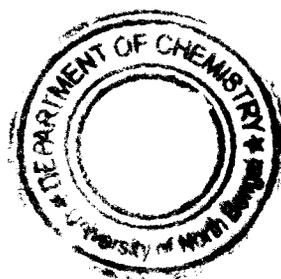


**STUDIES ON
SOLUTION PROPERTIES PREVAILING
IN SOME INDUSTRIAL SOLVENTS BY
PHYSICO-CHEMICAL METHODS**

A Thesis submitted to University of North Bengal for the
Degree of Doctor of Philosophy
in Chemistry, Faculty of Science.

2009



By

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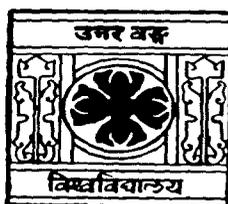
MY

Beloved Parents

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October, 2009

It gives me immense pleasure to certify that Mr. Prasanna Pradhan, M.Sc. in Chemistry has carried out his research work embodied in the thesis entitled "**Studies on Solution Properties Prevailing in Some Industrial Solvents by Physico-Chemical Methods**," based on his original work under my supervision and guidance.

He is going to submit his thesis for the award of Doctor of Philosophy degree in Chemistry in the Faculty of Science as per the rules and regulations of the University of North Bengal. The research work included in this thesis is original and has not been submitted previously in any form for the fulfillment of the Degree or Diploma to this University or any other University and research institutions.

I am very much impressed for his keen interest, research aptitudes and sincere attempt to study the various phenomena in connection with his research in the field of "**Solution Thermodynamics**" which demands far-reaching effects in the modern battery and medicinal industries including pharmaceuticals and cosmetics products. According to me, he is fit and proper person to be conferred with the degree of Doctor of Philosophy (**Ph.D.**) in Chemistry (Science) of the University of North Bengal.

Needless to say he is sober, honest, meritorious, energetic, active and industrious person and I venture to say that he will be able to prove himself worthy if he is placed in a higher position.

I wish him every success in life.

Mahendra Nath Roy
20.10.2009

Dr. Mahendra Nath Roy
READER IN CHEMISTRY
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Acknowledgement

The research work associated with my thesis was carried out by me at Department of Chemistry, University of North Bengal, Darjeeling-734013, India.

At first I feel tremendously excited and fortunate enough while expressing my deepest sense of gratitude and inner sentiments to my teacher and supervisor, Dr. Mahendra Nath Roy, Reader in Physical Chemistry, University of North Bengal, Darjeeling. He deserves my thanks because he has not only guided me during the completion of research work but also motivated me, encouraged me and for his being dynamic and mesmerizing one. I am deeply indebted to him for his keen interest, strong motivation, constant encouragement and sympathetic consideration. His subtle guidance, advice and suggestions have always helped me to think me positively and remain optimistic. The fruitful scientific discussions with him furthered my keen interest in Chemistry. He gave me the freedom to pursue an interesting research as well as trusted me often times more than myself and never let me get out of his office without a positive thought. I am fortunate to have had an opportunity under him. His presence in my life is very significant at times and will remain so throughout my life. Without his loving care, scrupulous guidance and precious supervision, it would not have been possible for me to bring the present contour to this thesis. I shall ever remain grateful to him.

I also express my profound sense of gratitude to all of my respected faculty members and thanks to the non-teaching staff, Department of Chemistry, University of North Bengal for their helpful assistance and continual inspiration during the course of my research work.

I am grateful to the University authority for providing library and laboratory amenities, especially Computer Centre and University Scientific Instrumentation Centre (USIC) for helping me in my research.

My special thanks are also due to Dr. Biswajit Sinha, Sri. Radhey Shayam Sah, Miss Rajani Dewan and Sri. Pran Kumar Roy of our research laboratory for their valuable assistance and cooperation during my research work.

It is impossible for me to express my gratitude to those authors of monographs, articles etc. from which I have collected information related to my research work. I can only hope that some measure of my gratitude is expressed by the references I have cited to their works.

I would like to acknowledge my thanks to my parents, sister and brother in law for their ceaseless inspiration, sincere help, constructive suggestion and whole-hearted cooperation in order to complete the work associated with my thesis and keeping me aloof from the family responsibilities

I shall be failing in my duty if I do not express my deep sense of gratitude to my friends and colleagues of K.M.N.H.S for their constant encouragement and self-belief

during my research work. I am also grateful to my best beloved friend , Ritika for her great forbearance, understanding, moral support and greatful sacrifice in shaping my Ph.D thesis in the present form.

Finally, I would also like to record my thankfulness to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No.F 540 / 27 / DRS / 2007, SAP-1) for financial and instrumental assistance in connection with my research work.

Prasanna Pradhan
20/10/2009.

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CHAPTER - I

1.1 Scope and Objective of the research

In recent years there has been an upsurge in the study of physico-chemical properties of various solvent-solvent and solute-solvent systems in interpreting the intermolecular interactions among mixed components. The determination of density, viscosity, sound speed and refractive index is a valuable tool to develop new theoretical models and learn about the liquid state [1] because of the close connection between liquid structure and macroscopic properties. Ultrasonic methods and refractive index measurements finds extensive applications owing to their ability of characterizing the physicochemical behavior of systems. Young [2] made the first systematic attempt in these directions by collecting a number of data on the thermodynamic and mechanical properties of liquid mixtures.

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

Rheology is the branch of science [3] that studies material deformation and flow, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied in the analysis of the viscous behavior of many pharmaceutical products [4-8], and to establish their stability and even bio-availability. Considering the rheological behavior,

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thermodynamic investigation is very important, since many products are formulated with more than one component in order to yield the desired physical structure and properties [9]. Synergy and antagonism gives the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components for 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 [10-11] is said to lack interaction. The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the product.

The importance and uses of the chemistry of electrolytes in non-aqueous and reactions in non-aqueous and mixed solvents have been summarized by Franks[12], Meck [13], Popovych [14], Bates [15, 16], Parker [17, 18], Criss and Salomon [19], Mercus [20] and others [21-23]. The solute-solute and solute - solvent interactions have been subject of wide interest as apparent from recent Faraday Trans. of the Chemical society [24].

Although a great deal of work and collection of data on various electrolytic and non-electrolytic solution in water have been made, the structure of water and the various types of interactions that water undergoes with electrolytes are yet to be understood properly. However, a great deal of information has been obtained on the thermodynamic properties of different electrolytes and non-electrolytes in aqueous solution. Also, the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties in aqueous solutions have been well studied.

Understanding of solute-solvent interactions in solution chemistry, forms the basis of explaining quantitatively the influence of solvent, the extent of interaction of ions in solvents and thus pave the way for real understanding of the different phenomena associated with solution chemistry. Estimate of solute- solvent interactions can be obtained

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thermodynamically and also from the measurement of partial molar volumes, viscosity B -coefficient and conductivity studies.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute and solute-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for physical chemists and interests in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry [25].

Research on non-aqueous electrolyte solutions has manifested their wide applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion 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 supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success [26, 27]. Other fields where non-aqueous solutions are broadly used include electro-chromic 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 ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions [28]. The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in

Object and Application of the Research Work

chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction [29, 30].

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents like water is substantially modified by the presence of solutes [31].

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, refractometric and conductometric behaviour 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 nature of intermolecular interactions among the mixed components can be revealed from the interpretation of excess properties through the rheological and thermodynamic study of physico-chemical properties. 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, isoentropic compressibility, refractive index [32, 33] etc.

Density of solvent mixtures and related volumetric properties like excess molar volume and apparent molar volume are of great importance in characterizing the properties and structural aspects of solutions. The sign and magnitude of excess molar volume imparts estimate of strength of unlike interactions in the binary and ternary solvent systems. The negative values of

Object and Application of the Research Work

excess molar volume (V^E) suggest specific interactions [34, 35] between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces 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. Similarly, the sign and magnitude of apparent molar volume (V_ϕ^o) also provides information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_v^*) provides information about ion-ion interactions [36].

Valuable information about the nature and strength of forces operating within and between the unlike molecules can be obtained from viscosity data. 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 [37, 38]. 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.

The refractive index is an important physical property of liquids and liquid mixtures, which affects the solution of different problems in chemical engineering in order to develop industrial processes. Knowledge of refractive index of multicomponent mixtures provides information regarding the interactions in these mixtures [39-41]. Prediction of refractive index of

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multicomponent liquid mixtures is essential for many physicochemical calculations, which include correlation of refractive index with density [42-44].

Drug transport across biological cells and membranes is dependent on physicochemical 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 [45, 46].

These facts therefore prompted us to undertake the study of binary or ternary solvent systems with some polar, weakly polar and non-polar solvents as well as with some solutes. Furthermore, the excess properties derived from experimental density, viscosity, speeds of sound data, refractive index and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

1.3 Choice and importance of solvents and solutes used

Alcohols, viz., methyl alcohol, amyl alcohol, isoamylalcohol; alkoxyethanols, viz., 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol; benzene and its derivatives, viz., anisole, chlorobenzene, nitrobenzene, toluene, acetophenone; Cyclohexane, cyclohexanone, cyclic ethers, viz., 1, 4 dioxane, tetrahydrofuran; carbontetrachloride, dichloromethane, ethane 1, 2-diol along with water were chosen as solvents for the research purpose.

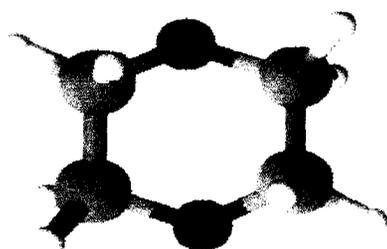
Catechol, phosphomolybdic acid, sodium molybdate, sodium tungstate, sodium iodide, sodium acetate, sodium thiocyanate, tetraalkylammonium iodides, viz., tetrabutylammonium iodide,

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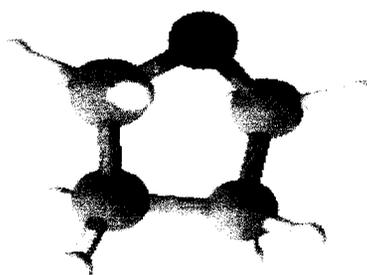
tetrapentylammonium iodide, tetrahexylammonium iodide, tetraheptylammonium iodide were considered as solutes.

The study of these solvents and solutes is of great importance because of their wide use as solvents, solutes and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

1, 4-dioxane (DO) and tetrahydrofuran (THF) are polar aprotic solvents of low permittivity, each with great present-day synthetic and industrial importance. They are frequently used in electrical conductance studies [47-48, 49-50] and in high-energy batteries [47-48, 49-50] has found its application in organic syntheses as manifested from the physico-chemical studies in this medium [51, 52].

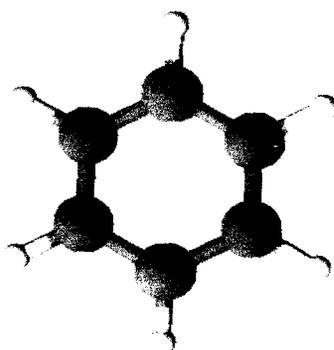


(1,4 D.O)



(T.H.F)

Benzene is used as solvents for fats and oils, dry-cleaner of woolen clothes, anti-knock gasoline and in manufacture of detergents, insecticides, etc.



(BENZENE)

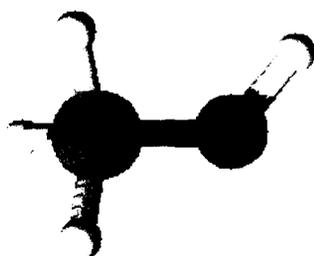
Object and Application of the Research Work

Ethane-1, 2 diol have received increasing attention as a class of substance widely used in different applications. They find a variety of applications in pharmaceutical, cosmetics [53], food and textiles fields [54].



(ETHANE 1,2-DIOL)

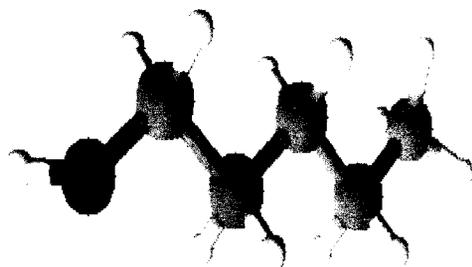
Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc. It is obtainable commercially in adequate purity for most purposes, the impurity being up to 0.05% water usually be removed by distillation, or by use of molecular sieves and calcium hydride.



(METHANOL)

The amyl alcohols are used fundamentally for the perfumes composition and the synthesis of fruit essences. They are also used as solvents for surfaces and lacquer baths, inks for print and dyes for wool as well as in the chemical production of photographic and pharmaceutical substances. Furthermore, they are an intermediate in the production of amyl acetate and other amyl esters.

Object and Application of the Research Work



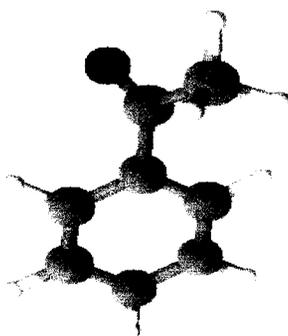
(AMYL ALCOHOL)

The importance of iso-amyl alcohol in research field is implied for its usefulness in gas chromatography. It can isolate high quality RNA from even the hardest to isolate samples for immediate use in micro array application and it is also useful in most DNA applications [55].



(ISO-AMYL ALCOHOL)

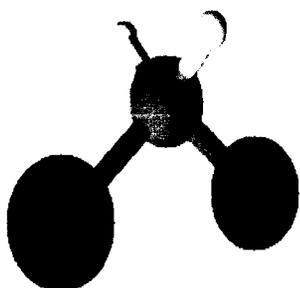
Acetophenone, a typical ketone is used in perfumery and as a hypotonic under the name "hypone". It is also used as a solvent for cellulose ethers.



(ACETOPHENONE)

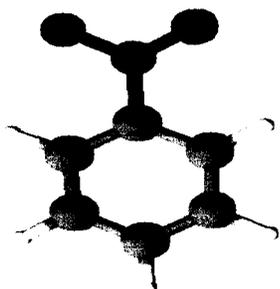
Dichloromethane is a very interesting solvent with appreciable industrial use in pharmaceutical industry, as paint stripping agent, aerosols and as adhesives etc. and also as it is a solvent exhibiting high density and low viscosity.

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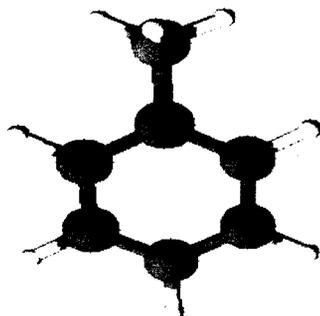
(DICHLOROMETHANE)

Nitrobenzene is used- (i) mainly for the manufacture of aniline and aniline dyes; (ii) as high-boiling industrial solvent; (iii) for the preparation of benzidine; and (iv) as an oxidising agent in organic synthesis [56].



(NITROBENZENE)

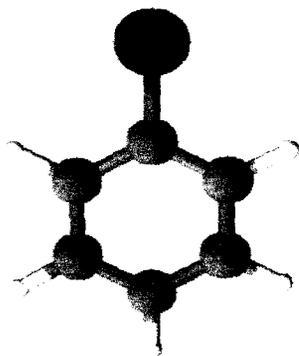
Toluene is used as a constituent of high-octane aviation and motor gasolines, as a solvent and as a raw material in the manufacture of benzene, caprolactam, phenol, many dyestuffs and various other chemicals.



(TOLUENE)

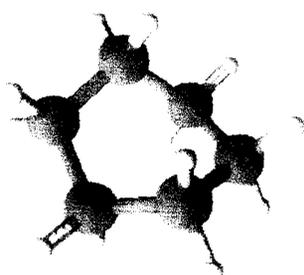
Chlorobenzene is used as an intermediate in the manufacture of other chemicals, particularly phenol, DDT and aniline.

Object and Application of the Research Work

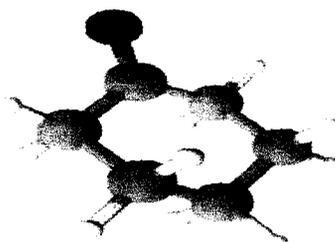


(CHLOROBENZENE)

Cyclohexane is inflammable. It is used as a solvent for oils, fats and waxes; and also as a paint remover. Cyclohexanone has also an important role in the manufacture of caprolactum, nylon, adipic acid, celluloid, artificial leather and printing inks [57].

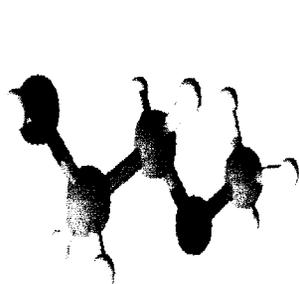


(CYCLOHEXANE)

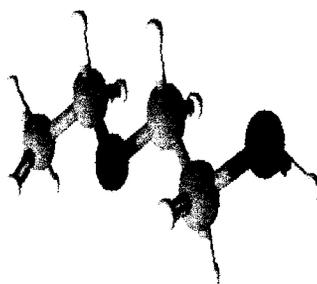


(CYCLOHEXANONE)

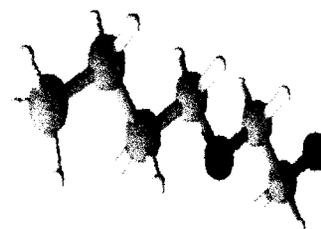
Alkoxyethanols have wide use as monomers in the production of polymers and emulsion formulations. They find a wide range of application of technological importance and these solvents are relevant to battery construction using suitable electrodes. They are also of considerable interest for studying the heteroproximity effects of the etheric oxygen on the -OH bond and, hence their influence on the associated nature of the species in these molecules.



(2-METHOXYETHANOL)



(2-ETHOXYETHANOL)



(2-BUTOXYETHANOL)

Object and Application of the Research Work

Phosphomolybdic acid is widely used to stain connective tissues by dyes. Phosphomolybdic acid not only yields an intense staining of connective tissue fibers by dyes with basic groups but also reduces the staining of cytoplasm, thus producing a specific staining of connective tissue fiber [58].

Sodium molybdate, sodium tungstate, sodium iodide, sodium acetate, sodium acetate sodium thiocyanate are the electrolytes with important roles in the study of ion-solvent interactions in pure or mixed solvent systems.

Tetraalkylammonium salts are bulky in nature and are known to orient water molecules around them depending on their alkyl chain [59, 60]. Salts like tetrabutylammonium iodide can give a better insight into the effect of electrostatic and hydrophobic interactions on the stability of vitamins as these salts are known to influence macromolecular conformations by weakening attraction or repulsion inter- and intracharge-charge interactions and by affecting hydrophobic interactions through the side chain of the alkyl groups.

Thus, evaluation of thermodynamics and bulk properties of these solvents and their mixtures with organic solvents may prove quite relevant to the design and implementation of the above-mentioned processes, especially for the establishment of reliable correlations and predictions.

Moreover, in recent years, the above-mentioned solvents have drawn much focused in electro-analytical investigation, still more studies on the electrolytic behavior in these non-aqueous medium can be explored.

1.4 Methods of Investigations

The existence of free ions, solvated ions, ion-pairs and triple-ions in aqueous and non-aqueous media depends upon the concentrations of the solvent systems. Hence, the study of various interactions and equilibrium of ions in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occurs in these systems.

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It is of interest to employ different experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed five important methods, namely, conductometric, viscometric, densitometry, ultrasonic interferometer and refractometric to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative to Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The *B*-coefficients are also separated into ionic components by the 'reference electrolyte' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. may be given.

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

1.5 Summary of the work 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

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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, refractive indices 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, refractive indices and acoustic properties.

Chapter IV

Electrical conductances of tetraalkylammonium iodides, R_4NI ($R =$ Pentyl to hexyl) have been measured at 298.15 K in low-permittivity mixtures of 1, 4-dioxane ($\epsilon=2.21$) and tetrahydrofuran ($\epsilon =7.58$). Minima in the conductometric curves (Λ versus \sqrt{C}) were observed for electrolyte concentrations dependent

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upon both the electrolyte and the binary solvent mixture. The conductance data have been analyzed by the Fuoss- Kraus theory of triple ions. A numerical evaluation of ion-pair and triple- ion formation constants (K_p and K_T) were made and the results have been discussed in terms of molecular scale model.

Chapter V

In this chapter the densities (ρ), viscosities (η), sound speeds (u) and refractive indices (n_D) of seven ternary mixtures of cyclic ether (tetrahydrofuran), methanol and cyclic compounds; benzene, toluene, chlorobenzene, nitrobenzene, anisole, cyclohexane and cyclohexanone are determined over the entire range of composition at 298.15K. From the experimental observations viscosity deviation ($\Delta\eta$), the viscous synergy and antagonism, synergic and antagonic index are derived by the equations developed by Kalentunc-Gencer and Peleg and Howell, respectively. Excess molar volume (V^E), excess isentropic compressibility (ΔK_S) and excess molar refraction (ΔR) has been calculated from the experimentally measured density, sound speed and refractive index values. The excess Gibb's free energy of activation (ΔG^E) has also been calculated. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

Chapter VI

Apparent molar volume (V_ϕ) and viscosity B -coefficients were estimated for sodium molybdate and sodium tungstate in aqueous binary mixture of ethane-1, 2-diol from measured solution density (ρ) and viscosity (η) at 298.15, 308.15 and 318.15K at various electrolyte concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data

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has been analyzed using Jones -Dole equation and the derived parameters, B and A , have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of sign of $(\partial\theta^0_{\text{E}}/\partial T)_{\text{P}}$.

Chapter VII

Precise measurements on electrical conductances of tetraalkylammonium iodides, R_4NI ($\text{R} =$ butyl to heptyl) in different mass% (20-80) of carbon tetrachloride + nitrobenzene at 298.15 K have been performed. Limiting molar conductances (Λ_0), association constants (K_A) and co-sphere diameter (R) for ion-pair formation in the mixed solvent mixtures have been evaluated using the Lee-Wheaton conductivity equation. However, the deviation of the conductometric curves (Λ versus \sqrt{c}) from linearity for the electrolytes in 80 mass% of carbon tetrachloride + nitrobenzene indicated triple ion formation and therefore corresponding conductance data have been analyzed by the Fuoss- Kraus theory of triple ions. Limiting ionic molar conductances (λ_0^\pm) have been calculated by the reference electrolyte method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_P \approx K_A$ and K_T); the results have been discussed in terms of solvent properties, configurational theory and molecular scale model.

Chapter VIII

In this chapter an attempt has been made to reveal the nature of various types of interactions prevailing in solution of phosphomolybdic acid in aqueous catechol from solution density (ρ) and viscosity (η) at 298.15, 308.15 and 318.15K at various solute concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data have been analyzed using Jones-Dole equation and the derived parameters, B

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and A , have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure-making or breaking capacity of the solute under investigation has been discussed in terms of sign of $(\partial\phi^0/\partial T)_P$. The activation parameters of viscous flow were determined and discussed by application of transition state theory.

CHAPTER IX

The excess molar volume (V^E), viscosity deviation ($\Delta\eta$), deviation in isentropic compressibility (ΔK_S), excess molar refraction (ΔR) and excess Gibbs free energy of activation (ΔG^E) of viscous flow have been investigated from the experimentally measured densities, viscosities, sound speeds and refractive indices for three binary mixtures of isoamyl alcohol with 2-methoxy ethanol (2-M.E), 2-ethoxy ethanol (2-E.E) and 2-butoxy ethanol (2-B.E) over the entire range of composition at 303.15, 313.15, and 323.15K. The calculated quantities are further fitted to the Redlich-Kister equation to estimate the binary fitting parameters and root mean square deviations from the regression lines. These excess properties have been used to discuss the presence of significant interactions between the component molecules in the binary mixtures. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures and have been discussed in terms of molecular interactions and structural changes.

Chapter X

The excess molar volume (V^E), viscosity deviation ($\Delta\eta$), deviation in isentropic compressibility (ΔK_S), excess molar refraction (ΔR) and excess Gibbs free energy of activation (ΔG^E) of viscous flow have been investigated from the experimentally measured densities, viscosities, sound speeds and refractive indices for three binary mixtures of acetophenone + amyl alcohol, acetophenone + dichloromethane and amyl alcohol + dichloromethane and

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their corresponding ternary mixtures at 298.15K over the entire composition range. The calculated quantities are further fitted to the Redlich-Kister equation to estimate the binary fitting parameters and root mean square deviations from the regression lines. These excess properties have been used to discuss the presence of significant interactions between the component molecules in the binary and ternary mixtures. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures and have been discussed in terms of molecular interactions and structural changes.

Chapter XI

Electrolytic conductivities of some sodium salts (NaI, NaSCN, CH₃COONa) have been studied in 0, 25, 50 and 75 mass% ethane-1, 2-diol + methyl alcohol mixtures at 293.15, 298.15 and 303.15K. The limiting molar conductivity (Λ°), the association constant (K_A) and the distance of closest approach of ion (R) have been evaluated using the Fuoss conductance equation (1978). The association constant (K_A) decreases with temperature while it tends to decrease in the order: 0 mass% > 25 mass% > 50 mass% > 75 mass% ethane-1, 2-diol + methyl alcohol mixtures. Thermodynamic parameters ΔH° , ΔG° and ΔS° along with the Walden products ($\Lambda^{\circ}\eta$) are obtained and discussed. The results have been interpreted in terms of ion-solvent interactions and structural changes in the mixed solvents.

Chapter XII

The dissertation ends with some concluding remarks in this chapter.

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CHAPTER II

2.1 Importance of Solution Chemistry

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

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

However, the exact structure of the solvent molecule is not known with certainty. The addition of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The assesment of ion-pairing in these systems is important because of its effect on the ionic mobility and hence on the ionic conductivity of the ions in solution. These phenomenon thus paves the path for research in solution chemistry to elucidate the nature of interaction through experimental studies involving densitometry, viscometry, interferrometry, refractometry and other suitable methods and to interpret the experimental data collected.

2.2. Ion-Solvent Interaction

Ion solvation is a phenomenon of primary interest in many contexts of chemistry because solvated ions are omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems [1, 2]. Solvated ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common [3, 4]. The exchange of solvent molecules around ions in solutions is fundamental to the understanding of the reactivity of ions in solution [5]. Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions [6].

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.

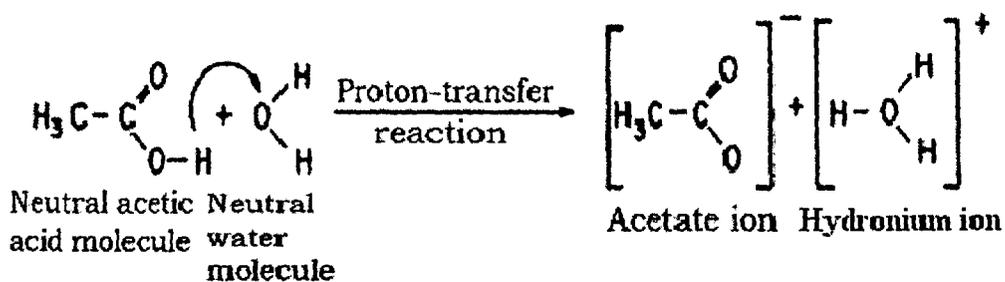


Figure 1: The chemical method of producing ionic solutions.

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 1, 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

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interaction between the ions and the solvent molecules. These interactions are collectively termed as ion- solvent interactions.

Ions orient dipoles. The spherically symmetrical electric field of the ion may tear solvent dipoles out of the solvent lattice and orient them with appropriate charged end toward the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. The majority of reactions occurring in solutions are chemical or biological in nature. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents [7-16].

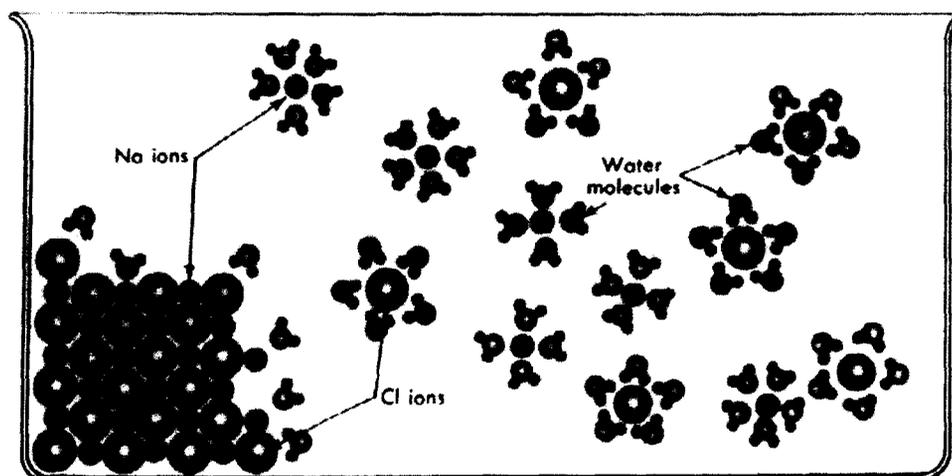


Figure 2: Dissolution of an ionic crystal by the action of a solvent.

Most chemical processes of individual and biological importance occur in solution. The role of solvent is so great that million fold rate changes take place in some reactions simply by changing the reaction medium. Our bodies contain 65 to 70 % water, which acts as a lubricant, as an aid to digestion and more specifically as a stabilizing factor to the double helix conformations of DNA. With the exceptions of heterogeneous catalytic reactions most reactions in technical importance occur in solutions. In addition, molecules not only have to travel through a solvent to their reaction partner before reacting, but also need to present a sufficiently unsolvated rate for collision. The solvent

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governs the movement and energy of the reacting species to such an extent that a reaction suffers a several-million fold change in rate when the solvent is changed. As water is the most abundant solvent in nature and its major importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic and equilibrium studies. But still our knowledge of molecular interactions in water is extremely limited.

Moreover, the uniqueness of water as a solvent has been questioned [17, 18] 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. The organic solvents have been classified on the basis of dielectric constants, organic group types, acid base properties or association through hydrogen bonding [16] donor-acceptor properties [19, 20] hard and soft acid-base principles [21] etc. As a result, the different solvents show a wide divergence of properties ultimately influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes or non electrolytes in various solvents would thus provide important information in this direction. Henceforth, in the development of theories of electrolytic solutions, much attention has been devoted to the controlling forces-'ion-solvent interactions' in infinitely dilute solutions wherein ion-ion interactions are almost absent. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a key role to understand the physico-chemical properties of solutions. One of the causes for the intricacies in solution chemistry is the uncertainty about the structure of the solvent molecules in solution. The introduction of a solute modifies the solvent structure to an uncertain magnitude, the solvent molecule and the interplay of forces like solute-solute, solute-solvent also modify the solute molecule and solvent-solvent

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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 [22, 23]. The spectral solvent shifts or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent interactions. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task. It is thus apparent that the real understanding of the ion-solvent interaction is a difficult task. The aspect embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc. and such thermodynamic properties as apparent and partial molar volumes and apparent molal adiabatic compressibility.

2.3. Ion-Ion Interaction

Ion-solvent interactions are only a part of the story of an ion related to its environment. The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions constitute the essential part- 'ion-ion interactions'. The degree of ion-ion interactions affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions, in general, are stronger than ion-solvent interactions. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but ion-solvent interactions or ion-solvation still remains a complex process. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the solvents significantly modify the majority of the solutes. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus

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

2.4. Theory of Mixed Solvents

As the mixed and non-aqueous solvents are increasingly used in chromatography, solvent extraction, in the elucidation of reaction mechanism, in preparing high density batteries, etc. a number of molecular theories, based on either the radial distribution function or the choice of suitable physical model, have been developed for mixed solvents. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. L. Jones and Devonshire [24] were first to evaluate the thermodynamic functions for a single fluid in terms of interchange energy parameters. They used "Free volume" or "Cell model". Prigogine and Garikian [25] extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans [26] developed a two fluid version of the cell model. They found that while excess molar volume (V^E) was negative for mixtures with molecules of almost same size, it was large positive for mixtures with molecules having small difference in their molecular sizes. Treszczanowicz *et al.* [27] 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

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studies [28-29]. It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi *et al.*[30] therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-interaction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Based on the principle of corresponding states as suggested by Pitzer [31], L. Huggins [32] 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.* [33-35] reformulated the average rules for Vander 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 [36]. A more successful approach is due to Flory who made the use of certain features of cell theory [37-39] and developed a statistical theory for predicting the excess properties of binary mixtures by using the equation of state and the properties of pure components along with some adjustable parameters. This theory is applicable to mixtures containing components with molecules of different shapes and sizes. Patterson and Dilamas [40] combined both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure, etc. to the excess thermodynamic properties. Recently, Heintz [41-43] and coworkers suggested a theoretical model based on a statistical mechanical derivation and accounts for self-association and cross association in hydrogen bonded solvent mixtures is termed as Extended Real Associated Solution model (ERAS). It combines the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory *et al.*[37-39]. Subsequently the ERAS

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model has been successfully applied by many workers [44-46] to describe the excess thermodynamic properties of alkanol-amine mixtures. Recently, a new symmetrical reformation on the Extended Real Association (ERAS) model has been described in the literature [47]. The symmetrical-ERAS (S-ERAS) model makes it possible to describe excess molar enthalpies and excess molar volumes of binary mixtures containing very similar compounds described by extremely small mixing functions. The symmetrical Extended Real Associated Solution Model (S-ERAS) is, in fact, a simple continuation of the ERAS model. It was developed in order to widen its applicability to the thermodynamic properties of systems that could not be satisfactorily described by the equations of the ERAS model [47, 48]. Gepert *et al.* [49] applied this model for studying some binary systems containing alcohols.

2.5. Density

The physicochemical properties of liquid mixtures have attracted much attention from both theoretical and engineering applications points of view. Many engineering applications require quantitative data on the density of liquid mixtures. They also provide information about the nature and molecular interactions between liquid mixture components.

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

interactions. The volumetric information may be of immense importance in this regard. Various concepts regarding molecular processes in solutions like electrostriction [50], hydrophobic hydration [51], micellization [52] and co-sphere overlap during solute-solvent interactions [53] have been derived and interpreted from the partial molar volume data of many compounds.

2.5.1. Apparent and Partial Molar Volumes

Density data can be used for the calculation of molar volume of a pure substance. However, the volume contributed to a solvent by the addition of 1 mole of an ion is difficult to determine. This is so because, upon entry into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the influence of the ion's electric field, i.e., electrostriction. Electrostriction is a general phenomenon and whenever there are electric fields of the order of 10^9 - 10^{10} V m⁻¹, the compression of ions and molecules is likely to be significant. The effective volume of an ion in solution, the partial molar volume, can be determined from a directly obtainable quantity- apparent molar volume (V_ϕ). The apparent molar volumes, (V_ϕ), of the solutes can be calculated by using the following relation [54].

$$V_\phi = \frac{M}{\rho_o} - \frac{1000(\rho - \rho_o)}{c\rho_o} \quad (1)$$

Where M is the molar mass of the solute, c is the molarity of the solution; ρ_o and ρ are the densities of the solvent and the solution respectively.

The partial molar volumes, \bar{V}_2 can be obtained from the equation [55]:

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

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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 [56], the Redlich-Meyer equation [57], the Owen-Brinkley equation [58], and the Pitzer equation [31]. Masson found that the apparent molar volume of electrolyte, V_ϕ , vary with the square root of the molar concentration by the linear equation:

$$V_\phi = V_\phi^o + S_V^* \sqrt{c} \quad (3)$$

where V_ϕ^o is the apparent molar volume (equal to the partial molar volume, \bar{V}_2^o) at infinite dilution and S_V^* the experimental slope. The majority of V_ϕ data in water [59] and nearly all V_ϕ data in non-aqueous [60-64] solvents have been extrapolated to infinite dilution through the use of equation (3).

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

$$V_\phi^o = a_0 + a_1 T + a_2 T^2 \quad (4)$$

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

The limiting apparent molar expansibilities (ϕ_E^o) can be obtained by the following equation: thus

$$\phi_E^o = \left(\frac{\partial V_\phi^o}{\partial T} \right)_P = a_0 + 2a_2 T \quad (5)$$

The limiting apparent molar expansibilities (ϕ_E^o) change in magnitude with the change of temperature. 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 tendency of any solute. Helper [65] developed a technique of examining the sign of $(\partial \phi_E^o / \partial T)_P$ for the solute in terms of long-

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range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows

$$\left(\frac{\partial\phi_E^0}{\partial T}\right)_P = 2a_2 \quad (6)$$

If the sign of $(\partial\phi_E^0/\partial T)_P$ is positive or small negative the electrolyte is a structure maker and when the sign of $(\partial\phi_E^0/\partial T)_P$ is negative, it is a structure breaker. Redlich and Meyer [57] have shown that an equation (3) cannot be any more than a limiting law where for a given solvent and temperature, the slope S_V^* should depend only upon the valence type. They suggested the equation

$$V_\phi = V_\phi^0 + S_V\sqrt{c} + b_v c \quad (7)$$

where

$$S_V = Kw^{\frac{3}{2}} \quad (8)$$

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

$$w = 0.5 \sum_i^j 2 \gamma_i Z_i^2 \quad (9)$$

$$\text{and, } K = N^2 e^2 \left(\frac{8\pi}{1000 \epsilon^3 RT} \right)^{\frac{1}{2}} (\partial \ln \epsilon / \partial P)_T - \frac{\kappa_S}{3} \quad (10)$$

In equation (10), κ_S is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation [57] adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies [66-68] on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for polyvalent electrolytes, the more

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complete Owen-Brinkley equation [58] 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 [58] which includes the ion-size parameter, a (cm), is given by

$$V_\phi = V_\phi^o + S_V \tau(Ka) \sqrt{c} + 0.5W_V \theta(Ka)c + 0.5K_V c \quad (11)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson [69] to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt $M_\gamma M X_\gamma X$ is

$$V_\phi = V_\phi^o + v |Z_M Z_X| A_V |2b \ln(1 + b\sqrt{I}) + 2\gamma_M \gamma_X RT [mB_{MX}^2 + m^2 \sqrt{(\gamma_M \gamma_X)} C_{MX}^V] \quad (12)$$

where the symbols have their usual significance.

2.5.2. Ionic Limiting Partial Molar Volumes

The individual partial ionic volumes provide information relevant to the general question of the structure near the ion, i.e., its 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 solutions to non-aqueous electrolyte solutions. In the last few years, the method suggested by Conway *et al.* [70] 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, $\bar{V}_{R_4X^+}^o$, for a series of these salts with a halide ion in common as a function of the formula

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weight of the cation, $M_{R_4N^+}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\bar{V}_{R_4NX}^o = \bar{V}_{X^-}^o + bM_{R_4N^+} \quad (13)$$

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

Uosaki *et al.* [71] used this method for the separation of some literature values and of their own $V_{R_4NX}^o$ values into ionic contributions in organic electrolyte solutions. Krungalz [72] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.5.3. Excess Molar Volumes

The excess molar volumes, V^E are calculated from the molar masses M_i and the densities of pure liquids and the mixtures according to the following equation [73, 74]

$$V^E = \sum_{i=1}^n x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (14)$$

where ρ_i and ρ are the density of the i^{th} component and density of the solution mixture respectively. V^E is the resultant of contributions from several opposing effects. These may be divided arbitrarily into three types, namely, chemical, physical and structural. Physical contributions, which are nonspecific interactions between the real species present in the mixture, contribute a positive term to V^E . The chemical or specific intermolecular interactions result in a volume decrease, thereby contributing negative V^E values. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume [13]. These phenomena are the results of difference in energies of interaction between molecules being in solutions and packing effects.

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Disruption of the ordered structure of pure component during formation of the mixture leads to a positive effect observed on excess volume while an order formation in the mixture leads to negative contribution.

2.6. Viscosity

As fundamental and important properties of liquids, viscosity and volume could also provide a lot of information on the structures and molecular interactions of liquid mixtures. Viscosity and volume are different types of properties of one liquid, and there is a certain relationship between them. So by measuring and studying them together, relatively more realistic and comprehensive information could be expected to be gained. The relationship between them could also be studied. The viscometric information includes 'Viscosity' as a function of composition on the basis 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 [77, 78]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, \bar{V}_2^o , 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.

2.6.1. Viscosity of Pure Liquids and Liquid Mixtures

Since the molecular motion in liquids is controlled by the influence of the neighbouring molecules, the transport of momentum in liquids takes place, in sharp contrast with gases at ordinary pressures, not by the actual movement of molecules but by the intense influence of intermolecular force fields. It is this aspect of the mechanism of momentum transfer which forms the basis of

the procedures for predicting the variations in the viscosity of liquids and liquid mixtures.

2.6.1.1. *Early theoretical considerations on liquid viscosity*

The theoretical development of liquid viscosity in early stages has been reviewed Andrade [79, 80] and Frenkel [81]. By considering the forces of collision to be the only important factor and assuming that at the melting point, the frequency of vibration is equal to that in the solid state and that one-third of the molecules are vibrating along each of the three directions normal to one another, Andrade [80] developed equations which checked well against data on monoatomic metals at the melting point. Frenkel [81] considered the molecules of a liquid to be spheres moving with an average velocity with respect to the surrounding medium and using Stokes' law and Einstein's relation for self diffusion-coefficient, arrived at a complicated expression for liquid viscosity with only limited applicability. Furth [82] assumed the momentum transfer to take place by the irregular Brownian movement of the holes [83] which were linked to clusters in a gas and thus, in analogy with the gas theory of viscosity and with assumption of the equipartition law of energy, showed that for liquids,

$$\eta = 0.915 \frac{RT}{V} \left(\frac{m}{\sigma} \right) e^{\frac{A}{RT}} \quad (15)$$

where η , V and m are viscosity, volume and mass, respectively, T is the temperature, R is the universal gas constant, s is the surface tension and A is the work function at the melting point. He compared his theory with experiment as well as with the theories of Andrade [81] and Ewell and Eyring [84] Auluck, De and Kothari [85] further modified the theory and successfully explained the variations of the viscosity with pressure. A critical review of these simple theories and their abilities to explain momentum transport in liquids is given by Eisenschitz [86].

2.6.1.2. The cell lattice theory and liquid viscosity

A model related to in the literature by various names such as cell, lattice, cage, free volume or one particle model was introduced by Lennard- Jones and Devonshire [87, 88] and further expanded by Pople [89]. Eizenschitz employing this model developed a theory of viscosity by considering the motion of the representative molecules to be Brownian and their distribution according to the Smoluchowski equation. Even with certain assumptions, the final expression showed shortcomings most of which were later overcome in a subsequent publication [90].

2.6.1.3. Statistical mechanical approach to liquid viscosity

The distribution functions for the liquid molecules were obtained on the basis of statistical mechanical theory mainly by the efforts of Kirkwood [91-92] Mayer and Montroll [93], Mayer [94], Born and Green [95] and the considerations on the basis of the general kinetic theory led Born and Green [95, 96] to develop a viscosity equation which provided explanation for several empirical equations [79, 80, 82] proposed for liquid viscosity. In this connection the theoretical contributions of Kirkwood and coworkers [83, 97-103] Zwanzig *et al.*, [104] Rice and coworkers [105-108] Longuet- Higgins and Valleau [109] and Davis and Coworkers [110, 111] are worth mentioning.

2.6.1.4. Principle of corresponding states and liquid viscosity

The principle of the corresponding states has been applied to liquids in the same way as to gases [112] the basic assumption being that the intermolecular potential between two molecules is a universal function of the reduced intermolecular separation. This assumption is a good approximation for spherically symmetric mono atomic non-polar molecules. For complicated molecules, the principle becomes increasingly crude. In general, more parameters are introduced in the corresponding state correlations on

somewhat empirical grounds in the hope that such modification in some way compensates the shortcomings of the above stated assumption. In this connection the studies by Rogers and Brickwedde [113], Boon and Thomaes [114-116] Boon, Legros and Thomaes [117], and Hollman and Hijmans [118] are worth mentioning.

2.6.1.5. *The reaction rate theory for viscous flow*

Considering viscous flow as a chemical reaction in which a molecule moving in a plane occasionally acquires the activation energy necessary to sleep over the potential barrier to the next equilibrium position in the same plane. Eyring [119] showed that the viscosity of the liquid is given by

$$\eta = \frac{\lambda_1 h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (16)$$

where λ is the average distance between the equilibrium positions in the direction of motion, λ_1 is the perpendicular distance between two neighbouring layers of molecules in relative motion, λ_2 is the distance between neighbouring molecules in the same direction and λ_3 is the distance from molecule to molecule in the plane normal to the direction of motion. The transmission coefficient (κ) is the measure of the chance that a molecule having once crossed the potential barrier will react and not recross in the reverse direction, F_n is the partition function of the normal molecules, F_a^* that of the activated molecule with a degree of freedom corresponding to flow, ΔE_{act} is the energy of activation for the flow process, h is Planck's constant and k is Boltzmann constant. Ewell and Eyring [84] argued that for a molecule to flow into a hole, it is not necessary that the latter be of the same size as the molecule. Consequently they assume that ΔE_{act} is a function of ΔE_{vap} for viscous flow because ΔE_{vap} is the energy required to make a hole in the liquid of the size of a molecule. Utilizing the idea and certain other relations [84, 120] finally gets

$$\eta = \frac{N_A h (2\pi m k T)^{\frac{1}{2}}}{V h} \frac{b R T V^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{n R T} \quad (17)$$

where n and b are constants. It was found that the theory could reproduce the trend in temperature dependence of η but the computed values are greater than the observed values by a factor of 2 or 3 for most liquids. Kincaid, Eyring and Stearn [121] have summarized all the working relations and the underlying

2.6.1.6. *The significant structure theory and liquid viscosity*

Eyring and coworkers [122-125] improved the “holes in solid” model theory [121-126] to picture the liquid state by identifying three significant structures- In brief, a molecule has solid like properties for the short time it vibrates about an equilibrium position and then it assumes instantly the gas like behaviour on jumping into the neighbouring vacancy. The above idea of significant structures leads to the following relation for the viscosity of liquid [127, 128].

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (18)$$

where V_s is the molar volume of the solid at the melting point and V is the molar volume of the liquid at the temperature of interest while η_s and η_g are the viscosity contributions from the solid-like and gas-like degrees of freedom, respectively. The expressions for η_s and η_g are given by Carlson, Eyring and Ree [128]. Eyring and Ree [129] have discussed in detail the evaluation of η_s from the reaction rate theory of Eyring [119] assuming that a solid molecule can jump into all neighbouring empty sites. The expression for η_s takes the following form [130]

$$\eta_s = \frac{N_A h}{Zk} \cdot \frac{V}{V_s} \cdot \frac{6}{2^2} \cdot \frac{1}{V - V_s} \cdot \frac{1}{1 - e^{-\frac{\theta}{T}}} \exp \frac{aE_s V_s}{(V - V_s)RT} \quad (19)$$

where N_A is Avogadro's number, Z is the number of nearest neighbours, θ is the Einstein characteristic temperature, E_s is the energy of sublimation and a' is the proportionality constant. On the other hand, the term η_g is obtained from the kinetic theory of gases [130] by the relation:

$$\eta_g = \frac{2}{3d^2} \left(\frac{mkT}{\pi^3} \right)^{\frac{1}{2}} \quad (20)$$

where d is the molecular diameter and m is the molecular mass.

2.6.2. Viscosity of Electrolytic Solutions

The viscosity relationships of electrolytic solutions are highly complicated. Because ion-ion and ion-solvent interactions are occurring in the solution and separation of the related forces is a difficult task. But, from careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system. As viscosity is a measure of the friction between adjacent, relatively moving parallel planes of the liquid, anything that increases or decreases the interaction between the planes will raise or lower the friction and thus, increase or decrease the viscosity. If large spheres are placed in the liquid, the planes will be keyed together in increasing the viscosity. Similarly, increase in the average degree of hydrogen bonding between the planes will increase the friction between the planes, thereby viscosity. An ion with a large rigid co-sphere for a structure-promoting ion will behave as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules

will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity. In 1905 Grüneisen [131] performed the first systematic measurement of viscosities of a number of electrolytic solutions over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole [132] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c):

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \quad (21)$$

The above equation can be rearranged as:

$$\frac{(\eta_r - 1)}{\sqrt{c}} = A + B\sqrt{c} \quad (22)$$

where A and B are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non aqueous solvent systems where there is no ionic association and has been used extensively. The term $A\sqrt{c}$, originally ascribed to Grüneisen effect, arose from the long-range coulombic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory [133] of inter-ionic attractions in 1923. The A -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [134-136] and is given by the Falkenhagen Vernon [136] equation:

$$A_{Theo} = \frac{0.2577\Lambda_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[1 - 0.6863 \left(\frac{\lambda_+^o \lambda_-^o}{\Lambda_o} \right)^2 \right] \quad (23)$$

where the symbols have their usual significance. In very accurate work on aqueous solutions [137], A -coefficient has been obtained by fitting η_r to equation (22) and compared with the values calculated from equation (23), the agreement was normally excellent. The accuracy achieved with partially aqueous solutions was however poorer [138]. A -coefficient suggesting that

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should be calculated from conductivity measurements. Crudden et al.[139] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_p \left(\frac{1 - \alpha}{\alpha} \right) \quad (24)$$

where A , B_i and B_p are characteristic constants and a is the degree of dissociation of ion pair. Thus, a plot of $(\eta_r - 1 - A\sqrt{\alpha c}) / \alpha c$ against $(1 - a) / a$, when extrapolated to $(1 - a) / a = 0$ gave the intercept B_i . However, for the most of the electrolytic solutions both aqueous and nonaqueous, the equation (22) is valid up to 0.1 (M) [77, 140, 141] within experimental errors. At higher concentrations the extended Jones-Dole equation (25), involving an additional coefficient D , originally used by Kaminsky, [142] has been used by several workers [143, 144] and is given below:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \quad (25)$$

The coefficient D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (22) is used by the most of the workers.

The plots of $(\eta/\eta_o - 1)/\sqrt{c}$ 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 [141,145,146]. Thus, instead of determining A - coefficient from the plots or by the least square method, the A -coefficient are generally calculated using Falkenhagen-Vernon equation (23). 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 [132]. The B -coefficient may be either positive or negative and it is actually the ion-solvent interaction

parameter. It is conditioned by the ionic 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 [147, 148]:

- (1) The effect of ionic solvation and the action of the field of the ion in producing long-range order in solvent molecules, increase η or B - value.
- (2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or depolymerization effect) decreases η values.
- (3) High molal volume and low dielectric constant, which yield high B - values for similar solvents.
- (4) Reduced B -values are obtained when the primary solvation of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

2.6.3. 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 [149]:

$$\eta = A \exp^{\frac{b}{T}} \quad (26)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [150-155] and the equation suggested by Angell [156-157] 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:

$$\frac{1}{\eta} = A \exp \left[-\frac{K_1}{N_o - N} \right] \quad (27)$$

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_o is the hypothetical concentration at which the system becomes glass. The equation

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was recast by Majumder *et al.* [158-160] introducing the limiting condition, that is $N \rightarrow 0, \eta \rightarrow \eta_o$; which is the viscosity of the pure solvent.

Thus, we have:

$$\ln \eta / \eta_o = \ln \eta_{Rel} = \frac{K_1 N}{N_o(N_o - N)} \quad (28)$$

The equation (28) predicts a straight line passing through the origin for the plot of $\ln \eta_{Rel}$ vs. $N/(N_o - N)$ if a suitable choice for N_o is made. Majumder *et al.* tested the equation (28) by using literature data as well as their own experimental data. The best choice for N_o and K_1 was selected by a trial and error methods. The set of K_1 and N_o producing minimum deviations between η_{Rel}^{Exp} and η_{Rel}^{Theo} was accepted.

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

$$\eta_{Rel} = \exp\left(\frac{K_1 N}{N_o^2}\right) \cong 1 + \frac{K_1 N}{N_o^2} \quad (29)$$

Equation (29) is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K_1/N_o^2$. 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 (28) can be written in the form:

$$\frac{N}{\ln \eta_{Rel}} = \frac{N_o^2}{K_1} - \left(\frac{N_o}{K_1}\right) N \quad (30)$$

It closely resembles the Vand's equation [153] for fluidity (reciprocal for viscosity):

$$\frac{2.5c}{2.3 \log \eta_{Rel}} = \frac{1}{V_h} - Qc \quad (31)$$

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

2.6.4. Division of B -coefficient into Ionic Values

The viscosity B -coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents [146, 161-191]. However, the B -coefficients as determined experimentally using the Jones-Dole equation, does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total solute-solvent interaction. The division of B -values into ionic components is quite arbitrary and based on some assumptions, the validity of which may be questioned. The following methods have been used for the division of B -values in the ionic components -

(1) Cox and Wolfenden [192] carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in LiIO_3 are proportional to the ionic volumes which are proportional to the third power of the ionic mobilities. The method of Gurney [193] and also of Kaminsky [142] is based on:

$$B_{K^+} = B_{Cl^-} \text{ (in water)} \quad (32)$$

The argument in favour of this assignment is based on the fact that the B -coefficients for KCl is very small and that the motilities' of K^+ and Cl^- are very similar over the temperature range 288.15 - 318.15 K. The assignment is supported from other thermodynamic properties. Nightingale [194], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron [143] 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 [195],

$$B = 0.0025\bar{V}_o \quad (33)$$

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and by having an accurate value of the partial molar volume of the ion, \bar{V}_o , it is possible to calculate the value of 0.359 for $B_{Et_4N^+}$ in water at 298.15 K. Recently, Sacco *et al.* proposed the "reference electrolytic" method for the division of B -values.

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

$$B_{BPh_4^-} = B_{PPh_4^+} + B_{BPh_4PPh_4}/2 \quad (34)$$

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

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \quad (35)$$

The values obtained are in good agreement with those obtained by other methods. The criteria adopted for the separation of B -coefficients in nonaqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilutions.

(a) Criss and Mastroianni assumed $B_{K^+} = B_{Cl^-}$ in ethanol based on equal mobilities of ions [196]. They also adopted $B_{Me_4N^+}^{25} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss [197] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.*, [198] $\lambda_{25}^0(Bu_4N^+) = 61.4$ and $\lambda_{25}^0(Ph_4B^-) = 58.3$ in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \quad (36)$$

(c) Gopal and Rastogi [147] resolved the B -coefficient in N-methyl propionamide solutions assuming that $B_{Et_4N^+} = B_{I^-}$ at all temperatures.

(d) In dimethyl sulphoxide, the division of B -coefficients were carried out by Yao and Beunion [146] assuming:

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

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate [199] solutions. The methods, however, have been strongly criticized by Krungalz [200]. 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 $\lambda_o^+ = \lambda_o^-$ in all solvents at all

temperatures. Thus, though $\lambda_K^+ = \lambda_{Cl}^-$ at 298.15 K in methanol, but is not so in ethanol or in any other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the B -coefficient values are calculated. Further, according to him, equality of dimensions of $(i-pe)_3BuN^+$ or $(i-Am)_3BuN^+$ and Ph_4B^- does not necessarily imply the equality of B - coefficients of these ions and they are likely to be solvent and ion-structure dependent. Krungalz [200, 201] 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 [202, 203] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B -values for large tetraalkylammonium ions, R_4N^+ (where $R > Bu$) in organic solvents are proportional to their ionic dimensions. So, we have:

$$B_{R_4NX} = a + br^3R_4N^+ \quad (38)$$

$a=B_X$. B and b is a constant dependent on temperature and solvent nature.

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

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

$$B_{R_4N^+} - B_{R_4N^+} = B_{R_4NX} - B_{R_4NX} \quad (39)$$

$$\frac{B_{R_4N^+}}{B_{R_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R_4N^+}} \quad (40)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [204]. Gill and Sharma [184] used Bu_4NBPh_4 as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that Bu_4N^+ and Ph_4B^- ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of Bu_4N^+ (5.00 Å) and Ph_4B^- (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \quad (41)$$

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (42)$$

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

$$B_{[(i-Am)_3Bu_4N^+]} = B_{Ph_4B^-} = 1/2 B_{Bu_4NBPh_4} \quad (43)$$

Recently, Lawrence and Sacco [187] used tetrabutylammonium tetrabutylborate

(Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal Vander Waals volume. Thus, we have:

$$\frac{B_{Bu_4N^+}}{B_{Bu_4B^-}} = \frac{V_{W(Bu_4N^+)}}{V_{W(Bu_4B^-)}} \quad (44)$$

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$$B_{\text{Bu}_4\text{N}^+} = \frac{B_{\text{Bu}_4\text{NBPh}_4}}{[1 + V_{W(\text{Bu}_4\text{B}^-)}/V_{W(\text{Bu}_4\text{N}^+)}]} \quad (45)$$

A similar division can be made for Ph_4PBPh_4 system.

Recently, Lawrence *et al.* made the viscosity measurements of tetraalkyl (from Propyl to Heptyl) ammonium bromides in DMSO and HMPT.

The B -coefficients $B_{\text{R}_4\text{NB}_r} = B_{\text{B}_r^-} + a[f_x R_4\text{N}^+]$ were plotted as functions of the Vander Waals volumes. The $B_{\text{B}_r^-}$ values thus obtained were compared with the accurately determined $B_{\text{B}_r^-}$ value using Bu_4NBBu_4 and Ph_4PBPh_4 as reference salts. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritchett [205] suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali metal halide salts by employing Fajan's competition principle [206] and 'volcano plots' of Morris [207]. The principle was extended to derive absolute single ion B coefficients for alkali metals and halides in water. They also observed that $B_{\text{Cs}^+} = B_{\text{I}^-}$ suggested by Krumgalz [202] to be more reliable than $B_{\text{K}^+} = B_{\text{Cl}^-}$ in aqueous solutions. However, we require more data to test the validity of this method.

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

2.6.5. Temperature Dependence of B - ion Values

A regularity in the behaviour of B_{\pm} and dB_{\pm}/dT has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by 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

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of periodic system, the temperature co-efficient of B_{Ion} values increase as the ionic radius. The results can be summarized as follows:

$$(i) A \text{ and } dA/dT > 0 \quad (46)$$

$$(ii) B_{Ion} < 0 \text{ and } dB_{Ion}/dT > 0 \quad (47)$$

characteristic of the structure breaking ions.

$$(iii) B_{Ion} > 0 \text{ and } dB_{Ion}/dT < 0 \quad (48)$$

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 [208], A, B, C Zones of Frank and Wen [209] and hydrated radius of Nightingale [194].

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_o) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation:

$$\eta = \eta_o + \eta^* + \eta^E + \eta^A + \eta^D = \eta_o + \eta(A\sqrt{c} + Bc) \quad (49)$$

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

$$\eta^E + \eta^A + \eta^D = \eta_o Bc \quad (50)$$

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

Following Stokes, Mills and Krungalz [200] we can write for B_{Ion} as:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{Reinf} \quad (51)$$

where as according to Lawrence and Sacco:

$$B_{Ion} = B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \quad (52)$$

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B_{Ion}^{Einst} is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^E or B_{Shape}). B_{Ion}^{Orient} is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to η^A or B_{Ord}). B_{Ion}^{Str} is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself 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 Vander Waals volume and the volume of the solvation of ions. Thus, small and highly charged cations like Li^+ and Mg^{2+} form a firmly attached primary solvation sheath around these ions (B_{Ion}^{Orient} or η^E positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in B_{Ion}^{Orient} (η^A), B_{Ion}^{Orient} (η^D) is small for these ions. Thus, B_{Ion} will be large and positive as $B_{Ion}^{Einst} + B_{Ion}^{Orient} > B_{Ion}^{Str}$. However, B_{Ion}^{Einst} and B_{Ion}^{Orient} would be small for ions of greatest crystal radii (within a group) like Cs^+ or I^- due to small surface charge densities resulting in weak orienting and structure forming effect. B_{Ion}^{Str} would be large due to structural disorder in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure.

Thus, $B_{Ion}^{Einst} + B_{Ion}^{Orient} < B_{Ion}^{Str}$ and B_{Ion} is negative.

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

Large molecular ions like tetraalkylammonium ions have large B_{Ion}^{Einst} because of large size but B_{Ion}^{Orient} and B_{Ion}^{Str} would be small, i.e., $B_{Ion}^{Einst} +$

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$B_{lon}^{Orient} \gg B_{lon}^{Str}$ would be positive and large. The value would be further reinforced in water arising from B_{lon}^{Reinf} due to hydrophobic hydrations.

The increase in temperature will have no effect on B_{lon}^{Einst} . But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in B_{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 coefficient 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_{lon} 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_{lon} values and increases in entropy of solvation and the mobility of ions. Moreover, the temperature induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So, there is a correlation between the viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic B -coefficient and the entropy of solvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication of structure making and structure breaking character of ions. The linear plot of ionic B -coefficients against the ratios of mobility viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney [208] 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:

$$\bar{S}_h^o = \bar{S}_{aq}^o - \bar{S}_g^o \quad (53)$$

Where, $\bar{S}_{aq}^o = \bar{S}_{ref}^o + \Delta S^o$, \bar{S}_g^o is the calculated sum of the translational and rotational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic B -coefficients for all mono atomic ions by equating the entropy of the hydrogen ion ($S_{H^+}^o$) to $-5.5 \text{ cal. mol}^{-1} \text{ deg}^{-1}$. Asmus [210] used the entropy of hydration to correlate ionic B values and Nightingale [194] showed that a single linear relationship could be obtained with it for both monoatomic and polyatomic ions. The correlation was utilized by Abraham *et al.* [211] to assign single ion B -coefficients so that a plot of ΔS_e^o [212, 213] the electrostatic entropy of solvation or $\Delta S_{I,II}^o$ 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^o and ΔS_I^o and the single ion B - coefficients. Both entropy criteria (ΔS_e^o and $\Delta S_{I,II}^o$) and B - ion values indicate that in water the ions Li^+ , Na^+ , Ag^+ and F^- are not structure makers, and the ions Rb^+ , Cs^+ , Cs^+ , Cl^- , Br^- , I^- and ClO_4^- are structure breakers and K^+ is a border line case.

2.6.6. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [214] approaches as:

$$\eta = A e^{\frac{E_{vis}}{RT}} = \left(\frac{hN_A}{V} \right) e^{\frac{\Delta G^*}{RT}} = \left(\frac{hN_A}{V} \right) e^{\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right)} \quad (54)$$

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.

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Nightingale and Benck [215] 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 $A c$ term).

Thus, we have:

$$R \left[\frac{d \ln \eta}{d(1/T)} \right] = r \left[\frac{d \ln \eta_o}{d(1/T)} \right] + \frac{R}{(1 + Bc)} \cdot \frac{d(1 + Bc)}{d(1/T)} \quad (55)$$

$$\Delta E_{\eta(\text{Soln})}^{\ddagger} = \Delta E_{\eta_o(\text{Soln})}^{\ddagger} + \Delta E_{\ddot{V}}^{\ddagger} \quad (56)$$

$\Delta E_{\ddot{V}}^{\ddagger}$ 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.* [216] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = \frac{(\bar{V}_1^o - \bar{V}_2^o)}{1000} + \frac{\bar{V}_1^o (\Delta \mu_2^{o\ddagger} - \Delta \mu_1^{o\ddagger})}{1000RT} \quad (57)$$

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

$$\Delta \mu_1^{o\ddagger} = \Delta G_1^{o\ddagger} = \frac{RT \ln \eta_1 \bar{V}_1^o}{h N_A} \quad (58)$$

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

$$\frac{d(\Delta \mu_2^{o\ddagger})}{dT} = -\Delta S_2^{o\ddagger} \quad (59)$$

$$\Delta H_2^{o\ddagger} = \Delta \mu_2^{o\ddagger} + T \Delta S_2^{o\ddagger} \quad (60)$$

2.6.7. Effects of Shape and Size

Stokes and Mills have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein [195] leads to the equation:

$$\frac{\eta}{\eta_o} = 1 + 2.5\phi \quad (61)$$

where ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by (i) Sinha [217] 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 (61):

$$2.5\phi = A\sqrt{c} + Bc \quad (62)$$

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:

$$2.5\bar{V}_1 = B \quad (63)$$

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:

$$B_{\pm} = 2.5\bar{V}_{\pm} = 2.5 \times \frac{4}{3} \left(\frac{\pi R_{\pm}^3 N_A}{1000} \right) \quad (64)$$

assuming that the ions behave like rigid spheres with a effective radii, R_{\pm} moving in a continuum. R_{\pm} , calculated using the equation (64) 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.

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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 [218]:

$$B_{\pm} = \frac{2.5}{1000(V_i + n_b V_s)} \quad (65)$$

where V_i is the molar volume of the base ion and V_s , the molar volume of the solvent. The equation (65) has been used by a number of workers to study the nature of solvation and solvation number.

2.6.8. Viscosity of Non-electrolytic Solutions

The equations of Vand [219], Thomas [220] and Moulik proposed mainly to account for the viscosity of the concentrated solutions of bigger spherical particles have been also found to correlate the mixture viscosities of the usual nonelectrolytes [221-223]. These equations are:

Vand equation:

$$\ln \eta_r = \frac{a}{1 - Q} = \frac{2.5V_h c}{1 - QV_h c} \quad (66)$$

Thomas equation:

$$\eta_r = 1 + 2.5V_h c + 10.05cV_h^2 c \quad (67)$$

Moulik equation:

$$\eta^2 = l + Mc^2 \quad (68)$$

where η_r is the relative viscosity, a is constant depending on axial ratios of the particles, Q is the interaction constant, V_h is the molar volume of the solute including rigidly held solvent molecules due to hydration, c is the molar concentration of the solutes; l and M are constants. The viscosity equation proposed by Eyring and coworkers for pure liquids on the basis of pure

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significant liquid structures theory, can be extended to predict the viscosity of mixed liquids also. The final expression for the liquid mixtures takes the following form [130]:

$$\eta_m = \frac{6N_A h}{\sqrt{2}r_m(V_m - V_{Sm})} \left[\sum_i^n \left\{ 1 - \exp\left(\frac{-\theta_i}{T}\right) \right\}^{-x_i} \right] \exp\left[\frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm})}\right] + \frac{V_m - V_{Sm}}{V_m} \left[\sum_i^n \frac{2}{3d_i^2} \left(\frac{m_i kT}{\pi^3}\right)^{\frac{1}{2}} x_i \right] \quad (69)$$

where n is 2 for binary and 3 for ternary liquid mixtures. The mixture parameters, r_m , E_{Sm} , V_m , V_{Sm} and a_m were calculated from the corresponding pure component parameters by using the following relations [130]:

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i \neq j} 2x_i x_j r_{ij} \quad (70)$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i \neq j} 2x_i x_j E_{Sij} \quad (71)$$

$$V_m = \sum_i^n x_i V_i \quad V_{Sm} = \sum_i^n x_i V_{Si} \quad a_m = \sum_i^n x_i a_i \quad (72)$$

$$r_{ij} = (r_i r_j)^{\frac{1}{2}} \quad \text{and} \quad E_{Sij} = (E_{Si} E_{Sj})^{\frac{1}{2}} \quad (73)$$

$$\theta = \frac{h}{\kappa 2\pi} \left(\frac{b}{m}\right)^{\frac{1}{2}} \quad (74)$$

$$b = 2Z\varepsilon \left[22.106 \left(\frac{N_A \sigma^2}{V_S}\right)^4 - 10.559 \left(\frac{N_A \sigma^3}{V_S}\right)^2 \right] \frac{1}{\sqrt{2}\sigma^2} \left(\frac{N_A \sigma^3}{V_S}\right)^{\frac{2}{3}} \quad (75)$$

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where σ and ε are Lennard-Jones potential parameters and the other symbols have their usual significance.

For interpolation and limited extrapolation purposes, the viscosities of ternary mixture can be correlated to a high degree of accuracy in terms of binary contribution by the following equations [224-230].

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2 x_3 [A_{23} \\ & + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_1 - x_2) \\ & + C_{31}(x_1 - x_2)^2] \end{aligned} \quad (76a)$$

The correlation of ternary is modified to the following form:

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2 x_3 [A_{23} \\ & + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] \\ & + A_{123}^* x_1 x_2 x_3 \end{aligned} \quad (76b)$$

However, a better result may be obtained using the following relation:

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2 x_3 [A_{23} \\ & + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] \\ & + x_1 x_2 x_3 [A_{123} + B_{123} x_1^2 (x_2 - x_3)^2 \\ & + C_{123} x_1^3 (x_2 - x_3)^3] \end{aligned} \quad (76c)$$

Where $A_{12}, B_{12}, B_{23}, A_{23}, B_{23}, C_{23}, A_{31}, B_{31}$ and C_{31} are constants for binary mixtures; $A_{123}^*, A_{123}, B_{123}$ and C_{123} are constants for the ternaries; and the other symbols have their usual significance.

2.6.9. Viscosity Deviation

Viscosity of liquid mixtures can also provide information for the elucidation of the fundamental behaviour of liquid mixtures, aid in the correlation of mixture viscosities with those of pure components, and may provide a basis for the selection of physico-chemical methods of analysis. Quantitatively, as per the absolute reaction rates theory [231], the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^j (x_i\eta_i) \quad (77)$$

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.

2.6.10. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow, ΔG^* can be calculated as [232]:

$$\Delta G^E = RT \left[\ln\eta V - \sum_{i=1}^j x_i \ln\eta_i V_i \right] \quad (78)$$

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

2.6.11 Viscous Synergy and Antagonism

Rheology is the branch of science that studies [233] material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products, [234-243] and to establish their stability and even bioavailability, since it has been firmly established that viscosity influences the drug absorption rate in the body [244, 245]. The study of the viscous behavior of pharmaceutical, foodstuffs, cosmetics or industrial products, etc.,

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is essential for conforming that their viscosity is appropriate for the contemplated use of the products.

Viscous synergy is the term used in the application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction [246, 247]

The method most widely used to analyze the synergic and antagonic behavior of the ternary liquid mixtures used here is that developed by Kaletunc- Gencer and Peleg [248] allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp} , with the viscosity expected in the absence of interaction, η_{cal} , as defined by the simple mixing rule as:

$$\eta_{cal} = \sum_{i=1}^J w_i \eta_i \quad (79)$$

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

Accordingly, when $\eta_{exp} > \eta_{cal}$, viscous synergy exists, while, when $\eta_{cal} > \eta_{exp}$, the system is said to exhibit viscous antagonism. The procedure is used when Newtonian fluids are involved, since in non-synergy indices are defined in consequence [249].

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_S) as introduced by Howell [250] is taken into account:

$$I_S = \frac{\eta_{exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \quad (80)$$

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

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

$$\rho_{cal} = \sum_{i=1}^j w_i \rho_i \quad (81)$$

where ρ_i is the experimentally measured density of the i^{th} component. Other symbols have their usual significance.

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

2.7. Ultrasonic Speed

In recent years, there has been considerably progress in the determination of thermodynamic, acoustic and transport properties of working liquids from ultrasonic speeds, density and viscosity measurement. The study of ultrasonic speeds and isentropic compressibilities of liquids, solutions and liquid mixtures provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic

speeds and densities in solutions. Isentropic compressibilities play a vital role in characterization of binary and ternary liquid mixtures particularly in cases where partial molar volume data alone fail to provide an unequivocal interpretation of the interactions.

2.7.1. Apparent Molal Isentropic Compressibility

Although for a long time attention has been paid to the apparent molal isentropic compressibility for electrolytes and other compounds in aqueous solutions [251-255] measurements in non-aqueous solvents are still scarce. It has been emphasized by many authors that the apparent molal isentropic compressibility data can be used as a useful parameter in elucidating the solute-solvent and solute-solute interactions. The most convenient way to measure the compressibility of a solvent/solution is from the speed of sound in it.

The isentropic compressibility (κ_S) of a solvent/solution can be calculated from the Laplace's equation [233][256]:

$$\kappa_S = \frac{1}{(u^2\rho)} \quad (82)$$

where ρ is the solution density and u is the ultrasonic speed in the solvent/solution. The isentropic compressibility (κ_S) determined by equation (82) is adiabatic, not an isothermal one, because the local compressions occurring when the ultrasound passes through the solvent/solution are too rapid to allow an escape of the heat produced.

The apparent molal isentropic compressibility (ϕ_K) of the solutions was calculated using the relation:

$$\phi_K = \frac{M\kappa_S}{\rho} + \frac{1000(\kappa_S\rho_o - \kappa_{S,o}\rho)}{m\rho\rho_o} \quad (83)$$

$\kappa_{S,o}$ 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 limiting apparent isentropic compressibility ϕ_K^o may be obtained by extrapolating the plots of ϕ_K versus the square root of the molal concentration of the solutes by the computerized least- square method according to the equation [252,255].

$$\phi_K = \phi_K^o + S_K^* \sqrt{m} \quad (84)$$

The limiting apparent molal isentropic compressibility (ϕ_K^o) 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 [257, 258]. This is reflected by the negative values of ϕ_K^o of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure. The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved. However, the poor fit of the solute molecules [259, 260] 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^o values have been reported in aqueous non-electrolyte [261] and non-aqueous non-electrolyte [262] solutions.

2.7.2. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility (ΔK_S) can be calculated using the following equation [263-265]:

$$\Delta K_S = K_S - \sum_{i=1}^j x_i K_{S,i} \quad (85)$$

where x_i , $K_{S,i}$ are the mole fraction and isentropic compressibility of i^{th} component in the mixture, respectively. The observed values of ΔK_S can be qualitatively explained by considering the factors, namely (i) the mutual disruption of associated species 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 [266]. The resultant values of ΔK_S for the present mixtures are due to the net effect of the combination of (i) to (iii) [267].

Moreover, the excess or deviation properties (V_m^E , $\Delta\eta$, ΔG^E and ΔK_S) have been fitted to Redlich-Kister [268] polynomial equation using the method of least squares involving the Marquardt algorithm [269] and the binary coefficients, a_i were determined as follows :

$$Y_{ij}^E = x_1 x_2 \sum_{i=1}^J a_i (x_1 - x_2)^i \quad (86)$$

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

$$\sigma = \left[\frac{(Y_{exp}^E - Y_{cal}^E)^2}{(n - m)} \right]^{\frac{1}{2}} \quad (87)$$

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

2.8. Conductance

One of the most precise and direct technique available to determine the extent of the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents is the "conductometric method." Conductance data in conjunction with viscosity measurements, gives much information regarding ion-ion and ion-solvent interaction.

General Introduction

The study of conductance measurements were pursued vigorously during the last five decades, both theoretically and experimentally and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents. The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager [270] 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:

$$\Lambda = \Lambda_o - S\sqrt{c} \quad (88)$$

where,

$$S = \alpha\Lambda_o + \beta \quad (89)$$

$$\alpha = \frac{(z^2)\kappa}{3(2 + \sqrt{2})\epsilon_r kT\sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(\epsilon_r T)^{\frac{3}{2}}} \quad (90a)$$

$$\beta = \frac{z^2 e F \kappa}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\epsilon_r T}} \quad (90b)$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent [271]. In the subsequent years, Pitts (1953) [272] and Fuoss and Onsager (1957) [261,273] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions. However, the Λ_o values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably [271] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned [257,274,275]. The original Fuoss-Onsager equation was further modified by Fuoss and Hsia [276] 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:

General Introduction

$$\Lambda = \frac{\Lambda_o - \alpha\Lambda_o\sqrt{c}}{(1 + \kappa a)} \left(\frac{1 + \kappa a}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1 + \kappa a)} + G(\kappa a) \quad (91)$$

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

$$\Lambda = \Lambda_o - S\sqrt{c} + Ec \ln c + J_1c - J_2\sqrt[3]{c} \quad (92)$$

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 [257,277,278]. Further correction of the equation (92) was made by Fuoss and Accascin [261]. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_o - S\sqrt{c} + Ec \ln c + J_1c + J_2\sqrt[3]{c} - F\Lambda c \quad (93)$$

where

$$Fc = \frac{4\pi R^3 N_A}{3} \quad (94)$$

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 [279].

2.8.1. Ionic Association

The equation (93) 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}^o is greater than Λ_{theo}^o , 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 ($\Lambda_{exp}^o < \Lambda_{theo}^o$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_o + \beta$) 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_{exp}^o and Λ_{theo}^o would be considerable with increasing association [280].

General Introduction

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



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

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (97)$$

where γ^{\pm} is the mean activity coefficient of the free ions at concentration ac .

For strongly associated electrolytes, the constant, K_A and Λ_o has been determined using Fuoss-Kraus equation [281] or Shedlovsky's equation[282].

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (98)$$

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

$$F(z) = 1 - z(1 - z(1 - \dots)^{-\frac{1}{2}})^{-\frac{1}{2}} \quad (99a)$$

and

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (99b)$$

A plot of $T(z)/\Lambda$ against $c \gamma_{\pm}^2 \Lambda / T(z)$ should be a straight line having $1/\Lambda_o$ for its intercept and K_A/Λ_o^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_o and K_A from equation (98).

The Fuoss-Hsia [276] conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_o - S\sqrt{ac} + E(ac) \ln(ac) + J_1(ac) - J_2(ac)^{\frac{3}{2}} - K_A \Lambda \gamma_{\pm}^2(ac) \quad (100)$$

The equation was modified by Justice [283]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

General Introduction

$$\Lambda = \alpha(\Lambda_o - S\sqrt{\alpha c}) + E(\alpha c) \ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{\frac{3}{2}} \quad (101)$$

$$\frac{(1 - \alpha)}{\alpha^2 c \gamma_{\pm}^2} = K_A \quad (102)$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1 + kR\sqrt{\alpha c})} \quad (103)$$

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

According to Justice the method of fixing the J -coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. Since the equation (101) is a series expansion truncated at the $c^{\frac{3}{2}}$ 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 [284]:

$$K_A = \frac{4\pi N_A a^3}{3000} \exp\left(\frac{e^2}{a\epsilon kT}\right) \quad (104)$$

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 [285].

$$K_A = \frac{4\pi N_A a}{1000} \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r\epsilon kT}\right) dr \quad (105)$$

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 [286].

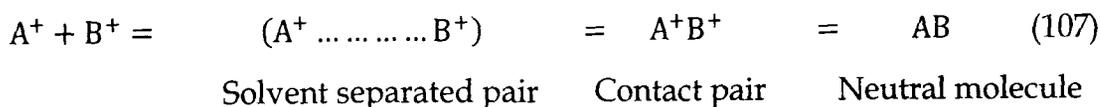
2.8.2. Ion size Parameter and Ionic Association

For plotting, equation (93) can be rearranged to the 'Λ' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Eclnc = \Lambda_0 + J_1c + J_2\sqrt[3]{c} = \Lambda_0 + J_1c \quad (106)$$

with J_2 term omitted.

Thus, a plot of Λ_0 vs. c gives a straight line with Λ_0 as intercept and J_1 as slope and 'a' values can be calculated from J_1 values. The 'a' values obtained by this method for DMSO were much smaller [280] than would be expected from sums of crystallographic radii. One of the reasons attributed to it is that ion-solvent interactions are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in 'a' values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction leads to a larger value of 'a' [287] but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J [288]. Fuoss [289] in 1975 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 neighbours 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:



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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 unpaired ion and $c(1 - \alpha)(1 - \gamma)$ and that of contact pair is $\alpha c(1 - \gamma)$.

The equation constants for (107S) are:

$$K_R = \frac{(1 - \alpha)(1 - \gamma)}{c\gamma^2 f^2} \quad (108)$$

$$K_S = \frac{\alpha}{1 - \alpha} = \exp\left(\frac{-E_S}{kT}\right) = e^{-\varepsilon} \quad (109)$$

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

Now,

$$(1 - \alpha) = \frac{1}{(1 + K_S)} \quad (110)$$

and the conductometric pairing constant is given by:

$$K_\Lambda = \frac{(1 - \alpha)}{c\gamma^2 f^2} = \frac{K_R}{(1 - \alpha)} = K_R(1 + K_S) \quad (111)$$

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

$$\Lambda = p \left[\Lambda_0 \left(\frac{1 + \Delta X}{X} \right) + \Delta\Lambda_e \right] = p[\Lambda_0(1 + R_X) + E_L] \quad (112)$$

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

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

$$p = 1 - \alpha(1 - \gamma) \quad (113)$$

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:

$$\Lambda = \gamma \left[\Lambda_0 \left(\frac{1 + \Delta X}{X} \right) \right] + \Delta\Lambda_e \quad (114)$$

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

$$K_\Lambda = \frac{(1 - \gamma)}{c\gamma^2 f^2} \approx K_R K_S \quad (115)$$

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

$$\gamma = 1 - \frac{K_R c \gamma^2 f^2}{(1 - \alpha)} \quad (116)$$

$$K_R = \left(\frac{4\pi N_A R^3}{3000} \right) \exp\left(\frac{\beta}{R}\right) \quad (117)$$

$$-\ln f = \frac{\beta_\kappa}{2(1 + \kappa R)}, \quad \beta = \frac{e^2}{\epsilon kT} \quad (118)$$

$$\kappa^2 = 8\pi\beta\gamma n = \frac{\pi\beta N_A \gamma c}{125} \quad (119)$$

$$-\varepsilon = \ln\left[\frac{\alpha}{1 - \alpha}\right] \quad (120)$$

The details of the calculations are presented in the 1978 paper [289]. 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. Lee-Wheaton Conductance Equation

As Fuoss 1978 conductance equation contained a boundary condition error, [290, 291] Fuoss introduced a slight modification to his model [292, 293]. According to him, the ion pairs (ion approaching with their Gurney co-sphere) are divided into two categories- contact pairs (with no contribution to conductance) and solvent separated ion pairs (which can only contribute to the net transfer of charge). To rectify the boundary errors contained in Fuoss 1978 conductance equation, Lee-Wheaton [294(a)] in the same year described in the derivation of a new conductance equation, based on the Gurney co-sphere model and henceforth the new equation is referred to as the Lee-Wheaton equation [294(b)]. The conductance data were analyzed by means of the Lee-Wheaton conductance equation [296] in the form:

$$\Lambda = \alpha_i \left\{ \Lambda_o [1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3] - \frac{\rho \kappa}{1 + \kappa R} \left[1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \right\} \quad (121)$$

The mass action law association [324] [297] is

$$K_{A,c} = \frac{(1 - \alpha_i) \gamma_A}{\alpha_i^2 c_i \gamma_{\pm}^2} \quad (122)$$

and the equation for the mean ionic activity coefficient:

$$\gamma_{\pm} = \exp \left[- \frac{q \kappa}{1 + \kappa R} \right] \quad (123)$$

where C_1 to C_5 are least square fitting coefficients as described by Pethybridge and Taba [295], Λ_o is the limiting molar conductivity, $K_{A,c}$ is the association constant, α_i is the dissociation degree, q is the Bjerrum parameter and γ the activity coefficient and $\beta = 2q$. The distance parameter R is the least distance that two free ions can approach before they merge into ion pair. The Debye parameter κ , the Bjerrum parameter q and ρ are defined by the expressions [295]:

$$\kappa = 16000 \pi N_A q c_i \alpha_i \quad (124)$$

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$$q = \frac{e^2}{8\varepsilon_0\varepsilon_r kT} \quad (125)$$

$$\rho = \frac{Fe}{299.79 \times 3\pi\eta} \quad (126)$$

where the symbols have their usual significance [298].

The equation (118) was resolved by an iterative procedure. For a definite R value the initial value of Λ_o and $K_{A,c}$, were obtained by the Kraus-Bray method [299]. The parameter Λ_o and $K_{A,c}$, were made to approach gradually their best values by a sequence of alternating linearization and least squares optimizations by the Gauss-Siedel method [300] until satisfying the criterion for convergence. The best value of a parameter is the one when equation (118) is best fitted to the experimental data corresponding to minimum standard deviation (σ_A) for a sequence of predetermined R value and standard deviation (σ_A) was calculated by the following equation:

$$\sigma_A^2 = \sum_{i=1}^n \frac{[\Lambda_i(calc) - \Lambda_i(obs)]^2}{n - m} \quad (127)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two parameter fit ($m=2$). For the electrolytes with no significant minima observed in the σ_A versus R curves, the R values were arbitrarily preset at the centre to centre distance of solvent-separated pair [301]:

$$R = a + d \quad (128)$$

where $a = r_c^+ + r_c^-$, i.e., the sum of the crystallographic radii of the cation and anion and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of d and related terms are described in the literature [301]. R was generally varied by a step 0.1 Å and the iterative process was continued with equation (118).

2.8.4. Limiting Equivalent Conductance

It is possible to isolate the contributions due to cations and anions by separating a number of molal functions of electrolytic solutions into ionic contributions. At present, a limiting equivalent conductance is the only function, which can be divided into ionic components by a commonly accepted direct method. The rigorous method for the separation of the limiting equivalent conductances (Λ^o) of electrolytes into ionic conductances (λ_{\pm}^o) is based on the use of transference numbers (t_{\pm}) for infinite dilutions.

$$\lambda_{+}^o = t_{+}\Lambda^o \quad \text{and} \quad \lambda_{-}^o = t_{-}\Lambda^o \quad (129)$$

However, accurate transference number determinations are limited to only a few solvents.

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

The method has been summarized by Krumgalz [302] and some important points are mentioned as follows:

- (i) Walden equation [303]

$$(\lambda_{\pm}^o)_{\text{water}}^{25} \cdot \eta_{o,\text{water}} = (\lambda_{\pm}^o)_{\text{acetone}}^{25} \cdot \eta_{o,\text{acetone}} \quad (130)$$

- (ii) $\lambda_{\text{pic}}^o \cdot \eta_o = 0.267$, $\lambda_{\text{Et}_4\text{N}^+}^o \cdot \eta_o = 0.269$ [303,304] based on

$$\Lambda_{\text{Et}_4\text{Npic}}^o = 0.563 \quad (131)$$

Walden considered the products to be independent of temperature and solvent. However, the $\Lambda_{\text{Et}_4\text{Npic}}^o$ values used by Walden was found to differ

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considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

$$(iii) \quad \lambda_{25}^{\circ}(\text{Bu}_4\text{N}^+) = \lambda_{25}^{\circ}(\text{Ph}_4\text{B}^-) \quad (132)$$

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

$$(iv) \quad \lambda_{25}^{\circ}(\text{Bu}_4\text{N}^+) = \lambda_{25}^{\circ}(\text{Bu}_4\text{B}^-) \quad [305] \quad (133)$$

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^- .

(iv) The equation suggested by Gill [306] is:

$$\lambda_{25}^{\circ}(\text{R}_4\text{N}^+) = \frac{ZF^2}{6\pi N_A \eta_o [r_i - (0.0103\epsilon_o + r_y)]} \quad (134)$$

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

However, large discrepancies were observed between the experimental and calculated values [302(a)]. In a paper, [302(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.

$$(v) \quad \lambda_{25}^{\circ}[(i - \text{Am})_3\text{BuN}^+] = \lambda_{25}^{\circ}(\text{Ph}_4\text{B}^-) [336] [307] \quad (135)$$

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

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$$(vi) \quad \lambda_{25}^o(\text{Ph}_4\text{B}^-) = 1.01 \lambda_{25}^o[(i-\text{Am})_4\text{B}^-] \quad |308| \quad (136)$$

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

Krumgalz 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_o 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:

$$r_s = \frac{|z|F^2}{A\pi\eta_o\lambda_{\pm}^o} \quad (137)$$

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

$$\lambda_{\pm}^o\eta_o = \text{constant} \quad (138)$$

This relation has been verified using λ_{\pm}^o 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^+ , Ph_4B^- ions and for tetraalkylammonium cation starting with Et_4N^+ . The relationship can be well utilized to determine λ_{\pm}^o of ions in other organic solvents from the determined Λ_o values.

2.8.5. Solvation



Figure 3: Solvation phenomena

Various types of interactions exist between the ions in solutions. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number. Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation.

$$V_s = \frac{4\pi}{3}(r_s^3 - r_c^3) \quad (139)$$

where r_c is the crystallographic radius of the ion. The solvation number n_s would then be obtained from

$$n_s = \frac{V_s}{V_o} \quad (140)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects [309], from

$$V_s^o = 4.35r_s^3 \quad (141)$$

where V_s^o is expressed in mol/lit. and r_s in angstroms. However, this method is not applicable to ions of medium size though a number of empirical and theoretical corrections [310-313] have been suggested in order to apply it to most of the ions.

2.8.6. Stokes' Law and Walden's Rule

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 as function only of the ionic radius and thus, under normal conditions, is constant. The limiting conductances λ_i^o of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^o = \frac{|z_i e| \hat{e} F}{6\pi\eta_o R_i} = \frac{0.819|z_i|}{\eta_o R_i} \quad (142)$$

where η_o = 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:

$$\lambda_i^o \eta_o = \frac{0.819|z_i|}{R_i} = \text{constant} \quad (143)$$

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This is known as the Walden rule [314]. The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

Robinson and Stokes [315], Nightingale [194] and others [316-318] have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of those large ions, a calibration curve was obtained for each solvent. However, the experimental results indicate that the method is incorrect as the method is based on the wrong assumption of the invariance of Walden's product with temperature. The idea of microscopic viscosity [319] was invoked without much success [320, 321] but it has been found that:

$$\lambda_i^o \eta^p = \text{constant} \quad (144)$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions [322, 323]. Gill [324] has pointed out the inapplicability of the Zwanzig theory [325] of dielectric friction for some ions in non-aqueous and mixed solvents and has proposed an empirical modification of Stokes' Law accounting for the dielectric friction effect quantitatively and predicts actual solvated radii of ions in solution. This equation can be written as:

$$r_i = \frac{|z|F^2}{6\pi N_A \eta_o \lambda_i^o} + 0.0103D + r_y \quad (145)$$

where r_i is the actual solvated radius of the ion in solution and r_y is an empirical constant dependent on the nature of the solvent [324, 325].

The dependence of Walden product on the dielectric constant led Fuoss [292] 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:

$$\lambda_{i,o}^o = \frac{Fe|z_i|}{6\pi R_\infty} \left(\frac{1+A}{\epsilon R_\infty^2} \right) \quad (146)$$

or,

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$$R_i = R_\infty + \frac{R}{\infty} \quad (147)$$

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.

Boyd [282] gave the expression:

$$\lambda_i^o = \frac{Fe|z_i|}{6\pi\eta_o r_i \left[\left(1 + \frac{2}{27}\pi\eta_o\right) \cdot \left(\frac{Z_i^2 e^2 \tau}{r_i^4 \epsilon_o}\right) \right]} \quad (148)$$

by considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles. Zwanzig [312] 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:

$$\lambda_i^o = \frac{z_i^2 e F}{\left\{ A_V \pi \eta_o r_i + A_D \left[\frac{z_i^2 e^2 (\epsilon_r^o - \epsilon_r^\infty) \tau}{\epsilon_r^o (2\epsilon_r^o + 1) r_i^3} \right] \right\}} \quad (149)$$

where ϵ_r^o and ϵ_r^∞ are the static and limiting high frequency (optical) dielectric constants. $A_V = 6$ and $A_D = 3/8$ for perfect sticking and $A_V = 4$ and $A_D = 3/4$ for perfect slipping. It has been found that Born's and Zwanzig's equations are very similar and both may be written in the form:

$$\lambda_i^o = \frac{A r_i^3}{(r_i^4 + B)} \quad (150)$$

The theory predicts [326] that λ_i^o passes through a maximum of $\frac{1}{27^{1/4}} A / 4B^{1/4}$ at $r_i = (3B)^{1/4}$. The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius. For comparison with results in different solvents, the equation (149) can be rearranged as [327]:

$$\frac{z_i^2 eF}{\lambda_i^o \eta_o} = \frac{A_V \pi r_i + A_D z_i^2}{r_i^3} \cdot \frac{e^2 (\epsilon_r^o - \epsilon_r^\infty)}{\epsilon_r^o (2\epsilon_r^o + 1)} \cdot \left(\frac{\tau}{\eta_o} \right) \quad (151)$$

$$\text{or,} \quad L^* = A_V \pi r_i + \frac{A_D z_i^2}{r_i^3 P^*} \quad (152)$$

In order to test Zwanzig's theory, the equation (152) was applied for Me_4N^+ and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol [326-331]. 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 .

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, [327] 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 [328].

(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 [327].

The Walden product in case of mixed solvents does not show any constancy but it shows a maximum in case of DMF + water and DMA + water

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[326-336] mixtures and other aqueous binary mixtures [337-340]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts [311,312,341] 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 [342] the major deviations in the Walden products are due to the variation in the electrochemical equilibrium between ions and solvent molecules of mixed polar solvent composition. In cases where more than one types of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Hubbard and Onsager [343] have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the concept of kinetic polarization deficiency has been introduced. However, quantitative expression is still awaited. Further, improvements [344, 345] naturally must be in terms of (i) sophisticated treatment of dielectric saturation, (ii) specific structural effects involving ion-solvent interactions. From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to explore this problem using different experimental techniques. We have, therefore, utilized four important methods, viz., volumetric, viscometric, interferometric and conductometric for the physico-chemical studies in different solvent media.

2.8.7. THERMODYNAMICS OF ION-PAIR FORMATION

The standard Gibbs energy changes (ΔG°) for the ion- association process can be calculated from the equation

$$\Delta G^\circ = -RT \ln K_A \quad (153)$$

The values of the standard enthalpy change, ΔH° and the standard entropy change, ΔS° , can be evaluated from the temperature dependence of ΔG° values as follows,

$$\Delta H^\circ = -T^2 \left[\frac{d(\Delta G^\circ/T)}{dT} \right]_p \quad (154)$$

$$\Delta S^\circ = -T^2 \left[\frac{d(\Delta G^\circ)}{dT} \right]_p \quad (155)$$

The ΔG° values can be fitted with the help of a polynomial of the type.

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (156)$$

and the coefficients of the fits can be compiled together with the σ % values of the fits. The standard values at 298.15 K are then:

$$\Delta G^\circ_{298.15} = c_0 \quad (157)$$

$$\Delta S^\circ_{298.15} = c_1 \quad (158)$$

$$\Delta H^\circ_{298.15} = c_0 + 298.15 c_1 \quad (159)$$

The main factors which govern the standard entropy of ion-association of electrolytes are: (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-columbic part of the Gibbs energy, ΔG^o , can also be calculated using the following equation:

$$\Delta G^o = N_A W_{\pm} \quad (160)$$

$$K_A = \left(\frac{4\pi N_A}{1000} \right) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}^*}{kT} \right) dr \quad (161)$$

where the symbols have their usual significance. The quantity $2q/r$ is the Columbic part of the interionic mean force potential and W_{\pm} is its non-columbic part. The procedure for the evaluation of the non-columbic part of the entropy and enthalpy (and ΔS^* and ΔH^* respectively) is the same as that used for obtaining ΔS^o and ΔH^o .

The ΔG^o values at different temperatures can be fitted to the polynomial:

$$\Delta G^* = c_0^* + c_1^*(298.15 - T) + c_2^*(298.15 - T)^2 \quad (162)$$

and the coefficients of the fits along with the $\sigma\%$ values can be determined.

The values of ΔG^* , ΔS^* and ΔH^* at 298.15 K are then easily obtained from the following equations.

$$\Delta G^o_{298.15} = c_0 \quad (163)$$

$$\Delta S^o_{298.15} = c_1 \quad (164)$$

$$\Delta H^o_{298.15} = c_0 + 298.15 c_1 \quad (165)$$

2.9. Solvation Models- Some Recent Trends

The interactions between particles in chemistry have been based upon empirical laws- principally on Coulomb's law. This is also the basis of the attractive part of the potential energy used in the SchÖdinger equation. Quantum mechanical approach for ion-water interactions was begun by

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Clementi in 1970 s.1 A quantum mechanical approach to solvation can provide information on the energy of the individual ion-water interactions provided it is relevant to solution chemistry, because it concerns potential energy rather than the entropic aspect of solvation. Another problem in quantum approach is the mobility of ions in solution affecting solvation number and coordination number. However, the Clementi calculations concerned stationary models and cannot have much to do with the dynamic solvation numbers. Covalent bond formation enters little into the aqueous calculations,¹ however, with organic solvents the quantum mechanical approaches to bonding may be essential. The trend pointing to the future is thus the molecular dynamics technique. In molecular dynamic approach, a limited number of ions and molecules and Newtonian mechanics of movement of all particles in solution is concerned. The foundation of such an approach is the knowledge of the intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last decade (1990-2000) witnessed some interesting trends in the development of solvation models and computer softwares. Based on a collection of experimental free energy of solvation data, C.J. Cramer, D.G. Truhlar and co-workers from the University of Minnesota, U.S.A. constructed a series of solvation models (SM1-SM5 series) to predict and calculate the free energy of solvation of a chemical compound [346-350]. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are, molecular formula, geometry, refractive index, surface tension, Abraham's a (acidity parameter) and b (basicity parameter) values, and, in the latest models, the dielectric constants. The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 KJ/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.* [351,352] 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.* [353] 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 [354,355] have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from the same continuity and hydrodynamic equations used in the more classical treatment; however, an important difference exists in the use of MSA expressions for the equilibrium and structural properties of the electrolytic solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem to be relatively small, it has been claimed that the performance of MSA equation is better with a much wider concentration range than that covered by the classical equations. However, no through study of the performance of the new equation at the experimental uncertainty level of conductivity measurement is yet available in the literature, except the study by Bianchi *et al.* [356]. 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 [357] 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).

2.11 Refractive Index

The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (n_D) for the substance.

$$\text{Refractive index } (n_D) \text{ of substance} = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}}$$

Whenever light changes speed as it crosses a boundary from one medium into another, its direction of travel also changes, i.e., it is refracted. The relationship between light's speed in the two mediums (V_A and V_B), the angles of incidence ($\sin \theta_A$) and refraction ($\sin \theta_B$) and the refractive indexes of the two mediums (n_A and n_B) is shown below:

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (166)$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact

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with the sample, it is possible to determine the refractive index of the sample quite accurately.

The molar refraction, $[R]$ can be evaluated from Lorentz-Lorenz relation [358] and gives more information than n_D about the mixture phenomenon because takes into account the electronic perturbation of molecular orbital during the liquid mixture process and $[R]$ is also directly related to the dispersion forces

$$[R] = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \cdot \left(\frac{M}{\rho} \right) \quad (167)$$

where $[R]$, n_D^2 , and M are, correspondingly, the molar refraction, the refractive index and the molar mass of the mixture respectively. Deviation from molar refraction was calculated from the following relation;

$$\Delta R = [R] - \sum_{i=1}^j x_i [R]_i \quad (168)$$

Where x_i and $[R]_i$ are the mole fraction and excess molar refraction of the i^{th} component.

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CHAPTER III

3.1. Source and Purification of the Chemicals used

3.1.1. Solvents

1,4-Dioxane ($C_4H_8O_2$, M.W: 88.11), Merck, India, was kept several days over potassium hydroxide (KOH), followed by refluxing over excess of sodium for 12 hours. Finally, it was distilled from sodium [1].

Tetrahydrofuran (C_4H_8O , M.W: 72.11), Merck, India, for synthesis, was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over $LiAlH_4$ [2].

Methanol (CH_3OH , M.W: 32.04, A.R. grade) Merck, India, was dried over $4A^{\circ}$ molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled [3].

n-amyl alcohol ($C_5H_{11}OH$, M.W: 88.15, A.R. grade) and iso-amyl alcohol ($C_5H_{11}OH$, M.W:88.15, A.R. grade) Merck, India, were dried with anhydrous K_2CO_3 . The middle fractions for both the liquids were collected and kept free from humidity with $3A^{\circ}$ molecular sieves [4].

Benzene (C_6H_6 , M.W: 78.11) Merck, India, was purified by means of a simple distillation technique with the first and last 20% of the distillate being discarded.

Toluene ($C_6H_5CH_3$, M.W: 92.14) Merck, India, was double distilled and the middle fraction was collected [5].

Nitrobenzene ($C_6H_5NO_2$, M.W: 123.11) Merck, India, was purified by distillation and stored over $4A^{\circ}$ molecular sieves [5].

Cyclohexane (C_6H_{12} , M.W: 84.16) and cyclohexanone ($C_6H_{10}O$, M.W: 98.15) Merck, India, were purified by distillation and stored over activated $4A^{\circ}$ molecular sieves to reduce water content.

Acetophenone (C_8H_8O , M.W: 120.15) Merck, India, was dried over

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anhydrous potassium carbonate for three days, filtered and then distilled. The middle fraction of the distillates was collected for use [6].

Ethane-1, 2-diol ($C_2H_6O_2$, M.W: 62.07 A.R.) S.D. Fine was first dried over fused CaO overnight and then distilled twice under vacuum. The middle fraction was further dried using $4A^{\circ}$ molecular sieves (Linde) and stored and protected against moisture and CO_2 [7].

2-methoxyethanol ($C_3H_8O_2$, M.W: 76.10), S. D. Fine Chemical Limited, Mumbai, India, was dried with potassium carbonate and distilled twice in an all-glass distillation set immediately before use. The middle fraction was collected for use [8]. 2-ethoxyethanol ($C_4H_{10}O_2$, M.W: 90.12) and 2-butoxyethanol ($C_6H_{14}O_2$, M.W: 118.17) were purified as described in the literature [5].

Chlorobenzene (C_6H_5Cl , M.W: 112.56), S. D. Fine Chemical Limited, Mumbai, India (A. R. grade, purity > 99.5%), was purified as described in the literature [5].

Water was first deionized and then distilled from an all glass distilling set using alkaline $KMnO_4$ solution [9]. The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled (TD) water had specific conductance less than $1 \times 10^{-6} \Omega^{-1}cm^{-1}$.

Densities and viscosities of the purified solvents were in good agreement with the literature values [10-29] and are listed in the respective chapters. The purity of most of the solvents finally obtained was better than 99.5 %. All solvents, pure or mixed, were stored over $3A^{\circ}$ molecular sieves for three days before use.

3.1.2. Solutes

Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$, M.W: 241.95) and sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, M.W: 329.86), were of A. R. grade (NICE, India) and were purified by re-crystallizing twice from conductivity water and then dried in a

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vacuum desiccator over P_2O_5 for 24 hours before use.

Commercial sample of catechol (C_6H_6OH , M.W: 110.1), was purified by repeated crystallization from mixture of chloroform-methanol. The sample was dissolved in chloroform in hot condition, filtered and to the filtrate dried and distilled methanol was added drop wise. Fine plate like crystal separated and was recovered by rapid filtration and ready for use.

Phosphomolybdic acid ($H_3[P(W_3O_{10})_4].24H_2O$, M.W: 2257.62) of analytical grade was purchased from Thomas Baker and was used without further purification. However, the salt was dried in a vacuum desiccator over P_2O_5 for 24 hours before use.

Sodium metal salts viz., Sodium iodide (NaI, M.W: 58.44), Sodium thiocyanate (NaSCN, M.W: 81.07), Sodium acetate (CH_3COONa , M.W: 82.03), A.R. grade were procured from Merck, India and purified as described in the literature [10, 11].

Tetraalkylammonium iodides viz., tetrabutylammonium iodide (Bu_4NI , M.W: 369.38), tetrapentylammonium iodide (Pen_4NI , M.W: 425.47), tetrahexylammonium (Hex_4NI , M.W. : 481.58) and tetraheptylammonium iodide (Hep_4NI , M.W. : 537.69) of Pruis grade were purchased from Aldrich, Germany and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium [5]. After filtration, the salts were dried in oven for few hours.

The purity of the solutes finally obtained was better than 99.0 % as checked by melting point determination. Stock solutions of different salts/solutes in different mixed solvents and in pure solvents were prepared by mass and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using the experimental density values. Utmost care was taken in minimizing evaporation losses and preventing moisture pick-up. All solutions were prepared afresh before use.

3.1.3. Mixed solvents

The research work has been carried out with binary or ternary solvent systems with methanol isoamyl alcohol, acetophenone, amyl alcohol, dichloromethane, carbontetrachloride, tetrahydrofuran, 1, 4 dioxane as primary solvents with some polar, weakly polar and non-polar solvents as well as with some solutes. For the preparation of mixed binary and ternary mixtures, pure components were taken separately in glass stoppered bottles and thermostated at the desired temperature for sufficient time. When the thermal equilibrium was ensured, the required volumes of each component were transferred in a different bottle which was already cleaned and dried thoroughly. Conversion of required mass of the respective solvents to volume was accomplished by using experimental densities of the solvents at experimental temperature. It was then stoppered and the mixed contents were shaken well before use. While preparing different binaries and ternaries care was taken to ensure that the same procedure was adopted throughout the entire work. The physical properties of different pure and mixed solvents have been presented in the respective chapters.

The following different binary and ternary solvent mixtures have been prepared and used for my research studies.

Binary mixtures studied:

Isoamyl alcohol (1) + 2-Methoxyethanol (2)

Isoamyl alcohol (1) + 2-Ethoxyethanol (2)

Isoamyl alcohol (1) + 2-Butoxyethanol (2)

Acetophenone (1) + Dichloromethane (2)

Acetophenone (1) + Amyl alcohol (2)

Amyl alcohol (1) + Dichloromethane (2)

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Ternary mixtures studied:

Tetrahydrofuran (1) + Methanol (2) + Benzene (3)

Tetrahydrofuran (1) + Methanol (2) + Toluene (3)

Tetrahydrofuran (1) + Methanol (2) + Chlorobenzene (3)

Tetrahydrofuran (1) + Methanol (2) + Nitrobenzene (3)

Tetrahydrofuran (1) + Methanol (2) + Anisole (3)

Tetrahydrofuran (1) + Methanol (2) + Cyclohexane (3)

Tetrahydrofuran (1) + Methanol (2) + Cyclohexanone (3)

Acetophenone (1) + Amyl alcohol (2) + Dichloromethane (3)

Solute-solute / ion-ion and solute-solvent / ion-solvent interactions studied in the following mixed solutions:

1,4-Dioxane (1) + Tetrahydrofuran (2) + Tetrapentylammonium iodide (3)

1,4-Dioxane (1) + Tetrahydrofuran (2) + Tetrahexylammonium iodide (3)

1,4-Dioxane (1) + Tetrahydrofuran (2) + Tetraheptylammonium iodide (3)

Water (1) + Ethane 1,2-diol (2) + Sodium molybdate (3)

Water (1) + Ethane 1,2-diol (2) + Sodium tungstate (3)

Water (1) + Catechol (2) + phosphomolybdic acid (3)

Methanol (1) + Ethane 1,2-diol (2) + Sodium acetate (3)

Methanol (1) + Ethane 1,2-diol (2) + Sodium iodide (3)

Methanol (1) + Ethane 1,2-diol (2) + Sodium thiocyanate (3)

Carbontetrachloride (1) + Nitrobenzene (2) + Tetrabutylammonium iodide (3)

Carbontetrachloride (1) + Nitrobenzene (2) + Tetrapentylammonium iodide (3)

Carbontetrachloride (1) + Nitrobenzene (2) + Tetrahexylammonium iodide (3)

Carbontetrachloride (1) + Nitrobenzene (2) + Tetraheptylammonium iodide (3)

3.2. Experimental Methods

3.2.1 Density Measurements

Densities (ρ) were measured with an Ostwald-Sprengel-type pycnometer having a bulb volume of 25cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 308.15 and 318.15 K with doubly distilled water and benzene using density and viscosity values from the literature [30, 31]. The pycnometer filled with air bubble free experimental liquid was kept vertically in a thermostatic water bath maintained at ± 0.01 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 $\pm 3 \times 10^{-4} \text{gm cm}^{-3}$. Figure 1 shows an Ostwald-Sprengel-type pycnometer (Single arm) used in our works.

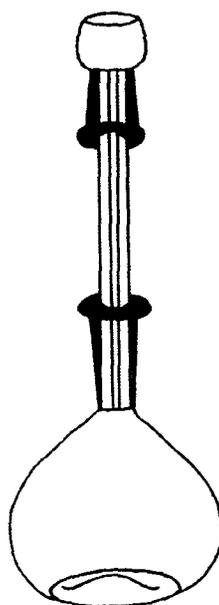


Figure 1: An Ostwald- Sprengel-type pycnometer.

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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 [32]. The solutions were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of the determining possible dispersion of the results obtained. Details of methods and techniques of density measurement is given in the literature [33-36].

3.2.2 Viscosity Measurements

The kinematic viscosities were measured by means of a suspended level Ubbelohde [37] 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 kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = \left(Kt - \frac{L}{t} \right) \quad (1)$$

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

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 2.4065×10^{-3} and -5.9535152 , respectively. The

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kinetic energy corrections were done from these values and they were found to be negligible.

Relative viscosities (η_r) were obtained using the equation:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \quad (3)$$

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. Figure 2 shows a suspended-level Ubbelohde viscometer used in our works.

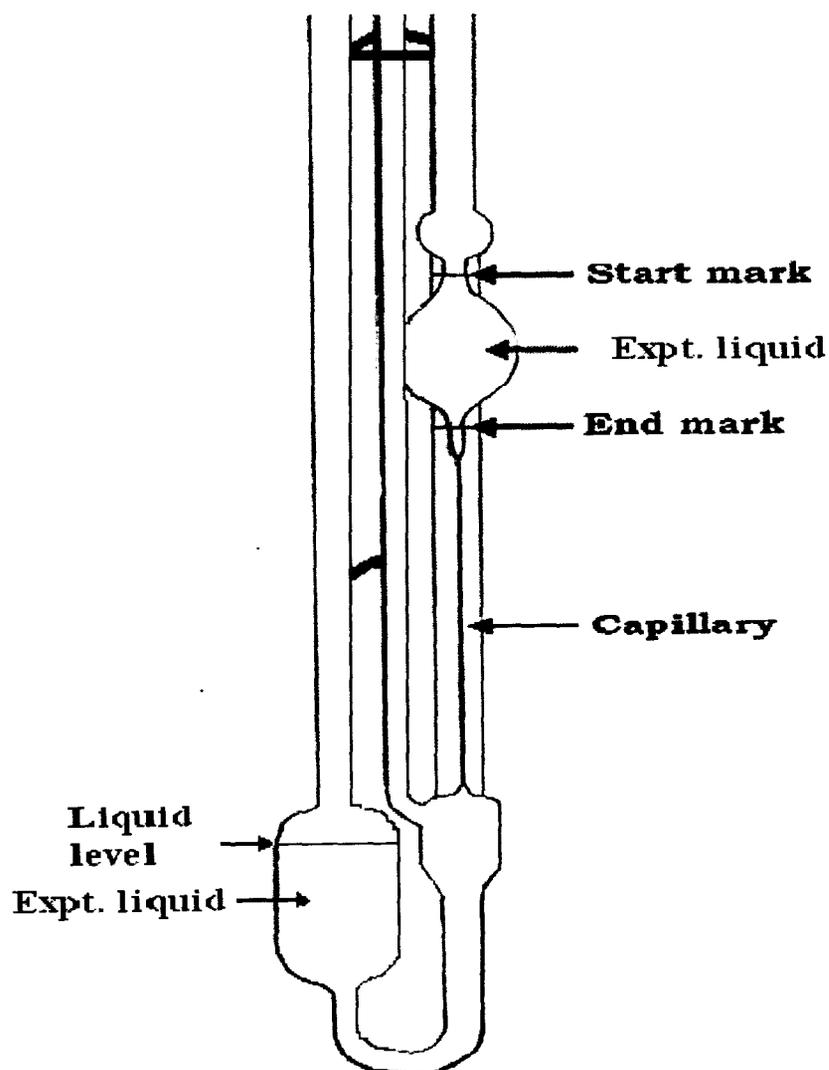


Figure 2: A suspended-level Ubbelohde viscometer.

3.2.3 Conductance Measurements

Systronic Conductivity meter- 308 was 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 Lindand co-workers [38]. 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. In order to minimize moisture contamination, all solutions were prepared in a dehumidified room with utmost care.

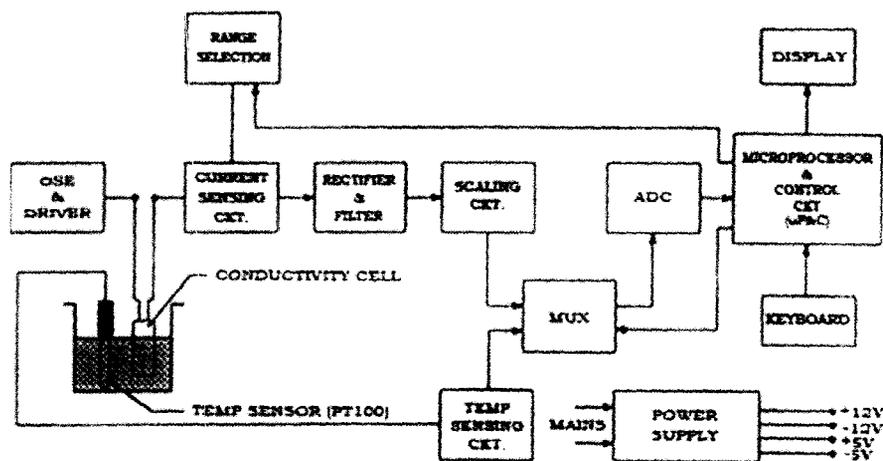


Figure 3: Block diagram of the Systronic Conductivity meter- 308.

3.2.4 Ultrasonic Sound Speeds Measurements

The speeds of sound (u) in pure liquids and solutions were measured with multi-frequency ultrasonic interferometer (supplied by Mittal Enterprise, New Delhi) with an accuracy of $\pm 0.3\%$. In the present work, a steel cell fitted with a quartz crystal of 2 MHz⁽³⁵⁾ - frequency was employed. This was calibrated with water, methanol, and benzene at the desired temperatures. The temperature stability was maintained within $\pm 0.01^\circ\text{C}$ by circulating thermostated water around the cell by a circulating pump.

The principle used in the measurement of the sound velocity (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. A movable metallic plate kept parallel to the quartz crystal reflects these waves. 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 gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelengths ($\lambda/2$) or integral multiple of it, anode current again becomes maximum. From the knowledge of the wavelength (λ), the velocity (u) can be obtained by the relation:

$$\text{Velocity } (u) = \text{Wavelength } (\lambda) \times \text{Frequency } (f) \quad (4)$$

Isentropic compressibility (κ_s) can then be calculated by the following relation:

$$\kappa_s = \frac{1}{u^2 \rho} \quad (5)$$

where ρ is the density of the experimental liquid.

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

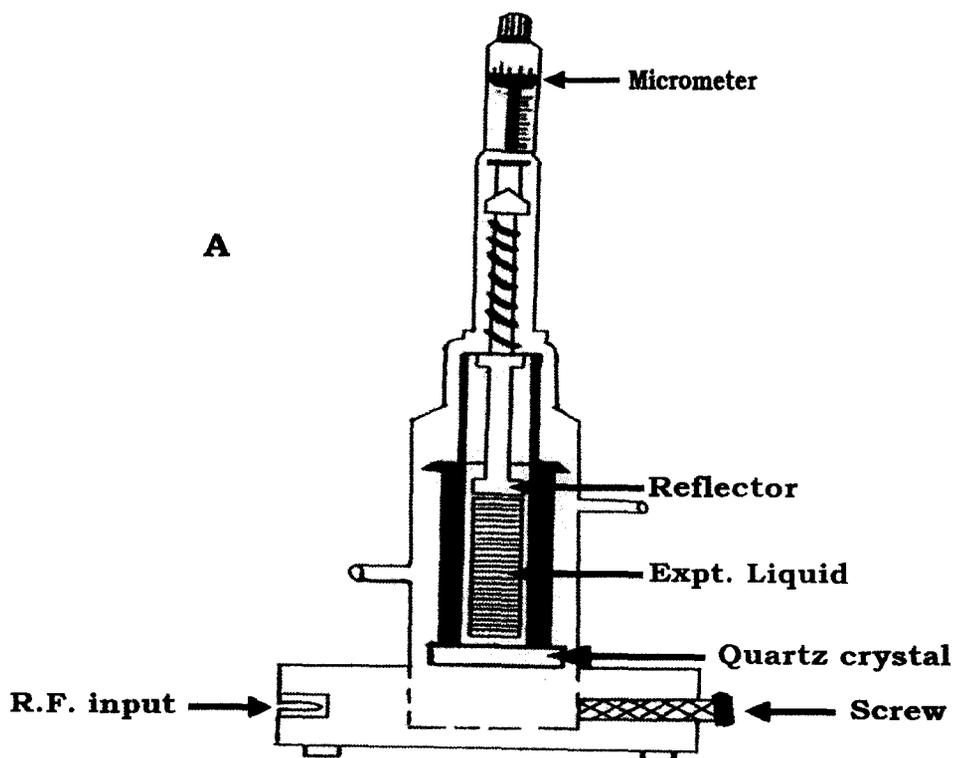
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shielded cable. The cell is filled with an experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal.

The micrometer is slowly moved till the anode current on the high frequency generator shows a maximum. A number of maximum readings of anode current are passed on and their number (n) is counted. The total distance (d) thus moved by the micrometer gives the value of wavelength (λ) with the following relation:

$$d = n \times \frac{\lambda}{2} \quad (6)$$

In Figure 3(A) Cross-section of the measuring cell of a Multifrequency Ultrasonic Interferometer and (B) Position of reflector vs. crystal current are depicted. The extra peaks (Figure 3B) in between minima and maxima occurs due to a number of reasons, but these do not effect the value of $\lambda / 2$.



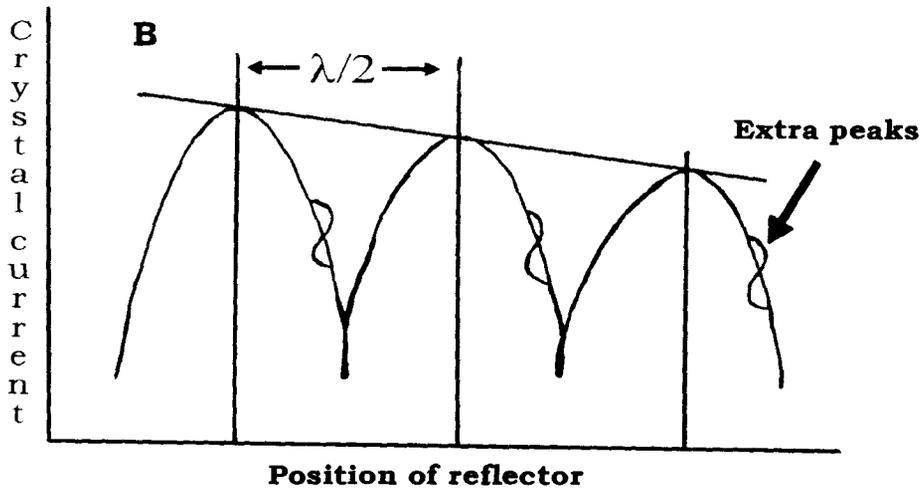


Figure 3: (A) Cross-section of the measuring cell of a Multifrequency Ultrasonic Interferometer and (B) Position of reflector vs. crystal current.

3.2.5 Refractive Index Measurements

Refractive index was measured with the help of Abbe-Refractometer (U.S.A). The accuracy of refractive index measurement was ± 0.0002 units. The refractometer was calibrated using twice distilled and deionized water, and calibration was checked after every few measurements. The temperature stability was maintained within $\pm 0.01\text{K}$ 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 refractive index is based on the difference of velocity of light in two different media.

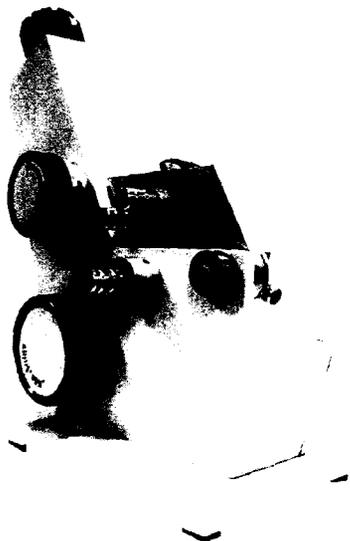


Figure 4: Abbe refractometer

Experimental Section

The speed of light in a vacuum is always the same, but when light moves through any other medium it travels more slowly since it is constantly being absorbed and reemitted by the atoms in the material. The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (n_D) for the substance.

$$\text{Refractive index } (n_D) \text{ of substance} = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}}$$

Whenever light changes speed as it crosses a boundary from one medium into another, its direction of travel also changes, i.e., it is refracted. The relationship between light's speed in the two mediums (V_A and V_B), the angles of incidence ($\sin \theta_A$) and refraction ($\sin \theta_B$) and the refractive indexes of the two mediums (n_A and n_B) is shown below:

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (7)$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample quite accurately. Nearly all refractometers utilize this principle, but may differ in their optical design. In the Abbe' refractometer the liquid sample is sandwiched into a thin layer between an illuminating prism and a refracting prism (Figure 2).

Experimental Section

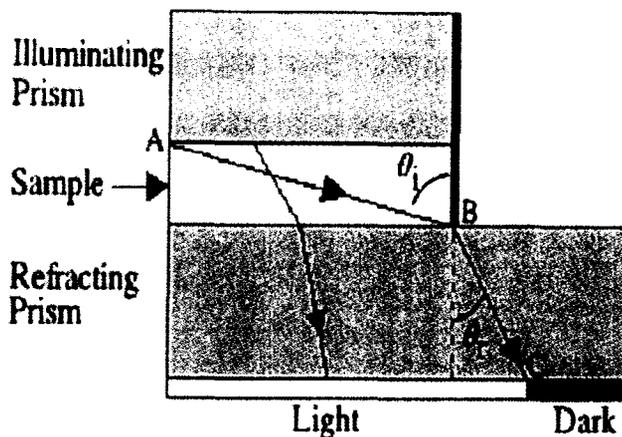


Figure 5: Cross-section of part of the optical path of an Abbe refractometer. The sample thickness has been exaggerated for clarity

The refracting prism is made of a glass with a high refractive index (e.g., 1.75) and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism. A light source is projected through the illuminating prism, the bottom surface of which is ground (i.e., roughened like a ground-glass joint), so each point on this surface can be thought of as generating light rays traveling in all directions. Inspection of Figure 2 shows that light traveling from point A to point B will have the largest angle of incidence (θ_i) and hence the largest possible angle of refraction (θ_r) for that sample. All other rays of light entering the refracting prism will have smaller θ_r and hence lie to the left of point C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right.

Samples with different refractive indexes will produce different angles of refraction (equation 7) and this will be reflected in a change in the position of the borderline between the light and dark regions. By appropriately calibrating the scale, the position of the borderline can be used to determine the refractive index of any sample. In an actual Abbe' refractometer there is not a detector on the back of the refracting prism, and there are additional optics, but this is the essential principle.

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As mentioned earlier, the speed of light in a substance is slower than in a vacuum since the light is being absorbed and reemitted by the atoms in the sample. Since the density of a liquid usually decreases with temperature, it is not surprising that the speed of light in a liquid will normally increase as the temperature increases. Thus, the index of refraction normally decreases as the temperature increases for a liquid. For many organic liquids the index of refraction decreases by approximately 0.0005 for every 1 °C increase in temperature. However for water the variation is only about -0.0001/°C. Most of the refractive index measurements reported in the text are determined at 298.15K and 303.15K.

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CHAPTER IV

Ion - Pair and Triple - Ion Formation by Some Tetraalkylammonium Iodides in Binary Mixtures of 1, 4-Dioxane + Tetrahydrofuran

4.1. Introduction

Progress in battery technology using the lithium electrolytes in ethereal solution [1] has occurred largely in the last decade. Recently, there has been a renewed interest,[2] in the study of association or dimerisation of electrolytes in the media of low permittivity. In media of low permittivity, salts are generally so associated that the states of the ionic species in solutions are most difficult to elucidate. A number of conductometric [3] and related studies of different electrolytes in non-aqueous solvents-specially mixed solvents have been made for their optimal use in high energy batteries [4] and for understanding organic reaction mechanisms [5]. Ionic association of salts in solution depends upon the mode of solvation of its ions [6-10] which in turn depends on the nature of the solvent or solvent mixtures. 1, 4-dioxane (DO) and tetrahydrofuran (THF) are polar aprotic solvents of low permittivity, each with great present-day synthetic and industrial importance. They are frequently used in electrical conductance studies [3,4,11,12] and in high-energy batteries [3, 4, 11-12]. Tetraalkylammonium salts are characterized by their low surface charge density and they are little or not solvated in solution [11, 12]. Hence in this paper we reported the electrical conductances of some tetraalkylammonium iodides, R_4NI (R=Pentyl to hexyl) in low-permittivity mixtures containing 10, 20 and 30 mass% of 1,4-dioxane in tetrahydrofuran (THF).

**Published in Journal of Chemical and Engineering Data 53 (2008) 141*

4.2. Experimental Section

4.2.1 Material

1,4-dioxane and tetrahydrofuran were purchased from Merck, India and purified as reported earlier [13, 14]. The salts Pen_4NI , Hex_4NI and Hep_4NI of pruss grade were purchased from Aldrich, Germany and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium [15]. After filtration, the salts were dried in oven for few hours.

4.2.2 Apparatus and Procedure

Binary solvent mixtures have been prepared by mixing required volume of 1,4-dioxane and tetrahydrofuran with earlier conversion of required mass of each liquid into volume at 298.15 K using literature densities [16]. A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The values of dielectric constant (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald et. al [17]. Densities (ρ) were measured with an Ostwald -Sprengel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The density values were reproducible to $\pm 3 \times 10^{-4}$ g.cm⁻³. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [18-20]. A thoroughly cleaned and perfectly dried viscometer filled with

experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The accuracy of the viscosity measurements, based on our work on several pure liquids, was ± 0.003 mPa.s. The details of the methods and measurement techniques had been described elsewhere [13, 14]. The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10 having cell constant $0.1 \pm 10\%$. Measurements were made in a water bath maintained within 298.15 ± 0.01 K and the cell was calibrated by Lind et. at method [21]. The conductance data were reported at a frequency of 1 KHz and the precision was $\pm 0.3\%$.

4.3. Results and discussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The concentrations (c) and equivalent conductances (Λ) of R_4NI (R=Pentyl to hexyl) in different binary solvent mixtures of 1,4-dioxane and tetrahydrofuran are given in Table 2. Figure 1-3 represents the plots of equivalent conductance (Λ) versus square root of salt concentration (\sqrt{c}) for the salts under investigations at 298.15 K in different binary mixtures of 1,4-dioxane and tetrahydrofuran. A minimum has been found for all the electrolytes suggesting the possible formation of triple-ions in these solutions. Fuoss and Krauss as early as in 1933 introduced the concept of triple ion formation from uni-univalent electrolytes to explain the minima in the relation between the equivalent conductance and the concentration of tetraisoamylammonium nitrate in 1,4-dioxane + water mixture ($\epsilon < 12$). The classical Fuoss-Kraus theory of triple ion [22] reads-

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_o}{\sqrt{K_p}} + \frac{\Lambda_o^{\tau}}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_o}\right) c \quad (1)$$

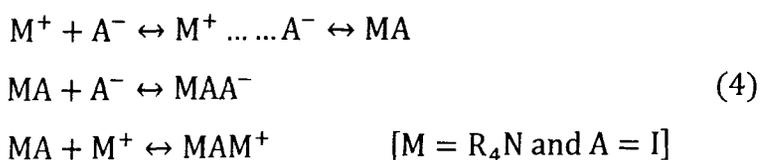
with

$$g(c) = \frac{\exp(-2.303\beta'\sqrt{c\Lambda}/\Lambda_0^{0.5})}{(1 - S\sqrt{c\Lambda}/\Lambda_0^{0.5})(1 - \Lambda/\Lambda_0)^{0.5}} \quad (2)$$

where β' is the Debye-Huckel activity coefficient term, defined by $\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5}$ and S is the Onsager conductance term, defined by

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{0.5}} \quad (3)$$

Also, Λ_0 is the sum of the equivalent conductance of the simple ions at infinite dilution and Λ_0^T is the sum of the conductances of the two triple ions $R_4N(I_2)^-$ and $(R_4N)^+I$ for R_4NI salts, K_p and K_T are the ion-pair and triple-ion formation constants. To make eq. 1 applicable, the symmetrical approximation of the two possible constant of triple ions equal to each other has been adopted and Λ_0 values for the studied electrolytes has been calculated following the scheme as suggested by B. S. Krungalz [12]. The calculated values have been listed in Table 3. Linear regression analysis of eq. 1 gives intercept and slope; the values have been listed in Table 3. In solving eq. 1, Λ_0^T , the triple ion conductance, was set equal to $2/3 \Lambda_0$. This has specially been done so for relative comparison of K_T values for the same electrolyte in different solvent mixtures. The K_p and K_T thus evaluated are listed in Table 4. A perusal of Table 4 shows that the major portion of the electrolytes exists as ion-pairs with only a negligible portion as triple ions. The observed difference in K_p and K_T values can be explained by molecular scale model [23, 24].



It is likely possible that association of R_4N^+ cations with solvent components shifts the above equilibrium towards left, thus decreasing K_p values and increasing K_T values. The ion-pair and triple-ion concentrations (C_p and C_T ,

respectively) of the electrolytes at the highest electrolyte concentration have been derived using eqs. 3-6 and listed in Table 4.

$$\alpha = (K_p c)^{-0.5} \quad (5)$$

$$\alpha_T = \frac{K_T}{\sqrt{K_P}} c^{0.5} \quad (6)$$

$$C_p = c(1 - \alpha - 3\alpha_T) \quad (7)$$

$$C_T = \frac{K_T}{\sqrt{K_P}} c^{1.5} \quad (8)$$

It was observed that dielectric constants of the binary solvent mixtures decreased as the amount of 1, 4-dioxane increased in the solvent mixtures. The concomitant increase in K_T and C_T values suggests that R_4N^+ cations are preferable more solvated by 1, 4-dioxane than by tetrahydrofuran. On the contrary, the steric hindrance caused by the CH_2- group adjacent to the ethereal group of the cyclic ethers may cause solvation hindrance favouring the anion I^- as a competitor for the first coordination shell of R_4N^+ cations. This may shift the above equilibrium towards right increasing K_p values.

Table 4 shows that for a particular solvent mixture i. e., for a particular value of dielectric constant of the solvent mixture, K_p values are in the order: $Pen_4NI > Hex_4NI > Hep_4NI$ and that of K_T values is: $Pen_4NI < Hex_4NI < Hep_4NI$. This suggests that smaller R_4N^+ cations tend to remain more as ion-pairs than larger ones, which in their turn has greater capacity to form triple ions. This also supports our earlier view of preferential solvation [10] of R_4N^+ cations by 1, 4-dioxane in the electrolyte solutions.

4.4 Conclusion

It may be concluded that all tetraalkylammonium salts existed as triple ions due to low dielectric constant of the solvent mixtures. However, it

was found that the smaller R_4N^+ cations tend to remain more as ion-pairs and exhibits higher tenency to form triple ions than larger ones.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

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TABLE 1. Density ρ , viscosity η , and dielectric constant ϵ , of different binary mixtures of 1,4-DO and THF at $T = 298.15$ K

Solvent Mixture	$\rho \times 10^{-3} (\text{kg m}^{-3})$		$\eta (\text{mPa s})$		ϵ
	Exp.	Lit.	Exp.	Lit.	
0 mass% of DO	0.8807	0.8807[16]	0.4630	0.4630[16]	7.58[11]
10 mass% of DO	0.8941	-	0.0049	-	7.04 ^a
20 mass% of DO	0.9071	-	0.0051	-	6.51 ^a
30 mass% of DO	0.9190	-	0.0053	-	5.96 ^a
100 mass% of DO	1.0305	1.0305[16]	1.2000	1.2000[16]	2.21[11]

^a Calculated using the scheme given at ref. no 17.

TABLE 2. The concentrations c and equivalent conductances Λ of R_4NI (R = Pentyl to hexyl) in different binary solvent mixtures of 1,4-DO and THF at $T = 298.15$ K

$c \times 10^4$ (mol dm ⁻³)	Λ (S. cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S. cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S. cm ² mol ⁻¹)
10 mass% of DO					
Pen ₄ NI		Hex ₄ NI		Hep ₄ NI	
0.8046	7.02	0.6367	8.12	0.3419	12.27
0.8138	6.86	0.6469	8.04	0.3754	11.64
0.8294	6.60	0.6541	7.98	0.4052	11.13
0.8385	6.46	0.6631	7.91	0.4319	10.77
0.8549	6.26	0.6696	7.88	0.4559	10.48
0.8674	6.46	0.6754	7.89	0.4776	10.52
0.8702	6.52	0.6806	7.93	0.4973	10.84
0.8726	6.59	0.6851	7.98	0.5153	11.33
20 mass% of DO					
0.4957	4.94	0.5460	3.98	0.6037	6.38
0.5016	4.83	0.5518	3.94	0.6142	4.94
0.5077	4.74	0.5598	3.88	0.6288	3.03
0.5122	4.76	0.5646	3.85	0.6376	1.94
0.5197	4.90	0.5694	3.83	0.6456	1.00
0.5229	4.98	0.5736	3.84	0.6541	0.55
0.4788	5.21	0.5764	3.86	0.6625	1.63
0.4839	5.12	0.5808	3.90	0.6672	2.53
30 mass% of DO					
0.2156	2.77	0.3125	4.97	0.5589	2.74
0.2564	2.70	0.3247	3.71	0.5675	2.30
0.2906	2.64	0.3420	2.13	0.5749	1.92
0.3481	2.56	0.3536	1.13	0.5813	1.63
0.3827	2.53	0.3657	0.35	0.5869	1.49
0.3986	2.53	0.3758	1.23	0.5917	1.62
0.4124	2.55	0.3819	2.13	0.5962	1.86
0.4274	2.58	0.3868	2.96	0.6001	2.09

TABLE 3. The calculated limiting conductance Λ_0 , slope and intercepts of eq.1 for R_4NI (R=Pentyl to hexyl) in different binary solvent mixtures of 1,4-DO and THF at $T = 298.15$ K

Solvent mixture	Λ ($S \cdot cm^2 \cdot mol^{-1}$)	Slope	Intercept
10 mass% of DO	Pen ₄ NI		
	199.21	0.0064	-0.011
		(± 0.0003)	(± 0.002)
	Hex ₄ NI		
	195.57	0.0346	-0.029
		(± 0.0002)	(± 0.003)
Hep ₄ NI			
193.34	0.0974	-0.050	
	(± 0.0001)	(± 0.001)	
20 mass% of DO	Pen ₄ NI		
	192.20	0.1315	-0.108
		(± 0.0002)	(± 0.001)
	Hex ₄ NI		
	188.68	0.2975	-0.225
		(± 0.0002)	(± 0.002)
Hep ₄ NI			
186.53	1.4633	-0.837	
	(± 0.0001)	(± 0.002)	
30 mass% of DO	Pen ₄ NI		
	185.92	5.1354	-1.042
		(± 0.0003)	(± 0.002)
	Hex ₄ NI		
	182.52	0.3102	-0.173
		(± 0.0001)	(± 0.003)
Hep ₄ NI			
180.44	0.5852	-0.585	
	(± 0.0004)	(± 0.006)	

TABLE 4. Maximum concentration c , ion-pair constant K_P , triple-ion constant K_T , ion-pair concentration C_P , and triple-ion concentration C_T for R_4NI (R=Pentyl to hexyl) in different binary solvent mixtures of 1,4-DO and THF at $T = 298.15$ K

Salt	$c \times 10^4$ (mol dm ⁻³)	$K_P \times 10^5$ / mol dm ⁻³	$K_T \times 10^5$ / mol dm ⁻³	$C_P \times 10^5$ / mol dm ⁻³	$C_T \times 10^{-10}$ / mol dm ⁻³
10 mass% of DO					
Pen ₄ NI	0.8726	3316.37	0.883	8.71	0.40
Hex ₄ NI	0.6851	450.34	1.783	6.72	1.51
Hep ₄ NI	0.5153	132.90	2.753	4.95	2.81
20 mass% of DO					
Pen ₄ NI	0.4839	31.55	1.823	4.81	3.98
Hex ₄ NI	0.5805	7.03	1.983	4.92	6.16
Hep ₄ NI	0.6672	0.50	2.622	3.85	13.40
30 mass% of DO					
Pen ₄ NI	0.4508	0.32	7.389	3.50	4.25
Hex ₄ NI	0.3868	11.12	2.688	3.25	6.64
Hep ₄ NI	0.6001	1.26	1.728	3.77	23.50

*Maximum concentrations at which calculations have been performed.

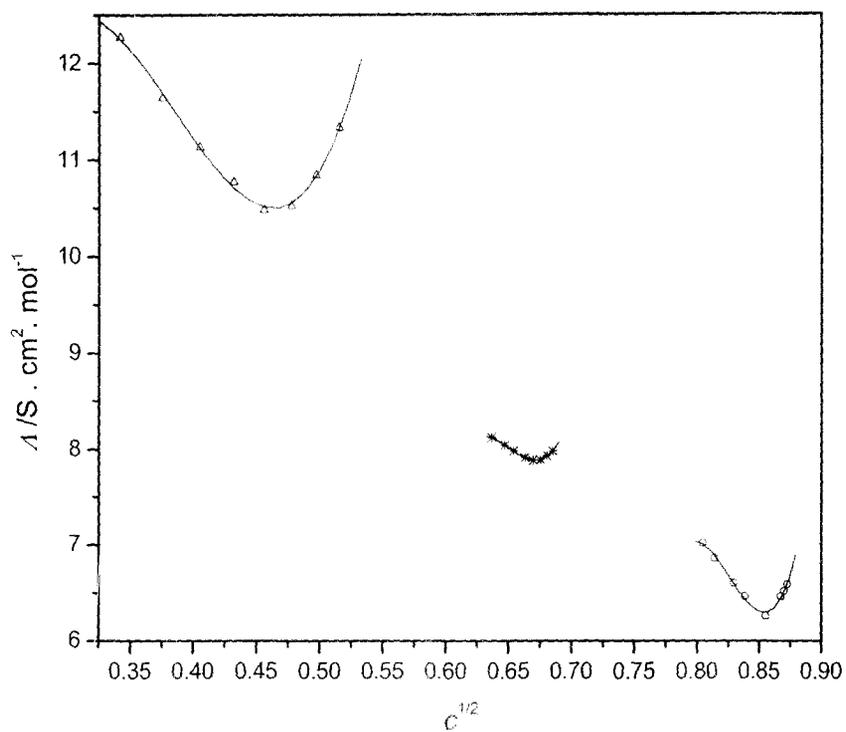


FIGURE 1. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at $T = 298.15$ K in 10 mass% of DO + THF solutions. O, Tetrapentylammonium iodide; *, Tetrahexylammonium iodide; Δ , Tetrheptylammonium iodide.

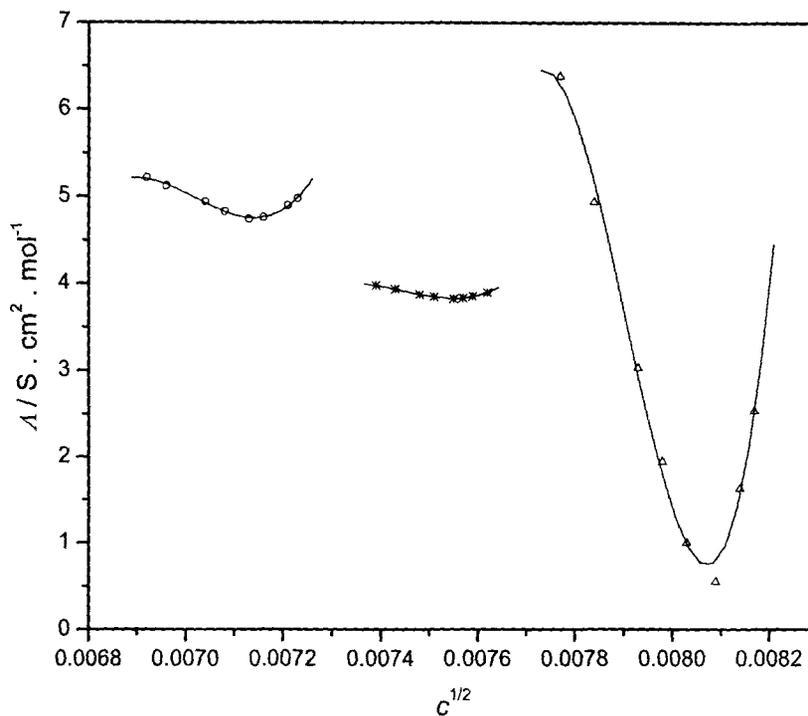


FIGURE 2. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at $T = 298.15$ K in 20 mass% of DO + THF solutions. O, Tetrapentylammonium iodide; *, Tetrahexylammonium iodide; Δ , Tetrheptylammonium iodide.

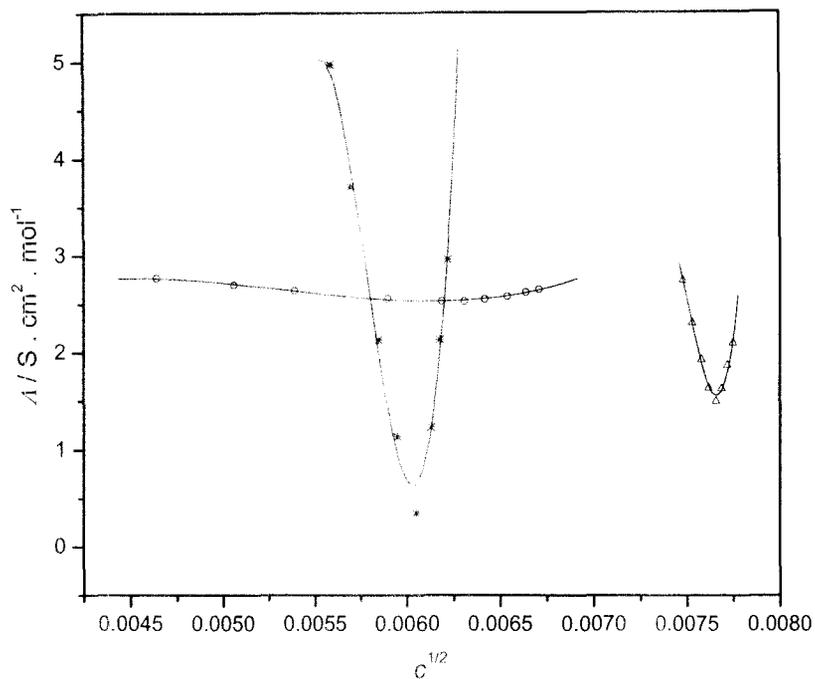


FIGURE 3. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at $T = 298.15$ K in 30 mass% of DO + THF solutions. O, Tetrapentylammonium iodide; *, Tetrahexylammonium iodide; Δ , Tetrheptylammonium iodide.

CHAPTER V

Viscous Synergy and Antagonism, Excess Molar Volume, Isoentropic Compressibility and Excess Molar Refraction of Ternary Mixtures Containing Tetrahydrofuran, Methanol and Six Membered Cyclic Compounds at 298.15K

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. Because of the close connection between liquid structure and macroscopic properties, determination of density, viscosity and ultrasonic speeds is a valuable tool to learn the liquid state [1, 2].

Rheology is the field of physics that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products, [3-12] and to establish their stability and even bioavailability, since it has been firmly established that viscosity influences the drug absorption rate in the body [13, 14].

The increasing use of the solvents tetrahydrofuran, methanol and their mixtures in benzene and benzene derivatives in industrial processes such as battery, pharmaceutical and cosmetics have greatly stimulated the need for extensive information on their various 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 [15, 16].

The present work contributes to the study of viscosity deviations, viscous antagonism, excess molar volumes, isentropic compressibility, excess molar refraction and excess Gibb's free energy of activation in ternary solutions of tetrahydrofuran (A) + methanol (B)+benzene, toluene, chlorobenzene, nitrobenzene, anisole, cyclohexane, cyclohexanone (C).

**Accepted for publication in Physics and Chemistry of Liquids*

5.2. Experimental section

5.2.1. Source and purity of samples

Tetrahydrofuran (T.H.F), methanol (MeOH), benzene, toluene, chlorobenzene, nitrobenzene, anisole, cyclohexane and cyclohexanone were obtained from Merck and L. R. These were further purified by standard methods [17]. The purity of the liquids was checked by measuring their densities, viscosities, refractive indices and sound velocities at 298.15K which was quite in agreement with the literature values as represented in Table 1.

5.2.2 Measurements

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostat bath controlled to ± 0.01 K. Viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4}$ mPas. 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 fractions was within ± 0.0002 . The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm⁻³.

Ultrasonic speeds of sound (u) were determined by a multifrequency ultrasonic interferometer (Mittal enterprise, New Delhi9, M-81) working at 1MHz, calibrated with triply distilled and purified water, methanol and benzene at 303.15K. The precision of ultrasonic speed measurements was ± 0.2

ms⁻¹. The details of the methods and techniques have been described in earlier papers [18-21]. Refractive index was measured with the help of Abbe-Refractometer (U.S.A). The accuracy of refractive index measurement was ± 0.0002 units. The refractometer was calibrated twice using distilled and deionized water, and calibration was checked after every few measurements.

5.3. Results and Discussion

The comparison of the experimentally determined densities, viscosities, sound speeds and refractive indices of the pure components at 298.15K with the literature values has been presented in Table 1.

5.3.1. Viscosity deviations

In Table 2, the calculated and experimentally determined viscosities of the ternary mixtures are shown along with the mole fraction of tetrahydrofuran (x_A) and methanol (x_B) at 298.15K. Viscosity deviation ($\Delta\eta$), synergic (I_S) and antagonic index (I_A) values are presented together in Table 2.

The viscosity deviations ($\Delta\eta$) [22] from linear dependence for ternary mixtures can be calculated as

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

where, η is the viscosity of the mixture and x_i , η_i are the mole fraction and viscosity of pure component i respectively.

The $\Delta\eta$ values are plotted against mole fraction of component (C) and are depicted graphically in Fig 4. The $\Delta\eta$ values are negative for the ternary mixture of THF + MeOH +(cyclohexane, cyclohexanone and nitrobenzene) over the entire range of composition suggesting dispersion and dipolar interaction between molecules whereas the values are positive for the ternary mixtures of tetrahydrofuran + methanol +(benzene, anisole, toluene and

chlorobenzene) which suggests hydrogen bonding interactions leading to the formation of complex species between molecules.

5.3.2. Viscous synergy and antagonism

The method most widely used to analyze the synergic and antagonic behavior of the ternary liquid mixtures used here is that developed by Kalentunc-Gencer and Peleg [23] allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp} , with the viscosity expected in the absence of interaction, η_{cal} defined by the simple mixing rule as

$$\eta_{cal} = x_A\eta_A + x_B\eta_B + x_C\eta_C \quad (2)$$

where x_A , x_B , x_C are the mole fraction of the systems A, B, C, and η_A , η_B , η_C are the viscosities, measured experimentally, of the systems A, B, C, respectively.

The result for η_{cal} and η_{exp} has been presented in Table 2 and is depicted graphically against mole fraction of component (C) in Fig 1 and 2 respectively. In order to secure more comparable viscous synergy result, the so called synergic interaction index (I_S) introduced by Howell [24] is taken into account:

$$I_S = \frac{(\eta_{exp} - \eta_{cal})}{\eta_{cal}} = \frac{\Delta\eta}{\eta_{cal}} \quad (3)$$

The negative values of I_S gives antagonic interaction (I_A). Table 2 gives the data for the I_S and I_A of the mixtures which has been graphically compared in Fig.3.

If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction [25, 26]. Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous

antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. Accordingly, when $\eta_{exp} > \eta_{cal}$, viscous synergy exists, while, when $\eta_{cal} > \eta_{exp}$, the system is said to exhibit viscous antagonism. This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other synergy indices are defined in consequence [27].

A perusal of Table 2 shows that for the ternary mixture of tetrahydrofuran (A) + methanol (B) + (cyclohexane, cyclohexanone, nitrobenzene) (C), the experimentally determined viscosities, η_{exp} are lower than those of its calculated values, η_{cal} which demonstrates viscous antagonism in the three mixtures studied here. The explanation of this behaviour is based on the known phenomenon of molecular dissociation, as a consequence of weakening the non-covalent bondings formed between the molecules producing a decrease in size of the molecular package which logically implies an increase in I_A [28].

On the other hand for the ternary mixtures of tetrahydrofuran (A) + methanol (B) + (benzene, toluene, chlorobenzene, anisole) (C), the experimentally determined viscosities, η_{exp} are higher than those of its calculated values, η_{cal} which demonstrates viscous synergy in the four mixtures studied here. The explanation of this type of behaviour is based on the known phenomenon of solvation as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture producing increase in size of the resulting molecular package, which logically implies a rise in viscosity.

5.3.3. Excess molar volume

The method used to analyze volume contraction and expansion is similar to that applied to viscosity, i.e., the density of the mixture is determined

experimentally, ρ_{exp} , and a calculation is made for ρ_{cal} based on the following expression:

$$\rho_{cal} = x_A\rho_A + x_B\rho_B + x_C\rho_C \quad (4)$$

where x_A , x_B , x_C are the mole fraction of the systems A, B, C, and ρ_A , ρ_B , ρ_C are the densities, measured experimentally, of the systems A, B, C, respectively.

The experimentally determined density value along with the derived parameter, V^E which is the excess molar volume is listed in Table 2. The excess molar volumes, V^E , are calculated from density data according to the following equation [29]:

$$V^E = \sum_{i=1}^3 x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (5)$$

where ρ is the density of the mixture and M_i , x_i , ρ_i are the molecular weight, mole fraction and viscosity of the i^{th} component in the mixture respectively.

Fig. 5 represent the V^E values for the seven ternary mixtures under examination. In general, V^E is found to be negative throughout for all the ternary mixtures except for tetrahydrofuran + methanol + cyclohexane. However, the values at first decreases to minima and then it increase with increasing x_C . 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 [30]: (1) dipolar interaction, (2) interstitial accommodation of one component into the other and (3) possible hydrogen bonded interactions between unlike molecules. The actual volume change would, therefore, depend on the relative strength of these three effects.

5.3.4 Isentropic Compressibility.

Isentropic compressibility, K_S and deviation in isentropic compressibility ΔK_S , for the ternary mixtures were calculated using the following relations:

$$K_S = \frac{1}{(u^2 \rho)} \quad (6)$$

$$\Delta K_S = K_S - \sum_{i=1}^3 x_i K_{S,i} \quad (7)$$

where u and K_S are the speed of sound and isentropic compressibility of the mixture and $K_{S,i}$, the isentropic compressibility of the i^{th} component in the mixture respectively. The experimental speed of sound, isentropic compressibility and deviation in isentropic compressibility are listed in Table 3 and are graphically represented in Fig. 6 as functions of mole fraction of the cyclic compounds. From Table 3 it is evident that except for the ternary mixture of tetrahydrofuran + methanol + cyclohexane, the deviation in isentropic compressibility ΔK_S are negative for all the ternary mixtures of tetrahydrofuran + methanol + (benzene, toluene, chlorobenzene, nitrobenzene, anisole, cyclohexanone). 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 [31]. The resultant values of ΔK_S for the present mixtures are due to the net effect of the combination of (i) to (iii) [32]. 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 [33-35]. These results are in excellent agreement with those of V^E discussed earlier.

5.3.5 Excess molar refraction

The molar refraction, $[R]$ can be evaluated from Lorentz-Lorenz relation [36] and gives more information than n_D about the mixture phenomenon because takes into account the electronic perturbation of molecular orbital during the liquid mixture process and $[R]$ is also directly related to the dispersion forces

$$[R] = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \cdot \left(\frac{M}{\rho} \right) \quad (8)$$

where $[R]$, n_D^2 , and M are, correspondingly, the molar refraction, the refractive index and the molar mass of the mixture respectively. Deviation from molar refraction was calculated from the following relation;

$$\Delta R = [R] - \sum_{i=1}^3 x_i [R]_i \quad (9)$$

The values of refractive indices and excess molar refraction (ΔR) for the ternary mixtures are presented in Table 3 and depicted graphically in Fig.7.

5.3.6 Excess Gibb's free energy of activation

On the basis of the theories of absolute reaction rates [37], the excess Gibbs energy of activation for viscous flow was calculated from the equation [38] for ternary systems.

$$\Delta G^E = RT \left[\ln \eta V - \sum_{i=1}^3 x_i \ln \eta_i V_i \right] \quad (10)$$

where R , T , V_i and V are the universal gas constant, experimental temperature in absolute scale, and the molar volumes of the pure component and the mixtures, respectively. From Table 3 and Fig. 8 it is evident that the ΔG^E values are negative for all the ternary mixtures over entire range of mole fraction.

5.4. Conclusion

From the experimental work it can be concluded that the experimentally determined viscosities, η_{exp} of the ternary mixture of tetrahydrofuran (A) + methanol (B) + (cyclohexane, cyclohexanone, nitrobenzene) (C), are lower than those of its calculated values, η_{cal} which demonstrates viscous antagonism while for the ternary mixtures of tetrahydrofuran (A) + methanol (B) + (benzene, toluene, chlorobenzene, anisole) (C), the experimentally determined viscosities, η_{exp} are higher than those of its calculated values, η_{cal} which demonstrates viscous synergy.

Acknowledgment. The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2007, SAP-2) for financial support.

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TABLE 1: Density (ρ), viscosity (η), sound speed (u) and refractive index (n_D) of pure liquids at 298.15K.

Pure components	$\rho \times 10^{-3} \text{kgm}^{-3}$		η/mPas		u/ms^{-1}		n_D	
	This work	Lit	This work	Lit	This work	Lit	This work	Lit
Tetrahydrofuran	0.8821	0.8819[39]	0.461	0.460[39]	1287.2	1228[39]	1.4050	1.4050[39]
Methanol	0.7865	0.7866[40]	0.544	0.545[40]	1104.1	1103[40]	1.3264	1.3264[40]
Benzene	0.8765	0.8728[41]	0.599	0.552[41]	1302.6	1301[41]	1.4970	1.4982[41]
Toluene	0.8645	0.8662[42]	0.579	0.552[42]	1303.8	1304[43]	1.4925	1.4930[43]
Chlorobenzene	1.1056	1.1010[44]	0.787	0.773[44]	1270.6	1271[44]	1.5220	1.5223[44]
Nitrobenzene	1.1985	1.1983[45]	1.686	1.686[45]	1642.8	1648[45]	1.5490	1.5493[45]
Anisole	0.9946	0.9893[46]	0.995	0.991[46]	1418.4	1418[46]	1.5140	1.5143[46]
Cyclohexane	0.7773	0.7740[47]	0.886	0.883[47]	1254.6	1254[47]	1.4240	1.4235[47]
Cyclohexanone	0.9462	0.9452[46]	1.965	1.963[46]	1415.2	1417[46]	1.4465	1.4500[46]

TABLE 2: Experimental (ρ_{exp} , η_{exp}) and calculated (ρ_{cal} , η_{cal}) density and viscosity, excess molar volume (V^E), viscosity deviation ($\Delta\eta$) and synergic index (I_S) for the ternary mixture of tetrahydrofuran (A) + methanol (B) +benzene derivatives (C) at 298.15K.

x_A	x_B	$\rho_{cal} \times 10^3$ kg m ³	$\rho_{cal} \times 10^3$ kg m ³	$V^E \times 10^6$ m ³ mol ⁻¹	$\eta_{exp}/$ mPas	$\eta_{cal} /$ mPas	$\Delta\eta /$ mPas	I_S
(A)Tetrahydrofuran + (B) methanol + (C) benzene								
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5025	0.5185	-0.0160	-0.0309
0.2982	0.6712	0.8398	0.8178	-0.3890	0.5153	0.5210	-0.0057	-0.0109
0.2872	0.6465	0.8426	0.8199	-0.4232	0.5256	0.5238	0.0018	0.0034
0.2743	0.6172	0.8455	0.8225	-0.4360	0.5332	0.5272	0.0060	0.0114
0.2587	0.5821	0.8484	0.8256	-0.4362	0.5428	0.5313	0.0115	0.0216
0.2396	0.5392	0.8518	0.8293	-0.4340	0.5523	0.5363	0.0160	0.0298
0.2157	0.4855	0.8554	0.8340	-0.4101	0.5606	0.5426	0.0180	0.0332
0.1850	0.4164	0.8596	0.8401	-0.3879	0.5677	0.5506	0.0171	0.0311
0.1440	0.3241	0.8642	0.8481	-0.3195	0.5758	0.5613	0.0145	0.0258
0.0865	0.1947	0.8695	0.8595	-0.2004	0.5834	0.5764	0.0070	0.0121
0.0000	0.0000	0.8756	0.8765	0.0000	0.5990	0.5990	0.0000	0.0000
(A)Tetrahydrofuran + (B) methanol +(C) toluene								
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328
0.2996	0.6743	0.8391	0.8172	-0.3846	0.5154	0.5201	-0.0047	-0.0090
0.2902	0.6531	0.8412	0.8187	-0.4072	0.5238	0.5220	0.0018	0.0035
0.2789	0.6276	0.8435	0.8205	-0.4360	0.5320	0.5242	0.0078	0.0149

0.2651	0.5966	0.8459	0.8226	-0.4530	0.5390	0.5270	0.0121	0.0229
0.2479	0.5580	0.8484	0.8253	-0.4580	0.5495	0.5304	0.0191	0.0360
0.2260	0.5087	0.8512	0.8288	-0.4598	0.5569	0.5347	0.0222	0.0415
0.1970	0.4433	0.8543	0.8334	-0.4530	0.5630	0.5405	0.0226	0.0417
0.1567	0.3527	0.8577	0.8397	-0.4149	0.5673	0.5485	0.0188	0.0343
0.0971	0.2186	0.8610	0.8492	-0.2750	0.5697	0.5603	0.0094	0.0168
0.0000	0.0000	0.8645	0.8645	0.0000	0.5796	0.5796	0.0000	0.0000

(A)Tetrahydrofuran + (B) methanol + (C) chlorobenzene

0.3076	0.6924	0.8373	0.8159	-0.3700	0.5015	0.5185	-0.0170	-0.0329
0.3010	0.6775	0.8503	0.8221	-0.4980	0.5167	0.5243	-0.0075	-0.0144
0.2932	0.6599	0.8649	0.8295	-0.6320	0.5304	0.5311	-0.0007	-0.0014
0.2837	0.6384	0.8806	0.8385	-0.7150	0.5506	0.5394	0.0111	0.0206
0.2719	0.6120	0.8984	0.8496	-0.7820	0.5752	0.5497	0.0255	0.0464
0.2570	0.5784	0.9190	0.8636	-0.8400	0.5991	0.5628	0.0363	0.0645
0.2374	0.5344	0.9434	0.8820	-0.8880	0.6292	0.5798	0.0493	0.0851
0.2107	0.4743	0.9719	0.9072	-0.8650	0.6615	0.6032	0.0583	0.0967
0.1720	0.3872	1.0065	0.9436	-0.7650	0.6979	0.6370	0.0609	0.0957
0.1109	0.2496	1.0489	1.0012	-0.4670	0.7349	0.6904	0.0445	0.0645
0.0000	0.0000	1.1056	1.1056	0.0000	0.7873	0.7873	0.0000	0.0000

(A) Tetrahydrofuran +(B) methanol + (C) nitrobenzene

0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328
0.3016	0.6788	0.8513	0.8234	-0.3906	0.5234	0.5414	-0.0180	-0.0332
0.2944	0.6625	0.8679	0.8324	-0.4520	0.5504	0.5688	-0.0184	-0.0323

0.2856	0.6427	0.8869	0.8433	-0.5050	0.5834	0.6022	-0.0188	-0.0312
0.2746	0.6181	0.9093	0.8569	-0.5673	0.6240	0.6437	-0.0197	-0.0306
0.2607	0.5867	0.9357	0.8743	-0.6270	0.6765	0.6967	-0.0202	-0.0290
0.2422	0.5450	0.9678	0.8973	-0.7026	0.7449	0.7669	-0.0220	-0.0287
0.2166	0.4874	1.0076	0.9292	-0.8000	0.8404	0.8640	-0.0236	-0.0273
0.1788	0.4024	1.0564	0.9762	-0.8078	0.9817	1.0074	-0.0257	-0.0255
0.1173	0.2641	1.1176	1.0526	-0.6100	1.2188	1.2405	-0.0217	-0.0175
0.0000	0.0000	1.1985	1.1985	0.0000	1.6857	1.6857	0.0000	0.0000

(A) Tetrahydrofuran +(B) methanol + (C) anisole

0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328
0.3008	0.6769	0.8448	0.8199	-0.3880	0.5151	0.5291	-0.0140	-0.0265
0.2926	0.6586	0.8532	0.8246	-0.4060	0.5353	0.5417	-0.0064	-0.0118
0.2828	0.6364	0.8628	0.8303	-0.4333	0.5602	0.5570	0.0032	0.0057
0.2706	0.6091	0.8739	0.8374	-0.4700	0.5843	0.5758	0.0084	0.0147
0.2553	0.5745	0.8865	0.8463	-0.4880	0.6145	0.5996	0.0149	0.0249
0.2352	0.5295	0.9016	0.8580	-0.5330	0.6490	0.6306	0.0184	0.0292
0.2080	0.4682	0.9192	0.8738	-0.5570	0.6948	0.6728	0.0220	0.0327
0.1690	0.3803	0.9402	0.8964	-0.5570	0.7536	0.7333	0.0203	0.0277
0.1081	0.2433	0.9650	0.9318	-0.4320	0.8387	0.8276	0.0111	0.0135
0.0000	0.0000	0.9946	0.9946	-0.0100	0.9950	0.9950	0.0000	0.0000

(A)Tetrahydrofuran + (B) methanol + (C) cyclohexanone

0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328
0.3001	0.6754	0.8430	0.8191	-0.3940	0.5220	0.5539	-0.0320	-0.0577

0.2912	0.6553	0.8495	0.8229	-0.4330	0.5413	0.5959	-0.0545	-0.0915
0.2805	0.6312	0.8569	0.8274	-0.4849	0.5661	0.6462	-0.0801	-0.1240
0.2673	0.6017	0.8651	0.8330	-0.5220	0.6023	0.7079	-0.1056	-0.1492
0.2509	0.5647	0.8743	0.8399	-0.5539	0.6510	0.7852	-0.1342	-0.1709
0.2297	0.5171	0.8848	0.8489	-0.5730	0.7126	0.8847	-0.1722	-0.1946
0.2014	0.4533	0.8968	0.8609	-0.5690	0.8117	1.0180	-0.2062	-0.2026
0.1616	0.3636	0.9106	0.8778	-0.5062	0.9670	1.2053	-0.2383	-0.1977
0.1014	0.2282	0.9266	0.9033	-0.3273	1.2380	1.4883	-0.2503	-0.1570
0.0000	0.0000	0.9462	0.9462	0.0000	1.9650	1.9650	0.0000	0.0000

(A) Tetrahydrofuran + (B) methanol + (C) cyclohexane

0.3076	0.6924	0.8373	0.8159	-0.3671	0.5150	0.5185	-0.0035	-0.0068
0.2989	0.6727	0.8324	0.8148	-0.3502	0.5203	0.5290	-0.0087	-0.0164
0.2886	0.6496	0.8256	0.8135	-0.2070	0.5268	0.5412	-0.0144	-0.0266
0.2764	0.6221	0.8189	0.8120	-0.0705	0.5332	0.5558	-0.0226	-0.0407
0.2617	0.5889	0.8122	0.8101	0.0619	0.5429	0.5734	-0.0305	-0.0532
0.2435	0.5479	0.8062	0.8079	0.1429	0.5610	0.5952	-0.0342	-0.0574
0.2205	0.4962	0.7989	0.8050	0.3478	0.5820	0.6226	-0.0406	-0.0652
0.1905	0.4287	0.7934	0.8012	0.3728	0.6149	0.6585	-0.0436	-0.0662
0.1497	0.3370	0.7869	0.7961	0.4796	0.6631	0.7071	-0.0440	-0.0622
0.0912	0.2053	0.7825	0.7887	0.2560	0.7428	0.7770	-0.0342	-0.0440
0.0000	0.0000	0.7773	0.7773	0.0000	0.8860	0.8860	0.0000	0.0000

TABLE 3 Sound speed (u), isoentropic compressibility (K_S), excess isoentropic compressibility (K_S^E), refractive index (n_D), molar refraction (ΔR) and excess Gibb's free energy of activation of viscous flow (ΔG^E) for the ternary mixture of tetrahydrofuran (A) + methanol (B) + benzene derivatives (C) at 298.15K.

x_A	x_B	u/ms^{-1}	$K_S \times 10^{12}$ /Pa $^{-1}$	$\Delta K_S \times 10^{12}$ /Pa $^{-1}$	n_D	$\Delta R \times 10^6$ (m 3 mol $^{-1}$)	$\Delta G^E \times 10^{-3}$ (Jmol $^{-1}$)
(A)Tetrahydrofuran + (B) methanol + ((C) benzene							
0.3076	0.6924	1162.4	883.9	2.8	1.3625	-0.0948	-581.13
0.2982	0.6712	1174.6	863.1	-11.6	1.3694	-0.0880	-504.22
0.2872	0.6465	1181.5	850.1	-17.1	1.3770	-0.0848	-439.23
0.2743	0.6172	1195.2	828.0	-30.4	1.3855	-0.0790	-385.64
0.2587	0.5821	1206.1	810.2	-37.5	1.3952	-0.0675	-321.52
0.2396	0.5392	1223.8	783.9	-50.9	1.4065	-0.0490	-257.23
0.2157	0.4855	1242.9	756.8	-61.8	1.4194	-0.0274	-197.65
0.1850	0.4164	1258.3	734.7	-63.1	1.4347	0.0013	-144.10
0.1440	0.3241	1278.7	707.7	-62.2	1.4527	0.0423	-89.15
0.0865	0.1947	1297.5	683.2	-47.6	1.4734	0.0570	-46.92
0.0000	0.0000	1302.6	672.0	0.0	1.4970	0.0000	0.12
(A)Tetrahydrofuran + (B) methanol +(C) toluene							
0.3076	0.6924	1137.89	922.4	41.3	1.3625	-0.0948	-586.148
0.2996	0.6743	1147.43	905.1	29.3	1.3695	-0.0794	-494.314
0.2902	0.6531	1158.56	885.7	16.0	1.3775	-0.0571	-428.101
0.2789	0.6276	1171.50	863.8	1.5	1.3860	-0.0478	-360.645
0.2651	0.5966	1183.30	844.3	-9.0	1.3960	-0.0218	-296.438
0.2479	0.5580	1200.32	818.1	-24.0	1.4071	0.0000	-213.892
0.2260	0.5087	1215.77	794.8	-33.0	1.4201	0.0380	-143.38
0.1970	0.4433	1235.43	766.9	-42.0	1.4350	0.0729	-78.936
0.1567	0.3527	1254.50	740.8	-41.8	1.4522	0.1100	-27.3329
0.0971	0.2186	1277.40	711.8	-32.0	1.4720	0.1403	-0.52299
0.0000	0.0000	1303.80	680.5	0.0	1.4925	0.0000	-0.1297
(A)Tetrahydrofuran + (B) methanol + (C) chlorobenzene							
0.3076	0.6924	1162.40	883.9	2.9	1.3625	-0.0944	-586.15
0.3010	0.6775	1166.30	864.5	-9.6	1.3705	-0.0682	-515.94

Viscous Synergy and..... Cyclic Compounds at 298.15K

0.2932	0.6599	1172.70	840.7	-25.3	1.3804	-0.0120	-455.95
0.2837	0.6384	1177.90	818.4	-37.6	1.3910	0.0467	-366.86
0.2719	0.6120	1184.10	793.9	-49.9	1.4030	0.1110	-263.36
0.2570	0.5784	1195.30	761.6	-66.7	1.4160	0.1600	-171.17
0.2374	0.5344	1210.80	734.1	-73.7	1.4315	0.2200	-65.06
0.2107	0.4743	1226.70	701.8	-78.2	1.4487	0.2540	32.10
0.1720	0.3872	1236.40	660.3	-79.4	1.4681	0.2380	111.47
0.1109	0.2496	1270.60	623.7	-52.3	1.4910	0.1584	124.42
0.0000	0.0000	1210.80	560.3	0.0	1.5220	0.0000	0.03

(A) Tetrahydrofuran +(B) methanol + (C) nitrobenzene

0.3076	0.6924	1162.40	883.9	2.8	1.3625	-0.0948	-586.15
0.3016	0.6788	1190.80	828.4	-41.4	1.3708	-0.0470	-515.92
0.2944	0.6625	1224.51	768.4	-88.0	1.3800	-0.0120	-436.61
0.2856	0.6427	1288.20	679.4	-160.6	1.3905	0.0281	-348.05
0.2746	0.6181	1322.70	628.6	-191.1	1.4023	0.0580	-252.29
0.2607	0.5867	1385.49	556.7	-237.0	1.4160	0.0836	-144.93
0.2422	0.5450	1453.07	489.4	-270.0	1.4325	0.1071	-34.19
0.2166	0.4874	1524.96	426.8	-285.0	1.4527	0.1220	79.70
0.1788	0.4024	1589.88	374.5	-267.0	1.4768	0.1030	180.17
0.1173	0.2641	1593.67	352.3	-175.0	1.5070	0.0500	224.63
0.0000	0.0000	1642.80	309.2	0.0	1.5490	0.0000	0.01

(A) Tetrahydrofuran + (B) methanol + (C) anisole

0.3076	0.6924	1162.40	887.6	6.6	1.3625	-0.0948	-586.15
0.3008	0.6769	1167.80	840.7	-29.1	1.3695	-0.0824	-528.07
0.2926	0.6586	1196.30	769.2	-87.2	1.3775	-0.0651	-443.82
0.2828	0.6364	1214.80	718.3	-121.9	1.3870	-0.0370	-347.44
0.2706	0.6091	1228.80	673.6	-146.6	1.3980	-0.0010	-266.28
0.2553	0.5745	1261.30	612.3	-182.7	1.4107	0.0430	-173.75
0.2352	0.5295	1290.43	559.1	-203.0	1.4257	0.0900	-89.00
0.2080	0.4682	1328.49	503.4	-214.0	1.4436	0.1550	0.85
0.1690	0.3803	1353.25	461.1	-192.0	1.4644	0.2030	69.78
0.1081	0.2433	1359.54	433.0	-120.0	1.4878	0.1900	92.76
0.0000	0.0000	1418.40	375.4	0.0	1.5140	0.0000	0.04

(A)Tetrahydrofuran + (B) methanol + (C) cyclohexanone

0.3076	0.6924	1159.73	888.0	6.9	1.3625	-0.0948	-586.15
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Viscous Synergy and..... Cyclic Compounds at 298.15K

0.3001	0.6754	1175.62	858.3	-14.1	1.3670	-0.0878	-540.39
0.2912	0.6553	1189.31	832.3	-29.9	1.3720	-0.0700	-515.45
0.2805	0.6312	1215.88	789.3	-60.5	1.3779	-0.0620	-485.09
0.2673	0.6017	1233.06	760.3	-74.5	1.3843	-0.0440	-432.24
0.2509	0.5647	1253.50	727.9	-88.0	1.3917	-0.0270	-369.44
0.2297	0.5171	1276.62	693.5	-98.1	1.4003	0.0130	-318.75
0.2014	0.4533	1301.43	658.3	-100.7	1.4100	0.0440	-237.36
0.1616	0.3636	1325.25	625.3	-88.0	1.4206	0.0690	-159.19
0.1014	0.2282	1352.79	589.7	-54.4	1.4327	0.0600	-87.00
0.0000	0.0000	1415.20	527.7	0.0	1.4465	0.0000	-40.00

(A) Tetrahydrofuran + (B) methanol + (C) cyclohexane

0.3076	0.6924	1162.40	883.9	2.8	1.3625	-0.0948	-520.23
0.2989	0.6727	1165.44	882.9	3.7	1.3660	-0.0870	-496.11
0.2886	0.6496	1170.16	881.8	4.7	1.3693	-0.0800	-463.50
0.2764	0.6221	1174.90	880.8	6.2	1.3727	-0.0660	-437.17
0.2617	0.5889	1180.10	879.4	7.9	1.3770	-0.0520	-403.03
0.2435	0.5479	1184.85	878.5	10.7	1.3822	-0.0340	-345.07
0.2205	0.4962	1191.84	876.3	13.3	1.3880	-0.0030	-288.55
0.1905	0.4287	1199.14	872.1	15.3	1.3954	0.0280	-220.25
0.1497	0.3370	1209.92	864.7	16.4	1.4032	0.0410	-143.02
0.0912	0.2053	1225.33	849.0	12.8	1.4132	0.0480	-64.25
0.0000	0.0000	1254.60	817.3	0.0	1.4240	0.0000	-0.07

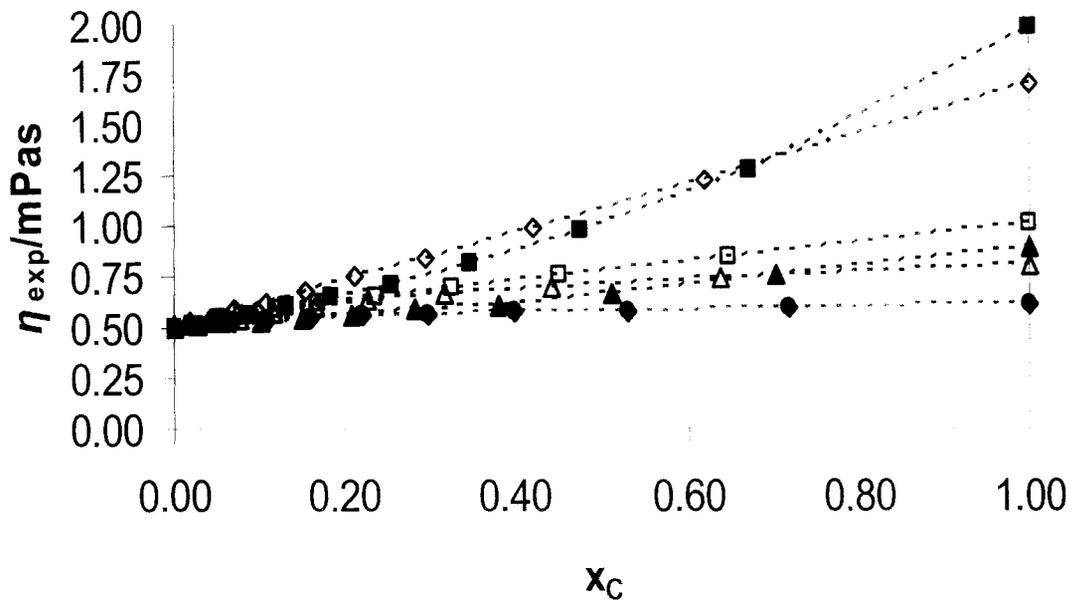


FIGURE 1. Plot of η_{exp} vs (x_c) for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

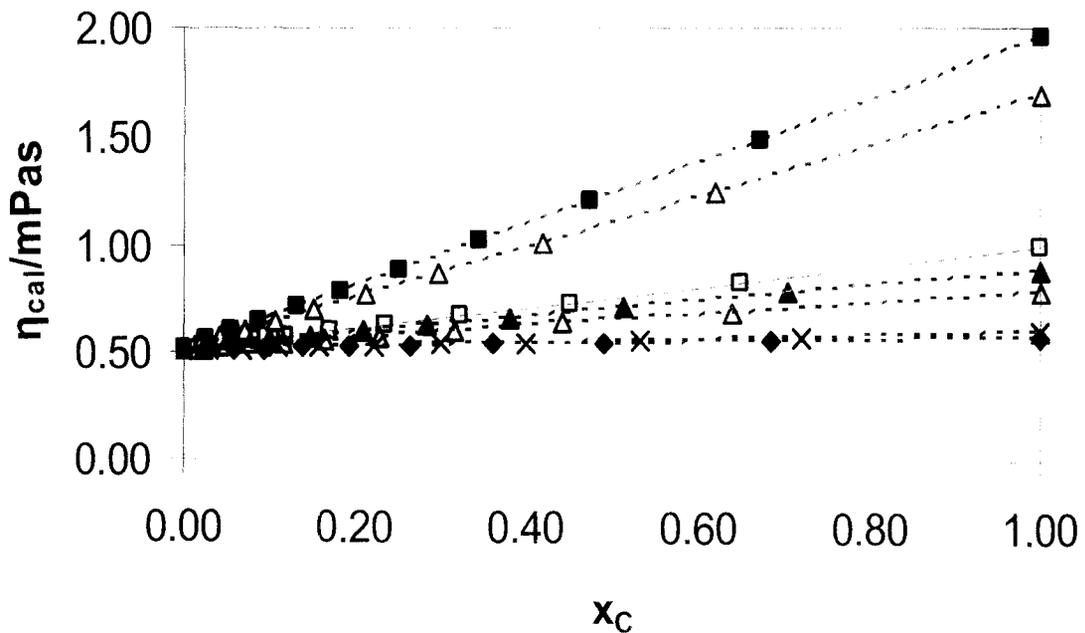


FIGURE 2. Plot of η_{cal} vs (x_c) for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene (C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone (C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

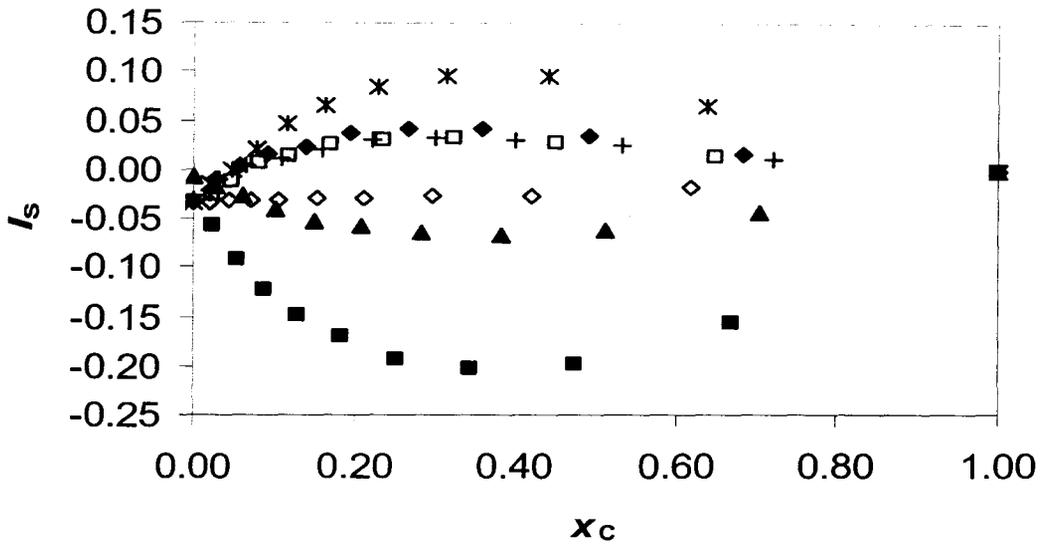


FIGURE 3. Plot of I_s vs x_c for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

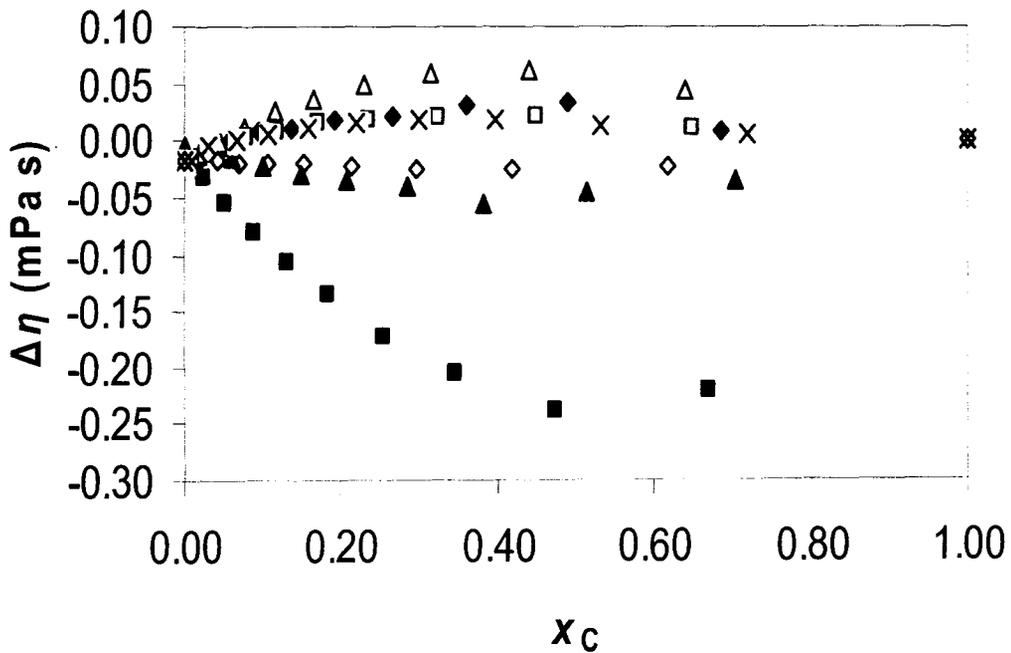


FIGURE 4. Plot of viscosity deviation $\Delta\eta$ (mPas) vs x_c for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

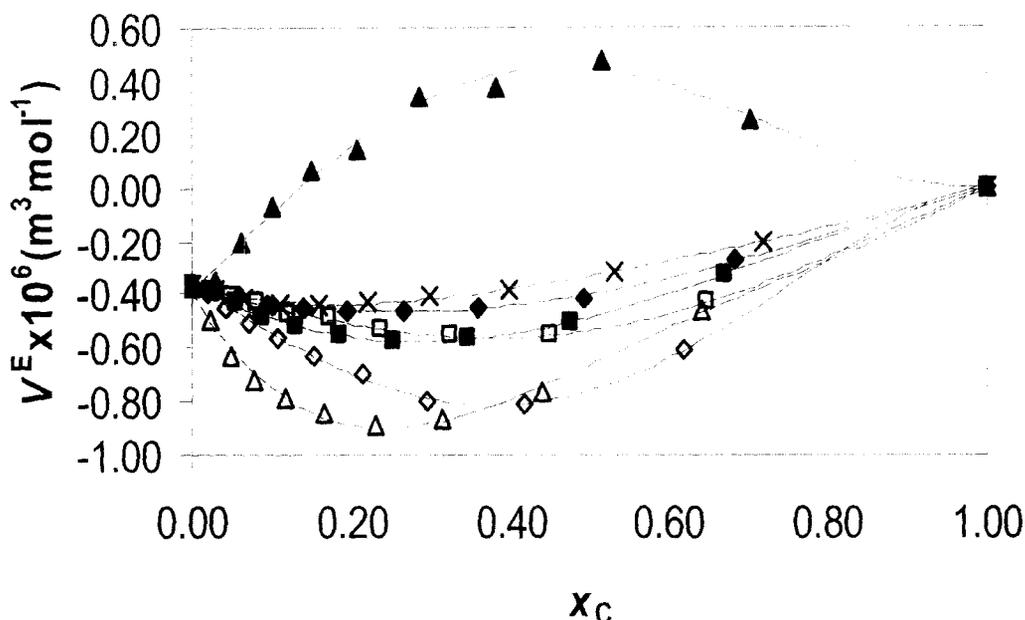


FIGURE 5. Plot of excess molar volume $V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$ vs x_c for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

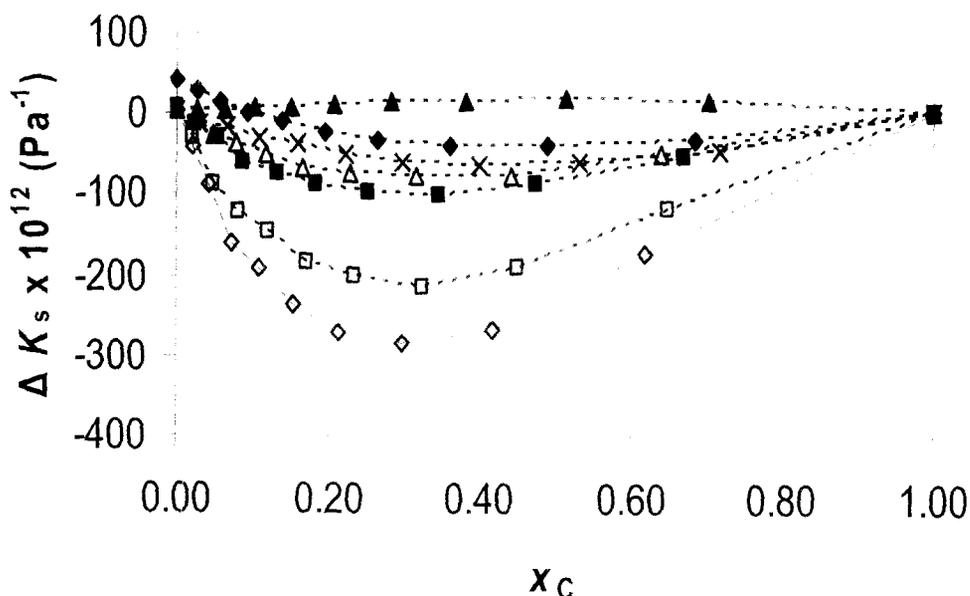


FIGURE 6. Plot of excess isentropic compressibility $\Delta K_s \times 10^{12} (\text{Pa}^{-1})$ vs x_c for the ternary mixtures at 298.15K. (x), T.H.F (A) + MeOH (B) + Benzene(C); (♦)T.H.F (A) + MeOH (B) + Toluene (C); (Δ), T.H.F (A) + MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A) + MeOH (B) + Nitrobenzene(C); (□), T.H.F (A) + MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A) + MeOH (B) + Cyclohexane(C).

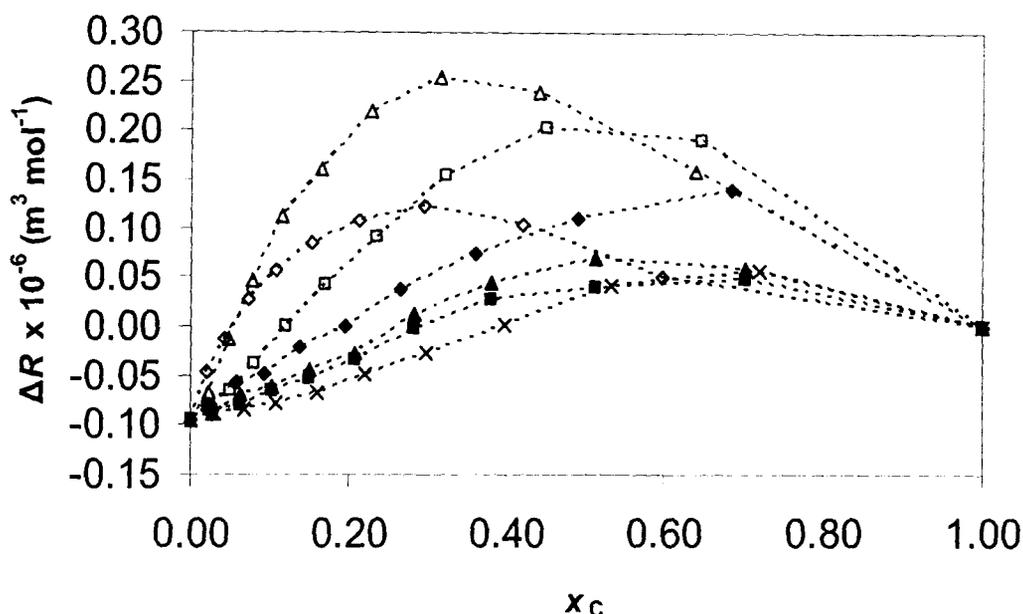


FIGURE 7. Plot of excess molar refraction $\Delta R \times 10^6 (\text{m}^3 \text{mol}^{-1})$ vs x_c for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

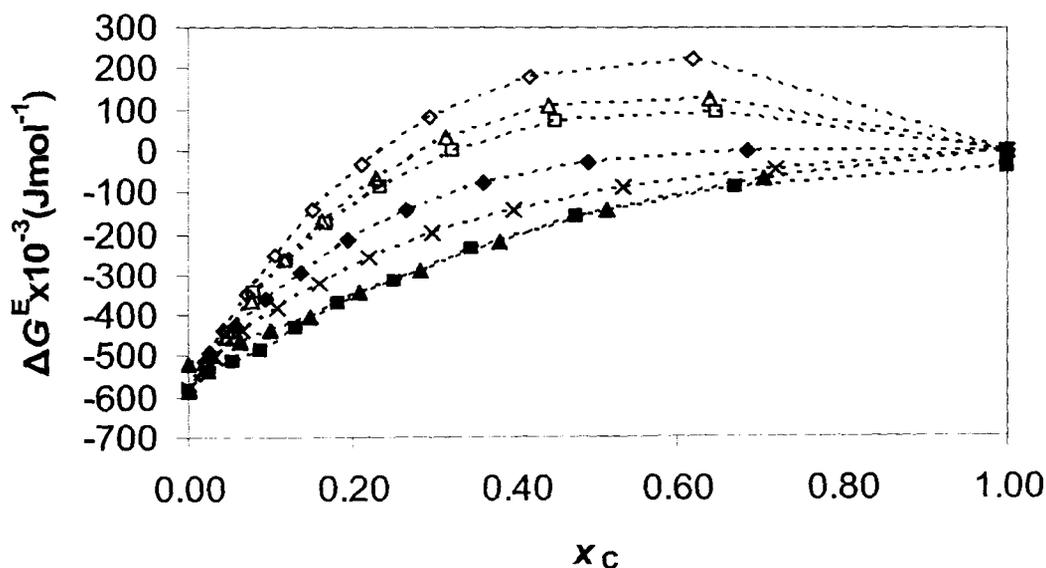


FIGURE 8. Plot of excess Gibbs energy of activation $\Delta G^E \times 10^{-3} (\text{Jmol}^{-1})$ vs x_c for the ternary mixtures at 298.15K. (x), T.H.F (A)+ MeOH (B) + Benzene(C); (♦)T.H.F (A)+ MeOH (B) + Toluene (C); (Δ), T.H.F (A)+ MeOH (B) + Chlorobenzene(C); (◇), T.H.F (A)+ MeOH (B) + Nitrobenzene(C); (□), T.H.F (A)+ MeOH (B) + Anisole (C); (■), T.H.F (A)+ MeOH (B) + Cyclohexanone(C); (▲), T.H.F (A)+ MeOH (B) + Cyclohexane(C).

CHAPTER VI

Ion -Solvent and Ion-Ion Interactions of Sodium Molybdate and Sodium Tungstate in mixtures of Ethane- 1, 2 diol and Water at 298.15, 308.15 and 318.15K.

6.1. Introduction

Studies on densities (ρ) and viscosities (η) of electrolyte solutions are of great importance in characterizing the properties and structural aspects of solutions. The addition of an electrolyte to an aqueous organic solution alters the pattern of ion solvation and causes phenomenal changes in the behavior of the dissolved electrolyte. Hence, studies on the limiting apparent molar volume and viscosity- B coefficients of electrolyte provide us valuable information regarding ion-ion, ion-solvent and solvent-solvent interactions [1-3]. It has been found by a number of workers [4-6] that the addition of an electrolyte could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various electrolyte concentrations and temperature.

In this paper we have attempted to report the limiting apparent molar volume (V_{ϕ}^0), experimental slopes (S_V^*) and viscosity B - coefficients for sodium molybdate and sodium tungstate in aqueous binary mixture of ethane-1, 2-diol at 298.15, 308.15 and 318.15K. The mixture of ethane-1, 2-diol with water was chosen because of its diverse application in pharmaceutical and cosmetic. However, the experiment was not performed in pure ethane-1, 2-diol due to the insolubility of the electrolytes. Since both molybdate and tungstate ions have similar structure [9] and sodium ion being a common cation for both the

Ion -Solvent and.....at 298.15, 308.15 and 318.15K.

electrolyte under investigation, the present work enables us to have a qualitative comparison of the role of anion in aqueous binary mixture of ethane-1,2-diol in terms of various derived parameters obtained from viscosity (η) and density (ρ) measurement.

6.2. Experimental section

6.2.1 Materials

Ethane-1, 2-diol (E.Merck, India) was purified by standard methods [10]. The purity of the solvent was checked by measuring the viscosity (η) and density (ρ) at 298.15K which was in good agreement with the literature values. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was used. Sodium tungstate and sodium molybdate (E.Merck, India) were purified by re-crystallizing twice from conductivity water and then dried in a vacuum dessicator over P_2O_5 for 24 hours before use. The purity of the solvents was ascertained by GLC and also by comparing experimental values of viscosity (η) and density (ρ) whenever available with those reported in the literature and are listed in Table 1.

6.2.2. Measurements

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of about 0.1 cm. The measurements were done in a thermostat bath controlled to $\pm 0.01 \text{ K}$. Viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to $\pm 0.1 \text{ s}$, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4} \text{ mPas}$. 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 fractions was within ± 0.0002 . The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$. Viscosity of the solution, η , is given by the following equation:

$$\eta = \left(Kt - \frac{l}{t} \right) \rho \quad (1)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.003 mPas.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere [11-14]. The electrolyte solutions studied here were prepared by mass and the conversion of molality into molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

6.3. Results and discussion

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation [3]:

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (2)$$

Where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volume (V_ϕ^0) was calculated using a least -squares treatment to the plots of V_ϕ versus \sqrt{c} using the following Masson equation [15]:

$$V_{\phi} = V_{\phi}^o + S_V^* \sqrt{c} \quad (3)$$

where V_{ϕ}^o is the apparent molar volume at infinite dilution and S_V^* the experimental slope. The plots of V_{ϕ} against square root of molar concentration (\sqrt{c}) were found to be linear as depicted graphically in Figure (1-6) with negative slopes. Values of V_{ϕ}^o and S_V^* are reported in Table 3.

As the systems under study are characterized by hydrogen bonding, the ion-solvent and ion-ion interactions can be interpreted in terms of structural changes, which arise due to hydrogen bonding between various components of the solvent and solution systems. V_{ϕ}^o can be used to interpret ion-solvent interactions. A perusal of Table 3 reveals that the V_{ϕ}^o values are positive and increases with rise in temperature and decreases with increase in the amount of ethane-1, 2-diol in the solvent mixture. This indicates the presence of strong ion-solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the amount of ethane-1, 2-diol in the solvent mixture under study, suggesting larger electrostriction at higher temperature and in lower amount of ethane-1, 2-diol in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous dimethylformamide [16] and aqueous tetrahydrofuran [17].

It is evident from Table 3 that the S_V^* values are negative for all temperatures for aqueous mixtures of ethane-1, 2-diol. Furthermore S_V^* values decreases with the increase of experimental temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion-ion interactions (ionic-dissociation) [18]. The S_V^* values increases with an increase in the amount of ethane-1,2-diol in the aqueous 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 ethane-1, 2-diol to the mixture. A quantitative comparison of the magnitude of values shows that V_{ϕ}^o

values are much greater in magnitude than those of S_V^* for all the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and at all experimental temperatures.

The variation of V_ϕ^o with temperature of sodium molybdate and sodium tungstate in solvent mixture follows the polynomial,

$$V_\phi^o = a_0 + a_1T + a_2T^2 \quad (4)$$

over the temperature range under study where T is the temperature in K.

Values of coefficients of the above equation for sodium molybdate and sodium tungstate for aqueous ethane-1, 2-diol mixtures are reported in Table 4.

The apparent molar expansibilities (ϕ_E^o) can be obtained by the following equation:

$$\phi_E^o = \left(\frac{\partial V_\phi^o}{\partial T} \right)_P = a_1 + 2a_2T \quad (5)$$

The values ϕ_E^o of for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. From Table it is evident that the values of ϕ_E^o for sodium molybdate increases with a rise in temperature and decreases with the increase in the amount of ethane-1, 2-diol in the mixture which can be ascribed to the absence of caging or packing effects [19]. However for sodium tungstate the ϕ_E^o values were found to be rather complicated to explain.

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 tendency of any solute. Helper [20] developed a technique of examining the sign of $(\partial \phi_E^o / \partial T)_P$ for the solute in terms of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows

$$\left(\frac{\partial\phi_E^0}{\partial T}\right)_P = 2a_2 \quad (6)$$

If the sign of $(\partial\phi_E^0/\partial T)_P$ is positive or small negative [21] the electrolyte is a structure maker and when the sign of $(\partial\phi_E^0/\partial T)_P$ is negative, it is a structure breaker. As is evident from Table 5, the electrolyte under investigation generally acts as a structure breaker. Thus it may be concluded that the electrolytes are characterized by the absence of caging effect [18, 22].

The viscosity data of solutions for the electrolytes in 0.0312, 0.0677, 0.1106 mole fraction (x_1) of ethane-1, 2-diol + water mixtures have been analyzed using Jones-Dole [23] equation:

$$\left(\frac{\eta}{\eta_0} - 1\right)/\sqrt{c} = A + B\sqrt{c} \quad (7)$$

Where η_0 and η are the viscosities of the solvent/solvent mixtures and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 6. From the Table it is evident that the values of the A coefficient are negative for all the solutions under investigation at all experimental temperatures. These results indicate the presence of weak ion-ion interactions, and these interactions further decrease with the rise of experimental temperatures suggesting an increase in ion-solvation while these interactions increase with an increase of ethane-1, 2-diol in the mixture. Interestingly, values are found to be more negative for sodium molybdate and hence it may be concluded that sodium molybdate is more soluble in aqueous ethane-1,2-diol solutions than sodium tungstate.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B -coefficient [24, 25]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B -coefficient of sodium molybdate and sodium tungstate in the studied solvent systems are positive, thereby suggesting the presence of strong ion - solvent interactions, and these type of interactions are

strengthened with a rise in temperature and weakened with an increase of ethane-1,2-diol in the mixture. These conclusions are in excellent agreement with those drawn from V° values discussed earlier.

It has been reported in a number of studies [26, 27] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 6 that the values of the B-coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of sodium molybdate and sodium tungstate in the solvent systems. A similar result was reported in a study [28] of viscosity of some salts in propionic acid and ethanol mixtures.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of the electrolytes, suggested by Feakins. et. al [29] using the following equation

$$\Delta\mu_2^{o\ddagger} = \Delta\mu_1^{o\ddagger} + \frac{(1000B + \bar{V}_2^{\circ} - \bar{V}_1^{\circ})RT}{\bar{V}_1^{\circ}} \quad (8)$$

Where \bar{V}_1° and \bar{V}_2° are the partial molar volumes of the solvent and the solute respectively. The contribution per mole of the solute to the free energy of activation of viscous flow ($\Delta\mu_2^{o\ddagger}$) of the solutions was determined from the above relation and are listed in Table 7. The free energy of activation of viscous flow of the pure solvent ($\Delta\mu_1^{o\ddagger}$) is given by the relation:

$$\Delta\mu_1^{o\ddagger} = \Delta G_1^{o\ddagger} = \frac{RT \ln \eta_1 \bar{V}_1^{\circ}}{hN_A} \quad (9)$$

Where N is the Avogadro's number and the other symbols have their usual significance. The values of $\Delta\mu_2^{o\ddagger}$ and $\Delta\mu_1^{o\ddagger}$ are reported in Table 7. From Table 7 it is evident that $\Delta\mu_1^{o\ddagger}$ is practically constant at all the solvent composition and at all temperatures, implying that $\Delta\mu_2^{o\ddagger}$ is mainly dependent on the viscosity B-coefficients and $(\bar{V}_2^{\circ} - \bar{V}_1^{\circ})$ terms. Also $\Delta\mu_2^{o\ddagger}$ values were found to positive at all the experimental temperatures and hence the formation of the

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transition state is less favorable in presence of these anions. A similar result was reported for sodium molybdate and sodium tungstate in aqueous acetonitrile solutions [21]. According to Feakins.et.al [29] $\Delta\mu_2^{o\ddagger} > \Delta\mu_1^{o\ddagger}$ for 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 [30]. The smaller values of $\Delta\mu_2^{o\ddagger}$ indicates the increased structure breaking tendency of the electrolyte. Thus from the values of $\Delta\mu_2^{o\ddagger}$ it can be inferred that both tungstate and molybdate ions have similar structure breaking tendencies. The entropy of activation for electrolytic solutions has been calculated using the following relation [29].

$$-\Delta S_2^{o\ddagger} = \frac{d(\Delta\mu_2^{o\ddagger})}{dT} \quad (10)$$

Where $\Delta S_2^{o\ddagger}$ has been determined from the negative slope of the plots of $\Delta\mu_2^{o\ddagger}$ against T by using a least square treatment.

The activation enthalpy ($\Delta H_2^{o\ddagger}$) has been calculated using the relation [29]:

$$\Delta H_2^{o\ddagger} = \Delta\mu_2^{o\ddagger} + T\Delta S_2^{o\ddagger} \quad (11)$$

the value of $\Delta S_2^{o\ddagger}$ and $\Delta H_2^{o\ddagger}$ are listed in Table 7 and they are found to be negative for all the electrolytic solutions and at all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state [29, 31].

6.4. Conclusion

In summary it can be concluded that both sodium molybdate and sodium tungstate shows similar trend of ion-solvent and ion-ion interactions, which can be ascribed to the similar structure of tungstate and molybdate ions [7]. From the values of apparent molar volume (V°_\emptyset) and viscosity *B*- coefficients

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it may be concluded that ion-solvent interaction increases with increasing temperature and decreases with increasing amount of ethane-1,2-diol in the aqueous mixture. Also the structure breaking tendencies of the two electrolytes were found to be similar.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

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TABLE 1: Density (ρ , kg m^{-3}) and viscosity (η , mPa s) of aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions (x_1) of ethane-1, 2-diol at different temperatures

Temperature (K)	$\rho \times 10^{-3} \text{kg m}^{-3}$		$\eta \text{ mPa s}$	
	This work	Lit	This work	Lit
$x_1=0.0312$				
298.15	1.0110	1.0116 [32]	1.1284	-
308.15	1.0071	1.0080 [32]	0.8922	-
318.15	1.0036	1.0038 [32]	0.7564	-
$x_1=0.0677$				
298.15	1.0238	1.0279 [32]	1.4244	-
308.15	1.0207	1.0239 [32]	1.1371	-
318.15	1.0167	1.0195 [32]	0.9440	-
$x_1=0.1106$				
298.15	1.0372	1.0432 [32]	1.8286	-
308.15	1.0352	1.0390 [32]	1.4302	-
318.15	1.0290	1.0343 [32]	1.1472	-

TABLE 2: Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_ϕ), and $\alpha = (\eta / \eta_o - 1) / c^{1/2}$ of sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions (x_1) of ethane-1, 2-diol at different temperatures

C mol dm ⁻³	$\rho \times 10^{-3}$ kg m ⁻³	η mPas	$V_\phi \times 10^6$ m ³ mol ⁻¹	α	c mol dm ⁻³	$\rho \times 10^{-3}$ kg m ⁻³	η mPas	$V_\phi \times 10^6$ m ³ mol ⁻¹	α
Sodium molybdate $x_1=0.0312$					Sodium tungstate $x_1=0.0312$				
298.15 K					298.15 K				
0.0250	1.0143	1.1429	109.228	0.0650	0.0250	1.0163	1.1471	116.278	0.1050
0.0350	1.0159	1.1493	101.895	0.0900	0.0350	1.0186	1.1582	110.767	0.1410
0.0450	1.0174	1.1549	97.665	0.1050	0.0450	1.0210	1.1669	106.845	0.1610
0.0550	1.0191	1.1619	93.236	0.1267	0.0550	1.0233	1.1750	104.213	0.1760
0.0750	1.0223	1.1748	90.621	0.1502	0.0750	1.0281	1.1902	100.921	0.2000
0.0850	1.0239	1.1820	89.663	0.1630	0.0850	1.0305	1.1998	99.7900	0.2170
308.15 K					308.15 K				
0.0249	1.0099	0.9044	127.605	0.0870	0.0249	1.0120	0.9094	133.908	0.1220
0.0348	1.0115	0.9102	114.742	0.1080	0.0349	1.0143	0.9173	121.999	0.1507
0.0448	1.0131	0.9183	107.597	0.1380	0.0448	1.0167	0.9245	115.189	0.1711

0.0548	1.0147	0.9256	103.106	0.1598	0.0548	1.0191	0.9325	110.818	0.1929
0.0747	1.0178	0.9383	98.545	0.1889	0.0747	1.0238	0.9472	105.575	0.2255
0.0846	1.0195	0.9442	94.498	0.2003	0.0846	1.0262	0.9543	103.732	0.2391
318.15K					318.15K				
0.0248	1.0060	0.7672	144.585	0.0910	0.0248	1.0081	0.7724	149.569	0.1346
0.0347	1.0076	0.7743	125.053	0.1273	0.0347	1.0105	0.7799	130.293	0.1667
0.0447	1.0093	0.7801	114.206	0.1485	0.0446	1.0130	0.7868	119.589	0.1903
0.0547	1.0110	0.7867	105.545	0.1712	0.0546	1.0154	0.7937	112.722	0.2110
0.0747	1.0144	0.7991	96.4701	0.2065	0.0744	1.0204	0.8076	104.345	0.2484
0.0847	1.0161	0.8047	92.9767	0.2195	0.0844	1.0228	0.8146	101.635	0.2649
Sodium molybdate $x_1=0.0677$					Sodium tungstate $x_1=0.0677$				
298.15K					298.15K				
0.0250	1.0274	1.4451	94.8690	0.0100	0.0250	1.0306	1.4460	101.479	0.0960
0.0350	1.0290	1.4527	91.4636	0.1130	0.0350	1.0331	1.4553	97.1661	0.1158
0.0450	1.0307	1.4633	86.8985	0.1350	0.0450	1.0355	1.4646	96.866	0.1330
0.0550	1.0324	1.4720	82.8316	0.1480	0.0550	1.0380	1.4738	94.961	0.1479
0.0750	1.0357	1.4906	81.3094	0.1746	0.0750	1.0428	1.4934	95.189	0.1770
0.0850	1.0374	1.4997	79.8219	0.1860	0.0850	1.0453	1.5016	94.153	0.1860

308.15K					308.15K				
0.0249	1.0236	1.1540	115.626	0.0960	0.0249	1.0267	1.1563	131.329	0.1070
0.0349	1.0252	1.1630	106.010	0.1236	0.0349	1.0292	1.1653	118.732	0.1330
0.0448	1.0268	1.1710	100.402	0.1419	0.0448	1.0317	1.1732	111.443	0.1500
0.0548	1.0283	1.1788	96.9554	0.1578	0.0548	1.0341	1.1797	107.973	0.1600
0.0747	1.0315	1.1940	93.3839	0.1841	0.0747	1.0390	1.1992	103.259	0.1998
0.0846	1.0330	1.2033	91.9710	0.2010	0.0847	1.0415	1.2065	101.803	0.2097
318.15K					318.15K				
0.0248	1.0193	0.9583	136.063	0.0950	0.0248	1.0224	0.9608	139.942	0.1130
0.0347	1.0208	0.9667	120.549	0.1280	0.0347	1.0248	0.9694	127.007	0.1444
0.0446	1.0223	0.9739	113.695	0.1487	0.0446	1.0272	0.9763	119.833	0.1619
0.0546	1.0240	0.9808	105.996	0.1659	0.0546	1.0297	0.9840	113.528	0.1816
0.0744	1.0271	0.9947	99.814	0.1962	0.0744	1.0346	0.9988	107.263	0.2127
0.0843	1.0287	1.0019	97.666	0.2104	0.0843	1.0371	1.0068	104.668	0.2290
Sodium molybdate $x_1=0.1106$					Sodium tungstate $x_1=0.1106$				
298.15K					298.15K				
0.0250	1.0410	1.8517	85.2862	0.0940	0.0250	1.0446	1.8553	85.2862	0.0924

0.0350	1.0428	1.8624	81.6000	0.1108	0.0350	1.0471	1.8648	81.6000	0.1057
0.0450	1.0443	1.8731	80.7124	0.1253	0.0450	1.0498	1.8760	80.7124	0.1221
0.0550	1.0462	1.8845	76.2873	0.1401	0.0550	1.0520	1.8874	76.2873	0.1370
0.0750	1.0495	1.9066	74.7013	0.1640	0.0750	1.0572	1.9109	74.7013	0.1643
0.0850	1.0513	1.9190	73.6711	0.1775	0.0850	1.0603	1.9214	73.6711	0.1740
Sodium molybdate $x_1=0.1106$					Sodium molybdate $x_1=0.1106$				
308.15K					318.15K				
0.0249	1.0385	1.4522	105.289	0.1070	0.0249	1.0240	1.4521	105.289	0.0976
0.0349	1.0401	1.4597	99.2167	0.1184	0.0349	1.0447	1.4615	99.2167	0.1170
0.0449	1.0416	1.4695	95.8562	0.1368	0.0449	1.0471	1.4687	95.8562	0.1270
0.0548	1.0431	1.4793	95.3671	0.1532	0.0549	1.0496	1.4798	95.3671	0.1480
0.0748	1.0460	1.5002	93.5430	0.1847	0.0748	1.0544	1.4979	93.5430	0.1731
0.0848	1.0483	1.5096	84.7810	0.1960	0.0847	1.0570	1.5089	84.7810	0.1892
318.15K					318.15K				
0.0248	1.0321	1.1679	114.771	0.1148	0.0248	1.0356	1.1660	114.771	0.1040
0.0347	1.0336	1.1756	105.395	0.1330	0.0347	1.0380	1.1746	105.395	0.1282
0.0446	1.0353	1.1840	98.2377	0.1520	0.0446	1.0405	1.1831	98.238	0.1483
0.0545	1.0369	1.1924	93.4467	0.1686	0.0545	1.0430	1.1914	93.447	0.1651
0.0743	1.0401	1.2106	90.0550	0.2029	0.0743	1.0479	1.2075	90.055	0.1928
0.0842	1.0418	1.2193	87.2167	0.2166	0.0842	1.0505	1.2157	87.217	0.2059

TABLE 3: Limiting apparent molar volumes (V_{ϕ}^o) and experimental slopes (S_V^*) of sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures

Mole fraction of ethane-1,2- diol	$V_{\phi}^o \times 10^6 (\text{m}^3 \text{mol}^{-1})$			$S_V^* \times 10^6 (\text{m}^3 \text{mol}^{-3/2} \text{dm}^{3/2})$		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
Sodium molybdate						
0.0312	129.27	159.40	196.73	-142.44	-229.13	-370.98
0.0677	112.07	138.58	174.46	-114.37	-167.67	-275.93
0.1106	98.401	123.80	142.76	-87.05	-124.49	-197.92
Sodium tungstate						
0.0312	133.53	163.74	196.65	-119.91	-215.01	-341.53
0.0677	107.08	159.28	176.10	-46.15	-207.53	-254.70
0.1106	95.53	134.31	146.72	-31.66	-141.55	-180.09

TABLE 4: Values of the coefficients of equation (4) for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol.

Mole fraction of ethane-1,2-diol	$a_0(\text{m}^3\text{mol}^{-1})$	$a_1(\text{m}^3\text{mol}^{-1}\text{K}^{-1})$	$a_2(\text{m}^3\text{mol}^{-1}\text{K}^{-2})$
Sodium molybdate			
0.0312	2538.441	-18.8138	0.0360
0.0677	3630.617	-25.7845	0.0469
0.1106	-3617.255	22.0628	-0.0322
Sodium tungstate			
0.0312	473.1154	-5.164	0.0135
0.0677	17701.946	112.475	-0.1769
0.1106	-13169.706	83.788	-0.1318

TABLE 5: Limiting partial molar expansibilities for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1, 2-diol at different temperatures

Mole fraction of ethane-1,2-diol	$\emptyset_E^0(\text{m}^3\text{mol}^{-1}\text{K}^{-1})$			$(\partial\emptyset_E^0/\partial T)_P$ ($\text{m}^3\text{mol}^{-1}\text{K}^{-2}$)
	298.15K	308.15K	318.15K	
Sodium molybdate				
0.0312	2.6530	3.3730	4.0930	0.0720
0.0677	2.1820	3.1200	4.0580	0.0938
0.1106	-2.8619	-2.2179	-1.5739	-0.0644
Sodium tungstate				
0.0312	2.8861	3.1561	3.4261	0.0270
0.0677	6.9890	3.4510	0.0870	-0.3538
0.1106	5.1957	2.5597	-0.0763	-0.2636

TABLE 6: Values of *A* and *B* coefficients for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures.

Mole fraction of ethane 1,2- diol	<i>A</i> , dm ^{3/2} mol ^{-1/2}			<i>B</i> , dm ³ mol ⁻¹		
	298.15 K	308.15K	318.15K	298.15K	308.15K	318.15K
Sodium molybdate						
0.0312	-0.0478	-0.0504	-0.0535	0.7272	0.8746	0.9493
0.0677	-0.0067	-0.0211	-0.0329	0.6606	0.7610	0.8445
0.1106	-0.0056	-0.0083	-0.0108	0.6226	0.6977	0.7792
Sodium tungstate						
0.0312	-0.0118	-0.0145	-0.0165	0.7891	0.8733	0.9720
0.0677	-0.0122	-0.0135	-0.0176	0.6842	0.7678	0.8494
0.1106	-0.0102	-0.0126	-0.0139	0.6311	0.6834	0.7608

TABLE 7: Values of \bar{V}_1^o , \bar{V}_2^o , $\Delta\mu_1^{o\neq}$, $\Delta\mu_2^{o\neq}$, $T\Delta S_2^{o\neq}$ and $\Delta H_2^{o\neq}$ for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions (x_1) of ethane-1,2-diol at different temperatures.

Parameter	mole fraction of ethane-1,2-diol $x_1=0.0312$			mole fraction of ethane-1,2-diol $x_1=0.0677$			mole fraction of ethane-1,2-diol $x_1=0.1106$		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
$\bar{V}_1^o \times 10^6$ $\text{m}^3\text{mol}^{-1}$	19.1855	20.8527	22.8122	18.9456	20.5749	22.5182	18.7008	20.2867	22.2491
$\Delta\mu_1^{o\neq}$, KJ mol^{-1}	27.0272	27.5454	28.2401	27.5736	28.1325	28.7919	28.1606	28.6840	29.2758
Sodium molybdate									
$\bar{V}_2^o \times 10^6$ $\text{m}^3\text{mol}^{-1}$	129.27	159.40	196.73	112.07	138.58	174.46	98.401	123.80	142.76
$\Delta\mu_2^{o\neq}$, KJ mol^{-1}	42.1900	45.6418	49.5068	40.6222	43.7739	47.6317	39.5501	42.6376	44.5292
$T\Delta S_2^{o\neq}$, KJ mol^{-1}	-109.122	-112.782	-116.442	-104.501	-108.006	-111.511	-74.239	-76.729	-79.2193
$\Delta H_2^{o\neq} \times 10^3$ KJ mol^{-1}	-66.9329	-67.1411	-66.936	-63.8793	-64.2326	-63.8798	-34.6889	-34.0914	-34.6901

Sodium tungstate									
$\bar{V}_2^o \times 10^6$ $\text{m}^3\text{mol}^{-1}$	133.53	163.74	196.65	107.08	159.28	176.10	95.53	134.31	146.72
$\Delta\mu_2^{o\ddagger}, \text{KJ}$ mol^{-1}	42.8203	46.1784	49.5238	40.0002	46.3599	47.8301	39.1810	43.9108	44.9781
$T\Delta S_2^{o\ddagger}, \text{KJ}$ mol^{-1}	-99.8802	-103.230	-106.580	-116.427	-120.332	-124.237	-86.3144	-89.2094	-92.1044
$\Delta H_2^{o\ddagger} \times 10^3$ KJ mol^{-1}	-57.0599	-57.0518	-57.0519	-76.4273	-73.9726	-76.4074	-47.1334	-45.2986	-47.1263

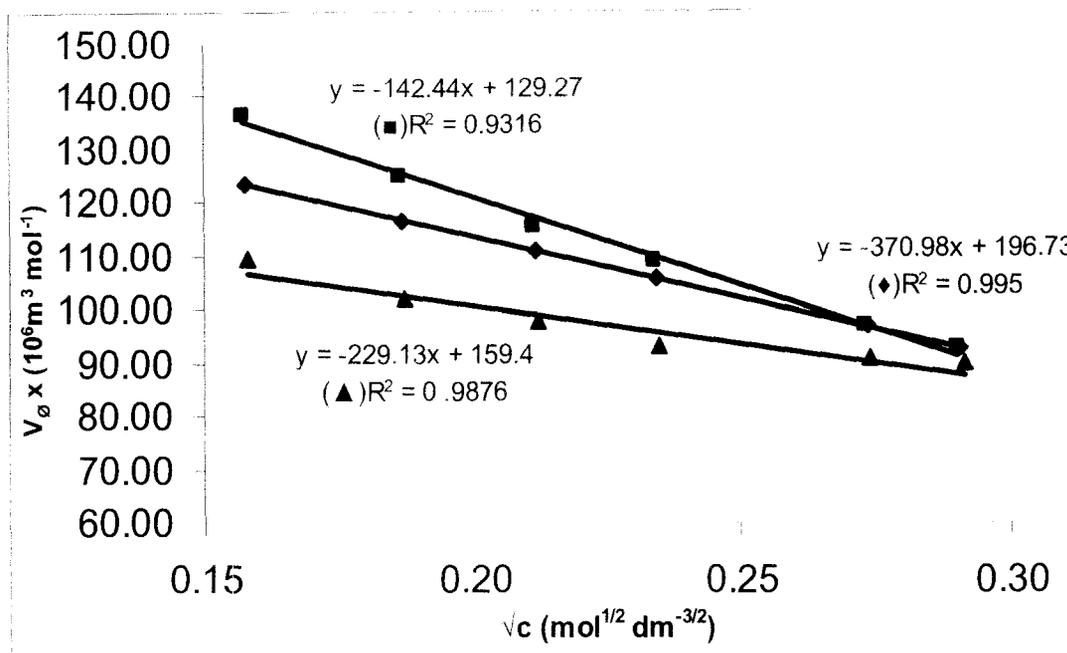


FIGURE 1. The apparent molar volume (V_{ϕ}^0) of sodium molybdate in the mixture of aqueous ethane-1, 2-diol ($x_1 = 0.0312$) as a function of square root of concentration (\sqrt{c}) at 298.15(▲), 308.15(◆) and 318.15 K(■). The lines represent the linear fits.

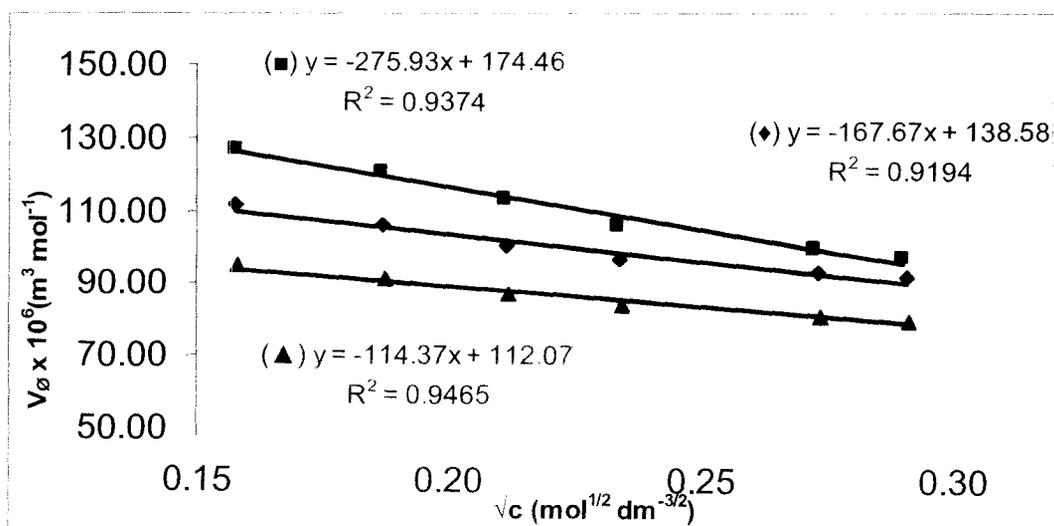


FIGURE 2. The apparent molar volume (V_{ϕ}^0) of sodium molybdate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.0677$) as a function of square root of concentration (\sqrt{c}) at 298.15(▲), 308.15(◆) and 318.15 K(■). The lines represent the linear fits.

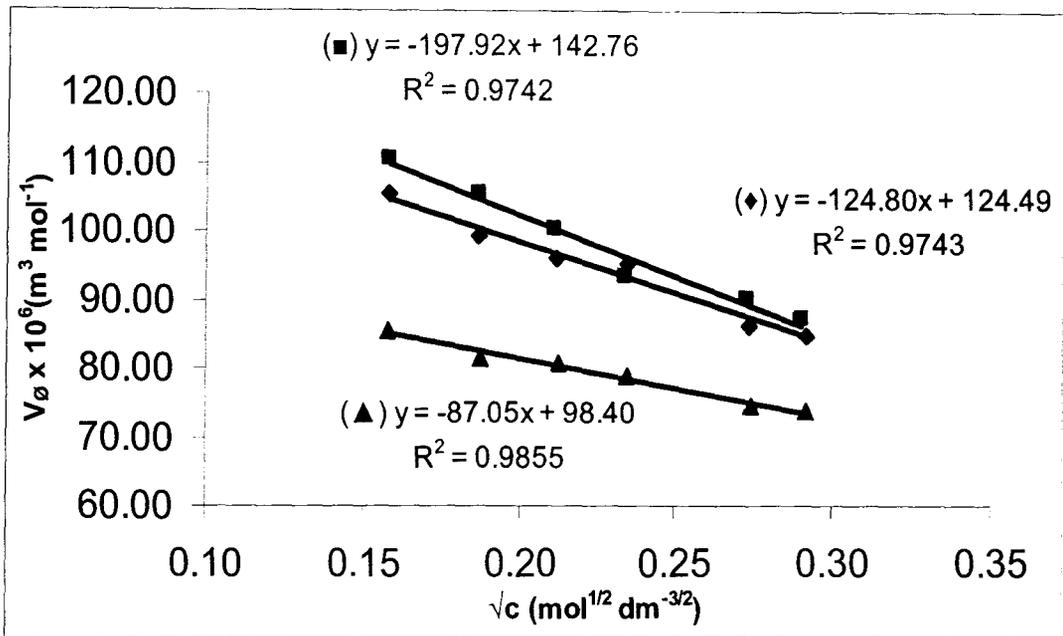


FIGURE 3. The apparent molar volume (V_{ϕ}°) of sodium molybdate in the mixture of aqueous ethane-1,2-diol ($x_1= 0.1106$) as a function of square root of concentration (\sqrt{c}) at 298.15(▲), 308.15(◆) and 318.15 K(■).The lines represent the linear fits.

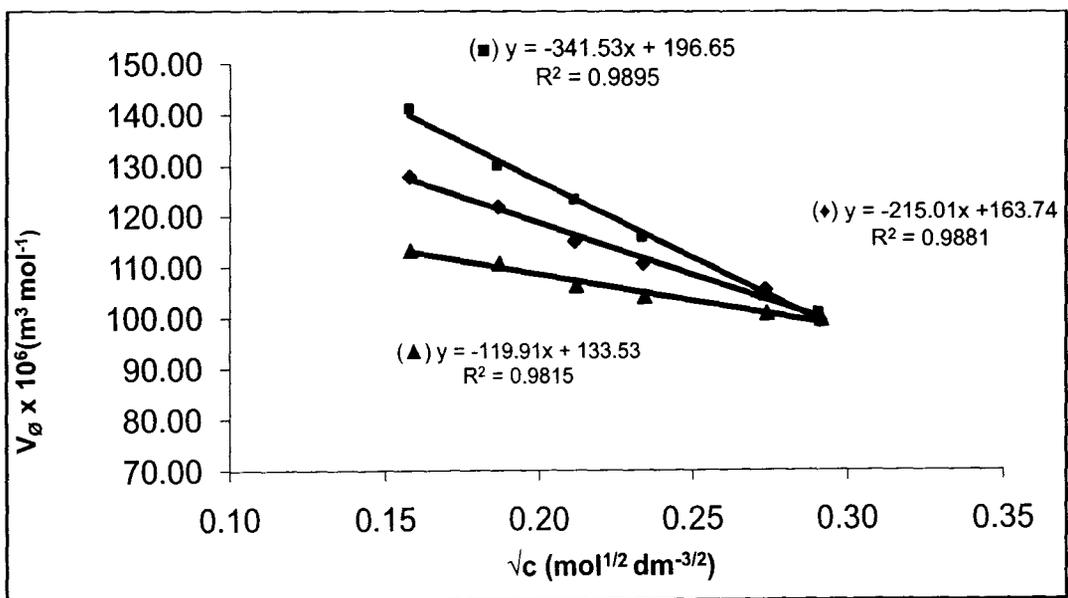


FIGURE 4. The apparent molar volume (V_{ϕ}°) of sodium tungstate in the mixture of aqueous ethane-1,2-diol ($x_1= 0.0312$) as a function of square root of concentration (\sqrt{c}) at 298.15(▲), 308.15(◆) and 318.15 K(■).The lines represent the linear fits.

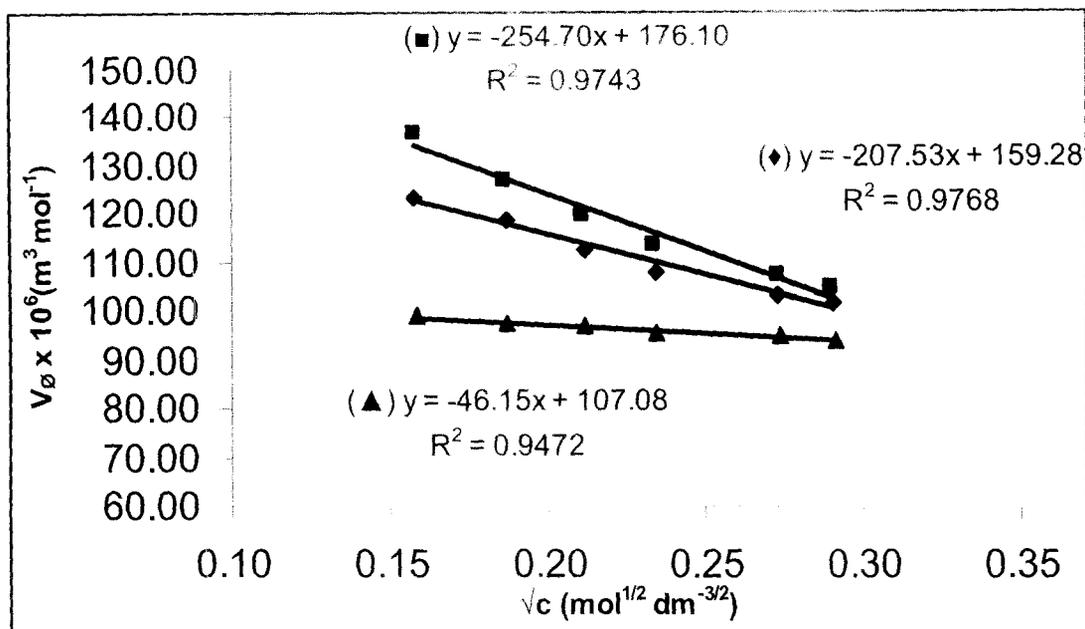


FIGURE 5. The apparent molar volume (V_{ϕ}^0) of sodium tungstate in the mixture of aqueous ethane-1,2-diol ($x_1= 0.0677$) as a function of square root of concentration (\sqrt{c}) at 298.15(▲), 308.15(◆) and 318.15 K(■).The lines represent the linear fits.

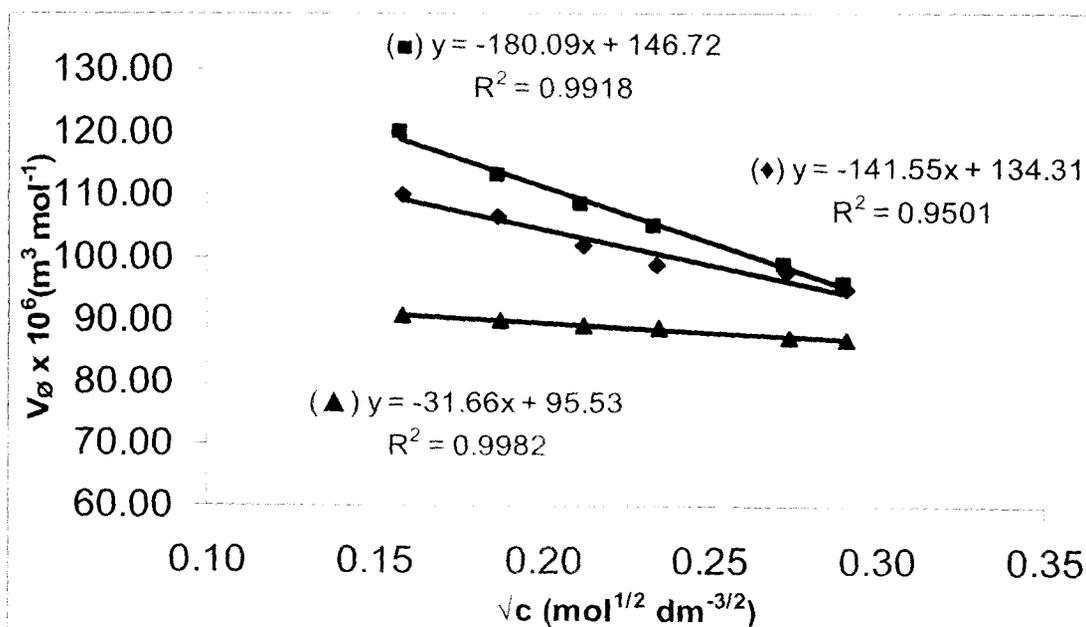


FIGURE 6. The apparent molar volume (V_{ϕ}^0) of sodium tungstate in the mixture of aqueous ethane-1,2-diol ($x_1= 0.1106$) as a function of square root of concentration (\sqrt{c}) at 298.15(▲), 308.15(◆) and 318.15 K(■).The lines represent the linear fits.

CHAPTER VII

Ion- Pair and Triple- Ion Formation by Some Tetraalkylammonium Iodides in Binary Mixtures of Carbontetrachloride + Nitrobenzene.

7.1. Introduction

Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore the ion-ion and ion-solvent interactions can be better studied. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration-dependence of the electrolyte conductivity. Consequently a number of conductometric [1] and related studies of different electrolytes in non-aqueous solvents, specially mixed organic solvents, have been made for their optimal use in high energy batteries [2] and for understanding organic reaction mechanisms [3]. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions [4-8], which in its turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Thus extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years [9-13] to examine the nature and magnitude of ion-ion and ion-solvent interactions. Also tetraalkylammonium salts are characterized by their low surface charge density and they show little or no solvation in solution [14, 15] as such they are frequently selected as desired electrolytes in conductance studies. In continuation of our investigation on electrical conductance [8,10,11] the present work deals with the conductance measurements of some tetraalkylammonium iodides, R_4NI (R=butyl to heptyl) in binary mixtures of carbon tetrachloride (CCl_4)- a nonpolar aprotic liquid and nitrobenzene ($PhNO_2$) polar aprotic liquid at 298.15 K.

**Published in Journal of Chemical and Engineering Data* 54 (2009) 2429

7.2. Experimental Section

7.2.1. Materials.

Carbon tetrachloride, CCl_4 and nitrobenzene, PhNO_2 were purchased from Merck, India and purified as reported earlier [16]. The purities as checked by gas chromatography were better than 99.5% for carbon tetrachloride and 99.6% for nitrobenzene. The salts Bu_4NI (*N,N,N*-tributyl-1-butaminium iodide, CAS: 311-28-4), Pen_4NI (*N,N,N*-tripentyl-1-pentaminium iodide, CAS: 2498-20-6), Hex_4NI (*N,N,N*-trihexyl-1-hexaminium iodide, CAS: 2138-24-1) and Hept_4NI (*N,N,N*-triheptyl-1-heptaminium iodide, CAS: 3535-83-9) of prouiss grade were purchased from Aldrich, Germany and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium [17]. After filtration, the salts were dried in an oven for few hours.

7.2.2. Apparatus and Procedure.

Binary solvent mixtures were prepared by mixing required volume of CCl_4 and PhNO_2 with earlier conversion of required mass of each liquid into volume at 298.15 K using experimental densities. A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The conversion of molality into molarity was accomplished using density values. The uncertainty of molarity of different salt solutions is evaluated to $\pm 0.0001 \text{ mol.dm}^{-3}$.

The values of relative permittivity (ϵ_r) of the solvent mixtures were obtained by interpolation of the solvent permittivity data from the literature [18] by cubic spline fitting. The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. Densities were measured with an Ostwald -Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene [19]. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at $\pm 0.01 \text{ K}$ of the desired temperature.

The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The uncertainty of density values is $\pm 3 \times 10^{-4}$ g.cm⁻³. Solvent viscosities were 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]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa.s. The details of the methods and measurement techniques had been described elsewhere [11, 23]. The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10 having cell constant $0.1 \pm 10\%$. Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K and the cell was calibrated by the method proposed by Lind et. al. [24]. The conductance data were reported at a frequency of 1 KHz and were uncertain to $\pm 0.3\%$.

7.3. Results and discussion

The concentrations and molar conductances Λ of R₄NI (R=butyl to heptyl) in different binary solvent mixtures of carbon tetrachloride and nitrobenzene are given in Table 2.

For the solvent mixtures in the range of higher to moderate relative permittivity ($\epsilon_r=29.66-17.45$), the conductance curves (Λ versus \sqrt{c}) were linear and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolytes, but as the relative permittivity (ϵ_r) dropped

to 10.22 for the solvent mixture containing 80 mass% of CCl₄ in PhNO₂ non-linearity (Figure 1) was observed in conductance curves. Thus the conductance data, in the solvent mixtures ($w_1 = 0.20 - 0.60$) wherein higher clusters other than ion-pair formation was not expected, were analyzed by the Lee-Wheaton conductance equation [25] in the form,

$$\Lambda = \alpha_i \left\{ \Lambda_o [1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3] - \frac{\rho \kappa}{1 + \kappa R} \left[1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \right\} \quad (1)$$

The mass action law association [26] is

$$K_A = \frac{(1 - \alpha_i) \gamma_A}{\alpha_i^2 c_i \gamma_{\pm}^2} \quad (2)$$

and the equation for the mean ionic activity coefficient

$$\gamma_{\pm} = \exp \left[- \frac{q \kappa}{1 + \kappa R} \right] \quad (3)$$

where C_1 to C_5 are least square fitting coefficients as described by Pethybridge and Taba [25], Λ_o is the limiting molar conductivity, K_A , is the association constant, α_i is the dissociation degree, q is the Bjerrum parameter and γ the activity coefficient and $\beta = 2q$. The distance parameter R is the least distance that two free ions can approach before they merge into ion pair. The Debye parameter κ , the Bjerrum parameter q and ρ [25] are defined by the expressions

$$\kappa = 16000 \pi N_A q c_i \alpha_i \quad (4)$$

$$q = \frac{e^2}{8 \epsilon_o \epsilon_r k T} \quad (5)$$

$$\rho = \frac{F e}{299.79 \times 3 \pi \eta} \quad (6)$$

where the symbols have their usual significance [27].

The Eq.1 was resolved by an iterative procedure. For a definite R value the initial value of Λ_o and K_A were obtained by the Kraus-Bray method [28]. The parameter Λ_o and K_A were made to approach gradually their best

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values by a sequence of alternating linearization and least squares optimizations by the Gauss-Siedel method [29] until satisfying the criterion for convergence. The best value of a parameter is the one when Eq.1 is best fitted to the experimental data corresponding to minimum standard deviation (σ_{Λ}) for a sequence of predetermined R value and standard deviation (σ_{Λ}) was calculated by the following equation,

$$\sigma_{\Lambda}^2 = \sum_{i=1}^n \frac{[\Lambda_i(\text{calc}) - \Lambda_i(\text{obs})]^2}{n - m} \quad (7)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two parameter fit ($m = 2$). As for the electrolytes studied in the solvent mixtures ($w_1 = 0.20 - 0.60$) no significant minima observed in the σ_{Λ} versus R curves and the R values were arbitrarily preset at the centre to centre distance of solvent-separated pair [8]:

$$R = a + d \quad (8)$$

where a is the sum of the crystallographic radii of the cation and anion and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of d and related terms have already been described in the literature [8]. R was generally varied by a step 0.1\AA and the iterative process was continued with Eq.1.

Table 3 reveals that the limiting molar conductances (Λ_o) for the electrolytes decreases with the increase of CCl_4 content in the solvent mixtures. This fact is in line with the decrease of the relative permittivity (ϵ_r) of the solvent mixtures [14, 30]. Although, the decreasing trend of viscosity for the solvent mixtures with increasing content of CCl_4 suggests concomitant increase in limiting molar conductances [14, 30] for the electrolytes, but we observed an opposite trend. This trend suggests predominance of relative permittivity (ϵ_r) over the solvent viscosity (η_o) in effecting the electrolytic conductances in these media. In a particular solvent mixture the limiting molar conductances

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(Λ_o) of the electrolytes under investigation decreases as the size of the alkyl group increases, in contraposition to the conductance behaviour of the alkali metal cations, as tetraalkylammonium salts are characterized by their low surface charge density [14, 15].

The decreasing trend of Walden products ($\Lambda_o\eta_o$) in Table 3 is mainly in accordance with the concomitant decrease of both the solvent viscosity and limiting molar conductance of the electrolytes. The ionic conductances (λ_o^\pm) for the various cations (R=butyl to hexyl) in different solvent mixtures ($w_1 = 0.20 - 0.60$) were calculated using tetrabutylammonium tetraphenyl borate (Bu_4NBPh_4) as a reference electrolyte following the scheme as suggested by B. Das et. al [31]. We calculated its limiting molar conductances (λ_o^\pm) in our solvent compositions by interpolation of conductance data from literature [18] using cubic spline fitting. The λ_o^\pm values were in turn utilizing for the calculation of Stoke's radii (r_s) according to the classical expression [32],

$$r_s = \frac{F^2}{6\pi N_A \eta_o \lambda_o^\pm} \quad (9)$$

Ionic Walden products ($\lambda_o^\pm\eta_o$), Stoke's radii (r_s) and crystallographic radii (r_c) are presented in Table 4. The trend in ionic Walden products ($\lambda_o^\pm\eta_o$) just mimics the trend in Walden product ($\Lambda_o\eta_o$) for all electrolytes in the solvent mixtures ($w_1 = 0.20 - 0.60$). The position of the curves in Figure 2 ($\Lambda_o\eta_o$ or $\lambda_o^\pm\eta_o$ versus w_1) suggest a relationship $\text{Bu}_4\text{NI}^+ < \text{Pen}_4\text{NI}^+ < \text{Hex}_4\text{NI}^+ < \text{Hep}_4\text{NI}^+$ for this radius, just similar to their ionic radii order. For tetraalkylammonium ions, the Stokes' radii are lower than their crystallographic radii (r_c), particularly for smaller ions. This suggests that these ions are comparatively less solvated than alkali metal ions due to their intrinsic low surface charge density.

The conductance data for all the electrolytes in 80 mass% of CCl_4 in PhNO_2 ($\epsilon_r=10.22$) was analyzed by the classical Fuoss-Kraus theory of triple ion formation in the form [33, 34]:

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_o}{\sqrt{K_p}} + \frac{\Lambda_o^T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_o}\right) c \quad (10)$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by:

$$g(c) = \frac{\exp(-2.303\beta'\sqrt{c\Lambda}/\Lambda_o^{0.5})}{(1 - S\sqrt{c\Lambda}/\Lambda_o^{0.5})(1 - \Lambda/\Lambda_o)^{0.5}} \quad (11)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5} \quad (12)$$

$$S = \alpha\Lambda_o + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_o + \frac{82.501}{\eta(\epsilon T)^{0.5}} \quad (13)$$

In the above equations, Λ_o is the sum of the molar conductance of the simple ions at infinite dilution and Λ_o^T is the sum of the conductances of the two triple ions $R_4N(I_2)^-$ and $(R_4N)^+I$ for R_4NI salts, $K_p \approx K_A$ and K_T) are the ion-pair and triple-ion formation constants. To make eq 10 applicable, the symmetrical approximation of the two possible constant of triple ions equal to each other has been adopted and Λ_o values for the studied electrolytes in 80 mass% of CCl_4 in $PhNO_2$ have been calculated using respective Λ_o and η_o values in 60 mass% of CCl_4 in $PhNO_2$ according to the Walden rule [14, 30]. Λ_o^T is calculated by setting the triple-ion conductance equal to $2/3 \Lambda_o$ [35]. The ratio Λ_o^T/Λ_o was thus set equal to 0.667 during linear regression analysis of eq 10.

Linear regression analysis of eq 10 for the electrolytes with an average regression constant, $R^2 = 0.9653$ gives intercepts and slopes; these permit the calculation of other derived parameters such as K_p and K_T listed in Table 5. A perusal of Table 5 shows that the major portion of the electrolytes exists as ion-pairs with a minor portion as triple ions. Using the K_p values, the inter-ionic distance parameter a_{ip} has been calculated with the aid of the Bjerrum's theory of ionic association [36] in the form:

$$K_p = \frac{4\pi N_A}{1000} \exp\left[\frac{e^2}{\epsilon_r kT}\right]^3 Q(b) \quad (14)$$

$$Q(b) = \int_2^b y^{-4} \exp(y) dy \quad (15)$$

$$b = \frac{e^2}{a_{IP} \epsilon_r kT} \quad (16)$$

The a_{IP} values obtained are given in Table 6. The $Q(b)$ and b values have been calculated by the literature procedure [36]. Table 6 reveals that a_{IP} values are almost similar for all the electrolytes though the actual ionic sizes varied by 0.28-0.35 Å. This may be due to easy penetration by I^- ion to some extent into the void spaces between the alkyl chains, as suggested by Abbott and Schiffrin [37]. Thus increase in chain length for tetraalkylammonium ions does not greatly affect the distance of closest approach between the two ions. The a_{IP} are much less in comparison with the crystallographic radii (r_c) suggesting probable contact ion-pairs for the iodides in solution [14]. This will cause a decrease in the degree of freedom for the cations in the ion-pair resulting in their loss of configurational entropy of the contact pair. Generally K_p values do not change significantly for quaternary ammonium ions with alkyl chain consisting of carbon atoms more than 3. The small changes in the K_p may thus be related to entropic contributions. The inter-ionic distance a_{TI} for triple ion can be calculated using the expressions [33]:

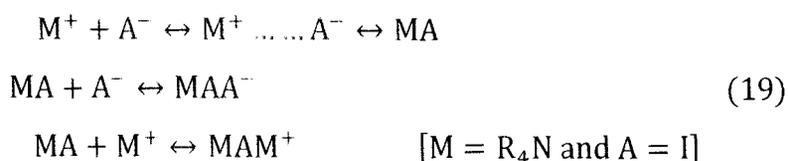
$$K_T = \frac{2\pi N_A a_{TI}^3}{1000} I(b_3) \quad (17)$$

$$b_3 = \frac{e^2}{a_{TI} \epsilon_r kT} \quad (18)$$

$I(b_3)$ is a double integral tabulated in the literature [33] for a range of values of b_3 . Since $I(b_3)$ is a function of a_{TI} , a_{TI} values have been calculated by an iterative computer program. The a_{TI} values (Table 6) for the electrolytes are greater than the corresponding a_{IP} values but are much less than the expected theoretical value $5a_{IP}$. This is probably due to repulsive forces between the two anions or cations in the triple ions $R_4N(I_2)^-$ and $(R_4N)^+I$ as suggested by Hazra et al [38].

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A perusal of Table 5 shows that the major portion of the electrolytes exists as ion-pairs with a minor portion as triple ions. The tendency of triple ion formation can be judged from the K_T/K_P ratios, which is highest for Hept₄NI. These ratios suggest that strong association between the ions is due to the coulombic interactions as well as to covalent forces in the solution. This results are in good agreement with those of Hazra and Muhuri et. al [39]. At very low permittivity of the solvent ($\epsilon_r < 15$) [30], electrostatic interactions are very strong permitting the ion-pair to attract free anions/cations from solution bulk and form triple ions [33,38] which acquire the charge of the combining ion, i.e.:



The effect of ternary association [40] thus removes some non-conducting species MA from solution and replace them by triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the electrolytes in 80 mass% of CCl₄ in PhNO₂.

The ion-pair and triple-ion concentrations (C_P and C_T , respectively) of the electrolytes at the highest electrolyte concentration have been derived using eqs [41] 20 to 23 and are listed in Table 5.

$$\alpha = (K_P c)^{-0.5} \quad (20)$$

$$\alpha_T = \frac{K_T}{\sqrt{K_P}} c^{0.5} \quad (21)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \quad (22)$$

$$C_T = \frac{K_T}{\sqrt{K_P}} c^{1.5} \quad (23)$$

Ion- Pair and Triple- Ion..... of Carbontetrachloride + Nitrobenzene.

While highest C_p value is for Bu_4NI , $Hept_4NI$ has the highest C_T value and our results supports the general view that the tendency of ion-pair and triple-ion formation depends on the size and the charge distribution of the ions as well as on the solvent polarity.

7.4. Conclusion

From the experimental work it is evident that the tetraalkyl ammonium salts exists as ion-pairs upto 60 mass% of solvent mixture but as the dielectric constant of the solvent mixture decreases in 80 mass% , there is a tendency for triple ion pair formation.

Acknowledgment. The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

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TABLE 1: Density (ρ), viscosity (η), and dielectric constant (ϵ_r) of CCl_4 (1) + PhNO_2 (2) at T=298.15 K

Solvent Mixture	$\rho \times 10^{-3}$ (kg m ⁻³)		η (mPa. s)		ϵ_r
	Exp.	Lit.	Exp.	Lit.	
$w_1 = 0.00$	1.1982	1.1985[40]	1.686	1.686[41]	34.69[18]
$w_1 = 0.20$	1.2614		1.613		29.66 ^b
$w_1 = 0.40$	1.3314		1.411		23.90 ^b
$w_1 = 0.60$	1.4067		1.224		17.45 ^b
$w_1 = 0.80$	1.4910		1.099		10.22 ^b
$w_1 = 1.00$	1.5843	1.5844[41]	0.902	0.9017[41]	2.25[41]

^bObtained by interpolation of literature data from Ref. No 18.

TABLE 2: The concentrations (c) and molar conductances (Λ) of R_4NI (R =Butyl to heptyl) in different binary solvent mixtures of CCl_4 (1) + $PhNO_2$ (2) at 298.15 K

Bu ₄ NI		Pen ₄ NI		Hex ₄ NI		Hept ₄ NI	
$c \times 10^4$	Λ						
(mol dm ⁻³)	(S. cm ² mol ⁻¹)	(mol dm ⁻³)	(S. cm ² mol ⁻¹)	(mol dm ⁻³)	(S. cm ² mol ⁻¹)	(mol dm ⁻³)	(S. cm ² mol ⁻¹)
$w_1 = 0.20$							
8.3	39.50	8.3	38.60	8.4	36.38	8.3	35.20
15.3	37.00	15.3	36.00	15.3	34.66	15.3	33.20
21.2	35.80	21.2	34.90	21.2	33.14	21.2	32.33
26.2	34.68	26.2	34.20	26.3	32.14	26.2	31.22
30.6	34.00	30.6	33.00	30.64	31.66	30.6	30.72
34.4	33.50	34.4	33.00	34.5	30.50	34.4	30.20
37.8	32.80	37.8	31.70	37.8	30.30	37.8	29.89
40.8	32.10	40.8	31.30	40.8	29.80	40.8	29.30
45.9	31.70	43.5	30.60	43.5	29.40	45.9	29.00
50.1	30.50	48.1	29.70	46.0	29.37	50.1	28.40
53.6	30.00	51.9	29.27	50.1	28.92	53.6	28.19
57.8	29.40	55.1	28.66	51.9	28.49	56.5	27.70
61.2	29.20	57.8	28.52	55.1	28.29	59.0	27.62

64.0	28.59	61.2	28.08	57.9	27.82	61.2	27.28
66.3	28.34	64.0	27.80	60.2	27.23	63.1	27.25
68.3	28.26	66.3	27.58	63.2	27.22	65.6	27.00
69.9	28.01	68.3	27.37	65.7	27.11	67.6	26.76
71.4	28.00	70.5	27.23	67.1	26.98	69.4	26.51
72.3	27.80	72.3	26.96	69.5	26.62	70.9	26.36
73.8	27.76	74.2	26.95	71.5	26.44	72.7	26.28
$w_1 = 0.40$							
4.4	38.80	4.4	36.89	4.4	35.50	4.6	34.61
8.1	37.00	6.3	36.00	6.3	35.25	6.6	33.82
11.3	35.80	8.1	35.20	8.0	34.18	8.4	32.71
13.9	34.56	9.7	34.56	9.7	33.86	10.1	32.31
16.3	33.37	11.2	34.00	11.1	33.39	11.6	31.84
18.3	32.83	13.9	32.90	12.8	32.47	13.1	31.35
20.1	32.30	16.2	32.34	13.8	32.10	14.4	30.91
23.1	31.50	18.2	31.43	14.9	32.04	15.7	30.54
25.6	30.43	20.0	30.70	17.1	31.23	17.9	29.82
27.6	30.19	21.6	30.50	19.0	30.86	19.9	29.66
29.3	29.81	23.0	30.14	20.7	30.30	21.6	29.16
31.4	29.32	24.3	29.38	22.2	29.75	23.2	28.61
33.1	28.97	26.5	29.30	23.5	29.21	24.6	28.60
34.4	28.44	28.4	29.06	24.7	29.16	25.9	28.24
35.6	28.36	29.9	28.68	25.8	28.77	27.0	27.99
36.9	27.91	31.2	28.22	27.7	28.41	29.0	27.54

37.9	27.66	32.9	27.94	29.3	27.64	30.7	27.37
39.0	27.40	34.3	27.69	30.7	27.73	32.1	26.95
39.9	27.29	35.5	27.35	31.9	27.48	33.4	26.81
40.7	27.29	36.7	26.94	33.4	26.93	34.5	26.40
$w_1 = 0.60$							
1.7	36.41	1.7	34.60	1.7	33.30	1.7	32.30
2.5	34.82	2.4	33.05	2.4	32.51	2.4	31.60
3.2	34.12	3.1	32.50	3.1	31.40	3.1	30.80
3.8	32.94	3.8	31.40	3.7	30.48	3.8	30.05
4.4	32.12	4.3	30.70	4.3	30.20	4.3	29.73
4.9	31.31	4.9	30.00	4.8	29.70	4.9	28.93
5.4	30.94	5.4	29.50	5.3	29.00	5.4	28.67
5.9	30.44	5.8	29.10	5.8	28.60	5.8	28.11
6.3	29.80	6.3	28.90	6.2	28.40	6.3	28.00
7.1	29.21	6.7	28.50	6.6	28.00	6.7	27.70
7.8	28.20	7.0	27.96	7.4	27.56	7.0	27.20
8.4	27.66	7.7	27.70	7.7	27.14	7.7	26.87
8.9	27.18	8.3	26.94	8.3	26.71	8.4	26.33
9.5	26.81	8.9	26.63	8.9	26.30	8.9	25.94
9.9	26.50	9.4	26.08	9.3	25.88	9.4	25.74
10.7	25.86	9.8	25.71	9.8	25.80	10.2	24.96
11.4	25.42	10.6	25.40	10.6	25.26	11.3	24.02
11.9	25.31	11.3	24.60	11.2	24.87	11.8	23.82
12.6	24.62	11.8	24.51	11.8	24.46	12.3	23.54
13.2	24.54	12.3	24.29	12.2	24.24	12.9	23.29

$w_1 = 0.80$

1.7	4.07	1.7	3.72	1.7	3.72	1.7	3.64
2.4	3.57	2.4	3.27	2.4	3.20	2.4	3.38
3.1	3.26	3.1	2.96	3.1	2.95	3.1	3.09
3.8	3.03	3.8	2.71	3.8	2.75	3.8	2.90
4.3	2.93	4.3	2.49	4.3	2.61	4.3	2.72
4.9	2.81	4.9	2.36	4.9	2.50	4.9	2.63
5.4	2.72	5.4	2.25	5.4	2.40	5.4	2.51
5.8	2.59	5.8	2.16	5.8	2.31	5.8	2.43
6.3	2.55	6.3	2.10	6.3	2.28	6.3	2.36
7.0	2.45	7.0	2.00	7.0	2.21	6.7	2.29
7.7	2.33	7.7	1.87	7.7	2.13	7.0	2.23
8.4	2.26	8.3	1.82	8.4	2.05	7.7	2.17
8.9	2.19	8.9	1.74	8.9	1.98	8.4	2.08
9.4	2.15	9.4	1.72	9.4	1.95	8.9	2.02
10.2	2.05	9.8	1.68	10.2	1.87	9.4	1.97
10.9	2.01	10.6	1.66	10.9	1.81	9.8	1.94

TABLE 3: Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R), standard deviations of experimental Λ from Eq.1 and Walden products for the electrolytes in different binary solvent mixtures of CCl_4 (1) + PhNO_2 (2) at 298.15 K

w_1	$\Lambda_o \times 10^4$ ($\text{S m}^2 \text{ mol}^{-1}$)	K_A	R (\AA)	$\Lambda_o \eta_o$ ($\text{S m}^2 \text{ mol}^{-1} \text{ mPa s}$)	σ
Bu ₄ NI					
0.20	46.23	159.89	12.01	74.57	0.24
0.40	45.71	301.14	12.36	64.49	0.22
0.60	44.94	330.52	12.67	54.99	0.25
Pen ₄ NI					
0.20	42.53	90.94	11.99	69.77	0.21
0.40	42.35	246.09	13.44	59.75	0.26
0.60	41.51	1075.34	12.65	50.79	0.26
Hex ₄ NI					
0.20	41.74	126.55	11.97	67.33	0.23
0.40	41.31	231.98	12.32	58.28	0.25
0.60	39.01	816.16	12.63	47.74	0.24
Hept ₄ NI					
0.20	39.59	99.62	11.95	63.86	0.12
0.40	39.30	195.84	12.29	55.44	0.14
0.60	38.51	851.97	12.61	47.13	0.16

TABLE 4: Limiting ionic conductance (λ_o^\pm), ionic Walden product ($\lambda_o^\pm \eta_o$), Stokes' radii (r_s) and crystallographic radii (r_c) at 298.15 K

Ion	λ_o^\pm (S m ² mol ⁻¹)	$\lambda_o^\pm \eta_o \times 10^4$ (S m ² mol ⁻¹ mPa s)	r_s (Å)	r_c (Å)
$w_1 = 0.20$				
Bu ₄ N ⁺	13.38	21.58	3.79	4.94
Pen ₄ N ⁺	9.68	15.61	5.25	5.29
Hex ₄ N ⁺	8.89	14.34	5.71	5.60
Hept ₄ N ⁺	8.74	10.87	7.53	5.88
I ⁻	32.85	52.99	1.76	2.16
$w_1 = 0.40$				
Bu ₄ N ⁺	14.97	21.12	3.93	4.94
Pen ₄ N ⁺	11.61	16.38	5.09	5.29
Hex ₄ N ⁺	10.57	14.91	5.60	5.60
Hept ₄ N ⁺	8.56	12.08	6.95	5.88
I ⁻	30.74	43.37	1.87	2.16
$w_1 = 0.60$				
Bu ₄ N ⁺	15.83	18.82	4.15	4.94
Pen ₄ N ⁺	12.40	15.18	5.26	5.29
Hex ₄ N ⁺	9.90	12.16	6.56	5.60
Hept ₄ N ⁺	9.40	11.50	6.89	5.88
I ⁻	29.11	35.62	2.32	2.16

TABLE 5: The calculated limiting molar conductance (Λ_o), slope and intercepts of Eq 1, maximum concentration (c), ion-pair formation constant K_p , triple-ion formation constant K_T , ion-pair concentration C_p , and triple-ion concentration C_T for R_4NI (R=butyl to heptyl) in 80 mass% of CCl_4 (1) + $PhNO_2$ (2) at 298.15 K

Λ_o $\times 10^4$ ($S\ m^2$ mol^{-1})	Slope	Intercept \times 10^2	$c \times 10^4$ ($mol\ dm^{-3}$)	K_p $\times 10^5$	K_T	C_p $\times 10^3$	C_T $\times 10^6$
			Bu ₄ NI				
50.04	9.069	6.164	13.3	6.59	220.57	1.24	13.10
			Pen ₄ NI				
46.22	5.824	5.265	10.6	7.71	165.84	1.01	6.54
			Hex ₄ NI				
43.44	7.121	5.408	13.1	6.45	194.42	1.23	11.48
			Hept ₄ NI				
42.88	15.422	5.235	12.3	6.71	441.69	1.12	23.31

* Maximum concentrations for which calculations have been performed

TABLE 6: Inter-ionic distance parameter (a_{TI}) and inter-ionic distance for triple ion (a_{TI}) in 80 mass% of CCl_4 (1) + $PhNO_2$ (2) at 298.15 K.

Electrolyte	a_{IP} (Å)	a_{TI} (Å)	$1.5a_{TI}$ (Å)
Bu ₄ NI	3.01	3.95	4.51
Pen ₄ NI	2.99	4.32	4.48
Hex ₄ NI	3.02	3.92	4.53
Hept ₄ NI	3.01	3.62	4.51

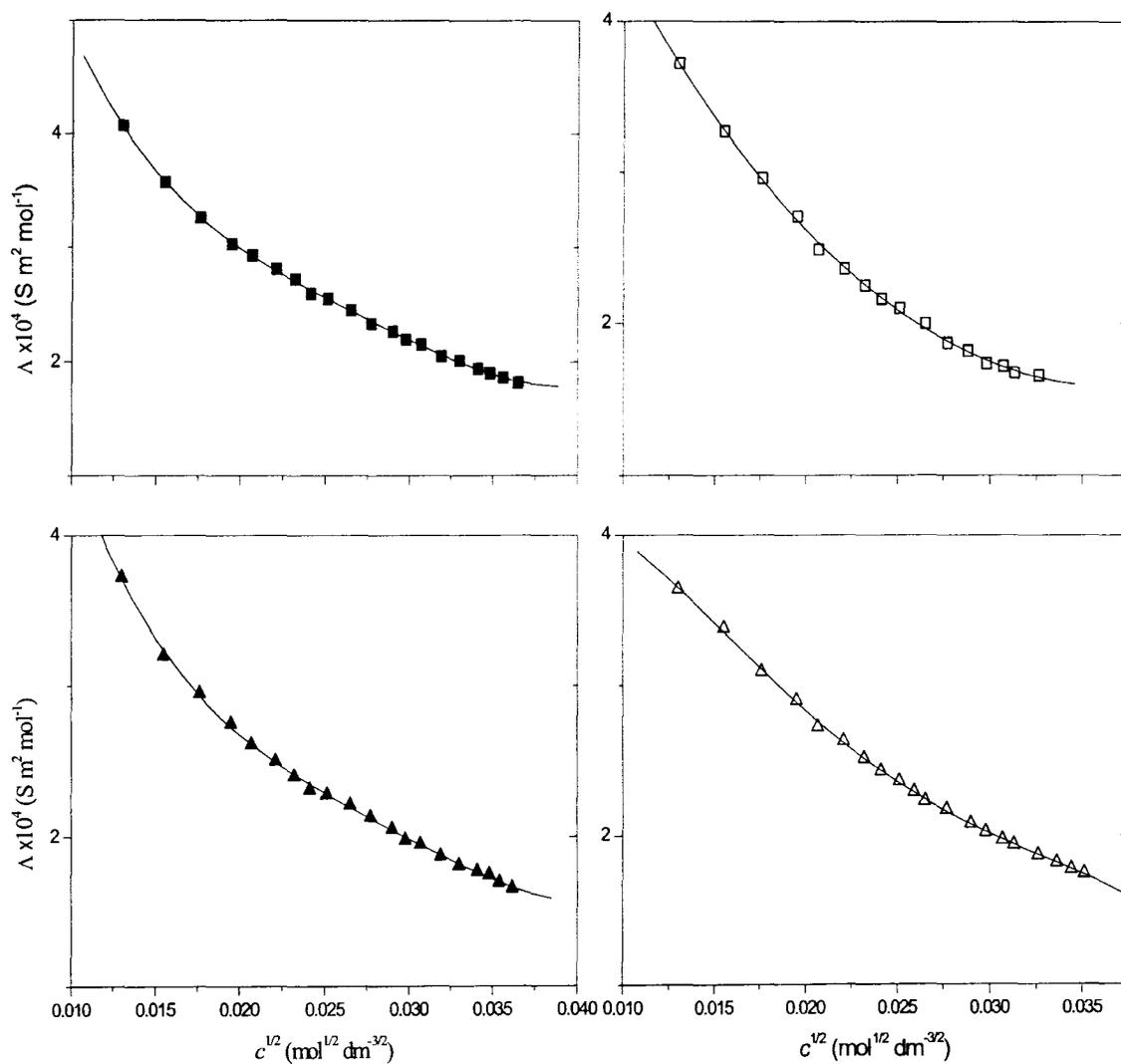


FIGURE 1: Molar conductance (Λ) versus square root of salt concentration ($c^{1/2}$) in $w_1 = 0.80$ of Carbon tetrachloride (1) + Nitrobenzene (2) at 298.15 K. Bu_4NI , \blacksquare ; Pen_4NI , \square ; Hex_4NI , \blacktriangle ; Hept_4N , \triangle .

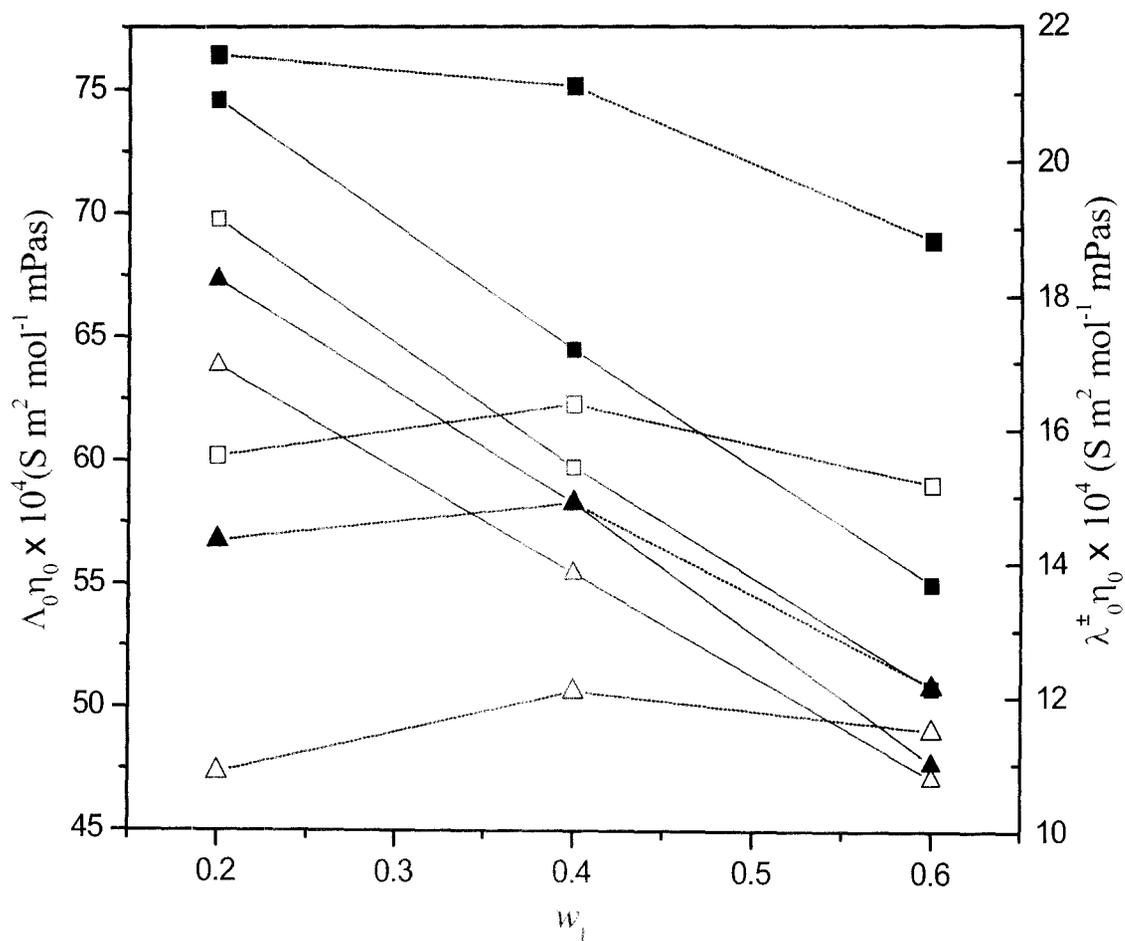


FIGURE 2: Walden products ($\Lambda_0 \eta_0$) for electrolytes and ionic Walden products ($\lambda_0^\pm \eta_0$) versus w_1 of Carbon tetrachloride (1) + Nitrobenzene (2) mixtures at 298.15 K. Solid lines, Walden products for electrolytes; dotted lines, ionic Walden products. Bu₄NI or Bu₄N⁺, ■; Pen₄NI or Pen₄N⁺, □; Hex₄NI or Hex₄N⁺, ▲; Hept₄N or Hept₄N⁺, Δ.

CHAPTER VIII

Ion-Solvent and Ion-Ion Interactions of Phosphomolybdic Acid in Aqueous Solution of Catechol at 298.15, 308.15 and 318.15K.

8.1. Introduction

Studies on densities (ρ) and viscosities (η) of solutions are of great importance in characterizing the properties and structural aspects of solutions. Hence studies on the limiting apparent molar volume and viscosity- B coefficients of electrolyte provide us valuable information regarding ion-ion, ion-solvent and solvent-solvent interactions [1-3]. It has been found by a number of workers [4-6] that the addition of a solute could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various solute concentrations and temperature.

In this paper we have attempted to report the limiting apparent molar volume (V_{ϕ}^0), experimental slopes (S_V^*) and viscosity B - coefficients for phosphomolybdic acid in aqueous catechol solution at 298.15, 308.15 and 318.15K.

Phosphomolybdic acid is widely used to stain connective tissues by dyes. It has been found that phosphomolybdic acid forms salts with connective tissues containing basic groups and hence the polyvalent phosphomolybdic acid appears to form a bridge between the basic group of the substrate and the basic group of the dye. In other words, addition of phosphomolybdic acid to connective tissues changes its acidophilia to basophilia. Phosphomolybdic acid not only yields an intense staining of

* *Published in Russian Journal of Physical Chemistry* 83 (2009) 1.

connective tissue fibers by dyes with basic groups but also reduces the staining of cytoplasm, thus producing a specific staining of connective tissue fiber [7].

8.2. Experimental Section

8.2.1 Materials

Commercial sample of catechol was purified by repeated crystallization from mixture of chloroform-methanol. The sample was dissolved in chloroform in hot condition, filtered and to the filtrate dried and distilled methanol was added drop wise. Fine plate like crystal separated and was recovered by rapid filtration and ready for use. Phosphomolybdic acid of analytical grade was purchased from Thomas Baker and was used without further purification. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was used for all measurements. Experimental values of viscosity (η), density (ρ) and pH are listed in Table 1.

8.2.2. Measurements

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of about 0.1 cm. the measurements were done in a thermostat bath controlled to $\pm 0.01 \text{ K}$. the viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to $\pm 0.1 \text{ s}$, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4} \text{ mPas}$. 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 fractions was within

±0.0002 units. The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ±0.01 mg. The precision of density measurements was ±3×10⁻⁴ g cm⁻³. Viscosity of the solution, η , is given by the following equation:

$$\eta = \left(Kt - \frac{l}{t} \right) \rho \tag{1}$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ±0.003 mPas.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere [8-11]. The electrolyte solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

8.3. Results and discussion

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation:

$$V_\phi = \frac{M}{\rho_o} - \frac{1000(\rho - \rho_o)}{c\rho_o} \tag{2}$$

Where M is the molar mass of the solute, c is the molarity of the solution; ρ_o and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volume (V_ϕ^o) was calculated using a least -squares treatment to the plots of V_ϕ versus \sqrt{c} using the following Masson equation [12].

$$V_{\phi} = V_{\phi}^{\circ} + S_V^* \sqrt{c} \quad (3)$$

where V_{ϕ}° is the apparent molar volume at infinite dilution and S_V^* the experimental slope. The plots of V_{ϕ} against square root of molar concentration (\sqrt{c}) were found to be linear with negative slopes. Values of V_{ϕ}° and S_V^* are reported in Table 3.

As the systems under study are characterized by hydrogen bonding, the ion-solvent and ion-ion interactions can be interpreted in terms of structural changes which arise due to hydrogen bonding between various components of the solvent and solution systems. V_{ϕ}° can be used to interpret ion-solvent interactions. Table 3 reveals that V_{ϕ}° values are positive and increases with rise in temperature and decreases with increase in the amount of catechol in the solvent mixture. This indicates the presence of strong ion-solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the amount of catechol in the solvent mixture under study, suggesting larger electrostriction at higher temperature and in lower amount of catechol in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous DMF [13] and aqueous THF [14].

It is evident from Table 3 that the S_V^* values are negative at all temperatures for aqueous mixtures of catechol. Furthermore S_V^* values decreases with the increase of experimental temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion-ion interactions (ionic-dissociation) [15]. A quantitative comparison of the magnitude of values shows that V_{ϕ}° values are much greater in magnitude than those of S_V^* for all the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and at all experimental temperatures.

The variation of V_{ϕ}° with temperature of phosphomolybdic acid in solvent mixture follows the polynomial,

$$V_{\phi}^{\circ} = a_0 + a_1 T + a_2 T^2 \quad (4)$$

over the temperature range under study where T is the temperature in K.

Values of coefficients of the above equation for phosphomolybdic acid in aqueous catechol mixtures are reported in Table 4.

The apparent molar expansibilities (ϕ_E^o) can be obtained by the following equation:

$$\phi_E^o = \left(\frac{\partial V_\phi^o}{\partial T} \right)_P = a_1 + 2a_2T \quad (5)$$

The values ϕ_E^o of for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. Table 5 reveals that ϕ_E^o value increases as temperature increases up to 0.05 mol. dm⁻³ of catechol mixtures but thereafter ϕ_E^o value decreases slightly with increasing temperature. This fact may be attributed to gradual disappearance of caging or packing effect [15,16] in the ternary solutions. 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 tendency of any solute. According to Helper [17] the sign of $(\partial \phi_E^o / \partial T)_P$ is a better criterion in characterizing the long-range structure-making and breaking ability of the solutes in solution. The general thermodynamic expression used is as follows

$$\left(\frac{\partial \phi_E^o}{\partial T} \right)_P = 2a_2 \quad (6)$$

If the sign of $(\partial \phi_E^o / \partial T)_P$ is positive or small negative [18] the solute is a structure maker otherwise it is a structure breaker. As is evident from Table 5, phosphomolybdic acid predominately acts as a structure maker, and its structure making ability decreases to some extent as the molarity of catechol increases in the solvent mixture. A similar result was observed in the study of nicotinamide in aqueous tetrabutylammonium bromide solution [19]. The small negative values of $(\partial \phi_E^o / \partial T)_P$ at 0.1 and 0.15 mol dm⁻³ aqueous catechol solution are probably due to higher structure promoting ability of catechol

than phosphomolybdic acid with comparatively higher V_{ϕ}° value in aqueous solution [20] originating from hydrophobic hydration with greater degree of hydrogen bonding than the bulk water [21].

Partial molar volume ΔV_{ϕ}° of transfer from water to different aqueous catechol solution has been determined using the following relation [22, 23]

$$\Delta V_{\phi}^{\circ} = V_{\phi}^{\circ} (\text{aqueous catechol solution}) - V_{\phi}^{\circ} (\text{water}) \quad (7)$$

The V_{ϕ}° value is independent from solute-solute interaction and provides information regarding solute and co-solute interaction [22]. Table 3 shows that the values of V_{ϕ}° is positive at all experimental temperatures and increases with the concentration of catechol in the ternary mixture. The concentration dependence of the thermodynamic properties of the solute in aqueous solution can be explained in terms of overlap of hydration co-sphere. According to the co-sphere model as developed by Friedman and Krishnan [24], the effect of the overlap of hydration co-sphere is destructive. The overlap of hydration co-spheres of two ionic species results in an increase in volume but that of hydration co-sphere of hydrophobic- hydrophobic group and ion- hydrophobic group results in a net volume decrease. The positive value of ΔV_{ϕ}° indicate that hydrophobic- hydrophobic and ion- hydrophobic group interaction are predominant and the overall effect of the hydration co-sphere of phosphomolybdic acid and catechol reduce the effect of electrostriction of water by phosphomolybdic acid molecule and these effect increases with the molarity of catechol in the ternary mixture as shown in the figure 1(ΔV_{ϕ}° vs. molarity of catechol in solution). In addition, standard partial molar volume of the solute has been explained by a simple model [25, 26].

$$V_{\phi}^{\circ} = V_{\phi_{vw}} + V_{\phi_{void}} - V_{\phi_s} \quad (8)$$

where $V_{\phi_{vw}}$ is the vander wall volume, $V_{\phi_{void}}$ is the volume associated with void or empty space and V_{ϕ_s} the shrinkage volume due to electrostriction. Considering the $V_{\phi_{vw}}$ and $V_{\phi_{void}}$ have the same magnitude in water and in aqueous catechol solution for the same solute [27]. The increase in V_{ϕ}^o values and the concomitant positive ΔV_{ϕ}^o can be attributed to the decrease in shrinkage volume of water by phosphomolybdic acid in presence of catechol. This fact suggests that catechol has a dehydrating effect on the hydrated phosphomolybdic acid.

The viscosity data of aqueous and aqueous catechol solution have been analyzed using Jones-Dole [28] equation:

$$\left(\frac{\eta}{\eta_o} - 1\right) / \sqrt{c} = A + B\sqrt{c} \quad (9)$$

where η_o and η are the viscosities of the solvent/solvent mixtures and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 6. From the Table it is evident that the values of the A coefficient are either negative or very small positive for all the solutions under investigation at all experimental temperatures. These results indicate the presence of very weak ion-ion interactions and these interactions further decrease with the rise of experimental temperatures and increase with an increase of catechol in the mixture.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B -coefficient [29, 30]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B -coefficient of phosphomolybdic acid in the studied solvent systems are positive, thereby suggesting the presence of strong ion - solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of catechol in the mixture. These

conclusions are in excellent agreement with those drawn from V_{ϕ}^o values discussed earlier.

Viscosity B -coefficient of transfer (ΔB) from water to different aqueous catechol solutions have been determined using the relation [22, 23]

$$\Delta B = B \text{ (aqueous catechol solution)} - B \text{ (water)} \quad (10)$$

The ΔB values as shown in Table 7 and depicted graphically in fig 2 (ΔB vs. molarity of catechol in solution) as a function of molarity of catechol in solution at the experimental temperature supports the result obtained from ΔV_{ϕ}^o as discussed above.

. The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of solutes as suggested by Feakings. et. al [31] using the following equation

$$\Delta\mu_2^{o\ddagger} = \Delta\mu_1^{o\ddagger} + \frac{(1000B + \bar{V}_2^o - \bar{V}_1^o)RT}{\bar{V}_1^o} \quad (11)$$

Where \bar{V}_1^o and \bar{V}_2^o are the partial molar volumes of the solvent and the solute respectively. The contribution per mole of the solute to the free energy of activation of viscous flow ($\Delta\mu_2^{o\ddagger}$) of the solutions was determined from the above relation and are listed in Table 8. The free energy of activation of viscous flow of the pure solvent ($\Delta\mu_1^{o\ddagger}$) is given by the relation:

$$\Delta\mu_1^{o\ddagger} = \Delta G_1^{o\ddagger} = \frac{RT \ln \eta_1 \bar{V}_1^o}{hN_A} \quad (12)$$

Where N is the Avogadro's number and the other symbols have their usual significance. The values of $\Delta\mu_2^{o\ddagger}$ and $\Delta\mu_1^{o\ddagger}$ are reported in Table 8. From Table 8 it is evident that $\Delta\mu_1^{o\ddagger}$ is practically constant at all the solvent composition and temperature, implying that $\Delta\mu_2^{o\ddagger}$ is mainly dependent on the

viscosity B -coefficients and $(\bar{V}_2^o - \bar{V}_1^o)$ terms. Also $\Delta\mu_2^{o\ddagger}$ values were found to be positive at all experimental temperatures and this suggests that the process of viscous flow becomes difficult as the temperature and molarity of catechol in solution increases. Hence the formation of transition becomes less favorable [31]. According to Feakings.et.al , $\Delta\mu_2^{o\ddagger} > \Delta\mu_1^{o\ddagger}$ for 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 [32] . The greater values of $\Delta\mu_2^{o\ddagger}$ supports the increased structure making tendency of the solute as discussed earlier. The entropy of activation for solutions has been calculated using the following relation [31].

$$-\Delta S_2^{o\ddagger} = \frac{d(\Delta\mu_2^{o\ddagger})}{dT} \quad (13)$$

Where $\Delta S_2^{o\ddagger}$ has been determined from the negative slope of the plots of $\Delta\mu_2^{o\ddagger}$ against T by using a least square treatment.

The activation enthalpy ($\Delta H_2^{o\ddagger}$) has been calculated using the relation [31]:

$$\Delta H_2^{o\ddagger} = \Delta\mu_2^{o\ddagger} + T\Delta S_2^{o\ddagger} \quad (14)$$

The value of $\Delta S_2^{o\ddagger}$ and $\Delta H_2^{o\ddagger}$ are listed in Table 8 and they are found to be negative for all the solutions and at all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state [31, 33].

8.4. Conclusion

The values of apparent molar volume (V_{ϕ}°) and viscosity B - coefficients for phosphomolybdic acid indicate the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperature and higher molarity of catechol in the ternary solutions. Also phosphomolybdic acid acts as a water-structure promoter due to hydrophobic hydration in the presence of catechol and catechol has a dehydration effect on the hydrated phosphomolybdic acid.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

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TABLE 1: Density (ρ , kg m^{-3}) and viscosity (η , mPa s) of aqueous catechol mixtures at different temperatures.

Temperature (K)	$\rho \times 10^{-3} \text{kg m}^{-3}$		$\eta \text{ mPa. s}$		pH	
	Exp	Lit	Exp	Lit	Exp	Lit
0.05(M)						
298.15	0.99650	-	0.9003	-	6.16	-
308.15	0.99371	-	0.7350	-	5.31	-
318.15	0.99222	-	0.6135	-		-
0.1(M)						
298.15	0.99797	-	0.9132	-	4.20	-
308.15	0.99509	-	0.7475	-	4.16	-
318.15	0.99303	-	0.6375	-	4.13	-
0.15(M)						
298.15	0.99910	-	0.9227	-	3.97	-
308.15	0.99621	-	0.7602	-	3.89	-
318.15	0.99429	-	0.6528	-	3.82	-

TABLE 2: Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_ϕ), and $\alpha = (\eta / \eta_o - 1) / c^{1/2}$ and pH of phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

C mol dm ⁻³	$\rho \times 10^{-3}$ kg m ⁻³	η mPas	$V_\phi \times 10^6$ m ³ mol ⁻¹	$(\eta / \eta_o - 1) / c^{1/2}$	pH
0.00(M)					
298.15 K					
0.0025	1.0003	0.8970	963.47	0.0754	2.56
0.0050	1.0042	0.9013	807.35	0.1213	2.29
0.0074	1.0085	0.9059	709.80	0.1585	2.13
0.0099	1.0125	0.9099	693.59	0.1829	1.99
0.0124	1.0169	0.9146	649.65	0.2107	1.91
0.0154	1.0223	0.9205	593.04	0.2432	1.83
308.15 K					
0.0025	0.9972	0.7234	980.42	0.0260	2.50
0.0049	1.0008	0.7275	880.58	0.0980	2.20
0.0074	1.0048	0.7318	803.29	0.1500	2.02
0.0098	1.0091	0.7365	725.12	0.1961	1.89
0.0123	1.0135	0.7404	677.66	0.2239	1.80
0.0151	1.0189	0.7454	617.43	0.2571	1.72
318.15K					
0.0024	0.9949	0.6042	1117.80	0.2110	2.40
0.0049	0.9989	0.6170	874.40	0.4530	2.08
0.0073	1.0032	0.6280	745.77	0.5860	1.90
0.0098	1.0072	0.6378	717.08	0.6720	1.79
0.0122	1.0114	0.6469	678.22	0.7400	1.69
0.0151	1.0169	0.6583	614.98	0.8200	1.59
0.05(M)					
298.15 K					
0.0024	1.0007	0.9071	504.87	0.0860	2.73
0.0048	1.0053	0.9116	431.73	0.1330	2.36

Ion-Solvent and..... at 298.15, 308.15 and 318.15K.

0.0076	1.0107	0.9162	391.32	0.1637	2.14
0.0101	1.0156	0.9190	365.77	0.1727	2.03
0.0125	1.0205	0.9229	339.99	0.1940	1.92
0.0149	1.0252	0.9270	329.77	0.2145	1.83
308.15 K					
0.0024	0.9978	0.7396	530.28	0.1280	2.66
0.0048	1.0023	0.7458	472.46	0.2130	2.29
0.0076	1.0075	0.7516	434.25	0.2600	2.08
0.0101	1.0123	0.7569	412.49	0.2970	1.98
0.0125	1.0170	0.7604	387.12	0.3100	1.85
0.0148	1.0217	0.7663	373.60	0.3492	1.77
318.15 K					
0.0024	0.9962	0.6217	569.2613	0.2750	2.58
0.0048	1.0004	0.6307	518.5812	0.4060	2.22
0.0076	1.0055	0.6421	484.1216	0.5364	1.99
0.0102	1.0094	0.6514	458.6212	0.6171	1.91
0.0126	1.0132	0.6583	424.2826	0.6560	1.83
0.0150	1.0174	0.6657	411.1519	0.7000	1.73
0.1(M)					
298.15K					
0.0024	1.0022	0.9199	510.13	0.1490	2.53
0.0048	1.0065	0.9254	491.94	0.1930	2.26
0.0076	1.0116	0.9306	471.79	0.2180	2.09
0.0101	1.0162	0.9343	456.38	0.2300	1.99
0.0125	1.0207	0.9375	440.59	0.2380	1.91
0.0149	1.0253	0.9411	423.41	0.2500	1.85
308.15 K					
0.0024	0.9992	0.7524	562.06	0.1340	2.58
0.0048	1.0034	0.7577	526.57	0.1970	2.24
0.0076	1.0084	0.7634	501.16	0.2440	2.04
0.0101	1.0130	0.7682	487.94	0.2762	1.94
0.0125	1.0173	0.7716	476.84	0.2881	1.83
0.0149	1.0219	0.7752	460.99	0.3040	1.75

Ion-Solvent and..... at 298.15, 308.15 and 318.15K.

318.15 K					
0.0024	0.9970	0.6441	600.01	0.2020	2.42
0.0048	1.0011	0.6518	572.64	0.3230	2.14
0.0076	1.0060	0.6604	551.50	0.4120	1.94
0.0101	1.0104	0.6662	533.72	0.4480	1.85
0.0125	1.0148	0.6731	514.62	0.5000	1.75
0.0150	1.0192	0.6806	498.54	0.5540	1.70
0.15(M)					
298.15K					
0.0024	1.0034	0.9309	480.50	0.1820	2.52
0.0050	1.0081	0.9354	462.59	0.1940	2.25
0.0076	1.0128	0.9400	458.51	0.2150	2.09
0.0102	1.0174	0.9434	445.89	0.2230	1.97
0.0125	1.0217	0.9474	439.35	0.2402	1.88
0.0151	1.0265	0.9512	428.72	0.2520	1.81
308.15 K					
0.0024	1.0002	0.7644	576.63	0.1140	2.45
0.0050	1.0047	0.7673	560.65	0.1320	2.16
0.0076	1.0092	0.771	548.45	0.1630	1.99
0.0102	1.0135	0.7737	537.49	0.1767	1.87
0.0125	1.0175	0.7770	535.19	0.1990	1.78
0.0151	1.0221	0.7807	524.59	0.2208	1.70
318.15 K					
0.0024	0.9983	0.1040	592.55	0.1040	2.40
0.0050	1.0027	0.1450	565.55	0.1450	2.09
0.0076	1.0072	0.1700	550.87	0.1700	1.89
0.0102	1.0116	0.1960	540.23	0.1960	1.79
0.0125	1.0156	0.2270	533.95	0.2270	1.70
0.0151	1.0204	0.2490	513.53	0.2490	1.62
0.0150	1.0192	0.6806	498.54	0.5540	1.70

TABLE 3: Limiting apparent molar volumes (V_{ϕ}^o) and experimental slopes (S_V^*) of of phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

Aqueous catechol solution	$V_{\phi}^o \times 10^6 (\text{m}^3 \text{mol}^{-1})$			$S_V^* \times 10^6 (\text{m}^3 \text{mol}^{-3/2} \text{dm}^{3/2})$		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
0.00(M)	1163.5	1227.3	1368.4	-4757.8	-4980.3	-6440.7
0.05(M)	607.3	626.2	673.7	-2372.1	-2128.5	-2185.7
0.10(M)	571.4	622.6	668.4	-1174.5	-1335.1	-1371.7
0.15(M)	513.4	609.9	639.5	-674.1	-697.1	-1000.7

TABLE 4: Values of the coefficients of equation (4) for phosphomolybdic acid in different aqueous catechol mixtures.

Aqueous catechol solution	$a_0 (\text{m}^3 \text{mol}^{-1})$	$a_1 (\text{m}^3 \text{mol}^{-1} \text{K}^{-1})$	$a_2 (\text{m}^3 \text{mol}^{-1} \text{K}^{-2})$
0.00(M)	34772.46	-227.96	0.3865
0.05(M)	13182.24	-84.81	0.1430
0.10(M)	-3389.25	21.18	-0.0265
0.15(M)	-33143.04	212.76	-0.3350

TABLE 5: Limiting partial molar expansibilities for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

Aqueous catechol solution	$\phi_E^0(\text{m}^3\text{mol}^{-1}\text{K}^{-1})$			$(\partial\phi_E^0/\partial T)_P$ ($\text{m}^3\text{mol}^{-1}\text{K}^{-2}$)
	298.15K	308.15K	318.15K	
0.00(M)	2.510	10.240	17.97	0.773
0.05(M)	0.459	3.319	6.179	0.286
0.10(M)	5.388	4.853	4.323	-0.053
0.15(M)	13.004	6.304	0.396	-0.670

TABLE 6: Values of *A* and *B* coefficients for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures

Aqueous catechol solution	A ($\text{dm}^{3/2}\text{mol}^{-1/2}$)			B ($\text{dm}^3\text{mol}^{-1}$)		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
0.00(M)	-0.0363	-0.1251	-0.1438	2.2454	3.1624	8.0839
0.05(M)	0.011	0.0010	-0.0025	1.663	2.8785	5.9650
0.10(M)	0.0941	0.0307	0.0010	1.3220	2.3322	4.5261
0.15(M)	0.1301	0.0355	0.0048	0.9717	1.4666	1.9682

TABLE 7: Apparent molar volumes V_{ϕ}^o and viscosity B -coefficients transfer from water to different aqueous catechol solutions for phosphomolybdic acid at different temperatures.

Aqueous catechol solution	$V_{\phi}^o \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	$\Delta V_{\phi}^o \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	$B \times 10^6$ ($\text{dm}^3 \text{mol}^{-1}$)	$\Delta B \times 10^6$ ($\text{dm}^3 \text{mol}^{-1}$)
298.15K				
0.00(M)	1163.5	0.00	2.2454	0.00
0.05(M)	607.33	556.17	1.663	0.5824
0.10(M)	571.38	592.12	1.3220	0.9234
0.15(M)	513.4	650.1	0.9717	1.2737
308.15K				
0.00(M)	1227.3	0.00	3.1624	0.00
0.05(M)	626.22	601.08	2.8785	0.2839
0.10(M)	622.56	604.74	2.3322	0.8302
0.15(M)	609.94	617.36	1.4666	1.6958
318.15K				
0.00(M)	1368.4	0.00	8.0839	0.00
0.05(M)	673.7	694.70	5.956	2.1279
0.10(M)	668.44	699.96	4.5261	3.5578
0.15(M)	639.48	728.92	1.9682	6.1157

TABLE 8: Values of \bar{V}_1^o , \bar{V}_2^o , $\Delta\mu_1^{o\neq}$, $\Delta\mu_2^{o\neq}$, $T\Delta S_2^{o\neq}$ and $\Delta H_2^{o\neq}$ for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

Parameter	298.15K	308.15K	318.15K
0.00(M)			
$(\bar{V}_2^o - \bar{V}_1^o) \times 10^6$ $\text{m}^3\text{mol}^{-1}$	1145.43	1209.17	1350.24
$\Delta\mu_1^{o\neq}$, kJ mol^{-1}	60.82	62.86	64.90
$\Delta\mu_2^{o\neq}$, kJ mol^{-1}	465.134	617.891	1373.86
$T\Delta S_2^{o\neq}$, kJ mol^{-1}	-13546.71	-14001.1	-14455.5
$\Delta H_2^{o\neq} \times 10^3$ kJ mol^{-1}	-13081.609	-13383.21	-13081.60
0.05(M)			
$(\bar{V}_2^o - \bar{V}_1^o) \times 10^6$ $\text{m}^3\text{mol}^{-1}$	589.10	607.89	655.32
$\Delta\mu_1^{o\neq}$, kJ mol^{-1}	60.84	62.89	64.93
$\Delta\mu_2^{o\neq}$, kJ mol^{-1}	222.02	317.90	349.47
$T\Delta S_2^{o\neq}$, kJ mol^{-1}	-1899.99	-1963.72	-2027.44
$\Delta H_2^{o\neq} \times 10^3$ kJ mol^{-1}	-1677.97	-1645.81	-1677.97
0.1(M)			
$(\bar{V}_2^o - \bar{V}_1^o) \times 10^6$ $\text{m}^3\text{mol}^{-1}$	553.12	604.20	650.00
$\Delta\mu_1^{o\neq}$, KJ mol^{-1}	60.85	62.90	64.94
$\Delta\mu_2^{o\neq}$, KJ mol^{-1}	187.13	228.51	257.89

Ion-Solvent and..... at 298.15, 308.15 and 318.15K.

$T\Delta S_2^{o\neq}$, KJ mol ⁻¹	-1054.85	-1090.23	-1125.61
$\Delta H_2^{o\neq} \times 10^3$ KJ mol ⁻¹	-867.72	-861.72	-867.72
0.15(M)			
$(\bar{V}_2^o - \bar{V}_1^o) \times 10^6$ m ³ mol ⁻¹	495.10	591.54	621.00
$\Delta\mu_1^{o\neq}$, KJ mol ⁻¹	60.86	62.90	64.96
$\Delta\mu_2^{o\neq}$, KJ mol ⁻¹	88.55	147.27	177.11
$T\Delta S_2^{o\neq}$, KJ mol ⁻¹	-1320.21	-1364.49	-1408.77
$\Delta H_2^{o\neq} \times 10^3$ KJ mol ⁻¹	-1231.66	-1217.22	-1231.66

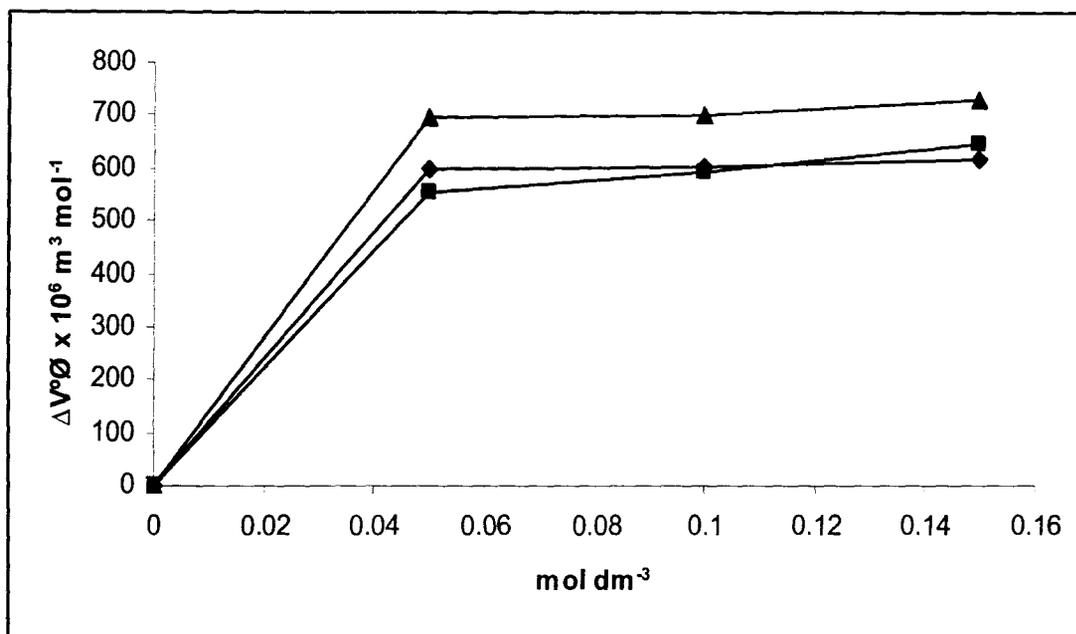


FIGURE 1. Plots of partial molar volume (ΔV_{ϕ}^0) against molality of aqueous catechol solution for the transfer from water to different aqueous catechol solution for phosphomolybdic acid at different temperatures ;T=298.15K (■); T=308.15K (◆); T=318.15K (▲).

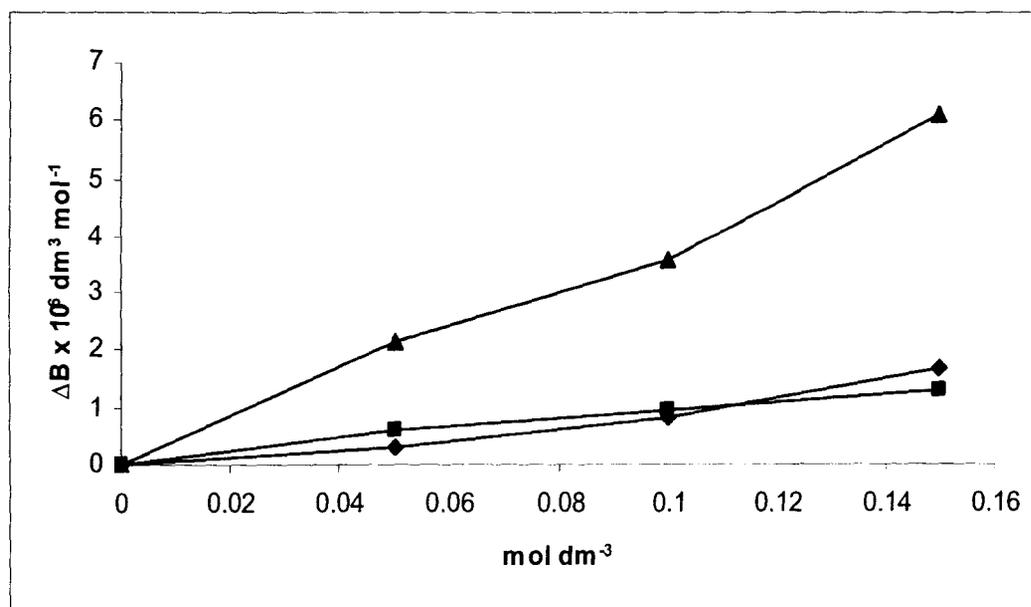


FIGURE 2. Plots of viscosity *B*-coefficient (ΔB) against molality of aqueous catechol solution for the transfer from water to different aqueous catechol solution for phosphomolybdic acid at different temperatures. T=298.15K (■); T=308.15K (◆); T=318.15K (▲).

CHAPTER IX

Investigation on Solvent-Solvent Interactions in Binary Mixtures of Isoamyl Alcohol with Some Alkoxyethanols.

9.1. 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. The determination of density, viscosity, speed of sound and refractive index is a valuable tool to develop new theoretical models and learn about the liquid state [1] because of the close connection between liquid structure and macroscopic properties. Ultrasonic methods and refractive index find extensive applications owing to their ability of characterizing the physico-chemical behavior of liquid systems. On the other hand, excess thermodynamic functions and deviations of non thermodynamic ones of binary liquid mixtures are fundamental for understanding the interactions between molecules in these types of binary mixtures.

There has been a recent upsurge of interest [2, 3] in the study of thermodynamic properties of binary liquid mixture which has been used extensively to obtain information on intermolecular interactions and stereochemical effects in these solvents. The present work reports density (ρ), viscosity (η) for the binary mixtures of iso-amyl alcohol (I.A.A) with 2-methoxy ethanol (2-M.E), 2-ethoxy ethanol (2-E.E) and 2-butoxy ethanol (2-B.E) over the entire range of composition at 303.15, 313.15, and 323.15K. Also ultrasonic speed (u) and refractive index (n_D) have been reported for the binary mixture at 303.15K.

**Communicated in International Journal of Thermophysics*

The amyl alcohols are used fundamentally for the perfumes composition and the synthesis of fruit essences. They are also used as solvents for surfaces and lacquer baths, inks for print and dyes for wool as well as in the chemical production of photographic and pharmaceutical substances. Furthermore, they are an intermediate in the production of amyl acetate and other amyl esters. In some of these uses, the knowledge of their physical properties are very important. It is well known that alkoxyethanols have wide use as monomers in the production of polymers and emulsion formulations. They are also of considerable interest for studying the heteroproximity effects of the etheric oxygen on the -OH bond and, hence their influence on the associated nature of the species in these molecules.

The excess or deviation properties were fitted to Redilch-Kister polynomial equation to obtain their coefficients and have been interpreted in terms of molecular interactions and structural effects. This work provides a test of various empirical equations to correlate viscosity, density, acoustic and refractive index data of binary mixtures in terms of pure component properties.

9.2 Experimental section

9.2.1. Chemicals

2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol (S.D. Fine Chemicals, AR, India) were purified as described in the literature [4]. Iso -amyl alcohol was procured from Merck, India and was used as purchased. The pure chemicals were stored over activated 4A° molecular sieves to reduce water content before use. The chemicals after purification were 99.8% pure and their purity was ascertained by GLC and also by comparing experimental values of density, viscosity and refractive index with those reported in the literature when available, as presented in Table I.

9.2.2 Measurements

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostat bath controlled to ± 0.01 K. Viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4}$ mPas. 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 fractions was within ± 0.0002 . The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm⁻³.

Ultrasonic speeds of sound (u) were determined by a multifrequency ultrasonic interferometer (Mittal enterprise, New Delhi, M-81) working at 1MHz, calibrated with triply distilled and purified water, methanol and benzene at 303.15K. The precision of ultrasonic speed measurements was ± 0.2 ms⁻¹. The details of the methods and techniques have been described in earlier papers [5-8]. Refractive index was measured with the help of Abbe-Refractometer (U.S.A). The accuracy of refractive index measurement was ± 0.0002 units. The refractometer was calibrated using twice distilled and deionized water, and calibration was checked after every few measurements.

9.3. Results and discussion

9.3.1 Excess molar volumes

The experimental densities (ρ), viscosities (η), excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 303.15, 313.15 and 323.15K are reported in Table 2.

The excess molar volume V^E , for the mixtures were calculated using the following equation [9],

$$V^E = \sum_{i=1}^2 x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (1)$$

where ρ is the density of the mixture and M_i , x_i , ρ_i are the molecular weight, mole fraction and viscosity of the i^{th} component in the mixture respectively.

Fig. (1-3) illustrates that the excess molar volumes, V^E for the binary system of I.A.A with 2-M.E, 2-E.E, 2-B.E. are positive over the entire range of composition and at all experimental temperature and follows the order 2-M.E > 2-E.E > 2-B.E.

The sign of excess volume (V^E) of a system depends on the relative magnitude of expansion/contraction on mixing of two liquids. If the factors causing expansion dominate the factors causing contraction, then V^E becomes positive. On the other hand, if the contractive factors dominate the expansive factors, then V^E becomes negative. The factors that are responsible for expansion in volume are as follows:

- (1) Loss of dipolar association (i.e., rupturing of H-bonding of component by the other or breaking up of associates held by weaker forces, namely, dipole-dipole or dipole-induced dipole interactions or by van der Waals forces)
- (2) The geometry of molecular structure, which does not allow fitting of one component in to other component.
- (3) Steric hindrance, which opposes the proximity of the constituent molecules.

Mixing of I.A.A with alkoxyethanols induces a decrease in the molecular order in the latter, resulting in an expansion in volume and hence positive V^E

values The positive values of V^E observed in the case of binary mixtures may be ascribed to molecular structure of I.A.A which does not allow it to pack well with the smaller molecules of alkoxyethanols resulting in the increase of the volume of the mixture. Furthermore the presence of etheric oxygen in alkoxyethanols facilitates the formation of intramolecular hydrogen bonding between the etheric oxygen and hydrogen of --OH group of the same molecule. Infrared, microwave and calorimetric studies [10-12] have also shown the presence of mostly ten-membered dimers and linear associates in $R\cdots O\cdots C_2H_5OH$ (where $R = -CH_3, -C_2H_5, C_4H_9,$ etc) and the positive values of V^E , for the alkoxyethanols under investigation may be attributed to the presence of weak hydrogen bond or dispersive forces between the mixing liquids. The values of excess molar volumes V^E were found to decrease with the increase of carbon chain length of alkoxyethanols. This may be attributed to the increased +I effect of the alkyl group, thereby decreasing the polarity of the $\cdots OH$ bond. A similar result was found in the study of binary mixtures of chloroform with propan-1-ol and butan-1-ol [13]. The V^E values were found to increase with rise in temperature over all composition range. Similar dependence of V^E values on temperature was reported elsewhere [14, 15].

9.3.2 Viscosity deviations

The viscosity deviations ($\Delta\eta$) from linear dependence on mole fraction were calculated [16] by,

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

where, η is the viscosity of the mixture and x_i, η_i are the mole fraction and viscosity of pure component i respectively.

Deviations in viscosity ($\Delta\eta$) for the mixture of I.A.A with alkoxyethanols are negative (Fig 4-6) and the magnitude of negative deviation

increases with increasing chain of alkoxy alkanols. The trend in negative deviation of $\Delta\eta$ is M.E >E.E>B.E. This suggests that the intermolecular interactions between I.A.A and B.E are stronger than for I.A.A and M.E mixtures. Increase in $\Delta\eta$ values with increase in chain length suggests that the forces between pair of unlike molecules are greater than the forces between pair of like molecules. The $\Delta\eta$ values show a systematic increase with increase in temperature for the binary mixture. The effect of temperature increase is to disrupt hetero and homo association of the molecules resulting in an increase in fluidity of the liquids giving higher $\Delta\eta$ values at higher temperatures. Similar results have been reported earlier [14]. Also, the deviations in $\Delta\eta$ values are found to be opposite to the sign of excess molar volumes V^E for all three binary mixtures, which is in agreement with the view proposed by Brocos et al. [17-18]. This further reinforces our earlier conclusions regarding the intermolecular interactions from the variations of V^E values of these mixtures.

A correlation between the sign of $\Delta\eta$ and V^E (Table 2) has been observed for a number of binary solvent systems [19-20] i.e., $\Delta\eta$ is positive when V^E is negative and vice-versa. In general, for systems where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative, whereas charge-transfer and hydrogen-bonding interactions lead to the formation of complex species between unlike molecules, thereby resulting in positive $\Delta\eta$ values [21].

9.3.3 Deviations in isentropic compressibility.

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

$$K_S = \frac{1}{(u^2\rho)} \quad (3)$$

$$\Delta K_S = K_S - \sum_{i=1}^3 x_i K_{S,i} \quad (4)$$

where u and K_S are the speed of sound and isentropic compressibility of the mixture and $K_{S,i}$, the isentropic compressibility of the i^{th} component in the mixture respectively. The experimental speed of sound, isentropic compressibility and deviation in isentropic compressibility are listed in Table 3 and are graphically represented in Fig. 8 as a function of mole fraction of I.A.A. From Fig.8, it is evident that the ΔK_S values are positive and the magnitude of positive values decreases with increasing chain length of the alcohols. This indicates that the mixtures are less compressible than the corresponding ideal mixture. Due to these interactions, the ultrasonic velocity decreases and the compressibility of these solutions increases until the maxima is reached and then these parameters follow the reverse trend. The order it follows is: 2-M.E > 2-E.E > 2-B.E. These results can be explained in terms of molecular interactions and structural effects. Positive ΔK_S values are due to the breaking of interactions and the corresponding disruption of molecular order in the pure components [22]. Interactions between the molecules of I.A.A and alkoxyalcohols are broken in the mixing process as already explained above which leads to positive ΔK_S values.

9.3.4 Excess molar refraction

The molar refraction, $[R]$ can be evaluated from Lorentz-Lorenz relation [23] and gives more information than n_D about the mixture phenomenon because takes into account the electronic perturbation of molecular orbital during the liquid mixture process and $[R]$ is also directly related to the dispersion forces

$$[R] = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \cdot \left(\frac{M}{\rho} \right) \quad (5)$$

where $[R]$, n_D^2 , and M are, correspondingly, the molar refraction, the refractive index and the molar mass of the mixture respectively. Deviation from molar refraction was calculated from the following relation;

$$\Delta R = [R] - \sum_{i=1}^2 x_i [R]_i \quad (6)$$

The value of ΔR is positive (Table 3) for all systems indicating that the dispersion forces are higher in the mixture than in the pure liquids. The deviations in refractive indices are shown in Fig.7. The ΔR values for the binary mixtures under study follows the order M.E>E.E>B.E with a maximum at around $x_1 \sim 0.3-0.4$.

9.3.5 Gibb's Free Energy

On the basis of the theories of absolute reaction rates [24], the excess Gibbs energy of activation for a viscous was calculated from the equation [25]

$$\Delta G^E = RT \left[\ln \eta V - \sum_{i=1}^3 x_i \ln \eta_i V_i \right] \quad (7)$$

where R , T , V_i and V are the universal gas constant, experimental temperature in absolute scale, and the molar volumes of the pure component and the mixtures, respectively.

In Table 2, the value of Gibbs excess energy of activation of viscous flow, i.e., ΔG^E is reported and is observed to negative for the binary systems under study over the entire range of composition and temperatures. Negative ΔG^E values for the systems under study (Fig. 9-11) follows the order M.E > E.E > B.E. It has been reported [26, 27] that the ΔG^E parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. Here it is observed that the magnitude of negative values decreases with increasing chain length of the alcohols. Alcohol molecules self-associate [28] very strongly (OH----OH interaction) which has a dramatic influence on the thermo-physical properties studied.

The excess properties (V^E , $\Delta \eta$, ΔK_S , ΔR , ΔG^E) were fitted to the Redlich-Kister polynomial equation [29],

$$Y_{ij}^E = x_1 x_2 \sum_{i=1}^k a_i (x_1 - x_2)^i \quad (8)$$

where Y^E refer to an excess property, x_1 is the mole fraction of I.A.A and x_2 is that of the other component.

The coefficients (a_i) were obtained by fitting equation (8) to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation. The estimated values of along with the standard deviations are summarized for all mixtures in Table 4. The standard deviation was calculated using the equation

$$\sigma = \left[\frac{(Y_{exp}^E - Y_{cal}^E)^2}{(n - m)} \right]^{\frac{1}{2}} \quad (9)$$

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

9.4. Conclusion

After a through study of the behavior of alkoxyethanols and iso-amyl alcohol, we get a clear idea about the molecular interaction between the components and it was found that the interactions between the solvent molecules increases with the increase in chain length of alkoxyethanols.

Acknowledgment

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

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TABLE 1: Density (ρ), viscosity (η), sound speed (u) and refractive index (n_D) of the pure component liquids at different temperatures.

T/K	$\rho \times 10^{-3} \text{kg m}^{-3}$		η/mPas		u/ms^{-1}		n_D	
	This work	Lit	This work	Lit	This work	Lit	This work	Lit
Iso-amyl alcohol								
303.15	0.8031	0.8032 [30]	3.2622	3.1111[30]	1197.4	1197.0 [30]	1.4035	-
313.15	0.7964	-	2.4409	-	-	-	-	-
323.15	0.7898	-	1.9396	-	-	-	-	-
2-Methoxyethanol								
303.15	0.9646	0.9558 [31]	1.5623	1.476 [31]	1324.3	1359.2 [32]	1.3983	-
313.15	0.9553	0.9462 [31]	1.3006	1.189 [31]	-	-	-	-
323.15	0.9469	-	1.0929	-	-	-	-	-
2-Ethoxyethanol								
303.15	0.9195	0.9212 [31]	1.6226	1.643 [31]	1301.5	1319.9 [32]	1.4065	-
313.15	0.9120	0.9123 [31]	1.3554	1.293 [31]	-	-	-	-
323.15	0.9038	-	1.1432	-	-	-	-	-
2-Butoxyethanol								
303.15	0.8920	0.8923 [31]	2.4864	2.408 [31]	1288.4	1322.0 [32]	1.4150	-
313.15	0.8842	0.8839 [31]	1.9788	1.869 [31]	-	-	-	-
323.15	0.8775	-	1.6525	-	-	-	-	-

TABLE 2: Experimental values of density, (ρ), viscosity, (η), excess molar volume, (V^E), deviations in viscosity ($\Delta\eta$), excess Gibb's free energy ΔG^E for the binary mixture under investigation at 303.15, 313.15 and 323.15K.

Mole fraction of I.A.A (x_1)	$\rho \times 10^3$ kg m ³	$\eta_{exp}/$ mPas	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\eta/\text{mPas}$	$\Delta G^E \times 10^{-3}$ (Jmol ⁻¹)
I.A.A (1) +2-M.E (2)		303.15K			
0.0000	0.9646	1.5623	0.0000	0.0000	0.0000
0.0875	0.6445	1.5889	0.0980	-0.1227	-0.1048
0.1775	0.9256	1.6011	0.1601	-0.2450	-0.2414
0.2701	0.9075	1.6434	0.2205	-0.3600	-0.3388
0.3653	0.8903	1.7433	0.2510	-0.4258	-0.3800
0.4633	0.8742	1.8209	0.2487	-0.5020	-0.4327
0.5643	0.8588	1.9365	0.2190	-0.5588	-0.4670
0.6683	0.8442	2.1366	0.1590	-0.5614	-0.4177
0.7754	0.8302	2.3674	0.0967	-0.5199	-0.3665
0.8860	0.8166	2.7203	0.0312	-0.4060	-0.2327
0.0000	0.8031	3.2622	0.0000	0.0000	0.0000
313.15K					
0.0000	0.9553	1.3006	0.0000	0.0000	0.0000
0.0875	0.9357	1.3226	0.1002	-0.0791	-0.0849
0.1775	0.9170	1.3503	0.1775	-0.1540	-0.1666
0.2701	0.8992	1.3845	0.2470	-0.2259	-0.2445
0.3653	0.8821	1.4396	0.2850	-0.2784	-0.2931
0.4633	0.8658	1.4999	0.3100	-0.3305	-0.3445
0.5643	0.8507	1.5898	0.2920	-0.3800	-0.3800
0.6683	0.8361	1.6964	0.2550	-0.3960	-0.3870
0.7754	0.8224	1.8467	0.1873	-0.3720	-0.3305
0.8860	0.8094	2.0739	0.0720	-0.2700	-0.2225
1.0000	0.7964	2.4409	0.0000	0.0000	0.0000
323.15K					
0.0000	0.9469	1.0929	0.0000	0.0000	0.0000
0.0875	0.9272	1.1230	0.1140	-0.0240	-0.0710
0.1775	0.9086	1.1382	0.1908	-0.0700	-0.1530
0.2701	0.8909	1.1626	0.2701	-0.1200	-0.2200
0.3653	0.8741	1.1972	0.3190	-0.2060	-0.2760
0.4633	0.8581	1.2372	0.341	-0.2512	-0.3180

Investigation on with Some Alkoxyethanols.

0.5643	0.8429	1.2867	0.3540	-0.2830	-0.3420
0.6683	0.8286	1.3734	0.3168	-0.3000	-0.3360
0.7754	0.8149	1.4865	0.2502	-0.2700	-0.2970
0.8860	0.8021	1.6560	0.1377	-0.2100	-0.1920
1.0000	0.7898	1.9396	0.0000	0.0000	0.0000

I.A.A (1) +2-E.E (2)			303.15K		
0.0000	0.9195	1.6226	0.0000	0.0000	0.0000
0.0875	0.9061	1.6885	0.0313	-0.1227	-0.0768
0.1775	0.8929	1.7610	0.0750	-0.2450	-0.1474
0.2701	0.8801	1.8121	0.1288	-0.3600	-0.2200
0.3653	0.8677	1.8916	0.1644	-0.4258	-0.2660
0.4633	0.8558	1.9937	0.1920	-0.5020	-0.2860
0.5643	0.8443	2.1244	0.2020	-0.5588	-0.2960
0.6683	0.8333	2.3012	0.1973	-0.5614	-0.2760
0.7754	0.8228	2.4957	0.1560	-0.5199	-0.2370
0.8860	0.8126	2.8067	0.1040	-0.4060	-0.1650
0.0000	0.8031	3.2622	0.0000	0.0000	0.0000

313.15K					
0.0000	0.9120	1.3554	0.0000	0.0000	0.0000
0.1020	0.8986	1.3851	0.0385	-0.0810	-0.0972
0.2036	0.8856	1.4245	0.0796	-0.1518	-0.1773
0.3047	0.8729	1.4688	0.1320	-0.2173	-0.2560
0.4053	0.8605	1.5295	0.1740	-0.2659	-0.2977
0.5055	0.8487	1.6041	0.1976	-0.3001	-0.3266
0.6053	0.8373	1.6804	0.2087	-0.3320	-0.3350
0.7046	0.8264	1.8119	0.2008	-0.3084	-0.3151
0.8035	0.8159	1.9451	0.1698	-0.2825	-0.2835
0.9020	0.8058	2.1431	0.1156	-0.1914	-0.1845
1.0000	0.7964	2.4409	0.0000	0.0000	0.0000

323.15K					
0.0000	0.9038	1.1432	0.0000	0.0000	0.0000
0.1020	0.8905	1.1695	0.0400	-0.0550	-0.0710
0.2036	0.8777	1.1963	0.0830	-0.1090	-0.1380
0.3047	0.8651	1.2221	0.1370	-0.1637	-0.1960
0.4053	0.8530	1.2627	0.1790	-0.2033	-0.2530
0.5055	0.8413	1.3098	0.2020	-0.2360	-0.2900
0.6053	0.8300	1.3771	0.2180	-0.2482	-0.3070
0.7046	0.8192	1.4598	0.2090	-0.2445	-0.2960

Investigation on with Some Alkoxyethanols.

0.8035	0.8088	1.5657	0.1850	-0.2174	-0.2510
0.9020	0.7990	1.7275	0.1230	-0.1340	-0.1510
1.0000	0.7898	1.9396	0.0000	0.0000	0.0000

I.A.A (1) +2-B.E (2) **303.15K**

0.0000	0.8920	2.4864	0.0000	0.0000	0.0000
0.1297	0.8822	2.4826	0.0142	-0.1043	-0.0875
0.2510	0.8725	2.4959	0.0282	-0.1852	-0.1535
0.3649	0.8631	2.5135	0.0370	-0.2560	-0.2115
0.4720	0.8539	2.5572	0.0400	-0.2953	-0.2404
0.5728	0.8450	2.5937	0.0364	-0.3370	-0.2737
0.6679	0.8386	2.6532	0.0313	-0.3514	-0.2827
0.7578	0.8277	2.7480	0.0231	-0.3262	-0.2575
0.8428	0.8193	2.8774	0.0158	-0.2629	-0.2023
0.9235	0.8111	3.0576	0.0080	-0.1452	-0.1073
1.0000	0.8031	3.2622	0.0000	0.0000	0.0000

313.15K

0.0000	0.8842	1.9788	0.0000	0.0000	0.0000
0.1297	0.8745	1.9694	0.0165	-0.0693	-0.0780
0.2510	0.8654	1.9674	0.0335	-0.1274	-0.1431
0.3649	0.8561	1.9873	0.0422	-0.1601	-0.1768
0.4720	0.8472	1.9969	0.0460	-0.2002	-0.2217
0.5728	0.8379	2.0284	0.0449	-0.2151	-0.2362
0.6679	0.8295	2.0671	0.0368	-0.2204	-0.2401
0.7578	0.8210	2.1207	0.0294	-0.2083	-0.2243
0.8428	0.8125	2.2001	0.0195	-0.1682	-0.1777
0.9235	0.8046	2.3034	0.0092	-0.1021	-0.1054
1.0000	0.7964	2.4409	0.0000	0.0000	0.0000

323.15K

0.0000	0.8775	1.6525	0.0000	0.0000	0.0000
0.1297	0.8677	1.6233	0.0190	-0.0664	-0.0700
0.2510	0.8582	1.6286	0.0356	-0.0960	-0.1255
0.3649	0.8488	1.6363	0.0495	-0.1209	-0.1658
0.4720	0.8398	1.6498	0.0540	-0.1382	-0.2000
0.5728	0.8310	1.6729	0.0514	-0.1440	-0.2070
0.6679	0.8223	1.7022	0.0473	-0.1420	-0.1960
0.7578	0.8193	1.7371	0.0383	-0.1329	-0.1820
0.8428	0.8057	1.7985	0.0280	-0.0960	-0.1281
0.9235	0.7976	1.8507	0.0190	-0.0669	-0.0892
1.0000	0.7898	1.9396	0.0000	0.0000	0.0000

Investigation on with Some Alkoxyethanols.

TABLE 3: Experimental values of ultrasonic speed, (u), isentropic compressibility, (K_S), deviation in isentropic compressibility, ΔK_S , refractive indices n_D excess molar refraction ΔR for the binary mixtures at 303.15K.

Mole fraction of I.A.A (x_1)	u/ms^{-1}	$K_S \times 10^{12} / \text{Pa}^{-1}$	$\Delta K_S \times 10^{12} / \text{Pa}^{-1}$	n_D	$\Delta R \times 10^6 (\text{m}^3 \text{mol}^{-1})$
I.A.A (1) +2-M.E (2) 303.15K					
0.0000	1324.3	591.1	0.0	1.3983	0.0000
0.0875	1312.1	615.0	21.8	1.3988	0.0254
0.1775	1299.2	640.1	40.3	1.3993	0.0356
0.2701	1287.4	664.9	53.9	1.3999	0.0457
0.3653	1274.8	691.1	63.5	1.4004	0.0483
0.4633	1261.2	719.2	68.7	1.4009	0.0467
0.5643	1248.8	746.6	67.8	1.4014	0.0414
0.6683	1235.7	775.7	61.2	1.4020	0.0316
0.7754	1223.3	805.0	48.0	1.4025	0.0209
0.8860	1210.5	835.8	27.9	1.4030	0.0117
1.0000	1197.4	868.4	0.0	1.4035	0.0000
I.A.A (1) +2-E.E (2) 303.15K					
0.0000	1301.5	1301.5	0.0	1.4065	0.0000
0.1020	1292.4	1292.4	16.8	1.4062	0.0175
0.2036	1282.4	1282.4	31.0	1.4059	0.0290
0.3047	1272.7	1272.7	41.3	1.4055	0.0392
0.4053	1262.9	1262.9	47.9	1.4052	0.0432
0.5055	1251.2	1251.2	51.6	1.4049	0.0396
0.6053	1240.6	1240.6	50.3	1.4046	0.0320
0.7046	1229.3	1229.3	44.9	1.4043	0.0223
0.8035	1219.2	1219.2	34.5	1.4040	0.0148
0.9020	1208.7	1208.7	19.6	1.4037	0.0065
1.0000	1197.4	1197.4	0.0	1.4035	0.0000
I.A.A (1) +2-B.E (2) 303.15K					
0.0000	1288.4	675.3	0.0	1.4150	0.0000
0.1297	1279.8	692.1	14.6	1.4138	0.0136
0.2510	1270.3	710.2	26.2	1.4127	0.0194
0.3649	1261.8	727.7	33.3	1.4115	0.0223
0.4720	1251.8	747.3	38.0	1.4104	0.0221
0.5728	1242.3	766.8	39.1	1.4093	0.0208
0.6679	1233.5	785.9	36.7	1.4080	0.0176
0.7578	1224.2	806.1	31.7	1.4069	0.0140
0.8428	1215.3	826.4	23.7	1.4058	0.0116
0.9235	1206.4	847.1	13.1	1.4047	0.0047
1.0000	1197.4	868.4	0.0	1.4035	0.0000

TABLE 4: Redlich-Kister coefficients and standard deviations (σ) for the binary mixtures at 303.15, 313.15 and 323.15K.

Excess property	T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ
I.A.A + 2-M.E								
$V^E \times 10^6$ $\text{m}^3\text{mol}^{-1}$	303.15	0.959	-0.535	-0.392	-	-	-	0.004
	313.15	-0.181	-0.035	0.502	-0.619	-1.267	-	0.003
	323.15	1.397	0.068	-	-	-	-	0.005
$\Delta\eta$ (mPa s)	303.15	-2.188	-0.912	-0.614	-0.378	-	-	0.011
	313.15	-1.355	-0.658	-0.529	-0.365	-	-	0.002
	323.15	-1.047	-0.608	-0.298	-0.298	-	-	0.003
ΔG^E $\times 10^{-3}$ (Jmol $^{-1}$)	303.15	-1.785	-0.309	-0.226	-0.356	-	-	0.013
	313.15	-1.447	-0.691	-0.338	-	-	-	0.005
	323.15	-1.312	-0.507	-0.325	-0.183	0.229	-	0.002
$\Delta K_S \times 10^{12}$ /Pa $^{-1}$	303.15	275.30	2.058	-	-	-	-	0.245
$\Delta R \times 10^6$ (m $^3\text{mol}^{-1}$)	303.15	0.178	-0.108	0.023	-	-	-	0.001
I.A.A + 2-E.E								
$V^E \times 10^6$ $\text{m}^3\text{mol}^{-1}$	303.15	0.757	0.450	-	-	-	-	0.004
	313.15	0.791	0.473	-	-	-	-	0.005
	323.15	0.803	0.416	0.718	-0.021	-6.382	1.755	0.001
$\Delta\eta$ (mPa s)	303.15	-1.822	-0.853	-0.223	-1.726	-0.629	1.366	0.006
	313.15	-1.212	-0.569	-0.236	-0.343	-0.389	-	0.006
	323.15	-0.932	-0.491	-0.214	-0.165	-	-	0.003
ΔG^E $\times 10^{-3}$ (Jmol $^{-1}$)	303.15	-1.312	-0.507	-0.325	-0.183	0.229	-	0.002
	313.15	-1.297	-0.349	-0.402	-0.500	-	-	0.004
	323.15	-1.152	-0.605	-0.148	-	-	-	0.002

Investigation on with Some Alkoxyethanols.

$\Delta K_S \times 10^{12}$ /Pa ⁻¹	303.15	205.28	27.07	-2.58	-7.13	-	-	0.204
$\Delta R \times 10^6$ (m ³ mol ⁻¹)	303.15	0.160	-0.124	-0.099	0.230	0.088	-0.235	0.001
I.A.A + 2-B.E								
$V^E \times 10^6$ m ³ mol ⁻¹	303.15	0.156	-0.035	-0.067	0.053	-	-	0.002
	313.15	0.184	-0.022	-0.070	0.032	-	-	0.001
	323.15	-0.007	-0.104	0.090	0.129	-	-	0.001
$\Delta\eta$ (mPa s)	303.15	-1.243	-0.789	-0.723	0.086	0.589	-	0.004
	313.15	-0.811	-0.462	-0.306	-	-	-	0.003
	323.15	-0.556	-0.172	-0.232	-	-	-	0.004
$\Delta G^E \times 10^{-3}$ (Jmol ⁻¹)	303.15	-1.014	-0.611	-0.559	0.173	0.574	-	0.003
	313.15	-0.896	-0.466	-0.282	-	-	-	0.004
	323.15	-0.798	-0.294	-0.075	-	-	-	0.006
$\Delta K_S \times 10^{12}$ /Pa ⁻¹	303.15	153.9	33.83	5.89	-	-	-	-
$\Delta R \times 10^6$ (m ³ mol ⁻¹)	303.15	0.087	-0.026	0.020	-	-	-	0.001

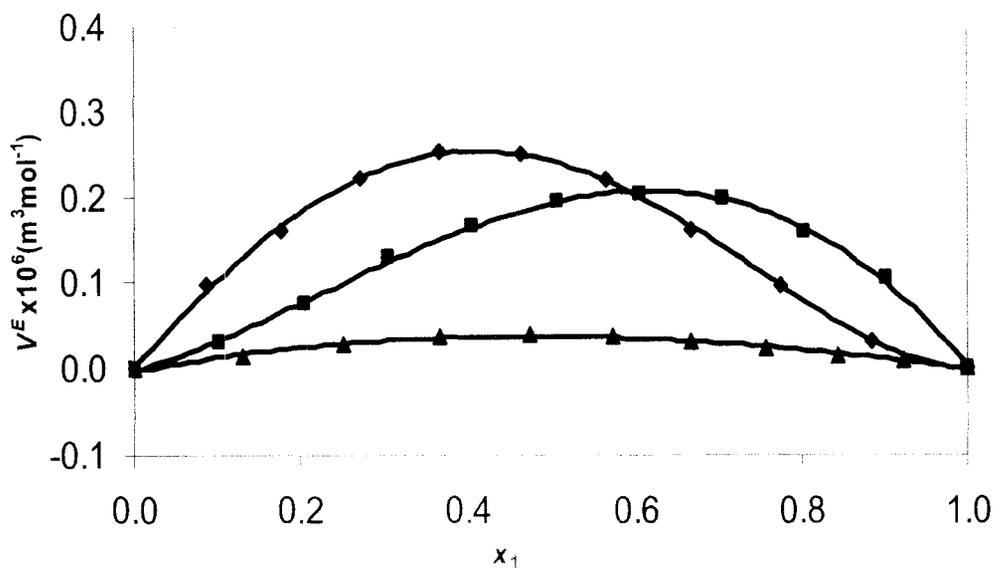


FIGURE 1. Plots of excess molar volumes $V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$ against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (\diamond), 2-ethoxyethanol (\blacksquare) and 2-butoxyethanol (\blacktriangle) at 303.15K.

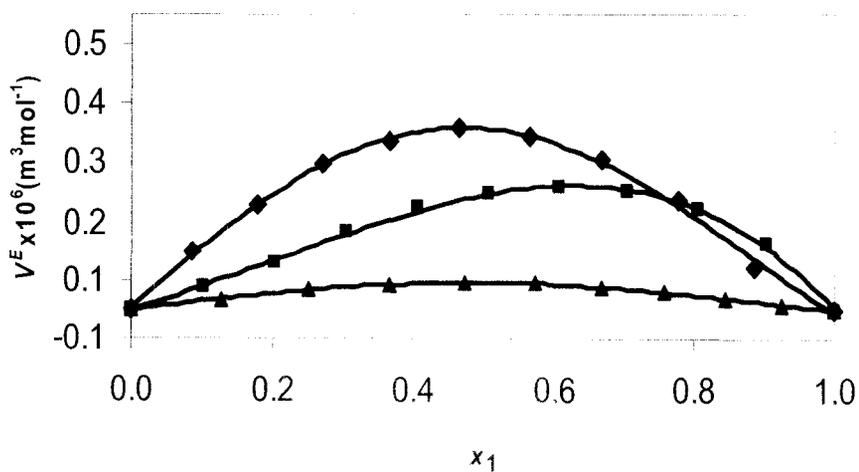


FIGURE 2. Plots of excess molar volumes $V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$ against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (\diamond), 2-ethoxyethanol (\blacksquare) and 2-butoxyethanol (\blacktriangle) at 313.15K.

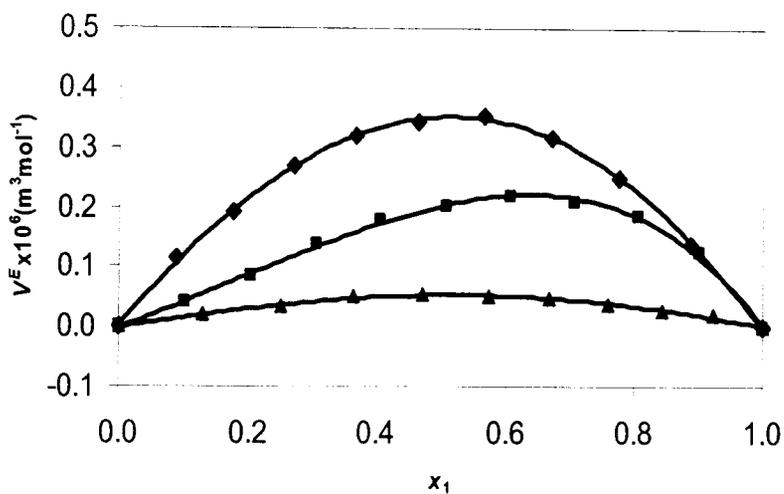


FIGURE 3. Plots of excess molar volumes $V^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (\blacklozenge), 2-ethoxyethanol (\blacksquare) and 2-butoxyethanol (\blacktriangle) at 323.15K.

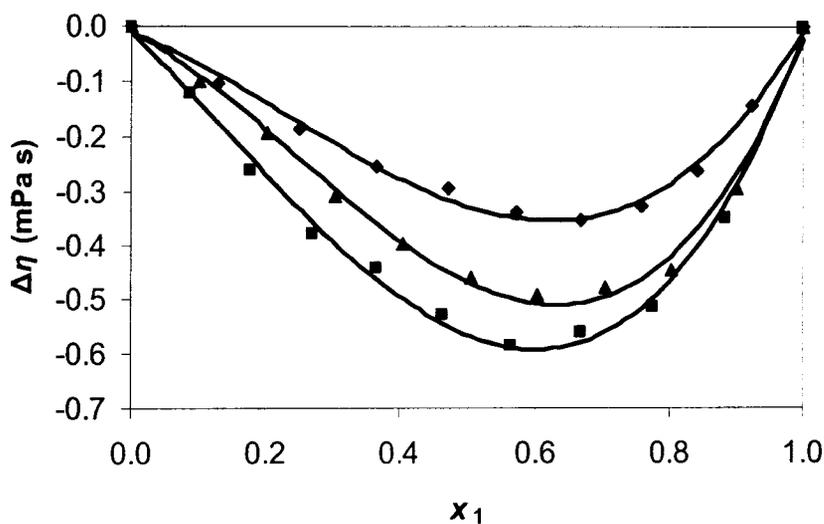


FIGURE 4. Plots of viscosity deviations, $\Delta\eta$ (mPa s) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (\blacksquare), 2-ethoxyethanol (\blacktriangle) and 2-butoxyethanol (\blacklozenge) at 303.15K.

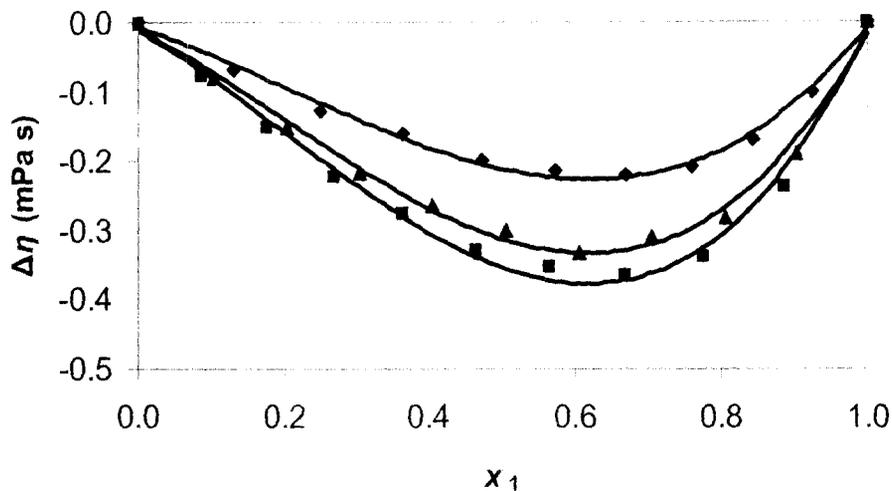


FIGURE 5. Plots of viscosity deviations, $\Delta\eta$ (mPa s) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (■), 2-ethoxyethanol (▲) and 2-butoxyethanol (◆) at 313.15K.

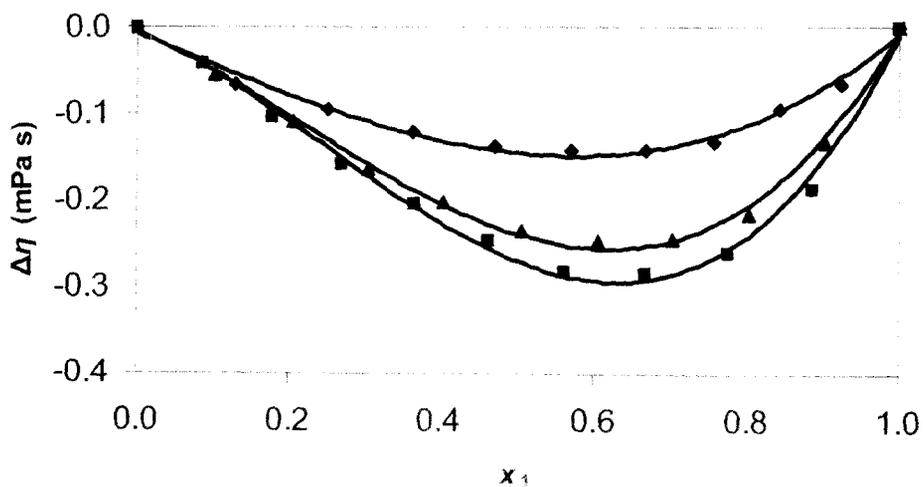


FIGURE 6. Plots of viscosity deviations, $\Delta\eta$ (mPa s) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (■), 2-ethoxyethanol (▲) and 2-butoxyethanol (◆) at 323.15K.

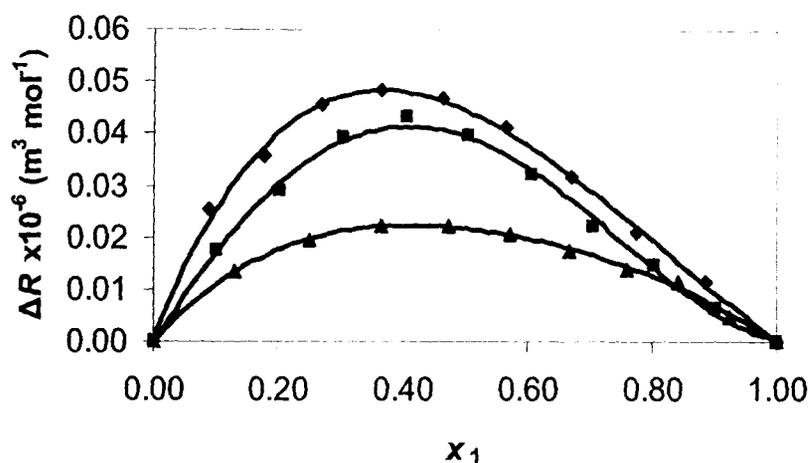


FIGURE 7. Plots of excess molar refraction $\Delta R \times 10^{-6} \text{ (m}^3 \text{ mol}^{-1})$ against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (♦), 2-ethoxyethanol (■) and 2-butoxyethanol (▲) at 303.15K.

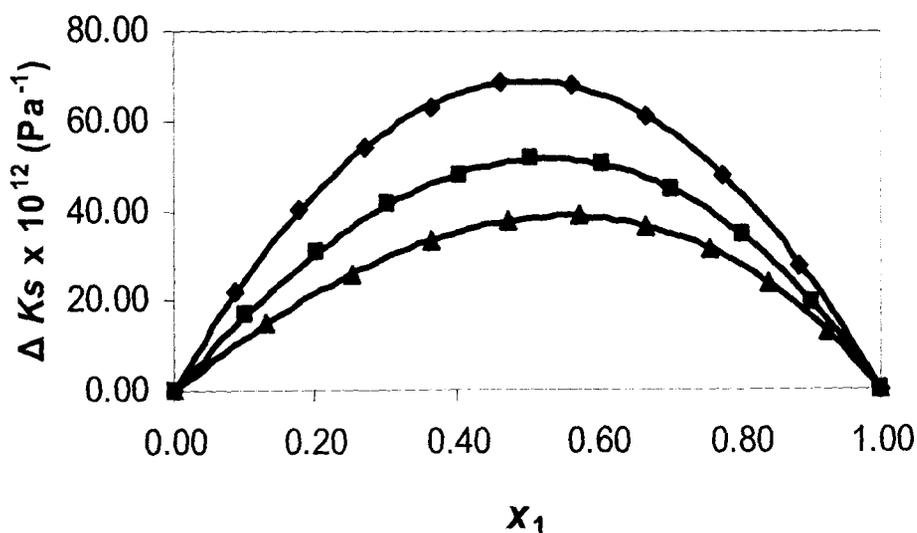


FIGURE 8. Plots of deviation in isentropic compressibility $\Delta K_s \times 10^{12} \text{ (Pa}^{-1})$ against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (♦), 2-ethoxyethanol (■) and 2-butoxyethanol (▲) at 303.15K.

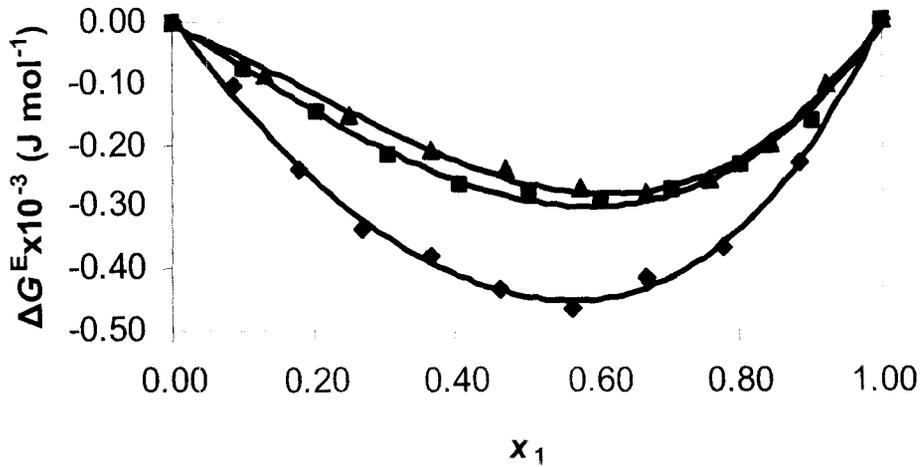


FIGURE 9. Plots of deviation in excess Gibbs free energy $\Delta G^E \times 10^{-3}$ (Jmol^{-1}) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (\blacklozenge), 2-ethoxyethanol (\blacksquare) and 2-butoxyethanol (\blacktriangle) at 303.15K

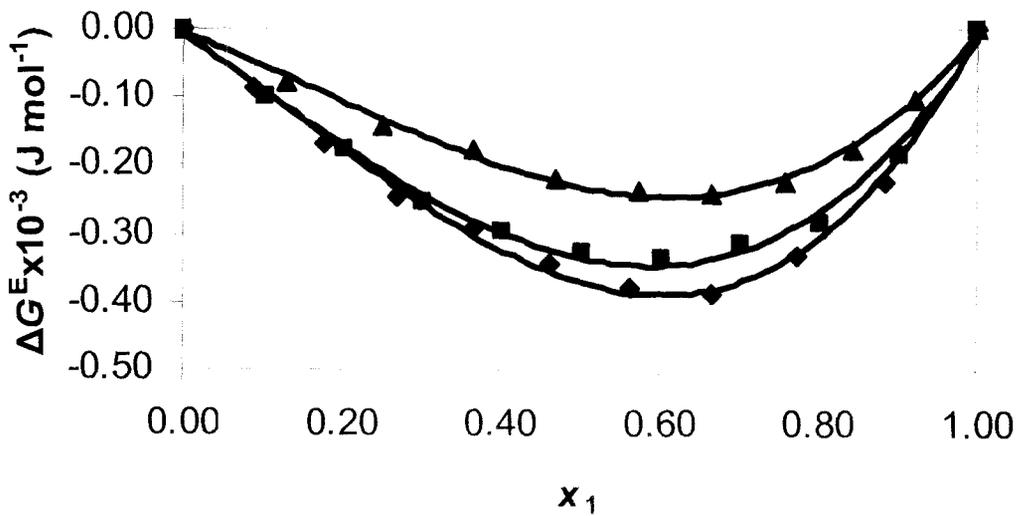


FIGURE 10. Plots of deviation in excess Gibbs free energy $\Delta G^E \times 10^{-3}$ (Jmol^{-1}) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (\blacklozenge), 2-ethoxyethanol (\blacksquare) and 2-butoxyethanol (\blacktriangle) at 313.15K

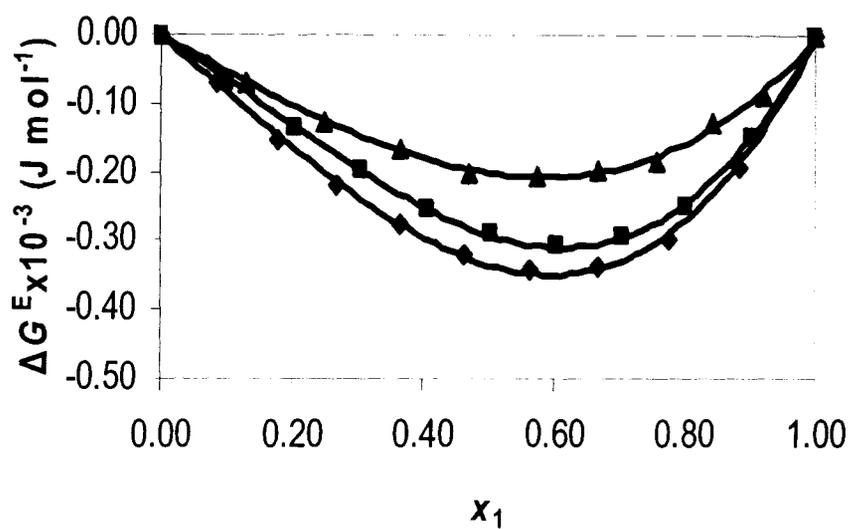


FIGURE 11. Plots of deviation in excess Gibbs free energy $\Delta G^E \times 10^{-3}$ (Jmol⁻¹) against mole fraction (x_1) of iso-amyl alcohol with 2-methoxyethanol (◆), 2-ethoxyethanol (■) and 2-butoxyethanol (▲) at 323.15K

CHAPTER X

Studies on Solution Properties of Ternary Mixture of Acetophenone + Amyl alcohol + Dichloromethane and its Corresponding Binaries at 298.15 K.

10.1. Introduction

In recent years, measurements of thermodynamic and transport properties of binary and ternary liquid mixtures have been adequately employed in understanding the nature of molecular systems and physico-chemical behaviour in liquid mixtures [1]. It is also possible to investigate molecular packing, molecular motion, various types and extent of intermolecular interaction influenced by the size, shape and chemical nature of component molecules and microscopic structure of liquids.

Acetophenone, a typical ketone is used in perfumery and as a hypotonic under the name "hypone". It is also used as a solvent for cellulose ethers. Dichloromethane is a very interesting solvent with appreciable industrial use in pharmaceutical industry, as paint stripping agent, aerosols and as adhesives etc. and also as it is a solvent exhibiting high density and low viscosity.

Considering all of these aspects we undertook investigations on the thermodynamic and transport properties of binary and ternary mixtures involving acetophenone (A.P), amyl alcohol (A.L) and dichloromethane (D.C.M).

In this paper are reported excess molar volume (V^E), viscosity deviations ($\Delta\eta$), deviations in isentropic compressibility (ΔK_S), excess molar refraction (ΔR) and Gibbs excess free energy of activation for viscous flow (ΔG^E) for three binary mixtures of A.P + A.L, A.P + D.C.M, A.L + D.C.M and

**Communicated in Monatshefte fur Chemie.*

their corresponding ternary mixtures at 298.15K over the entire range of composition. The excess or deviation properties of binary mixtures were fitted to Redlich-Kister polynomial equation to obtain their coefficients and have been interpreted in terms of molecular interactions and structural effects.

10.2. Experimental

10.2.1 *Experimental materials*

Acetophenone, amyl alcohol and dichloromethane were procured from S.d.fine-Chem Limited, Mumbai, India. Acetophenone was dried over anhydrous potassium carbonate for 3 days, filtered, and then distilled. The middle fraction of the distillate was retained [2]. Dichloromethane was dried over calcium hydride and distilled. Amyl alcohol was used as purchased. The purity of each substance was evaluated by comparing experimental values of density, viscosity, sound speed and refractive index with those reported in the literature whenever available, as presented in

10.2.2 *Measurements*

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostat bath controlled to ± 0.01 K. Viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4}$ mPas. 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 fractions was within ± 0.0002 . The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm⁻³.

Ultrasonic speeds of sound (u) were determined by a multifrequency ultrasonic interferometer (Mittal enterprise, New Delhi9, M-81) working at 1MHz, calibrated with triply distilled and purified water, methanol and benzene at 303.15K. The precision of ultrasonic speed measurements was ± 0.2 ms⁻¹. The details of the methods and techniques have been described in earlier papers [3-6]. Refractive index was measured with the help of Abbe-Refractometer (U.S.A). The accuracy of refractive index measurement was ± 0.0002 units. The refractometer was calibrated twice using distilled and deionized water, and calibration was checked after every few measurements.

10.3. Results and discussion

We have calculated excess molar volume (V^E), viscosity deviations ($\Delta\eta$), deviations in isentropic compressibility (ΔK_s), excess molar refraction (ΔR) and Gibbs excess free energy of activation for viscous flow (ΔG^E) at 298.15K for the binary mixtures of acetophenone, dichloromethane and amyl alcohol over all composition range. The variations of the excess properties over the entire range of composition for the binary mixtures are depicted in Figs. 1-5.

10.3.1 Excess molar volume

The density (ρ) values have been used to calculate the excess molar volumes (V^E) for binary ($n=2$) and ternary ($n=3$) mixture using the following equation [7]

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

where ρ is the density of the mixture and M_i , x_i , ρ_i are the molecular weight, mole fraction and viscosity of the i^{th} component in the mixture respectively

V^E is the resultant of contributions from several opposing effects. These may be divided arbitrarily into three types, namely, chemical, physical and structural. Physical contributions, which are nonspecific interactions between the real species present in the mixture, contribute a positive term to V^E . The chemical or specific intermolecular interactions result in a volume decrease, thereby contributing negative V^E values. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume [8].

The values of excess molar volume (V^E) are found to be negative for binary mixtures of A.P+A.L and A.L+D.C.M over the entire range of compositions but for A.P+D.C.M the V^E values are positive.

These phenomena are the results of difference in energies of interaction between molecules being in solutions and packing effects. Disruption of the ordered structure of pure component during formation of the mixture leads to a positive effect observed on excess volume while an order formation in the mixture leads to negative contribution. The carbonyl group is highly polar and has a high percentage of ionic character [9]. There is a negative charge on the carbonyl oxygen atom of acetophenone. The weaker interactions in binary mixture of A.P and D.C.M may be attributed to the internal interaction between the π -electrons of C=O bond and the π electrons of benzene ring [10]. The positive V^E values may also be due to repulsion between the highly electronegative chlorine atom of D.C.M and π electrons of benzene ring of acetophenone. Thus, for this binary mixture the factors which are responsible for expansion in volume are dominant over the entire composition range. The negative V^E values indicate the specific interactions such as intermolecular hydrogen bonding between the (-OH group of amyl alcohol and π electrons of C=O bond of acetophenone and also between -OH group of amyl alcohol and electronegative chlorine atom of dichloromethane) mixing components and also interstitial accommodation of the mixing components because of the difference in molar volumes. The negative V^E values may also be due to the

difference in the dielectric constants of the liquid components of the binary mixtures [11]. The negative V^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 [12].

The density (ρ) values and excess molar volume (V^E) for the ternary mixture (A.P+A.L+D.C.M) are reported in Table 5. From Table 5 it is evident that the V^E values are negative in the low mole fraction region of D.C.M suggesting specific intermolecular interaction between the two components (A.P+A.L), but as the mole fraction of D.C.M in the ternary mixture increases the magnitude of V^E decreases suggesting that dispersion forces now begins to operate. Thus, it can be said that the addition of D.C.M to binary mixture of A.L+A.P causes a decrease in intermolecular interaction between the mixing components. This is in agreement with our earlier discussion of binary mixtures.

10.3.2 Viscosity deviation

The measured η values for binary systems are listed in Table 2 and depicted graphically in Fig. 2. The viscosity deviations ($\Delta\eta$) [13] from linear dependence for binary ($n=2$) and ternary ($n=3$) mixtures can be calculated as

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

where, η is the viscosity of the mixture and x_i , η_i are the mole fraction and viscosity of pure component i respectively. The values of $\Delta\eta$ are positive for A.P+A.L and A.L+D.C.M and negative for A.P+D.C.M over the entire range of compositions. Also, the deviations in $\Delta\eta$ values are found to be opposite to the sign of excess molar volumes V^E or all three binary mixtures, which is in agreement with the view proposed by Brocos et al. [14, 15]. This further

reinforces our earlier conclusions regarding the intermolecular interactions from the variations of V^E values of these mixtures.

A correlation between the sign of $\Delta\eta$ and V^E (Table 2) has been observed for a number of binary solvent systems [16, 17] i.e., $\Delta\eta$ is positive when V^E is negative and vice-versa. In general, for systems where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative, whereas charge-transfer and hydrogen-bonding interactions lead to the formation of complex species between unlike molecules, thereby resulting in positive $\Delta\eta$ values [18].

10.3.3 Viscosity model and interaction parameter

Several semi empirical models have been proposed to estimate the dynamic viscosity, η of the binary liquid mixtures in terms of pure component data [19, 20] one of which is discussed below.

Grunberg and Nissan [21] have suggested the following logarithmic relation between the viscosity of binary liquid mixtures and of pure components

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2d_{12} \quad (3)$$

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 negative for all the binary liquid mixtures except that of acetophenone with dichloromethane over the entire range of compositions. The positive values of d_{12} may be attributed to the presence of specific interactions [22, 23] between the mixing components in the mixtures, whereas the negative values of d_{12} indicate the presence of dispersion forces [23] between them.

The viscosity (η) values and deviation in viscosity ($\Delta\eta$) values are reported in Table 5. It is seen from Table 5 that $\Delta\eta$ values are positive in the low mole fraction region of D.C.M but as the mole fraction of D.C.M in the ternary mixture increases the values of $\Delta\eta$ gradually decreases and becomes negative in higher mole fraction region of D.C.M. This in accordance with the inference of V^E values of ternary mixture.

10.3.4 Deviation in Isentropic Compressibility.

Isentropic compressibility, K_S and deviation in isentropic compressibility ΔK_S , for binary ($n=2$) and ternary ($n=3$) mixtures were calculated using the following relations:

$$K_S = \frac{1}{(u^2\rho)} \tag{4}$$

$$\Delta K_S = K_S - \sum_{i=1}^3 x_i K_{S,i} \tag{5}$$

where u and K_S are the speed of sound and isentropic compressibility of the mixture and $K_{S,i}$, the isentropic compressibility of the i^{th} component in the mixture respectively.

An examination of deviation in isentropic compressibility (ΔK_S) data in Table 3 and Fig.3 suggest that the quantity is positive for binary mixture of A.P+D.C.M and negative for A.P+A.L, D.C.M+A.L binary mixtures. These may be attributed to the relative strength of effects which influenced the free space between component molecules. The negative ΔK_S values arise from changes of "free volume" and polar interactions in the real mixture and positive ΔK_S values are due to the dispersion interactions between unlike molecules. These results support our earlier discussion arising from excess molar volumes.

10.3.5 Deviation in Molar Refraction.

The molar refraction, $[R]$ can be evaluated from Lorentz-Lorenz relation [24] and gives more information than n_D about the mixture phenomenon because takes into account the electronic perturbation of molecular orbital during the liquid mixture process and $[R]$ is also directly related to the dispersion forces

$$[R] = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \cdot \left(\frac{M}{\rho} \right) \quad (6)$$

Where $[R]$, n_D^2 , and M are, correspondingly, the molar refraction, the refractive index and the molar mass of the mixture respectively. Deviation from molar refraction was calculated from the following relation;

$$\Delta R = [R] - \sum_{i=1}^3 x_i [R]_i \quad (7)$$

The values of refractive indices and excess molar refraction (ΔR) for the binary mixtures are presented in Table 3 and depicted graphically in Fig.4 and the data for ternary mixture are reported in Table 6.

10.3.6 Excess Gibb's free energy of activation

On the basis of the theories of absolute reaction rates [25], the excess Gibbs energy of activation for viscous flow was calculated from the equation [26] for binary ($n=2$) and ternary ($n=3$) systems.

$$\Delta G^E = RT \left[\ln \eta V - \sum_{i=1}^3 x_i \ln \eta_i V_i \right] \quad (8)$$

where R , T , V_i and V are the universal gas constant, experimental temperature in absolute scale, and the molar volumes of the pure component and the mixtures, respectively. From Table 3 and Fig. 5 it is evident that the ΔG^E

values are positive for A.P + D.C.M and negative for A.P + A.L and A.L + D.C.M binary mixtures over entire range of mole fraction. The positive values indicate the specific interaction between unlike molecules compared to like molecules, while the negative values of ΔG^E indicate the dominance of dispersion forces in these mixtures.

The ΔG^E values of ternary mixture are reported in Table 5. The ΔG^E values decreases in the low mole fraction region of D.C.M and becomes negative but as the mole fraction of D.C.M increases, the magnitude of ΔG^E begins to increase and becomes positive in higher mole fraction region of D.C.M. Thus, it can be said that specific interaction between unlike molecules increases with the increase of D.C.M in the ternary mixture.

The excess properties ($(V^E, \Delta\eta, \Delta K_S, \Delta R, \Delta G^E)$) for the binary mixtures were fitted to the Redlich-Kister polynomial equation [27],

$$Y_{ij}^E = x_1 x_2 \sum_{i=1}^2 a_i (x_1 - x_2)^i \quad (9)$$

where Y^E refer to an excess property, x_1 is the mole fraction of I.A.A and x_2 is that of the other component.

The coefficients (a_i) were obtained by fitting Eq. (8) to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation. The estimated values of along with the standard deviations are summarized for all mixtures in Table 4. The standard deviation was calculated using the equation

$$\sigma = \left[\frac{(Y_{exp}^E - Y_{cal}^E)^2}{(n - m)} \right]^{\frac{1}{2}} \quad (10)$$

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

10.4. Conclusion

It may be concluded that in the low mole fraction region of D.C.M, intermolecular interaction between the two components (A.P+A.L), but as the mole fraction of D.C.M in the ternary mixture increases dispersion forces begins to operate. Thus, it can be said that the addition of D.C.M to binary mixture of A.L+A.P causes a decrease in intermolecular interaction between the mixing components.

Acknowledgment

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2007, SAP-2) for financial support.

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TABLE 1: Density (ρ), viscosity (η), sound speed (u) and refractive index (n_D) of the pure component liquids at different temperatures.

Pure components	$\rho \times 10^{-3} \text{kg m}^{-3}$		η/mPas		u/ms^{-1}		n_D	
	This work	Lit	This work	Lit	This work	Lit	This work	Lit
	Acetophenone	1.0291	1.0241[28]	1.6663	1.680[28]	1519.4	-	1.5340
amyl alcohol	0.8164	0.8110[30]	3.1858	3.056[31]	1271.6	1256[32]	1.4100	1.4078[30]
dichloromethane	1.3162	1.3163[33]	0.4652	0.406[34]	1071.3	1035[33]	1.4210	1.4228[33]

[29]^a Value reported at 293.15K

TABLE 2: Densities (ρ), viscosities(η), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), interaction parameter (d_{12}) and excess Gibbs energy of activation (ΔG^E) for binary mixtures of acetophenone, dichloromethane amyl alcohol.

x_1	$\rho \times 10^3$ kg m ³	$\eta_{exp}/$ mPas	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\eta$ /mPas	d_{12}	$\Delta G^E \times 10^{-3}$ (Jmol ⁻¹)
(x_1) acetophenone + (1- x_1)dichloromethane						
0.0000	1.3162	0.4652	0.0000	0.0000		0.0000
0.0728	1.2899	0.5046	0.1321	-0.0480	-0.171	9.3000
0.1501	1.2608	0.5598	0.3706	-0.0857	-0.051	19.7945
0.2324	1.2299	0.6209	0.6697	-0.1234	-0.044	28.0000
0.3201	1.2005	0.6967	0.8474	-0.1530	-0.021	45.0000
0.4139	1.1704	0.7804	1.0167	-0.1820	-0.045	60.0000
0.5144	1.1419	0.8931	1.0240	-0.1900	-0.017	74.3000
0.6224	1.1145	1.0357	0.8800	-0.1770	0.027	82.3386
0.7386	1.0867	1.2123	0.6684	-0.1400	0.080	80.0000
0.8641	1.0594	1.4220	0.2992	-0.0810	0.127	54.3000
1.0000	1.0291	1.6663	0.0000	0.0000		0.0000
(x_1)acetophenone + (1- x_1) amyl alcohol						
0.0000	0.8164	3.1858	0.0000	0.0000		0.0000
0.0754	0.8388	3.1043	-0.4083	0.0330	0.329	42.1548
0.1550	0.8495	3.0163	-0.5623	0.0660	0.349	120.6803
0.2392	0.8672	2.9183	-0.7467	0.0960	0.370	177.2188
0.3285	0.8859	2.8007	-0.8582	0.1140	0.381	221.3045
0.4232	0.9062	2.6567	-0.9433	0.1140	0.379	243.2884
0.5240	0.9280	2.4976	-0.9796	0.1080	0.386	250.8472
0.6313	0.9508	2.3096	-0.8895	0.0830	0.376	228.1293
0.7459	0.9745	2.1024	-0.6520	0.0500	0.358	178.6798
0.8685	1.0008	1.8981	-0.3810	0.0320	0.394	117.9123
1.0000	1.0291	1.6663	0.0000	0.0000		0.0000
(x_1)amyl alcohol + (1- x_1) dichloromethane						
0.0000	1.3162	0.4652	0.0000	0.0000		0.0000
0.0966	1.2400	0.7741	-0.3062	0.0460	3.704	773.7460
0.1940	1.1722	1.0969	-0.5479	0.1040	3.099	1144.5033
0.2921	1.1110	1.3908	-0.6950	0.1310	2.579	1275.3330
0.3909	1.0558	1.6686	-0.7650	0.1400	2.206	1261.3701

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0.4905	1.0056	1.9296	-0.7434	0.1300	1.916	1156.8684
0.5908	0.9603	2.1816	-0.6768	0.1090	1.690	991.2391
0.6919	0.9197	2.4367	-0.6050	0.0890	1.523	783.5470
0.7938	0.8820	2.6879	-0.4269	0.0630	1.385	545.4065
0.8965	0.8481	2.9273	-0.2730	0.0230	1.234	272.8385
1.0000	0.8164	3.1858	0.0000	0.0000		0.0000

TABLE 3: Ultrasonic speed (u), isentropic compressibility (K_S), deviation in isentropic compressibility (ΔK_S), refractive indices (n_D) and excess molar refraction (ΔR) for binary for binary mixtures of acetophenone, dichloromethane and amyl alcohol at 298.15K.

x_1	u/ms^{-1}	$K_S \times 10^{12}$ / Pa^{-1}	$\Delta K_S \times 10^{12}$ / Pa^{-1}	n_D	$\Delta R \times 10^6$ ($\text{m}^3\text{mol}^{-1}$)
(x_1) acetophenone + (1- x_1)dichloromethane					
0.0000	1071.30	662.00	0.00	1.4210	0.0000
0.0728	1091.31	650.95	6.50	1.4400	0.0626
0.1501	1116.37	636.42	10.60	1.4566	0.1200
0.2324	1146.94	618.08	12.10	1.4695	0.1084
0.3201	1180.31	597.92	13.10	1.4820	0.1020
0.4139	1219.21	574.80	12.60	1.4918	0.0450
0.5144	1262.78	549.18	11.20	1.5011	-0.0250
0.6224	1312.85	520.56	8.60	1.5097	-0.1100
0.7386	1371.47	489.24	5.30	1.5179	-0.1500
0.8641	1439.73	455.39	1.70	1.5263	-0.1450
1.0000	1519.40	420.92	0.00	1.5340	0.0000
(x_1)acetophenone + (1- x_1)amyl alcohol					
0.0000	1271.60	757.53	0.00	1.4100	0.0000
0.0754	1286.95	719.86	-12.30	1.4232	0.0330
0.1550	1321.15	674.45	-30.90	1.4300	0.0842
0.2392	1348.82	633.80	-43.20	1.4409	0.1340
0.3285	1368.40	602.80	-44.15	1.4519	0.1510
0.4232	1384.17	575.97	-39.10	1.4637	0.1610
0.5240	1402.94	547.46	-33.70	1.4760	0.1357
0.6313	1426.23	517.03	-28.00	1.4890	0.1142
0.7459	1451.80	486.86	-19.60	1.5020	0.0540
0.8685	1483.20	454.22	-10.97	1.5171	0.0200
1.0000	1519.40	420.92	0.00	1.5340	0.0000
(x_1)amyl alcohol + (1- x_1) dichloromethane					
0.0000	1071.30	662.00	0.00	1.4210	0.0000
0.0966	1098.30	668.58	-3.30	1.4190	-0.0490
0.1940	1123.57	675.79	-5.90	1.4170	-0.1400
0.2921	1148.71	682.13	-9.30	1.4155	-0.1800
0.3909	1172.21	689.28	-11.81	1.4140	-0.2300

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0.4905	1193.17	698.47	-12.20	1.4130	-0.2373
0.5908	1212.41	708.39	-11.80	1.4120	-0.2209
0.6919	1228.46	720.53	-9.10	1.4115	-0.1820
0.7938	1243.96	732.70	-6.30	1.4110	-0.1240
0.8965	1258.21	744.80	-3.50	1.4105	-0.0400
1.0000	1271.60	757.53	0.00	1.4100	0.0000

TABLE 4: Redlich-Kister coefficients and standard deviations (σ) for binary liquid mixtures at 298.15K.

Excess property	A_0	A_1	A_2	A_3	A_4	A_5	σ
(x_1) acetophenone + (1- x_1) dichloromethane							
$V^E \times 10^6$ $m^3 mol^{-1}$	4.0824	-0.6338	-1.7676	0.9017	-	1.5929	0.018
$\Delta\eta$ (mPa s)	-0.7056	-0.3702	-	-	-	-	0.004
$\Delta G^E \times 10^{-3}$ (Jmol $^{-1}$)	289.402	262.168	26.544	-81.231	-	-	1.073
$\Delta K_S \times 10^{12}$ /Pa $^{-1}$	45.7807	-34.9423	-0.2823	-23.9907	-	-	0.146
$\Delta R \times 10^6$ (m $^3 mol^{-1}$)	-0.0635	-1.4624	-0.1939	-	-	-	0.007
(x_1) acetophenone + (1- x_1) amyl alcohol							
$V^E \times 10^6$ $m^3 mol^{-1}$	-3.8344	0.5163	-	-	-	-	0.020
$\Delta\eta$ (mPa s)	0.4557	-0.0921	-0.1845	-	-	-	0.003
$\Delta G^E \times 10^{-3}$ (Jmol $^{-1}$)	1001.28 5	-132.586	-136.136	485.046	-	-	4.958
$\Delta K_S \times 10^{12}$ /Pa $^{-1}$	- 144.016 4	125.208 4	-83.6329	-	-	-	1.951
$\Delta R \times 10^6$ (m $^3 mol^{-1}$)	0.6373	-0.1529	-0.5202	-	-	-	0.005
(x_1) amylalcohol + (1- x_1) dichloromethane							
$V^E \times 10^6$ $m^3 mol^{-1}$	-2.9834	0.9074	-0.33454	-0.7695	-	-	0.013
$\Delta\eta$ (mPa s)	0.5065	-0.3149	0.2584	0.2111	-0.6720	-	0.002

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$\Delta G^E \times 10^{-3}$ (Jmol ⁻¹)	4679.077	-2656.448	1513.940	-947.285	528.753	632.36	0.008
$\Delta K_S \times 10^{12}$ /Pa ⁻¹	-48.9707	-2.7738	25.1304	-	-	-	0.320
$\Delta R \times 10^6$ (m ³ mol ⁻¹)	-0.9516	-0.0615	0.5962	-	-	-	0.003

TABLE 5: Densities (ρ), viscosities(η), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and excess Gibbs energy of activation (ΔG^E) for ternary mixtures of acetophenone, amyl alcohol and dichloromethane at 298.15K.

(1- x_1 - x_2)	$\rho \times 10^3$ kg m ³	$\eta_{exp}/$ mPas	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\eta/mPas$	$\Delta G^E \times 10^{-3}$ (Jmol ⁻¹)
(x_1)acetophenone+(x_2)amyl alcohol +(1- x_1 - x_2)dichloromethane					
0.0000	0.9116	1.8698	-1.9657	0.8962	624.78
0.0624	0.9392	1.6192	-4.0630	0.6748	450.41
0.1302	0.9716	1.3917	-5.4352	0.4791	269.37
0.2043	1.0039	1.2036	-6.2341	0.3258	131.89
0.2854	1.0385	1.0550	-6.9236	0.2151	53.05
0.3746	1.0763	0.8967	-7.3003	0.0986	-73.97
0.4733	1.1183	0.7779	-7.2811	0.0259	-118.99
0.5829	1.1621	0.6797	-6.7043	-0.0209	-102.19
0.7055	1.2106	0.6032	-5.5657	-0.0400	-1.87
0.8435	1.2655	0.5418	-3.5475	-0.0367	181.02
1.0000	1.3241	0.4652	-0.4003	-0.0400	322.40

 TABLE 6: Ultrasonic speed (u), isentropic compressibility (K_S), deviation in isentropic compressibility (ΔK_S), refractive indices (n_D) and excess molar refraction (ΔR) for ternary mixtures of acetophenone, amyl alcohol and dichloromethane at 298.15K.

(1- x_1 - x_2)	u/ms^{-1}	$K_S \times 10^{12}$ /Pa ⁻¹	$\Delta K_S \times 10^{12}$ /Pa ⁻¹	n_D	$\Delta R \times 10^6$ (m ³ mol ⁻¹)
(x_1)acetophenone+(x_2)amyl alcohol +(1- x_1 - x_2)dichloromethane					
0.0000	1381.81	574.50	-36.88	1.4635	-0.0364
0.0624	1345.86	587.81	-18.00	1.4620	-0.4302
0.1302	1277.42	630.71	8.66	1.4595	-0.8879
0.2043	1243.04	644.67	18.19	1.4560	-1.2357
0.2854	1202.73	665.70	33.85	1.4530	-1.4516
0.3746	1180.89	666.27	38.30	1.4490	-1.6099
0.4733	1152.76	672.90	43.50	1.4445	-1.6728
0.5829	1128.73	675.44	41.30	1.4405	-1.5144
0.7055	1092.76	691.73	32.00	1.4350	-1.2433
0.8435	1084.10	672.38	16.12	1.4300	-0.7490
1.0000	1071.62	657.64	-3.96	1.4210	-0.0978

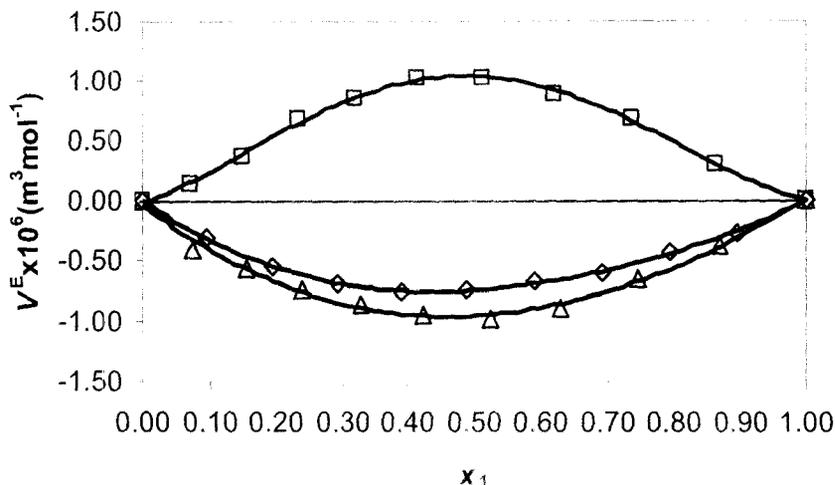


FIGURE 1. Excess molar volumes $V^E \times 10^6$ (m³ mol⁻¹) versus mole fraction (x_1) for the three binary subsystems at 298.15K. □(x_1) A.P + (1- x_1) D.C.M, ◇ (x_1) A.L + (1- x_1) D.C.M, △(x_1) A.P + (1- x_1) A.L.

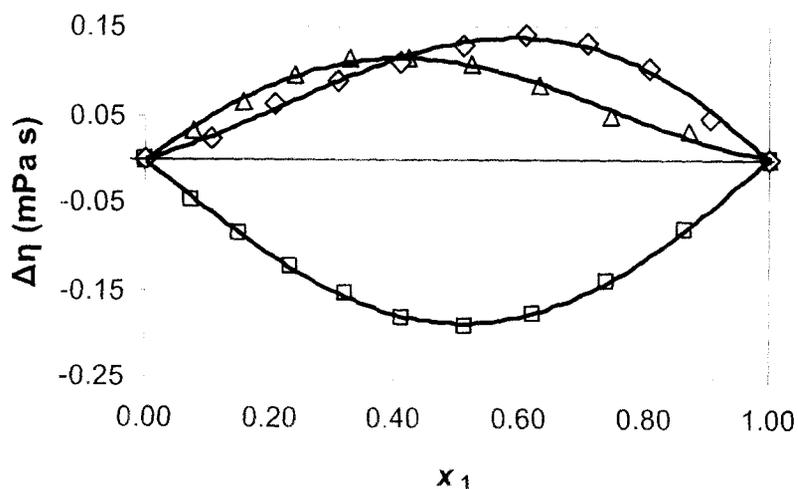


FIGURE 2. Viscosity deviations, $\Delta\eta$ (mPa s) versus mole fraction (x_1) for the three binary subsystems at 298.15K. □(x_1) A.P + (1- x_1) D.C.M, ◇ (x_1) A.L + (1- x_1) D.C.M, △(x_1) A.P + (1- x_1) A.L.

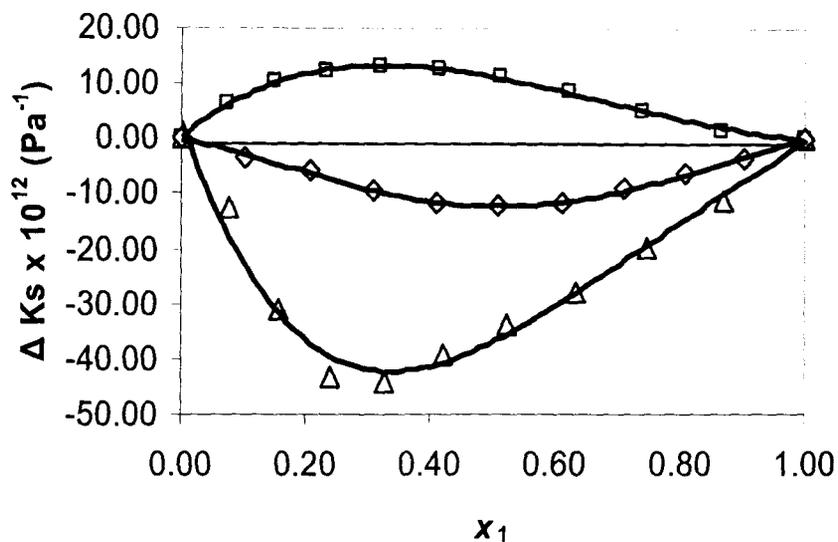


FIGURE 3. Deviation in isentropic compressibility $\Delta K_S \times 10^{12}$ (Pa^{-1}) versus mole fraction (x_1) for the three binary subsystems at 298.15K. $\square(x_1)$ A.P + (1- x_1) D.C.M, $\diamond(x_1)$ A.L + (1- x_1) D.C.M, $\Delta(x_1)$ A.P + (1- x_1) A.L.

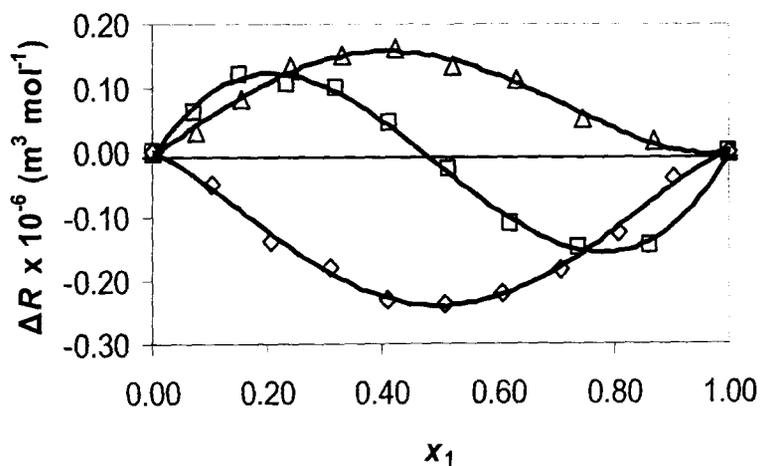


FIGURE 4. Molar refraction $\Delta R \times 10^{-6}$ ($\text{m}^3 \text{mol}^{-1}$) versus mole fraction (x_1) for the three binary subsystems at 298.15K. $\square(x_1)$ A.P + (1- x_1) D.C.M, $\diamond(x_1)$ A.L + (1- x_1) D.C.M, $\Delta(x_1)$ A.P + (1- x_1) A.L.

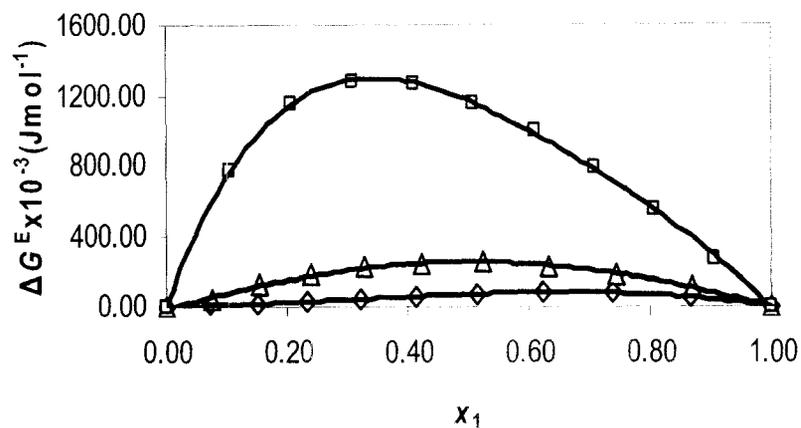


FIGURE 5. Deviation of excess Gibbs energy of activation $\Delta G^E \times 10^{-3} \text{ (J mol}^{-1}\text{)}$ versus mole fraction (x_1) for the three binary subsystems at 298.15K. $\square(x_1)$ A.P + (1- x_1) D.C.M, $\diamond(x_1)$ A.L + (1- x_1) D.C.M, $\Delta(x_1)$ A.P + (1- x_1) A.L.

CHAPTER XI

Study on Ion-Solvent Interactions of Alkali Metal Salts in Pure Methanol and its Binary Mixtures with Ethane 1, 2-Diol by a Conductometric Technique.

11.1. Introduction

Studies on the transport properties of electrolytes in different solvent media are of great importance for obtaining information concerning the behavior of electrolyte solutions. The use of mixed solvents enables the variation of properties such as dielectric constant or viscosity and therefore the ion-ion and ion-solvent interactions can be better studied. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration dependence of the electrolyte conductivity. In the present study, an attempt has been made to ascertain the nature of ion-solvent interactions of sodium salts (NaI, NaSCN, CH₃COONa) in ethane 1, 2-diol + methyl alcohol mixtures using the conductometric technique as literature survey revealed that very scarce work has been carried out in the solvent mixture considered. Thermodynamic parameters are also evaluated and discussed.

11.2. Experimental Section

Sodium metal salts (A.R. grade) were procured from Merck, India and purified as described in the literature [1, 2]. Ethane-1, 2-diol (E. Merck, India) and methyl alcohol (E. Merck, India) was purified by standard methods [3].

A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The conversion of molality into molarity was accomplished using density values [4].

**Published in Fluid Phase Equilibria 282 (2009) 51.*

The values of relative permittivity (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner [5].

Densities were measured with an Ostwald -Sprengel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostat water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The density values were reproducible to $\pm 3 \times 10^{-3}$ g.cm⁻³. The details of the method have been discussed elsewhere [6].

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 [7-9]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa.s. The details of the methods and measurement techniques had been described elsewhere [10, 11].

The conductance measurements were carried out in a Systronic 308 conductivity bridge (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10 having cell constant $0.1 \pm 10\%$. The cell was calibrated by the method of Lind et al. [12] using aqueous potassium chloride solutions.

11.3. Results and Discussion

The solvent properties of ethane1, 2-diol + methyl alcohol mixtures are reported in Table. 1, where ϵ is the dielectric constant, ρ the density of the solvent mixture and η the viscosity of the solvent mixture. The conductance data have been analyzed using the Fuoss conductance equation [13, 14]. For a given set of conductivity values ($c_j, \Lambda_j, j = 1, \dots, n$) three adjustable parameters, the limiting molar conductivity (Λ^0), the association constant (K_A), and the distance of closest approach of ions (R) are derived from the following set of equations.

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

$$P = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \frac{\beta \kappa}{2(1 + \kappa R)} \quad (4)$$

$$\beta = \frac{e^2}{Dk_B T} \quad (5)$$

$$K_A = \frac{K_R}{(1 - \alpha)} = \frac{K_R}{(1 + K_S)} \quad (6)$$

where the terms have their usual significance.

The computations were performed using a program suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set ($c_j, \Lambda_j, j = 1, \dots, n$), n, D, η, T , initial values of Λ^0 , and an instruction to cover a preselected range of R values.

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

$$\delta^2 = \sum \frac{[\Lambda_j(\text{calc}) - \Lambda_j(\text{obsv})]^2}{(n - 2)} \quad (7)$$

for a sequence of R values and then plotting δ against R ; the best-fit R corresponds to the minimum of the δ - R versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increment to locate the minimum, but no significant minima were found in the δ - R curves for all the salts studied here; thus, R values are 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 is given by

$$d(A^\circ) = 1.183 \left(\frac{M}{\rho} \right)^{1/3} \quad (8)$$

where M is the molar mass of the solvent and ρ is its density. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by

$$M_{\text{av}} = \frac{M_1 M_2}{(W_1 M_2 + W_2 M_1)} \quad (9)$$

where W_1 is the mass fraction of the first component of molar mass M_1 . The values of Λ° , K_A and R obtained by this procedure are reported in Table 3.

A perusal of Table 3 reveals that the values of Λ° of all salts decreases as the concentration of ethane 1, 2-diol in the solvent mixture increases. But as the temperature increases, Λ° values increase for all of ethane 1, 2-diol + methyl alcohol mixtures. The trend in Λ° can be discussed through another characteristic function called the Walden product, $\Lambda^\circ \eta$. From Table 3 and 4 it is seen that although Λ° decreases as the concentration of ethane 1, 2-diol increases, the Walden product increases with increasing concentration of

ethane 1, 2-diol for most of the solvent mixtures which can be attributed to the increase in viscosity (η) with increasing concentration of ethane 1, 2-diol suggesting the predominance of η over $\Lambda^o\eta$. Changes in Walden product with concentration are common and they can be attributed to changes in ion-solvation and ion-solvent interaction.

From Table 3, we see that Λ^o of sodium salts of common cations follows the sequence $\text{SCN}^- > \text{I}^- > \text{CH}_3\text{COO}^-$. Furthermore, Λ^o of the studied electrolyte is enhanced in the following order: $\text{NaSCN} > \text{NaI} > \text{CH}_3\text{COONa}$. It is evident from the crystallographic radii of these ions the acetate ion (CH_3COO^-) due to its small size is most solvated while iodide ion (I^-) and thiocyanate ion (SCN^-) have preferentially larger crystallographic radii and thus shows less tendency towards solvation.

There are marked characteristics behaviors in the K_A values. K_A values generally decreases as the temperature is increased; the thermal motion probably destroys the solvent structure. However, K_A of all salts decreases as the concentration of ethane 1, 2- diol increases in the mixture.

As the conductance of an ion depends on the rate of movement, it seems reasonable to treat the conductance in a manner analogous to that employed for other processes taking place at a definite rate which increases with temperature. On this basis it would be possible to write;

$$\Lambda^o = Ae^{-E/RT} \quad (10)$$

$$\ln \Lambda^o = \ln A - \frac{E}{RT} \quad (11)$$

where A is the frequency factor, R is the universal gas constant, and E is the Arrhenius activation energy of transport processes.

From the plot of $\log \Lambda^o$ versus $1/T$ for the sodium salts for all solvent mixtures, E values have been computed from the slope [15] and are recorded in Table 4.

The Gibbs energy change (ΔG°) for association is calculated from the relation [16].

$$\Delta G^\circ = -RT \ln K_A \quad (11)$$

The enthalpy of association (ΔH°) is obtained by studying the association constant (K_A) over a range of temperature by means of Van't Hoff's isochore, where $\log K_A$ values are plotted against $1/T$ giving a straight line with slope $-\Delta H^\circ/R$. The negative ΔH° values obtained are found to decrease systematically with the concentration of ethane 1, 2-diol in the mixture.

The entropy change (ΔS°) is calculated from the Gibb's-Helmholtz equation;

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The values of these thermodynamic functions are given in Table 5.

If we consider that from a rudimentary standpoint the ion pair is formed with only the action of the Columbic force in a continuum medium, the values of ΔH° and ΔS° of the ion-pair formation will be negative. Therefore, all the experimental values of ΔH° and ΔS° are negative for all the sodium salts studied here. The negative sign of ΔH° means that the association process is exothermic.

11.4 Conclusion

It can be concluded that Λ° of sodium salts of common cations follows the sequence $\text{SCN}^- > \text{I}^- > \text{CH}_3\text{COO}^-$ while Λ° of the studied electrolyte is enhanced in the following order: $\text{NaSCN} > \text{NaI} > \text{CH}_3\text{COONa}$ which may be explained from the crystallographic radii of these ions.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2007, SAP-1) for financial support.

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TABLE 1. Values of density (ρ), viscosity (η) and dielectric constant (ϵ) of ethane 1, 2-diol + methyl alcohol mixtures at various temperatures.

Mass%(w_1)(ethane 1, 2-diol)	Temp K	$\rho \times 10^{-3}(\text{kg m}^{-3})$		η (mPa. s)		ϵ^a
		This work	Lit	This work	Lit	This work
$w_1=0.00$	293.15	0.7910	0.7915[17]	0.5814	0.5820[17]	33.1[5]
	298.15	0.7859	0.7866[17]	0.5436	0.5445[17]	32.7[5]
	303.15	0.7814	0.7820[17]	0.5112	0.5120[17]	31.9[5]
$w_1=0.25$	293.15	0.8647		1.1268		35.2[5]
	298.15	0.8609		1.0295		34.7[5]
	303.15	0.8586		0.9454		33.7[5]
$w_1=0.50$	293.15	0.9383		2.2692		37.3[5]
	298.15	0.9338		2.0452		36.7[5]
	303.15	0.9321		1.8101		35.6[5]
$w_1=0.75$	293.15	1.0234		5.7998		39.3[5]
	298.15	1.0196		4.9040		38.7[5]
	303.15	1.0173		4.2319		37.4[5]

^a Calculated using the scheme given at ref. no [5].

TABLE 2. Molar conductance (Λ) and molar concentration of various sodium salts in ethane 1, 2-diol (1) + methyl alcohol (2) mixtures at different temperatures.

$c \times 10^4$ (mol dm ⁻³)	Λ (S. cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S. cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S. cm ² mol ⁻¹)
293.15 K		298.15 K		303.15 K	
NaSCN ($w_1=0.00$)					
6.9857	95.60	6.9857	103.50	6.9857	108.50
10.0229	94.07	10.0229	102.45	12.8071	106.00
15.3685	92.71	15.3685	101.00	15.3685	105.07
17.7329	91.92	17.7329	100.14	17.7329	104.50
23.8477	89.93	21.9550	99.36	21.9550	103.14
25.6142	89.50	23.8477	98.71	23.8477	102.71
31.6410	88.36	25.6142	98.21	25.6142	102.14
34.1522	87.84	31.6410	97.07	31.6410	100.80
38.4212	87.20	34.1522	96.75	34.1522	100.14
41.9141	86.64	36.3991	96.16	36.3991	99.79
43.4327	86.80	41.9141	95.07	41.9141	98.64
48.3823	85.78	47.2877	94.14	48.3823	97.35
50.3451	85.41	54.8875	92.93	50.3451	97.13
56.6208	84.77	58.5467	92.50	56.0742	96.00
63.3614	83.96	60.1376	92.29	62.6124	94.93
NaI ($w_1 = 0.00$)					
7.0053	83.44	7.0053	88.14	7.0053	98.00
10.0511	82.36	10.0511	86.86	10.0511	95.40
15.4116	80.40	15.4116	84.64	15.4116	92.46
17.7827	79.69	17.7827	84.07	17.7827	91.48
23.9146	78.40	19.9780	83.29	22.0166	90.14
25.6861	77.86	23.9146	82.50	23.9146	89.60
30.3562	76.88	25.6861	81.71	25.6861	89.07
35.4051	76.00	31.7298	80.19	31.7298	85.20
37.5412	75.56	34.2481	79.56	34.2481	84.60
41.2172	75.00	36.5012	79.07	36.5012	84.00
46.8393	74.31	42.0317	77.91	42.0317	82.50

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50.9367	73.56	47.4204	76.97	48.5181	80.40
56.5093	72.88	49.5374	76.63	50.4864	80.00
61.7991	71.94	55.0415	75.71	56.2316	78.20
65.2936	71.50	60.3064	77.94	62.5189	76.00

CH₃COONa (w₁ = 0.00)

7.0375	76.13	7.0375	83.50	7.0375	89.30
10.0972	74.97	10.0972	82.40	10.0972	85.70
15.4824	73.06	12.9020	81.07	15.4824	80.40
17.8643	72.75	17.8643	79.49	17.8643	78.60
24.0245	71.59	20.0698	78.93	20.0698	78.00
25.8040	71.31	24.0245	77.88	24.0245	75.40
31.8756	69.94	25.8040	77.32	25.8040	74.00
34.4054	69.47	31.8756	75.79	31.8756	71.40
36.6689	69.13	34.4054	75.29	34.4054	69.60
42.2248	68.25	36.6689	74.75	36.6689	69.20
47.6382	67.59	42.2248	73.71	42.2248	68.00
49.7649	67.32	47.6382	72.63	48.7410	64.30
55.9088	66.36	49.7649	71.94	50.7183	63.40
57.5629	66.36	55.2944	71.25	56.4899	62.00
62.5252	65.57	58.9807	70.44	59.8185	61.20
64.9263	65.30	60.0231	70.10	62.8061	61.20

NaSCN (w₁ = 0.25)

8.6155	50.60	8.3564	74.90	8.2592	82.10
12.3613	49.30	11.9896	73.00	11.8501	78.60
21.8700	46.30	21.2123	70.00	20.9656	72.63
24.5700	44.60	23.8311	68.80	23.5540	70.70
27.0771	44.60	26.2629	68.30	25.9574	68.60
29.4114	43.30	30.6400	67.12	30.2837	66.40
33.6281	42.00	32.6168	66.00	34.0691	65.00
37.3336	41.60	36.2109	65.00	37.4092	64.00
42.1200	40.70	42.2335	63.60	43.0347	61.40
47.3850	39.00	47.0810	63.20	47.5886	60.00
49.6414	38.60	49.1665	61.80	49.5551	58.00
56.8620	36.90	56.5662	60.40	57.2025	56.12
59.6700	36.40	61.7823	58.67	61.5442	54.76
65.1544	35.60	63.1950	58.11	65.6146	53.80
72.2057	34.00	65.6571	57.50	71.1008	51.40

Study on Ion-Solvent..... Conductometric Technique.

NaI ($w_1 = 0.25$)

8.6155	50.60	8.2955	61.50	8.6155	67.40
12.3613	49.30	11.9022	59.00	12.3613	66.90
21.8700	46.30	21.0577	56.37	21.8700	64.60
24.5700	44.60	23.6574	55.50	24.5700	64.00
27.0771	44.60	26.0714	54.50	27.0771	62.90
29.4114	43.30	30.4167	54.00	29.4114	61.50
33.6281	42.00	34.2188	52.50	33.6281	61.10
37.3336	41.60	37.5735	53.00	39.0229	59.73
42.1200	40.70	43.2237	52.00	42.1200	59.28
47.3850	39.00	47.7976	52.00	47.3850	58.67
49.6414	38.60	49.7727	50.43	51.6927	58.21
56.8620	36.90	56.8160	50.69	56.8620	57.64
59.6700	36.40	62.2817	49.00	60.9236	56.80
65.1544	35.60	65.5458	48.00	68.4450	56.20
72.2057	34.00	72.0395	47.50	71.6554	55.60

CH₃COONa ($w_1 = 0.25$)

8.1791	44.90	8.3118	53.60	8.1791	59.50
11.7352	43.50	11.9257	52.30	11.7352	59.00
20.7623	42.00	15.2383	49.71	20.7623	56.83
23.3256	41.70	21.0992	48.94	23.3256	56.16
25.7057	41.70	26.1229	48.40	25.7057	55.24
29.9900	40.90	30.4767	47.74	29.9900	55.02
33.7388	40.00	37.6476	47.40	33.7388	53.94
37.0465	40.00	45.7150	46.80	37.0465	54.00
42.6174	39.20	49.8709	46.40	42.6174	52.56
47.1271	38.40	52.5236	46.11	47.1271	52.50
50.8526	38.20	58.7764	45.69	49.0745	51.00
58.9459	37.10	68.5725	44.80	56.6478	50.30
63.5082	36.80	73.1440	44.66	60.9474	49.50
66.9008	36.30	78.3686	44.00	64.2643	49.79
71.6088	35.80	82.6000	43.52	71.6088	48.60

NaSCN ($w_1 = 0.50$)

10.0164	35.13	10.2782	38.07	10.0164	43.93
14.3713	34.91	18.8433	37.47	14.3713	43.46
22.0360	34.66	22.6120	37.19	18.3633	43.00

Study on Ion-Solvent..... Conductometric Technique.

25.4262	34.47	26.0908	36.96	22.0360	42.73
28.5652	34.39	35.0876	36.53	25.4262	42.56
31.4800	34.31	37.6867	36.35	31.4800	41.93
36.7267	34.15	42.3975	36.09	34.1938	41.80
41.3175	34.07	46.5541	35.93	36.7267	41.74
45.3682	33.94	50.2489	35.73	41.3175	41.44
48.9689	33.90	56.5300	35.47	45.3682	41.14
52.1905	33.80	63.9035	35.27	48.9689	40.97
55.0900	33.71	67.8360	35.13	55.0900	40.71
62.2757	33.63	71.1859	34.96	62.2757	40.30
69.3726	33.45	73.5600	33.85	66.1080	40.07
72.1869	33.39	75.6400	33.61	76.7921	39.73

NaI ($w_1 = 0.50$)

10.0556	28.14	9.5582	33.90	10.0556	36.83
14.4276	27.99	13.7139	33.50	14.4276	36.06
18.4353	27.84	21.0280	33.10	18.4353	35.60
22.1223	27.76	24.2631	32.80	22.1223	35.14
25.5258	27.67	27.2585	32.67	25.5258	34.91
31.6033	27.50	35.0467	32.33	28.6771	34.60
34.3278	27.48	39.4275	32.13	34.3278	33.94
36.8706	27.40	43.2929	31.96	39.2493	33.49
41.4794	27.29	46.7289	31.76	41.4794	33.27
45.5460	27.24	49.8032	31.64	45.5460	32.93
49.1608	27.15	56.2377	31.36	49.1608	32.73
55.3059	27.08	62.2257	31.13	55.3059	32.29
60.3337	27.02	67.5900	30.93	60.3337	31.90
64.5235	26.93	72.2838	30.80	68.0687	31.43
72.4697	26.79	73.5600	30.10	71.1075	31.34

CH₃COONa ($w_1 = 0.50$)

9.8449	25.15	9.8082	27.99	9.8449	31.23
14.1253	24.83	14.0726	27.73	14.1253	30.67
18.0490	24.59	24.8977	27.35	18.0490	30.29
21.6588	24.39	27.9715	27.21	21.6588	30.00
24.9909	24.28	33.4831	27.00	24.9909	29.64
28.0762	24.08	35.9633	26.96	30.9411	29.30
30.9411	24.00	44.4253	26.68	33.6084	29.09
36.0979	23.80	47.9511	26.61	40.6102	28.63
44.5916	23.50	51.1058	26.55	44.5916	28.40
54.1469	23.20	57.7086	26.34	48.1306	28.20

Study on Ion-Solvent..... Conductometric Technique.

59.0693	23.10	60.9813	26.30	51.2971	28.07
63.1714	22.95	66.3938	26.16	56.7253	27.85
66.6423	22.89	73.0868	26.00	59.0693	27.52
72.1959	22.72	74.6300	25.86	63.1714	27.31
73.5600	22.12	75.6200	24.98	73.3603	26.98

NaSCN ($w_1 = 0.75$)

11.6059	16.91	11.6059	18.86	11.6059	20.71
16.6519	16.73	16.6519	18.73	16.6519	20.65
21.2774	16.63	21.2774	18.61	21.2774	20.60
25.5329	16.43	25.5329	18.54	25.5329	20.56
33.0982	16.25	33.0982	18.43	33.0982	20.50
36.4755	16.16	36.4755	18.38	36.4755	20.48
42.5548	16.04	42.5548	18.29	42.5548	20.44
47.8742	15.88	47.8742	18.23	47.8742	20.41
52.5677	15.86	52.5677	18.17	52.5677	20.37
56.7397	15.73	56.7397	18.12	56.7397	20.35
63.8322	15.59	63.8322	18.04	63.8322	20.31
69.6351	15.50	69.6351	17.98	69.6351	20.28
78.5627	15.38	78.5627	17.91	78.5627	20.23
82.0700	15.29	83.6422	17.86	83.6422	20.22
86.4823	15.19	87.7693	17.81	91.1889	20.17

NaI ($w_1 = 0.50$)

11.6233	14.40	11.6233	16.01	11.6233	18.68
16.6769	14.30	16.6769	15.93	16.6769	18.59
21.3093	14.22	21.3093	15.90	21.3093	18.53
25.5712	14.12	25.5712	15.85	25.5712	18.45
29.5052	14.04	33.1479	15.80	33.1479	18.35
33.1479	13.97	36.5303	15.78	36.5303	18.34
36.5303	13.92	42.6187	15.75	42.6187	18.23
42.6187	13.87	47.9460	15.73	47.9460	18.18
47.9460	13.78	52.6466	15.69	52.6466	18.16
52.6466	13.72	56.8249	15.68	60.5634	18.10
56.8249	13.66	63.9280	15.66	63.9280	18.07
60.5634	13.62	74.5827	15.61	69.7396	18.02
69.7396	13.56	80.5019	15.59	74.5827	17.99
78.6806	13.47	85.2373	15.57	82.1931	17.93
83.7677	13.41	89.1118	15.56	91.3257	17.89

CH₃COONa ($w_1 = 0.50$)

11.5835	11.79	11.5835	13.39	11.5835	16.23
16.6198	11.69	16.6198	13.22	16.6198	15.92
21.2365	11.57	21.2365	13.09	21.2365	15.69
25.4837	11.50	25.4837	13.02	25.4837	15.50
29.4043	11.43	29.4043	12.94	29.4043	15.34
36.4054	11.34	33.0345	12.87	33.0345	15.26
42.4729	11.23	36.4054	12.80	36.4054	15.08
47.7820	11.15	42.4729	12.71	42.4729	14.91
52.4665	11.10	47.7820	12.64	47.7820	14.78
56.6306	11.05	52.4665	12.58	52.4665	14.66
60.3562	11.00	60.3562	12.49	60.3562	14.46
66.7431	10.94	66.7431	12.39	66.7431	14.25
76.4512	10.83	76.4512	12.28	72.0193	14.16
81.9120	10.79	84.9458	12.17	78.4115	14.03
86.3159	10.71	88.8070	12.14	83.4812	13.90

TABLE 3. Derived conductivity parameters for sodium salts in ethane 1, 2-diol (1) + methyl alcohol (2) mixtures at various temperatures.

Mass%(w_1)(ethane 1, 2-diol)	T (K)	Λ° ($S \cdot cm^2 mol^{-1}$)	K_A ($dm^3 mol^{-1}$)	R (A°)	δ
NaSCN					
$w_1 = 0.00$	293.15	93.64	83.52	6.11	2.81
	298.15	108.17	52.07	6.12	0.13
	303.15	113.49	38.04	6.33	0.08
$w_1 = 0.25$	293.15	76.26	51.63	6.17	1.67
	298.15	82.90	35.63	6.17	0.66
	303.15	100.25	24.63	6.18	0.92
$w_1 = 0.50$	293.15	26.14	22.42	6.42	0.03
	298.15	39.65	18.89	6.47	0.04
	303.15	45.74	12.79	6.38	0.05
$w_1 = 0.75$	293.15	17.66	10.53	6.58	0.03
	298.15	19.41	6.73	6.59	0.01
	303.15	21.36	4.32	6.61	0.01
NaI					
$w_1 = 0.00$	293.15	94.55	65.54	6.16	2.69
	298.15	97.41	49.31	6.17	0.86
	303.15	106.86	28.48	6.18	0.78
$w_1 = 0.25$	293.15	60.03	43.65	6.22	0.67
	298.15	65.64	34.08	6.22	0.60
	303.15	72.85	21.63	6.23	0.45
$w_1 = 0.50$	293.15	28.97	31.65	6.51	0.01
	298.15	35.25	21.04	6.57	0.04

Study on Ion-Solvent..... Conductometric Technique.

	303.15	39.21	12.23	6.53	0.06
	293.15	14.90	16.82	6.53	0.02
$w_1 = 0.75$	298.15	16.38	14.68	6.84	0.01
	303.15	19.21	10.48	6.65	0.02
CH ₃ COONa					
	293.15	79.80	44.95	6.24	0.15
$w_1 = 0.00$	298.15	88.58	32.52	6.25	0.13
	303.15	102.74	25.09	6.26	0.49
	293.15	48.14	36.81	6.31	0.27
$w_1 = 0.25$	298.15	56.35	28.17	6.32	0.31
	303.15	64.31	21.63	6.33	0.42
	293.15	26.74	33.46	6.39	0.52
$w_1 = 0.50$	298.15	28.99	22.87	6.60	0.04
	303.15	32.97	17.68	6.61	0.08
	293.15	12.27	17.82	6.71	0.01
$w_1 = 0.75$	298.15	13.88	17.41	6.72	0.01
	303.15	17.14	12.53	6.73	0.03

TABLE 4. Values of activation energy (E) and Walden products ($\Lambda^o\eta$) of sodium salts in ethane 1, 2-diol (1) + methyl alcohol (2) mixtures at various temperatures.

Mass%(w_1) (ethane 1, 2-diol)	E (kJ mol ⁻¹)	$\Lambda^o\eta \times 10^3$ (S. cm ² mol ⁻¹ Pa. s)		
		293.15K	298.15K	303.15K
NaSCN				
$w_1 = 0.00$	14.24	54.44	58.80	58.01
$w_1 = 0.25$	20.16	85.93	85.35	94.78
$w_1 = 0.50$	41.46	59.32	81.09	82.79
$w_1 = 0.75$	14.05	102.42	95.19	90.39
NaI				
$w_1 = 0.00$	9.02	54.97	52.95	54.63
$w_1 = 0.25$	14.3	67.64	67.58	68.87
$w_1 = 0.50$	22.4	65.74	72.09	70.97
$w_1 = 0.75$	18.74	86.42	80.33	81.29
CH ₃ COONa				
$w_1 = 0.00$	18.65	46.40	48.15	52.52
$w_1 = 0.25$	21.41	54.24	58.01	60.80
$w_1 = 0.50$	15.46	60.68	59.29	59.68
$w_1 = 0.75$	24.66	71.16	68.07	72.54

TABLE 5. Thermodynamic functions for association of sodium salts in ethane 1, 2-diol (1) + methyl alcohol (2) mixtures at various temperatures.

Mass%(w_1)(ethane 1, 2-diol)	T (K)	$-\Delta H^o$ (KJ mol ⁻¹)	$-\Delta G^o$ (KJ mol ⁻¹)	$-\Delta S^o$ (J K ⁻¹ mol ⁻¹)
NaSCN				
$w_1 = 0.00$	293.15	58.18	10.79	161.66
	298.15		9.80	162.27
	303.15		9.17	161.67
$w_1 = 0.25$	293.15	54.9	9.61	154.49
	298.15		8.86	154.42
	303.15		8.07	154.48
$w_1 = 0.50$	293.15	41.39	7.58	115.33
	298.15		7.28	114.41
	303.15		6.42	115.36
$w_1 = 0.75$	293.15	35.83	5.74	102.64
	298.15		4.74	104.28
	303.15		3.69	106.02
NaI				
$w_1 = 0.00$	293.15	61.48	10.19	174.96
	298.15		9.66	173.81
	303.15		8.44	174.96
$w_1 = 0.25$	293.15	51.8	9.20	185.16
	298.15		8.75	183.57
	303.15		7.75	183.84
$w_1 = 0.50$	293.15	40.2	8.42	108.41
	298.15		7.55	109.51
	303.15		6.31	111.79

Study on Ion-Solvent..... Conductometric Technique.

$w_1 = 0.75$	293.15	25.1	6.88	62.15
	298.15		6.66	61.85
	303.15		6.26	62.15
CH ₃ COONa				
$w_1 = 0.00$	293.15	43.11	9.28	115.40
	298.15		8.63	115.65
	303.15		8.12	115.42
$w_1 = 0.25$	293.15	39.29	8.79	104.04
	298.15		8.27	104.04
	303.15		7.75	104.04
$w_1 = 0.50$	293.15	31.19	8.56	77.20
	298.15		7.76	78.58
	303.15		7.24	79.00
$w_1 = 0.75$	293.15	25.9	7.02	64.40
	298.15		7.08	63.12
	303.15		6.35	64.49

CHAPTER: XII

Concluding Remarks

Various interactions such as solute-solute, solute-solvent and solvent-solvent prevailing in aqueous, non-aqueous and mixed solvent systems in various concentration regions has been studied in our research work.

1, 4-dioxane (DO) and tetrahydrofuran (THF) are polar aprotic solvents of low permittivity, each with great present-day synthetic and industrial importance. They are frequently used in electrical conductance studies and in high-energy batteries has found its application in organic syntheses as manifested from the physico-chemical studies in this medium.

Ethane-1, 2 diol have received increasing attention as a class of substance widely used in different applications. They find a variety of applications in pharmaceutical, cosmetics, food and textiles fields .

Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc.

Tetraalkylammonium salts are bulky in nature and are known to orient water molecules around them depending on their alkyl chain. Salts like tetrabutylammonium iodide can give a better insight into the effect of electrostatic and hydrophobic interactions on the stability of vitamins.

Most of the present day knowledge on non-aqueous solutions have come from studies on various thermodynamics properties e.g. apparent molar volumes, adiabatic compressibilities, heat capacities etc. as well as on transport properties, e.g. conductance, viscosity and transference numbers.

The study of apparent molar volumes and apparent molal isentropic compressibilities of electrolyte solutions is very useful to obtain information on ion-ion, ion-solvent and solvent-solvent interactions. The relative magnitude of the limiting apparent molar volumes, and the limiting apparent

Concluding Remarks

molal isentropic compressibilities, would enable us to provide information about the strengths of interactions between ions and solvent molecules. Measurements of the apparent molar volumes as a function of temperature can give an indication of electrostriction or concentration of solvent molecules around an ion.

The excess molar volume (V^E), viscosity deviation ($\Delta\eta$), deviation in isentropic compressibility (ΔK_S), excess molar refraction (ΔR) and excess Gibbs free energy of activation (ΔG^E) of viscous flow have been investigated from the experimentally measured densities, viscosities, sound speeds and refractive indices for three binary mixtures

One of the most precise and direct technique available to determine the extent of the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents is the "conductometric method." Conductance data in conjunction with viscosity measurements, gives much information regarding ion-ion and ion-solvent interaction.

The study of conductance measurements were pursued vigorously during the last five decades, both theoretically and experimentally and a number of important theoretical equations have been derived..

From chapter IV it was found that all tetraalkylammonium salts existed as triple ions due to low dielectric constant of the solvent mixtures. However, it was found that the smaller R_4N^+ cations tend to remain more as ion-pairs and exhibits higher tenency to form triple ions than larger ones.

Chapter VI revealed that the experimentally determined viscosities, η_{exp} of the ternary mixture of tetrahydrofuran (A) + methanol (B) + (cyclohexane, cyclohexanone, nitrobenzene) (C), are lower than those of its calculated values, η_{cal} which demonstrates viscous antagonism while for the ternary mixtures of tetrahydrofuran (A) + methanol (B) + (benzene, toluene, chlorobenzene, anisole) (C), the experimentally determined viscosities, η_{exp} are higher than those of its calculated values, η_{cal} which demonstrates viscous synergy.

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From the experimentally determined density and viscosity it was found from chapter VI that both sodium molybdate and sodium tungstate shows similar trend of ion-solvent and ion-ion interactions, which can be ascribed to the similar structure of tungstate and molybdate ions. From the values of apparent molar volume (V_{ϕ}^0) and viscosity B - coefficients it may be concluded that ion-solvent interaction increases with increasing temperature and decreases with increasing amount of ethane-1,2-diol in the aqueous mixture. Also the structure breaking tendencies of the two electrolytes were found to be similar.

In chapter VII conductivity studies of tetraalkyl ammonium salts were carried out in various molefractions of carbon tetrachloride and nitrobenzene and it was found that the tetraalkylammonium salts exists as ion-pairs upto 60 mass% of solvent mixture but as the dielectric constant of the solvent mixture decreases in 80 mass% , there is a tendency for triple ion pair formation.

Chapter VIII revealed that the values of apparent molar volume (V_{ϕ}^0) and viscosity B - coefficients for phosphomolybdic acid indicate the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperature and higher molarity of catechol in the ternary solutions. Also phosphomolybdic acid acts as a water-structure promoter due to hydrophobic hydration in the presence of catechol and catechol has a dehydration effect on the hydrated phosphomolybdic acid.

After a through study of the behavior of alkoxyethanols and iso-amyl alcohol in chapter IX we get a clear idea about the molecular interaction between the components and it was found that the interactions between the solvent molecules increases with the increase in chain length of alkoxyethanols.

It may be concluded from chapter X that in the low mole fraction region of D.C.M, intermolecular interaction between the two components (A.P+A.L), but as the mole fraction of D.C.M in the ternary mixture increases

Concluding Remarks

dispersion forces begins to operate. Thus, it can be said that the addition of D.C.M to binary mixture of A.L+A.P causes a decrease in intermolecular interaction between the mixing components.

Chapter XI dealt with conductivity studies of alkali metal salts in mixed solvents of ethane 1,2-diol and methanol and it was found that It can be concluded that Λ° of sodium salts of common cations follows the sequence $\text{SCN}^{-} > \text{I}^{-} > \text{CH}_3\text{COO}^{-}$ while Λ° of the studied electrolyte is enhanced in the following order: $\text{NaSCN} > \text{NaI} > \text{CH}_3\text{COONa}$.

To conclude, more extensive studies of the different thermodynamic, transport, refractometric and acoustic properties of the electrolytes will be of sufficient help in understanding the nature of the various molecular interactions and the role of solvents in different physico-chemical processes.

The proper understanding of ion-ion and ion-solvent interaction may form the basis of explaining quantitatively the influence of the solvent and the ions in solution and thus pave the way for understanding of different phenomena associated with solution chemistry.

LIST OF PUBLICATIONS

- [1] *Ion-pair and Triple-Ion Formation by Some Tetraalkylammonium Iodides in binary Mixtures of 1, 4-Dioxane + Tetrahydrofuran.* **Journal of Chemical and Engineering Data**, 53 (2008) 1417.



(Reprint of the paper enclosed)

- [2] *Ion -Solvent and Ion-Ion Interactions of sodium Molybdate and Sodium Tungstate in mixtures of Ethane- 1, 2 diol and Water at 298.15, 308.15 and 318.15K.* **Journal of Molecular Liquids**, 144 (2009) 149.



(Reprint of the paper enclosed)

- [3] *Ion- Pair and Triple- Ion Formation by Some Tetraalkylammonium Iodides in Binary mixtures of Carbontetrachloride and Nitrobenzene.* **Journal of Chemical and Engineering Data**, 54 (2009) 2429 .



(Reprint of the paper enclosed)

- [4] *Ion-Solvent and Ion-Ion Interactions of Phosphomolybdic acid in Aqueous solution of Catechol at at 298.15, 308.15 and 318.15K.* **Russian Journal of Physical Chemistry**, 83 (2009) 1.



(Reprint of the paper enclosed)

- [5] *Study on Ion-Solvent Interactions of Alkali Metal Salts in Pure Methanol and its Binary Mixtures with Ethane 1, 2-Diol by a Conductometric Technique.* **Fluid Phase Equilibria**. 282 (2009) 51.



(Reprint of the paper enclosed)

- [6] *Viscous synergy and antagonism, excess molar volume, isoentropic compressibility and excess molar refraction of ternary mixtures containing tetrahydrofuran, methanol and some six membered cyclic compounds at 298.15K. **Physics and Chemistry of Liquids** (In Press).*



(Galley proof of the paper enclosed)

- [7] *Investigation on Solvent-Solvent Interactions in Binary Mixtures of Isoamyl Alcohol with Some Alkoxyethanols. **International Journal of Thermophysics** (Communicated).*
- [8] *Studies on solution properties of ternary mixture of Acetophenone + Amyl alcohol + Dichloromethane and its Corresponding Binaries at 298.15 K. **Monatshefte fur Chemie** (Communicated).*

Seminar / Symposium /convention attended:

- **Sixth CRSI, National Symposium (Kolkata Chapter)**, organized by Department of Chemistry, North Bengal University, Darjeeling, India on August 2, 2008 as Delegate.
- **Trends in Surface Science and Related Areas (TSSRA) V**, organized by Department of Chemistry, North Bengal University, Darjeeling and Indian Society for Surface Science and Technology, Jadavpur University, Kolkata, India on December 06, 2008 as Delegate.
- **Symposium on "Acharya Prafulla Chandra Roy Memeorial Symposium on Chemistry Today (2009)"**, organized by Indian Chemical Society, held at Kolkata during August 01, 2009 as Speaker.

Trends in Surface Science and Related Areas (TSSRA) V

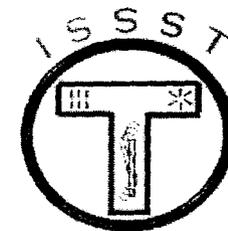
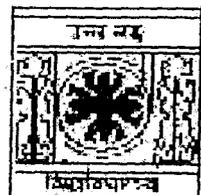
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Department of Chemistry
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Darjeeling 734 013

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Indian Society for Surface Science & Technology
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Kolkata 700 032

December 06, 2008



*Certified that Prof./Dr./Mr./Ms. Prasanna K. Pradhan, R/S Department of Chemistry
of University of North Bengal.....has participated
in the Trends in Surface Science and Related Areas (TSSRA) V held at the Department of
Chemistry, University of North Bengal as Invited Speaker/Speaker/Delegate.*

December 06, 2008


Head, Department of Chemistry
University of North Bengal


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Organizing Committee

SIXTH CRSI (KOLKATA CHAPTER) SYMPOSIUM

Organized by

DEPARTMENT OF CHEMISTRY

University of North Bengal

Darjeeling 734 013



August 02, 2008

Certified that Prof./Dr./Mr./MS *Prasanna Pradhan*
of *Department of Chemistry, North Bengal University* has participated
the Sixth CRSI (Kolkata Chapter) Symposium, Organized by the Department of Chemistry, University
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CERTIFICATE OF MERIT

Certified that Mr. Prasanna Pradhan, Chem. Deptt. Univ. of North Bengal, Darjeeling is
awarded the Certificate of Merit for his / ~~her~~ presentation of paper entitled
“Study of Ion-Pair and Triple-Ion of Some Measurement” in
the Symposium on “Acharya Prafulla Chandra Ray Memorial Symposium
on Chemistry Today (2009)” held at Kolkata during August 01-02, 2009.

2nd August, 2009
Kolkata

Girjesh Govil
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P. Majumder
Professor P. L. Majumder
Convener of the Symposium on
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on Chemistry Today (2009)”
& Honorary Secretary, Indian Chemical Society

Articles

Ion-Pair and Triple-Ion Formation by Some Tetraalkylammonium Iodides in Binary Mixtures of 1,4-Dioxane + Tetrahydrofuran

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Electrical conductances of tetraalkylammonium iodides, R_4NI ($R =$ pentyl to heptyl) have been measured at 298.15 K in low-permittivity mixtures of 1,4-dioxane ($\epsilon = 2.21$) and tetrahydrofuran ($\epsilon = 7.58$). Minima in the conductometric curves (Λ versus \sqrt{c}) were observed for electrolyte concentrations dependent upon both the electrolyte and the binary solvent mixture. The conductance data have been analyzed by the Fuoss–Kraus theory of triple ions. A numerical evaluation of ion-pair and triple-ion formation constants (K_p and K_T) was made, and the results have been discussed in terms of a molecular scale model.

Introduction

Progress in battery technology using the lithium electrolytes in etheral solution¹ has occurred largely in the past decade. Recently, there has been a renewed interest² in the study of association or dimerization of electrolytes in a media of low permittivity. In a media of low permittivity, salts are generally so associated that the states of the ionic species in solutions are difficult to elucidate. A number of conductometric³ and related studies of different electrolytes in nonaqueous solvents, especially mixed solvents, have been made for their optimal use in high-energy batteries⁴ and for understanding organic reaction mechanisms.⁵ Ionic association of salts in solution depends upon the mode of solvation of its ions,^{6–10} which in turn depends on the nature of the solvent or solvent mixtures. 1,4-Dioxane and tetrahydrofuran are polar aprotic solvents of low permittivity, each with great present-day synthetic and industrial importance. They are frequently used in electrical conductance studies^{3,4,11,12} and in high-energy batteries.^{3,4,11,12} Tetraalkylammonium salts are characterized by their low surface charge density, and they show little or no solvation in solution.^{11,12} Hence, in this paper, we reported the electrical conductances of some tetraalkylammonium iodides, R_4NI ($R =$ pentyl to heptyl), in low-permittivity mixtures where mass fractions of 1,4-dioxane in tetrahydrofuran are 10, 20, and 30, respectively.

Experimental Section

Materials. 1,4-Dioxane and tetrahydrofuran were purchased from Merck, India, and purified as reported earlier.^{13,14} The salts Pen_4NI , Hex_4NI , and $Hept_4NI$ of puriss grade were purchased from Aldrich, Germany, and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium.¹⁵ After filtration, the salts were dried in an oven for a few hours.

Apparatus and Procedure. Binary solvent mixtures were prepared by mixing a required volume of 1,4-dioxane and

Table 1. Density ρ , Viscosity η , and Dielectric Constant ϵ , for 1,4-Dioxane (1) + Tetrahydrofuran (2) at $T = 298.15$ K

solvent mixture	$\rho \cdot 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$		$\eta / (\text{mPa} \cdot \text{s})$		ϵ
	exptl	lit.	exptl	lit.	
$w_1 = 0.00$	0.8807	0.8807 ¹⁶	0.463	0.4630 ¹⁶	7.58 ¹¹
$w_1 = 0.10$	0.8941	–	0.490	–	7.04 ²
$w_1 = 0.20$	0.9071	–	0.510	–	6.51 ²
$w_1 = 0.30$	0.9190	–	0.530	–	5.96 ²
$w_1 = 1.00$	1.0305	1.0305 ¹⁶	1.200	1.2000 ¹⁶	2.21 ¹¹

² Calculated using the scheme given in ref 17.

tetrahydrofuran with earlier conversion of required mass of each liquid into volume at 298.15 K using literature densities.¹⁶ A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality into molarity was accomplished using density values. The uncertainty of molarity of different salt solutions is evaluated to $\pm 0.0001 \text{ mol} \cdot \text{dm}^{-3}$.

>The values of relative permittivity (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner.¹⁷

Densities were measured with an Ostwald–Sprenge-type pycnometer having a bulb volume of about 25 cm³ 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.¹⁸ The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried, and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurements was taken into account. The uncertainty of density values is $\pm 3 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. 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.^{19–21}

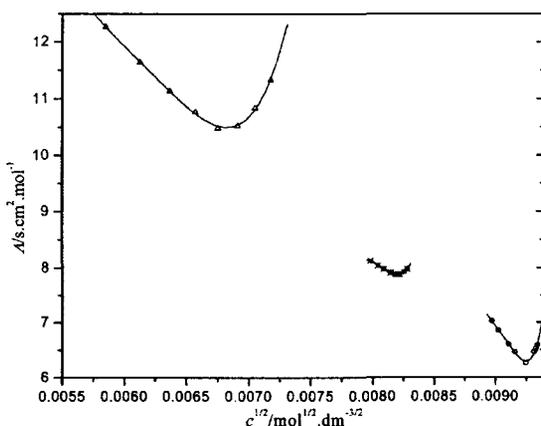
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Table 2. Concentrations c and Molar Conductances Λ of R_4NI ($R =$ Pentyl to Heptyl) in Different Binary Solvent Mixtures of 1,4-Dioxane (1) and Tetrahydrofuran (2) at $T = 298.15$ K

Pen ₄ NI		Hex ₄ NI		Hept ₄ NI	
$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ
mol·dm ⁻³	S·cm ² ·mol ⁻¹	mol·dm ⁻³	S·cm ² ·mol ⁻¹	mol·dm ⁻³	S·cm ² ·mol ⁻¹
			$w_1 = 0.10$		
0.8046	7.02	0.6367	8.12	0.3419	12.27
0.8138	6.86	0.6469	8.04	0.3754	11.64
0.8294	6.60	0.6541	7.98	0.4052	11.13
0.8385	6.46	0.6631	7.91	0.4319	10.77
0.8549	6.26	0.6696	7.88	0.4559	10.48
0.8674	6.46	0.6754	7.89	0.4776	10.52
0.8702	6.52	0.6806	7.93	0.4973	10.84
0.8726	6.59	0.6851	7.98	0.5153	11.33
			$w_1 = 0.20$		
0.4957	4.94	0.5460	3.98	0.6037	6.38
0.5016	4.83	0.5518	3.94	0.6142	4.94
0.5077	4.74	0.5598	3.88	0.6288	3.03
0.5122	4.76	0.5646	3.85	0.6376	1.94
0.5197	4.90	0.5694	3.83	0.6456	1.00
0.5229	4.98	0.5736	3.84	0.6541	0.55
0.4788	5.21	0.5764	3.86	0.6625	1.63
0.4839	5.12	0.5808	3.90	0.6672	2.53
			$w_1 = 0.30$		
0.2156	2.77	0.3125	4.97	0.5589	2.74
0.2564	2.70	0.3247	3.71	0.5675	2.30
0.2906	2.64	0.3420	2.13	0.5749	1.92
0.3481	2.56	0.3536	1.13	0.5813	1.63
0.3827	2.53	0.3657	0.35	0.5869	1.49
0.3986	2.53	0.3758	1.23	0.5917	1.62
0.4124	2.55	0.3819	2.13	0.5962	1.86
0.4274	2.58	0.3868	2.96	0.6001	2.09
0.4406	2.62				
0.4508	2.65				

**Figure 1.** Plots of molar conductance (Λ) versus square root of salt concentration ($c^{1/2}$) at $T = 298.15$ K in $w_1 = 0.10$ of 1,4-dioxane (1) + tetrahydrofuran (2). O, Pen₄NI; * Hex₄NI; Δ, Hept₄NI.

A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa·s. The details of the methods and measurement techniques have been described elsewhere.^{13,14} The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of 0.1 ± 10 %. Measurements were made in a water bath maintained within

$T = (298.15 \pm 0.01)$ K, and the cell was calibrated by Lind et al.²² The conductance data were reported at a frequency of 1 KHz and were uncertain to ± 0.3 %.

Results and Discussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The concentrations and molar conductances Λ of R_4NI ($R =$ pentyl to heptyl) in different binary solvent mixtures of 1,4-dioxane and tetrahydrofuran are given in Table 2.

Figures 1 to 3 represent the plots of molar conductance Λ versus square root of salt concentration \sqrt{c} for the salts under investigations at 298.15 K in different binary mixtures of 1,4-dioxane and tetrahydrofuran. A minimum has been found for all the electrolytes suggesting the possible formation of triple-ions in these solutions. Fuoss and Krauss as early as 1933 introduced the concept of triple-ion formation from univalent electrolytes to explain the minima in the relation between the equivalent conductance and the concentration of tetraisoamylammonium nitrate in 1,4-dioxane + water mixtures ($\epsilon < 12$). A result of the classical Fuoss–Kraus theory²³ of triple-ion formation can be presented by the eq^{24,25}

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

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by and $\beta' = 1.8247 \cdot 10^6 / (\epsilon T)^{3/2}$ is the Debye–Huckel term of the activity coefficient, $f = \exp[-(2.303/\Lambda_0^{1/2})\beta'(c\Lambda^{1/2})]$, and S is the Onsager conductance term of the conductance equation $\Lambda = \Lambda_0 - S(c\Lambda/\Lambda_0)^{1/2}$, defined by

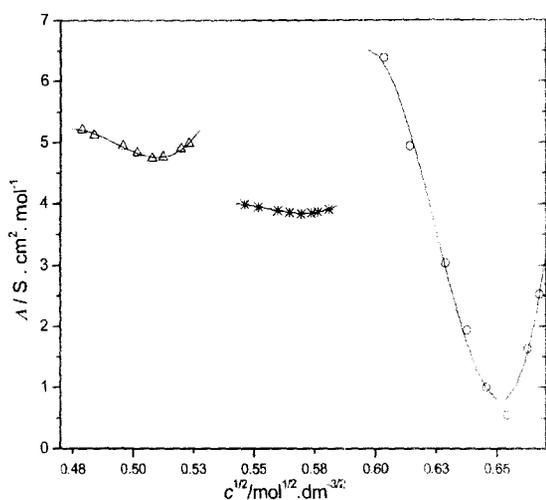


Figure 2. Plots of molar conductance (Λ) versus square root of salt concentration ($c^{1/2}$) at $T = 298.15$ K in $w_1 = 0.20$ of 1,4-dioxane (1) + tetrahydrofuran (2). \circ , Pen₄NI; $*$, Hex₄NI; Δ , Hept₄NI.

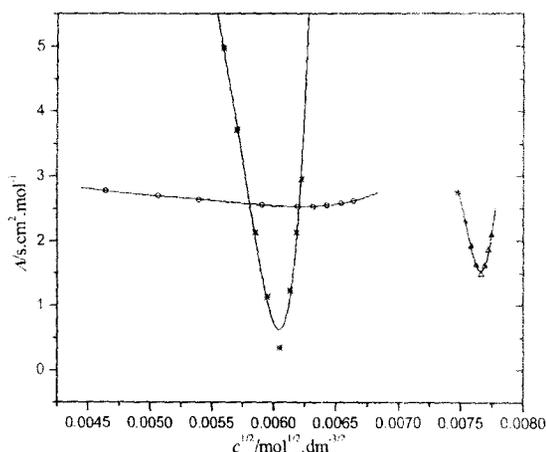


Figure 3. Plots of molar conductance (Λ) versus square root of salt concentration (\sqrt{c}) at $T = 298.15$ K in $w_1 = 0.30$ of 1,4-dioxane (1) + tetrahydrofuran (2). \circ , Pen₄NI; $*$, Hex₄NI; Δ , Hept₄NI.

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \cdot 10^6}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{1/2}}$$

where the units of Λ_0 and η are $S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ and poise, respectively. Also, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution and Λ_0^{\ddagger} is the sum of the conductances of the two triple ions $R_4N(I_2)^{\ddagger}$ and $(R_4N)^{\ddagger}_2 I$ for R_4NI salts. K_p and K_T are the ion-pair and triple-ion formation constants. To make eq 1 applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted² and Λ_0 values for the studied electrolytes have been calculated following the scheme as suggested by Krumgalz.¹²

The calculated values have been listed in Table 3. Linear regression analysis of eq 1 gives the intercept and slope, and the values have been listed in Table 3. The K_T and K_p , calculated from the slopes and intercepts, are listed in Table 4. A perusal of Table 4 shows that the major portion of the electrolytes exists as ion pairs with only a negligible portion as triple ions. The

Table 3. Calculated Limiting Molar Conductance Λ_0 , Slope, and Intercepts of Equation 1 for R_4NI ($R =$ Pentyl to Heptyl) in Different Binary Solvent Mixtures of 1,4-Dioxane (1) and Tetrahydrofuran (2) at $T = 298.15$ K

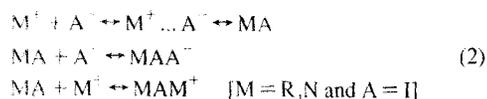
solvent mixture	Λ_0		intercept
	$S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	slope	
$w_1 = 0.10$	Pen ₄ NI		
	199.21	0.0064 (± 0.0003)	-0.011 (± 0.002)
	Hex ₄ NI		
$w_1 = 0.20$	195.57	0.0346 (± 0.0002)	-0.029 (± 0.003)
	Hept ₄ NI		
	193.34	0.0974 (± 0.0001)	-0.050 (± 0.001)
$w_1 = 0.30$	192.20	0.1315 (± 0.0002)	-0.108 (± 0.001)
	Hex ₄ NI		
	188.68	0.2975 (± 0.0002)	-0.225 (± 0.002)
$w_1 = 0.40$	Hept ₄ NI		
	186.53	1.4633 (± 0.0001)	-0.837 (± 0.002)
	Pen ₄ NI		
$w_1 = 0.50$	185.92	5.1354 (± 0.0003)	-1.042 (± 0.002)
	Hex ₄ NI		
	182.52	0.3102 (± 0.0001)	-0.173 (± 0.003)
$w_1 = 0.60$	Hept ₄ NI		
	180.44	0.5852 (± 0.0004)	-0.585 (± 0.006)
	Pen ₄ NI		

Table 4. Maximum Concentration c , Ion-Pair Formation Constant K_p , Triple-Ion Formation Constant K_T , Ion-Pair Concentration c_p , and Triple-Ion Concentration c_T for R_4NI ($R =$ Pentyl to Heptyl) in Different Binary Solvent Mixtures of 1,4-Dioxane (1) and Tetrahydrofuran (2) at $T = 298.15$ K

salt	$c^{\ddagger} \cdot 10^3$	$K_p \cdot 10^5$	K_T	$c_p \cdot 10^5$	$c_T \cdot 10^{10}$
	$\text{mol} \cdot \text{dm}^{-3}$	$\text{mol}^{-1} \cdot \text{dm}^3$	$\text{mol}^{-1} \cdot \text{dm}^3$	$\text{mol} \cdot \text{dm}^{-3}$	$\text{mol} \cdot \text{dm}^{-3}$
$w_1 = 0.10$					
Pen ₄ NI	0.8726	3316.37	0.883	8.71	0.40
Hex ₄ NI	0.6851	450.34	1.783	6.72	1.51
Hept ₄ NI	0.5153	132.90	2.753	4.95	2.81
$w_1 = 0.20$					
Pen ₄ NI	0.4839	31.55	1.823	4.81	3.98
Hex ₄ NI	0.5805	7.03	1.983	4.92	6.16
Hept ₄ NI	0.6672	0.50	2.622	3.85	13.40
$w_1 = 0.30$					
Pen ₄ NI	0.4508	0.32	7.389	3.50	4.25
Hex ₄ NI	0.3868	11.12	2.688	3.25	6.64
Hept ₄ NI	0.6001	1.26	1.728	3.77	23.50

^a Maximum concentrations at which calculations have been performed.

observed difference in K_p and K_T values can be explained by the molecular scale model^{26,27}



It is likely possible that association of R_4N^{\ddagger} cations with solvent components shifts the above equilibrium toward the left, thus decreasing K_p values and increasing K_T values. The ion-pair and triple-ion concentrations (c_p and c_T , respectively) of the electrolytes at the highest electrolyte concentration have been derived using eqs 25–27, 3 to 6 and are listed in Table 4.

$$\alpha = (K_p c)^{-1/2} \quad (3)$$

$$\alpha_T = \frac{K_T}{K_p^{3/2} c^{1/2}} \quad (4)$$

$$c_p = c(1 - \alpha - 3\alpha_T) \quad (5)$$

$$c_T = \frac{K_T}{K_P^{1/2}} c^{3/2} \quad (6)$$

It was observed that dielectric constants of the binary solvent mixtures decreased as the amount of 1,4-dioxane increased in the solvent mixtures. The concomitant increase in K_T and C_T values suggests that R_4N^+ cations are preferably more solvated by 1,4-dioxane than by tetrahydrofuran. On the contrary, the steric hindrance caused by the CH_2- group adjacent to the ethereal group of the cyclic ethers may cause solvation hindrance favoring the anion I^- as a competitor for the first coordination shell of R_4N^+ cations. This may shift the above equilibrium toward right increasing K_P values.

Table 4 shows that for a particular solvent mixture, i. e., for a particular value of dielectric constant of the solvent mixture, K_P values are in the order $Pen_4NI > Hex_4NI > Hept_4NI$, and that of K_T values is $Pen_4NI < Hex_4NI < Hept_4NI$. This suggests that smaller R_4N^+ cations tend to remain more as ion-pairs than larger ones, which in turn has greater capacity to form triple ions. This also supports our earlier view of preferential solvation¹⁰ of R_4N^+ cations by 1,4-dioxane in the electrolyte solutions.

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Received for review August 23, 2007. Accepted March 27, 2008. The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 5406/DRS/2002, SAP-1), for financial support.

JE7004787



Ion–solvent and ion–ion interactions of sodium molybdate and sodium tungstate in mixtures of ethane-1,2-diol and water at 298.15, 308.15 and 318.15 K

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ARTICLE INFO

Article history:

Received 3 June 2008

Received in revised form 31 October 2008

Accepted 3 November 2008

Available online 11 November 2008

Keywords:

Ethane-1,2-diol

Sodium tungstate

Sodium molybdate

Apparent molar volume

ABSTRACT

Apparent molar volume (V_{ϕ}) and viscosity B -coefficients were estimated for sodium molybdate and sodium tungstate in aqueous binary mixture of ethane-1,2-diol from measured solution density (ρ) and viscosity (η) at 298.15, 308.15 and 318.15 K at various electrolyte concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion–solvent and ion–ion interactions. The viscosity data has been analyzed using Jones–Dole equation and the derived parameters, B and A , have also been interpreted in terms of ion–solvent and ion–ion interactions respectively. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of sign of $(\delta^2 V_{\phi}^0 / \delta T^2)_i$. The activation parameters of viscous flow were also determined and were discussed by the application of transition state theory.

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1. Introduction

Studies on densities (ρ) and viscosities (η) of electrolyte solutions are of great importance in characterizing the properties and structural aspects of solutions. The addition of an electrolyte to an aqueous organic solution alters the pattern of ion solvation and causes phenomenal changes in the behavior of the dissolved electrolyte. Hence studies on the limiting apparent molar volume and viscosity– B coefficients of electrolyte provide us valuable information regarding ion–ion, ion–solvent and solvent–solvent interactions [1–3]. It has been found by a number of workers [4–6] that the addition of an electrolyte could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various electrolyte concentrations and temperature.

In this paper we have attempted to report the limiting apparent molar volume (V_{ϕ}^0), experimental slopes (S_{ϕ}^*) and viscosity B -coefficients for sodium molybdate and sodium tungstate in aqueous binary mixture of ethane-1,2-diol at 298.15, 308.15 and 318.15 K. The mixture of ethane-1,2-diol with water was chosen because of its diverse application in pharmaceutical and cosmetic industries [7,8]. However, the experiment was not performed in pure ethane-1,2-diol due to the insolubility of the

electrolytes. Since both molybdate and tungstate ions have similar structure [9] and sodium ion being a common cation for both the electrolyte under investigation, the present work enables us to have a qualitative comparison of the role of anion in aqueous binary mixture of ethane-1,2-diol in terms of various derived parameters obtained from viscosity (η) and density (ρ) measurement.

2. Experimental section

2.1. Materials

Ethane-1,2-diol (E. Merck, India) was purified by standard methods [10]. The purity of the solvent was checked by measuring the viscosity (η) and density (ρ) at 298.15 K which was in good agreement with the literature values. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ was used. Sodium tungstate and sodium molybdate (E. Merck, India) were purified by re-crystallizing twice from conductivity water and then dried in a vacuum dessicator over P_2O_5 for 24 h before use. The purity of the solvents was ascertained by GLC and also by comparing experimental values of viscosity (η) and density (ρ) whenever available with those reported in the literature and is listed in Table 1.

2.2. Measurements

Densities (ρ) were measured with an Ostwald–Sprenzel type pycnometer having a bulb volume of about 25cm^3 and an internal diameter of about 0.1 cm. The measurements were done in a thermostat bath controlled to $\pm 0.01 \text{K}$. Viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply

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Table 1
Density (ρ , kg m⁻³) and viscosity (η , mPa s) of aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions (x_1) of ethane-1,2-diol at different temperatures

Temperature (K)	$\rho \times 10^{-3}$ kg m ⁻³		η mPa s	
	This work	Lit.	This work	Lit.
$x_1 = 0.0312$				
298.15	1.0110	1.0116 [32]	1.1284	-
308.15	1.0071	1.0080 [32]	0.8922	-
318.15	1.0036	1.0038 [32]	0.7564	-
$x_1 = 0.0677$				
298.15	1.0238	1.0279 [32]	1.4244	-
308.15	1.0207	1.0239 [32]	1.1371	-
318.15	1.0167	1.0195 [32]	0.9440	-
$x_1 = 0.1106$				
298.15	1.0372	1.0432 [32]	1.8286	-
308.15	1.0352	1.0390 [32]	1.4302	-
318.15	1.0290	1.0343 [32]	1.1472	-

distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4}$ 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 fractions was within ± 0.0002 . The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm⁻³. Viscosity of the solution, η , is given by the following equation:

$$\eta = (Kt - L/t)\rho \quad (1)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.003 mPa s.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere [11–14]. The electrolyte solutions studied here were prepared by mass and the conversion of molality into molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

3. Results and discussion

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following Eq. [3]:

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (2)$$

where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volumes V_ϕ^0 was calculated using a least-squares treatment to the plots of V_ϕ versus \sqrt{c} using the following Masson equation [15]:

$$V_\phi = V_\phi^0 + S_\phi^* \sqrt{c} \quad (3)$$

where V_ϕ^0 is the apparent molar volume at infinite dilution and S_ϕ^* is the experimental slope. The plots of V_ϕ against square root of molar concentration (\sqrt{c}) were found to be linear as depicted graphically in Figs. 1–6 with negative slopes. Values of V_ϕ^0 and S_ϕ^* are reported in Table 3.

As the systems under study are characterized by hydrogen bonding, the ion–solvent and ion–ion interactions can be interpreted in terms of structural changes, which arise due to hydrogen bonding between various components of the solvent and solution systems. V_ϕ^0 can be used to interpret ion–solvent interactions. A perusal of Table 3 reveals that the V_ϕ^0 values are positive and increases with rise in temperature and decreases with increase in the amount of ethane-1,2-diol in the solvent mixture. This indicates the presence of strong ion–solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the amount of ethane-1,2-diol in the solvent mixture under study, suggesting larger electrostriction at higher temperature and in lower amount of ethane-1,2-diol in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous dimethylformamide [16] and aqueous tetrahydrofuran [17].

It is evident from Table 3 that the S_ϕ^* values are negative for all temperatures for aqueous mixtures of ethane-1,2-diol. Furthermore S_ϕ^* values decrease with the increase of experimental temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion–ion interactions (ionic-dissociation) [18]. The S_ϕ^* values increase with an increase in the amount of ethane-1,2-diol in the aqueous 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 ethane-1,2-diol to the mixture. A quantitative comparison of the magnitude of values shows that V_ϕ^0 values are much greater in magnitude than those of S_ϕ^* for all the solutions. This suggests that ion–solvent interactions dominate over ion–ion interactions in all the solutions and at all experimental temperatures.

The variation of V_ϕ^0 with temperature of sodium molybdate and sodium tungstate in solvent mixture follows the polynomial,

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \quad (4)$$

over the temperature range under study where T is the temperature in K.

Values of coefficients of the above equation for sodium molybdate and sodium tungstate for aqueous ethane-1,2-diol mixtures are reported in Table 4.

The apparent molar expansibilities (ϕ_E^0) can be obtained by the following equation:

$$\phi_E^0 = \left(\delta V_\phi^0 / \delta T \right)_p = a_1 + 2a_2 T \quad (5)$$

The values of ϕ_E^0 for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. From the table it is evident that the values of ϕ_E^0 for sodium molybdate increases with a rise in temperature and decreases with the increase in the amount of ethane-1,2-diol in the mixture which can be ascribed to the absence of caging or packing effects [19]. However for sodium tungstate the ϕ_E^0 values were found to be rather complicated to explain.

During the past few years it has been emphasized by a number of workers that S_ϕ^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. Hepler [20] developed a technique of examining the sign of $(\delta \phi_E^0 / \delta T)_p$ for the solute in terms of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows

$$\left(\delta \phi_E^0 / \delta T \right)_p = 2a_2 \quad (6)$$

If the sign of $(\delta \phi_E^0 / \delta T)_p$ is positive or small negative [21] the electrolyte is a structure maker and when the sign of $(\delta \phi_E^0 / \delta T)_p$ is negative, it is a structure breaker. As is evident from Table 5, the electrolyte under investigation generally acts as a structure breaker.

Table 2

Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_a), and $\alpha = (\eta/\eta_0 - 1)/c^{1/2}$ of sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions (x_1) of ethane-1,2-diol at different temperatures

c mol dm ⁻³	$\rho \times 10^{-3}$ kg m ⁻³	η mPa s	$V_a \times 10^6$ m ³ mol ⁻¹	α	c mol dm ⁻³	$\rho \times 10^{-3}$ kg m ⁻³	η mPa s	$V_a \times 10^6$ m ³ mol ⁻¹	α
Sodium molybdate $x_1 = 0.0312$					Sodium tungstate $x_1 = 0.0312$				
298.15 K					298.15 K				
0.0250	1.0143	1.1429	109.228	0.0650	0.0250	1.0163	1.1471	116.278	0.1050
0.0350	1.0159	1.1493	101.895	0.0900	0.0350	1.0186	1.1582	110.767	0.1410
0.0450	1.0174	1.1549	97.665	0.1050	0.0450	1.0210	1.1669	106.845	0.1610
0.0550	1.0191	1.1619	93.236	0.1267	0.0550	1.0233	1.1750	104.213	0.1760
0.0750	1.0223	1.1748	90.621	0.1502	0.0750	1.0281	1.1902	100.921	0.2000
0.0850	1.0239	1.1820	89.663	0.1630	0.0850	1.0305	1.1998	99.7900	0.2170
308.15 K					308.15 K				
0.0249	1.0099	0.9044	127.605	0.0870	0.0249	1.0120	0.9094	133.908	0.1220
0.0348	1.0115	0.9102	114.742	0.1080	0.0349	1.0143	0.9173	121.999	0.1507
0.0448	1.0131	0.9183	107.597	0.1380	0.0448	1.0167	0.9245	115.189	0.1711
0.0548	1.0147	0.9256	103.106	0.1598	0.0548	1.0191	0.9325	110.818	0.1929
0.0747	1.0178	0.9383	98.545	0.1889	0.0747	1.0238	0.9472	105.575	0.2255
0.0846	1.0195	0.9442	94.498	0.2003	0.0846	1.0262	0.9543	103.732	0.2391
318.15 K					318.15 K				
0.0248	1.0060	0.7672	144.585	0.0910	0.0248	1.0081	0.7724	149.569	0.1346
0.0347	1.0076	0.7743	125.053	0.1273	0.0347	1.0105	0.7799	130.293	0.1667
0.0447	1.0093	0.7801	114.206	0.1485	0.0446	1.0130	0.7868	119.589	0.1903
0.0547	1.0110	0.7867	105.545	0.1712	0.0546	1.0154	0.7937	112.722	0.2110
0.0747	1.0144	0.7991	96.4701	0.2065	0.0744	1.0204	0.8076	104.345	0.2484
0.0847	1.0161	0.8047	92.9767	0.2195	0.0844	1.0228	0.8146	101.635	0.2649
Sodium molybdate $x_1 = 0.0677$					Sodium tungstate $x_1 = 0.0677$				
298.15 K					298.15 K				
0.0250	1.0274	1.4451	94.8690	0.0100	0.0250	1.0306	1.4460	101.479	0.0960
0.0350	1.0290	1.4527	91.4636	0.1130	0.0350	1.0331	1.4553	97.1661	0.1158
0.0450	1.0307	1.4633	86.8985	0.1350	0.0450	1.0355	1.4646	96.866	0.1330
0.0550	1.0324	1.4720	82.8316	0.1480	0.0550	1.0380	1.4738	94.961	0.1479
0.0750	1.0357	1.4906	81.3094	0.1746	0.0750	1.0428	1.4934	95.189	0.1770
0.0850	1.0374	1.4997	79.8219	0.1860	0.0850	1.0453	1.5016	94.153	0.1860
308.15 K					308.15 K				
0.0249	1.0236	1.1540	115.626	0.0960	0.0249	1.0267	1.1563	131.329	0.1070
0.0349	1.0252	1.1630	106.010	0.1236	0.0349	1.0292	1.1653	118.732	0.1330
0.0448	1.0268	1.1710	100.402	0.1419	0.0448	1.0317	1.1732	111.443	0.1500
0.0548	1.0283	1.1788	96.9554	0.1578	0.0548	1.0341	1.1797	107.973	0.1600
0.0747	1.0315	1.1940	93.3839	0.1841	0.0747	1.0390	1.1992	103.259	0.1998
0.0846	1.0330	1.2033	91.9710	0.2010	0.0847	1.0415	1.2065	101.803	0.2097
318.15 K					318.15 K				
0.0248	1.0193	0.9583	136.063	0.0950	0.0248	1.0224	0.9608	139.942	0.1130
0.0347	1.0208	0.9667	120.549	0.1280	0.0347	1.0248	0.9694	127.007	0.1444
0.0446	1.0223	0.9739	113.695	0.1487	0.0446	1.0272	0.9763	119.833	0.1619
0.0546	1.0240	0.9808	105.996	0.1659	0.0546	1.0297	0.9840	113.528	0.1816
0.0744	1.0271	0.9947	99.814	0.1962	0.0744	1.0346	0.9998	107.263	0.2127
0.0843	1.0287	1.0019	97.666	0.2104	0.0843	1.0371	1.0068	104.668	0.2290
Sodium molybdate $x_1 = 0.1106$					Sodium tungstate $x_1 = 0.1106$				
298.15 K					298.15 K				
0.0250	1.0410	1.8517	85.2862	0.0940	0.0250	1.0446	1.8553	85.2862	0.0924
0.0350	1.0428	1.8624	81.6000	0.1108	0.0350	1.0471	1.8648	81.6000	0.1057
0.0450	1.0443	1.8731	80.7124	0.1253	0.0450	1.0498	1.8760	80.7124	0.1221
0.0550	1.0462	1.8845	76.2873	0.1401	0.0550	1.0520	1.8874	76.2873	0.1370
0.0750	1.0495	1.9066	74.7013	0.1640	0.0750	1.0572	1.9109	74.7013	0.1643
0.0850	1.0513	1.9190	73.6711	0.1775	0.0850	1.0603	1.9214	73.6711	0.1740
308.15 K					308.15 K				
0.0249	1.0385	1.4522	105.289	0.1070	0.0249	1.0240	1.4521	105.289	0.0976
0.0349	1.0401	1.4597	99.2167	0.1184	0.0349	1.0447	1.4615	99.2167	0.1170
0.0449	1.0416	1.4695	95.8562	0.1368	0.0449	1.0471	1.4687	95.8562	0.1270
0.0548	1.0431	1.4793	95.3671	0.1532	0.0549	1.0496	1.4798	95.3671	0.1480
0.0748	1.0460	1.5002	93.5430	0.1847	0.0748	1.0544	1.4979	93.5430	0.1731
0.0848	1.0483	1.5096	84.7810	0.1960	0.0847	1.0570	1.5089	84.7810	0.1892
318.15 K					318.15 K				
0.0248	1.0321	1.1679	114.771	0.1148	0.0248	1.0356	1.1660	114.771	0.1040
0.0347	1.0336	1.1756	105.395	0.1330	0.0347	1.0380	1.1746	105.395	0.1282
0.0446	1.0353	1.1840	98.2377	0.1520	0.0446	1.0405	1.1831	98.238	0.1483
0.0545	1.0369	1.1924	93.4467	0.1686	0.0545	1.0430	1.1914	93.447	0.1651
0.0743	1.0401	1.2106	90.0550	0.2029	0.0743	1.0479	1.2075	90.055	0.1928
0.0842	1.0418	1.2193	87.2167	0.2166	0.0842	1.0505	1.2157	87.217	0.2059

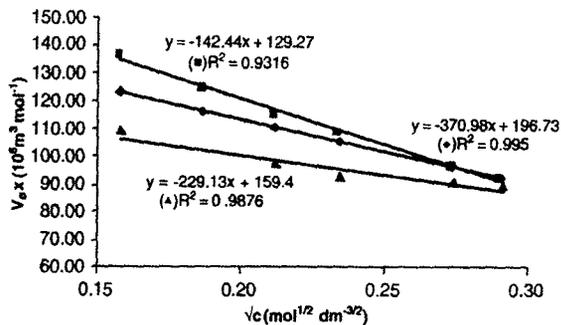


Fig. 1. The apparent molar volume of sodium molybdate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.0312$) as a function of square root of concentration at 298.15 (▲), 308.15 (◆) and 318.15 K (■). The lines represent the linear fits.

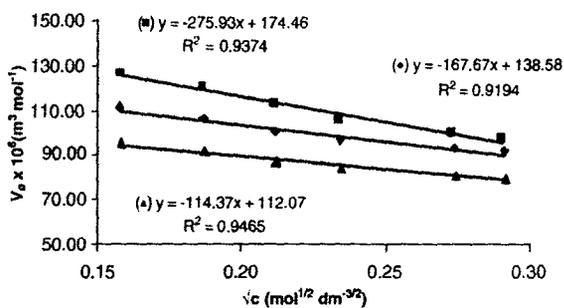


Fig. 2. The apparent molar volume of sodium molybdate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.0677$) as a function of square root of concentration at 298.15 (▲), 308.15 (◆) and 318.15 K (■). The lines represent the linear fits.

Thus it may be concluded that the electrolytes are characterized by the absence of caging effect [18,22].

The viscosity data of solutions for the electrolytes in 0.0312, 0.0677, 0.1106 mole fraction (x_1) of ethane-1,2-diol+water mixtures have been analyzed using Jones–Dole [23] equation:

$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2} \quad (7)$$

where η_0 and η are the viscosities of the solvent/solvent mixtures and solution respectively. A and B are the constants estimated by least-

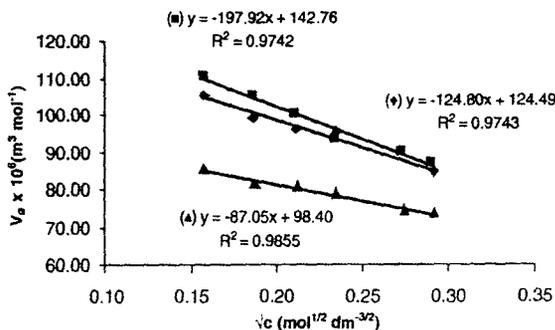


Fig. 3. The apparent molar volume of sodium molybdate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.1106$) as a function of square root of concentration at 298.15 (▲), 308.15 (◆) and 318.15 K (■). The lines represent the linear fits.

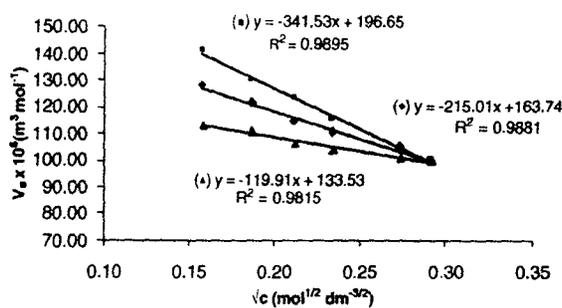


Fig. 4. The apparent molar volume of sodium tungstate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.0312$) as a function of square root of concentration at 298.15 (▲), 308.15 (◆) and 318.15 K (■). The lines represent the linear fits.

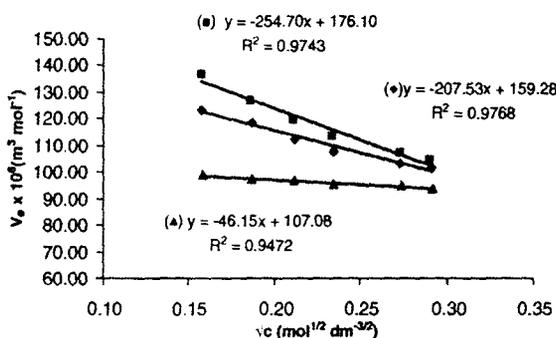


Fig. 5. The apparent molar volume of sodium tungstate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.0677$) as a function of square root of concentration at 298.15 (▲), 308.15 (◆) and 318.15 K (■). The lines represent the linear fits.

squares method and are reported in Table 6. From the table it is evident that the values of the A coefficient are negative for all the solutions under investigation at all experimental temperatures. These results indicate the presence of weak ion–ion interactions, and these interactions further decrease with the rise of experimental temperatures suggesting an increase in ion–solvation while these interactions increase with an increase of ethane-1,2-diol in the mixture. Interestingly, values are found to be more negative for sodium molybdate and

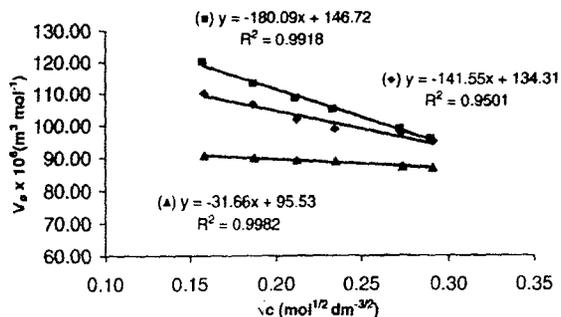


Fig. 6. The apparent molar volume of sodium tungstate in the mixture of aqueous ethane-1,2-diol ($x_1 = 0.1106$) as a function of square root of concentration at 298.15 (▲), 308.15 (◆) and 318.15 K (■). The lines represent the linear fits.

Table 3

Limiting apparent molar volumes (V_{ϕ}^0) and experimental slopes (S_{ϕ}^*) of sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures

Mole fraction of ethane-1,2-diol	$V_{\phi}^0 \times 10^6 \text{ m}^3 \text{ mol}^{-1}$			$S_{\phi}^* \times 10^6 \text{ m}^3 \text{ mol}^{-3/2} \text{ dm}^{3/2}$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Sodium molybdate						
0.0312	129.27	159.40	196.73	-142.44	-229.13	-370.98
0.0677	112.07	138.58	174.46	-114.37	-167.67	-275.93
0.1106	98.401	123.80	142.76	-87.05	-124.49	-197.92
Sodium tungstate						
0.0312	133.53	163.74	196.65	-119.91	-215.01	-341.53
0.0677	107.08	159.28	176.10	-46.15	-207.53	-254.70
0.1106	95.53	134.31	146.72	-31.66	-141.55	-180.09

hence it may be concluded that sodium molybdate is more soluble in aqueous ethane-1,2-diol solutions than sodium tungstate.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B -coefficient [24,25]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B -coefficient of sodium molybdate and sodium tungstate in the studied solvent systems are positive, thereby suggesting the presence of strong ion-solvent interactions, and these type of interactions are strengthened with a rise in temperature and weakened with an increase of ethane-1,2-diol in the mixture. These conclusions are in excellent agreement with those drawn from V_{ϕ}^0 values discussed earlier.

It has been reported in a number of studies [26,27] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B -coefficient. It is found from Table 6 that the values of the B -coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of sodium molybdate and sodium tungstate in the solvent systems. A similar result was reported in a study [28] of viscosity of some salts in propionic acid and ethanol mixtures.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of the electrolytes, suggested by Feakins et al. [29] using the following equation

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + \left(1000B + \bar{V}_2^0 - \bar{V}_1^0\right)RT/\bar{V}_1^0 \quad (8)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and the solute respectively. The contribution per mole of the solute to the free energy of activation of viscous flow ($\Delta\mu_2^{0*}$) of the solutions was determined from the above relation and is listed in Table 7. The free

Table 4

Values of the coefficients of Eq. (4) for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol

Mole fraction of ethane-1,2-diol	$a_0 (\text{m}^3 \text{ mol}^{-1})$			$a_1 (\text{m}^3 \text{ mol}^{-1} \text{ K}^{-1})$			$a_2 (\text{m}^3 \text{ mol}^{-1} \text{ K}^{-2})$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Sodium molybdate									
0.0312	2538.441			-18.8138			0.0360		
0.0677	3630.617			-25.7845			0.0469		
0.1106	-3617.255			22.0628			-0.0322		
Sodium tungstate									
0.0312	473.1154			-5.164			0.0135		
0.0677	17,701.946			112.475			-0.1769		
0.1106	-13,169.706			83.788			-0.1318		

Table 5

Limiting partial molar expansibilities for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures

Mole fraction of ethane-1,2-diol	$\phi_{\phi}^0 (\text{m}^3 \text{ mol}^{-1} \text{ K}^{-1})$			$(\partial\phi_{\phi}^0/\partial T)_{\phi}$ ($\text{m}^3 \text{ mol}^{-1} \text{ K}^{-2}$)
	298.15 K	308.15 K	318.15 K	
Sodium molybdate				
0.0312	2.6530	3.3730	4.0930	0.0720
0.0677	2.1820	3.1200	4.0580	0.0938
0.1106	-2.8619	-2.2179	-1.5739	-0.0644
Sodium tungstate				
0.0312	2.8861	3.1561	3.4261	0.0270
0.0677	6.9890	3.4510	0.0870	-0.3538
0.1106	5.1957	2.5597	-0.0763	-0.2636

energy of activation of viscous flow of the pure solvent ($\Delta\mu_1^{0*}$) is given by the relation:

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RT \ln \left(\eta_0 \bar{V}_1^0 \right) / hN_0 \quad (9)$$

where N is the Avogadro's number and the other symbols have their usual significance. The values of $\Delta\mu_2^{0*}$ and $\Delta\mu_1^{0*}$ are reported in Table 7. From Table 7 it is evident that $\Delta\mu_2^{0*}$ is practically constant at all the solvent composition and at all temperatures, implying that $\Delta\mu_2^{0*}$ is mainly dependent on the viscosity B -coefficients and $(\bar{V}_2^0 - \bar{V}_1^0)$ terms. Also $\Delta\mu_2^{0*}$ values were found to positive at all the experimental temperatures and hence the formation of the transition state is less favorable in the presence of these anions. A similar result was reported for sodium molybdate and sodium tungstate in aqueous acetonitrile solutions [21]. According to Feakins et al. [29] $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$ for 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 [30]. The smaller values of $\Delta\mu_2^{0*}$ indicate the increased structure breaking tendency of the electrolyte. Thus from the values of $\Delta\mu_2^{0*}$ it can be inferred that both tungstate and molybdate ions have similar structure breaking tendencies. The entropy of activation for electrolytic solutions has been calculated using the following relation [29].

$$\Delta S_2^{0*} = -d(\Delta\mu_2^{0*})/dT \quad (10)$$

where ΔS_2^{0*} has been determined from the negative slope of the plots of $\Delta\mu_2^{0*}$ against T by using a least square treatment.

Table 6

Values of A and B coefficients for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures

Mole fraction of ethane-1,2-diol	$A, \text{dm}^{3/2} \text{ mol}^{-1/2}$			$B, \text{dm}^3 \text{ mol}^{-1}$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Sodium molybdate						
0.0312	-0.0478	-0.0504	-0.0535	0.7272	0.8746	0.9493
0.0677	-0.0067	-0.0211	-0.0329	0.6606	0.7610	0.8445
0.1106	-0.0056	-0.0083	-0.0108	0.6226	0.6977	0.7792
Sodium tungstate						
0.0312	-0.0118	-0.0145	-0.0165	0.7891	0.8733	0.9720
0.0677	-0.0122	-0.0135	-0.0176	0.6842	0.7678	0.8494
0.1106	-0.0102	-0.0126	-0.0139	0.6311	0.6834	0.7608

Table 7

Values of V_1^0 , V_2^0 , $\Delta\mu_1^0$, $\Delta\mu_2^0$, $T\Delta S_2^{0*}$ and ΔH_2^{0*} for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions (x_1) of ethane-1,2-diol at different temperatures

Parameter	Mole fraction of ethane-1,2-diol $x_1=0.0312$			Mole fraction of ethane-1,2-diol $x_1=0.0677$			Mole fraction of ethane-1,2-diol $x_1=0.1106$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
$\bar{V}_1^{0*} \times 10^6 \text{ m}^3 \text{ mol}^{-1}$	19.1855	20.8527	22.8122	18.9456	20.5749	22.5182	18.7008	20.2867	22.2491
$\Delta\mu_1^0, \text{ kJ mol}^{-1}$	27.0272	27.5454	28.2401	27.5736	28.1325	28.7919	28.1606	28.6840	29.2758
Sodium molybdate									
$\bar{V}_2^{0*} \times 10^6 \text{ m}^3 \text{ mol}^{-1}$	129.27	159.40	196.73	112.07	138.58	174.46	98.401	123.80	142.76
$\Delta\mu_2^0, \text{ kJ mol}^{-1}$	42.1900	45.6418	49.5068	40.6222	43.7739	47.6317	39.5501	42.6376	44.5292
$T\Delta S_2^{0*}, \text{ kJ mol}^{-1}$	-109.1229	-112.7829	-116.4429	-104.5015	-108.0065	-111.5115	-74.239	-76.729	-79.2193
$\Delta H_2^{0*} \times 10^3 \text{ kJ mol}^{-1}$	-66.9329	-67.1411	-66.936	-63.8793	-64.2326	-63.8798	-34.6889	-34.0914	-34.6901
Sodium tungstate									
$\bar{V}_2^{0*} \times 10^6 \text{ m}^3 \text{ mol}^{-1}$	133.53	163.74	196.65	107.08	159.28	176.10	95.53	134.31	146.72
$\Delta\mu_2^0, \text{ kJ mol}^{-1}$	42.8203	46.1784	49.5238	40.0002	46.3599	47.8301	39.1810	43.9108	44.9781
$T\Delta S_2^{0*}, \text{ kJ mol}^{-1}$	-99.8802	-103.2302	-106.5802	-116.4275	-120.3325	-124.2375	-86.3144	-89.2094	-92.1044
$\Delta H_2^{0*} \times 10^3 \text{ kJ mol}^{-1}$	-57.0599	-57.0518	-57.0519	-76.4273	-73.9726	-76.4074	-47.1334	-45.2986	-47.1263

The activation enthalpy (ΔH_2^{0*}) has been calculated using the relation [29]:

$$\Delta H_2^{0*} = \Delta\mu_2^0 + T\Delta S_2^{0*} \quad (11)$$

the value of ΔS_2^{0*} and ΔH_2^{0*} are listed in Table 7 and they are found to be negative for all the electrolytic solutions and at all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state [29,31].

4. Conclusion

In summary it can be concluded that both sodium molybdate and sodium tungstate show similar trend of ion–solvent and ion–ion interactions, which can be ascribed to the similar structure of tungstate and molybdate ions [7]. From the values of apparent molar volume (V_0^0) and viscosity B -coefficients it may be concluded that ion–solvent interaction increases with increasing temperature and decreases with increasing amount of ethane-1,2-diol in the aqueous mixture. Also the structure breaking tendencies of the two electrolytes were found to be similar.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for financial support.

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Ion Pair and Triple Ion Formation by Some Tetraalkylammonium Iodides in Binary Mixtures of Carbon Tetrachloride + Nitrobenzene[†]

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Electrical conductances of tetraalkylammonium iodides, R₄NI (R = butyl to heptyl), in different mass % (20 to 80) of carbon tetrachloride (CCl₄) + nitrobenzene (PhNO₂) have been measured at 298.15 K. Limiting molar conductances Λ_0 , association constants K_A , and cosphere diameter R for ion pair formation in the mixed solvent mixtures have been evaluated using the Lee–Wheaton conductivity equation. However, the deviation of the conductometric curves (Λ versus \sqrt{c}) from linearity for the electrolytes in 80 mass % of CCl₄ + PhNO₂ indicated triple ion formation, and therefore corresponding conductance data have been analyzed by the Fuoss–Kraus theory of triple ions. Limiting ionic molar conductances λ_{i0}^\ddagger have been calculated by the reference electrolyte method along with a numerical evaluation of ion pair and triple ion formation constants ($K_P \approx K_A$ and K_T); the results have been discussed in terms of solvent properties and configurational theory.

Introduction

Mixed solvents enable the variation of properties such as dielectric constant or viscosity, and therefore the ion–ion and ion–solvent interactions can be better studied. Furthermore, different quantities strongly influenced by solvent properties can be derived from concentration dependence of the electrolyte conductivity. Consequently, a number of conductometric¹ and related studies of different electrolytes in nonaqueous solvents, especially mixed organic solvents, have been made for their optimal use in high-energy batteries² and for understanding organic reaction mechanisms.³ Ionic association of electrolytes in solution depends upon the mode of solvation of its ions,^{4–8} which in turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent–solvent interactions. Thus, extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years^{9–13} to examine the nature and magnitude of ion–ion and ion–solvent interactions. Also, tetraalkylammonium salts are characterized by their low surface charge density, and they show little or no solvation in solution.^{14,15} As such, they are frequently selected as desired electrolytes in conductance studies. In continuation of our investigation on electrical conductances,^{8,10,11} the present work deals with the conductance measurements of some tetraalkylammonium iodides, R₄NI (R = butyl to heptyl), in binary mixtures of CCl₄—a nonpolar aprotic liquid—and PhNO₂—a polar aprotic liquid—at 298.15 K.

Experimental Section

Materials. CCl₄ (carbon tetrachloride, CAS: 56-23-5) and PhNO₂ (nitrobenzene, CAS: 98-95-3) were purchased from Merck, India, and purified as reported earlier.¹⁶ The mole percent

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[†] Part of the “William A. Wakeham Festschrift”

Table 1. Density ρ , Viscosity η , and Dielectric Constant ϵ_r for CCl₄ (1) + PhNO₂ (2) at $T = 298.15$ K

solvent mixture	$(\rho \cdot 10^{-3})/(\text{kg} \cdot \text{m}^{-3})$		$(\eta)/(\text{mPa} \cdot \text{s})$		ϵ_r
	exptl	lit.	exptl	lit.	
$w_1 = 0.00$	1.1982	1.1985 ⁴⁰ 1.1983 ⁴¹	1.686	1.686 ⁴¹	34.69 ¹⁸
$w_1 = 0.20$	1.2614		1.613		29.66 ^a
$w_1 = 0.40$	1.3314		1.411		23.90 ^a
$w_1 = 0.60$	1.4067		1.224		17.45 ^a
$w_1 = 0.80$	1.4910		1.099		10.22 ^a
$w_1 = 1.00$	1.5843	1.5844 ⁴¹	0.902	0.9017 ⁴¹	2.25 ⁴¹

^a Obtained by interpolation of literature data from ref 18.

purities for the liquids used as checked by GC (HP6890) using an FID detector were better than 99. The salts Bu₄NI (*N,N,N*-tributyl-1-butanaminium iodide, CAS: 311-28-4), Pen₄NI (*N,N,N*-tripentyl-1-pentanaminium iodide, CAS: 2498-20-6), Hex₄NI (*N,N,N*-triethyl-1-hexanaminium iodide, CAS: 2138-24-1), and Hept₄NI (*N,N,N*-triheptyl-1-heptanaminium iodide, CAS: 3535-83-9) of puriss grade were purchased from Aldrich, Germany, and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium.¹⁷ After filtration, the salts were dried in an oven for a few hours.

Apparatus and Procedure. Binary solvent mixtures were prepared by mixing a required volume of CCl₄ and PhNO₂ with earlier conversion of required mass of each liquid into volume at 298.15 K using experimental densities. A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The uncertainty of molarity of different salt solutions is evaluated to $\pm 0.0001 \text{ mol} \cdot \text{dm}^{-3}$.

The values of relative permittivity ϵ_r of the solvent mixtures were obtained by interpolation of the solvent permittivity data from the literature¹⁸ by cubic spline fitting. The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. Densities were measured with an Ostwald–Sprengel-type pycnometer having a bulb volume of about 25 cm³ 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.¹⁹ The pycnometer with experimental liquid was equilibrated in a glass-walled thermostatted water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried, and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The uncertainty of density values is $\pm 3 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. Solvent viscosities were 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} A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is $\pm 0.003 \text{ mPa} \cdot \text{s}$. The details of the methods and measurement techniques had been described elsewhere.^{11,23} The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 10) %. Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K, and the cell was calibrated by the method proposed by Lind et al.²⁴ The conductance data were reported at a frequency of 1 kHz and were uncertain to ± 0.3 %.

Results and Discussion

The concentrations and molar conductances Λ of R_4NI ($R =$ butyl to heptyl) in different binary solvent mixtures of CCl_4 and PhNO_2 are given in Table 2.

For the solvent mixtures in the range of moderate relative permittivity ($\epsilon_r = 29.66$ to 17.45), the conductance curves (Λ versus \sqrt{c}) were linear, and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolytes; however, as the relative permittivity ϵ_r dropped to 10.22 for the solvent mixture containing 80 mass % of CCl_4 in PhNO_2 , nonlinearity (Figure 1) was observed in conductance curves. Thus the conductance data, in the solvent mixtures ($w_1 = 0.20$ to 0.60) wherein higher clusters other than ion pair formation was not expected, were analyzed by the Lee–Wheaton conductance equation²⁵ in the form

$$\Lambda = \alpha_i \left\{ \Lambda_0 [1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3] - \frac{\rho \kappa}{1 + \kappa R} \left[1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \right\} \quad (1)$$

The mass action law association²⁶ is

$$K_A = (1 - \alpha_i) \gamma_A / \alpha_i^2 c_i \gamma_{\pm}^2 \quad (2)$$

and the equation for the mean ionic activity coefficient

$$\gamma_{\pm} = \exp \left[-\frac{q \kappa}{1 + \kappa R} \right] \quad (3)$$

where C_1 to C_5 are least-squares fitting coefficients as described by Pethybridge and Taba;²⁵ Λ_0 is the limiting molar conductivity; K_A is the association constant; α_i is the dissociation degree; q is the Bjerrum parameter; γ is the activity coefficient; and $\beta = 2q$. The distance parameter R is the least distance that two free ions can approach before they merge into an ion pair. The Debye parameter κ , the Bjerrum parameter q , and ρ^{25} are defined by the expressions

$$\kappa = 16000 \pi N_A q c_i \alpha_i \quad (4)$$

$$q = \frac{e^2}{8 \epsilon_0 \epsilon_r \kappa T} \quad (5)$$

$$\rho = \frac{F e}{299.79 \cdot 3 \pi \eta} \quad (6)$$

where the symbols have their usual significance.²⁷

Equation 1 was resolved by an iterative procedure. For a definite R value, the initial values of Λ_0 and K_A were obtained by the Kraus–Bray method.²⁸ The parameters Λ_0 and K_A were made to approach gradually their best values by a sequence of alternating linearization and least-squares optimizations by the Gauss–Siedel method²⁹ until satisfying the criterion for convergence. The best value of a parameter is the one when eq 1 is best fitted to the experimental data corresponding to minimum standard deviation σ_{Λ} for a sequence of predetermined R values, and standard deviation σ_{Λ} was calculated by the following equation

$$\sigma_{\Lambda}^2 = \sum_{i=1}^n \frac{[\Lambda_i(\text{calcd}) - \Lambda_i(\text{obsd})]^2}{n - m} \quad (7)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two-parameter fit ($m = 2$). As for the electrolytes studied in the solvent mixtures ($w_1 = 0.20$ to 0.60), no significant minima were observed in the σ_{Λ} versus R curves, and the R values were arbitrarily preset at the center to center distance of the solvent-separated pair⁸

$$R = a + d \quad (8)$$

where a is the sum of the crystallographic radii of the cation and anion and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of d and related terms have already been described in the literature.⁸ R was generally varied by a step of 0.1 \AA , and the iterative process was continued with eq 1.

Table 3 reveals that the limiting molar conductances Λ_0 for the electrolytes decrease with the increase of CCl_4 content in the solvent mixtures. This fact is in line with the decrease of the relative permittivity ϵ_r of the solvent mixtures.^{14,30} Although the decreasing trend of viscosity for the solvent mixtures with increasing content of CCl_4 suggests concomitant increase in limiting molar conductances^{14,30} for the electrolytes, we observed an opposite trend. This trend suggests predominance of relative permittivity ϵ_r over the solvent viscosity η_0 in effecting the electrolytic conductances of the electrolytes under study in these media. In a particular solvent mixture, the limiting molar conductances Λ_0 of the electrolytes under investigation decrease as the size of the alkyl group increases, in contraposition to the conductance behavior of the alkali metal cations, as tetraalkylammonium salts are characterized by their low surface charge density.^{14,15}

The decreasing trend of Walden products $\Lambda_0 \eta_0$ in Table 3 is mainly in accordance with the concomitant decrease of both the solvent viscosity and limiting molar conductance of the electrolytes. The ionic conductances $\lambda_{\text{R}}^{\circ}$ for the various R_4N^+ cations ($R =$ butyl to hexyl) in different solvent mixtures ($w_1 = 0.20$ to 0.60) were calculated using tetrabutylammonium tetraphenyl borate (Bu_4NBP_4) as a reference electrolyte following the scheme as suggested by B. Das et al.³¹ We calculated its limiting molar conductances $\lambda_{\text{R}}^{\circ}$ in our solvent compositions by interpolation of conductance data from the literature¹⁸ using

Table 2. Concentrations c and Molar Conductances Λ of R_4NI ($R =$ Butyl to Heptyl) in Different Binary Solvent Mixtures of CCl_4 (1) + $PhNO_2$ (2) at $T = 298.15$ K

Bu ₄ NI		Pen ₄ NI		Hex ₄ NI		Hept ₄ NI	
($c \cdot 10^4$)	(Λ)	($c \cdot 10^4$)	(Λ)	($c \cdot 10^4$)	(Λ)	($c \cdot 10^4$)	(Λ)
(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)	(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)	(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)	(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)
$w_1 = 0.20$							
8.3	39.50	8.3	38.60	8.4	36.38	8.3	35.20
15.3	37.00	15.3	36.00	15.3	34.66	15.3	33.20
21.2	35.80	21.2	34.90	21.2	33.14	21.2	32.33
26.2	34.68	26.2	34.20	26.3	32.14	26.2	31.22
30.6	34.00	30.6	33.00	30.64	31.66	30.6	30.72
34.4	33.50	34.4	33.00	34.5	30.50	34.4	30.20
37.8	32.80	37.8	31.70	37.8	30.30	37.8	29.89
40.8	32.10	40.8	31.30	40.8	29.80	40.8	29.30
45.9	31.70	43.5	30.60	43.5	29.40	45.9	29.00
50.1	30.50	48.1	29.70	46.0	29.37	50.1	28.40
53.6	30.00	51.9	29.27	50.1	28.92	53.6	28.19
57.8	29.40	55.1	28.66	51.9	28.49	56.5	27.70
61.2	29.20	57.8	28.52	55.1	28.29	59.0	27.62
64.0	28.59	61.2	28.08	57.9	27.82	61.2	27.28
66.3	28.34	64.0	27.80	60.2	27.23	63.1	27.25
68.3	28.26	66.3	27.58	63.2	27.22	65.6	27.00
69.9	28.01	68.3	27.37	65.7	27.11	67.6	26.76
71.4	28.00	70.5	27.23	67.1	26.98	69.4	26.51
72.3	27.80	72.3	26.96	69.5	26.62	70.9	26.36
73.8	27.76	74.2	26.95	71.5	26.44	72.7	26.28
$w_1 = 0.40$							
4.4	38.80	4.4	36.89	4.4	35.50	4.6	34.61
8.1	37.00	6.3	36.00	6.3	35.25	6.6	33.82
11.3	35.80	8.1	35.20	8.0	34.18	8.4	32.71
13.9	34.56	9.7	34.56	9.7	33.86	10.1	32.31
16.3	33.37	11.2	34.00	11.1	33.39	11.6	31.84
18.3	32.83	13.9	32.90	12.8	32.47	13.1	31.35
20.1	32.30	16.2	32.34	13.8	32.10	14.4	30.91
23.1	31.50	18.2	31.43	14.9	32.04	15.7	30.54
25.6	30.43	20.0	30.70	17.1	31.23	17.9	29.82
27.6	30.19	21.6	30.50	19.0	30.86	19.9	29.66
29.3	29.81	23.0	30.14	20.7	30.30	21.6	29.16
31.4	29.32	24.3	29.48	22.2	29.75	23.2	28.61
33.1	28.97	26.5	29.30	23.6	29.21	24.6	28.60
34.4	28.44	28.4	29.06	24.7	29.16	25.9	28.24
35.6	28.36	29.9	28.68	25.8	28.77	27.0	27.99
36.9	27.91	31.2	28.22	27.7	28.41	29.0	27.54
37.9	27.66	32.9	27.94	29.4	27.64	30.7	27.37
39.0	27.40	34.3	27.69	30.7	27.73	32.1	26.95
39.9	27.29	35.5	27.35	31.9	27.48	33.4	26.81
40.7	27.29	36.7	26.94	33.4	26.93	34.5	26.40
$w_1 = 0.60$							
1.7	36.41	1.7	34.60	1.7	33.30	1.7	32.30
2.5	34.82	2.4	33.05	2.4	32.51	2.4	31.60
3.2	34.12	3.1	32.50	3.1	31.40	3.1	30.80
3.8	32.94	3.8	31.40	3.7	30.48	3.8	30.05
4.4	32.12	4.3	30.70	4.3	30.20	4.3	29.73
4.9	31.31	4.9	30.00	4.8	29.70	4.9	28.93
5.4	30.94	5.4	29.50	5.3	29.00	5.4	28.67
5.9	30.44	5.8	29.10	5.8	28.60	5.8	28.11
6.3	29.80	6.3	28.90	6.2	28.40	6.3	28.00
7.1	29.21	6.7	28.50	6.6	28.00	6.7	27.70
7.8	28.20	7.0	27.96	7.4	27.56	7.0	27.20
8.4	27.66	7.7	27.70	7.7	27.14	7.7	26.87
8.9	27.18	8.3	26.94	8.3	26.71	8.4	26.33
9.5	26.81	8.9	26.63	8.9	26.30	8.9	25.94
9.9	26.50	9.4	26.08	9.3	25.88	9.4	25.74
10.7	25.86	9.8	25.71	9.8	25.80	10.2	24.96
11.4	25.42	10.6	25.40	10.6	25.26	11.3	24.02
11.9	25.31	11.3	24.60	11.2	24.87	11.8	23.82
12.6	24.62	11.8	24.51	11.8	24.46	12.3	23.54
13.2	24.54	12.3	24.29	12.3	24.24	12.9	23.29
$w_1 = 0.80$							
1.7	4.07	1.7	3.72	1.7	3.72	1.7	3.64
2.4	3.57	2.4	3.27	2.4	3.20	2.4	3.38
3.1	3.26	3.1	2.96	3.1	2.95	3.1	3.09
3.8	3.03	3.8	2.71	3.8	2.75	3.8	2.90
4.3	2.93	4.3	2.49	4.3	2.61	4.3	2.72
4.9	2.81	4.9	2.36	4.9	2.50	4.9	2.63
5.4	2.72	5.4	2.25	5.4	2.40	5.4	2.51
5.8	2.59	5.8	2.16	5.8	2.31	5.8	2.43
6.3	2.55	6.3	2.10	6.3	2.28	6.3	2.36
7.0	2.45	7.0	2.00	7.0	2.21	7.0	2.29
7.7	2.33	7.7	1.87	7.7	2.13	7.7	2.23

Table 2. (Continued)

Bu ₄ NI		Pen ₄ NI		Hex ₄ NI		Hept ₄ NI	
(c·10 ⁴)	(Λ)						
(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)	(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)	(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)	(mol·dm ⁻³)	(S·cm ² ·mol ⁻¹)
8.4	2.26	8.3	1.82	8.4	2.05	7.7	2.17
8.9	2.19	8.9	1.74	8.9	1.98	8.4	2.08
9.4	2.15	9.4	1.72	9.4	1.95	8.9	2.02
10.2	2.05	9.8	1.68	10.2	1.87	9.4	1.97
10.9	2.01	10.6	1.66	10.9	1.81	9.8	1.94
11.6	1.94			11.6	1.77	10.6	1.87
12.1	1.90			12.1	1.75	11.3	1.82
12.7	1.86			12.5	1.70	11.8	1.78
13.3	1.82			13.1	1.66	12.3	1.75

cubic spline fitting. The λ_{δ}^{\pm} values were in turn utilized for the calculation of Stokes' radii r_s according to the classical expression³²

$$r_s = \frac{F^2}{6\pi N_A \lambda_{\delta}^{\pm} \eta_0} \quad (9)$$

Ionic Walden products $\lambda_{\delta}^{\pm} \eta_0$, Stokes' radii r_s , and crystallographic radii r_c are presented in Table 4. The trends in ionic

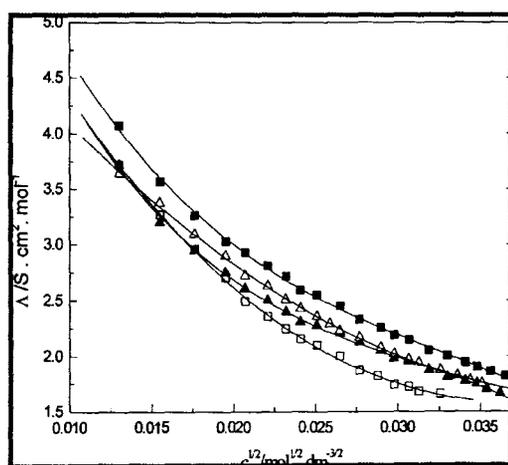


Figure 1. Plots of molar conductance, Λ , versus square root of salt concentration, $c^{1/2}$, in $w_1 = 0.80$ of CCl_4 (1) + PhNO_2 (2) at $T = 298.15$ K. ■, Bu_4NI ; □, Pen_4NI ; ▲, Hex_4NI ; △, Hept_4NI .

Table 3. Limiting Molar Conductance Λ_0 , Association Constant K_A , Cosphere Diameter R , and Standard Deviations σ of Experimental Λ from Equation 1 and Walden Products for the Electrolytes in Different Binary Solvent Mixtures of CCl_4 (1) + PhNO_2 (2) at $T = 298.15$ K

w_1	Λ_0		R		$\Lambda_0 \eta_0$	σ
	(S·cm ² ·mol ⁻¹)	K_A	Å	(S·cm ² ·mol ⁻¹ ·mPa·s)		
Bu ₄ NI						
0.20	46.23	159.9	12.0	74.57	0.24	
0.40	45.71	301.1	12.4	64.49	0.22	
0.60	44.94	330.5	12.7	54.99	0.25	
Pen ₄ NI						
0.20	42.53	90.9	11.9	69.77	0.21	
0.40	42.35	246.1	13.4	59.75	0.26	
0.60	41.51	1075.3	12.6	50.79	0.26	
Hex ₄ NI						
0.20	41.74	126.5	11.9	67.33	0.23	
0.40	41.31	231.9	12.3	58.28	0.25	
0.60	39.01	816.2	12.6	47.74	0.24	
Hept ₄ NI						
0.20	39.59	99.6	11.9	63.86	0.12	
0.40	39.30	195.8	12.3	55.44	0.14	
0.60	38.51	851.9	12.6	47.13	0.16	

Table 4. Limiting Ionic Conductance λ_{δ}^{\pm} , Ionic Walden Product $\lambda_{\delta}^{\pm} \eta_0$, Stokes' Radii r_s , and Crystallographic Radii r_c at $T = 298.15$ K

ion	λ_{δ}^{\pm}	$\lambda_{\delta}^{\pm} \eta_0$	r_s	r_c^a
	(S·cm ² ·mol ⁻¹)	(S·cm ² ·mol ⁻¹ ·mPa·s)	Å	Å
$w_1 = 0.20$				
Bu ₄ N ⁺	13.38	21.58	3.79	4.94
Pen ₄ N ⁺	9.68	15.61	5.25	5.29
Hex ₄ N ⁺	8.89	14.34	5.71	5.60
Hept ₄ N ⁺	8.74	10.87	7.53	5.88
I ⁻	32.85	52.99	1.76	2.16
$w_1 = 0.40$				
Bu ₄ N ⁺	14.97	21.12	3.93	4.94
Pen ₄ N ⁺	11.61	16.38	5.09	5.29
Hex ₄ N ⁺	10.57	14.91	5.60	5.60
Hept ₄ N ⁺	8.56	12.08	6.95	5.88
I ⁻	30.74	43.37	1.87	2.16
$w_1 = 0.60$				
Bu ₄ N ⁺	15.83	18.82	4.15	4.94
Pen ₄ N ⁺	12.40	15.18	5.26	5.29
Hex ₄ N ⁺	9.90	12.16	6.56	5.60
Hept ₄ N ⁺	9.40	11.50	6.89	5.88
I ⁻	29.11	35.62	2.32	2.16

^a r_c values are taken from ref 14.

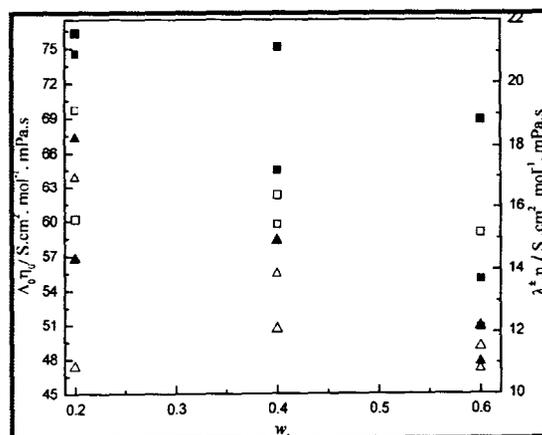


Figure 2. Plots of Walden products, $\Lambda_0 \eta_0$, for electrolytes and ionic Walden products, $\lambda_{\delta}^{\pm} \eta_0$, versus w_1 of CCl_4 (1) + PhNO_2 (2) mixtures at $T = 298.15$ K. ■, Bu_4NI or Bu_4N^+ ; □, Pen_4NI or Pen_4N^+ ; ▲, Hex_4NI or Hex_4N^+ ; △, Hept_4NI or Hept_4N^+ .

Walden products $\lambda_{\delta}^{\pm} \eta_0$ and Walden products $\Lambda_0 \eta_0$ for all the electrolytes in the solvent mixtures ($w_1 = 0.20$ to 0.60) are depicted in Figure 2. It shows that Walden products $\Lambda_0 \eta_0$ for all electrolytes decrease almost linearly as the CCl_4 content increases in the solvent mixtures, but the trend in ionic Walden products $\lambda_{\delta}^{\pm} \eta_0$ for R_4N^+ ions is rather irregular. However, the I^- ion shows a similar trend with the electrolytes in this regard.

Table 5. Calculated Limiting Molar Conductance Λ_0 , Slope and Intercepts of Equation 10, Maximum Concentration c , Ion Pair Formation Constant K_P , Triple Ion Formation Constant K_T , Ion Pair Concentration c_P , and Triple Ion Concentration c_T for R_4NI ($R =$ Butyl to Heptyl) in 80 Mass % of CCl_4 (1) + $PhNO_2$ (2) at $T = 298.15$ K

Λ_0 ($S \cdot cm^2 \cdot mol^{-1}$)	slope	intercept $\cdot 10^2$	$c^a \cdot 10^4$ ($mol \cdot dm^{-3}$)	$K_P \cdot 10^5$	K_T	$c_P \cdot 10^3$	$c_T \cdot 10^6$
50.04	9.069 (± 0.003)	6.164 (± 0.002)	Bu ₄ NI 13.3	6.6	220.6	1.24	13.1
46.22	5.824 (± 0.002)	5.265 (± 0.003)	Pen ₄ NI 10.6	7.7	165.8	1.01	6.5
43.44	7.121 (± 0.004)	5.408 (± 0.001)	Hex ₄ NI 13.1	6.4	194.4	1.23	11.5
42.88	15.422 (± 0.001)	5.235 (± 0.001)	Hept ₄ NI 12.3	6.7	441.7	1.12	23.3

^a Maximum concentrations used in calculations.

Thus, it seems that the I^- ion plays a predominating role in characterizing the conductance behavior of the electrolytes under study in these media. The position of the curves in Figure 2. $\Lambda_0\eta_0$ or $\lambda_0^+\eta_0$ versus w_1 , suggests a relationship $Bu_4N^+ < Pen_4N^+ < Hex_4N^+ < Hept_4N^+$ for Stokes' radius just similar to their ionic radii order. For tetraalkylammonium ions, the Stokes' radii are either lower or comparable to their crystallographic radii r_c , particularly for smaller ions. This suggests that these ions are comparatively less solvated than alkali metal ions due to their intrinsic low surface charge density.

The conductance data for all the electrolytes in 80 mass % of CCl_4 in $PhNO_2$ ($\epsilon_r = 10.22$) were analyzed by the classical Fuoss–Kraus theory of triple ion formation in the form^{33,34}

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0 K_T}{\sqrt{K_P}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (10)$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by

$$g(c) = \frac{\exp\{-(2.303/\Lambda_0^{1/2})\beta(c\Lambda^{1/2})\}}{\{1 - (S/\Lambda_0^{3/2})(c\Lambda)^{1/2}\}(1 - \Lambda/\Lambda_0)^{1/2}} \quad (11)$$

$$\beta = 1.8247 \cdot 10^6 / (\epsilon T)^{3/2} \quad (12)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \cdot 10^6}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{1/2}} \quad (13)$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution; Λ_0^+ is the sum of the conductances of the two triple ions $R_4N(I_2)^-$ and $(R_4N)_2^+I$ for R_4NI salts; and $K_P \approx K_A$ and K_T are the ion pair and triple ion formation constants. To make eq 10 applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted, and Λ_0 values for the studied electrolytes in 80 mass % of CCl_4 in $PhNO_2$ have been calculated using respective Λ_0 and η_0 values in 60 mass % of CCl_4 in $PhNO_2$ according to the Walden rule.^{14,30} Λ_0^+ is calculated by setting the triple ion conductance equal to $2/3\Lambda_0$.²⁵ The ratio Λ_0^+/Λ_0 was thus set equal to 0.667 during linear regression analysis of eq 10.

Linear regression analysis of eq 10 for the electrolytes with an average regression constant, $R^2 = 0.9653$, gives intercepts and slopes. These permit the calculation of other derived parameters such as K_P and K_T listed in Table 5. A part of Table 5 shows that the major portion of the electrolytes exists

Table 6. Interionic Distance Parameter a_{IP} and Interionic Distance for Triple Ion a_{TI} in 80 mass % of CCl_4 in $PhNO_2$ at $T = 298.15$ K

electrolyte	$a_{IP}/\text{\AA}$	$a_{TI}/\text{\AA}$	$1.5a_{IP}/\text{\AA}$
Bu ₄ NI	3.01	3.95	4.51
Pen ₄ NI	2.99	4.32	4.48
Hex ₄ NI	3.02	3.92	4.53
Hept ₄ NI	3.01	3.62	4.51

as ion pairs with a minor portion as triple ions. Using the K_P values, the interionic distance parameter a_{IP} has been calculated with the aid of the Bjerrum's theory of ionic association³⁶ in the form

$$K_P = \frac{4\pi N_A}{1000} \left[\frac{e^2}{\epsilon_r kT} \right]^3 Q(b) \quad (14)$$

$$Q(b) = \int_2^b y^{-4} \exp(y) dy \quad (15)$$

$$b = \frac{e^2}{a_{IP} \epsilon_r kT} \quad (16)$$

The a_{IP} values obtained are given in Table 6. The $Q(b)$ and b values have been calculated by the literature procedure.³⁶ Table 6 reveals that a_{IP} values are almost similar for all the electrolytes though the actual ionic sizes varied by (0.28 to 0.35) \AA . This may be due to easy penetration by the I^- ion to some extent into the void spaces between the alkyl chains, as suggested by Abbott and Schiffrin.³⁷ Thus, an increase in chain length for tetraalkylammonium ions does not affect the distance of closest approach between the two ions. The a_{IP} are much less in comparison with the crystallographic radii (r_c) suggesting probable contact ion pairs for the iodides in solution.¹⁴ This will cause a decrease in the degree of freedom for the cations in the ion pair resulting in their loss of configurational entropy of the contact pair. Generally, K_P values do not change significantly for quaternary ammonium ions with the alkyl chain consisting of more than 3 carbon atoms. The small changes in the K_P may thus be related to entropic contributions. The interionic distance a_{TI} for the triple ion can be calculated using the expressions³³

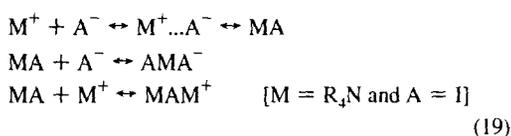
$$K_T = \frac{2\pi N_A a_{TI}^3}{1000} I(b_3) \quad (17)$$

$$b_3 = \frac{e^2}{a_{TI} \epsilon_r kT} \quad (18)$$

$I(b_3)$ is a double integral tabulated in the literature³³ for a range of values of b_3 . Since $I(b_3)$ is a function of a_{TI} , a_{TI} values have

been calculated by an iterative computer program. The α_T values (Table 6) for the electrolytes are greater than the corresponding α_P values but are much less than the expected theoretical value 1.5 α_P . This is probably due to repulsive forces between the two anions or cations in the triple ions $R_4N(l_2)^-$ and $(R_4N)_2^+I$ as suggested by Hazra et al.³⁸

A perusal of Table 5 shows that the major portion of the electrolytes exists as ion pairs with a minor portion as triple ions. The tendency of triple ion formation can be judged from the K_T/K_P ratios, which are highest for Hept₄NI. These ratios suggest that strong association between the ions is due to the Coulombic interactions as well as to covalent forces in the solution. At very low permittivity of the solvent ($\epsilon_r < 15$),³⁰ electrostatic interactions are very strong permitting the ion pair to attract free anions/cations from solution bulk and from triple ions^{33,38} which acquire the charge of the combining ion, i.e.



The effect of ternary association³⁹ thus removes some nonconducting species MA from solution and replaces them by triple ions which increase the conductance manifested by nonlinearity observed in conductance curves for the electrolytes in 80 mass % of CCl₄ in PhNO₂.

The ion pair and triple ion concentrations (c_P and c_T , respectively) of the electrolytes at the highest electrolyte concentration have been derived using eqs³⁸ 20 to 23 and are listed in Table 5.

$$\alpha = (K_P c)^{-1/2} \quad (20)$$

$$\alpha_T = \frac{K_T}{K_P^{0.5} c} \quad (21)$$

$$c_P = c(1 - \alpha - 3\alpha_T) \quad (22)$$

$$c_T = \frac{K_T}{K_P^{1/2} c} \quad (23)$$

While the highest c_P value was found for Bu₄NI, the highest c_T value was found for Hept₄NI.

Note Added after ASAP Publication: This paper was published ASAP on May 11, 2009. A change was made to an author name. The revised paper was reposted on May 18, 2009.

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Received for review November 20, 2008. Accepted April 17, 2009. The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. F 540/27/DRS/2007, SAP-I), for financial support.

1E800885H

PHYSICAL CHEMISTRY
OF SOLUTIONS

Ion–Solvent and Ion–Ion Interactions of Phosphomolybdic Acid in Aqueous Solution of Catechol at 298.15, 308.15, and 318.15 K*

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Abstract—Apparent molar volume (V_{ϕ}°) and viscosity B -coefficients were measured for phosphomolybdic acid in aqueous solution of catechol from solution density (ρ) and viscosity (η) at 298.15, 308.15, and 318.15 K at various solute concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion–solvent and ion–ion interactions. The viscosity data have been analyzed using Jones–Dole equation and the derived parameters, B and A , have been interpreted in terms of ion–solvent and ion–ion interactions respectively. The structure-making or breaking capacity of the solute under investigation has been discussed in terms of sign of $(\delta^2 V_{\phi}^{\circ} / \delta T^2)_{\rho}$. The activation parameters of viscous flow were determined and discussed by application of transition state theory.

DOI: 10.1134/S0036024409110144

INTRODUCTION

Studies on densities (ρ) and viscosities (η) of solutions are of great importance in characterizing the properties and structural aspects of solutions. Hence studies on the limiting apparent molar volume and viscosity- B coefficients of electrolyte provide us valuable information regarding ion–ion, ion–solvent, and solvent–solvent interactions [1–3]. It has been found by a number of workers [4–6] that the addition of a solute could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various solute concentrations and temperature.

In this paper we have attempted to report the limiting apparent molar volume (V_{ϕ}°), experimental slopes (S_v^*), and viscosity B -coefficients for phosphomolybdic acid in aqueous catechol solution at 298.15, 308.15, and 318.15 K. Phosphomolybdic acid is widely used to stain connective tissues by dyes. It has been found that phosphomolybdic acid forms salts with connective tissues containing basic groups and hence the polyvalent phosphomolybdic acid appears to form a bridge between the basic group of the substrate and the basic group of the dye. In other words, addition of phosphomolybdic acid to connective tissues changes its acidophilia to basophilia. Phosphomolybdic acid not only yields an intense staining of connective tissue fibers by dyes with basic groups but also reduces the staining of cytoplasm, thus producing a specific staining of connective tissue fiber [7].

EXPERIMENTAL

Commercial sample of catechol was purified by repeated crystallization from mixture of chloroform–methanol. The sample was dissolved in chloroform in hot condition, filtered and to the filtrate dried and distilled methanol was added drop wise. Fine plate like crystal separated and was recovered by rapid filtration and ready for use. Phosphomolybdic acid of analytical grade was purchased from Thomas Baker and was used without further purification. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was used for all measurements. Experimental values of viscosity (η), density (ρ), and pH are listed in Table 1.

Densities (ρ) were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of about 0.1 cm. The measurements were done in a thermostat bath controlled to $\pm 0.01 \text{ K}$. the viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to $\pm 0.1 \text{ s}$, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4} \text{ mPa s}$. The mixtures were prepared by mixing known volume of pure liquids in air-tight-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 fractions 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

* The text was submitted by the authors in English.

Table 1. Experimental value of density (ρ , kg m⁻³) and viscosity (η , mPa s) of aqueous catechol mixtures at different temperatures

Temperature, K	$\rho \times 10^{-3}$, kg m ⁻³	η , mPa s	pH
0.05 M			
298.15	0.99650	0.9003	6.16
308.15	0.99371	0.7350	5.31
318.15	0.99222	0.6135	
0.1 M			
298.15	0.99797	0.9132	4.20
308.15	0.99509	0.7475	4.16
318.15	0.99303	0.6375	4.13
0.15 M			
298.15	0.99910	0.9227	3.97
308.15	0.99621	0.7602	3.89
318.15	0.99429	0.6528	3.82

precision of density measurements was $\pm 3 \times 10^{-4}$ g cm⁻³. Viscosity of the solution, η , is given by the following equation:

$$\eta = (Kt - L/t)\rho \quad (1)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.003 mPa s.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere [8–11]. The electrolyte solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

RESULTS AND DISCUSSION

The apparent molar volumes (V_{ϕ}) were determined from the solution densities using the following equation [3]:

$$V_{\phi}^{\circ} = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0, \quad (2)$$

where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volumes V_{ϕ}° was calculated using a least-square treatment to the plots of V_{ϕ} versus $c^{1/2}$ using the following Masson equation [12]:

$$V_{\phi} = V_{\phi}^{\circ} + S_v^* c^{1/2}, \quad (3)$$

where V_{ϕ}° is the partial molar volume at infinite dilution and S_v^* the experimental slope. The plots of V_{ϕ} against square root of molar concentration ($c^{1/2}$) were found to be linear with negative slopes. Values of V_{ϕ}° and S_v^* are reported in Table 3.

As the systems under study are characterized by hydrogen bonding, the ion–solvent and ion–ion interactions can be interpreted in terms of structural changes which arise due to hydrogen bonding between various components of the solvent and solution systems. V_{ϕ}° can be used to interpret ion–solvent interactions. Table 3 reveals that V_{ϕ}° values are positive and increases with rise in temperature and decreases with increase in the amount of catechol in the solvent mixture. This indicates the presence of strong ion–solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the amount of catechol in the solvent mixture under study, suggesting larger electrostriction at higher temperature and in lower amount of catechol in the mixture. Similar results were obtained for some 1 : 1 electrolytes in aqueous DMF [13] and aqueous THF [14].

It is evident from Table 3 that the S_v^* values are negative at all temperatures for aqueous mixtures of catechol. Furthermore S_v^* values decreases with the increase of experimental temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion–ion interactions (ionic-dissociation) [15]. A quantitative comparison of the magnitude of values shows that V_{ϕ}° values are much greater in magnitude than those of S_v^* for all the solutions. This suggests that ion–solvent interactions dominate over ion–ion interactions in all the solutions and at all experimental temperatures.

The variation of V_{ϕ}° with temperature of phosphomolybdic acid in solvent mixture follows the polynomial,

$$V_{\phi}^{\circ} = a_0 + a_1 T + a_2 T^2 \quad (4)$$

over the temperature range under study where T is the temperature in K. Values of coefficients of the above equation for phosphomolybdic acid in aqueous catechol mixtures are reported in Table 4.

The apparent molar expansibilities (ϕ_E°) can be obtained by the following equation:

$$\phi_E^{\circ} = (\delta V_{\phi}^{\circ} / \delta T)_p = a_0 + 2a_2 T. \quad (5)$$

The values ϕ_E° of for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are

Table 2. Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_{ϕ}), $(\eta/\eta_0 - 1)/c^{1/2}$, and pH of phosphomolybdic acid in different aqueous catechol mixtures at different temperatures (c_c is concentration of catechol in aqueous solution)

c , mol dm ⁻³	$\rho \times 10^{-3}$, kg m ⁻³	η , mPa s	$V_{\phi} \times 10^6$, m ³ mol ⁻¹	$(\eta/\eta_0 - 1)/c^{1/2}$	pH
$c_c = 0.298.15$ K					
0.0025	1.0003	0.8970	963.4739	0.0754	2.56
0.0050	1.0042	0.9013	807.3489	0.1213	2.29
0.0074	1.0085	0.9059	709.8034	0.1585	2.13
0.0099	1.0125	0.9099	693.5894	0.1829	1.99
0.0124	1.0169	0.9146	649.6547	0.2107	1.91
0.0154	1.0223	0.9205	593.0401	0.2432	1.83
$c_c = 0.308.15$ K					
0.0025	0.9972	0.7234	980.4210	0.0260	2.50
0.0049	1.0008	0.7275	880.5810	0.0980	2.20
0.0074	1.0048	0.7318	803.2913	0.1500	2.02
0.0098	1.0091	0.7365	725.1210	0.1961	1.89
0.0123	1.0135	0.7404	677.6658	0.2239	1.80
0.0151	1.0189	0.7454	617.4291	0.2571	1.72
$c_c = 0.318.15$ K					
0.0024	0.9949	0.6042	1117.8019	0.2110	2.40
0.0049	0.9989	0.6170	874.4041	0.4530	2.08
0.0073	1.0032	0.6280	745.7746	0.5860	1.90
0.0098	1.0072	0.6378	717.0760	0.6720	1.79
0.0122	1.0114	0.6469	678.2216	0.7400	1.69
0.0151	1.0169	0.6583	614.9841	0.8200	1.59
$c_c = 0.05$ M, 298.15 K					
0.0024	1.0007	0.9071	504.8713	0.0860	2.73
0.0048	1.0053	0.9116	431.7338	0.1330	2.36
0.0076	1.0107	0.9162	391.3216	0.1637	2.14
0.0101	1.0156	0.9190	365.7746	0.1727	2.03
0.0125	1.0205	0.9229	339.9873	0.1940	1.92
0.0149	1.0252	0.9270	329.7652	0.2145	1.83
$c_c = 0.05$ M, 308.15 K					
0.0024	0.9978	0.7396	530.2752	0.1280	2.66
0.0048	1.0023	0.7458	472.4611	0.2130	2.29
0.0076	1.0075	0.7516	434.2549	0.2600	2.08
0.0101	1.0123	0.7569	412.4919	0.2970	1.98
0.0125	1.0170	0.7604	387.1231	0.3100	1.85
0.0148	1.0217	0.7663	373.6044	0.3492	1.77
$c_c = 0.05$ M, 318.15 K					
0.0024	0.9962	0.6217	569.2613	0.2750	2.58
0.0048	1.0004	0.6307	518.5812	0.4060	2.22
0.0076	1.0055	0.6421	484.1216	0.5364	1.99
0.0102	1.0094	0.6514	458.6212	0.6171	1.91
0.0126	1.0132	0.6583	424.2826	0.6560	1.83
0.0150	1.0174	0.6657	411.1519	0.7000	1.73

Table 2. (Contd.)

c , mol dm ⁻³	$\rho \times 10^{-3}$, kg m ⁻³	η , mPa s	$V_{\infty} \times 10^6$, m ³ mol ⁻¹	$(\eta/\eta_0 - 1)/c^{1/2}$	pH
$c_c = 0.1$ M, 298.15K					
0.0024	1.0022	0.9199	510.1307	0.1490	2.53
0.0048	1.0065	0.9254	491.9397	0.1930	2.26
0.0076	1.0116	0.9306	471.7912	0.2180	2.09
0.0101	1.0162	0.9343	456.3825	0.2300	1.99
0.0125	1.0207	0.9375	440.5892	0.2380	1.91
0.0149	1.0253	0.9411	423.4132	0.2500	1.85
$c_c = 0.1$ M, 308.15 K					
0.0024	0.9992	0.7524	562.0561	0.1340	2.58
0.0048	1.0034	0.7577	526.5677	0.1970	2.24
0.0076	1.0084	0.7634	501.1550	0.2440	2.04
0.0101	1.0130	0.7682	487.9350	0.2762	1.94
0.0125	1.0173	0.7716	476.8405	0.2881	1.83
0.0149	1.0219	0.7752	460.9899	0.3040	1.75
$c_c = 0.1$ M, 318.15 K					
0.0024	0.9970	0.6441	600.0121	0.2020	2.42
0.0048	1.0011	0.6518	572.6434	0.3230	2.14
0.0076	1.0060	0.6604	551.5000	0.4120	1.94
0.0101	1.0104	0.6662	533.7240	0.4480	1.85
0.0125	1.0148	0.6731	514.6262	0.5000	1.75
0.0150	1.0192	0.6806	498.5364	0.5540	1.70
$c_c = 0.15$ M, 298.15K					
0.0024	1.0034	0.9309	480.5001	0.1820	2.52
0.0050	1.0081	0.9354	462.5995	0.1940	2.25
0.0076	1.0128	0.9400	458.5057	0.2150	2.09
0.0102	1.0174	0.9434	445.8924	0.2230	1.97
0.0125	1.0217	0.9474	439.3518	0.2402	1.88
0.0151	1.0265	0.9512	428.7236	0.2520	1.81
$c_c = 0.15$ M, 308.15 K					
0.0024	1.0002	0.7644	576.6336	0.1140	2.45
0.0050	1.0047	0.7673	560.6523	0.1320	2.16
0.0076	1.0092	0.771	548.4545	0.1630	1.99
0.0102	1.0135	0.7737	537.4861	0.1767	1.87
0.0125	1.0175	0.7770	535.1857	0.1990	1.78
0.0151	1.0221	0.7807	524.5887	0.2208	1.70
$c_c = 0.15$ M, 318.15 K					
0.0024	0.9983	0.1040	592.5463	0.1040	2.40
0.0050	1.0027	0.1450	565.5505	0.1450	2.09
0.0076	1.0072	0.1700	550.8687	0.1700	1.89
0.0102	1.0116	0.1960	540.2304	0.1960	1.79
0.0125	1.0156	0.2270	533.9527	0.2270	1.70
0.0151	1.0204	0.2490	513.5327	0.2490	1.62

Table 3. Limiting apparent molar volumes (V_{ϕ}°) and experimental slopes (S_{ϕ}^*) for phosphomolybdic acid at different temperatures (c_c is concentration of catechol in aqueous solution)

$c_c, \text{mol dm}^{-3}$	$V_{\phi}^{\circ} \times 10^6, \text{m}^3 \text{mol}^{-1}$			$-S_{\phi}^* \times 10^6, \text{m}^3 \text{mol}^{-1}$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0.00	1163.5	1227.3	1368.4	4757.8	4980.3	6440.7
0.05	607.33	626.22	673.7	2372.1	2128.5	2185.7
0.1	571.38	622.56	668.44	1174.5	1335.1	1371.7
0.15	513.4	609.94	639.48	674.12	697.1	1000.7

reported in Table 5. Table 5 reveals that ϕ_E° value increases as temperature increases up to 0.05 mol. dm⁻³ of catechol mixtures but thereafter ϕ_E° value decreases slightly with increasing temperature. This fact may be attributed to gradual disappearance of caging or packing effect [15, 16] in the ternary solutions. During the past few years it has been emphasized by a number of workers that S_{ϕ}^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. According to Helper [17] the sign of $(\delta\phi_E^{\circ}/\delta T)_p$ is a better criterion in characterizing the long-range structure-making and breaking ability of the solutes in solution. The general thermodynamic expression used is as follows

$$(\delta\phi_E^{\circ}/\delta T)_p = 2a_2. \quad (6)$$

If the sign of $(\delta\phi_E^{\circ}/\delta T)_p$ is positive or small negative [18] the solute is a structure maker otherwise it is a structure breaker. As is evident from Table 5, phosphomolybdic acid predominately acts as a structure maker and its structure making ability decreases to some extent as the molarity of catechol increases in the solvent mixture. A similar result was observed in the study of nicotinamide in aqueous tetrabutylammonium bromide solution [19]. The small negative values of $(\delta\phi_E^{\circ}/\delta T)_p$ at 0.1 and 0.15 mol dm⁻³ aqueous catechol solution are probably due to higher structure promoting ability of catechol than phosphomolybdic acid with comparatively higher V_{ϕ}° value in aqueous solution [20] originating from hydrophobic hydration with greater degree of hydrogen bonding than the bulk water [21].

Partial molar volume ΔV_{ϕ}° of transfer from water to different aqueous catechol solution has been determined using the following relation [22, 23]

$$\Delta V_{\phi}^{\circ} = V_{\phi}^{\circ}(\text{aqueous catechol solution}) - V_{\phi}^{\circ}(\text{water}). \quad (7)$$

The V_{ϕ}° value is independent from solute-solute interaction and provides information regarding solute and co-solute interaction [22]. Table 3 shows that the values of V_{ϕ}° is positive at all experimental temperatures and increases with the concentration of catechol in the ternary mixture. The concentration dependence of the thermodynamic properties of the solute in aqueous solution can be explained in terms of overlap of hydration co-sphere. According to the co-sphere model as developed by Friedman and Krishnan [24], the effect of the overlap of hydration co-sphere is destructive. The overlap of hydration co-spheres of two ionic species results in an increase in volume but that of hydration co-sphere of hydrophobic-hydrophobic group and ion-hydrophobic group results in a net volume decrease. The positive value of ΔV_{ϕ}° indicate that hydrophobic-hydrophobic and ion-hydrophobic group interaction are predominant and the overall effect of the hydration co-sphere of phosphomolybdic acid and catechol reduce the effect of electrostriction of water by phosphomolybdic acid molecule and these effect increases with the molarity of catechol in the ternary mixture as shown in the Fig. 1 (ΔV_{ϕ}° vs. molarity of catechol in solution). In addition, standard partial molar volume of the solute has been explained by a simple model [25, 26].

$$V_{\phi}^{\circ} = V_{\phi}^{\circ}{}_{\text{vw}} + V_{\phi}^{\circ}{}_{\text{void}} - V_{\phi}^{\circ}{}_{\text{s}}, \quad (8)$$

Table 4. Values of the coefficients of Eq. (4) for phosphomolybdic acid in different aqueous catechol mixtures (cm³ mol⁻¹)

$c_c, \text{mol dm}^{-3}$	a_0	a_1	a_2
0.00	34772.46	-227.96	0.3865
0.05	13182.24	-84.81	0.1430
0.1	-3389.23	21.18	-0.0265
0.15	-33143.04	212.76	-0.3350

Table 5. Limiting partial molar expansibilities for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures

Aqueous catechol solution, c_c , mol dm ⁻³	\varnothing_E° , m ³ mol ⁻¹ K ⁻¹			$(\delta\varnothing_E^\circ/\delta T)_P$
	298.15 K	308.15 K	318.15 K	
0.00	2.5100	10.2400	17.97	0.7730
0.05	0.4590	3.3190	6.1790	0.2860
0.1	5.3884	4.8531	4.3231	-0.0530
0.15	13.0040	6.3040	0.3960	-0.6700

where $V_{\varnothing_{vw}}$ is the vander wall volume, $V_{\varnothing_{void}}$ is the volume associated with void or empty space and V_{\varnothing_s} the shrinkage volume due to electrostriction. Considering the $V_{\varnothing_{vw}}$ and $V_{\varnothing_{void}}$ have the same magnitude in water and in aqueous catechol solution for the same solute [27]. The increase in V_{\varnothing}° values and the concomitant positive $\Delta V_{\varnothing}^\circ$ can be attributed to the decrease in shrinkage volume of water by phosphomolybdic acid in presence of catechol. This fact suggests that catechol has a dehydrating effect on the hydrated phosphomolybdic acid.

The viscosity data of aqueous and aqueous catechol solution have been analyzed using Jones–Dole [28] equation:

$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2}, \quad (9)$$

where η_0 and η are the viscosities of the solvent–solvent mixtures and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 6. From the Table it is evident that the values of the A -coefficient are either negative or very small positive for all the solutions under investiga-

tion at all experimental temperatures. These results indicate the presence of very weak ion–ion interactions and these interactions further decrease with the rise of experimental temperatures and increase with an increase of catechol in the mixture.

The effects of ion–solvent interactions on the solution viscosity can be inferred from the B -coefficient [29, 30]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B -coefficient of phosphomolybdic acid in the studied solvent systems are positive, thereby suggesting the presence of strong ion–solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of catechol in the mixture. These conclusions are in excellent agreement with those drawn from V_{\varnothing}° values discussed earlier.

Viscosity B -coefficient of transfer (ΔB) from water to different aqueous catechol solutions have been determined using the relation [22, 23]

$$\Delta B = B(\text{aqueous catechol solution}) - B(\text{water}). \quad (10)$$

The ΔB values as shown in Table 7 and depicted graphically in Fig. 2 (ΔB vs. molarity of catechol in solution) as a function of molarity of catechol in solution at the experimental temperature supports the result obtained from $\Delta V_{\varnothing}^\circ$ as discussed above.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of solutes as suggested by Feakings et. al [31] using the following equation:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + (1000B + \bar{V}_2^0 - \bar{V}_1^0)RT/\bar{V}_1^0, \quad (11)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and the solute respectively. The contribution

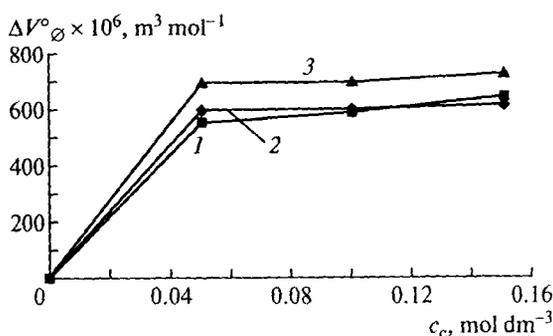
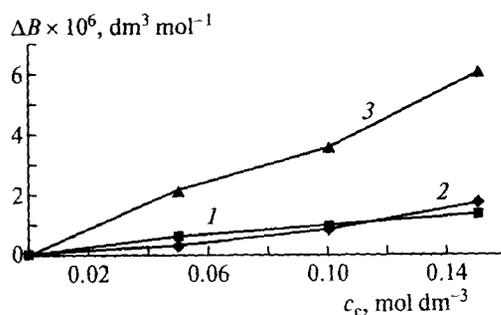
**Fig. 1.** Plots of partial molar volume ($\Delta V_{\varnothing}^\circ$) against molarity for the transfer from water to different aqueous catechol solution for phosphomolybdic acid at different temperatures: (1) 298.5 K, (2) 308.15 K, (3) 318.15**Fig. 2.** Plots of partial molar volume (ΔB) against molarity for the transfer from water to different aqueous catechol solution for phosphomolybdic acid at different temperatures: (1) 298.5 K, (2) 308.15 K, (3) 318.15

Table 6. Values of A and B coefficients for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures

$c_c, \text{mol dm}^{-3}$	$A, \text{m}^{3/2} \text{mol}^{-1/2}$			$B, \text{m}^{3/2} \text{mol}^{-1/2}$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0.00	-0.0363	-0.1251	-0.1438	2.2454	3.1624	8.0839
0.05	0.011	0.0010	-0.0025	1.663	2.8785	5.9650
0.1	0.0941	0.0307	0.0010	1.3220	2.3322	4.5261
0.15	0.1301	0.0355	0.0048	0.9717	1.4666	1.9682

per mole of the solute to the free energy of activation of viscous flow ($\Delta\mu_2^{0\ddagger}$) of the solutions was determined from the above relation and are listed in Table 8. The free energy of activation of viscous flow of the pure solvent ($\Delta\mu_1^{0\ddagger}$) is given by the relation:

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln(\eta_0 \bar{V}_1^0) / hN, \quad (12)$$

where N is the Avogadro's number and the other symbols have their usual significance. The values of $\Delta\mu_2^{0\ddagger}$ and $\Delta\mu_1^{0\ddagger}$ are reported in Table 8. From Table 8 it is evident that $\Delta\mu_1^{0\ddagger}$ is practically constant at all the solvent composition and temperature, implying that $\Delta\mu_2^{0\ddagger}$ is mainly dependent on the viscosity B -coefficients and $(\bar{V}_2^0 - \bar{V}_1^0)$ terms. Also $\Delta\mu_2^{0\ddagger}$ values were found to be positive at all experimental temperatures and this suggests that the process of viscous flow becomes difficult as the temperature and molarity of catechol in solution increases. Hence the formation of transition becomes less favorable [31]. According to Feakings et. al, $\Delta\mu_2^{0\ddagger} > \Delta\mu_1^{0\ddagger}$ for 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 [32]. The greater values of $\Delta\mu_2^{0\ddagger}$ supports the increased structure making tendency of the solute as discussed earlier. The entropy of activation for solutions has been calculated using the following relation [31]:

$$\Delta S_2^{0\ddagger} = -d(\Delta\mu_2^{0\ddagger})/dT, \quad (13)$$

where $\Delta S_2^{0\ddagger}$ has been determined from the negative slope of the plots of $\Delta\mu_2^{0\ddagger}$ against T by using a least square treatment.

The activation enthalpy ($\Delta H_2^{0\ddagger}$) has been calculated using the relation [31]:

$$\Delta H_2^{0\ddagger} = \Delta\mu_2^{0\ddagger} + T\Delta S_2^{0\ddagger}. \quad (14)$$

The value of $\Delta S_2^{0\ddagger}$ and $\Delta H_2^{0\ddagger}$ are listed in Table 8 and they are found to be negative for all the solutions and at all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mecha-

Table 7. Partial molar volumes V_∞^0 and viscosity B -coefficients ΔB of transfer from water to different aqueous catechol solutions for phosphomolybdic acid at different temperatures ($\text{m}^3 \text{mol}^{-1}$)

$c_c, \text{mol dm}^{-3}$	$V_\infty^0 \times 10^6$	$\Delta V_\infty^0 \times 10^6$	$B \times 10^6$	$\Delta B \times 10^6$
298.15 K				
0.00	1163.5	0.00	2.2454	0.00
0.05	607.33	556.17	1.663	0.5824
0.10	571.38	592.12	1.3220	0.9234
0.15	513.4	650.1	0.9717	1.2737
308.15 K				
0.00	1227.3	0.00	3.1624	0.00
0.05	626.22	601.08	2.8785	0.2839
0.10	622.56	604.74	2.3322	0.8302
0.15	609.94	617.36	1.4666	1.6958
318.15 K				
0.00	1368.4	0.00	8.0839	0.00
0.05	673.7	694.70	5.956	2.1279
0.10	668.44	699.96	4.5261	3.5578
0.15	639.48	728.92	1.9682	6.1157

Table 8. Values of $\bar{V}_1^0 - \bar{V}_2^0$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$, and $\Delta H_2^{0\neq}$ (kJ mol⁻¹) for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures

Parameter	298.15 K	308.15 K	318.15 K
$c_c = 0$			
$(\bar{V}_1^0 - \bar{V}_2^0) \times 10^6$	1145.43	1209.17	1350.24
$\Delta\mu_1^{0\neq}$	60.82	62.86	64.90
$\Delta\mu_2^{0\neq}$	465.134	617.891	1373.86
$-T\Delta S_2^{0\neq}$	13546.71	14001.1	14455.5
$-\Delta H_2^{0\neq} \times 10^3$	13081.609	13383.21	13081.60
$c_c = 0.05 \text{ mol dm}^{-3}$			
$(\bar{V}_1^0 - \bar{V}_2^0) \times 10^6$	589.10	607.89	655.32
$\Delta\mu_1^{0\neq}$	60.84	62.89	64.93
$\Delta\mu_2^{0\neq}$	222.02	317.90	349.47
$-T\Delta S_2^{0\neq}$	1899.99	1963.72	2027.44
$-\Delta H_2^{0\neq} \times 10^3$	1677.97	1645.81	1677.97
$c_c = 0.1 \text{ mol dm}^{-3}$			
$(\bar{V}_1^0 - \bar{V}_2^0) \times 10^6$	553.12	604.20	650.00
$\Delta\mu_1^{0\neq}$	60.85	62.90	64.94
$\Delta\mu_2^{0\neq}$	187.13	228.51	257.89
$-T\Delta S_2^{0\neq}$	1054.85	1090.23	1125.61
$-\Delta H_2^{0\neq} \times 10^3$	867.72	861.72	867.72
$c_c = 0.15 \text{ mol dm}^{-3}$			
$(\bar{V}_1^0 - \bar{V}_2^0) \times 10^6$	495.10	591.54	621.00
$\Delta\mu_1^{0\neq}$	60.86	62.90	64.96
$\Delta\mu_2^{0\neq}$	88.55	147.27	177.11
$-T\Delta S_2^{0\neq}$	1320.21	1364.49	1408.77
$-\Delta H_2^{0\neq} \times 10^3$	1231.66	1217.22	1231.66

nism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state [31, 33].

CONCLUSIONS

The values of apparent molar volume (V_ϕ^0) and viscosity B -coefficients for phosphomolybdic acid indicate the presence of strong solute–solvent interactions

and these interactions are further strengthened at higher temperature and higher molarity of catechol in the ternary solutions. Also phosphomolybdic acid acts as a water-structure promoter due to hydrophobic hydration in the presence of catechol and catechol has a dehydration effect on the hydrated phosphomolybdic acid.

ACKNOWLEDGMENTS

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (no. 540/6/DRS/2002, SAP-1) for financial support.

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Study on ion–solvent interactions of alkali metal salts in pure methanol and its binary mixtures with ethane-1,2-diol by a conductometric technique

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ARTICLE INFO

Article history:

Received 9 February 2009

Received in revised form 27 February 2009

Accepted 3 March 2009

Available online 18 March 2009

Keywords:

Association constant

Limiting conductance

Walden products

Ethane-1,2-diol

Methyl alcohol

ABSTRACT

Electrolytic conductivities of some sodium salts (NaI, NaSCN, CH₃COONa) have been studied in 0, 25, 50 and 75 mass% ethane-1,2-diol + methyl alcohol mixtures at 293.15, 298.15 and 303.15 K. The limiting molar conductivity (Λ°), the association constant (K_A) and the distance of closest approach of ion (R) have been evaluated using the Fuoss conductance equation (1978). The association constant (K_A) decreases with temperature while it tends to decrease in the order: 0 mass% > 25 mass% > 50 mass% > 75 mass% ethane-1,2-diol + methyl alcohol mixtures. Thermodynamic parameters ΔH° , ΔG° and ΔS° along with the Walden products ($\Lambda^\circ\eta$) are obtained and discussed. The results have been interpreted in terms of ion–solvent interactions and structural changes in the mixed solvents.

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1. Introduction

Studies on the transport properties of electrolytes in different solvent media are of great importance for obtaining information concerning the behavior of electrolyte solutions. The use of mixed solvents enables the variation of properties such as dielectric constant or viscosity and therefore the ion–ion and ion–solvent interactions can be better studied. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration dependence of the electrolyte conductivity. In the present study, an attempt has been made to ascertain the nature of ion–solvent interactions of sodium salts (NaI, NaSCN, CH₃COONa) in ethane-1,2-diol + methyl alcohol mixtures using the conductometric technique as literature survey revealed that very scarce work has been carried out in the solvent mixture considered. Thermodynamic parameters are also evaluated and discussed.

2. Experimental

Sodium metal salts (A.R. grade) were procured from Merck, India and purified as described in the literature [1,2]. Ethane-1,2-diol (E. Merck, India) and methyl alcohol (E. Merck, India) was purified by standard methods [3].

A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The conversion

of molality into molarity was accomplished using density values [4].

The values of relative permittivity (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner [5].

Densities were measured with an Ostwald–Sprenzel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostat water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The density values were reproducible to $\pm 3 \times 10^{-3}$ g cm⁻³. The details of the method have been discussed elsewhere [6].

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 [7–9]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa.s. The details

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Table 1

Values of density (ρ), viscosity (η) and dielectric constant (ϵ^a) of ethane-1,2-diol + methyl alcohol mixtures at various temperatures.

Mass% (w_1) (ethane-1,2-diol)	Temp (K)	$\rho \times 10^{-3}$ (kg m ⁻³)		η (mPa s)		ϵ^a
		This work	Lit	This work	Lit	
$w_1 = 0.00$	293.15	0.7910	0.7915 [17]	0.5814	0.5820 [17]	33.1 [5]
	298.15	0.7859	0.7866 [17]	0.5436	0.5445 [17]	32.7 [5]
	303.15	0.7814	0.7820 [17]	0.5112	0.5120 [17]	31.9 [5]
$w_1 = 0.25$	293.15	0.8647		1.1268		35.2 [5]
	298.15	0.8609		1.0295		34.7 [5]
	303.15	0.8586		0.9454		33.7 [5]
$w_1 = 0.50$	293.15	0.9383		2.2692		37.3 [5]
	298.15	0.9338		2.0452		36.7 [5]
	303.15	0.9321		1.8101		35.6 [5]
$w_1 = 0.75$	293.15	1.0234		5.7998		39.3 [5]
	298.15	1.0196		4.9040		38.7 [5]
	303.15	1.0173		4.2319		37.4 [5]

^a Calculated using the scheme given in Ref. [5].

Table 2

Molar conductance (Λ) and molar concentration of various sodium salts in ethane-1,2-diol (1) + methyl alcohol (2) mixtures at different temperatures.

$c \times 10^4$ (mol dm ⁻³)	Λ (S cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S cm ² mol ⁻¹)
293.15 K		298.15 K		303.15 K	
NaSCN ($w_1 = 0.00$)					
6.9857	95.60	6.9857	103.50	6.9857	108.50
10.0229	94.07	10.0229	102.45	12.8071	106.00
15.3685	92.71	15.3685	101.00	15.3685	105.07
17.7329	91.92	17.7329	100.14	17.7329	104.50
23.8477	89.93	21.9550	99.36	21.9550	103.14
25.6142	89.50	23.8477	98.71	23.8477	102.71
31.6410	88.36	25.6142	98.21	25.6142	102.14
34.1522	87.84	31.6410	97.07	31.6410	100.80
38.4212	87.20	34.1522	96.75	34.1522	100.14
41.9141	86.64	36.3991	96.16	36.3991	99.79
43.4327	86.80	41.9141	95.07	41.9141	98.64
48.3823	85.78	47.2877	94.14	48.3823	97.35
50.3451	85.41	54.8875	92.93	50.3451	97.13
56.6208	84.77	58.5467	92.50	56.0742	96.00
63.3614	83.96	60.1376	92.29	62.6124	94.93
NaI ($w_1 = 0.00$)					
7.0053	83.44	7.0053	88.14	7.0053	98.00
10.0511	82.36	10.0511	86.86	10.0511	95.40
15.4116	80.40	15.4116	84.64	15.4116	92.46
17.7827	79.69	17.7827	84.07	17.7827	91.48
23.9146	78.40	19.9780	83.29	22.0166	90.14
25.6861	77.86	23.9146	82.50	23.9146	89.60
30.3562	76.88	25.6861	81.71	25.6861	89.07
35.4051	76.00	31.7298	80.19	31.7298	85.20
37.5412	75.56	34.2481	79.56	34.2481	84.60
41.2172	75.00	36.5012	79.07	36.5012	84.00
46.8393	74.31	42.0317	77.91	42.0317	82.50
50.9367	73.56	47.4204	76.97	48.5181	80.40
56.5093	72.88	49.5374	76.63	50.4864	80.00
61.7991	71.94	55.0415	75.71	56.2316	78.20
65.2936	71.50	60.3064	77.94	62.5189	76.00
CH ₃ COONa ($w_1 = 0.00$)					
7.0375	76.13	7.0375	83.50	7.0375	89.30
10.0972	74.97	10.0972	82.40	10.0972	85.70
15.4824	73.06	12.9020	81.07	15.4824	80.40
17.8643	72.75	17.8643	79.49	17.8643	78.60
24.0245	71.59	20.0698	78.93	20.0698	78.00
25.8040	71.31	24.0245	77.88	24.0245	75.40
31.8756	69.94	25.8040	77.32	25.8040	74.00
34.4054	69.47	31.8756	75.79	31.8756	71.40
36.6689	69.13	34.4054	75.29	34.4054	69.60
42.2248	68.25	36.6689	74.75	36.6689	69.20
47.6382	67.59	42.2248	73.71	42.2248	68.00
49.7649	67.32	47.6382	72.63	48.7410	64.30
55.9088	66.36	49.7649	71.94	50.7183	63.40
57.5629	66.36	55.2944	71.25	56.4899	62.00
62.5252	65.57	58.9807	70.44	59.8185	61.20
64.9263	65.30	60.0231	70.10	62.8061	61.20

Table 2 (Continued)

$c \times 10^4$ (mol dm ⁻³)	A (Scm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	A (Scm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	A (Scm ² mol ⁻¹)
NaSCN ($w_1 = 0.25$)					
8.6155	50.60	8.3564	74.90	8.2592	82.10
12.3613	49.30	11.9896	73.00	11.8501	78.60
21.8700	46.30	21.2123	70.00	20.9656	72.63
24.5700	44.60	23.8311	68.80	23.5540	70.70
27.0771	44.60	26.2629	68.30	25.9574	68.60
29.4114	43.30	30.6400	67.12	30.2837	66.40
33.6281	42.00	32.6168	66.00	34.0691	65.00
37.3336	41.60	36.2109	65.00	37.4092	64.00
42.1200	40.70	42.2335	63.60	43.0347	61.40
47.3850	39.00	47.0810	63.20	47.5886	60.00
49.6414	38.60	49.1665	61.80	49.5551	58.00
56.8620	36.90	56.5662	60.40	57.2025	56.12
59.6700	36.40	61.7823	58.67	61.5442	54.76
65.1544	35.60	63.1950	58.11	65.6146	53.80
72.2057	34.00	65.6571	57.50	71.1008	51.40
NaI ($w_1 = 0.25$)					
8.6155	50.60	8.2955	61.50	8.6155	67.40
12.3613	49.30	11.9022	59.00	12.3613	66.90
21.8700	46.30	21.0577	56.37	21.8700	64.60
24.5700	44.60	23.6574	55.50	24.5700	64.00
27.0771	44.60	26.0714	54.50	27.0771	62.90
29.4114	43.30	30.4167	54.00	29.4114	61.50
33.6281	42.00	34.2188	52.50	33.6281	61.10
37.3336	41.60	37.5735	53.00	39.0229	59.73
42.1200	40.70	43.2237	52.00	42.1200	59.28
47.3850	39.00	47.7976	52.00	47.3850	58.67
49.6414	38.60	49.7727	50.43	51.6927	58.21
56.8620	36.90	56.8160	50.69	56.8620	57.64
59.6700	36.40	62.2817	49.00	60.9236	56.80
65.1544	35.60	65.5458	48.00	68.4450	56.20
72.2057	34.00	72.0395	47.50	71.6554	55.60
CH₃COONa ($w_1 = 0.25$)					
8.1791	44.90	8.3118	53.60	8.1791	59.50
11.7352	43.50	11.9257	52.30	11.7352	59.00
20.7623	42.00	15.2383	49.71	20.7623	56.83
23.3256	41.70	21.0992	48.94	23.3256	56.16
25.7057	41.70	26.1229	48.40	25.7057	55.24
29.9900	40.90	30.4767	47.74	29.9900	55.02
33.7388	40.00	37.6476	47.40	33.7388	53.94
37.0465	40.00	45.7150	46.80	37.0465	54.00
42.6174	39.20	49.8709	46.40	42.6174	52.56
47.1271	38.40	52.5236	46.11	47.1271	52.50
50.8526	38.20	58.7764	45.69	49.0745	51.00
58.9459	37.10	68.5725	44.80	56.6478	50.30
63.5082	36.80	73.1440	44.66	60.9474	49.50
66.9008	36.30	78.3686	44.00	64.2643	49.79
71.6088	35.80	82.6000	43.52	71.6088	48.60
NaSCN ($w_1 = 0.50$)					
10.0164	35.13	10.2782	38.07	10.0164	43.93
14.3713	34.91	18.8433	37.47	14.3713	43.46
22.0360	34.66	22.6120	37.19	18.3633	43.00
25.4262	34.47	26.0908	36.96	22.0360	42.73
28.5652	34.39	35.0876	36.53	25.4262	42.56
31.4800	34.31	37.6867	36.35	31.4800	41.93
36.7267	34.15	42.3975	36.09	34.1938	41.80
41.3175	34.07	46.5541	35.93	36.7267	41.74
45.3682	33.94	50.2489	35.73	41.3175	41.44
48.9689	33.90	56.5300	35.47	45.3682	41.14
52.1905	33.80	63.9035	35.27	48.9689	40.97
55.0900	33.71	67.8360	35.13	55.0900	40.71
62.2757	33.63	71.1859	34.96	62.2757	40.30
69.3726	33.45	73.5600	33.85	66.1080	40.07
72.1869	33.39	75.6400	33.61	76.7921	39.73
NaI ($w_1 = 0.50$)					
10.0556	28.14	9.5582	33.90	10.0556	36.83
14.4276	27.99	13.7139	33.50	14.4276	36.06
18.4353	27.84	21.0280	33.10	18.4353	35.60
22.1223	27.76	24.2631	32.80	22.1223	35.14
25.5258	27.67	27.2585	32.67	25.5258	34.91
31.6033	27.50	35.0467	32.33	28.6771	34.60
34.3278	27.48	39.4275	32.13	34.3278	33.94
36.8706	27.40	43.2929	31.96	39.2493	33.49
41.4794	27.29	46.7289	31.76	41.4794	33.27

Table 2 (Continued)

$c \times 10^4$ (mol dm ⁻³)	Λ (S cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S cm ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	Λ (S cm ² mol ⁻¹)
45.5460	27.24	49.8032	31.64	45.5460	32.93
49.1608	27.15	56.2377	31.36	49.1608	32.73
55.3059	27.08	62.2257	31.13	55.3059	32.29
60.3337	27.02	67.5900	30.93	60.3337	31.90
64.5235	26.93	72.2838	30.80	68.0687	31.43
72.4697	26.79	73.5600	30.10	71.1075	31.34
CH₃COONa (w₁ = 0.50)					
9.8449	25.15	9.8082	27.99	9.8449	31.23
14.1253	24.83	14.0726	27.73	14.1253	30.67
18.0490	24.59	24.8977	27.35	18.0490	30.29
21.6588	24.39	27.9715	27.21	21.6588	30.00
24.9909	24.28	33.4831	27.00	24.9909	29.64
28.0762	24.08	35.9633	26.96	30.9411	29.30
30.9411	24.00	44.4253	26.68	33.6084	29.09
36.0979	23.80	47.9511	26.61	40.6102	28.63
44.5916	23.50	51.1058	26.55	44.5916	28.40
54.1469	23.20	57.7086	26.34	48.1306	28.20
59.0693	23.10	60.9813	26.30	51.2971	28.07
63.1714	22.95	66.3938	26.16	56.7253	27.85
66.6423	22.89	73.0868	26.00	59.0693	27.52
72.1959	22.72	74.6300	25.86	63.1714	27.31
73.5600	22.12	75.6200	24.98	73.3603	26.98
NaSCN (w₁ = 0.75)					
11.6059	16.91	11.6059	18.86	11.6059	20.71
16.6519	16.73	16.6519	18.73	16.6519	20.65
21.2774	16.63	21.2774	18.61	21.2774	20.60
25.5329	16.43	25.5329	18.54	25.5329	20.56
33.0982	16.25	33.0982	18.43	33.0982	20.50
36.4755	16.16	36.4755	18.38	36.4755	20.48
42.5548	16.04	42.5548	18.29	42.5548	20.44
47.8742	15.88	47.8742	18.23	47.8742	20.41
52.5677	15.86	52.5677	18.17	52.5677	20.37
56.7397	15.73	56.7397	18.12	56.7397	20.35
63.8322	15.59	63.8322	18.04	63.8322	20.31
69.6351	15.50	69.6351	17.98	69.6351	20.28
78.5627	15.38	78.5627	17.91	78.5627	20.23
82.0700	15.29	83.6422	17.86	83.6422	20.22
86.4823	15.19	87.7693	17.81	91.1889	20.17
NaI (w₁ = 0.50)					
11.6233	14.40	11.6233	16.01	11.6233	18.68
16.6769	14.30	16.6769	15.93	16.6769	18.59
21.3093	14.22	21.3093	15.90	21.3093	18.53
25.5712	14.12	25.5712	15.85	25.5712	18.45
29.5052	14.04	33.1479	15.80	33.1479	18.35
33.1479	13.97	36.5303	15.78	36.5303	18.34
36.5303	13.92	42.6187	15.75	42.6187	18.23
42.6187	13.87	47.9460	15.73	47.9460	18.18
47.9460	13.78	52.6466	15.69	52.6466	18.16
52.6466	13.72	56.8249	15.68	60.5634	18.10
56.8249	13.66	63.9280	15.66	63.9280	18.07
60.5634	13.62	74.5827	15.61	69.7396	18.02
69.7396	13.56	80.5019	15.59	74.5827	17.99
78.6806	13.47	85.2373	15.57	82.1931	17.93
83.7677	13.41	89.1118	15.56	91.3257	17.89
CH₃COONa (w₁ = 0.50)					
11.5835	11.79	11.5835	13.39	11.5835	16.23
16.6198	11.69	16.6198	13.22	16.6198	15.92
21.2365	11.57	21.2365	13.09	21.2365	15.69
25.4837	11.50	25.4837	13.02	25.4837	15.50
29.4043	11.43	29.4043	12.94	29.4043	15.34
36.4054	11.34	33.0345	12.87	33.0345	15.26
42.4729	11.23	36.4054	12.80	36.4054	15.08
47.7820	11.15	42.4729	12.71	42.4729	14.91
52.4665	11.10	47.7820	12.64	47.7820	14.78
56.6306	11.05	52.4665	12.58	52.4665	14.66
60.3562	11.00	60.3562	12.49	60.3562	14.46
66.7431	10.94	66.7431	12.39	66.7431	14.25
76.4512	10.83	76.4512	12.28	72.0193	14.16
81.9120	10.79	84.9458	12.17	78.4115	14.03
86.3159	10.71	88.8070	12.14	83.4812	13.90

of the methods and measurement techniques had been described elsewhere [10,11].

The conductance measurements were carried out in a Systronic 308 conductivity bridge (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10 having cell constant $0.1 \pm 10\%$. The cell was calibrated by the method of Lind et al. [12] using aqueous potassium chloride solutions.

3. Discussion

The solvent properties of ethane-1,2-diol + methyl alcohol mixtures are reported in Table 1, where ϵ is the dielectric constant, ρ the density of the solvent mixture and η the viscosity of the solvent mixture. The values of equivalent conductance (Λ) at various concentrations are presented in Table 2 and the conductance data have been analyzed using the Fuoss conductance equation [13,14]. For a given set of conductivity values (c_j , Λ_j , $j = 1, \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ°), the association constant (K_A), and the distance of closest approach of ions (R) are derived from the following set of equations:

$$\Lambda = P[\Lambda^\circ(1 + R\kappa) + E_L] \quad (1)$$

$$P = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c_j \gamma^2 f^2 \quad (3)$$

$$-\ln f = \frac{\beta \kappa}{2(1 + \kappa R)} \quad (4)$$

$$\beta = \frac{e^2}{Dk_B T} \quad (5)$$

$$K_A = \frac{K_R}{1 - \alpha} = \frac{K_R}{1 + K_S} \quad (6)$$

where the terms have their usual significance.

The computations were performed using a program suggested by Fuoss. The initial Λ° values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set (c_j , Λ_j , $j = 1, \dots, n$), n , D , η , T , initial values of Λ° , and an instruction to cover a preselected range of R values (Table 2).

In practice, calculations are performed by finding the values of Λ° and α which minimize the standard deviation:

$$\delta^2 = \sum \frac{[\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2}{n - 2} \quad (7)$$

for a sequence of R values and then plotting δ against R ; the best-fit R corresponds to the minimum of the δ - R versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increment to locate the minimum, but no significant minima were found in the δ - R curves for all the salts studied here; thus, R values are 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 is given by

$$d(\Lambda^\circ) = 1.183 \left(\frac{M}{\rho} \right)^{1/3} \quad (8)$$

where M is the molar mass of the solvent and ρ is its density. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by

$$M_{av} = \frac{M_1 M_2}{W_1 M_2 + W_2 M_1} \quad (9)$$

where W_1 is the mass fraction of the first component of molar mass M_1 . The values of Λ° , K_A and R obtained by this procedure are reported in Table 3.

A perusal of Table 3 reveals that the values of Λ° of all salts decreases as the concentration of ethane-1,2-diol in the solvent

Table 3
Derived conductivity parameters for sodium salts in ethane-1,2-diol (1) + methyl alcohol (2) mixtures at various temperatures.

Mass% (w_1) (ethane-1,2-diol)	T (K)	Λ° ($\text{S cm}^2 \text{ mol}^{-1}$)	K_A ($\text{dm}^3 \text{ mol}^{-1}$)	R (Å)	δ
NaSCN					
$w_1 = 0.00$	293.15	93.64	83.52	6.11	2.81
	298.15	108.17	52.07	6.12	0.13
	303.15	113.49	38.04	6.33	0.08
$w_1 = 0.25$	293.15	76.26	51.63	6.17	1.67
	298.15	82.90	35.63	6.17	0.66
	303.15	100.25	24.63	6.18	0.92
$w_1 = 0.50$	293.15	26.14	22.42	6.42	0.03
	298.15	39.65	18.89	6.47	0.04
	303.15	45.74	12.79	6.38	0.05
$w_1 = 0.75$	293.15	17.66	10.53	6.58	0.03
	298.15	19.41	6.73	6.59	0.01
	303.15	21.36	4.32	6.61	0.01
NaI					
$w_1 = 0.00$	293.15	94.55	65.54	6.16	2.69
	298.15	97.41	49.31	6.17	0.86
	303.15	106.86	28.48	6.18	0.78
$w_1 = 0.25$	293.15	60.03	43.65	6.22	0.67
	298.15	65.64	34.08	6.22	0.60
	303.15	72.85	21.63	6.23	0.45
$w_1 = 0.50$	293.15	28.97	31.65	6.51	0.01
	298.15	35.25	21.04	6.57	0.04
	303.15	39.21	12.23	6.53	0.06
$w_1 = 0.75$	293.15	14.90	16.82	6.53	0.02
	298.15	16.38	14.68	6.84	0.01
	303.15	19.21	10.48	6.65	0.02
CH₃COONa					
$w_1 = 0.00$	293.15	79.80	44.95	6.24	0.15
	298.15	88.58	32.52	6.25	0.13
	303.15	102.74	25.09	6.26	0.49
$w_1 = 0.25$	293.15	48.14	36.81	6.31	0.27
	298.15	56.35	28.17	6.32	0.31
	303.15	64.31	21.63	6.33	0.42
$w_1 = 0.50$	293.15	26.74	33.46	6.39	0.52
	298.15	28.99	22.87	6.60	0.04
	303.15	32.97	17.68	6.61	0.08
$w_1 = 0.75$	293.15	12.27	17.82	6.71	0.01
	298.15	13.88	17.41	6.72	0.01
	303.15	17.14	12.53	6.73	0.03

Table 4
Values of activation energy (E) and Walden products ($\Lambda^\circ \eta$) of sodium salts in ethane-1,2-diol (1) + methyl alcohol (2) mixtures at various temperatures.

Mass% (w_1) (ethane-1,2-diol)	E (kJ mol^{-1})	$\Lambda^\circ \eta$ ($\times 10^3 \text{ S cm}^2 \text{ mol}^{-1} \text{ Pa s}$)		
		293.15 K	298.15 K	303.15 K
NaSCN				
$w_1 = 0.00$	14.24	54.44	58.80	58.01
$w_2 = 0.25$	20.16	85.93	85.35	94.78
$w_3 = 0.50$	41.46	59.32	81.09	82.79
$w_4 = 0.75$	14.05	102.42	95.19	90.39
NaI				
$w_1 = 0.00$	9.02	54.97	52.95	54.63
$w_2 = 0.25$	14.3	67.64	67.58	68.87
$w_3 = 0.50$	22.4	65.74	72.09	70.97
$w_4 = 0.75$	18.74	86.42	80.33	81.29
CH₃COONa				
$w_1 = 0.00$	18.65	46.40	48.15	52.52
$w_2 = 0.25$	21.41	54.24	58.01	60.80
$w_3 = 0.50$	15.46	60.68	59.29	59.68
$w_4 = 0.75$	24.66	71.16	68.07	72.54

mixture increases. But as the temperature increases, Λ° values increase for all of ethane-1,2-diol+methyl alcohol mixtures. The trend in Λ° can be discussed through another characteristic function called the Walden product, $\Lambda^\circ\eta$. From Tables 3 and 4 it is seen that although Λ° decreases as the concentration of ethane 1, 2-diol increases, the Walden product $\Lambda^\circ\eta$ increases with increasing concentration of ethane 1, 2-diol for most of the solvent mixtures, which can be attributed to the increase in viscosity (η) with increasing concentration of ethane 1, 2-diol suggesting the predominance of η over Λ° . Changes in Walden product with concentration are common and they can be attributed to changes in ion-solvation and ion-solvent interaction.

From Table 3, we see that Λ° of sodium salts of common cations follows the sequence $\text{SCN}^- > \text{I}^- > \text{CH}_3\text{COO}^-$. Furthermore, Λ° of the studied electrolyte is enhanced in the following order: $\text{NaSCN} > \text{NaI} > \text{CH}_3\text{COONa}$. It is evident from the crystallographic radii of these ions the acetate ion (CH_3COO^-) due to its small size is most solvated while iodide ion (I^-) and thiocyanate ion (SCN^-) have preferentially larger crystallographic radii and thus shows less tendency towards solvation.

Table 5
Thermodynamic functions for association of sodium salts in ethane-1,2-diol (1)+methyl alcohol (2) mixtures at various temperatures.

Mass%(w_1) (ethane-1,2-diol)	T(K)	$-\Delta H^\circ$ (kJ mol $^{-1}$)	$-\Delta G^\circ$ (kJ mol $^{-1}$)	$-\Delta S^\circ$ (JK $^{-1}$ mol $^{-1}$)
NaSCN				
$w_1 = 0.00$	293.15	58.18	10.79	161.66
	298.15		9.80	162.27
	303.15		9.17	161.67
$w_1 = 0.25$	293.15	54.9	9.61	154.49
	298.15		8.86	154.42
	303.15		8.07	154.48
$w_1 = 0.50$	293.15	41.39	7.58	115.33
	298.15		7.28	114.41
	303.15		6.42	115.36
$w_1 = 0.75$	293.15	35.83	5.74	102.64
	298.15		4.74	104.28
	303.15		3.69	106.02
NaI				
$w_1 = 0.00$	298.15	61.48	10.19	174.96
	303.15		9.66	173.81
	303.15		8.44	174.96
$w_1 = 0.25$	293.15	51.8	9.20	185.16
	298.15		8.75	183.57
	303.15		7.75	183.84
$w_1 = 0.50$	293.15	40.2	8.42	108.41
	298.15		7.55	109.51
	303.15		6.31	111.79
$w_1 = 0.75$	293.15	25.1	6.88	62.15
	298.15		6.66	61.85
	303.15		6.26	62.15
CH₃COONa				
$w_1 = 0.00$	293.15	43.11	9.28	115.40
	298.15		8.63	115.65
	303.15		8.12	115.42
$w_1 = 0.25$	293.15	39.29	8.79	104.04
	298.15		8.27	104.04
	303.15		7.75	104.04
$w_1 = 0.50$	293.15	31.19	8.56	77.20
	298.15		7.76	78.58
	303.15		7.24	79.00
$w_1 = 0.75$	293.15	25.9	7.02	64.40
	298.15		7.08	63.12
	303.15		6.35	64.49

There are marked characteristic behaviors in the K_A values. K_A values generally decreases as the temperature is increased; the thermal motion probably destroys the solvent structure. However, K_A of all salts decreases as the concentration of ethane-1,2-diol increases in the mixture.

As the conductance of an ion depends on the rate of movement, it seems reasonable to treat the conductance in a manner analogous to that employed for other processes taking place at a definite rate which increases with temperature. On this basis it would be possible to write:

$$\Lambda^\circ = \Lambda e^{-E/RT}$$

$$\ln \Lambda^\circ = \ln \frac{A-E}{RT} \tag{10}$$

where A is the frequency factor, R is the universal gas constant, and E is the Arrhenius activation energy of transport processes.

From the plot of $\log \Lambda^\circ$ versus $1/T$ for the sodium salts for all solvent mixtures, E values have been computed from the slope [15] and are recorded in Table 4.

The Gibbs energy change (ΔG°) for association is calculated from the relation [16]:

$$\Delta G^\circ = -RT \ln K_A \tag{11}$$

The enthalpy of association (ΔH°) is obtained by studying the association constant (K_A) over a range of temperature by means of Van't Hoff's isochore, where $\log K_A$ values are plotted against $1/T$ giving a straight line with slope $-\Delta H^\circ/R$. The negative ΔH° values obtained are found to decrease systematically with the concentration of ethane-1,2-diol in the mixture.

The entropy change (ΔS°) is calculated from the Gibb's-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{12}$$

The values of these thermodynamic functions are given in Table 5.

If we consider that from a rudimentary standpoint the ion pair is formed with only the action of the Columbic force in a continuum medium, the values of ΔH° and ΔS° of the ion-pair formation will be negative. Therefore, all the experimental values of ΔH° and ΔS° are negative for all the sodium salts studied here. The negative sign of ΔH° means that the association process is exothermic.

List of symbols

- ϵ dielectric constant
- ρ density
- η viscosity
- C concentration
- Λ° limiting molar conductivity
- K_A association constant
- R_X relaxation field effect
- E_L electrophoretic counter current constant
- γ fraction of solute present as unpaired ion
- f activity coefficient
- β twice the Bjerrum distance
- κ radius of ionic atmosphere
- e electric charge
- K_B Boltzmann constant
- R distance of closest approach of ions
- A frequency factor
- R universal gas constant
- E Arrhenius activation energy
- ΔG° Gibbs energy change
- ΔH° enthalpy of association
- ΔS° entropy change

Subscript

- av average

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2007, SAP-1) for financial support.

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Viscous synergy and antagonism, excess molar volume, isentropic compressibility and excess molar refraction of ternary mixtures containing tetrahydrofuran, methanol and six membered cyclic compounds at 298.15 K

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(Received 18 May 2009; final version received 27 June 2009)

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The densities (ρ), viscosities (η), sound speeds (u) and refractive indices (n_D) of seven ternary mixtures of cyclic ether (tetrahydrofuran), methanol and cyclic compounds; benzene, toluene, chlorobenzene, nitrobenzene, anisole, cyclohexane and cyclohexanone are determined over the entire range of composition at 298.15 K. From the experimental observations, viscosity deviation ($\Delta\eta$), the viscous synergy and antagonism, synergic and antagonistic index are derived by the equations developed by Kalentunc-Gencer and Peleg [J. Texture Stud. 17, 61 (1986)] and Howell [Proceedings of the Seventh International Conference, Wales, 1993], respectively. Excess molar volume (V^E), excess isentropic compressibility (ΔK_S) and excess molar refraction (ΔR) have been calculated from the experimentally measured density, sound speed and refractive index values. The excess Gibb's free energy of activation (ΔG^E) has also been calculated. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

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Keywords: viscous synergy and antagonism; viscosity deviations; excess molar volumes; isentropic compressibilities; excess molar refraction

25

1. Introduction

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Grouping of solvents into classes is often based on the nature of the inter-molecular forces, because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. Because of the close connection between liquid structure and macroscopic properties, determination of density, viscosity and ultrasonic speeds is a valuable tool to learn the liquid state [1,2].

35

Rheology is the field of physics that studies material deformation and flow, and is increasingly applied to analyse the viscous behaviour of many pharmaceutical products, [3–12] and to establish their stability and even bioavailability; since it has been firmly established that viscosity influences the drug absorption rate in the body [13,14].

The increasing use of the solvents tetrahydrofuran, methanol and their mixtures in benzene and benzene derivatives in industrial processes such as battery.

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pharmaceutical and cosmetics have greatly stimulated the need for extensive
40 information on their various 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 [15,16].

The present work contributes to the study of viscosity deviations, viscous
45 antagonism, excess molar volumes, isentropic compressibility, excess molar refraction
and excess Gibb's free energy of activation in ternary solutions of
tetrahydrofuran (A) + methanol (B) + benzene, toluene, chlorobenzene, nitrobenzene,
anisole, cyclohexane, cyclohexanone (C).

2. Experimental

2.1. Source and purity of samples

Tetrahydrofuran (T.H.F), methanol MeOH, benzene, toluene, chlorobenzene,
nitrobenzene, anisole, cyclohexane and cyclohexanone were obtained from Merck
and LR. These were further purified by standard methods [17]. The purity of the
liquids was checked by measuring their densities, viscosities, refractive indices and
55 sound velocities at 298.15 K which was quite in agreement with the literature values
as represented in Table 1.

2.2. Measurements

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a
bulb volume of about 25 cm³ and an internal diameter of the capillary of about
60 0.1 cm. The measurements were done in a thermostat bath controlled to ± 0.01 K.
Viscosity (η) was measured by means of suspended Ubbelohde type viscometer,
calibrated at 298.15 K with triply distilled water and purified methanol using density
and viscosity values from literature. The flow times were accurate to ± 0.1 s, and the
uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4}$ mPas. The mixtures were

Table 1. Density (ρ), viscosity (η), sound speed (u) and refractive index (n_D) of pure liquids at 298.15 K.

Pure components	$\rho \times 10^{-3}$ (kg m ⁻³)		η (mPas)		u (ms ⁻¹)		n_D	
	This work	Lit	This work	Lit	This work	Lit	This work	Lit
Tetrahydrofuran	0.8821	0.8819[39]	0.461	0.460[39]	1287.2	1228[39]	1.4050	1.4050[39]
Methanol	0.7865	0.7866[40]	0.544	0.545[40]	1104.1	1103[40]	1.3264	1.3264[40]
Benzene	0.8765	0.8728[41]	0.599	0.552[41]	1302.6	1301[41]	1.4970	1.4982[41]
Toluene	0.8645	0.8662[42]	0.579	0.552[42]	1303.8	1304[43]	1.4925	1.4930[43]
Chlorobenzene	1.1056	1.1010[44]	0.787	0.773[44]	1270.6	1271[44]	1.5220	1.5223[44]
Nitrobenzene	1.1985	1.1983[45]	1.686	1.686[45]	1642.8	1648[45]	1.5490	1.5493[45]
Anisole	0.9946	0.9893[46]	0.995	0.991[46]	1418.4	1418[46]	1.5140	1.5143[46]
Cyclohexane	0.7773	0.7740[47]	0.886	0.883[47]	1254.6	1254[47]	1.4240	1.4235[47]
Cyclohexanone	0.9462	0.9452[46]	1.965	1.963[46]	1415.2	1417[46]	1.4465	1.4500[46]

65 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 minimise evaporation losses
70 during the actual measurements. The reproducibility in mole fractions was within
 ± 0.0002 . The mass measurements were done on a Mettler AG-285 electronic balance
with a precision of ± 0.01 mg. The precision of density measurements was
 $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$.

75 Ultrasonic speeds of sound (u) were determined by a multifrequency ultrasonic
interferometer (Mittal enterprise, New Delhi 9, M-81) working at 1 MHz, calibrated
with triply distilled and purified water, methanol and benzene at 303.15 K. The
precision of ultrasonic speed measurements was $\pm 0.2 \text{ ms}^{-1}$. The details of the
methods and techniques have been described in earlier papers [18-21]. Refractive
index was measured with the help of Abbe-Refractometer (USA). The accuracy of
80 refractive index measurement was ± 0.0002 units. The refractometer was calibrated
twice using distilled and deionised water, and calibration was checked after every few
measurements.

3. Results and discussions

The comparison of the experimentally determined densities, viscosities, sound speeds
and refractive indices of the pure components at 298.15 K with the literature values
85 has been presented in Table 1.

3.1. Viscosity deviations

In Table 2, the calculated and experimentally determined viscosities of the ternary
mixtures are shown along with the mole fraction of tetrahydrofuran (x_A) and
methanol (x_B) at 298.15 K. Viscosity deviation ($\Delta\eta$), synergic (I_S) and antagonic
90 index (I_A) values are presented together in Table 2.

The viscosity deviations ($\Delta\eta$) [22] from linear dependence for ternary mixtures
can be calculated as

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

where, η is the viscosity of the mixture and x_i , η_i are the mole fraction and viscosity
of pure component i respectively.

95 The $\Delta\eta$ values are plotted against mole fraction of component (C) and are
depicted graphically in Figure 1. The $\Delta\eta$ values are negative for the ternary
mixture of T.H.F + MeOH + (cyclohexane, cyclohexanone and nitrobenzene) over
the entire range of composition suggesting dispersion and dipolar interaction
between molecules whereas the values are positive for the ternary mixtures of
100 tetrahydrofuran + methanol + (benzene, anisole, toluene and chlorobenzene) which
suggests hydrogen bonding interactions leading to the formation of complex
species between molecules.

Table 2. Experimental (ρ_{exp} , η_{exp}) and calculated (ρ_{cal} , η_{cal}) density and viscosity, excess molar volume (V^E), viscosity deviation ($\Delta\eta$) and synergic index (I_S) for the ternary mixture of tetrahydrofuran (A) + methanol (B) + benzene derivatives (C) at 298.15 K.

x_A	x_B	$\rho_{\text{exp}} \times 10^{-3} \text{ (kg m}^{-3}\text{)}$	$\rho_{\text{cal}} \times 10^{-3} \text{ (kg m}^{-3}\text{)}$	$V^E \times 10^6 \text{ (m}^3 \text{mol}^{-1}\text{)}$	$\eta_{\text{exp}} \text{ (mPas)}$	$\eta_{\text{cal}} \text{ (mPas)}$	$\Delta\eta \text{ (mPas)}$	I_S
(A) Tetrahydrofuran + (B) methanol + (C) benzene								
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5025	0.5185	-0.0160	-0.0309
0.2982	0.6712	0.8398	0.8178	-0.3890	0.5153	0.5210	-0.0057	-0.0109
0.2872	0.6465	0.8426	0.8199	-0.4232	0.5256	0.5238	0.0018	0.0034
0.2743	0.6172	0.8455	0.8225	-0.4360	0.5332	0.5272	0.0060	0.0114
0.2587	0.5821	0.8484	0.8256	-0.4362	0.5428	0.5313	0.0115	0.0216
0.2396	0.5392	0.8518	0.8293	-0.4340	0.5523	0.5363	0.0160	0.0298
0.2157	0.4855	0.8554	0.8340	-0.4101	0.5606	0.5426	0.0180	0.0332
0.1850	0.4164	0.8596	0.8401	-0.3879	0.5677	0.5506	0.0171	0.0311
0.1440	0.3241	0.8642	0.8481	-0.3195	0.5758	0.5613	0.0145	0.0258
0.0865	0.1947	0.8695	0.8595	-0.2004	0.5834	0.5764	0.0070	0.0121
0.0000	0.0000	0.8756	0.8765	0.0000	0.5990	0.5990	0.0000	0.0000
(A) Tetrahydrofuran + (B) methanol + (C) toluene								
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328
0.2996	0.6743	0.8391	0.8172	-0.3846	0.5154	0.5201	-0.0047	-0.0090
0.2902	0.6531	0.8412	0.8187	-0.4072	0.5238	0.5220	0.0018	0.0035
0.2789	0.6276	0.8435	0.8205	-0.4360	0.5320	0.5242	0.0078	0.0149
0.2651	0.5966	0.8459	0.8226	-0.4530	0.5390	0.5270	0.0121	0.0229
0.2479	0.5580	0.8484	0.8253	-0.4580	0.5495	0.5304	0.0191	0.0360
0.2260	0.5087	0.8512	0.8288	-0.4598	0.5569	0.5347	0.0222	0.0415
0.1970	0.4433	0.8543	0.8334	-0.4530	0.5630	0.5405	0.0226	0.0417
0.1567	0.3527	0.8577	0.8397	-0.4149	0.5673	0.5485	0.0188	0.0343
0.0971	0.2186	0.8610	0.8492	-0.2750	0.5697	0.5603	0.0094	0.0168
0.0000	0.0000	0.8645	0.8645	0.0000	0.5796	0.5796	0.0000	0.0000
(A) Tetrahydrofuran + (B) methanol + (C) chlorobenzene								
0.3076	0.6924	0.8373	0.8159	-0.3700	0.5015	0.5185	-0.0170	-0.0329
0.3010	0.6775	0.8503	0.8221	-0.4980	0.5167	0.5243	-0.0075	-0.0144
0.2932	0.6599	0.8649	0.8295	-0.6320	0.5304	0.5311	-0.0007	-0.0014
0.2837	0.6384	0.8806	0.8385	-0.7150	0.5506	0.5394	0.0111	0.0206

0.2719	0.6120	0.8984	0.8496	-0.7820	0.5752	0.5497	0.0255	0.0464	
0.2570	0.5784	0.9190	0.8636	-0.8400	0.5991	0.5628	0.0363	0.0645	
0.2374	0.5344	0.9434	0.8820	-0.8880	0.6292	0.5798	0.0493	0.0851	
0.2107	0.4743	0.9719	0.9072	-0.8650	0.6615	0.6032	0.0583	0.0967	
0.1720	0.3872	1.0065	0.9436	-0.7650	0.6979	0.6370	0.0609	0.0957	
0.1109	0.2496	1.0489	1.0012	-0.4670	0.7349	0.6904	0.0445	0.0645	
0.0000	0.0000	1.1056	1.1056	0.0000	0.7873	0.7873	0.0000	0.0000	
(A) Tetrahydrofuran + (B) methanol + (C) nitrobenzene									
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328	
0.3016	0.6788	0.8513	0.8234	-0.3906	0.5234	0.5414	-0.0180	-0.0332	
0.2944	0.6625	0.8679	0.8324	-0.4520	0.5504	0.5688	-0.0184	-0.0323	
0.2856	0.6427	0.8869	0.8433	-0.5050	0.5834	0.6022	-0.0188	-0.0312	
0.2746	0.6181	0.9093	0.8569	-0.5673	0.6240	0.6437	0.0197	0.0306	
0.2607	0.5867	0.9357	0.8743	-0.6270	0.6765	0.6967	0.0202	0.0290	
0.2422	0.5450	0.9678	0.8973	-0.7026	0.7449	0.7669	0.0220	0.0287	
0.2166	0.4874	1.0076	0.9292	-0.8000	0.8404	0.8640	-0.0236	-0.0273	
0.1788	0.4024	1.0564	0.9762	-0.8078	0.9817	1.0074	-0.0257	-0.0255	
0.1173	0.2641	1.1176	1.0526	-0.6100	1.2188	1.2405	-0.0217	-0.0175	
0.0000	0.0000	1.1985	1.1985	0.0000	1.6857	1.6857	0.0000	0.0000	
(A) Tetrahydrofuran + (B) MeOH + (C) anisole									
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328	
0.3008	0.6769	0.8448	0.8199	-0.3880	0.5151	0.5291	-0.0140	-0.0265	
0.2926	0.6586	0.8532	0.8246	-0.4060	0.5353	0.5417	-0.0064	-0.0118	
0.2828	0.6364	0.8628	0.8303	-0.4333	0.5602	0.5570	0.0032	0.0057	
0.2706	0.6091	0.8739	0.8374	-0.4700	0.5843	0.5758	0.0084	0.0147	
0.2553	0.5745	0.8865	0.8463	-0.4880	0.6145	0.5996	0.0149	0.0249	
0.2352	0.5295	0.9016	0.8580	-0.5330	0.6490	0.6306	0.0184	0.0292	
0.2080	0.4682	0.9192	0.8738	-0.5570	0.6948	0.6728	0.0220	0.0327	
0.1690	0.3803	0.9402	0.8964	-0.5570	0.7536	0.7333	0.0203	0.0277	
0.1081	0.2433	0.9650	0.9318	-0.4320	0.8387	0.8276	0.0111	0.0135	
0.0000	0.0000	0.9946	0.9946	-0.0100	0.9950	0.9950	0.0000	0.0000	
(A) Tetrahydrofuran + (B) MeOH + (C) cyclohexanone									
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5015	0.5185	-0.0170	-0.0328	
0.3001	0.6754	0.8430	0.8191	-0.3940	0.5220	0.5539	-0.0320	-0.0577	

(Continued)

Table 2. Continued.

x_A	x_B	$\rho_{\text{exp}} \times 10^{-3} \text{ (kg m}^{-3}\text{)}$	$\rho_{\text{cal}} \times 10^{-3} \text{ (kg m}^{-3}\text{)}$	$V^E \times 10^6 \text{ (m}^3 \text{ mol}^{-1}\text{)}$	$\eta_{\text{exp}} \text{ (mPas)}$	$\eta_{\text{cal}} \text{ (mPas)}$	$\Delta\eta \text{ (mPas)}$	I_S
0.2912	0.6553	0.8495	0.8229	-0.4330	0.5413	0.5959	-0.0545	-0.0915
0.2805	0.6312	0.8569	0.8274	-0.4849	0.5661	0.6462	-0.0801	-0.1240
0.2673	0.6017	0.8651	0.8330	-0.5220	0.6023	0.7079	-0.1056	-0.1492
0.2509	0.5647	0.8743	0.8399	-0.5539	0.6510	0.7852	-0.1342	-0.1709
0.2297	0.5171	0.8848	0.8489	-0.5730	0.7126	0.8847	-0.1722	-0.1946
0.2014	0.4533	0.8968	0.8609	-0.5690	0.8117	1.0180	-0.2062	-0.2026
0.1616	0.3636	0.9106	0.8778	-0.5062	0.9670	1.2053	-0.2383	-0.1977
0.1014	0.2282	0.9266	0.9033	-0.3273	1.2380	1.4883	-0.2503	-0.1570
0.0000	0.0000	0.9462	0.9462	0.0000	1.9650	1.9650	0.0000	0.0000
(A) Tetrahydrofuran + (B) MeOH + (C) cyclohexane								
0.3076	0.6924	0.8373	0.8159	-0.3671	0.5150	0.5185	-0.0035	-0.0068
0.2989	0.6727	0.8324	0.8148	-0.3502	0.5203	0.5290	-0.0087	-0.0164
0.2886	0.6496	0.8256	0.8135	-0.2070	0.5268	0.5412	-0.0144	-0.0266
0.2764	0.6221	0.8189	0.8120	-0.0705	0.5332	0.5558	-0.0226	-0.0407
0.2617	0.5889	0.8122	0.8101	0.0619	0.5429	0.5734	-0.0305	-0.0532
0.2435	0.5479	0.8062	0.8079	0.1429	0.5610	0.5952	-0.0342	-0.0574
0.2205	0.4962	0.7989	0.8050	0.3478	0.5820	0.6226	-0.0406	-0.0652
0.1905	0.4287	0.7934	0.8012	0.3728	0.6149	0.6585	-0.0436	-0.0662
0.1497	0.3370	0.7869	0.7961	0.4796	0.6631	0.7071	-0.0440	-0.0622
0.0912	0.2053	0.7825	0.7887	0.2560	0.7428	0.7770	-0.0342	-0.0440
0.0000	0.0000	0.7773	0.7773	0.0000	0.8860	0.8860	0.0000	0.0000

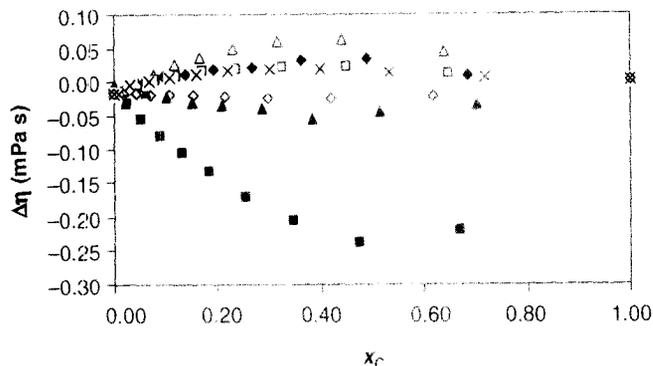


Figure 1. Plot of viscosity deviation $\Delta\eta$ (mPa s) vs. x_C for the ternary mixtures at 298.15 K. (\times), T.H.F (A)+MeOH (B)+ Benzene (C); (\blacklozenge), T.H.F (A)+ MeOH (B)+ Toluene (C); (Δ), T.H.F (A)+ MeOH (B)+ Chlorobenzene (C); (\diamond), T.H.F (A)+ MeOH (B)+ Nitrobenzene (C); (\square), T.H.F (A)+ MeOH (B)+ Anisole (C); (\blacksquare), T.H.F (A)+ MeOH (B)+ Cyclohexanone (C); (\blacktriangle), T.H.F (A)+ MeOH (B)+ Cyclohexane (C).

150 **3.2. Viscous synergy and antagonism**

The method most widely used to analyse the synergic and antagonic behaviour of the ternary liquid mixtures and which is used here is the one developed by Kalentunc-Gencer and Peleg [23], allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp} , with the viscosity expected in the absence of interaction, η_{calc} defined by the simple mixing rule as

$$\eta_{calc} = x_A\eta_A + x_B\eta_B + x_C\eta_C \quad (2)$$

where x_A , x_B , x_C are the mole fraction of the systems A, B, C, and η_A , η_B , η_C are the viscosities, measured experimentally, of the systems A, B, C, respectively.

160 The result for η_{calc} and η_{exp} has been presented in Table 2 and is depicted graphically against mole fraction of component (C) in Figures 2 and 3, respectively. In order to secure more comparable viscous synergy result, the so called synergic interaction index (I_S) introduced by Howell [24] is taken into account:

$$I_S = (\eta_{exp} - \eta_{calc})/\eta_{calc} = \Delta\eta/\eta_{calc} \quad (3)$$

165 The negative values of I_S gives antagonic interaction (I_A). Table 2 gives the data for the I_S and I_A of the mixtures which has been graphically compared in Figure 4.

If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction [25,26]. Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. Accordingly, when $\eta_{exp} > \eta_{calc}$, viscous synergy exists, while, when $\eta_{calc} > \eta_{exp}$, the system is said to

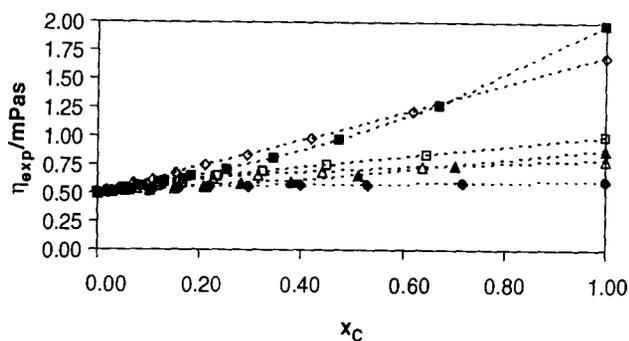


Figure 2. Plot of η_{exp} vs. (x_c) for the ternary mixtures at 298.15 K. (\times), T.H.F (A) + MeOH (B) + Benzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Toluene (C); (\triangle), T.H.F (A) + MeOH (B) + Chlorobenzene (C); (\diamond), T.H.F (A) + MeOH (B) + Nitrobenzene (C); (\square), T.H.F (A) + MeOH (B) + Anisole (C); (\blacksquare), T.H.F (A) + MeOH (B) + Cyclohexanone (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Cyclohexane (C).

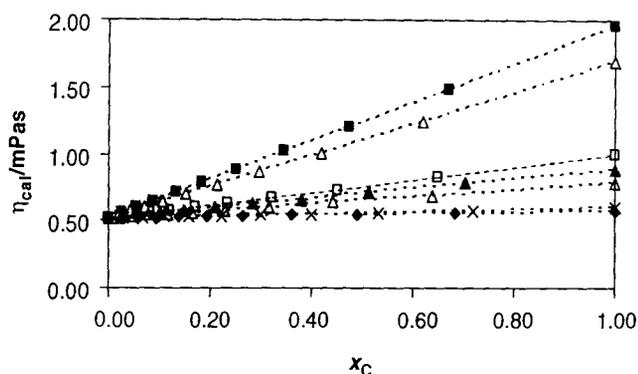


Figure 3. Plot of η_{cal} vs. (x_c) for the ternary mixtures at 298.15 K. (\times), T.H.F (A) + MeOH (B) + Benzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Toluene (C); (\triangle), T.H.F (A) + MeOH (B) + Chlorobenzene (C); (\diamond), T.H.F (A) + MeOH (B) + Nitrobenzene (C); (\square), T.H.F (A) + MeOH (B) + Anisole (C); (\blacksquare), T.H.F (A) + MeOH (B) + Cyclohexanone (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Cyclohexane (C).

175 exhibit viscous antagonism. This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other synergy indices are defined in consequence [27].

A perusal of Table 2 shows that for the ternary mixture of tetrahydrofuran (A) + methanol (B) + (cyclohexane, cyclohexanone, nitrobenzene) (C), the experimentally determined viscosities, η_{exp} are lower than those of its calculated values, η_{cal} which demonstrates viscous antagonism in the three mixtures studied here. The explanation of this behaviour is based on the known phenomenon of molecular dissociation; as a consequence of weakening the non-covalent bondings formed between the molecules produced a decrease in size of the molecular package which logically implies an increase in I_A [28].

185 On the other hand, for the ternary mixtures of tetrahydrofuran (A) + methanol (B) + (benzene, toluene, chlorobenzene, anisole) (C), the experimentally determined

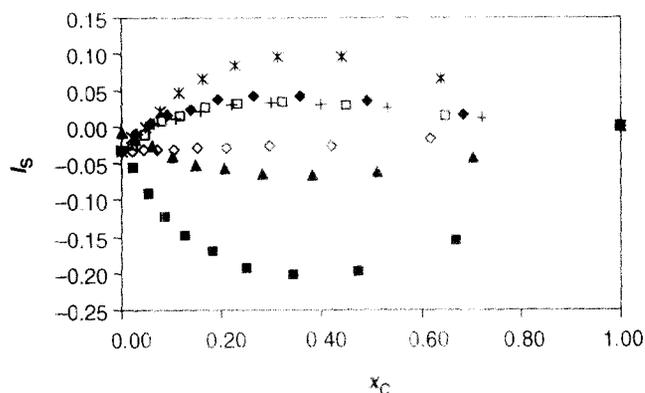


Figure 4. Plot of I_S vs. x_C for the ternary mixtures at 298.15 K. (x), T.H.F (A)+MeOH (B)+ Benzene (C); (◆), T.H.F (A)+MeOH (B)+Toluene (C); (Δ), T.H.F (A)+MeOH (B)+ Chlorobenzene (C); (◇), T.H.F (A)+MeOH (B)+ Nitrobenzene (C); (□), T.H.F (A)+MeOH (B)+ Anisole (C); (■), T.H.F (A)+MeOH (B)+ Cyclohexanone (C); (▲), T.H.F (A)+MeOH (B)+ Cyclohexane (C).

viscosities, η_{exp} are higher than those of its calculated values, η_{cal} which demonstrates viscous synergy in the four mixtures studied here. The explanation of this type of behaviour is based on the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture produced increase in size of the resulting molecular package, which logically implies a rise in viscosity.

3.3. Excess molar volume

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

$$\rho_{calc} = x_A \rho_A + x_B \rho_B + x_C \rho_C \quad (4)$$

where x_A , x_B , x_C are the mole fraction of the systems A, B, C, and ρ_A , ρ_B , ρ_C are the densities, measured experimentally, of the systems A, B, C, respectively.

The experimentally determined density value along with the derived parameter, V^E , which is the excess molar volume, is listed in Table 2. The excess molar volumes, V^E , are calculated from density data according to the following equation [29]:

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

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

Figure 5 represents the V^E values for the seven ternary mixtures under examination. In general, V^E is found to be negative throughout for all the ternary mixtures except for tetrahydrofuran + methanol + cyclohexane. However, the values

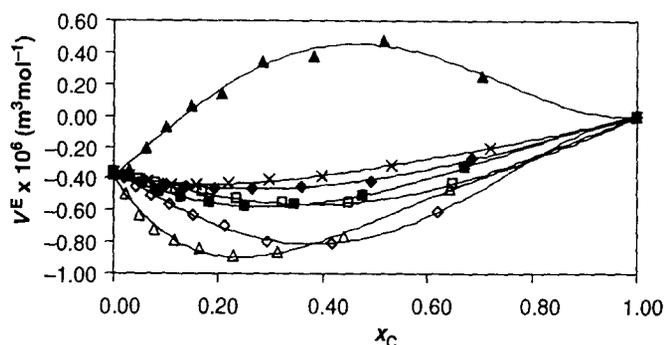


Figure 5. Plot of excess molar volume $V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$ vs. x_C for the ternary mixtures at 298.15 K. (\times), T.H.F (A) + MeOH (B) + Benzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Toluene (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Chlorobenzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Nitrobenzene (C); (\square), T.H.F (A) + MeOH (B) + Anisole (C); (\blacksquare), T.H.F (A) + MeOH (B) + Cyclohexanone (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Cyclohexane (C).

at first decrease to minima and then they increase with increasing x_C . 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 [30]:
 210 (1) dipolar interaction, (2) interstitial accommodation of one component into the other and (3) possible hydrogen bonded interactions between unlike molecules. The actual volume change would, therefore, depend on the relative strength of these three effects.

215 3.4. Isentropic compressibility

Isentropic compressibility, K_S and deviation in isentropic compressibility ΔK_S , for the ternary mixtures were calculated using the following relations:

$$K_S = (\mu^2 \rho)^{-1} \quad (6)$$

$$\Delta K_S = K_S - \sum_{i=1}^3 K_{Si} \quad (7)$$

where u and K_S are the speed of sound and isentropic compressibility of the mixture and K_{Si} , the isentropic compressibility of the i th component in the mixture respectively. The experimental speed of sound, isentropic compressibility and deviation in isentropic compressibility are listed in Table 3 and are graphically represented in Figure 6 as functions of mole fraction of the cyclic compounds. From Table 3, it is evident that except for the ternary mixture of tetrahydrofuran + methanol + cyclohexane, the deviation in isentropic compressibility ΔK_S are negative for all the ternary mixtures of tetrahydrofuran + methanol + (benzene, toluene, chlorobenzene, nitrobenzene, anisole, cyclohexanone). 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,
 225 (ii) the formation of weak bonds by dipole-induced dipole interaction between unlike molecules and (iii) geometrical fitting of component molecules into each
 230

Table 3. Sound speed (u), isoentropic compressibility (K_S), excess isoentropic compressibility (K_S^E), refractive index (n_D), molar refraction (ΔR) and excess Gibbs free energy of activation of viscous flow (ΔG^*E) for the ternary mixture of tetrahydrofuran (A) + methanol (B) + benzene derivatives (C) at 298.15 K.

x_A	x_B	u (ms ⁻¹)	$K_S \times 10^{12}$ (Pa ⁻¹)	$\Delta K_S \times 10^{12}$ (Pa ⁻¹)	n_D	$\Delta R \times 10^{-6}$ (m ³ mol ⁻¹)	$\Delta G^E \times 10^{-3}$ (J mol ⁻¹)
(A) Tetrahydrofuran + (B) methanol + (C) benzene							
0.3076	0.6924	1162.4	883.9	2.8	1.3625	-0.0948	-581.13
0.2982	0.6712	1174.6	863.1	-11.6	1.3694	-0.0880	-504.22
0.2872	0.6465	1181.5	850.1	-17.1	1.3770	-0.0848	-439.23
0.2743	0.6172	1195.2	828.0	-30.4	1.3855	-0.0790	-385.64
0.2587	0.5821	1206.1	810.2	-37.5	1.3952	-0.0675	-321.52
0.2396	0.5392	1223.8	783.9	-50.9	1.4065	-0.0490	-257.23
0.2157	0.4855	1242.9	756.8	-61.8	1.4194	-0.0274	-197.65
0.1850	0.4164	1258.3	734.7	-63.1	1.4347	0.0013	-144.10
0.1440	0.3241	1278.7	707.7	-62.2	1.4527	0.0423	-89.15
0.0865	0.1947	1297.5	683.2	-47.6	1.4734	0.0570	-46.92
0.0000	0.0000	1302.6	672.0	0.0	1.4970	0.0000	0.12
(A) Tetrahydrofuran + (B) methanol + (C) toluene							
0.3076	0.6924	1137.89	922.4	-41.3	1.3625	-0.0948	-586.148
0.2996	0.6743	1147.43	905.1	-29.3	1.3695	-0.0794	-494.314
0.2902	0.6531	1158.56	885.7	-16.0	1.3775	-0.0571	-428.101
0.2789	0.6276	1171.50	863.8	-1.5	1.3860	-0.0478	-360.645
0.2651	0.5966	1183.30	844.3	-9.0	1.3960	-0.0218	-296.438
0.2479	0.5580	1200.32	818.1	-24.0	1.4071	0.0000	-213.892
0.2260	0.5087	1215.77	794.8	-33.0	1.4201	0.0380	-143.38
0.1970	0.4433	1235.43	766.9	-42.0	1.4350	0.0729	-78.936
0.1567	0.3527	1254.50	740.8	-41.8	1.4522	0.1100	-27.3329
0.0971	0.2186	1277.40	711.8	-32.0	1.4720	0.1403	-0.52299
0.0000	0.0000	1303.80	680.5	0.0	1.4925	0.0000	-0.1297
(A) Tetrahydrofuran + (B) methanol + (C) chlorobenzene							
0.3076	0.6924	1162.40	883.9	2.9	1.3625	-0.0944	-586.15
0.3010	0.6775	1166.30	864.5	-9.6	1.3705	-0.0682	-515.94
0.2932	0.6599	1172.70	840.7	-25.3	1.3804	-0.0120	-455.95
0.2837	0.6384	1177.90	818.4	-37.6	1.3910	0.0467	-366.86
0.2719	0.6120	1184.10	793.9	-49.9	1.4030	0.1110	-263.36
0.2570	0.5784	1195.30	761.6	-66.7	1.4160	0.1600	-171.17
0.2374	0.5344	1210.80	734.1	-73.7	1.4315	0.2200	-65.06
0.2107	0.4743	1226.70	701.8	-78.2	1.4487	0.2540	32.10
0.1720	0.3872	1236.40	660.3	-79.4	1.4681	0.2380	111.47
0.1109	0.2496	1270.60	623.7	-52.3	1.4910	0.1584	124.42
0.0000	0.0000	1210.80	560.3	0.0	1.5220	0.0000	0.03
(A) Tetrahydrofuran + (B) MeOH + (C) nitrobenzene							
0.3076	0.6924	1162.40	883.9	2.8	1.3625	-0.0948	-586.15
0.3016	0.6788	1190.80	828.4	-41.4	1.3708	-0.0470	-515.92
0.2944	0.6625	1224.51	768.4	-88.0	1.3800	-0.0120	-436.61
0.2856	0.6427	1288.20	679.4	-160.6	1.3905	0.0281	-348.05
0.2746	0.6181	1322.70	628.6	-191.1	1.4023	0.0580	-252.29
0.2607	0.5867	1385.49	556.7	-237.0	1.4160	0.0836	-144.93
0.2422	0.5450	1453.07	489.4	-270.0	1.4325	0.1071	-34.19
0.2166	0.4874	1524.96	426.8	-285.0	1.4527	0.1220	79.70
0.1788	0.4024	1589.88	374.5	-267.0	1.4768	0.1030	180.17

(Continued)

Table 3. Continued.

x_A	x_B	u (ms ⁻¹)	$K_S \times 10^{12}$ (Pa ⁻¹)	$\Delta K_S \times 10^{12}$ (Pa ⁻¹)	n_D	$\Delta R \times 10^{-6}$ (m ³ mol ⁻¹)	$\Delta G^E \times 10^{-3}$ (Jmol ⁻¹)
0.1173	0.2641	1593.67	352.3	-175.0	1.5070	0.0500	224.63
0.0000	0.0000	1642.80	309.2	0.0	1.5490	0.0000	0.01
(A) Tetrahydrofuran + (B) MeOH + (C) anisole							
0.3076	0.6924	1162.40	887.6	6.6	1.3625	-0.0948	-586.15
0.3008	0.6769	1167.80	840.7	-29.1	1.3695	-0.0824	-528.07
0.2926	0.6586	1196.30	769.2	-87.2	1.3775	-0.0651	-443.82
0.2828	0.6364	1214.80	718.3	-121.9	1.3870	-0.0370	-347.44
0.2706	0.6091	1228.80	673.6	-146.6	1.3980	-0.0010	-266.28
0.2553	0.5745	1261.30	612.3	-182.7	1.4107	0.0430	-173.75
0.2352	0.5295	1290.43	559.1	-203.0	1.4257	0.0900	-89.00
0.2080	0.4682	1328.49	503.4	-214.0	1.4436	0.1550	0.85
0.1690	0.3803	1353.25	461.1	-192.0	1.4644	0.2030	69.78
0.1081	0.2433	1359.54	433.0	-120.0	1.4878	0.1900	92.76
0.0000	0.0000	1418.40	375.4	0.0	1.5140	0.0000	0.04
(A) Tetrahydrofuran + (B) MeOH + (C) cyclohexanone							
0.3076	0.6924	1159.73	888.0	6.9	1.3625	-0.0948	-586.15
0.3001	0.6754	1175.62	858.3	-14.1	1.3670	-0.0878	-540.39
0.2912	0.6553	1189.31	832.3	-29.9	1.3720	-0.0700	-515.45
0.2805	0.6312	1215.88	789.3	-60.5	1.3779	-0.0620	-485.09
0.2673	0.6017	1233.06	760.3	-74.5	1.3843	-0.0440	-432.24
0.2509	0.5647	1253.50	727.9	-88.0	1.3917	-0.0270	-369.44
0.2297	0.5171	1276.62	693.5	-98.1	1.4003	0.0130	-318.75
0.2014	0.4533	1301.43	658.3	-100.7	1.4100	0.0440	-237.36
0.1616	0.3636	1325.25	625.3	-88.0	1.4206	0.0690	-159.19
0.1014	0.2282	1352.79	589.7	-54.4	1.4327	0.0600	-87.00
0.0000	0.0000	1415.20	527.7	0.0	1.4465	0.0000	-40.00
(A) Tetrahydrofuran + (B) MeOH + (C) cyclohexane							
0.3076	0.6924	1162.40	883.9	2.8	1.3625	-0.0948	-520.23
0.2989	0.6727	1165.44	882.9	3.7	1.3660	-0.0870	-496.11
0.2886	0.6496	1170.16	881.8	4.7	1.3693	-0.0800	-463.50
0.2764	0.6221	1174.90	880.8	6.2	1.3727	-0.0660	-437.17
0.2617	0.5889	1180.10	879.4	7.9	1.3770	-0.0520	-403.03
0.2435	0.5479	1184.85	878.5	10.7	1.3822	-0.0340	-345.07
0.2205	0.4962	1191.84	876.3	13.3	1.3880	-0.0030	-288.55
0.1905	0.4287	1199.14	872.1	15.3	1.3954	0.0280	-220.25
0.1497	0.3370	1209.92	864.7	16.4	1.4032	0.0410	-143.02
0.0912	0.2053	1225.33	849.0	12.8	1.4132	0.0480	-64.25
0.0000	0.0000	1254.60	817.3	0.0	1.4240	0.0000	-0.07

other structure. The first factor contributes to positive ΔK_S values, whereas the remaining two factors lead to negative ΔK_S values [31]. The resultant values of ΔK_S for the present mixtures are due to the net effect of the combination of (i) to (iii) [32]. 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 [33–35]. These results are in excellent agreement with those of V^E discussed earlier.

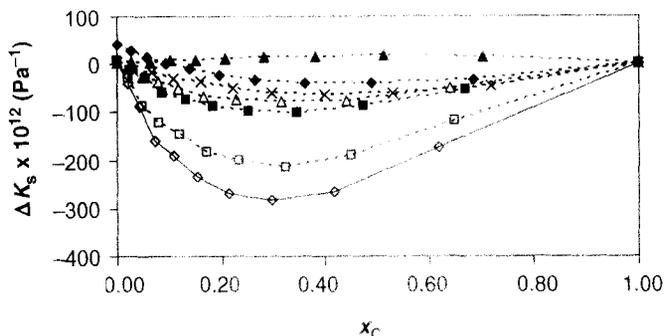


Figure 6. Plot of excess isentropic compressibility $\Delta K_s \times 10^{12} \text{ (Pa}^{-1}\text{)}$ vs. x_c for the ternary mixtures at 298.15 K. (\times), T.H.F (A) + MeOH (B) + Benzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Toluene (C); (Δ), T.H.F (A) + MeOH (B) + Chlorobenzene (C); (\diamond), T.H.F (A) + MeOH (B) + Nitrobenzene (C); (\square), T.H.F (A) + MeOH (B) + Anisole (C); (\blacksquare), T.H.F (A) + MeOH (B) + Cyclohexanone (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Cyclohexane (C).

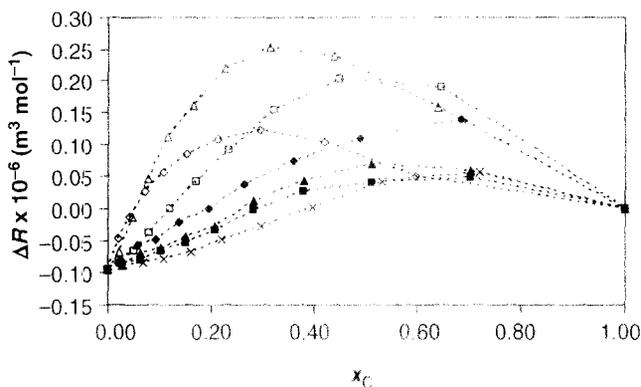


Figure 7. Plot of excess molar refraction $\Delta R \times 10^{-6} \text{ (m}^3 \text{ mol}^{-1}\text{)}$ vs. x_c for the ternary mixtures at 298.15 K. (\times), T.H.F (A) + MeOH (B) + Benzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Toluene (C); (Δ), T.H.F (A) + MeOH (B) + Chlorobenzene (C); (\diamond), T.H.F (A) + MeOH (B) + Nitrobenzene (C); (\square), T.H.F (A) + MeOH (B) + Anisole (C); (\blacksquare), T.H.F (A) + MeOH (B) + Cyclohexanone (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Cyclohexane (C).

3.5. Excess molar refraction

240 The molar refraction, $[R]$ can be evaluated from Lorentz-Lorenz relation [36] and gives more information than n_D about the mixture phenomenon because it takes into account the electronic perturbation of molecular orbital during the liquid mixture process and $[R]$ is also directly related to the dispersion forces

$$[R] = (n_D^2 - 1/n_D^2 + 2)(M/\rho) \quad (8)$$

245 where $[R]$, n_D^2 and M are, correspondingly, the molar refraction, the refractive index and the molar mass of the mixture respectively. Deviation from molar refraction was calculated from the following relation:

$$\Delta R = [R] - (x_1[R]_1 + x_2[R]_2) \quad (9)$$

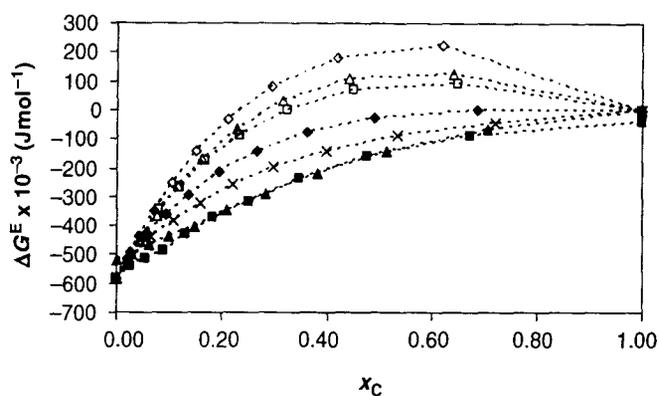


Figure 8. Plot of excess Gibbs energy of activation $\Delta G^{E*} \times 10^{-3} (\text{J mol}^{-1})$ vs. x_C for the ternary mixtures at 298.15 K. (\times), T.H.F (A) + MeOH (B) + Benzene (C); (\blacklozenge), T.H.F (A) + MeOH (B) + Toluene (C); (Δ), T.H.F (A) + MeOH (B) + Chlorobenzene (C); (\diamond), T.H.F (A) + MeOH (B) + Nitrobenzene (C); (\square), T.H.F (A) + MeOH (B) + Anisole (C); (\blacksquare), T.H.F (A) + MeOH (B) + Cyclohexanone (C); (\blacktriangle), T.H.F (A) + MeOH (B) + Cyclohexane (C).

The values of refractive indices and excess molar refraction (ΔR) for the binary mixtures are presented in Table 3 and depicted graphically in Figure 7.

3.6. Excess Gibb's free energy of activation

250 On the basis of the theories of absolute reaction rates [37], the excess Gibbs energy of activation for viscous flow was calculated from the equation [38] for ternary systems.

$$\Delta G^E = RT \left[\ln \eta V - \sum_{i=1}^3 (x_i \ln \eta_i V_i) \right] \quad (10)$$

where R , T , V_i and V are the universal gas constant, experimental temperature in absolute scale, and the molar volumes of the pure component and the mixtures, respectively. From Table 3 and Figure 8 it is evident that the ΔG^E values are negative
255 for all the ternary mixtures over entire range of mole fraction.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2007, SAP-2) for financial support.

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