x_1 , x_2 ; ρ_1 , ρ_2 ; and M_1 , M_2 are the mole fractions, densities, and molecular weights of pure components 1 (formamide) and 2 of the binary liquid mixtures, respectively. The

values of excess molar volume, V_m^E , have been represented in Table 2. The estimated uncertainty for excess molar volume, V_m^E , is $(\pm 0.005 \times 10^6 \text{ m}^3 \cdot \text{mol}^{-1})$. A perusal of Table 2 shows that the values of V_m^E are negative for all the binary mixtures over the entire range of compositions and temperatures. The negative values of excess molar volume for the three systems are in the order: formamide + 1,2 dimethoxyethane > formamide + acetonitrile > formamide + 2-methoxyethanol > formamide + dimethylsulfoxide > formamide + acetophenone. The plots of excess molar volume, V_m^E , vs mole fraction of formamide, x_1 , at 298.15 K are presented in Figure 1.

The negative values of excess molar volume, V_m^E , suggest specific interactions²⁴ between the mixing components in the mixtures, whereas its positive values suggest dominance of dispersion forces^{26,27} between them. The negative V_m^E values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also interstitial accommodation of the mixing components because of the difference in molar volumes. The negative V_m^E values may also be due to the difference in the dielectric constants of the liquid components of the binary mixtures.²⁵ The negative V_m^E values for all the systems studied may be attributed to dipole-induced dipole interactions between the component liquids of the mixtures resulting in the formation of electron donor-acceptor complexes.²⁸ Thus, it is seen that the strength of interaction between the mixing components follows the order: formamide + 1,2- dimethoxyethane > formamide + acetonitrile > formamide + 2-methoxyethanol > formamide + dimethylsulfoxide > formamide + acetophenone.

A perusal of Table 2 also shows that the V_m^E values become more negative as the temperature is increased from (298.15 to 318.15) K. This indicates a gradually decreasing trend in the degree of the inter hydrogen bonds in the associated formamide molecules as the experimental temperature increases and dipole-dipole interactions between the hetero molecules are increased leading to greater contraction in the mixture volumes.¹⁴

Viscosity Deviation: The viscosity deviation, $\Delta\eta$, was calculated by using the relation²⁴

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

where η and ρ are the viscosity and density of the binary mixtures. x_1 ; x_2 and ρ_1 , ρ_2 are the mole fractions and viscosities of pure components 1 (formamide) and 2 of the binary

liquid mixtures, 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 positive for all the studied binary mixtures except those of 1,2-dimethoxyethane and acetonitrile over the entire composition range and at all the experimental temperatures, and they have been presented in Figure 2 as a function of the mole fraction of formamide at 298.15 K. The negative values imply the presence of dispersion forces²⁹ between the mixing components in the mixtures, and the positive values may be attributed to the presence of specific interactions²⁹ between them.

It is also evident from Table 2 that $\Delta\eta$ values of the mixtures decrease as the experimental temperatures increases, thereby suggesting an increase in the fluidity of the mixtures.³⁰

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.^{31,32} Some of them we examined are as follows:

- (i) ***Grunberg*** and ***Nissan***³³ have suggested the following logarithmic relation between the viscosity of binary liquid mixtures and of pure components

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad (3)$$

where d_{12} is a constant, proportional to interchange energy, and the other symbols have their usual significance. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The calculated d_{12} values of the binary mixtures at different temperatures are listed in Table 2. Table 2 shows that the values of d_{12} are positive for all the binary liquid mixtures except that of formamide with acetonitrile over the entire range of compositions and at all the experimental temperatures. The positive values of d_{12} may be attributed to the presence of specific interactions^{29,34} between the mixing components in the mixtures, whereas the negative values of d_{12} indicate the presence of dispersion forces²⁹ between them.

(ii) *Tamura and Kurata*³⁵ put forward the following equation for the viscosity of binary liquid mixtures

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2 (x_1 x_2 \phi_1 \phi_2)^{0.5} \cdot T_{12} \quad (4)$$

where T_{12} is the interaction parameter which depends on temperature and composition of the mixture and ϕ_1 [$\phi_1 = x_1 V_1 / (x_1 V_1 + x_2 V_2)$] and ϕ_2 [$\phi_2 = 1 - \phi_1$] are the volume fractions of pure components 1 and 2, respectively.

(iii) *Hind et al*³⁶ suggested the following equation for the viscosity of the binary liquid mixture

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 H_{12} \quad (5)$$

where H_{12} is the Hind interaction parameter and is attributed to the unlike pair interactions.³⁷

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. A perusal of Table 2 shows that the T_{12} and H_{12} values do not differ appreciably with a change in the composition of the binary mixtures at all the experimental temperatures. This is in agreement with the view put forward by Fort and Moore²⁹ in regard to the nature of parameter T_{12} and H_{12} .

Deviation in Isentropic Compressibility: The isentropic compressibility, K_S , values were calculated using the relation⁵

$$K_S = 1 / (u^2 \rho) \quad (6)$$

where u and ρ are the experimental values of ultrasonic speed of sound and density, respectively, for the binary mixtures.

The deviations in isentropic compressibility, ΔK_S , for the binary mixtures have been derived using the relation⁵

$$\Delta K_S = K_S - (x_1 K_{S,1} + x_2 K_{S,2}) \quad (7)$$

where x_1 , x_2 and $\Delta K_{S,1}$, $\Delta K_{S,2}$ are the mole fractions and isentropic compressibilities of pure components 1 (formamide) and 2 of the binary liquid mixtures, respectively.

The experimental values of density, ρ , ultrasonic speed of sound, u , the isentropic compressibility, K_S , and the deviation in isentropic compressibility, ΔK_S , at 298.15 K as a function of the composition of the binary mixtures have been presented in Table 3.

Table 3 shows that ΔK_S values are positive for the binary mixtures of 2-methoxyethanol, dimethylsulfoxide, and acetophenone and negative for those of 1,2-dimethoxyethane and acetonitrile over the entire range of compositions at 298.15 K, and the deviations in isentropic compressibility, ΔK_S , have been plotted against mole fraction of formamide, x_1 , for the binary mixtures at 298.15 K in Figure 3.

The observed values of ΔK_S can be qualitatively explained by considering the factors, namely (i) the mutual disruption of associated present in the pure liquids, (ii) the formation of weak bonds by dipole-induced dipole interaction between unlike molecules, and (iii) geometrical fitting of component molecules into each other structure. The first factor contributes to positive ΔK_S values, whereas the remaining two factors lead to negative ΔK_S values.³⁸ The resultant values of ΔK_S for the present mixtures are due to the net effect of the combination of (i) to (iii).³⁹

In the present investigation, the negative deviation in isentropic compressibility is an indication of strong interactions, whereas positive deviation is a sign for weak interactions between component molecules.^{1, 29, 40-42}

From Table 3, it is also seen that the values of deviation in isentropic compressibility, ΔK_S , are more negative for the formamide + acetonitrile mixture than the formamide + 1,2-dimethoxyethane mixture. Higher values of the Grunberg-Nissan interaction parameter, d_{12} , in Table 2 for the formamide + 1,2-dimethoxyethane mixture than for the formamide + acetonitrile mixture are an indication of its higher molecular interactions than the formamide + acetonitrile mixture.⁶

Therefore, from Table 3, Figure 3, and the values of d_{12} in Table 2, it is seen that the strength of interaction between the binary mixtures follows the order: formamide + 1,2-dimethoxyethane > formamide + acetonitrile > formamide + 2-methoxyethanol > formamide + dimethylsulfoxide > formamide + acetophenone. Thus, the graded behavior of this function, ΔK_S , over the entire range of compositions at 298.15 K supports the results obtained earlier.

Redlich-Kister Polynomial Equation: The excess or deviation properties were fitted to the Redlich-Kister polynomial equation⁴³ of the type

$$X^E = x_1 x_2 \left[\sum_{i=0}^k A_i (x_1 - x_2)^i \right] \quad (8)$$

where X^E represents an excess or deviation property. The coefficients, A_i , of eq 8, were evaluated using a least-squares method and have been presented in Table 4 along with their standard deviations. The standard deviation σ was evaluated by using the following relation

$$\sigma (X^E) = [(X^E_{(obs.)} - X^E_{(cal.)})^2 / (n-p)]^{0.5} \quad (9)$$

where n is the total number of experimental points and p is the number of A_i coefficients considered. The σ values lie between $0.013 \text{ m}^3 \cdot \text{mol}^{-1}$ and $0.001 \text{ m}^3 \cdot \text{mol}^{-1}$ for V_m^E , between $0.022 \text{ m Pa} \cdot \text{s}$ and $0.001 \text{ m Pa} \cdot \text{s}$ for $\Delta\eta$, and between 0.011 Pa^{-1} and 0.001 Pa^{-1} for ΔK_S , respectively. The largest σ value corresponds to the formamide + acetonitrile system for V_m^E and the formamide + acetophenone system for $\Delta\eta$ and ΔK_S , respectively. It is seen that the fit is quite satisfactory as revealed by the values of standard deviation.

12.4. Conclusion

The present study reveals that the order of specific interaction for the binary mixtures of formamide follows the order: formamide + 1,2-dimethoxyethane > formamide + acetonitrile > formamide + 2-methoxyethanol > formamide + dimethylsulfoxide > formamide + acetophenone. This may be attributed to intermolecular hydrogen bonding and interstitial accommodation between the mixing components. The graded pattern can also be partly due to the difference in the dielectric constants of the mixing components.

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Table 1. Densities ρ , Viscosities η , and Speeds of Sound u of the Pure Liquids at Different Temperatures

Table 1. Densities ρ , Viscosities η , and Speeds of Sound u of the Pure Liquids at Different Temperatures

pure liquids	T/K	ρ (kg·m ⁻³)		η (mPa·s)		u (m·s ⁻¹)	
		exptl	lit.	exptl	lit.	exptl	lit.
formamide	298.15	1129.2	1129.2 ¹⁰	3.302	3.302 ¹⁰	1591.3	–
	308.15	1120.5	1120.2 ¹¹	2.542	2.59 ¹¹		1580 ¹²
	318.15	1111.1	1111.9 ¹³	2.001	2.00 ¹³		
2-methoxyethanol	298.15	959.7	959.79 ⁵	1.543	1.543 ⁵	1339.4	1339.31 ⁵
	308.15	951.5	952.51 ⁵	1.257	1.257 ⁵		
	318.15	945.9	946.23 ⁵	1.051	1.050 ⁵		
acetophenone	298.15	1023.1	1023.1 ⁶	1.653	1.652 ⁶	1296.4	–
	308.15	1014.8	–	1.412	–		
	318.15	1007.5	–	1.117	–		
acetonitrile	298.15	776.0	776.86 ⁷	0.344	0.3446 ⁷	1260.2	–
	308.15	766.3	765.64 ⁷	0.313	0.3125 ⁷		1237.2 ¹⁴
	318.15	755.0	754.98 ⁷	0.289	0.2893 ⁷		
1,2-dimethoxyethane	298.15	861.5	861.09 ¹⁵	0.409	0.4089 ¹⁵	1146.2	1146.0 ¹⁶
	308.15	850.7	850.01 ¹⁵	0.366	0.3659 ¹⁵		
	318.15	839.6	838.85 ¹⁵	0.330	0.3302 ¹⁵		
dimethylsulfoxide	298.15	1095.4	1095.4 ¹⁷	2.042	2.0418 ¹⁷	1493.0	1493.0 ¹⁷
	308.15	1085.9	1085.9 ¹⁷	1.568	1.5682 ¹⁷		
	318.15	1076.9	1076.7 ¹⁷	1.485	1.4847 ¹⁷		

Table 2. Values of Density ρ , Viscosity η , Excess Molar Volume V_m^E , Viscosity Deviation $\Delta\eta$, and Various Interaction Parameters d_{12} , T_{12} , and H_{12} for the Binary Mixtures of Formamide from $T = (298.15 \text{ to } 308.15) \text{ K}$ as a Function of Mole Fraction x_1 at $p = 0.1 \text{ mPa}$

Formamide (1) + 2-Methoxyethanol (2)															
x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	T_{12}	H_{12}	x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	T_{12}	H_{12}
	$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$					$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$			
$T = 298.15 \text{ K}$															
0.0000	959.7	1.543	0.000	0.000	—	—	—	0.7171	1060.2	3.331	-0.265	0.527	1.104	4.053	3.721
0.1581	977.0	1.912	-0.200	0.091	0.707	3.319	2.764	0.7977	1076.7	3.395	-0.191	0.449	1.126	4.058	3.813
0.2969	994.2	2.291	-0.325	0.226	0.812	3.525	2.964	0.8711	1093.8	3.399	-0.129	0.324	1.133	4.030	3.808
0.4199	1010.9	2.659	-0.368	0.377	0.922	3.738	3.196	0.9383	1111.1	3.348	-0.057	0.155	1.051	3.881	3.759
0.5297	1027.6	2.963	-0.374	0.488	1.001	3.892	3.402	1.0000	1129.2	3.302	0.000	0.000	—	—	—
0.6282	1044.1	3.173	-0.339	0.525	1.040	3.965	3.546	—	—	—	—	—	—	—	—
$T = 308.15 \text{ K}$															
0.0000	951.5	1.257	0.000	0.000	—	—	—	0.7171	1052.3	2.485	-0.300	0.307	0.871	2.925	2.656
0.1581	969.1	1.515	-0.224	0.055	0.567	2.507	2.106	0.7977	1068.7	2.541	-0.220	0.259	0.880	2.921	2.702
0.2969	986.2	1.759	-0.351	0.121	0.609	2.587	2.189	0.8711	1085.7	2.562	-0.153	0.186	0.879	2.900	2.728
0.4199	1002.8	1.997	-0.390	0.200	0.685	2.696	2.309	0.9383	1102.9	2.550	-0.076	0.088	0.807	2.808	2.656
0.5297	1019.4	2.206	-0.395	0.268	0.759	2.797	2.437	1.0000	1120.5	2.542	0.000	0.000	—	—	—
0.6282	1035.9	2.367	-0.361	0.303	0.816	2.867	2.548	—	—	—	—	—	—	—	—
$T = 318.15 \text{ K}$															
0.0000	945.9	1.051	0.000	0.000	—	—	—	0.7171	1045.3	1.929	-0.333	0.197	0.718	2.223	2.012
0.1581	963.5	1.225	-0.248	0.024	0.387	1.899	1.616	0.7977	1061.5	1.978	-0.261	0.169	0.735	2.228	2.049
0.2969	980.3	1.394	-0.373	0.061	0.437	1.958	1.672	0.8711	1078.1	2.016	-0.189	0.137	0.804	2.271	2.136
0.4199	996.5	1.561	-0.407	0.111	0.514	2.037	1.754	0.9383	1094.6	2.003	-0.104	0.061	0.707	2.179	2.053
0.5297	1012.8	1.709	-0.410	0.155	0.583	2.106	1.837	1.0000	1111.1	2.001	0.000	0.000	—	—	—
0.6282	1029.1	1.831	-0.388	0.183	0.644	2.162	1.918	—	—	—	—	—	—	—	—
Formamide (1) + Acetophenone (3)															
x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	T_{12}	H_{12}	x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	T_{12}	H_{12}
	$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$					$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$			
$T = 298.15 \text{ K}$															
0.0000	1023.1	1.653	0.000	0.000	—	—	—	0.8001	1084.4	3.819	-0.009	0.847	1.775	5.457	5.125
0.2286	1052.9	2.234	-0.012	0.204	0.811	4.157	3.056	0.8616	1095.3	3.735	-0.006	0.602	1.838	5.307	5.253
0.4001	1042.9	2.795	-0.021	0.482	1.034	4.582	3.481	0.9143	1106.4	3.590	-0.004	0.430	1.827	5.180	5.222
0.5334	1053.1	3.267	-0.023	0.735	1.255	4.955	3.954	0.9600	1117.7	3.439	-0.003	0.204	1.788	4.983	5.134
0.6401	1063.3	3.596	-0.019	0.888	1.452	5.223	4.405	1.0000	1129.2	3.302	0.000	0.000	—	—	—
0.7273	1073.8	3.778	-0.013	0.926	1.631	5.396	4.812	—	—	—	—	—	—	—	—
$T = 308.15 \text{ K}$															
0.0000	1014.8	1.412	0.000	0.000	—	—	—	0.8001	1076.3	2.779	-0.031	0.463	1.292	3.764	3.424
0.2286	1024.9	1.762	-0.042	0.092	0.495	2.972	2.237	0.8616	1087.0	2.748	-0.022	0.363	1.338	3.718	3.499
0.4001	1035.1	2.077	-0.061	0.213	0.628	3.153	2.420	0.9143	1097.9	2.685	-0.013	0.240	1.343	3.634	3.508
0.5334	1045.3	2.355	-0.064	0.341	0.797	3.354	2.662	0.9600	1109.1	2.608	-0.006	0.112	1.288	3.508	3.435
0.6401	1055.5	2.587	-0.056	0.452	0.995	3.564	2.958	1.0000	1120.5	2.542	0.000	0.000	—	—	—
0.7273	1065.8	2.724	-0.041	0.490	1.157	3.694	3.212	—	—	—	—	—	—	—	—
$T = 318.15 \text{ K}$															
0.0000	1007.5	1.117	0.000	0.000	—	—	—	0.8001	1068.2	2.141	-0.055	0.317	1.152	2.844	2.550
0.2286	1017.5	1.377	-0.052	0.058	0.431	2.281	1.724	0.8616	1078.7	2.111	-0.044	0.232	1.134	2.761	2.532
0.4001	1027.5	1.607	-0.078	0.136	0.542	2.399	1.843	0.9143	1089.4	2.068	-0.030	0.143	1.059	2.662	2.472
0.5334	1037.6	1.825	-0.085	0.236	0.722	2.569	2.033	0.9600	1100.1	2.027	-0.016	0.061	0.939	2.541	2.354
0.6401	1047.7	1.988	-0.079	0.305	0.882	2.697	2.221	1.0000	1111.1	2.001	0.000	0.000	—	—	—
0.7273	1057.9	2.100	-0.067	0.340	1.045	2.806	2.416	—	—	—	—	—	—	—	—

Viscosity, Density, and Speed of Sound for the Binary Mixturesat Different Temperatures

Formamide (1) + Acetonitrile (4)

x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	Γ_{12}	H_{12}	x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	Γ_{12}	H_{12}
	$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$					$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$			
$T = 298.15 \text{ K}$															
0.0000	776.0	0.344	0.000	0.000	--	--	--	0.5775	965.2	1.168	-0.467	-0.884	-0.343	0.261	0.011
0.0919	803.8	0.402	-0.175	-0.214	-0.626	0.608	0.541	0.6802	1002.9	1.507	-0.412	-0.849	-0.282	0.179	-0.128
0.1856	832.8	0.485	-0.302	-0.408	-0.507	0.567	0.473	0.7847	1042.6	1.945	-0.311	-0.720	-0.251	0.070	-0.308
0.2809	863.4	0.593	-0.401	-0.582	-0.452	0.506	0.382	0.8913	1085.1	2.540	-0.193	-0.440	-0.169	0.008	-0.448
0.3779	895.8	0.733	-0.469	-0.729	-0.419	0.431	0.272	1.0000	1129.2	3.302	0.000	0.000	--	--	--
0.4768	929.2	0.921	-0.471	-0.833	-0.374	0.353	0.153	--	--	--	--	--	--	--	--
$T = 308.15 \text{ K}$															
0.0000	766.3	0.313	0.000	0.000	--	--	--	0.5775	956.6	0.978	-0.527	-0.622	-0.286	0.343	0.152
0.0919	794.9	0.366	-0.237	-0.151	-0.400	0.583	0.523	0.6802	994.4	1.239	-0.463	-0.589	-0.219	0.305	0.073
0.1856	824.1	0.432	-0.381	-0.294	-0.429	0.532	0.454	0.7847	1034.7	1.569	-0.377	-0.492	-0.182	0.251	-0.029
0.2809	855.1	0.522	-0.495	-0.416	-0.373	0.496	0.396	0.8913	1076.9	1.999	-0.228	-0.300	-0.126	0.212	-0.121
0.3779	887.4	0.635	-0.560	-0.520	-0.354	0.446	0.321	1.0000	1120.5	2.542	0.000	0.000	--	--	--
0.4768	921.2	0.786	-0.566	-0.589	-0.307	0.402	0.247	--	--	--	--	--	--	--	--
$T = 318.15 \text{ K}$															
0.0000	755.0	0.289	0.000	0.000	--	--	--	0.5775	950.7	0.847	-0.780	-0.431	-0.176	0.411	0.262
0.0919	785.6	0.339	-0.378	-0.108	-0.242	0.552	0.498	0.6802	989.4	1.046	-0.731	-0.408	-0.141	0.385	0.207
0.1856	815.8	0.396	-0.579	-0.211	-0.298	0.513	0.447	0.7847	1029.3	1.295	-0.590	-0.338	-0.114	0.356	0.145
0.2809	847.4	0.472	-0.719	-0.298	-0.265	0.490	0.407	0.8913	1071.6	1.615	-0.417	-0.200	-0.043	0.359	0.113
0.3779	879.9	0.565	-0.774	-0.371	-0.260	0.458	0.356	1.0000	1111.1	2.001	0.000	0.000	--	--	--
0.4768	914.0	0.687	-0.783	-0.418	-0.227	0.431	0.307	--	--	--	--	--	--	--	--

Formamide (1) + 1,2-Dimethoxyethane (5)

x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	Γ_{12}	H_{12}	x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	Γ_{12}	H_{12}
	$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$					$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$			
$T = 298.15 \text{ K}$															
0.0000	861.5	0.409	0.000	0.000	--	--	--	0.7501	1022.2	2.296	-0.974	-0.283	0.846	2.144	1.100
0.1819	893.1	0.603	-1.101	-0.332	0.058	1.196	0.739	0.8236	1048.3	2.627	-0.752	-0.164	0.964	2.351	1.291
0.3334	920.1	0.848	-1.411	-0.525	0.151	1.281	0.674	0.8889	1073.7	2.899	-0.462	-0.081	1.034	2.501	1.445
0.4616	946.0	1.164	-1.464	-0.580	0.331	1.449	0.688	0.9474	1100.3	3.120	-0.201	-0.029	1.072	2.605	1.564
0.5715	971.8	1.545	-1.395	-0.517	0.534	1.695	0.799	1.0000	1129.2	3.302	0.000	0.000	--	--	--
0.6668	997.3	1.925	-1.229	-0.413	0.704	1.915	0.926	--	--	--	--	--	--	--	--
$T = 308.15 \text{ K}$															
0.0000	850.7	0.366	0.000	0.000	--	--	--	0.7501	1013.6	1.806	-1.074	-0.192	0.761	1.731	0.942
0.1819	883.5	0.522	-1.252	-0.240	0.014	1.014	0.647	0.8236	1039.4	2.045	-0.809	-0.113	0.856	1.867	1.065
0.3334	910.4	0.713	-1.536	-0.378	0.096	1.081	0.603	0.8889	1065.7	2.243	-0.536	-0.057	0.914	1.966	1.165
0.4616	936.3	0.952	-1.563	-0.418	0.249	1.202	0.613	0.9474	1092.7	2.408	-0.264	-0.019	0.964	2.048	1.265
0.5715	962.3	1.243	-1.487	-0.366	0.472	1.393	0.706	1.0000	1120.5	2.542	0.000	0.000	--	--	--
0.6668	988.5	1.536	-1.339	-0.281	0.639	1.574	0.821	--	--	--	--	--	--	--	--
$T = 318.15 \text{ K}$															
0.0000	839.6	0.330	0.000	0.000	--	--	--	0.7501	1007.5	1.427	-1.348	-0.156	0.600	1.368	0.749
0.1819	874.6	0.459	-1.527	-0.175	0.005	0.879	0.576	0.8236	1033.3	1.614	-1.038	-0.092	0.709	1.478	0.849
0.3334	902.6	0.609	-1.874	-0.278	0.053	0.923	0.540	0.8889	1059.2	1.775	-0.707	-0.040	0.815	1.582	0.963
0.4616	929.4	0.785	-1.927	-0.316	0.140	0.992	0.529	0.9474	1085.5	1.903	-0.376	-0.010	0.895	1.663	1.065
0.5715	955.9	0.994	-1.834	-0.291	0.296	1.107	0.572	1.0000	1111.1	2.001	0.000	0.000	--	--	--
0.6668	982.2	1.218	-1.647	-0.226	0.469	1.245	0.657	--	--	--	--	--	--	--	--

Viscosity, Density, and Speed of Sound for the Binary Mixturesat Different Temperatures

Formamide (1) + Dimethylsulfoxide (6)

x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	T_{12}	H_{12}	x_1	ρ	η	$V_m^E \cdot 10^6$	$\Delta\eta$	d_{12}	T_{12}	H_{12}
	$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$					$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$			
$T = 298.15 \text{ K}$															
0.0000	1095.4	2.042	0.000	0.000	-	-	-	0.7224	1115.8	3.652	-0.016	0.700	1.168	4.562	4.417
0.1616	1099.3	2.457	-0.032	0.212	0.794	3.943	3.454	0.8019	1119.1	3.626	-0.010	0.574	1.189	4.533	4.478
0.3025	1102.8	2.868	-0.047	0.445	0.921	4.193	3.726	0.8740	1122.5	3.540	-0.007	0.397	1.183	4.453	4.475
0.4264	1106.3	3.214	-0.047	0.635	1.017	4.381	3.969	0.9398	1125.8	3.426	-0.004	0.200	1.165	4.358	4.442
0.5363	1109.5	3.468	-0.039	0.751	1.094	4.513	4.182	1.0000	1129.2	3.302	0.000	0.000	-	-	-
0.6343	1112.6	3.608	-0.026	0.767	1.140	4.564	4.325								
$T = 308.15 \text{ K}$															
0.0000	1085.9	1.568	0.000	0.000	-	-	-	0.7224	1107.6	2.653	-0.050	0.382	0.883	3.154	3.007
0.1616	1090.7	1.859	-0.082	0.134	0.681	2.901	2.549	0.8019	1110.7	2.639	-0.032	0.291	0.841	3.078	2.971
0.3025	1094.9	2.135	-0.127	0.272	0.769	3.034	2.699	0.8740	1113.9	2.613	-0.021	0.194	0.804	3.010	2.936
0.4264	1098.5	2.365	-0.129	0.382	0.838	3.134	2.836	0.9398	1117.2	2.571	-0.010	0.088	0.717	2.895	2.833
0.5363	1101.6	2.520	-0.106	0.430	0.866	3.169	2.919	1.0000	1120.5	2.542	0.000	0.000	-	-	-
0.6343	1104.6	2.621	-0.077	0.435	0.893	3.189	2.993								
$T = 318.15 \text{ K}$															
0.0000	1076.9	1.485	0.000	0.000	-	-	-	0.7224	1099.5	2.118	-0.103	0.260	0.696	2.484	2.391
0.1616	1082.7	1.640	-0.152	0.072	0.379	2.223	2.009	0.8019	1102.3	2.083	-0.074	0.184	0.624	2.394	2.322
0.3025	1087.3	1.823	-0.212	0.182	0.545	2.393	2.174	0.8740	1105.3	2.054	-0.049	0.118	0.579	2.334	2.279
0.4264	1090.9	1.968	-0.214	0.263	0.631	2.477	2.280	0.9398	1108.2	2.021	-0.024	0.051	0.493	2.246	2.194
0.5363	1093.9	2.059	-0.182	0.297	0.670	2.503	2.340	1.0000	1111.1	2.001	0.000	0.000	-	-	-
0.6343	1096.7	2.112	-0.140	0.300	0.704	2.516	2.389								

Table 3. Values of density ρ , ultrasonic speed of sound u , isentropic compressibility K_S , and deviation in isentropic compressibility ΔK_S for the binary mixtures of formamide at $T=298.15$ K and $p = 0.1$ mPa as a function of mole fraction x_1

x_1	ρ kg·m ⁻³	u m·s ⁻¹	$K_S \cdot 10^{10}$ Pa ⁻¹	$\Delta K_S \cdot 10^{10}$ Pa ⁻¹	x_1	ρ kg·m ⁻³	u m·s ⁻¹	$K_S \cdot 10^{10}$ Pa ⁻¹	$\Delta K_S \cdot 10^{10}$ Pa ⁻¹
Formamide (1) + 2-Methoxyethanol (2)									
0.0000	959.7	1339.4	5.808	0.000	0.7171	1060.2	1478.3	4.316	0.165
0.1581	977.0	1353.6	5.586	0.143	0.7977	1076.7	1506.0	4.095	0.130
0.2969	994.2	1373.7	5.329	0.208	0.8711	1093.8	1533.9	3.885	0.090
0.4199	1010.9	1397.5	5.065	0.227	0.9383	1111.1	1564.3	3.678	0.038
0.5297	1027.6	1423.8	4.800	0.216	1.0000	1129.2	1591.3	3.497	0.000
0.6282	1044.1	1451.1	4.548	0.192					
Formamide (1) + Acetophenone (3)									
0.0000	1023.1	1296.4	5.816	0.000	0.8001	1084.4	1456.5	4.347	0.386
0.2286	1032.9	1304.8	5.686	0.400	0.8616	1095.3	1488.4	4.122	0.303
0.4001	1042.9	1323.3	5.475	0.587	0.9143	1106.4	1527.3	3.875	0.179
0.5334	1053.1	1345.8	5.243	0.663	0.9600	1117.7	1558.9	3.682	0.091
0.6401	1063.3	1379.3	4.943	0.611	1.0000	1129.2	1591.3	3.497	0.000
0.7273	1073.8	1413.6	4.661	0.531					
Formamide (1) + Acetonitrile (4)									
0.0000	776.0	1260.2	8.114	0.000	0.5775	965.2	1412.8	5.190	-0.257
0.0919	803.8	1277.7	7.620	-0.069	0.6802	1002.9	1449.0	4.749	-0.225
0.1856	832.8	1299.6	7.109	-0.148	0.7847	1042.6	1488.8	4.327	-0.164
0.2809	863.4	1322.8	6.619	-0.198	0.8913	1085.1	1529.8	3.938	-0.061
0.3779	895.8	1349.6	6.129	-0.240	1.0000	1129.2	1591.3	3.497	0.000
0.4768	929.2	1380.8	5.644	-0.269					
Formamide (1) + 1,2-Dimethoxyethane (5)									
0.0000	861.5	1146.2	8.835	0.000	0.7501	1022.2	1441.9	4.705	-0.126
0.1819	893.1	1200.3	7.771	-0.093	0.8236	1048.3	1480.5	4.352	-0.087
0.3334	920.1	1254.3	6.908	-0.147	0.8889	1073.7	1518.5	4.039	-0.051
0.4616	946.0	1306.2	6.195	-0.176	0.9474	1100.3	1556.1	3.753	-0.025
0.5715	971.8	1355.0	5.604	-0.180	1.0000	1129.2	1591.3	3.497	0.000
0.6668	997.3	1399.9	5.116	-0.160					
Formamide (1) + Dimethylsulfoxide (6)									
0.0000	1095.4	1493.0	4.095	0.000	0.7224	1115.8	1512.7	3.917	0.253
0.1616	1099.3	1480.1	4.153	0.154	0.8019	1119.1	1526.4	3.835	0.219
0.3025	1102.8	1480.6	4.136	0.222	0.8740	1122.5	1543.7	3.738	0.165
0.4264	1106.3	1483.9	4.105	0.265	0.9398	1125.8	1561.2	3.644	0.111
0.5363	1109.5	1492.3	4.047	0.273	1.0000	1129.2	1591.3	3.497	0.000
0.6343	1112.6	1502.9	3.979	0.263					

Table 4. Coefficients A_i of the Redlich-Kister Equation and the Standard Deviation σ for the Binary Mixtures of Formamide from $T=(298.15$ to $318.15)$ K

binary mixture	excess property	T/K	A_0	A_1	A_2	A_3	σ	
formamide (1) + 2-methoxyethanol (2)	$V_m^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-1.508	0.252	0.391	-	0.005	
		308.15	-1.595	0.230	0.142	-	0.004	
		318.15	-1.659	0.154	-0.246	-	0.004	
	$\Delta\eta / (\text{mPa} \cdot \text{s})$	298.15	1.840	1.705	-0.282	0.847	0.004	
		308.15	1.015	0.983	-	-	0.011	
		318.15	0.569	0.819	0.358	-0.264	0.005	
formamide (1) + acetophenone (3)	$\Delta K_S \cdot 10^{10} / (\text{Pa}^{-1})$	298.15	0.886	-0.221	0.099	-	0.003	
		$V_m^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-0.092	-0.002	0.147	0.032	0.001
			308.15	-0.261	0.017	0.204	0.058	0.001
	318.15		-0.329	-0.045	-	-	0.002	
	$\Delta\eta / (\text{mPa} \cdot \text{s})$	298.15	2.714	3.537	0.859	4.677	0.002	
		308.15	1.221	2.088	2.178	-0.174	0.002	
318.15		0.941	1.428	-	-	0.022		
formamide (1) + acetonitrile (4)	$\Delta K_S \cdot 10^{10} / (\text{Pa}^{-1})$	298.15	2.612	0.646	-1.141	-1.290	0.011	
		$V_m^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-1.917	0.112	-0.113	-	0.007
			308.15	-2.242	0.624	-0.215	-1.923	0.001
	318.15		-3.148	0.131	-1.741	-	0.013	
	$\Delta\eta / (\text{mPa} \cdot \text{s})$	298.15	-3.40449	-1.339	-0.280	0.117	0.002	
		308.15	-2.40623	-0.818	-0.106	-	0.002	
318.15		-1.69780	-0.496	-	-	0.002		
formamide (1) + 1,2-dimethoxyethane (5)	$\Delta K_S \cdot 10^{10} / (\text{Pa}^{-1})$	298.15	-1.05601	-0.102	0.111	0.393	0.005	
		$V_m^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-5.815	1.014	-1.024	2.051	0.012
			308.15	-6.196	0.929	-2.312	4.658	0.008
	318.15		-7.639	1.094	-2.352	4.833	0.006	
	$\Delta\eta / (\text{mPa} \cdot \text{s})$	298.15	-2.263	0.806	1.369	-	0.004	
		308.15	-1.634	0.774	1.805	-2.595	0.001	
318.15		-1.255	0.337	1.149	-0.036	0.001		
formamide (1) + dimethylsulfoxide(6)	$\Delta K_S \cdot 10^{10} / (\text{Pa}^{-1})$	298.15	-0.721	-0.152	0.262	0.828	0.001	
		$V_m^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-0.161	0.148	-	-	0.002
			308.15	-0.461	0.477	0.140	-0.373	0.001
	318.15		-0.775	0.649	-0.013	-0.336	0.001	
	$\Delta\eta / (\text{mPa} \cdot \text{s})$	298.15	2.881	1.807	-0.638	-0.637	0.002	
		308.15	1.690	0.853	-0.636	-0.550	0.003	
318.15		1.178	0.604	-0.738	-0.364	0.004		
$\Delta K_S \cdot 10^{10} / (\text{Pa}^{-1})$	298.15	1.091	0.155	0.162	0.186	0.005		

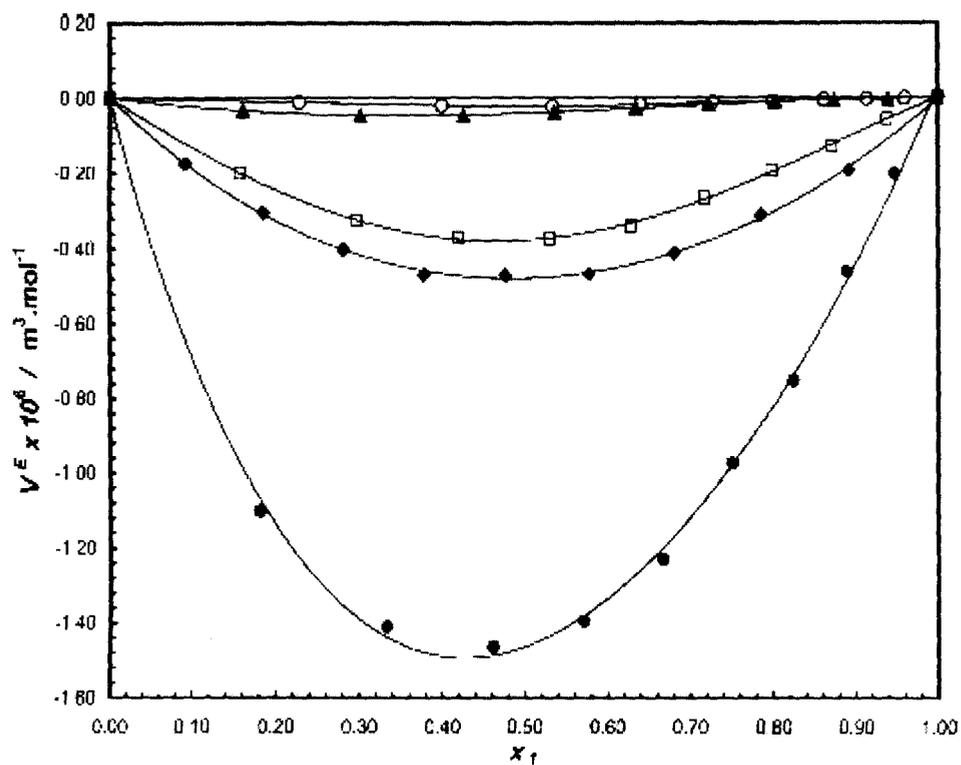


Figure 1. Excess molar volumes, V_m^E , for binary mixtures of formamide (1) at $T = 298.15 \text{ K}$ with: \square , 2-methoxyethanol (2); \circ , acetophenone (3); \blacklozenge , acetonitrile (4); \bullet , 1,2-dimethoxyethane (5); and \blacktriangle , dimethylsulfoxide (6).

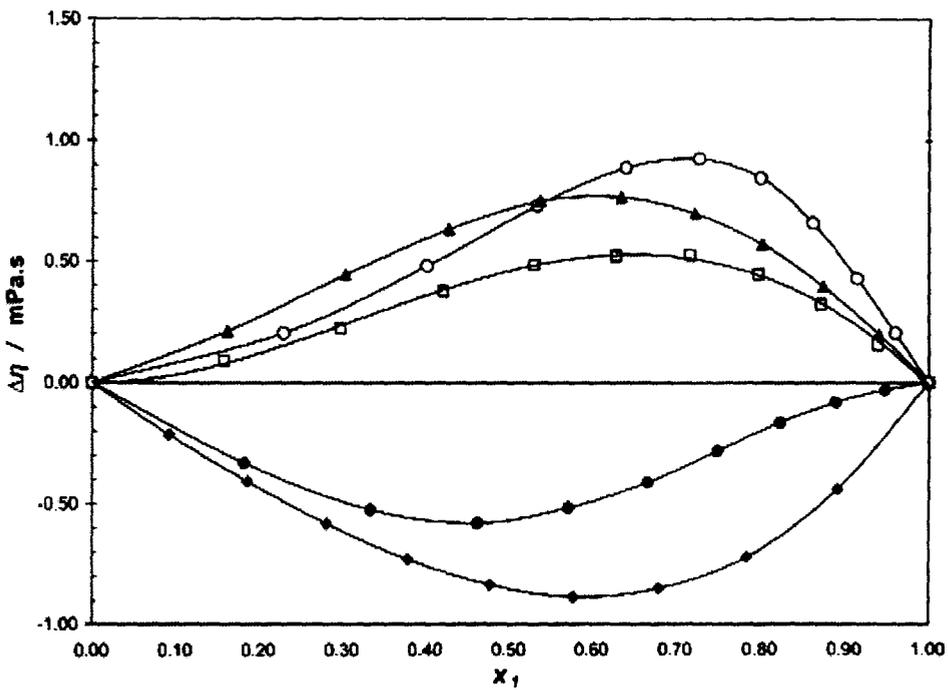


Figure 2. Viscosity deviations, $\Delta\eta$, for binary mixtures of formamide (1) at $T = 298.15$ K with: \square , 2-methoxyethanol (2); \circ , acetophenone (3); \blacklozenge , acetonitrile (4); \bullet , 1,2-dimethoxyethane (5); and \blacktriangle , dimethylsulfoxide (6).

CHAPTER XIII

Concluding Remarks

The aim of the works embodied in this thesis was to investigate the viscous synergy and antagonism and various type of interactions prevailing in mono, binary and ternary solvent systems.

After a thorough study in chapter IV, of the behavior of monoalkanols on aqueous DMF solution, we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about synergy. The lower monoalkanols are found to associate more with others molecules whereas self-association between the alcohol molecules was found to increase with increasing chain length.

After a thorough study in chapter V, of the behavior of some ether on DMF + C₆H₆ mixtures we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about antagonism. The explanation of this behavior is based on the known phenomenon of molecular dissociation, as a consequence of weakening the non-covalent bonding formed between the molecules producing a decrease in size of the molecular package. It also seen that though there is a similarity in the working formula of antagonistic interaction index and viscosity deviation would probably indicate that the two properties are similar but a close comparison between these two parameters has given the clear distinction.

An extensive study was done in chapter VI, on the behavior of the tetraalkylammonium halides in THF + CCl₄ mixtures through conductometric measurements. It becomes clear that a major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions. The tendency of the ion-pair and triple-ion formation of R₄NX depends on the size and the charge distribution of the ions. Further, it was found that Oct₄NCl had the highest amount of triple-ions and the lowest number of ion-pairs formed in different binary solvent mixtures of THF + CCl₄ as compared to the other electrolytes.

The study in chapter VII revealed that proteins are complex molecules and their behaviour in solutions is governed by a combination of many specific interactions. To

study the interactions in systems containing smaller biomolecules, such as amino acids, reveals that although ion-ion or hydrophilic-hydrophilic group interactions are predominant for glycine and L-alanine, ion-hydrophobic or hydrophobic-hydrophobic group interactions are predominant for L-valine and L-leucine in aqueous resorcinol solutions. These interactions are a function of the molality of resorcinol in the ternary solutions. Also, it is evident that resorcinol has a dehydration effect on these amino acids in aqueous resorcinol solutions. The size and number of carbon atoms of the alkyl chain groups of the amino acids also play a pivotal role in determining the nature and strength of the interactions in these solvent media.

The study in chapter VIII revealed that for ammonium, sodium and potassium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in both aqueous THF and aqueous 1,3 DO solvent mixtures. The Stokes' radius of the thiocyanate ion is, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that this ion is scarcely solvated in both solvent mixtures. This also supports our earlier contention, derived from the Walden products of those ions. It also shown that the aqueous THF mixtures have higher ΔG° than aqueous 1,3 DO mixtures. This indicates greater degree of ion-pair formation and lower extent of association in presence of THF molecules, attributing to its higher D than 1,3 DO. The results further indicate that the coulombic forces play a major role in the ion association processes.

In chapter IX an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of some sulphate salts in formamide + water mixtures. The sulphates under investigation were found has a positive value of $(\delta^2 V_\phi^\circ / \delta T^2)_p$, indicating all are structure maker in the given mixture. Also the compressibility data indicated electrostriction of the solvent molecules around the cations.

Study of electrical conductances of some tetraalkylammonium halides have been measured in chapter X indicate that Hep_4NBr had the highest amount of triple-ions and the lowest number of ion-pairs formed in different binary solvent mixtures of THF + C_6H_6 as compared to the other electrolytes. It is observed for all the salts in all solvent composition that the amount of triple-ions in the solution mixture increases with the increase in concentration of the salt as well as increase in the amount of benzene the

solvent mixture. The large association between the ions may be due to the coulombic interactions as well as to covalent bonding forces between the ions ($R_4N^+ \dots X^-$).

The study of V_ϕ° and viscosity B -coefficient values for different thiocyanate, in chapter XI indicate the presence of strong ion–solvent interactions and these interactions are further strengthened with rise in temperature and with decrease in the amount of 1,3-dioxolane in the mixtures. It also seen that all studied thiocyanate salts in different composition of 1,3-Dioxolane + water mixture acts as a structure breaker.

Study in chapter XII reveals that the order of specific interaction for the binary mixtures of formamide follows the order: formamide + 1,2-dimethoxyethane > formamide + acetonitrile > formamide + 2-methoxyethanol > formamide + dimethylsulfoxide > formamide + acetophenone. This may be attributed to intermolecular hydrogen bonding and interstitial accommodation between the mixing components. The graded pattern can also be partly due to the difference in the dielectric constants of the mixing components.

In recent years to interpreting the intermolecular interactions and the mechanism of such interactions among mixed components at microscopic and macroscopic levels thermodynamic, transport and acoustic studies on mono, binary and ternary solvent systems are highly useful. Numerous forces may operate between the molecules in solvent mixtures 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.

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 immense help in understanding the nature of 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.

A P P E N D I X

List of Publications

- [1] Study of Ion-Solvent Interactions of Some Tetraalkylammonium Halides in THF + CCL₄ mixtures by Conductance measurements. *Journal of Fluid Phase equilibria*, 269 (2008) 134.
- [2] Viscosity, Density, and Speed of Sound for the Binary Mixtures of Formamide with 2-Methoxyethanol, Acetophenone, Acetonitrile, 1,2-Dimethoxyethane, and Dimethylsulfoxide at Different Temperatures. *Journal of Chemical Engineering & Data*, 52 (2007) 1630.
- [3] Viscous Synergy, Excess Molar volumes, Viscosity Deviations and Isentropic Compressibility of some Primary Monoalkanols in Aqueous N, N- dimethylformamide Mixtures, *Russian Journal of Physical Chemistry- A*, (under revision)
- [4] Conductivity Study of Some 1-1 Electrolytes in Aqueous Binary Mixtures of Tetrahydrofuran and 1,3-dioxolane at 298.15 K. *Journal of Chemical Thermodynamics*. (under review)
- [5] Studies on Ion-pair and Triple-ion Formation of Some Tetraalkyl ammonium Salts in Binary Solvent Mixtures of Tetrahydrofuran and Benzene at 298.15 K, *Journal of Fluid Phase equilibria*. (under review)

Seminar / Symposium /convention attended:

- [1] 6th CRSI, National Symposium (Kolkata Chapter) in Chemistry, August 2, 2008, at the Department of Chemistry, North Bengal University, Darjeeling, India.
- [2] 45th Annual Conventoin of Chemistry of Chemist 2008, Dharwad, November 23-27, 2008 Organized by Indian Chemical Society and hosted by P.G.Department of Chemistry, Karnataka University, India.

