ION PAIR AND TRIPLE ION FORMATIONS OF SOME SELECTED COMPOUNDS IN AQUEOUS AND BINARY SOLUTIONS AT DIFFERENT TEMPERATURES

A Thesis submitted
in partial fulfilment of the requirements for the Degree of

Doctor of Philosophy
in
Chemistry

By
LALZAWNPUIA
Regd. No. : MZU/Ph.D./468 of 15/05/2012

DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
MIZORAM UNIVERSITY
TANHRIL, AIZAWL- 796004

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CERTIFICATE

This is to certify that the thesis entitled "*Ion pair and triple ion formations of some selected compounds in aqueous and binary solutions at different temperatures*" submitted by ***Mr.Lalzawnpuia***, (**Regd. No. : MZU/Ph.D./468 of 15/05/2012)**, for the degree of ***Doctor of Philosophy*** in Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted for any degree in any other university.

Dated:__________________ (N.MOHONDAS SINGH)
Supervisor

Declaration of the Candidate

Mizoram University

September, 2016

I, Lalzawnpuia, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to do the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

This is being submitted to the Mizoram University for the degree of Doctor of Philosophy in Chemistry.

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1. INTRODUCTION

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 [Pandey and Yasmin, 1997]. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. Thermo-physical and bulk properties of solutions are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover, knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research. 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 arraangements. 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 certainity. 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 two main types of electrochemistry, physically chemistry of ionically conducting solutions (ionics) and the physical chemistry of electrically charged interfaces (electrodics). There are four aspects of ionic electrochemistry: ion-solvent interactions, ion-ion interactions, ion transport in solution, and ionic liquids. The physical chemistry of ionic solutions deals with ions and solvents and how ions interact dynamically with water as they move about in solutions [Goodisman, 1987].

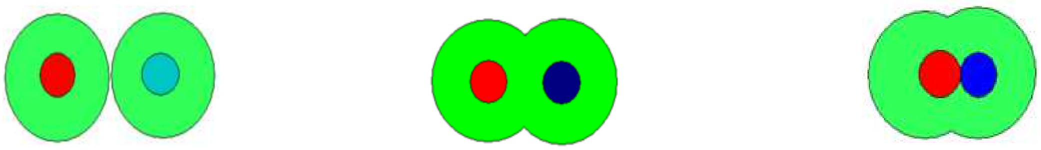
1.1. DEFINITION OF ION PAIRS AND TRIPLE IONS

The partial association of oppositely charged ions in electrolyte solution to form distinct chemical species called ion pairs [Fouss, 1978]. Ion-pairs may be defined as a neutral species formed by electrostatic attraction between oppositely charged ions in solution, which are often sufficiently lipophilic to dissolve in non-aqueous solvents [Quinanar-Guerrero *et al.*, 1997; Irwin *et al.*, 1969]. It should be emphasized that the formation of an ion pair is due only to outer sphere interaction and even though this molecular interaction can be written according to the mass action law, no chemical bond of any kind is formed. Ion-association is a chemical reaction whereby ions of opposite electrical charge come together in solution to form a distinct chemical entity. Ion-associates are classified, according to the number of ions that associate with each other, as ion-pairs, ion-triplets, etc. Ion-pairs are also classified according to the nature of the interaction as contact, solvent-shared or solvent-separated. The most important factor to determine the extent of ion-association is the dielectric constant of the solvent. Ion-associates have been characterized by means of vibrational spectroscopy.

Ion-pairs are formed when a cation and anion come together. $A^{n+} + B^{m-} \leftrightarrows AB^{(n-m)+}$

There are three distinct types of ion-pair, depending on the extent of solvation of the two ions.

Schematic representations of ion-pairs



fully solvated solvent-shared or solvent-separated contact

The sizes are arbitrary and not necessarily similar as illustrated. The cation is coloured red and the anion is coloured blue. The green area represents solvent molecules in a primary solvation shell: secondary solvation is ignored. When both ions have a complete primary solvation sphere the ion-pair may be termed fully solvated. When there is about one solvent molecule between cation and anion, the ion-pair may be termed solvent-shared. Lastly when the ions are in contact with each other the ion-pair is termed a contact ion-pair. Even in a contact ion-pair, however, the ions retain most of their solvation shell. The nature of this solvation shell is generally not known with any certainty. In aqueous solution and in other donor solvents, metal cations are surrounded by between four and nine solvent molecules in the primary solvation shell but the nature of solvation of anions is mostly unknown [Burgess, 1978]

For dilute salts solutions in a polar solvents such as propanone a fraction of the salt is described as being present as ion pairs formed by association of cations and anions. With further decrease in the permittivity of the solvent higher clusters are envisaged; e.g. triple ions, quadruple ions [Hammet, 1970; Grunwald, 1997]. Simple electrostatic theory show that a system of two charged spheres placed symmetrically on each side of an oppositely charged sphere, all three being of the same size, has energy 50 per cent greater than that of two oppositely charged spheres. Thus, there is reason to believe that triple ions (+ - +) or (- + -) might be formed in solvent of low dielectric constant. The following treatment is taken from Fuoss and Kraus. It must be note that by selecting a solvent of such low dielectric constant the calculation has been capable of simplification by neglecting the interionic effects. For a solvent of higher dielectric constant, the interionic forces are no longer negligible and the computation is not so straightforward. Fuoss and Kraus were able to carry the argument one stage further: by treating the approach of a negative ion towards the positive ion of an ion-pair, subject to coulomb forces only, they were able to show that there is a certain value of the distance which is critical: once the approaching ion is within this critical distance it is to be regarded as forming a triple ion [Robinson and Stokes, 1959]. From the conductance point of view, ion pairs and triple ions behave quite differently. The ion-pair, being uncharged, do not respond to an external field; the triple ion are charged and respond to the external field by drifting and contributing to the conductance. The extent of ion-pair formation is governed by the equilibrium between free ions and ion pairs. In like fashion, the extent of triple ion formation depends on the equilibrium between ion pairs and triple ions. Thus, the greater the stoichiometric concentration, the greater is the ion-pair formation and triple-ion formation. However, polar species are not readily amenable to formation in low ε solvents, which is why the Gibbs energies of transfer from aqueous solution into low ε solvents are generally positive for polar complexes and negative for non-polar species. Triple ions in low ε solvents are considered to be linear (i.e., are formed from monatomic or spherical species) because this is their most energetically stable configuration. Because of the opposite direction of the two dipoles, and will have a zero dipole moment. Therefore, if the triple-ion concentration is significant there should be a decrease in the polarization of the solution that should lead to an observable decrease in the dielectric permittivity, contrary to what is observed in many cases upon increasing the electrolyte concentration [Fuoss-Kraus, 1933].

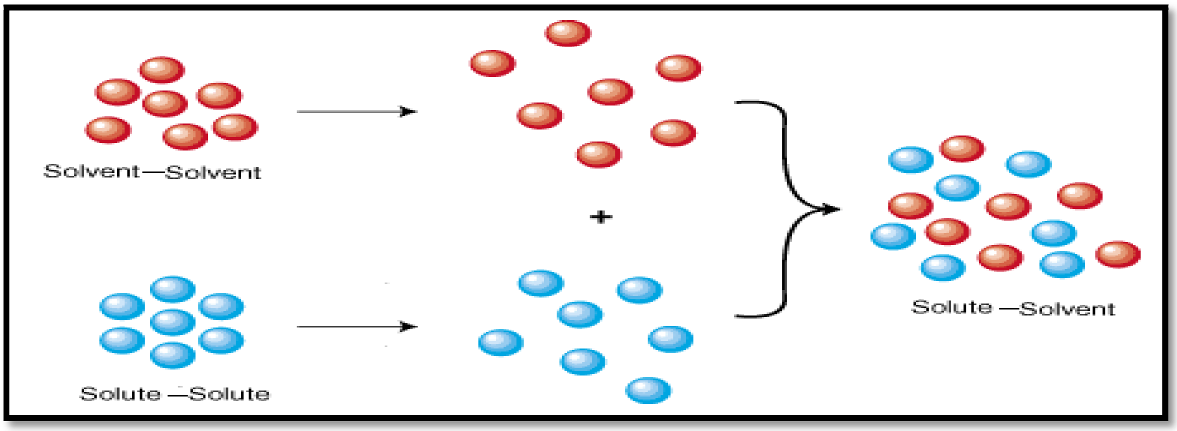
1.2. VARIOUS TYPES OF INTERACTIONS

There are three types of interactions in the solution process:

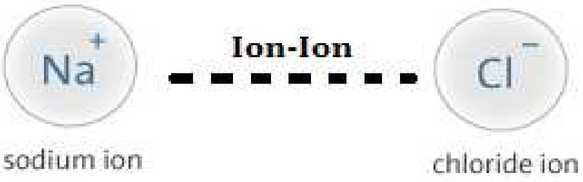
Solvent – solvent interactions

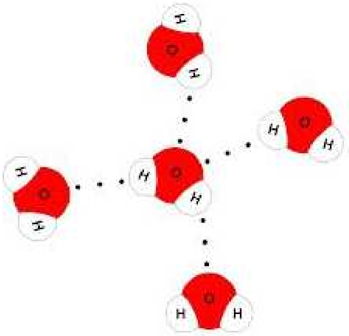
Solute – solute/ ion – ion interactions

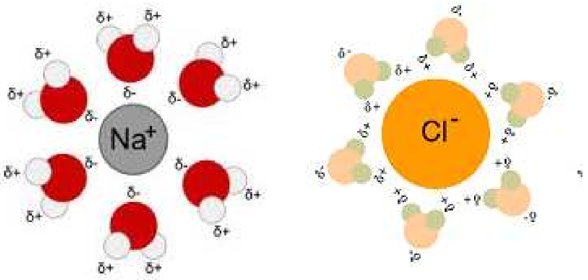
Solute – solvent/ ion – solvent interaction



Let us consider that Sodium Chloride (NaCl) dissolves in water (H_2O). The interactions are shown below:




Solvent-Solvent Interaction



Ion-Solvent Interaction

The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes of free energy, enthalpy and entropy, etc. associated with a particular reaction can be qualitatively and quantitatively evaluated using various physico-chemical techniques from which conclusions regarding the factors associated with the ion-solvent interactions can be worked out. 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. 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, and solvent-solvent interactions in some solvent media. The organic solvents have been classified based on the dielectric constants, organic group types, acid base properties or association through hydrogen bonding, [Franks and Wen, 1957], donor-acceptor properties [Gutmann, 1976], hard and soft acid-base principles [Pearson, 1973]. As a result, the different solvent systems show a wide divergence of properties which would naturally be reflected on the thermodynamic, transport and acoustic properties of electrolytes and non-electrolytes in these solvents. The presence of solvation shell is reflected in the fact that the Stokes radius of the solvation ion is substantially greater than that predicted for the bare ion. An ion possessing a tight solvation shell may approach a counter-ion without hindrance until its solvation shell contacts the partner [Murray and Yeager, 1973]. Thereafter, either the associate maintains its structure as a loose, solvent-separated ion-pair, or the solvent molecules separating the partners are squeezed out and a tight contact ion-pair is formed. This implies that solvent-separated ion-pairs may exist only in those media in which the free ions acquire tight solvation shells; otherwise, only tight contact ion-pair is formed. It is important to mention that Bjerrum’s original concept of a pair of solvated ions that are held together by coulombic attraction, in a solvent of a low dielectric constant, remains valid without modification despite the presence of a solvation shell [Braunstein, 1971].

1.3. CONCEPT OF ION PAIR AND TRIPLE ION FORMATION

Ion pair states are unusual compared to most electronic states of neutral molecules in that they appear at high energies but can be quite strongly bound. Bjerrum first introduced the concept of ion pair into the evaluation of the inter-ionic force in electrolytic solution in 1926 [Bjerrum, 1926] and its tendency of ions to associate into ion pairs depends on the balanced between the electrostatic force and thermal energy. Ion pair formation refers to the association of cations and anions in solution. An ion-pair is defined to exist when the cation and an anion are close enough in space with a common solvation shell, the energy associated with their electrostatic attraction being larger than the thermal energy (kT) available to separate them [Kortum, 1965]. The ions need also to stay associated longer than the time required for Brownian motion to separate non-interacting species [Lacour and Moraleda, 2009].

The first inter-ionic theory of electrolytic solution by Debye-Huckel has been used remarkably in interpreting the behavior of ions in dilute solutions [Debye and Huckel, 1923]. The theoretical calculation for the decreased of ionic mobility with increasing concentration considered two effects. Firstly, when an ion moves through under the influence of an applied electric field, it tends to disturb the surrounding ionic atmosphere which exerts an opposing electric force and, secondly, the ion comprising the ionic atmosphere produced a counter-current of solvent; which also retards the motion of the central ion. The Debye-Huckel model assumed the ions to be in almost random thermal motion and therefore, in almost random positions. The ion of the pair together formed an ionic dipole on which the net charge is zero. As the dielectric constant is increased the extents of association should (and does) decrease, but it should never become zero because there is always a non-zero chance that anion-cation contacts will occur. Conductance of 1:1 electrolytes has been extensively studied [Das and Patnaik, 1996] by using Shedlovsky equation. It is very important to realize that these forces holding the ions together are therefore independent of the chemical nature of the ions. On this basis, it would be expected that electrolytes which have ions of the same charge and are of similar size would have equilibrium constants of similar magnitude if the associated species is an ion pair [Azzari and Kraus, 1952]. This is found for some 2:2 sulphates, and for some cations of similar size which associated with Cl^- (aq) or I^- (aq). The ions of the ion pair move together as a single unit and are held together by electrostatic forces of the coulomb type acting over the short distances that the ions are apart in the ion pair [Marcus and Hefter, 2006]. These Coulombic forces impose a certain degree of cohesion on the unit and this is sufficiently great to overcome the tendency for normal thermal motion to cause the ions to move around as separate particles each with its own translational degrees of freedom. Because the forces holding the ions together are of this physical nature, they depend on three factors, the charges on the ions, the sizes of the ions and the relative permittivity of the solvent in the vicinity of the ion [Shehata and El-Bary, 1996].

The Debye-Huckel model assumed the ions to be in almost random thermal motion and therefore, in almost random positions. The slight deviation from randomness was pictured as giving rise to an ionic cloud around a given ion, a positive ion (of charge $+ze_0$) being surrounded by a cloud of excess negative charge ($-ze_0$). However, the possibility was not considered that some negative ions in the cloud would get sufficiently close to the central positive ion in the course of their quasi-random solution movements so that their thermal translational energy would not be sufficient for them to continue their independent movements in the solution [Pura and Atun, 2003]. Bjerrum suggested that a pair of oppositely charged ions may get trapped in each other Coulombic field. An ion-pair may be formed [Persson, 1986].

Species are generally describe as ion pairs if two oppositely charged ions in solution stay together at a separation, r, which is smaller than some specified cutoff distance, R. Ions farther apart than R considered “free’’. Various theories have been proposed for choosing the value of R and for describing the properties of the ion pairs and free ions that together produce the observed behavior of electrolyte solutions. However, when the ion association is weak, there is a strong correlation between these non-specific ion-ion interactions [Nelson and Errington, 2005] (characterized in terms of activity coefficients) and ion pair formation (characterized in terms of association constant). It is generally accepted that ions cannot approach each other more closely than some 'distance of closest approach,' a, due to the strong repulsive forces of the electron shells of the ions, even if polarizable [Samoilov and Ya, 1957]. The distance, a is understood to bear some relation to the sum of the (crystal ionic) radii of the oppositely charged ions, generally $a \geq r_+ + r_-$. In summary, two ions of oppositely sign are considered to form an ion pair if their distance apart is between a and R for a time longer than the time needed to diffuse over such a distance. Once ions are paired, they are thought to have no tendency to associate with other ions in dilute solutions, although, at higher electrolyte concentrations, ion triplets, quadruplets, or larger aggregates may form [Marcus, 2008]. Very short- range interactions (hard or nearly-hard sphere repulsions) involve the mutual exclusion of ions at $r > a$. However at distance $a < r < R$, solvation of the constituent ions must be considered. On this basis an ion pair may be classified as (double) separated ion pair (2SIP), when the primary solvation shells of both ions remain essentially intact, as a solvent-shared ion pair (SIP), if a single solvent layer exists in the space between the ion partners of the pair, or as a contact ion pair (CIP), if no solvent exists between the partners and the ions are in direct contact [Marcus and Hefter, 2006]. The long-range electrostatic forces that keep the partners of an ion pair together are non-directional. The type of association that is involved, in most cases, is not true chemical association where a bond, complex or contact pair is formed between two ions. The electrostatic association, defined by Bjerrum mode is simply a convenient way of representing strong coulombic interactions at short interionic distances, where the limiting law approximation fail. Justice has shown that Bjerrum association model is actually consistent with statistical thermodynamics and linear reversible processes and in fact, takes into account higher terms of the limiting Debye-Huckel theory. Many modern conductance theories now incorporate the Bjerrum association concept [Barthel *et al*., 1979]. In any solution of an electrolyte there is always the possibility that the ions of the electrolyte might not be fully dissociated in solution. The extent of association into ion-pairs depends on many factors, with the most important being the nature, charges and sizes of the ions, the characteristics of the solvent and the temperature. Although ion-pair formation has been considered only for solvents with a low dielectric constants (Bjerrum's ion-pair), the existence of the ion-pair in water or in other highly structured (bonded) solvents is possible when the ions involved are largely hydrophobic. In this case, ion-pairing is due to a solvent mediated effect rather than to an electrostatic interaction [Lee *et al*., 1987; Florence and Attwood, 1988]. The term "water structure enforced" ion-pairing was introduced by Diamond [Diamond, 1963] in order to explain the existence of ion-pairs in aqueous systems. If both the cation and anion are large hydrophobic species, the hydrogen-bonded water structure forces them together to maximize the water-water interactions and to minimize the structural perturbation. Water structure enforced ion-pairing involves both electrostatic and hydrophobic interactions, the relative contribution of which is dependent upon both ions structures and on their immediate environment. Despite the possibility to form ion-pairs in aqueous solution, the usefulness of this phenomenon is very limited due to the low association constant; furthermore, the ion-pairs exist only at very low concentration, because of the poor solubility of the ions [Lee, 1987; Freiser, 1969].

The study of conductance measurements were pursued vigorously both theoretically and experimentally during the last fifty years and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects and our discussion will be related 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 [Onsager, 1927] in deriving the Kohlrausch's equation:

$$\Lambda = \Lambda_0 \; + \; S\sqrt{c} \qquad \text{... (1)}$$

where, $$S = \alpha\Lambda_0 + \beta \qquad \text{…(2)}$$

$$\alpha = \frac{(ze^2)k}{3(2+\sqrt{2})\varepsilon{,}KT\sqrt{c}} = \frac{82.406 \text{ x } 10^4 z^3}{(\varepsilon{,}T)^{3/2}} \qquad \text{…(3)}$$

$$\beta = \frac{ze^2Fk}{3\pi\eta\sqrt{c}} = \frac{82.487z^3}{\eta\sqrt{\varepsilon T}} \qquad \text{…(4)}$$

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 [Fuoss, 1978]. In the subsequent years, Pitts and Fuoss and Onsager [Fouss and Onsager, 1955] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions. However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably [Fouss, 1978] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned [Pitts *et al.*, 1969]. The original F.O. equation was modified by Fuoss and Hsia [Fuoss and Hsia, 1967] who recalculated the relaxation field, retaining the terms which had previously been neglected.

The equation usually employed is of the form:

$$\Lambda = \Lambda_0 \; - \frac{\alpha\Lambda_0\sqrt{c}}{(1+ka)(1+\frac{ka}{\sqrt{2}})} - \frac{\beta\sqrt{c}}{(1+ka)} + G(ka) \qquad \text{…(5)}$$

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

$$\Lambda = \Lambda_0 \; - S\sqrt{c} + \; Ec\ln c + \; J_1 c - J_2\sqrt[3]{c} \qquad \text{…(6)}$$

is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini [Fernandez-Prini, 1973]. Further, correction of the equation (05) was made by Fuoss and Accascina [Fuoss and Accascina, 1959]. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2\sqrt[3]{c} - B\Lambda_0 c \qquad \ldots(7)$$

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 [Fernandez *et al.*, 1980]

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

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

$$M^{z+} + A^{z+} = MA \qquad \ldots(8)$$

$$K_A = \frac{(1-\alpha)}{\alpha^2 c\gamma_{\pm}^2} \qquad \ldots(9)$$

and

$$\alpha = 1 - \alpha^2 K_A c \gamma_\pm^2 \qquad \ldots(10)$$

For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation [Fouss and Kraus, 1933] or Shedlovsky's equation [Shedlovsky and Franklin, 1938]

$$\frac{T(Z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_A}{\Lambda_0^2} x \, \frac{c\gamma_\pm^2 \Lambda}{T(Z)} \qquad \ldots(11)$$

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

$$F(z) = 1 - z(1 - z(1 - \cdots)^{1/2}))^{1/2} \qquad \ldots(12)$$

and

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \qquad \ldots(13)$$

The plot of T(Z) /Λ against c $\gamma_\pm^2\Lambda/T(Z)$ should be a straight line having $1/\Lambda_0$ for its intercept and $K_A/(\Lambda_0)^2$ for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (11).

The Fuoss-Hsia [Fuoss and Hsia, 1967] conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 \; - S\sqrt{\alpha c} + \; E(\alpha c)\ln(\alpha c) + \; J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A \Lambda B \gamma_\pm^2 (\alpha c \quad \ldots(14)$$

The equation was modified by Justice [Justice *et al*., 1968]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 \; - S\sqrt{\alpha c)} + \; E(\alpha c)\ln(\alpha c) + \; J_1(\alpha c) - J_2(R)(\alpha c)^{\frac{3}{2}} \qquad \ldots(15)$$

$$\frac{(1-\alpha)}{\alpha^2 c \gamma_\pm^2} = K_A \qquad \ldots(16)$$

$$\ln\gamma_{\pm} = \frac{-k\sqrt{q}}{1+kR\sqrt{\alpha c}} \qquad ...(17)$$

The conductance parameters are obtained from a least square treatment after setting:

$$R = q = \frac{e^2}{2\varepsilon kT} \text{(Bjerrum}' \text{scritical distance)} \qquad \ldots(18)$$

According to Justice, the method of fixing the J-coefficient by setting R = q clearly permits a better defined value of K_A to be obtained. Since the equation (14) is a series expansion truncated at the c $^{3/2}$ term, it would be preferable that the resulting errors be absorbed as must as possible by J_2 rather than by K_A, whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction.

From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach, a^0, of two free ions to form an ion-pair. The following equation has been proposed by Fuoss [Fuoss and Accascina, 1959]

$$K_A = \left(\frac{4\pi N_A a^3}{3000}\right) \exp\left(\frac{e^2}{a\varepsilon KT}\right) \qquad \ldots(19)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a^0. The distance parameter was finally determined from the more general equation due to Bjerrum [Bjerrum, 1926]

$$K_A = \left(\frac{4\pi N_A a}{1000}\right) \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r\varepsilon KT}\right) dr \qquad \ldots(20)$$

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 [Tissier and Douheret, 1978]

The conductance-concentration curves of electrolytes in solvents of dielectric constant below about 15 contain minima which appear at lower and lower concentrations as the dielectric constant falls. In a classic paper, Fuoss and Kraus proposed as an explanation the formation of triple ions + - + and - + - and even of higher aggregates. In very dilute solutions, simple cations and anions are present and the molar conductance decreases with rising concentration as a result of ion pairing. At still higher concentrations triplet ions are produced and the molar conductance rises accordingly. For the triple-ion concept, the conductivity data have been analyzed by the Fuoss-Kraus triple-ion theory in the form [Fuoss-Kraus, 1933]

$$\Lambda\{g(c)\}c^{1/2} = \frac{\Lambda_0}{K_P^{1/2}} + \frac{\Lambda_0^T K_T}{K_P^{1/2}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c, \qquad \ldots(21)$$

$$g(c) = \frac{\exp\{(\frac{-2.303\beta'}{\Lambda_0^{\frac{1}{2}}}\left((c\Lambda)^{\frac{1}{2}}\right)\}}{1-\frac{S}{\Lambda_0^{\frac{3}{2}}}(c\Lambda)^{1/2}(1-\frac{\Lambda}{\Lambda_0})^{1/2}} \qquad \ldots(22)$$

$$\beta' = \frac{1.8247 \text{ x } 10^6}{(\varepsilon T)^{3/2}} \qquad \ldots(23)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8206 \text{ x } 10^6}{(\varepsilon T)^{3/2}}\Lambda_0 + \frac{82.501}{\eta_0(\varepsilon T)^{1/2}} \qquad \ldots(24)$$

β' is the Debye-Hückel activity coefficient and S is the limiting Onsager slope coefficient of the conductivity equation $\Lambda = \Lambda_0 - S(c\Lambda/\Lambda_0)^{1/2}$, and the other terms have their usual significance. Λ_0 and Λ_0^T are the limiting equivalent conductivities of the two possible triple ions. Neglecting Λ/Λ_0 compared to 1, and assuming for interionic attraction that g(c) = 1 in equation (1), we get,

$$\Lambda c^{1/2} = \frac{\Lambda_0}{K_P^{1/2}} + \Lambda_0^T \frac{K_T}{K_P^{1/2}} c \qquad \ldots(25)$$

$$c_P = c(1 - \alpha - 3\alpha_T) \qquad \ldots(26)$$

$$\alpha = (K_P c_P)^{-1/2} \quad \ldots(27)$$

$$\alpha_T = (K_T/K_P^{1/2})\, c^{1/2} \quad \ldots(28)$$

$$c_T = (K_T/K_P^{1/2}) c^{3/2} \quad \ldots(29)$$

1.4. EFFECT 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 [Einstein, 1906] leads to the equation

$$\frac{\eta}{\eta_0} = 1 + 2.5\text{Ø} \quad \ldots(30)$$

where Ø is the volume fraction occupied by the particles. Modifications of the equation have been proposed by Sinha on the basis of departures from spherical shape and 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 (30):

$$2.5\text{Ø} = A\sqrt{c} + Bc \quad \ldots(31)$$

Since A√ c term can be neglected in comparison with Bc and Ø = $C\text{Ø}^0_{v,1}$ where $\text{Ø}^0_{v,1}$ is the partial molar volume of the ion, we get:

$$2.5\text{Ø}^0_{V,1} = B \quad \ldots(32)$$

In the ideal case, the B -coefficient is a linear function of partial molar volume of the solute, $\text{Ø}^0_{v,1}$ with slope to 2.5. Thus, B± can be equated to:

$$B_{\pm} = 2.5\text{Ø}^0_{\pm} = \frac{2.5 \text{ x } 4(\pi R^3_{\pm})}{3 \text{ x } 1000} \quad \ldots(33)$$

assuming that the ions behave like rigid spheres with a effective radii, $R_{\pm}$ moving in a continuum. $R_{\pm}$ calculated using the equation (33) should be close to crystallographic radii or corrected Stoke's radii if the ions are scarcely solvated and behave as spherical entities. But, in general, $R_{\pm}$ values of the ions are higher than the crystallographic radii indicating appreciable solvation. The number n_b of solvent molecules bound to the ion in the primary solvation shell can be easily calculated by comparing the Jones-Dole equation with the Einstein's equation:

$$B_{\pm} = \frac{2.5}{1000(\text{Ø}_i + n_b \text{Ø}_s)} \qquad \ldots(34)$$

where Ø_i is the molar volume of the base ion and Ø_s, the molar volume of the solvent. The equation (34) has been used by a number of workers to study the nature of solvation and solvation number.There is no doubt that most ions are solvated in solution though it is difficult to assess precisely the extent of solvation, and hence the size of the solvated ion. Likewise, the ion pair will be solvated, and some estimate of its size is required. Furthermore, the change in solvation pattern on forming the ion pair is of crucial importance. However, both inner and outer-sphere ion pairs are still solvated as the composite unit, and are described as contact or solvent separated. Although the definitions can be quite unambiguous, experimental classification into contact or solvent separated or inner and outer sphere ion pairs most certainly is not unambiguous, and may even, at best, be only a guess. This is exactly the same problem as is encountered when discussing the formal and experimental distinctions between complexes and ion pairs [Fernandez-Prini, 1973].

1.5. SOLVATION NUMBER

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 easily be determined from the Stokes' law. The volume of the solvation shell V_S, can be written as:

$$V_s = \left(\frac{4\pi}{3}\right)(r_s^3 - r_c^3) \qquad \ldots(35)$$

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

$$n_s = \frac{V_s}{V_0} \qquad \ldots(36)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects [Stokes and Robinson, 1957] from:

$$V_s^0 = 4.35 r_s^3 \qquad \ldots(37)$$

where $V_S{}^0$ is expressed in mol/litre and r_S in angstroms. However, the method of determination of solvation number is not applicable to ions of medium size though a number of empirical equations [Born, 1920] and theoretical corrections [Boyd, 1961; Zwanzig, 1963] have been suggested to make the general method.

1.6. LIMITING EQUIVALENT CONDUCTANCE AND WALDEN PRODUCT

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

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \qquad \ldots(38)$$

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

$$\lambda_+^0 = t_+\Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_-\Lambda_0 \qquad \ldots(39)$$

Thus, from accurate value of λ^0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions [Padova, 1972]. However, accurate transference number determinations are limited to few solvents only. Spiro [Spiro, 1920] and Krumgalz [Krumgalz, 1983] have made extensive reviews on the subject. In absence of experimentally measured transference numbers, it would be useful to develop indirect methods to obtain the limiting equivalent conductances in organic solvents for which experimental transference numbers are not yet available. The methods have been summarized by Krumgalz [Krumgalz, 1985] and some important points [Walden *et al.*, 1926; Fuoss and Hirsch, 1960; Takezawa *et al.*, 1973] are mentioned below:

(i) Walden equation, $(\lambda_\pm^0)_{\text{water}}^{25}\, n_{0,\text{water}} = (\lambda_\pm^0)_{\text{acetone}}^{25}\, n_{0,\text{acetone}}$ …(40)

(ii) $$\begin{bmatrix} \lambda_{\text{pic}}^0 n_0 & = & 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^0 n_0 & = & 0.296 \end{bmatrix} \quad \text{based on} \Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^0 = 0.563 \qquad \ldots(41)$$

Walden considered the products to be independent of temperature and solvent. However the Λ^0Et$_4$Npic values used by Walden was found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

(iii) $\lambda_{25}^0(\text{Bu}_4\text{N}^+) = \lambda_{25}^0(\text{Ph}_4\text{B}^-)$ …(42)

The equality holds goods in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane. 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 [Gill *et al.*, 1985] is:

$$\lambda_{25}^{0}(R_4N^+) = zF^2/6\pi N_A n_0[r_i - (0.0103\varepsilon_0 + r_y)] \qquad \ldots(43)$$

where Z and r_i are charge and crystallographic radius of proper ion, respectively; η_0 and ε_0 are solvent viscosity and dielectric constant of the medium, respectively; r_y = adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents respectively. However, large discrepancies were observed between the experimental and calculated values [Krumgalz, 1983]. Krumgalz [Krumgal, 1985] 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) $\lambda_{25}^{0}[(i-Am)_3BuN^+] = \lambda_{25}^{0}(Ph_4B^-)$ …(44)

It has been found from transference number measurements that the $\lambda^0_{25[(i\text{-}Am)3\,BuN^+]}$ and $\lambda^0_{25\,Ph4B^-}$ values differ from one another by 1%.

(vi) $\lambda_{25}^{0}(Ph_4B^-) = 1.01\lambda_{25}^{0}(i-Am_4B^-)$ …(45)

The value is found to be true for various organic solvents. Krumgalz [Krumgalz, 1983] suggested a method for determining the limiting ion conductances in organic solvents. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_0 values into ionic components for non-aqueous electrolytic solutions.

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

$$r_s = \frac{|z|F^2}{A\pi n_0 \lambda_{\pm}^0} \qquad \ldots(46)$$

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:

$$\lambda_{\pm}^0 n_0 = \text{constant} \qquad \ldots(47)$$

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

1.7. LIMITATION OF THE CONCEPT OF ION PAIRS AND TRIPLE ION

When the concentration of ions is too high, the concept of ion pairs and triple ion is useless [Szwarc, 1972] For example, it would be impossible to differentiate between free ions and ion-pairs in a fused sodium chloride. Of course, each sodium ion has some chloride ions as its nearest neighbours and vice-versa, but it is impossible and unprofitable to assign two oppositely charged ions to a lasting pair. Such a system is better described by a suitable distribution function and not by equilibrium between the free ions and ion pairs.

1.8. SCOPE OF THE STUDY

Higuchi *et al*. have reported numerous methods for performing extraction of ionized solutes into organic phases in which ions of opposite charge are added to the aqueous phases, resulting ion-pairing between the solute ion and pairing ion. Ion-pairing was initially investigated in the field of physical chemistry; the concept was rapidly adopted in colloidal chemistry, analytical chemistry, and the pharmaceutical sciences. The ion-pair extraction method is widely used in the pharmaceutical and analytical sciences. There is very little report of comparative studies for the wide range temperature dependence of ion pair and triple ion formation of transition metal complexes and ionic liquids in pure and mixed solvents. We also considered that the conductance measurements in pure solvents will give the ion solvent interactions and in mixed solvents an all over view of the main aspects of solvation.

The purpose for this study is to expand the present status of the ion pair and triple ion formation and illustrate it with examples of well characterized ion pairs and triple ion formation in electrolyte solutions in various solvents. The formation of ion pairs is strongly influenced by the solvation of the ions; hence, the transfer of ion pairs between solvents of different solvation abilities will be discussing here. The useful methodology of ion pair formation is widely employed for separation and synthetic purposes. Ionic association is an important for electrolytes in most non-aqueous system, as well as for aqueous solutions of electrolytes at high temperature and pressure and multivalent electrolytes at any temperature. This research will also focus on the study of ion association and triple ion formation phenomena by studying limiting molar/equivalent conductance (Λ_0) and limiting molar/equivalent conductance of triple ion (Λ_0^T) at infinite dilution in different solutions and association constant (K_A) and triple ion constant (K_T) at different temperatures and to evaluate thermodynamic parameters including the activation energy to have a better understanding of association phenomena. This research will also study temperature effect on Λ_0, Λ_0^T and K_A, K_T to calculate the Walden products ($\Lambda_0\eta_0$) for measuring the influence of mixed solvent composition and calculation of radius (Å) for ion pair formation for the salts.

The following transition metal compounds and ionic liquids in pure and mixed solvents were chosen for our study.

Sl.No.	Salt	Solvent
1.	Tetraammine Cu(II) sulfate and tris(ethylenediamine) Cu(II) sulfate	Water
2.	N-[(benzoyl-amino) thioxomethyl] cystein manganese (II) chloride, N-[(benzoyl-amino) thioxomethyl] cystein cobalt (II) chloride, N-[(benzoyl-amino) thioxomethyl] cystein nickel (II) chloride and N-[(benzoyl-amino) thioxomethyl] cystein copper (II) chloride	Water
3.	N-[(benzoyl-amino)- thioxomethyl]- serine manganese (II) chloride and N-[(benzoyl-amino)-thioxomethyl]- serine nickel (II) chloride	Methanol + Water
4.	N-[(benzoyl-amino)- thioxomethyl]- histidine manganese (II) chloride and N-[(benzoyl-amino)-thioxomethyl]- histidine nickel (II) chloride	Methanol + Water
5.	1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$]	Methanol + Water, Acetonitrile + Water, Dimethylsulfoxide + Water
6.	[emim]NO$_3$, [emim]CH$_3$SO$_3$, [emim]Tos)	Tetrahydrofuran + Water
7.	1-butyl-3-methylimidazonium hexafluorophosphate and 1-benzyl-3-methylimidazolium hexafluorophosphate	AN, MeOH, DMF, DMA and DMSO

2. REVIEW

2.1. CONDUCTOMETRIC METHOD

Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent. Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore ion-ion and ion-solvent interactions can be better studied. Ionic association of electrolytes in solution depends on the mode of solvation of its ions [Das and Hazra, 2002; Guha *et al*., 2003; Roy *et al*., 2006] which in turn depends on the nature of the solvent or solvent mixtures. Solvent properties such 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. Conductance measurement, besides providing information on the mobility of ionic species in solution, is the most direct and accurate techniques available at present to determine the extent to which ions associate in solution [Debye-Huckel, 1923]. Thus, extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years [Das and Saha, 2000; Roy *et al*., 2008; Chanda and Roy, 2008; Parvatalu and Srivastava, 2003] to examine the nature and magnitude of ion-ion and ion-solvent interactions. Behavior of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity. Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolytic solutions. Because of its relative simplicity and versatility, the measurements of the conductivity of electrolyte solutions which can be carried out to a very high precision, remains an important tool to obtain information about electrolytes in different solvents

[Bianchi *et al.*, 2000]. Conductivity of aqueous system has recently provided valuable information about the influence of the solvent number-density in the low fluid-density regime and its effect on the ion-pairing equilibrium [Gruskiewiez and Wood, 1997; Zimmerman *et al.*, 1997]

2.2. ION PAIR AND TRIPLE ION FORMATION IN 2:1 AND 1:1 COMPLEXES

Notwithstanding the non-specific role of water in many non-aqueous solutions, in some cases it may have specific effects due to ion-water interactions which depend on the particular nature of the ions and solvent. Thus the conductance of associated $AgNO_3$ and $(CH_3)_2TlI$ in dimethylformamide increase with the water content in contrast to the decrease found for dissociated salts, In methanol and ethanol, the conductance of perchloric acid decreases significantly upon addition of 0.3% water [Goldenberg and Amis, 1962]. This was attributed to the change in the proton transport mechanism.

Yeager and Kratochvil [Yeager and Kratochvil, 1975] have recently reported conductance data for Cu(I), Ag(I) and Tl(I) salts in AN which shows that the salts of the two first cations are essentially dissociated, while Tl(I) salts are associated similarly to KSCN. The Λ^0 values indicate that Cu(I) is a very large solvodynamic unit, probably in the form $Cu(AN)_4^+$. The association of $AgNO_3$ and $AgClO_4$ in AC and Cyclohexanone [Griffiths *et al.*, 1958] can be reasonably accounted for by electrostatic interactions, but $AgNO_3$ in benzonitrile and $AgNO_3$ and MeTl(I) in DMF require too small α values (1.6, 1.3 and 1.1Å) if association is considered purely electrostatic.

Using conductance method Steekumar, Rajendran and Kalidas had studied ion-solvent interactions of copper (ll) Perchlorate in both water-DMSO and water-Pyridine. It was observed that the Λ_0 (equivalent conductance) of copper (ll) Perchlorate first decrease sharply on addition of pyridine upto 20 wt%, then gradually decreases upto 60 wt% pyridine and finally it increases. The Λ_0 also decreases continuously with the addition of DSMO mixtures. The Walden product of copper (II) perchlorate decreases continuously with the addition of DSMO in water-DSMO mixtures. In case of pyridine, it first decreases sharply with the addition of pyridine and then it increases slightly and subsequently decreases with the addition of pyridine. It may be of interest to point out that strong solvent-solvent interaction resulting in the formation of water-DSMO complexes compete with the ion solvent interactions and presumably give rise to the complex behavior.

Recently, Rajmuhon and Bag [Bag *et al*., 2009] had studied the conductance and ion association of bis (1-amidino-O-methylurea copper (II) acetate in aqueous medium at 5-40^{o}C using Shedlovsky equation. As evident from experimental values of Stoke's radius of anion ($^{r}CH_3COO^{-}$) is more or less constant with the variation of temperature. The Stoke’s radii for the complex cations increase with temperature which indicates that the cations become more hydrated as the temperature rises. Walden product ($\Lambda_0\eta_0$) of the ions is most nearly constant for those of large size due to their being polyatomic or extensive hydration. The ion association process will occur spontaneously and exothermic in nature which is supported by the positive value of ΔS^0 and the negative value of ΔH^0. Then the variation of ΔG^0 with temperature reveals that the ion association process is favored at low temperature. Singh, Rajmuhon and Manihar had studied the electrical conductivities and ion pair-formation of bis-l-amidino-O-methylurea-, bis-l-amidino-O-ethylurea-copper (II) halides and nitrates in aqueous solution at 18^{o}, 25^{o}and 35^{o}C. From the values of association constants of these complexes at different temperatures, the thermodynamic functions can be estimated in order to understand the nature of ion-association. The limiting equivalent conductivities (Λ_0) of the complexes were determined by Onsagar method of extrapolation. The sizes of ion pairs were evaluated from Bjerrum equation, Stokes' law and Dennison-Ramsey theory. The observed values of association constants (K_A) for bis 1-amidino-Omethylurea copper(II) and bis 1 -amidino-O-ethylurea copper(II) chloride, bromide, iodide and nitrate are followed the order:

(i) $\{[Cu(AMUH)_2]Cl]^+ > \{[Cu(AMUH)_2]Br] > \{[Cu(AMUH)^2]NO_3]^+ > \{[Cu(AMUH)_2]I]^+$

(ii) $\{[Cu(AEUH)_2Cl]^+ > \{[Cu(AEUH)_2]Br]^+ > \{[Cu(AEUH)_2]NO_3]^+ > \{[Cu(AEUH)_2]I]^+$

(iii) $\{[Cu(AMUH)_2]X]^+ > \{ [Cu(AEUH)_2]X]^+$

Using conductivity, Butler, Schiff and Gordon [Butler *et al.*, 1951] found for NaCl solutions in methanol the relative decrease of Λ for 1% of added water varies with the concentration of the salt, extrapolating precisely to the percentage decrease of the fluidity of methanol containing 1% of water when the concentration of salt is zero. Barthel [Barthel *et al.*, 1977] observed the same behavior when water was added to $NaOCH_3$ in methanol. Similar effects have seen found for nitromethane [Unni *et al.*, 1963], dimethylformamide [Prue and Sherrington, 1961], and sulpholane [Fernandez-Prini, 1973] solutions upon addition of water. The observed conductance change can be essentially explained in terms of viscosity change introduced in the media by the addition of water and may be considered of non-specific nature. This is justifies the use by some workers of hydrates instead of the anhydrous salts, the first being more readily soluble in some non-aqueous solvents [Dawson *et al.*, 1963]. D'Aprano and Fuoss [D'Aprano and Fuoss, 1963] found a very large increase in the conductance of picric acid dissolved in acetonitrile as water was added (Λ increases ten times for 0.02% of water). Ammonia, which is a likely impurity in acetonitrile, also increases the conductance of picric acid probably due to formation of the ammonium salt which is highly conducting. The abnormal variation of conductance with concentration for transition metal and aluminium salts in N-methylacetamide was attributed to the presence of acetates [Dawson *et al.*, 1962] a common impurity in the solvent.

The conductance of Alkali metal (M) halides in methanol, ethanol and propanol of $MClO_4$ and MNO_3 in methanol [Copley and Hartley, 1930], and of MSCN [Butler *et al.*, 1951] in propanol were determined before the extension of the conductance theory. Many of the results have been reanalyzed [Prue and Sherrington, 1961; Kay and Evan, 1964] using the conductance equations. For these electrolytic solutions, Λ^0 increases with the size of the ions; that is, the solvodynamic units are larger for the smaller ions. In methanol, alkali metal salts are essentially dissociated except the nitrates. Kay and Hawes have measured the conductance of CsCl in methanol and ethanol [Kay and Hawes, 1965]. Analysis of the data in the former solvent using Fuoss and Hsia's equation yields for d = 7.00 Å, $K_A = 20.8$ mol^{-1}l corresponding to $\alpha = 3.6$ Å. Recent data [Conti and Pistoia, 1968] for $KCLO_4$ and $CsCLO_4$ in methanol are at variance with the behavior described above and indicate both salts are associated. $AgNO_3$ in methanol [Busby and Griffiths, 1963] and ethanol [Griffiths *et al*., 1958; Parfitt and Smith, 1963] is more associated than MNO_3. MPic [Coplan and Fuoss, 1964] and $MBPh_4$ [Kunze and Fuoss, 1963] are dissociated in methanol excepy M=K. However, $KBPh_4$ can be considered a dissociated electrolyte with $\alpha = 5.6$ Å, if Fuoss and Hsia's equation is used to evaluate the data. Lithium and Caesium dinonylnapthalene-sulphonates [Little and Singleterry, 1964] are probably associated in methanol but definitely so in ethanol and butanol. The association of lithium and ammonium halides in butanol [Venkatasetty and Brown, 1963] in the range 0-50^{0}C agrees with Bjerrum's model if $\alpha = 3.7$ Å. The Walden product is almost constant in this range of temperatures. Alkali metal salts in alcohols show in general a behavior which may be accounts for by the electrostatic model if the ions are considered solvated. In addition, association is larger for large M^+ indicating that ion pairs are solvent separated. Interesting exceptions are the MRO bases in ROH [Barthel *et al*., 1977] (R= Me. or Et.). For R = Me the salts were considered dissociated but the contact distances increase from 1.74 Å for Li^+ to 3.13 Å for Cs^+. When = Et the bases are associated and K_A goes through a minimum at the potassium salt (K_A=176 for Li^+, 36 for K^+, and 65 for

Cs^+). Barthel and his groups assumed that large cations form solvent-separated pairs but the small ones polarize the solvent molecules around them such that contact pairs are formed.

This assumption is akin to the hypothesis of localized hydrolysis invoked by Robinson and Harned [Robinson and Harned, 1941] to explain the reversal of the order of activity coefficients of alkali metal hydroxides, fluorides, acetates and formates in water.

The mobilities and association constants of tetraalkylammonium (R_4N) halides are larger for iodides suggesting solvation of the anions through hydrogen bonds. In general R_4NI are more associated in ROH than in dipolar aprotic solvents through a minimum for R=Pr. Both these effects shows that the effect is especially marked for bulky cations. Kay, Evans and coworkers [Kay and Evans, 1968; Evan and Broadwater, 1968] have invoked a two step association process similar to the equilibria to explain these results.

The conductance of acids dissolved in alcohols indicates that the proton has excess mobility [Murgulescu *et al*., 1965; Shedlovsky, 1959; Spivey and Shedlovsky, 1967] due to a proton-jump mechanism of transport. HCL is associated in methanol (K_A= 17 $mol^{-1}l$) and in ethanol [Bezman and Verhoek, 1967] (K_A= 48 $mol^{-1}l$). Picric acid is strongly associated in both solvents [DAprano and Fuoss, 1963] (K_A= 3960 and 5870 $mol^{-1}l$ respectively). The amides and N-monoalkylamides have very large dielectric constants such that no association would be expected for (1:1) salts (l =1.5Å in N-monomethylacetamide (NMA) at 32^0C and 2.5Å in formamide (F) at 25^0C). However, a large number of uni-univalent salts show negative deviations from the Onsager limiting law in these solvents and also produce a considerable increase in the viscosity of the solution with increasing concentration. Positive deviations were observed for some uni-univalent salts in acetamide at 94^0C. In F (1:1) salts give small positive deviations [Tewari and Johari, 1963; Dawson *et al*., 1955] with the exceptions of $LiNO_3$, sodium acetate, and Tl^+ salts. Notley and Spiro [Notley and Spiro, 1966] reassessed the conductance of salts in F with equation finding an average α = 1.8 Å. If the conductances are corrected for the increased viscosity of the solution α becomes 3.8 Å. Λ^0 in F increases with the size of the alkali metal and halide ions, while the opposite holds for R_4N^+. In NMA the conductance of alkali metal halides [Dawson *et al*., 1955; French and Glover, 1955] varies linearly with $C^{1/2}$ but the slopes is 5-10% more negative. Even when viscosity corrections were applied to Λ no satisfactory interpretation was found for KCL in NMA [Kortum *et al*., 1968] and in N-methylpropionamide (NMP) [Hoover, 1964]. R_4N salts in NMA give larger negative deviations than alkali metal halides [Dawson *et al*., 1958] and there is evidence [Singh *et al*., 1968] that these salts disrupt the structure of the solvent. A similar behavior was found for 1:1 salts in N-methylformamide (NMF). The suggestion that the continuum model fails in these solvents because ions would depolymerise the solvent chains producing a local region of lower dielectric constant, seems unlikely in view of self-diffusion studies in NMA [Williams *et al*., 1957], of the increase in viscosity produced by increasing electrolyte concentration, and of the fact that polyvalent salts behave according to the continuum model even if conductances are not corrected for viscosity effects. Alkaline earth halides and perchlorates in NMA [Dawson *et al*., 1958] show positive deviations which increase from Ba^{2+} to Mg^{2+} as expected for solvated ions. Johari and Tewari found bivalent sulphates to dissociated in F [Johari and Tewari, 1965] but having small α values, $MgSO_4$ may also be considered slightly associated in F but is completely dissociated in NMF(α=3.38Å). Copper m-benzenedisulphonate shows positive deviations in NMP [Hoover, 1964]. The conductance of 3:3 salts in F [Johari and Tewari, 1965] is in good agreement with the simple electrostatic model, eg., $LaFe(CN)_6$ and $Co(en)_3Co(CN)_6$ have K_A= 243 and 605 respectively, corresponding to α =10.08 and 7.0Å. The values of Λ^0 and K_A indicate that La^{3+} is a larger species in F than the complex ions $Co(en)^{3+}$ or $Co(NH_3)_6{}^{3+}$. The behavior found for the conductance of 1:1 electrolytes in these solvents agrees with some evidence of abnormal equilibrium properties [Held and Criss, 1965; Bonner *et al.*, 1969]. As was in the case for alcohols, it is probable that hydrogen bonded solvents affect the behavior of electrolytes in a way not predicted by the continuum model, this effect being more noticeable with smaller electrostatic interaction between ions.

Conductance measurements of acids in NMA [Dawson *et al.*, 1957] and F [Dawson *et al.*, 1954] indicate that the protons have no excess mobility. Partially substituted ammonium salts show the same behavior as R_4N salts in NMA [Dawson *et al.*, 1955]. In formic acid (1:1) salts were found to be dissociated [Wehman and Popov, 1968]. HCL is associated(K_A=90 mol^{-1}l) due to the acidic nature of the solvent, and formate and H^+ ions have excess mobility suggesting a proton-jump transport mechanism for these ions. Association of weak bases in acetic acid has been studied by conductance. Brewster, Schmid and Schaap [Brewster *et al.*, 1959] found that the anomalous conductances reported in ethanolamine [Briscoe and Dirkse, 1940] are due to solvent impurities. In this solvent small ions are more solvated as indicated by Λ^0, halides are slightly associated and the nitrates, nitrites and thiocyanates more associated. In ethylene and propylene diamines, Br^- has a lower conductance than I^- and R_4NI are more associated than KI [Fowles and McGregor, 1964]. The difference of K_A in both solvents can be accounted for by the change in ε_r.

The large number of conductance measurements for R_4N salts in dipolar aprotic solvents in dipolar aprotic solvents are in fair agreement with the continuum model, with their association being larger for small R. R_4N salts are essentially dissociated in nitromethanes (NM) [Coplan and Fuoss, 1964] with the exception of the bromides and chlorides of R= Me and Et. The Stokes radius of i-Am_4NBPh_4 is 8.3Å in NM [Coetzee *et al.*, 1965], almost the same as in acetonitrile (AN). In nitrobenzene (NB) tetraalkylammonium salts associated [Kay and Evans, 1964] with the association being larger for the smaller cations. They have, however, more associated than in other dipolar aprotic solvents of similar ε_r [Boyd, 1961] suggesting NB is a poor solvating medium. Alkenes carbonates are solvents with large dielectric constants. In ethylene carbonate [Kempa and Lee, 1961], R_4N salts show small negative deviations but the restricted concentration range employed for the conductance measurements does not allow a more detailed analysis of the data. In propylene carbonate (PC) they are dissociated [Fuoss and Hirsch, 1960].

In sulpholane ($TMSO_2$), R_4NClO_4 [Della Monica and Lamanna, 1968] and Et_4NI are slightly associated (K_A=3-6mol^{-1}l) aacording to the Pitts equation with d=5.0Å). In dimethylsulpholane [Eliassaf *et al.*, 1970], $PhMe_3NI$ is associated but Ph_4AsI is not. Recent measurements of conductance of R_4N salts in dimethylsulphoxide (DMSO) show the salts to be essentially dissociated. Unfortunately the study was restricted to very dilute solutions so that not much weight can be put on the ɑ values obtained.

Evans, Zawoyski and Kay analysed data for R_4N salts in acetone (AC) [Reynolds and Kraus, 1948; McDowell and Kraus, 1951; Walden *et al.*, 1926] with the Fuoss-Onsager equation. They found K_A decreases with cation size, and for the anions, association decreases in the order Bu_4NBr (K_A =264)>I^-(143)≅ NO_3^->ClO_4^-(80)>Pic^-(17). This agrees with the data for methylehtylketones [Hughes and White, 1966]. The fact that association of Bu_4NClO_4 [Inami *et al.*, 1961] in AC, benzonitrile, and mehtylehtylketone corresponding to ɑ =4.85Å for the three solvents, indicates formation of contact ion pairs. Tetraalkylammonium halides in dimethylformamides (DMF) [Sears *et al.*, 1955] have small association constants when the data are evaluated with Shedlovsky's equation. When the data for Me_4NPic in DMF [Sears *et al.*, 1956] is assessed with Fuoss and Hsia's equation, ɑ =6.0Å

Acetonitrile (AN) is probably the most commonly employed dipolar aprotic solvent medium for studies of electrolytic conductance. Picrates and halides, hexafluorophosphates [Eliassaf *et al.*, 1970], perchlorates [Springer *et al.*, 1969], nitrates [Berns and Fuoss, 1961] and substituted borates [Brown and Fuoss, 1960] of R_4N^+ cations have been studied conductometrically in AN. Older conductance data for R_4N salts in AN [Walden and Birr, 1929; Kortum *et al.*, 1955; French and Muggleton, 1957] have been re- evaluated. These results show that the association constants for salts of a given R_4N^+ cation vary with change of anion as in AC, hexafluorophosphates and substituted borates being practically dissociated in AN. No association is found for solutions of Am_4N^+ salts and some Bu_4N^+ salts in AN. The behavior of tetraalkylammonium salts in adiponitrile [Sears *et al.*, 1967] is similar to that in AN. Et_4NClO_4 in valeronitrile [Banewicz *et al.*, 1968] has an association corresponding to $\alpha = 3.3$ Å and for Bu_4N^+ in phenylacetonitrile, $\alpha = 5$Å independent of the temperature.

Janz and Dasnyluk [Janz and Danyluk, 1960] have reviewed the conductance data for acids in dipolar aprotic solvents upto 1959. Variations of the conductance of acids with time have been reported for some solvents. The conductances of aged solutions of HBr [Janz and Ahmad, 1964] in benzonitrile and AN and of HCL in the former solvent [Janz and Tomkin, 1973] show the acids are very associated. However, the Λ^0 values obtained are much smaller than expected, e.g., $\Lambda^0_{HBr}=11.8$, $\Lambda^0_{HCL}=1.5$ compared to $\Lambda^0_{HClO4}=51.5$ Ω^{-1} cm^2mol^{-1} in benzonitrile. In AC and nitriles, $HClO_4$ is more associated than Bu_4NClO_4 [Coetzee and McGuire, 1963], the addition of small amounts of water to the acid in AN reduces its association to half of its value due to the efficiency of H_2O in solvating the ions CH_3CNH^+ and ClO_4^-. In DMSO, HCL has $\Lambda^0= 38.7$ Ω^{-1} cm^2mol^{-1} and $K_A=1.15 \times 10^2 mol^{-1}l$ [Bolzan and Arvia, 1970]. In DMF, HPic is more dissociated than HBr, HCL having an even larger association K_A (HCl)=3.5×10^3 at 20^0C) [Thomas and Rochow, 1957]. In AN, HPic is strongly associated [Yeager *et al.*, 1973] suggesting that AN is a poorer solvating medium than DMF and DMSO.

Prue and Sherrington measured the conductance of alkali metal(M) salts in DMF and reassessed existing data for some of these salts in DMSO [Sears *et al*., 1956], dimethylacetamide (DMA) [Lester *et al*., 1956], and dimethylpropionamide (DMP) [Wilhoit and Sears, 1956]. Alkali metal salts are dissociated in in these solvents with the exception of nitrates and LiCl in DMF. The sum of the Stokes' radii for alkali metal salts corresponds to large solvodynamic units, e.g., for KI it is 5.3 Å in DMF, 5.6Å in DMP, and 5.1Å in DMSO. $MClO_4$ in $TMSO_2$ [Della Monica and Lamanna, 1968] and AN [Conti and Pistoia, 1968] are slightly associated while $MBPh_4$ in AN are dissociated [Kay and Evans, 1968] except for $CsBPh_4$. For all these electrolytic solutions the mobilities (excepting Li^+ in $TMSO_2$) and K_A increase with the size of M^+. However, it has been reported [Della Monica and Lamanna, 1968] that for MSCN in $TMSO_2$ association is larger for M=Na.

Irregularities occur in the behavior of salts of small M^+ ions, particularly Li^+, in dipolar aprotic solvents [Fernandez-Prini, 1973]. The association of lithium halides in $TMSO_2$ and AC [Savedoff, 1966] is 2000 times greater for the Cl^- than for I^-. LiCl is 30 times more associated than LiBr in PC. The association constants for these solutions are given where α_{Bj} is the constant distance according to Bjerrum's expression for K_A. Abnormally large K_A values have been reported also for Li p-toluene-sulphonate in AC, for $LiClO_3$ in AN (K_A=401 compared to 5 $mol^{-1}l$ in methanol) for MPic in AC and NB (the effect being larger in NB which is a poorer electron donor). On the other hand NaPic and KPic in DMF [Sears *et al*., 1956] are dissociated (α=4.6 and 5.0Å) according to the Fuoss-Hsia conductance equation. For these picrate solutions, association increases from K^+ to Li^+. The same trend was reported for K_A of alkali metal salicylates [Hughes and White, 1966] in acetophenone and methylethylketone, opposite to the trend for iodides in these solvents. If Bjerrum's model for ion association is applied, the resulting α values for the salicylates are in the range 1.4-1.9Å in methylethylketone and 1.5-2.5Å in acetophenone, compared to α=3.6-3.9 and 6.4-7.6Å for the iodides. The formation of contact ion pairs by the salicylates is supported by the distinct decrease in association when 1% of water is added to the solvent. Stabilisation of ion pairs by the solvent dipoles, invoked by Hyne [Hyne, 1963] to explain the behavior of Bu_4NBr in NB, does not explain the anomalies observed for some alkali metal salts in dipolar aprotic solvents. This hypothesis cannot account for the large increase in K_A when going from LiI to LiCl. Parker has shown that if the ability of dipolar aprotic solvents to solvate cations varies in the order DMSO=DMA>DMF>AC=$TMSO_2$>AN=NM>benzonitrile=NB, many properties of electrolytes in these solvents can be explained. This ordering coincides with that found by Drago and co-workers [Drago *et al.*, 1963] for the electron donating power of dipolar aprotic solvents. It is interesting to note that the anomalies in conductance behavior have been encountered most frequently in the solvents having lower cations solvating power.

At low dielectric constant (ε_r <12), electrostatic ionic interactions are very large and often triple ion formation is encountered. The conductance has been observed to pass through a minimum with concentration, indicating the formation of triple ions, for R_4N-p-toluenesulphonated in triaryl phosphides [French and Tomlinson, 1961], for LiCl and bivalent chlorides in tetrahydrofuran (THF) [Strohmeier *et al.*, 1961], and for $MeEt_3NI$ in CH_2Cl_2 [Beard and Plesch, 1964]. In o-dichlorobenzene (oDCB), Bu_4NHPic [Ralph and Gilkerson, 1964] has very low Λ^0 probably because it dissociates according to the equilibria. The bromide and iodide in oDCB and the picrate in chlorobenzene form triple ions. When only pair formation is observed in these solvents it is usually not necessary to evaluate the data. The simpler Shedlovsky or Fuoss expressions may be employed since the concentration of free ions is very small. However, Treiner and Justice [Treiner and Justice, 1969] have recently used the complete equation with $d=l$ to evaluate the conductance of Bu_4NClO_4 in THF (ε_r=7.39) finding the data can be fitted with extreme precision upto $c = 1.12 \times 10^{-4}$ molar; the value of K_A corresponds to α=4.4Å. The conductance of Bu_4NPic in chlorobenzene, mDCB, and oDCB indicates that the association varies according to the values of the dielectric constant. The Bierrum α values of R_4NPic in oDCB [Curry and Gilkerson, 1957] are lower than expected. Inami, Bodenseh and Ramsey [Inami *et al.*, 1961] observed that the association of Bu_4NClO_4 in ethylene chloride and 1,2 dichloropropane is smaller than that predicted from their dielectric constants and the association found for this salt in other solvents. They pointed out that spectroscopic and dielectric constant measurements give evidence that, in the presence of an electric field, both solvents (Which are in isomeric equilibria between a gauche (polar) form and trans (non-polar) form show an increase in the amount of polar isomer. They suggested that the microscopic ε_r is larger in the neighbourhood of the ions than in the pure solvent, thus decreasing the electrostatic interaction between ions.$MeBu_3NClO_4$ is also less associated in ethylene chloride than in oDCB [Gilkerson and Ezell, 1965] having a similar ε_r. The addition of triphenylphosphine oxide produces a decrease in Λ^0 and K_A, due to specific solvation of the ions. An association smaller than expected in ethylene chloride has been also reported for other substituted ammonium salts [Accascina *et al*., 1953; Zwolenik and Fuoss, 1964]. The association and Λ^0 values of R_4NPic in oDCB decrease with the size of the cations. The contact distance of Bu_4NBr in ethylidene chloride [Bosenseh and Ramsey, 1965] agrees with that found for this salt in other solvents. Evidence for the existence of solvent-separated and contact ion pairs in solutions of alkali metal salts in cyclic ethers has been reported. The conductances of $MBPh_4$ and R_4NBPh_4 [Carvajal *et al*., 1965; Bhattacharyya *et al*., 1965] in THF and dimethoxyethane(DME) indicate that the latter is a better solvating medium. In THF the association of $MBPh_4$ is similar to that of R_4NBPh_4 except for the caesium salt which is much more associated. Stokes' radii are 4.3 and 2.4Å for M=Na and Cs respectively suggesting $CsBPh_4$ forms contact ionic pairs while the the other M^+ only form solvent-separated pairs. In DME, the Stokes' radii for $CsBPh_4$ are very similar and the former is only marginally more associated than $NaBPh_4$. The contact distance for solvent-separated pair is large, e.g., α=7.5 and 7.3Å for $NaBPh_4$ in THF and DME. Spectroscopic and conductance measurements of alkali metal salts of fluorenyl radicals [Ellingsen and Smid, 1969] also indicate that DME is a better solvating medium than THF and that solvent-separated and contact pairs are present in the solutions.

Conductance and NMR measurements agree in suggesting that THF solvates the sodium ion specially [Hammonds *et al.*, 1969]. The conductance of $NaAlBu_4$ in cyclohexane increases abruptly upon the addition of THF to the solution until the ratio salt/THF is 1. This is due to a decrease in association because $NasTHF^+$ is formed. As the concentration of THF increases, Λ decreases slightly up to a value of ¼ for the ratio salt/THF due to formation of $Na\ (THF)_4^+$. From this point onwards, Λ increases according to the variation of ε_r of the solvent mixture. No evidence of solvation was found when benzene or toluene was added to $NaAlBu_4$ in cyclohexane [Hammonds *et al.*, 1969]. For $NaAlEt_4$ in toluene, Λ increases upon addition of diethylether (Et_2O) until $NaEt_2O^+$ is formed [Davies, 1963].

2.3. SOLVENT MIXTURES

In binary mixtures of MeOH, AN and NM having an almost constant ε_r, i-Am_3BuN^+ [Coplan and Fuoss, 1964] salts are dissociated; but the variation of the walden product with solvent composition suggests specific ion-solvent interactions. D'Aprano and Fuoss [D'Aprano and Fuoss, 1963] observed specific effects on the conductance of the Pic^-, Br^- and BPh_4^- of Bu_4N^+ in isodielectric mixtures of dioxin with water, MeOH, AN and p-nitroaniline(PNA). K_A and the Walden products of the salts are reduced when PNA is present in the solvent mixture, the effect being largest for Br^- and least for BPh_4^-, due to anion-PNA interactions which are stronger for the bromide. HPic would in interact with anions even more strongly than PNA

[D'Aprano and Fuoss, 1963]. These interactions seem to depend not on the dipole moment of the added substance but primarily on the facility with which it hydrogen bonds to the anions [Treiner and Justice, 1969].

In MeOH-AN mixtures, $CsClO_4$ and $KClO_4$ [Conti and Pistoia, 1968] become fully dissociated when the medium has 60% of AN, inspite of the small and monotonous change in ε_r with solvent composition. For Bu_4NBr in binary mixtures of NB, EtOH and MeOH with CCl_4 [Sadek and Fuoss, 1959], association is somewhat larger than predicted by the electrostatic model. The excess association decreases in the order NB>EtOH>MeOH which agrees with the solvating power of these solvents. In NB-MeOH mixtures with practically constant ε_r, anomalies are observed in the association of Bu_4NBr [Kay and Evans, 1964; Hyne, 1963]. Specific interactions have been reported between Ag^+ in AC and cycloalkenes [Griffiths *et al.*, 1958], and for the same ion in MeOH when nitroalkanes are added [Busby and Griffiths, 1963]. The association constants of Me_4NNO_3 and Bu_4NNO_3 in AN-CCl_4 [Coetzee *et al.*, 1965], vary according to the predictions of the electrostatic model with contact distances of 4.01 and 5.41Å respectively. In AN-dioxan and MeOH-dioxan mixtures, $LiClO_3$ has α=3.70 and 5.04Å compared to 6.8Å in the water-dioxan mixture, showing that contact pairs are favored in dipolar aprotic solvents and solvent-separated pairs in the protic solvents. Agreement with the electrostatic model has been reported [Treiner and Justice, 1969] for the association of Bu_4NClO_4 and Bu_4NBr in THF with less than 15% of water(α=4.4 and 4.9Å respectively), for CsCl and KCl in EtOH-H_2O, for Bu_4NBPh_4 [Kay and Hawes, 1965](α=7Å) in NB-CCl_4 and in AC-CCL_4 [Berns and Fuoss, 1960; Accascina and Petrucci, 1959]. Alkali metal halides in mixtures of NMA-DMF [Dawson and Wharton, 1960] provide no evidence of specific interactions. Et_4NPic in MeOH-EtOH does not show the anomalies encountered in ROH-H_2O mixtures.

2.4. EFFECTS OF PRESSURE ON THE ELECTROLYTIC CONDUCTANCE

Measurements of conductance at different pressures and temperatures may be used to test the predictions of the continuum model, especially as regards association, and to study the mechanism of the ionic transport.

Skinner and Fuoss measured the conductance of i-Am_4NPic in diethylether and benzene upto 5 x 10^6 Nm^{-2}. Ion pairs and triplets are present because ε_r is small. Since ε_r increases with pressure, the variation of Λ may be expected to depend on the ratio of both associated species. If pairs dominate Λ will increase with pressure. On the other hand, if triple ions predominate. Λ decreases, the actual variation depending on whether the concentration of the solution is smaller or bigger than that corresponding to the minimum conductance. According to the predictions, Λ is found to increase in benzene and to decrease in diethylether where α = 4.9Å for the ion pairs. This behavior was also encountered for Bu_4NPic in where the variation of Λ with pressure depends on the concentration of the solution. The effect of pressure on the conductance of salts and HBr in MeOH has been studied. The mobility of H^+ decreases less with pressure than that of the other ions. For HPic solutions in MeOH, Λ increases with the pressure because the enhanced dissociation of the acid dominates the variation of mobilities. In MeOH, Bu_4NBPh_4 has Walden product constant upto 5 x $10^6 Nm^{-2}$, NaBr shows an increase in the Walden product with pressure, and the R_4N bromides are intermediate cases. Variations of K_A values with pressure were also observed to depend on the particular salt.

Brummer and Hills derived relations between the activation parameters and the variations of conductance with temperature and pressure according to an activated transport mechanism. They have emphasized the importance of the isochoric activation energy in characterizing the energetic of activated transport. Barreira and Hills found that for R_4NPic in NB, E_v is similar for all R and also to the isochoric activation energy for viscous flow of the pure solvent. The activation volume is also practically the same for all the salts. If the rate determining step in ionic transport is displacement of solvent molecules in the neighbourhood of the ions, the different ionic mobilities are due to the fact that the effective movement of the ions caused by the solvent displacement depends on their size.

Similar behavior was found for salts in MeOH and in NB. In DMF at various pressures the conductance of picrates shows that only for large cations is activation volume independent of cationic size. The variation of conductance with temperature and pressure for R_4NI in AC [Adams, 1967] show activation volume for transport is almost independent of ionic size. It is found to be similar for conductance of dilute solutions, solvent self-diffusion and viscosity for a number of solvents. There is evidence that ions are not followed by their solvation sheaths when they move. From these studies it is suggested that the free volume of the solvent is an important parameter in determining the mobility of ions.

2.5. SPECTROPHOTOMERIC/SPECTROSCOPIC METHOD

Infrared Spectroscopy has been a widely used tool for the study of organic solvent systems for many years and the techniques involved can be learned from many good monographs [Luthian, 1969; Alpert *et al*., 1970; Davies, 1963; Bauman, 1962; Colthup *et al*., 1964]. Raman spectroscopy has also been employed to provide significant information about the constitution and physical properties of the systems. Infrared and Raman are complementary forms of spectroscopy. Both provide information about the vibrational and rotational modes of motion of polyatomic molecules and crystals. The absorption of infrared radiation occurs when the dipole moment changes during a vibration. The frequency of the absorbed radiation is directly relatable to the frequency of the vibration. This change may occur when no dipole moment change occurs, as during a symmetric stretching vibration of a homonuclear diatomic molecule. Many non-aqueous solvents possess a rich vibrational spectrum of their own. This presents the spectroscopic with severe problem. Although, for electrochemical reasons, it may wish to study a particular solute in a particular solvent, the interference resulting from overlap of bands of the solvent with those generated by the solute, or species such as ion pairs or solvates formed after dissolution, may make the interpretation impossible. In addition to the normal modes of vibration, combinations, and overtones, many organic liquids generate low frequency Raman lines (30-85 cm^{-1} region) [Blatz, 1967; Waldstein and Blatz, 1967]. The low frequency lines shift and intensity changes occur on addition of a solute such as $AgNO_3$ or $Zn(NO_3)_2$. Such modes are also found in the far infrared spectra of polar solvents and have been attributed to dipole-dipole complexes or clusters [Jakobsen and Brasch, 1964; Bulkin, 1969]

In 1965, Edgell and co-workers [Edgell and Watts, 1965] reported an infrared band, from solutions of alkali metal salts of $Co(CO)_4^-$ dissolved in tetrahydrofuran (THF), which was assigned to the cation vibrating in a solvent cage. French and Wood also studied salts of BPh_4^-. The value of 175 cm^{-1} which they report for $NaBPh_4$ in THF has not been reproduced and 194 to 198 cm^{-1} appears to be a better value. Because the frequency was insensitive to solvent for $NaBPh_4$ in Py, D, Pip and THF they ascribed the band to contact ion pairs. The change of extinction coefficient with solvent, cation and concentration, and the isotopic shift were also reported while possible ion-pair potential functions were considered.

Electrolyte chemists turn to non-aqueous solvents to explore the effect of a changing, and usually low, dielectric constant on the degree of ion pair formation and to observe differences attributed to a changed solvation sphere, specific solvation or changed solvent structure. The stretching vibration of an ion pair M^+ - A^- may be detectable by infrared spectroscopy. If A^- is a polyatomic anion, however, new lines characteristic of a ‘bound’ species may be detected. Janz and co-workers have observed that the stretching mode of nitrate ion can be resolved into two Raman active components at 1041 and 1036 cm^{-1} for $AgNO_3$-CH_3CN. Because the lines are very intense it has been possible to follow the intensity ratio down to 0.034M. Good agreement was obtained between the degree of ion-pair formation measured by and that obtained from conductance using the Wishaw-Stokes equation.

In order to elucidate the mechanism of extraction of nitrates by tri-n-butyl phosphate (TBP) several authors have examined the infrared frequencies of metal nitrates in TBP [Ferraro, 1959; Katzin, 1962].The magnitude of the separation of a component lines in the region of 1380 cm^{-1} was considered to be a measure of the dis-symmetry induced in the nitrate group. The presence of a diagnostic metal-nitrate Raman vibration provides the strongiest evidence for covalence in such an interaction [Irish, 1971]. The splitting in tri-n-octyl phosphine oxide (TOPO) in CCl_4 and tri-octyl amine nitrate was inferred, the metal being the principal factor controlling the magnitude of the separation; the influence of the medium is small [Verstegen, 1964]. Infrared bands of inorganic nitrates in acetone have also been tabulated [Nortwitz and Chasan, 1969].

Solvation of Zn^{2+} by acetonitrile in the system $ZnCl_2$-CH_3CN-H_2O was inferred from Raman spectral studies by Evans and Lo [Evans and Lo, 1965]. Bands characteristic of two distinct forms of CH_3CN, in equilibrium, were observed. The complex involved zinc-containing species and was not influenced greatly by the nature and number of other ligands attached to zinc. It was shown that the complex formation caused an increase in the C-N stretching force constant. Raman spectra of $ZnCl_2$, $HgCl_2$, LiCl and HCL in methanol have been investigated [Kecki, 1962]. A set of equilibria involving $ZnCl_2L_4$, $ZcCl_4L_2^{2-}$ and a possible $(ZnCl_2)_{2n}$ polymer were invoked for $ZnCl_2$, somewhat as in aqueous solution [Irish *et al*., 1968] although no attempt was made to measure species concentrations. Similar complex ions were proposed for mercuric chloride and evidence for ion pairs was discovered in methanol solutions of LiCl and $CaCl_2$. The vibrational spectrum of zinc chloride in triphosphate (TBP) diluted with benzene, acetone or pyridine has also been studied. Bands at

345 cm^{-1} and 305 cm^{-1} were attributed to a $ZnCl_2$ species of symmetry (bent molecule) when TBP: $ZnCl_2$ ratio is less than 2:1.[Coates and Ridley, 1964]

Silver thiocyanate-pyridine solutions have been investigated with infrared spectroscopy [Larsson and Miezis, 1968]. The intensities of the C-N stretching vibration of free SCN^- (2059 cm^{-1}) and S-bonded mononuclear complexes (2089 cm^{-1}) were measured for various compositions. Stability constants were obtained by the graphical method of Fronaeus [Fronaeus, 1963] for the species AgSCN, $Ag(SCN)_2$, $Ag(SCN)_3$. Minc, Kecki and Kryzwicki [Minc *et al.*, 1963] had also noted that LiCl and $LiClO_4$ affect the molar intensity in opposite ways. Explanations in terms of ion pairs were advanced. A correlation between molar intensity of v (C-O) and cation electric-field intensity is discussed in terms of bond polarity [Kurowski and Minc, 1963]. A new line at 1112 cm^{-1} has been tentatively assigned to a LiCl complex in methanol [Hester and Plane, 1967]. Bufalini and stern [Bufalini and Stern, 1959] have reported on the effect of a number of electrolyts on the infrared spectra of some hydrogen bonded compounds (methanol, 1-butanol, t-butanol, N-methylacetamide) when both are dissolved in dilute benzene solution. They noted that the absorption maximum of methanol associated to the electrolyte decreased with increasing anion radius, $ClO_4^- < NO_3^- < Br^- < Cl^-$. Picrate produced no shifted peak. Lund [Lund, 1958] reported a similar correlation with apparent molar volume of the anions, for a series of tetrabutylammonium salts in chloroform containing 0.10 M p-cresol; for the same series the apparent integrated intensity increased when the apparent molar volume decreased. Minc et al., [Minc *et al.*, 1963] in a more extensive Raman study of perchlorates in acetone, show that the cation affects the line positions and integrated molar intensities in the order $Na^+ < Li^+ < Ba^{2+}$. The perchlorate ion spectrum was most perturbed for $LiClO_4$. Perchlorate ion and hexane were both found to cause destruction of the the dipole structure of acetone. The acetone-cation interaction is considered to be a similar to hydrogen bond formation, causing the C=O bond to weaken and the C-C-C angle to decrease. The larger size of Ba^{2+} is partly responsible for greater affects on the lines of acetone, whereas formation of Li^{+}-ClO_4^{-} ion pairs could cause the pronounced changes of the perchlorate spectrum and reduce the Li^{+} -acetone interaction. Changes in the infrared spectra of acetonitrile caused y dissolved $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, NaI or LiI were studied by Perelygin [Perelygin, 1962]. Perchlorate ion had no effect on the absorption bands. The blue shift of the C≡N vibration and C-C vibration and the increase of intensity of the CH_3 band were attributed to binding to cations. Evidence that I^{-} binds to the CH_3 group was also presented. Kecki [Kecki, 1970] has reported that the C-C and C≡N infrared stretching bands of acetonitrile are split into two components on addition of Cu^{2+}, Ni^{2+}, Co^{2+} and Na^{+}. One band is at the position of the pure solvent. The second, at higher frequencies, is attributed to acetonitrile solvating the cations; the shift is larger for the transition metal ions.

Vibrational spectra of many inorganic crystalline compounds, in which molecules of interest to the non-aqueous solution chemist are bonded to metal ions, have been tabulated by Adams [Adams, 1967] and Nakamoto [Nakamoto, 1970]. Frequencies of similar species in solution will be displaced from those of the solids because of the change of state, but the latter provide guidance for the assignment of the former. The intensities of polarized Raman bands of binary mixtures of many solvents have been studied over a wide concentration range by Fini and his groups [Fini *et al.*, 1968]. The scattering coefficient increases, in most cases linearly, with the refractive index of the mixture and is in good agreement with a theoretical formula, derived from Onsager’s theory of dielectric polarization [Mirone, 1966].

Spectroscopic methods have been employed extensively to study ion-pairing phenomena and often have advantages over other techniques, especially for the study of very complicated equilibria. They have provided valuable information about the binding sites of multidentate ligands and on the kinetics and structures of many species in solution. IR-

Spectrometry is a powerful tool for investigating fast equilibria between free ions and associated species in non-aqueous solution [Irish *et al*., 1963]. IR spectroscopy resembles Raman spectroscopy in that it provides information on the vibrational and rotational energy levels of a species, but it differs from the latter techniques in that it is based on studying the light transmitted through a medium after absorption and not that scattering by light [Das, 2008]. In most cases internal vibration of the polyatomic anions are used as probes of cation-anion interactions [Debye and Huckel, 1923]. The technique of Raman and IR spectroscopy are generally considered complementary in the gas and solid phases because some of the species under study may reveal themselves in only one of the techniques. Nevertheless, it must be stressed that Raman scattering is not affected by an aqueous medium, whereas the strong absorption in the infrared shown by water proves to be a troublesome interfering factor in the study of aqueous solution by the IR method.

3. METHODOLOGY

3.1. Methods

Solvent properties such 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. Conductance study is a very important tool in obtaining the information regarding the solvation and association behavior of ions in solutions [Dogonadze *et al.*, 1986]. Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The solvation behavior of ions in solutions can well understand in terms of ion-solvent, ion-ion and solvent-solvent interactions. Variation in the dielectric constant and viscosity in solvents due to mixing, leads to a better understanding of ion-ion and ion-solvent interactions. The use of mixed solvents in high energy batteries has also extended the horizon in the field of mixed solvent systems [Aurbach, 1999; Roy *et al.*, 2006]. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent. The electrical conductivities of the pure and mixed solvent solutions of the selected salts were measured at different temperatures. The limiting equivalent molar conductance (Λ_0), the association constant (K_A) of ion pair and limiting equivalent of triple ion(Λ_0^T) and triple ion formation(K_T) of the selected salts were calculated by using Shedlovsky [Shedlovsky, 1932], Fuoss [Fuoss, 1978] and Fuoss-Kraus method [Fuoss & Kraus, 1933]. The molar conductances (Λ) for all studied solution system have been calculated using following equation [El-Dossoki, 2010]

$$\Lambda = 1000\kappa/c \qquad \ldots(48)$$

A brief account on theories and equation used in our investigation are outlined below:

3.2. Evaluation of limiting molar conductance (Λ_0) and association Constant (K_A) of electrolytic salts by Shedlovsky technique.

The conductance data of the chosen simple and complex salts were analyzed by using Shedlovsky method [Shedlovsky, 1932].

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right) \qquad \ldots(49)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are given by [Shedlovsky and Kay, 1956]

$$S(z) = \left(\frac{z}{2}\sqrt{1+\left(\frac{z}{2}\right)^2}\right)^2 \;; \qquad Z = \left[\frac{\propto\Lambda_o+\beta}{\Lambda_o^{s/z}}\right](C\Lambda)^{1/2}$$

Applying the Debye-Huckel-Onsager conductance equation, α and β values were found as follows:

$$\Lambda = \Lambda_o - \left[\frac{29.15 \text{ X } 3\sqrt{3}}{(DT)^{1/2}} + \frac{9.90 \text{ X } 10^5}{(DT)^{3/2}}\Lambda_o W\right]\sqrt{C(Z_+ + Z_-)}$$

$$= \Lambda_o - \beta + \alpha\Lambda_o)\sqrt{C}$$

Therefore,

$$\beta = \frac{151.47}{(DT)^{1/2}\eta}, \; \alpha = \frac{17.147 \text{ X } 10^5}{(DT)^{1/2}}W, \qquad \text{(for 2:1 electrolytes)}$$

$$\beta = \frac{82.501}{\eta(DT)^{3/2}}, \; \alpha = \frac{0.8204 \text{ x } 10^6}{(DT)^{3/2}}, \qquad \text{(for 1:1 electrolytes)}$$

Where, $w = Z_+Z_- \frac{2q}{1+q^{1/2}}$

$$q = \frac{Z_+Z_-}{Z_+ + Z_-}\frac{\lambda_+\lambda_-}{Z_+\lambda_- + Z_-\lambda_+}$$

Z and λ are the valence and conductance of the ions respectively excluding their signs, D the dielectric constant of the medium, η the viscosity coefficient of the medium. The degree of dissociation (τ) is related to S(Z) by the equation.

$$-\log f_\pm = \frac{Az_+z_-\mu^{1/2}}{1+BR\mu^{1/2}} \qquad \ldots(50)$$

Where, $A = \frac{1.8247x10^6}{(DT)^{3/2}}$; $B = \frac{0.5029x10^{10}}{(DT)^{1/2}}$;$\mu = \frac{1}{2}\sum_i(c_i\tau_i)z_i^2$

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no precise method [Hogman *et al.*, 1956] for determining the value of R'. In order to treat the data in our system, the R' value is assumed to be R' = a + d, where 'a' is the sum of crystallographic radii of the ions approximately equal to 5A^0 and 'd' is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by [Fuoss and Onsager, 1955]

$$d = 1.183\left({}^{M}/_{\rho}\right)^{1/3} \text{Å} \qquad \ldots(51)$$

Where M is the molecular weight of the solvent and ρ is the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{avg} = \frac{M_1M_2}{X_1M_2 + X_2M_1} \qquad \ldots(52)$$

X_1 is the mole fraction of methanol of molecular weight M_1 and X_2 that of water of molecular weight M_2. An initial value of Λ_0 was obtained by least square method (Λ and concentration C was introduced as input in a computer programmed). The mean activity coefficient $f_{\pm}$ was determined by equation (13) for the above chosen simple and complex salts [Akhadov, 1981]. From the linear plot of $1/\Lambda S(Z)$ versus $C\,\Lambda f_{\pm}^{2}S(Z)$; Λ_0 and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope (K_A/Λ_0^2) respectively [Glasstone, 1942].

As per Shedlovsky method, an initial value of λ^o was obtained from the intercept of the linear Onsager plot of Λ versus $c^{1/2}$, λ^o is obtained from the literature at 25°C and at other temperatures it was obtained by using the following equation [Bag *et al.*, 2009]:

$$\lambda_t^0 = \lambda_{25}^0[1 + \alpha'(t - 25)] \qquad \ldots(53)$$

α' is constant. Using these values of Λ_o, λ^o_-, λ^o_+, z, s(z) and r values were calculated. The mean activity coefficient f was determined by equation (20) for the above chosen complex salts. From the linear plot of $1/\Lambda S(Z)$ versus $C\,\Lambda f_{\pm}^{2}S(Z)$; Λ_o and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope K_A/Λ_0^2 respectively [Nelson and Errington, 2005] . The procedure was repeated using these new values of Λ_0 and K_A.

3.3. Evaluation of limiting molar conductance (Λ_0) and association Constant (K_A) of electrolytic salts by Fuoss technique.

The conductance data in mixed solvents have been analyzed in terms of the limiting molar conductance (Λ_0) and the ion-association constant ($K_{A,c}$) of the electrolytes using Fuoss conductance-concentration equation, resolved by an iterative procedure programmed in a computer as suggested by Fuoss [Fuoss, 1978]. So with a given set of conductivity values $(c_j, \Lambda_j,\ j = 1, \ldots\ldots n)$, three adjustable parameters, the limiting molar conductance (Λ_0), the association constant ($K_{A,c}$) and the distance of closest approach of ions (R) are derived from the Fuoss conductance equation. Since there is no precise method [Per, 1977] for determining the R-value and for the electrolytes studied no significant minima were observed obtained in the σ_Λ versus R- curves and thus in order to treat the data in our system, R-values were preset at the centre-to centre distance of solvent separated ion-pairs, i.e., R = a + d; where $a = (r_+ + r_-)$ is the sum of the crystallographic radii of the cation (r_+) and anion (r_-) and d is the average distance corresponding to the side of a cell occupied by a solvent molecule.

The Fuoss conductance equation may be represented as follows:

$$\Lambda = P\Lambda_0[(1 + R_X) + E_L) \quad \ldots(54)$$

$$P = 1 - \alpha(1 - \gamma) \quad \ldots(55)$$

$$\gamma = 1 - K_A c\gamma^2 f^2 \quad \ldots(56)$$

$$-\ln f = \beta\kappa/2(1 + \kappa R) \quad \ldots(57)$$

$$\beta = e^2/(\varepsilon_r k_B T) \quad \ldots(58)$$

$$K_A = K_R/(1 - \alpha) = K_R/(1 + K_S) \quad \ldots(59)$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current, k^{-1} is the radius of the ion atmosphere, ε_r is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall paring constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance. The computations were performed using a program suggested by Fuoss.

The best value of a parameter is the one when equations is best fitted to the experimental data corresponding to minimum standard deviation δ for a sequence of predetermined R values, and standard deviation δ was calculated by the following equation

$$\delta^2 = \sum[\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2/(n - m) \quad \ldots(60)$$

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).

3.4. Evaluation of limiting molar conductance of triple ion (Λ_0^T) and triple ion formation constant (K_T) of electrolytic salts by Fuoss- Kraus technique.

The conductance data have been analyzed by the classical Fuoss-Kraus theory of triple-ion formation [Fuoss-Kraus, 1933] in the form

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right) c \qquad \ldots(61)$$

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

$$g(c) = \frac{\exp\{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \qquad \ldots(62)$$

$$\beta' = 1.8247 \text{ X } 10^6/(\varepsilon T)^{1.5} \qquad \ldots(63)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \text{ X } 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad \ldots(64)$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution, $\mathbf{\Lambda_0^T}$is the sum of the conductance value of the two triple-ions and $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants respectively and S is the limiting Onsager coefficient.

Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T, respectively, have also been calculated using the following equations [Nandi *et al.*, 1993]

$$\alpha = 1/(K_P^{\frac{1}{2}}.c^{\frac{1}{2}}) \qquad \ldots(65)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \qquad \ldots(66)$$

$$C_P = c(1-\alpha-3\alpha_T) \qquad \ldots(67)$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \qquad \ldots(68)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions present in the salt-solutions.

3.5. Evaluation of thermodynamic parameters

Thermodynamics properties for the association, viz., changes free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) for the ion-pair formation have been calculated from the values of association constants at different temperatures. The enthalpy change (ΔH^0_{ass}) is related to the changes in the number and strength of the bond in the process. The entropy change (ΔS^0_{ass}) is a measure of the change of randomness when comparing the association constant of some selected transition metals in pure and mixed solvents, one need a comparison of ΔG^0_{ass} for the process. The ΔG^0_{ass} can be calculated by using the Van't hoff isothermal correlation.

$$\Delta G^0 = \Delta H^0_{ass} - T\Delta S^0_{ass} \qquad \ldots(69)$$

Free energy of association process (ΔG^0_{ass}) was calculated from the equation

$$\Delta G^0 = -RT\ln K_A \qquad \ldots(70)$$

The entropy change of association (ΔH^0_{ass}) was obtained from the slope of log $K_A$vs 1/T. the change of association entropy (ΔS^0_{ass}) was calculated from the Gibbs Helmholtz equation

$$\Delta S^o_{ass} = \frac{\Delta H^o_{ass} - \Delta G^o_{ass}}{T} \qquad \ldots(71)$$

3.6. Calculation of walden product

The trend in Λ_o and ion-association can be discussed through another characteristic function called the Walden product ($\Lambda_0\eta_0$) (product of the limiting molar conductance at infinite dilution and solvent viscosity) This is justified as the Walden product of an ion or solute is inversely proportional to the effective solvated radius (r_{eff}) of the ion or solute in a particular solvent/solvent mixtures [Bhat and Bindu, 1995].

$$\Lambda_0\eta_0 = \frac{1}{6\pi r_{eff}T} \qquad ...(72)$$

Therefore, variation of Walden product ($\Lambda_0\eta_0$) with the change in the composition of the solvent reflects the solvation of the ions [Conway *et al.*, 1965]. Another suggestion that has been made to explain this fact is that the ion in solution is so completely surrounded by solvent molecules [Conway, 1978] which move with it, it is so extensively 'solvated' that its motion through the medium is virtually the same as the movement of the solvent molecules past one another in viscous flow of the solvent. The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ($\lambda_0^{\pm}\eta_0$), (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant.

The $\lambda_0^{\pm}$ values were in turn utilized for the calculation of Stokes' radii (r_s**)** according to the classical expression [Robinson and Stokes, 1959]

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^{\pm} r_c} \qquad \ldots(73)$$

where, r_s is the Stokes' radii, r_c is the crystallographic radii, N_A is the Avogadro's no., $\lambda_o^{\pm}$ is the limiting ionic conductance and F is the Faraday Constant.

The significance of the term had since then been realized due to the development Debye-Hückel theory [Debye and Hückel, 1923] of inter-ionic attractions in 1923. The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory and is given by the Falkenhagen and Vernon [Falkenhagen and Vernon,1983] equation:

$$A_{\text{Theo}} = \frac{0.2577\Lambda_0}{\eta_0(\varepsilon T)^{0.5}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0\lambda_-^0}{\Lambda_0}\right)^2\right] \qquad \ldots(74)$$

where the symbols have their usual significance. If A-coefficient is negative and very small, shows that the existence of the ion-ion interaction negligible, as compared to the ion-solvent interaction in the studied solvents.

3.7. Calculation of solvation number n_s

The number of solvent molecules that are involved in the solvation of the ion is called solvation number (n_s). 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 as well as the ILs.

If the limiting conductance of the ions ($\lambda_o^{\pm}$) of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law and the volume of the solvation shell is given by the equation.

$$V_s = \left(\frac{4\pi}{3}\right)(r_s^3 - r_c^3) \qquad \ldots(75)$$

where r_c and r_s is the crystallographic and Stokes' radius of the ions. The solvation number n_s would then be obtained from

$$n_s = \frac{V_s}{V_0} \qquad \ldots(76)$$

Where V_o is the volume of the solvent molecules.

3.8. Calculation of diffusion coefficient (D)

The diffusion coefficient (D) is obtained using the Stokes-Einstein Relation:

$$D = \frac{K_B T}{6\pi\eta_0 r_s} \qquad ...(77)$$

Where k_B is the Boltzmann’s constant, T is the temperature, η_0 is the solvent viscosity and r_s is the Stoke’s radius.

The ionic mobility was obtained using the following equation

$$i_{\pm} = \frac{z_{\pm}F}{R_g T} D \qquad …(78)$$

where $z_{\pm}$, F, R_g, T and D is the ionic charge, Faraday constant, universal gas constant, temperature and diffusion co-efficient respectively.

3.9. Physical Measurements

3.9.1. Conductance Measurements: The electrical conductivities were measured by using EUTECT- PC-700 Conductivity Bench top meter with Epoxy 2 cell (K=1.0) digital conductivity bridge (accuracy ± 0.1%) with a dip type immersion conductivity cell.

3.9.2. Temperature Control

The temperature was control in the range of 10-40^{o}C by using refrigerated Bath and Circulator - Cole-Palmer, Polystat R6L with the help of thermometer. The accuracy of the temperature measurement was ± 0.01^{o}C.

3.9.3. Measurement of Weights

The measurement of weights was done accurately by using a METTER Balance, Model-Ae260, Delta Range.

3.9.4. Computations

The computations were performed using a program suggested by Shedlovsky, Fuoss and Fuoss-Kraus.

The complexes, Ionic Liquids were verified by comparing their IR spectrums obtained from NICOLET iS10 FT-IR spectrometer with the IR spectrums obtained from **Gaussian 09W.Gaussian 09W, Revision A.02**, program package (Gaussian Inc.) is a computational software with which **Gauss View 5.0.9** is used for graphical interface which is necessary for input and output analysis. In Gaussian calculation, the geometrical optimization and harmonic vibrational frequencies of the complexes are calculated under gas phase using the Density Functional Theory (DFT) with B3LYP three- parameter hybrid functional proposed by Becke [Becke, 1993]. The B3LYP functional comprises an exchange-correlation functional that mixes the nonlocal Fock exchange with the gradient-corrected form of Becke [Becke, 1988] and adds the correlation functional proposed by Lee et al. [Lee *et al.,* 1988]. Unrestricted calculations are needed for processes such as bond dissociation which requires the separation of an electron pair [Foresman *et al.,* 1996] and diffuse functions are necessary for describing the weak bond interaction. Therefore, for all calculation u6-311++G basis set is used. Gauss View 5.0.9 is a graphical user interface designed to help me prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. Gauss View 5.0.9 is not integrated with the computational module of Gaussian, but rather is a front-end/back-end processor to aid in the use of Gaussian. Gauss View 5.0.9 provides me three main benefits as Gaussian users (Gaussian.com, 2016).

First, through its advanced visualization facility, Gauss View 5.0.9 allows me to rapidly sketch in even very large molecules, then rotate, translate and zoom in on these molecules through simple mouse operations. It can also import standard molecule file formats such as PDB files.

Secondly, Gauss View 5.0.9 makes it easy to set up many types of Gaussian calculations. It makes preparing complex input easy for both routine job types and advanced methods like ONIOM, STQN transition structure optimizations, CASSCF calculations, periodic boundary conditions (PBC) calculations, and many more. Gauss View 5.0.9 can be used to launch jobs as well if Gaussian is installed on the same computer. Lastly, default can be define and named calculation templates, known as schemes, to speed up the job setup process. Finally, Gauss View 5.0.9 lets me examine the results of Gaussian calculations using a variety of graphical techniques. Gaussian results that can be viewed graphically include the following:

Optimized molecular structures.

Molecular orbitals.

Electron density surfaces from any computed density.

Electrostatic potential surfaces.

Surfaces for magnetic properties.

Surfaces can also be viewed as contours.

Atomic charges and dipole moments.

Animation of the normal modes corresponding to vibrational frequencies.

IR, Raman, NMR, VCD and other spectra.

Molecular stereochemistry information.

3.10. Materials

3.10.1. Ligands

The following ligands were selected for the preparation of the mixed ligand complexes

(i) Cystein

(ii) Serine

(iii) Histidine
(iv) Benzoyl isothiocyanate
(v) N-(benzyolamino)-thiozomethyl]-cystein
(vi) N-(benzyolamino)-thiozomethyl]-serine
(vii) N-(benzyolamino)-thiozomethyl]-histidine
(viii) The cystein, serine and histidine of analytical reagent grade were directly purchased from Merck Company and used as such. The ligands, N-(benzyolamino)-thiozomethyl]-cystein, N-(benzyolamino)-thiozomethyl]-histidine and N-(benzyolamino)-thiozomethyl]-serine were prepared for the following methods of A.T. Kabbani and co-workers [Kabanni *et al.*, 2005; El-Hammamy *et al.*, 2010].

i. Preparation of benzoyl isothiocyanate

A mixture of Benzoyl chloride (0.01mol) and ammonium thiocyanate (0.01mol) in 25ml acetone was refluxed with stirring for 1 hour, then filtered and the filtrate was used for further reaction.

ii. Preparation of N-(benzyolamino)-thiozomethyl]-cystein

0.01 mol of cystein from 25ml pure dry acetone were added rapidly onto the solution of benzoyl isothiocyanate and refluxed for 6 hrs, after which excess cracked ice was poured into the mixture with vigorous stirring. The resulting solid was collected, washed with water and then with acetone and recrystallized from ethanol. (m.p=176^{o}C).

iii. Preparation of N-(benzyolamino)-thiozomethyl]-serine

0.01 mol of serine from 25ml pure dry acetone were added rapidly onto the solution of benzoyl isothiocyanate and refluxed for 6 hrs, after which excess cracked ice was poured into the mixture with vigorous stirring. The resulting solid was collected, washed with water and then with acetone and recrystallized from ethanol. (m.p=210^{o}C).

iv. Preparation of N-(benzyolamino)-thiozomethyl]-histidine

A 0.01 mol of histidine from 25ml pure dry acetone were added rapidly onto the solution of benzoyl isothiocyanate and refluxed for 6 hrs, after which excess cracked ice was poured into the mixture with vigorous stirring. The resulting solid was collected, washed with water and then with acetone and recrystallized from ethanol. (m.p=125^{o}C).

3.10.2. Preparation of the compounds/ Complexes

i. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein manganese (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of manganese (II) chloride tetrahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight**.**

ii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein cobalt (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of cobalt (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight**.**

iii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein nickel (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of nickel (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight**.**

iv. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein copper (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of copper (II) chloride dihydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight**.**

v. Preparation of N-[(benzoyl-amino)-thioxomethyl]-serine manganese (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-serine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of manganese (II) chloride tetrahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight

vi. Preparation of N-[(benzoyl-amino)-thioxomethyl]-serine nickel (II) chloride

1.24 mmol of N-(benzyolamino)-thiozomethyl]-serine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of nickel (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight

vii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-histidine manganese (II) chloride

1.24 mmol of N-(benzyolamino)-thiozomethyl]-histidine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of manganese (II) chloride tetrahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitates appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

viii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-histidine nickel (II) chloride

1.24 mmol of N-(benzyolamino)-thiozomethyl]-histidine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of nickel (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

ix. Preparation of Tetraammine Copper (II) sulfate.

The complex was synthesized as described by [Glemser and Sauer *et al.*, 1963]. 6 g of copper(II) sulphate pentahydrate dissolves in 15 mL of deionized water. The solution was then heated to the fume hood and adds conc NH_3 until the precipitate that initially forms has dissolved. Cool the deep blue solution in an ice bath. Cool 20 mL of 95% ethanol to ice bath temperature and then slowly add it to the solution. The blue, solid complex is then form and filtered in a filter paper, washed with two 5-mL portions of cold 95% ethanol and 5 mL of acetone. The product was dried at room temperature. The amount of the product is 6g, corresponding to a yield of 96%.

x. Preparation of Tris(ethylenediamine) copper (II) sulphate pentahydrate:

The complex was synthesized as described by [Girolami *et al.*, 1999]. 6 g of copper(II) sulphate pentahydrate dissolve in 10 mL of warm deionized water. The solution cooled in an ice bath and slowly adds 10 mL ethylenediamine. The mixture cooled again in an ice bath. The cold 15 mL of 95% ethanol slowly add it to the solution. The mixture allows settling for complete precipitation. The precipitate filtered in a filter paper, washed with two 5-mL portions of cold 95% ethanol and 5 mL of acetone. The product was dried at room temperature. The amount of the product is 6g, corresponding to a yield of 95%.

xi. 1-butyl-4-methylpyridinium hexafluorophosphate[4MBPPF$_6$]

xii. 1-ethyl-3-methylimidazolium nitrate [EMIm]NO$_3$

xiii. 1-ethyl-3-methylimidazolium methanesulfonate [EMIm]CH$_3$SO$_3$

xiv. 1-ethyl-3-methylimidazolium tosylate [EMIm]Tos

xv. 1-butyl-3-methylimidazolium hexafluorophosphate [BMimPF$_6$]

xvi. 1-benzyl-3-methylimidazolium hexafluorophosphate [BZMimPF$_6$]

Also the above six ILs selected for the present work puriss grade was procured from Sigma-Aldrich, Germany and the mass fraction purity of the ILs was$\geq$ 0.95.

3.11. Elemental analysis of few complexes

Table 1: Elemental analysis data of some N-[(benzoyl-amino)-thioxomethyl]-amino acids and their metal complexes.

Compound	Stoichiometry	% C		% H		% N	
		Calc.	(Found)	Calc.	(Found)	Calc.	(Found)
N-[(benzoyl-amino)-thioxomethyl]-cystein + $MnCl_2$	MLCl	34.95	(34.40)	2.67	(2.42)	7.25	(7.20)
N-[(benzoyl-amino)-thioxomethyl]-cystein + $CoCl_2$	MLCl	35.19	(34.39)	2.75	(2.41)	7.27	(7.19)
N-[(benzoyl-amino)-thioxomethyl]-cystein + $NiCl_2$	MLCl	35.31	(34.44)	2.81	(2.43)	7.30	(7.18)
N-[(benzoyl-amino)-thioxomethyl]-cystein + $CuCl_2$	MLCl	35.55	(34.43)	2.87	(2.48)	7.32	(7.21)
N-[(benzoyl-amino)-thioxomethyl]-serine + $MnCl_2$	MLCl	33.98	(31.81)	2.61	(2.52)	7.21	(7.15)
N-[(benzoyl-amino)-thioxomethyl]-serine + $NiCl_2$	MLCl	34.65	(33.52)	2.67	(2.57)	7.29	(7.20)
N-[(benzoyl-amino)-thioxomethyl]-histidine + $MnCl_2$	MLCl	31.64	(29.89)	2.53	(2.46)	7.20	(7.17)
N-[(benzoyl-amino)-thioxomethyl]-histidine + $NiCl_2$	MLCl	31.28	(29.87)	2.63	(2.49)	7.27	(7.21)

4. RESULTS AND DISCUSSIONS

4.1. Ion association of copper complexes in aqueous medium at different temperature: A conductance method.

4.1.1. Introduction

Inorganic compounds are used as catalysts, pigments, coatings, surfactants, medicines, fuel and more. They often have high melting points and specific high or low electrical conductivity properties, which make them useful for specific purposes [Elschenbroich and Salzer, 1992; Cotton, 1990]. The salts selected for the present work, ie., Tetraammine Cu (II) sulfate and tris(ethylenediamine) Cu (II) sulfate complexes. Tetraammine Cu (II) sulfate is often used as starting material to make ammonium sulfate. Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides and fungicides. Tetraammine Cu (II) sulfate is an excellent chemical to dye fabrics [Morrison, 1969]. Water is a universal solvent. A greater number of substances dissolve in it than in any other liquid, a good solvent for dissolving many solids, serving as an excellent coolant both mechanically and biologically, and acting as a reactant in many chemical reactions [Debenedetti and Stanley, 2003]. Among the various methods' the conductance method is one of the most sensitive and widely used methods for investigation of physico-chemical nature of ion-pair formation of simple and mixed solvents [Conway, 1981; Schwartz, 1995; Ue, 1994]. Ion pair formation process is a kind of very important chemical reaction whose theoretical and experimental studies are significant to the revealing of the microscopic dynamics of gas phase, liquid-phase reaction and the upper-space atmospheric reaction. In solvents of low dielectric constant ,where the electrostatic potential energy of an anion and a cation at contact is large compared to mean thermal energy kT, it is expected the association of ions as non conducting pairs. As the dielectric constant is increased the extents of association should decrease, but it should never become a non-zero chance that anion-cation contact will occur.

In the present work we have studied the conductance and ion association of 1:1 electrolyte salts, Tetraammine Cu (II) sulfate and tris(ethylenediamine) Cu (II) sulfate complexes in aqueous medium at 298.15 to 313.15K using Shedlovsky equation.

4.1.2. Experimental

4.1.2.1. Preparation of ligands and compounds

The salts selected for the present work, ie., Tetraammine Cu (II) sulfate and tris(ethylenediamine) Cu (II) sulfate complexes was synthesized according to the reported procedure 3.8.2. (ix) & (x) [Glemser and Sauer, 1963]**.**

4.1.2.2. Conductivity measurements

Water was distilled twice (specific conductivity ≈ 10^{-6} S cm^{-1}) and KCL (Merck, India) was dried for six hours at 393.15K before use. The solutions of different concentrations (1 x10^{-4}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water. All the viscosity, dielectric constant and density values were interpolated from literature values [Hodgman *et al.*, 1956; Akhadov, 1981; Timmermanns, 1960]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used. Conductivity measurements were carried out over the temperature range of 25^{o}C – 40^{o} C. The temperature control in the ranges of 25-40^{0}C were made by using refrigerated water bath and Circulator - Cole-Palmer, Polystat R6L and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg).

Table 2(a): Molar conductivities (Λ) of Tetraammine Cu (II) sulfate in aqueous medium at different temperatures.

Conc. x 10^{-3}	298.15K	303.15K	308.15K	313.15K
1.000	292.10	297.13	312.20	318.16
0.976	293.03	298.16	313.52	319.67
0.952	293.07	299.37	314.08	320.38
0.930	294.62	300.00	315.05	321.51
0.909	294.83	300.33	315.73	322.33
0.889	295.84	301.46	316.08	322.83
0.869	296.89	302.65	317.61	323.36
0.851	297.29	303.17	318.45	324.32
0.833	298.92	304.92	320.51	326.53
0.816	300.24	305.15	321.08	328.43

Table 2(b): Molar conductivities (Λ) of tris(ethylenediamine) Cu (II) sulfate in aqueous medium at different temperatures.

Conc. x 10^{-3}	298.15K	303.15K	308.15K	313.15K
1.000	271.04	278.31	287.16	296.20
0.976	272.32	279.09	288.12	297.45
0.952	273.45	280.28	289.03	298.17
0.930	274.02	281.20	290.01	299.34
0.909	274.87	281.78	290.67	300.12
0.889	275.49	282.35	291.03	300.76
0.869	275.49	283.09	292.43	301.26
0.851	276.34	283.87	293.29	302.42
0.833	277.09	284.67	293.98	303.53
0.816	278.27	285.75	294.71	304.51

4.1.3. Evaluation of limiting molar conductance and association constant

The molar conductances (Λ) for studied solution system have been calculated using following equation [El-Dossoki, 2010]

$$\Lambda = 1000\kappa/c$$

Where c is the molar concentration and κ is the measured specific conductance of the studied solutions. From the observed molar conductivities of TetraammineCu(II) sulfate and tris(ethylenediamine) Cu(II) sulfate complexes at various concentrations, the limiting molar conductivity (Λ_0) of the salts were determined by Shedlovsky extrapolation method [Shedlovsky, 1932]

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right) \qquad \ldots(79)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 the limiting equivalent conductance and K_A the observed association constant. The other symbols are given by [Shedlovsky and Kay, 1956]

$$S(z) = \left(\frac{z}{2}\sqrt{1+\left(\frac{z}{2}\right)^2}\right)^2 ; \qquad Z = \left|\frac{\propto\Lambda_o+\beta}{\Lambda_o^{s/z}}\right|(C\Lambda)^{1/2} \quad ; \qquad \propto = \frac{17.147x105W}{(DT)^{3/2}}$$

$$w = z_+z_-\frac{2q}{1+q^{1/2}} \qquad ; \qquad q = \frac{z_+z_-}{z_++z_-}x\frac{\lambda_++\lambda_-}{z_+\lambda_-+z_-\lambda_+} \; ; \quad \beta = \frac{151.47}{\eta(DT)^{1/2}}$$

Z and λ are the valence and conductance of the ions respectively, excluding their signs. D is the dielectric constant of the medium, η the viscosity (c.p). The degree of dissociation (τ) is related to S(z) by the equation, $\tau = \Lambda S(z)/\Lambda_o$

$f_\pm$ is the activity coefficient of the free ions and was calculated using the equation

$$-logf_\pm = \frac{Az_+z_-\mu^{1/2}}{1+BR\mu^{1/2}} \qquad \ldots(80)$$

Where, $A = \frac{1.8247x10^6}{(DT)^{3/2}}$; $B = \frac{0.5029x10^{10}}{(DT)^{1/2}}$;$\mu = \frac{1}{2}\sum_i(c_i\tau_i)z_i^2$

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no method of determining the value of R precisely [Bag *et al.*, 2000]. In order to treat the data in our system the R value is assumed to be R = a + d, where a, the sum of crystallographic radii of the ions, is approximately equal to 5A^0 and d (A^0) is given by [Akhadov, 1981]

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

Where M is the molecular weight of the solvent and ρ is the density of the solution. As per Shedlovsky method, an initial value of λ^o was obtained from the intercept of the linear Onsager plot of Λ versus $c^{1/2}$, λ^o is obtained from the literature at 25°C and at other temperatures it was obtained by using the following equation [Bag *et al.*, 2009]:

$$\lambda_t^0 = \lambda_{25}^0[1 + \alpha'(t - 25)]$$

α' is constant. Using these values of Λ_o, λ^o_-, λ^o_+, z, s(z) and r values were calculated. The mean activity coefficient f was determined by equation (20) for the above chosen complex salts. From the linear plot of $1/\Lambda S(Z)$ versus $C\,\Lambda f_\pm^2 S(Z)$; Λ_0 and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope K_A/Λ_0^2 respectively [Nelson and Errington, 2005] . The procedure was repeated using these new values of Λ_0 and K_A. The results of Limiting molar conductance (Λ_0) and association constant (K_A) at different temperatures are summarized in Table 3 (a) & Table 3 (b).

Table 3(a): The value of limiting molar conductance Λ_0 (Scm^2mol^{-1}) and association constants K_A ($dm^3\ mol^{-1}$) obtained for Tetraammine Cu (II) sulfate in aqueous solution at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**
$\mathbf{\Lambda_0}$	350.29	363.42	379.07	396.16
$\mathbf{K_A}$	291.61	306.57	325.82	345.55
$\mathbf{LogK_A}$	2.465	2.487	2.513	2.539

Table 3(b): The value of limiting molar conductance Λ_0 (Scm^2mol^{-1}) and association constants K_A ($dm^3\ mol^{-1}$) obtained for tris(ethylenediamine) Cu (II) sulfate in aqueous solution at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**
$\mathbf{\Lambda_0}$	326.34	337.15	350.37	364.64
$\mathbf{K_A}$	274.73	286.53	301.91	320.43
$\mathbf{LogK_A}$	2.439	2.457	2.480	2.506

From Tables 3(a) &3(b), the value of Λ_0 for the electrolytes increased invariably with increase in temperature in aqueous medium indicating less solvation or higher mobility of ions [Das, 2008]. This is due to the fact that the increase thermal energy results in bond breaking and leads to higher frequency and higher mobility of the ions. Values of Λ_0 for Tetraammine Cu (II) sulfate complexes are always greater than those values of complex tris(ethylenediamine) Cu (II) sulfate complexes is most prone to the variation in vibrational, rotational and translational energy levels with temperature [Jenkins and Monk, 1951]. The values of the K_As for these two complexes increase with rise in temperature.

The higher K_A values in case of Tetraammine Cu (II) sulfate salt compared to complexes salt may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the metal ion and sulfate ion [Pura and Atun, 2003]. This is so because the charge density of metal ion is greater than that of the charge density of the metal ion for tris(ethylenediamine) Cu (II) sulfate.

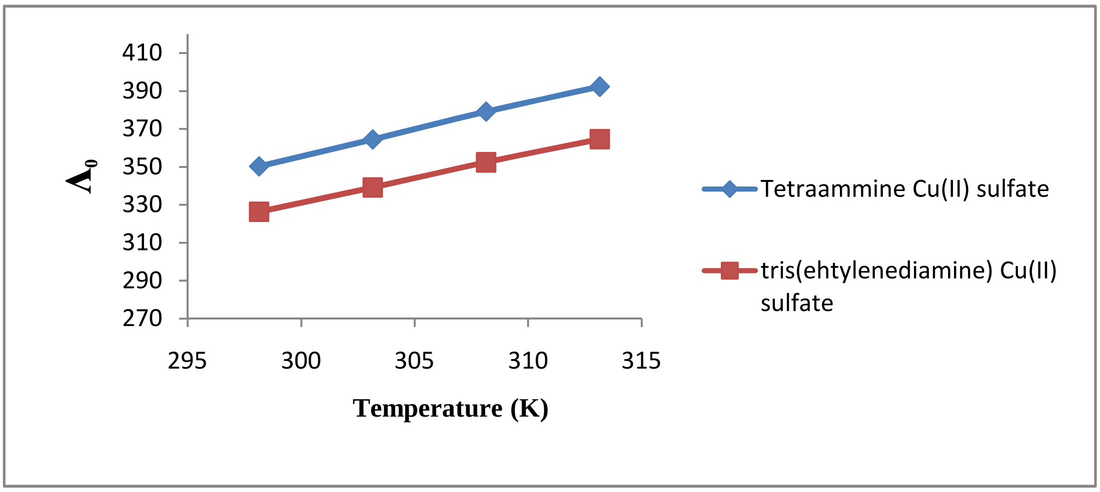


Figure 1: Plot of Limiting molar conductance (Λ_0) vs Temperature (K) for Tetraammine Cu (II) sulfate and tris(ethylenediamine) Cu (II) sulfate in aqueous solution at different temperatures.

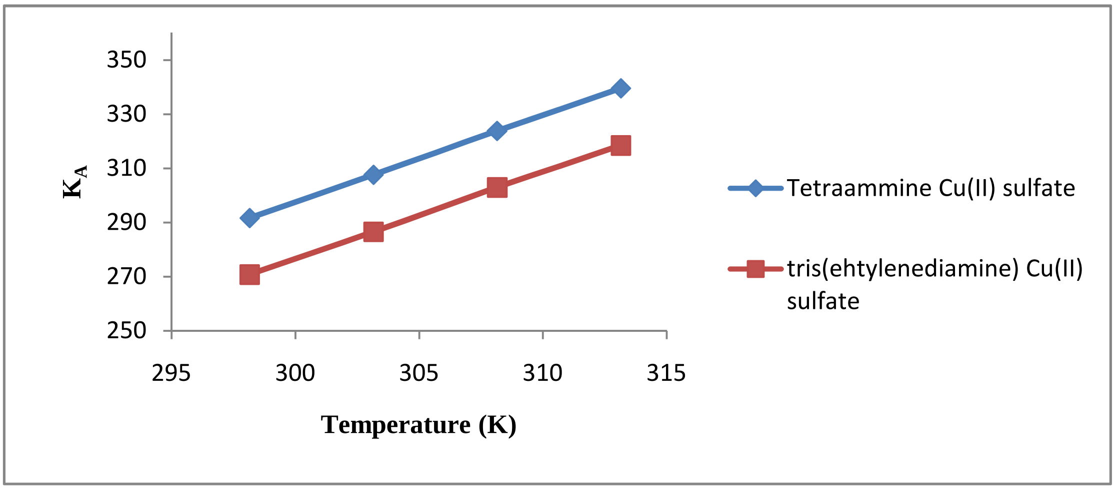


Figure 2: Temperature dependence of ion association constant for Tetraammine Cu (II) sulfate and tris(ethylenediamine) Cu (II) sulfate in aqueous solution at different temperatures.

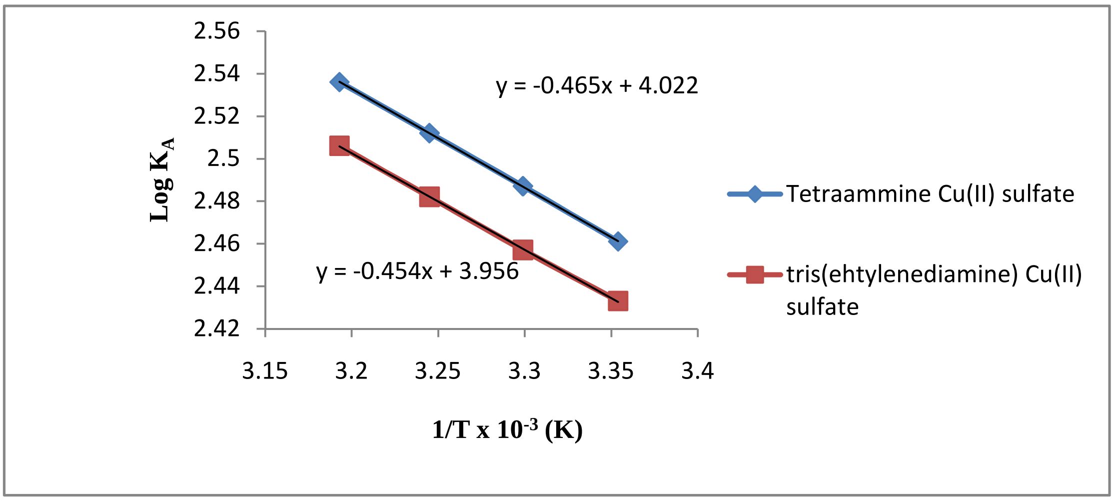


Figure 3: Plot of Log K_A vs Temperature (K) for Tetraammine Cu (II) sulfate and tris(ethylenediamine) Cu (II) sulfate in aqueous solution at different temperatures.

4.1.4. Evaluation of thermodynamic parameters:

The free energy change (ΔG^0) for association is calculated from the relation $\Delta G^0 = -RT \ln K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A vs 1/T (figure 3). The entropy change (ΔS^0) is calculated from the Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - \Delta S^0 T$. The values of thermodynamic functions are given in table 4(a) & 4(b). The positive values of ΔS^0 and negative values of ΔH^0 indicate that ion association process will occur spontaneously at all temperatures [Marusak and Lappin, 1989]. The negative value of ΔH^0 indicates that ion association processes are exothermic at all temperatures [Singh *et al.*, 2008].

Table 4(a): Thermodynamic parameters ΔG^0 (kJmol^{-1}), ΔH^0 (kJmol^{-1}) and ΔS^0 (kJK^{-1} mol^{-1}) obtained by Shedlovsky technique for Tetraammine Cu (II) sulfate in aqueous solutions at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**
ΔG^0	-14.072	-14.436	-14.827	-15.224
ΔH^0	-0.465			
10^3 x ΔS^0	45.534	45.984	46.507	47.032

Table 4(b): Thermodynamic parameters ΔG^0 ($kJmol^{-1}$), ΔH^0 ($kJmol^{-1}$) and ΔS^0 ($kJK^{-1}\ mol^{-1}$) obtained for tris(ethylenediamine) Cu (II) sulfate in aqueous solutions at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**
ΔG^0	-13.924	-14.255	-14.633	-15.026
ΔH^0	-0.454			
10^3 x ΔS^0	45.199	45.545	46.033	46.553

Out of these two complexes, negative values of ΔG^0 is more in Tetraammine Cu (II) sulfate and this complex is more favored in ion – pair formation. A positive entropy change is broken when association takes place leading to an increase in the degree of disorderliness [Ue and Mori, 1995].

The limiting equivalent conductance (Λ_0) increased linearly with the increase in temperature and the association constant K_A values increase with rise in temperature. Both the reactions are exothermic which is determined by negative values of ΔH^0 [Girolami *et al*., 1999]. A positive entropy change ΔS^0 is broken when association takes place leading to increase in the degree of disorderliness [Bag and Singh, 2009]. Among these two salts, the negative values of ΔG^0_{ass} become more in Tetraammine Cu (II) sulfate salt, indicating that the ion pair association is favored with lowering size of the complex cation.

The Cu (II) complexes show ion pair formation within the experimental different temperature ranges; which is supported by negative values of ΔG^o. The K_A values for both complexes are determined and found in order:

Tetraammine Cu (II) sulfate > tris(ethylenediamine) Cu (II) sulfate

4.2. Study of N-[(benzoyl-amino)-thioxomethyl]-cystein metal (II) chloride complexes in aqueous medium at different temperatures.

4.2.1. Introduction

Ion pair formation process is a kind of very important chemical reaction whose theoretical and experimental studies are significant to the revealing of the microscopic dynamics of gas phase, liquid-phase reaction and the upper-space atmospheric reaction. The ion of the pair together formed an ionic dipole on which the net charge is zero. Within the ionic cloud, the locations of such ion-pairs are completely random, since, being uncharged, they are not acted upon the Coulombic field of the central ion. Furthermore, on the average, a certain fractions of the ions in the electrolytic solution will be stack together in the form of ion-pairs [Bjerrum, 1926]. In solvents of low dielectric constant, where the electrostatic potential energy of an anion and a cation at contact is large compared to mean thermal energy kT, it is expected the association of ions as non-conducting pairs. As the dielectric constant is increased the extents of association should decrease, but it should never become a non-zero chance that anion-cation contact will occur. Conductance of 1:1 electrolytes has been extensively studied by using Shedlovsky equation [Bag *et al.*, 2000]. For higher valent unsymmetrical electrolytes limited work has been done. In the present work we have studied the conductance and ion association of 2:1 electrolyte salts N-[(Benzoyl-amino)-thioxomethyl]-cystein Metal (II) chloride complexes in aqueous medium at 298.15 to 313.15 K using Shedlovsky equation. The equivalent conductance at infinite dilution (Λ_0) and the association constant (K_A) for the complex salt have been evaluated .The thermodynamic parameters viz., ΔG^0, ΔH^0 and ΔS^0 have also been calculated from the temperature variations of the association constants. The present work aims at determining the molar conductance values of the solutions of the title electrolyte in aqueous medium at 298.15-313.15K to examine the validity of Shedlovsky technique.

4.2.2. Experimental

4.2.2.1. Preparation of ligands and compounds

The salts selected for the present work, ie N-[(benzoyl-amino)-thioxomethyl]-cystein manganese (II) chloride, N-[(benzoyl-amino)-thioxomethyl]-cystein cobalt (II) chloride, N-[(benzoyl-amino)-thioxomethyl]-cystein nickel (II) chloride and N-[(benzoyl-amino)-thioxomethyl]-cystein copper (II) chloride were prepared according to chapter-3, section 3.8.2 (i), 3.8.2 (ii), 3.8.2 (iii) & 3.8.2 (iv). The purity of the sample was determined by conventional chemical analysis and spectral measurements and the values are in good agreement with the literature values [Kabbani *et al*., 2005].

4.2.2.2. Conductivity measurements

Water was distilled twice (specific conductivity ≈ 10^{-6} S cm^{-1}) and KCL (Merck, India) was dried for six hours at 393.15K before use. The solutions of different concentrations (1 x10^{-4}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water. All the viscosity, dielectric constant and density values were interpolated from literature values [Hodgman *et al*., 1956; Akhadov, 1981; Timmermanns, 1960]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used. Conductivity measurements were carried out over the temperature range of 25^{o}C – 40^{o}C. The temperature control in the ranges of 25-40^{0}C were made by using refrigerated water bath and Circulator - Cole-Palmer, Polystat R6L and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg).

Table 5(a): Molar conductivities (Λ) of N-[(benzoyl-amino)-thioxomethyl]-cystein manganese (II) chloride in aqueous medium at different temperatures.

Conc. x 10^{-3}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.000	86.30	90.50	94.80	99.30
0.976	86.48	90.68	94.98	99.49
0.952	86.87	90.97	95.27	99.79
0.930	86.10	91.29	95.60	100.22
0.909	87.24	91.86	95.93	100.55
0.889	87.51	92.01	96.18	100.90
0.869	87.80	90.17	96.55	101.15
0.851	88.13	92.36	96.71	101.41
0.833	88.48	92.68	97.08	101.68
0.816	88.60	92.77	97.18	101.96

Table 5(b): Molar conductivities (Λ) of N-[(benzoyl-amino)-thioxomethyl]-cystein cobalt (II) chloride in aqueous medium at different temperatures.

Conc. x 10^{-3}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.000	122.70	126.10	287.16	133.20
0.976	123.32	126.72	129.7	134.00
0.952	123.83	127.13	130.53	134.55
0.930	124.18	127.42	131.06	134.80
0.909	124.59	127.91	131.38	135.18
0.889	125.07	128.37	131.61	135.61
0.869	125.32	128.51	132.28	136.21
0.851	125.67	128.86	132.49	136.47
0.833	126.01	129.43	132.87	136.72
0.816	126.16	129.67	133.29	137.20

Table 5(c): Molar conductivities (Λ) of N-[(benzoyl-amino)-thioxomethyl]-cystein nickel (II) chloride in aqueous medium at different temperatures.

Conc. x 10^{-3}	298.15K	303.15K	308.15K	313.15K
1.000	141.00	144.80	148.40	151.90
0.976	141.80	145.70	149.39	152.97
0.952	142.32	146.43	150.00	153.68
0.930	142.58	146.67	150.32	153.98
0.909	142.99	147.09	150.94	154.35
0.889	143.69	147.36	151.63	154.89
0.869	143.97	147.87	151.90	155.47
0.851	144.42	148.30	152.06	155.58
0.833	144.74	148.62	152.58	156.32
0.816	145.18	149.26	152.70	156.62

Table 5(d): Molar conductivities (Λ) of N-[(benzoyl-amino)-thioxomethyl]-cystein copper (II) chloride in aqueous medium at different temperatures.

Conc. x 10^{-3}	298.15K	303.15K	308.15K	313.15K
1.000	163.10	167.30	171.40	175.00
0.976	164.02	168.03	172.13	176.02
0.952	164.57	168.49	172.69	176.89
0.930	164.87	168.92	173.01	177.20
0.909	165.39	169.42	173.60	177.78
0.889	165.99	170.08	174.47	178.63
0.869	166.41	170.66	174.68	178.83
0.851	166.93	171.09	175.21	179.31
0.833	167.73	171.67	175.86	179.95
0.816	167.91	171.94	176.47	180.39

4.2.3. Evaluation of limiting molar conductance and association constant

The limiting molar conductances (Λ_0) and ion association constants (K_A) have been computed using Shedlovsky method [Shedlovsky, 1932].

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are same as given in chapter 3, section 3.1.1.1.

Table 6(a): The value of limiting molar conductances Λ_0 (Scm^3) and Association constants K_A(dm^{-3}mol^{-1}) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride in aqueous solution at different temperatures.

Symbol	298.15K	303.15K	308.15K	313.15K
Λ_0	102.38	109.99	115.55	121.58
K_A	283.42	292.98	300.42	309.65
LogK_A	2.452	2.467	2.478	2.491

Table 6(b): The value of limiting molar conductances Λ_0 (Scm^3) and Association constants K_A(dm^{-3}mol^{-1}) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride in aqueous solution at different temperatures.

Symbol	298.15K	303.15K	308.15K	313.15K
Λ_0	148.27	154.46	159.80	164.73
K_A	294.71	306.70	316.54	325.83
LogK_A	2.469	2.487	2.500	2.513

Table 6(c): The value of limiting molar conductances Λ_0 (Scm^3) and Association constants K$_A$(dm^{-3}mol^{-1}) obtained by Shedlovsky technique for N-[(Benzoylamino)-thioxomethyl]-cystein Ni (II) chloride in aqueous solution at different temperatures.

Symbol	298.15K	303.15K	308.15K	313.15K
Λ_0	172.30	178.08	183.52	188.74
K_A	300.04	312.54	323.38	334.05
LogK$_A$	2.477	2.495	2.510	2.524

Table 6(d): The value of limiting molar conductances Λ_0 (Scm^3) and Association constants K$_A$(dm^{-3}mol^{-1}) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride in aqueous solution at different temperatures.

Symbol	298.15K	303.15K	308.15K	313.15K
Λ_0	198.10	205.86	211.98	218.18
K_A	309.99	318.01	329.40	342.96
LogK$_A$	2.491	2.502	2.518	2.535

The higher K$_A$ values in the case of N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride compared to other three complexes viz., N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride and N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the complex ion and Chloride ion. This is because the charge density of N-[(Benzoylamino)-thioxomethyl]-cystein Cu (II) ion is greater than that of the charge density of the other three metal complexes ions.

The negative value of ΔH^0 indicates that ion association processes are exothermic at all temperatures. Out of all complexes, negative values of ΔG^0 is more in N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride and this complex is more favored in ion-pair formation. A positive entropy change is broken when association takes place leading to an increase in the degree of disorderliness.

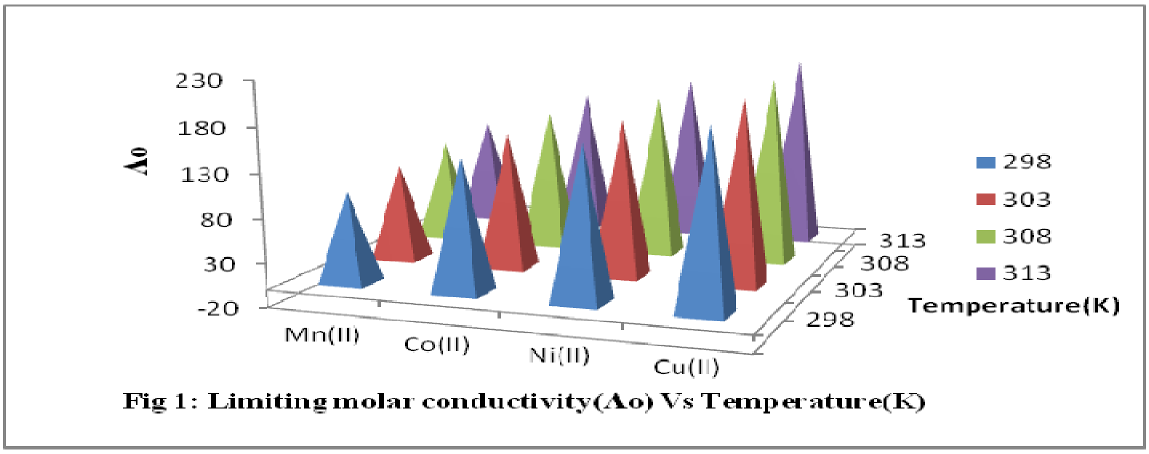


Figure 4: Plot of Limiting molar conductance (Λ_0) vs Temperature (K) for N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride and N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride in aqueous solution at different temperatures.

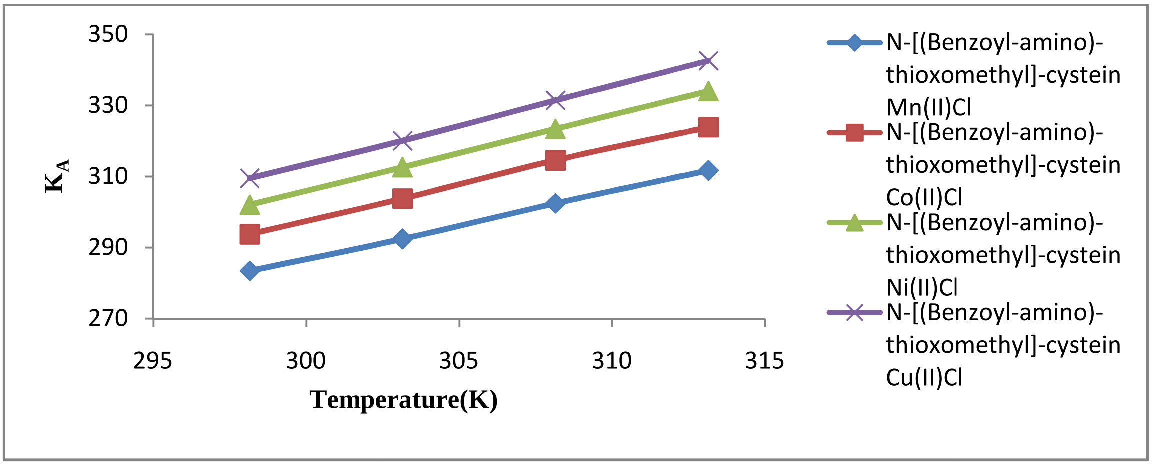


Figure 5: Temperature dependence of ion association constant for N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride and N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride in aqueous solution at different temperatures.

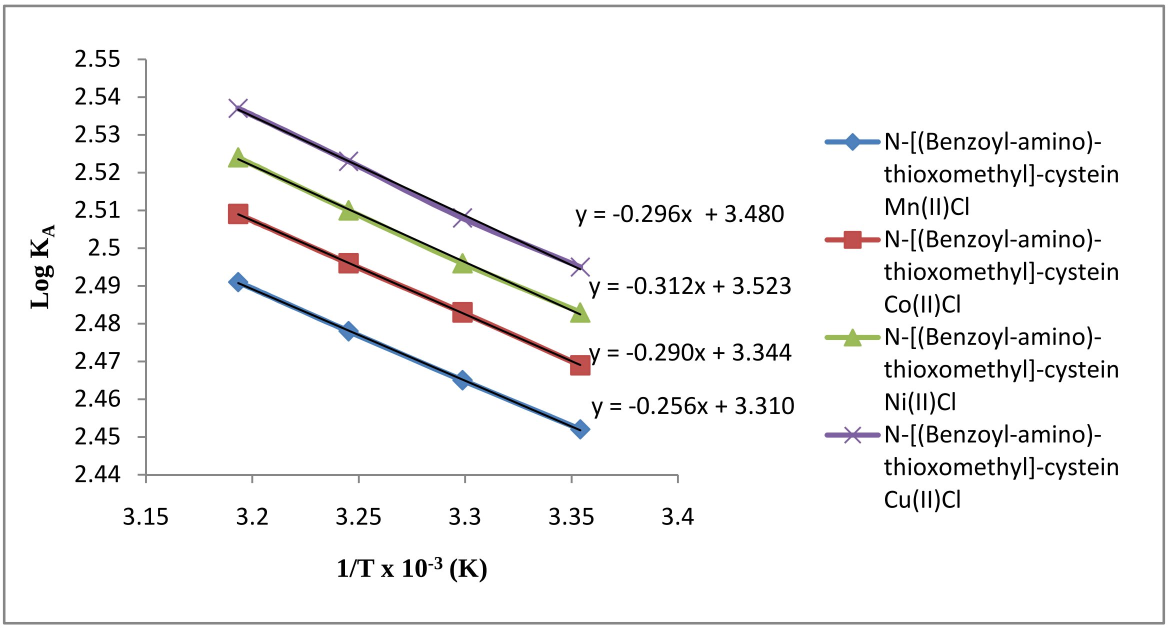


Figure 6: Plot of Log $K_A$vs Temperature (K) for N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride, N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride and N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride in aqueous solution at different temperatures.

4.2.4. Evaluation of thermodynamic parameters

Table 7(a): Thermodynamic parameters ΔG^0 ($kJmol^{-1}$), ΔH^0 ($kJmol^{-1}$) andΔS^0 ($kJK^{-1}mol^{-1}$) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride in aqueous solution at different temperatures.

Symbol	298.15K	303.15K	308.15K	313.15K
ΔG^0	-13.998	-14.320	-14.621	-14.936
ΔH^0	-0.256			
10^{-3}x ΔS^0	46.091	46.393	46.617	46.879

Table 7(b): Thermodynamic parameters ΔG^0 ($kJmol^{-1}$), ΔH^0 ($kJmol^{-1}$) andΔS^0 ($kJK^{-1}mol^{-1}$) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride in aqueous solution at different temperatures.

Symbol	**298.15K**	**303.15K**	**308.15K**	**313.15K**
$\mathbf{\Delta G^0}$	-14.095	-14.436	-14.751	-15.068
$\mathbf{\Delta H^0}$	-0.290			
$\mathbf{10^{-3} x\ \Delta S^0}$	46.302	46.663	46.928	47.191

Table 7(c): Thermodynamic parameters ΔG^0 ($kJmol^{-1}$), ΔH^0 ($kJmol^{-1}$) andΔS^0 ($kJK^{-1}mol^{-1}$) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride in aqueous solution at different temperatures.

Symbol	**298.15K**	**303.15K**	**308.15K**	**313.15K**
$\mathbf{\Delta G^0}$	-14.141	-14.482	-14.809	-15.138
$\mathbf{\Delta H^0}$	-0.312			
$\mathbf{10^{-3} x\ \Delta S^0}$	46.383	46.743	47.045	47.345

Table 7(d): Thermodynamic parameters ΔG^0 ($kJmol^{-1}$), ΔH^0 ($kJmol^{-1}$) andΔS^0 ($kJK^{-1}mol^{-1}$) obtained by Shedlovsky technique for N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride in aqueous solution at different temperatures.

Symbol	**298.15K**	**303.15K**	**308.15K**	**313.15K**
$\mathbf{\Delta G^0}$	-14.220	-14.523	-14.857	-15.200
$\mathbf{\Delta H^0}$	-0.296			
$\mathbf{10^{-3} x\ \Delta S^0}$	46.701	46.931	47.253	47.594

The free energy change (ΔG^0) for association is calculated from the relation $\Delta G^0 = -RT \ln K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A vs 1/T (fig. 6). The entropy change (ΔS^0) is calculated from the Gibbs-Helmholtz equation $\Delta G^0 = \Delta H^0 - \Delta S^0 T$. The values of thermodynamic function are given in Table 7(a), (b), (c) and (d). The negative value of ΔH^0 indicates that ion association processes are exothermic at all temperature. The positive values of ΔS^0 and negative value of ΔH^0 indicates that ion association process will occur spontaneously at all temperatures [De *at el*., 2006].

The present work reports conductometric properties, thermodynamic behavior of transition Metal (II) complexes in water at different temperatures ranging from 25 - 40^{0}C. The limiting equivalent conductance (Λ_0) increased linearly with the increase in temperature and the association constant K_A values increase with rise in temperature. All the reactions are exothermic which is determined by negative values of ΔH^0. The complexes show ion pair association within experimental obtained by the negative values of ΔG^0 at different temperatures. The positive values of ΔS^0 and negative values of ΔH^0 indicate that the ion association process will occur spontaneously at all temperatures. The K_A values for all metal complexes are determined and found in order: N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride > N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride > N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride > N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride.

4.3. Physico-chemical studies of some transition metal (II) chlorides in pure methanol and water and their binaries at different temperatures

4.3.1. Introduction

Variation in the dielectric constant and viscosity in solvents due to mixing, leads to a better understanding of ion-ion and ion-solvent interactions. The use of mixed solvents in high energy batteries has also extended the horizon in the field of mixed solvent systems [Aurbach, 1999]. Ion solvation is one of the most important factors determining the rate and mechanism of various physico-chemical processes occurring in solutions with ionic species as intermediates [Chatterjee and Das, 2006]. Conductance study is a very important tool in obtaining the information regarding the solvation and association behavior of ions in solutions [Dogonadze *et al*., 1986]. Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent [Saito *et al*., 1976]. 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 [Roy *et al*., 2009]. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration-dependence of the electrolyte conductivity. The theories of conductance have revealed one feature in common that the solvent is assumed as a continuum of permittivity D and viscosity η. This assumption is hardly valid when discussing strong ion- solvent interaction, since the size of solvent molecules are comparable to those of solute molecules, since the size of solvent molecules are also considered as rigid uniformity charged unpolarizable sphere [Fuoss, 1978; De *et al*., 2006]. Here, we have investigated the conductance behavior of two inorganic salts(transition metal salt) with common anion ie N-[Benzoylamino)-thioxomethyl]-serine Ni (II) chloride and N-[Benzoylamino)-thioxomethyl]-serine Mn (II) chloride in different mass fraction

(0.0000, 0.0588, 0.1942, 0.3600, 0.5676. 0.8351 and 1.0000) of methanol (CH_3OH) in water (H_2O) at different temperatures ranging from 283.15, 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15K. Experimental results were treated by Shedlovsky equation to obtain the limiting molar conductance (Λ_0) and the association constant (K_A) which served further to calculate Walden product ($\Lambda_0\eta_0$) and other thermodynamic quantities of the ion association reaction (ΔG^0, ΔH^0, ΔS^0). The calculation was further extended to derive Arrhenius activation energy (E^a) for ion-association reaction and described accordingly.

4.3.2. Experimental

4.3.2.1. Preparation of ligands and compounds

The salts selected for the present work, ie N-[(benzoyl-amino)-thioxomethyl]-serine manganese (II) chloride and N-[(benzoyl-amino)- thioxomethyl]-serine nickel (II) chloride were prepared according to chapter-3, section 3.8.2 (v) & 3.8.2 (vi). The purity of the sample was determined by conventional chemical analysis and spectral measurements and the values are in good agreement with the literature values [Kabbani *et al.*, 2005].

4.3.2.2. Conductivity measurements

Water was distilled twice (specific conductivity ≈ 10^{-6} S cm^{-1}) and KCL (Merck, India) was dried for six hours at 393.15K before use. Methanol (Merck, India, absolutely, 99.8% pure) was used without further purification. The solutions of different concentrations (1 x10^{-4}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water. All the viscosity, dielectric constant and density values were interpolated from literature values [Pura and Atun, 2003; Shedlovsky and Kay, 1956]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used.

Conductivity measurements were carried out over the temperature range of 10–40° C. The temperature control in the ranges of 10-40^{0}C were made by using refrigerated water bath and circulator Model D8-G of HAAKE Mess-Technik) and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg).

Table: 8(a). The values of molar conductance (Λ) obtained for N-[(benzoyl-amino)-thioxomethyl]-serine nickel (II) chloride in various methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	258.67	281.39	298.48	309.50	324.01	341.68	361.08
0.9091	259.82	282.45	299.41	310.29	324.74	342.36	361.67
0.8333	260.76	283.34	300.26	310.98	325.43	342.94	362.23
0.7692	261.59	284.13	301.04	311.62	326.00	343.47	362.72
0.7143	262.35	284.85	301.73	312.13	326.47	343.96	363.15
0.6667	263.07	285.49	302.34	312.64	326.92	344.40	363.57
0.6250	263.70	286.04	302.83	313.05	327.29	344.75	363.91
0.5882	264.27	286.53	303.32	313.46	327.68	345.14	364.26
0.5556	264.78	286.99	303.83	313.83	328.04	345.46	364.58
0.5263	265.23	287.42	304.32	314.18	328.37	345.78	364.87

X_1=0.0588

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	229.93	244.16	255.26	272.60	283.01	294.86	313.97
0.9091	230.99	245.23	256.21	273.49	283.79	295.55	314.63
0.8333	231.96	246.12	257.02	274.21	284.45	296.13	315.22
0.7692	232.83	246.90	257.70	274.87	285.01	296.71	315.74
0.7143	233.56	247.55	258.35	275.45	285.52	297.19	316.21
0.6667	234.27	248.21	258.95	275.96	286.00	297.62	316.62
0.6250	234.83	248.78	259.44	276.41	286.43	297.99	316.96
0.5882	235.42	249.34	259.88	276.87	286.82	298.34	317.34
0.5556	235.91	249.81	260.32	277.29	287.17	298.67	317.65
0.5263	236.41	250.27	260.70	277.63	287.50	298.95	317.96

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	194.40	204.94	211.60	227.00	240.20	253.80	270.96
0.9091	195.38	205.91	212.53	227.86	240.89	254.49	271.55
0.8333	196.22	206.74	213.32	228.56	241.52	255.04	272.06
0.7692	197.04	207.50	214.01	229.17	242.06	255.56	272.54
0.7143	197.72	208.16	214.61	229.75	242.55	256.00	272.97
0.6667	198.33	208.72	215.16	230.22	243.00	256.46	273.36
0.6250	198.82	209.24	215.62	230.70	243.39	256.81	273.70
0.5882	199.31	209.73	216.10	231.09	243.76	257.16	274.01
0.5556	199.77	210.21	216.53	231.50	244.13	257.47	274.33
0.5263	200.23	210.60	216.89	231.89	244.46	257.77	274.62

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	170.75	185.85	203.50	215.80	228.00	244.01	264.95
0.9091	171.61	186.75	204.38	216.71	228.82	244.78	265.62
0.8333	172.42	187.56	205.15	217.45	229.53	245.45	266.24
0.7692	173.13	188.29	205.87	218.12	230.17	246.02	266.76
0.7143	173.75	188.92	206.52	218.69	230.73	246.54	267.23
0.6667	174.31	189.51	207.13	219.23	231.22	247.03	267.66
0.6250	174.82	189.99	207.60	219.72	231.64	247.44	268.01
0.5882	175.29	190.47	208.09	220.17	232.06	247.82	268.38
0.5556	175.80	190.91	208.51	220.61	232.45	248.15	268.72
0.5263	176.22	191.28	208.91	221.00	232.81	248.47	269.01

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	184.45	197.51	215.43	230.19	238.94	257.30	270.81
0.9091	185.51	198.52	216.45	231.27	239.92	258.24	271.65
0.8333	186.42	199.45	217.35	232.14	240.75	259.08	272.38
0.7692	187.27	200.22	218.18	232.93	241.52	259.77	273.04
0.7143	188.00	200.93	218.92	233.60	242.14	260.38	273.63
0.6667	188.71	201.60	219.60	234.21	242.77	260.92	274.15
0.6250	189.29	202.14	220.14	234.82	243.30	261.41	274.61
0.5882	189.87	202.68	220.66	235.33	243.79	261.90	275.03
0.5556	190.38	203.16	221.17	235.81	244.23	262.34	275.44
0.5263	190.91	203.62	221.63	236.27	244.62	262.73	275.82

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	205.53	217.41	233.75	248.40	257.22	277.12	288.10
0.9091	206.87	218.67	234.98	249.63	258.40	278.28	289.08
0.8333	207.96	219.76	236.07	250.62	259.39	279.26	289.93
0.7692	208.95	220.71	237.00	251.57	260.27	280.14	290.69
0.7143	209.88	221.55	237.87	252.42	261.07	280.90	291.38
0.6667	210.67	222.34	238.66	253.19	261.81	281.53	292.05
0.6250	211.39	223.00	239.28	253.85	262.40	282.15	292.61
0.5882	212.10	223.65	239.91	254.51	262.97	282.72	293.14
0.5556	212.75	224.24	240.49	255.13	263.53	283.24	293.58
0.5263	213.36	224.80	241.00	255.65	264.07	283.71	294.09

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	225.55	237.43	255.44	269.11	278.93	298.84	310.84
0.9091	226.99	238.91	256.98	270.56	280.32	300.19	312.09
0.8333	228.42	240.19	258.29	271.72	281.51	301.30	313.13
0.7692	229.54	241.31	259.34	272.72	282.56	302.32	314.09
0.7143	230.58	242.32	260.33	273.86	283.55	303.26	314.95
0.6667	231.51	243.28	261.26	274.78	284.40	304.08	315.71
0.6250	232.30	244.05	262.03	275.54	285.14	304.83	316.35
0.5882	233.12	244.86	262.79	276.25	285.80	305.54	316.96
0.5556	233.73	245.55	263.48	276.97	286.46	306.18	317.61
0.5263	234.41	246.18	264.09	277.56	287.07	306.80	318.14

Table 8(b): The values of molar conductance (Λ) obtained for N-[(benzoyl-amino)-thioxomethyl]-serine manganese (II) chloride in various methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	238.19	260.06	278.10	289.15	303.67	322.41	338.21
0.9091	239.11	261.01	278.89	289.84	304.25	323.01	338.77
0.8333	239.86	261.84	279.55	290.45	305.74	323.52	339.22
0.7692	240.54	262.57	280.13	290.97	305.18	323.94	339.65
0.7143	241.19	263.16	280.62	291.45	305.58	324.30	340.00
0.6667	241.75	263.73	281.08	291.85	305.91	324.63	340.35
0.6250	242.28	264.18	281.45	292.23	306.22	324.89	340.64
0.5882	242.80	264.60	281.87	292.58	306.50	325.20	340.91
0.5556	243.25	265.02	282.19	292.89	306.77	325.45	341.16
0.5263	243.64	265.41	282.50	293.15	307.01	325.70	341.39

X_1=0.0588

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	209.12	223.34	234.58	252.42	261.53	273.51	296.33
0.9091	210.11	224.23	235.36	253.16	262.22	274.13	296.89
0.8333	210.91	225.02	236.07	253.83	262.77	274.67	297.38
0.7692	211.68	225.73	236.66	254.40	263.28	275.13	297.84
0.7143	212.35	226.36	237.25	254.94	263.73	275.54	298.23
0.6667	212.96	226.92	237.75	255.38	264.11	275.92	298.60
0.6250	213.47	227.44	238.18	255.79	264.46	276.24	298.91
0.5882	213.95	227.91	238.59	256.16	264.81	276.55	299.23
0.5556	214.46	228.33	239.01	256.53	265.12	276.83	299.51
0.5263	214.87	228.76	239.37	256.86	265.38	277.09	299.77

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	173.38	184.77	190.88	206.76	219.96	233.56	251.38
0.9091	174.21	185.59	191.64	207.45	220.57	234.15	251.92
0.8333	174.93	186.36	192.31	208.04	221.08	234.61	252.38
0.7692	175.61	187.05	192.93	208.59	221.53	235.02	252.79
0.7143	176.22	187.64	193.46	209.10	221.94	235.42	253.14
0.6667	176.79	188.16	193.98	209.48	222.32	235.77	253.48
0.6250	177.26	188.60	194.37	209.89	222.63	236.05	253.74
0.5882	177.71	189.06	194.78	210.27	222.92	236.34	254.02
0.5556	178.10	189.45	195.15	210.61	223.21	236.58	254.25
0.5263	178.46	189.80	195.46	210.92	223.49	236.85	254.49

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	149.99	166.11	183.23	194.41	206.61	223.69	245.09
0.9091	150.76	166.86	183.99	195.15	207.29	224.32	245.70
0.8333	151.41	167.52	184.73	195.74	207.94	224.83	246.21
0.7692	152.06	168.17	185.34	196.36	208.50	225.31	246.68
0.7143	152.59	168.73	185.86	196.85	208.99	225.72	247.11
0.6667	153.10	169.24	186.39	197.34	209.44	226.09	247.48
0.6250	153.51	169.64	186.82	197.76	209.85	226.41	247.83
0.5882	153.95	170.08	187.21	198.15	210.19	226.72	248.14
0.5556	154.32	170.51	187.59	198.52	210.51	227.01	248.43
0.5263	154.69	170.90	187.98	198.84	210.83	227.30	248.69

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	163.51	176.52	194.78	208.50	216.15	235.51	249.22
0.9091	164.54	177.46	195.62	209.42	216.97	236.32	249.94
0.8333	165.35	178.22	196.41	210.21	217.71	237.03	250.54
0.7692	166.08	178.89	197.12	210.87	218.34	237.68	251.08
0.7143	166.75	179.54	197.73	211.49	218.92	238.24	251.57
0.6667	167.32	180.12	198.30	211.98	219.45	238.76	252.00
0.6250	167.84	180.59	198.81	212.44	219.90	239.22	252.39
0.5882	168.33	181.06	199.32	212.90	220.38	239.61	252.76
0.5556	168.77	181.48	199.75	213.37	220.79	240.00	253.14
0.5263	169.21	181.91	200.20	213.78	221.20	240.33	253.41

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	184.51	196.39	216.47	229.08	235.30	256.31	270.29
0.9091	185.60	197.45	217.59	230.21	236.27	257.32	271.18
0.8333	186.62	198.33	218.53	231.17	237.11	258.20	271.95
0.7692	187.51	199.21	219.40	231.99	237.94	258.96	272.68
0.7143	188.31	199.97	220.14	232.73	238.63	259.67	273.32
0.6667	189.10	200.67	220.84	233.44	239.24	260.25	273.91
0.6250	189.71	201.25	221.43	233.99	239.78	260.76	274.39
0.5882	190.30	201.84	222.00	234.61	240.32	261.27	274.89
0.5556	190.81	202.37	222.53	235.18	240.80	261.72	275.30
0.5263	191.35	202.89	223.02	235.67	241.25	262.13	275.68

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	204.53	216.41	235.49	249.16	257.59	274.94	289.76
0.9091	205.90	217.75	236.85	250.47	258.87	276.15	290.95
0.8333	207.06	218.89	237.95	251.49	259.95	277.15	291.94
0.7692	208.08	219.88	239.00	252.48	260.93	278.12	292.78
0.7143	209.02	220.74	239.92	253.34	261.76	278.97	293.57
0.6667	209.84	221.56	240.69	254.15	262.53	279.70	294.26
0.6250	210.57	222.31	241.41	254.78	263.18	280.31	294.85
0.5882	211.27	222.98	242.06	255.50	263.80	280.95	295.43
0.5556	211.85	223.60	242.69	256.16	264.41	281.50	296.02
0.5263	212.47	224.23	243.25	256.73	264.94	282.03	296.48

4.3.3. Evaluation of limiting molar conductance, association constant, walden product and effective radius

The limiting molar conductances (Λ_0) and ion association constants (K_A) have been computed using Shedlovsky method [Shedlovsky, 1932].

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are same as given in chapter 3, section 3.1.1.1.

Table 9(a): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) obtained by Shedlovsky technique for N-[(benzoyl-amino)-thioxomethyl]-serine nickel (II) chloride in various methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r
		T=283.15K				**T=288.15K**		
0.0000	279.13	517.73	363.71	5.154	292.24	438.28	332.57	5.539
0.0588	245.39	615.03	396.80	4.724	257.75	528.67	372.71	4.942
0.1942	208.31	714.12	454.12	4.128	219.46	617.43	429.92	4.285
0.3600	193.78	791.06	482.71	3.884	204.97	706.45	465.90	3.954
0.5676	199.92	911.81	395.84	4.736	211.15	803.63	356.63	5.165
0.8351	227.98	999.37	241.89	7.750	239.51	884.12	231.13	7.970
1.0000	261.11	1065.16	180.69	10.38	274.04	953.08	170.73	10.79
		T=293.15K				**T=298.15K**		
0.0000	305.67	364.72	306.28	5.912	320.49	311.26	285.56	6.234
0.0588	269.96	447.19	338.26	5.353	282.01	375.67	309.65	5.749
0.1942	230.49	539.53	387.22	4.676	241.86	471.09	349.25	5.098
0.3600	216.46	617.83	389.20	4.652	228.67	541.62	359.47	4.953
0.5676	222.48	703.82	336.61	5.379	234.14	616.34	313.51	5.678
0.8351	251.26	774.35	219.60	8.245	263.28	683.17	211.94	8.399
1.0000	285.42	838.16	170.40	10.63	298.89	743.72	162.60	10.95

$X_{Methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
		T=303.15K				**T=308.15K**		
0.0000	334.26	268.11	266.74	6.564	348.21	233.59	250.71	6.870
0.0588	295.81	325.53	290.49	6.027	309.08	281.82	270.45	6.369
0.1942	253.85	412.89	323.66	5.409	266.50	360.39	296.08	5.818
0.3600	241.11	475.92	328.63	5.328	254.73	414.55	305.17	5.644
0.5676	246.85	541.42	292.27	5.991	259.28	473.24	274.32	6.279
0.8351	276.01	598.54	200.38	8.738	288.85	524.78	194.40	8.861
1.0000	311.13	656.45	158.68	11.03	323.80	577.09	158.66	10.86
		T=313.15K						
0.0000	362.04	205.22	236.77	7.159				
0.0588	323.67	249.17	256.67	6.604				
0.1942	279.81	322.34	276.73	6.125				
0.3600	268.74	365.76	280.83	6.036				
0.5676	272.80	410.79	258.07	6.568				
0.8351	302.37	453.34	187.47	9.041				
1.0000	337.04	497.80	153.69	11.03				

Table 9(b): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) obtained by Shedlovsky technique for N-[(benzoyl-amino)-thioxomethyl]-serine manganese (II) chloride in various methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0	K_A	$\Lambda_0\eta_0$	r	Λ_0	K_A	$\Lambda_0\eta_0$	r
	Scm^2mol^{-1}	dm^3mol^{-1}			Scm^2mol^{-1}	dm^3mol^{-1}		
		T=283.15K				**T=288.15K**		
0.0000	250.94	616.87	326.97	5.733	266.38	530.31	303.14	6.077
0.0588	222.80	687.07	360.27	5.203	235.12	599.02	339.98	5.418
0.1942	185.60	748.16	404.61	4.633	195.96	675.17	383.89	4.798
0.3600	172.78	809.92	430.39	4.356	185.58	726.01	384.71	4.788
0.5676	177.95	902.42	352.34	5.320	189.79	785.44	320.56	5.746
0.8351	202.48	986.08	214.83	8.726	215.87	878.72	208.31	8.843
1.0000	238.26	1072.01	164.88	11.37	252.18	959.61	157.11	11.73
		T=293.15K				**T=298.15K**		
0.0000	281.86	474.98	282.42	6.411	297.23	420.52	264.83	6.722
0.0588	248.27	533.83	311.08	5.820	261.11	468.89	286.70	6.209
0.1942	207.56	591.18	348.70	5.193	219.17	521.84	316.48	5.625
0.3600	197.75	653.47	355.55	5.092	210.06	572.52	330.21	5.391
0.5676	202.00	709.00	305.63	5.924	213.95	632.63	286.48	6.214
0.8351	227.89	782.84	199.18	9.091	240.82	709.34	193.86	9.183
1.0000	263.14	863.71	157.09	11.53	277.22	786.03	150.81	11.81

$X_{Methanol}$	Λ_0	K_A	$\Lambda_0\eta_0$	r	Λ_0	K_A	$\Lambda_0\eta_0$	r
	Scm^2mol^{-1}	dm^3mol^{-1}			Scm^2mol^{-1}	dm^3mol^{-1}		
		T=303.15K				**T=308.15K**		
0.0000	313.06	374.39	249.82	7.009	329.44	335.92	237.20	7.262
0.0588	275.16	409.35	270.21	6.480	290.11	367.38	253.85	6.786
0.1942	231.04	457.33	294.58	5.944	244.28	405.63	271.40	6.347
0.3600	222.28	513.12	302.97	5.779	235.58	455.32	282.22	6.103
0.5676	226.57	569.53	268.26	6.527	239.81	511.98	253.72	6.789
0.8351	254.75	638.48	184.95	9.467	269.65	573.12	181.47	9.492
1.0000	292.11	716.11	148.98	11.75	303.81	638.34	148.87	11.57
		T=313.15K						
0.0000	345.88	302.38	226.21	7.493				
0.0588	304.76	326.43	241.67	7.014				
0.1942	258.97	360.74	256.12	6.618				
0.3600	248.83	406.98	260.03	6.519				
0.5676	253.42	449.67	239.74	7.070				
0.8351	283.26	512.32	175.62	9.651				
1.0000	318.71	569.01	145.33	11.66				

Table 9 (a) & (b) shows that for both the complex salts studied, the limiting molar conductances (Λ_0) increase as the temperature increases but decrease as the mass fraction of methanol in the solvent mixtures increases upto $X_{MeOH} = 0.3600$. The variation of Walden product ($\Lambda_0\eta_0$) increase in $X_{MeOH} = 0.3600$ and thereafter it decreases rapidly. The viscosity of M + W mixtures passes through a maximum at about $X_{MeOH} = 0.3600$. This trend in limiting molar conductances can be well described by the viscosity behavior of the solvent media. It is interesting to note that the Λ_0 values of salts decrease upto this mole fraction and then increase in methanol rich region at all temperatures. Changes in Walden product with concentration are common and they can be attributed to change in ion-solvation and ion-solvent interaction. The value of $\Lambda_0\eta_0$ would be constant only if the effective radius of the ions were the same in different media. The increase of Walden product indicates the weak solvation of ions which attains a maximum value at $X_{MeOH} = 0.3600$ and decrease of Walden product indicates an increase of the hydrophobic solvation with increasing concentration of methanol. The variation of Walden product with X_{MeOH} is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions on the other with the change in composition of the mixed solvents and the temperature of the solution [Raju *et al.*, 1990]. On the water-rich side there exists a region, where water structure remains more or less intact as methanol molecules are added interstitially into cavities in the structure. As more and more methanol is added the cavities are progressively filled, water-methanol interactions become stronger and in turn producing maximum Walden product. As the methanol content increases, progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture. The effective radius(r) of ion or solute can be calculated as

$$\Lambda_0 n_0 = \frac{1}{6\pi r T}$$

It has been possible to derive the values of r for the cation of Ni^{II} complexes. The calculated values of r decrease with increase in methanol content upto $X_{MeOH} = 0.36$ and thereafter increase in methanol rich regions. The smaller $\Lambda_0\eta_0$ values in methanol rich region may be due to the large effective radius of the cation, whereas the maximum values of $X_{MeOH} = 0.36$ correspond to minimum values of r. Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employed for rate processes taking place with change of temperature, i.e.,

$\Lambda_0 = Ae^{-E^a/RT}$ or $\ln \Lambda_0 = \ln A - E^a/RT$

Where A is the frequency factor, R the ideal gas constant and E^a is Arrhenius activation energy of transport processes. E^a values can be computed from the slope of the plot of log Λ_o versus 1/T (Fig 9 & 10) and are shown in Table 10 (a) & (b).

4.3.4. Evaluation of thermodynamic parameters

Table 10(a): Thermodynamic parameters ΔG^0 (kJmol^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3} A for N-[(benzoyl-amino)-thioxomethyl]-serine Ni (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
			X_1=0.0000				
ΔG^0	-14.72	-14.58	-14.38	-14.23	-14.10	-13.97	-13.86
ΔH^0	-25.87						
10^3 ΔS^0	-39.40	-39.20	-39.19	-39.03	-38.84	-38.60	-38.34
E^a	7.06						
10^{-3}A	5.64						
			X_1=0.0588				
ΔG^0	-15.12	-15.03	-14.88	-14.70	-14.58	-14.46	-14.37
ΔH^0	-24.42						
10^3 ΔS^0	-32.84	-32.61	-32.55	-32.47	-32.45	-32.34	-32.10
E^a	7.19						
10^{-3}A	4.07						

			X_1=0.1942				
ΔG^0	-15.47	-15.40	-15.33	-15.26	-15.18	-15.09	-15.04
ΔH^0	-24.01						
$10^3\ \Delta S^0$	-30.15	-29.89	-29.59	-29.35	-29.12	-28.96	-28.65
E^a	7.55						
$10^{-3}A$	4.46						
			X_1=0.3600				
ΔG^0	-15.71	-15.70	-15.67	-15.61	-15.54	-15.44	-15.37
ΔH^0	-23.65						
$10^3\ \Delta S^0$	-28.03	-27.52	-27.24	-26.98	-26.75	-26.63	-26.45
E^a	8.79						
$10^{-3}A$	8.06						
			X_1=0.5676				
ΔG^0	-16.05	-16.03	-15.98	-15.93	-15.87	-15.78	-15.67
ΔH^0	-23.12						
$10^3\ \Delta S^0$	-24.98	-24.61	-24.35	-24.13	-23.93	-23.81	-23.79
E^a	8.23						
$10^{-3}A$	7.34						
			X_1=0.8351				
ΔG^0	-16.26	-16.25	-16.22	-16.18	-16.12	-16.05	-15.93
ΔH^0	-22.72						
$10^3\ \Delta S^0$	-22.80	-22.43	-22.19	-21.93	-21.77	-21.65	-21.69
E^a	7.69						
$10^{-3}A$	5.91						

			X_1=1.0000				
ΔG^0	-16.44	-16.43	-16.41	-16.39	-16.35	-16.29	-16.17
ΔH^0	-22.22						
$10^3\,\Delta S^0$	-20.51	-20.07	-19.82	-19.55	-19.36	-19.24	-19.21
E^a	7.09						
10^{-3}A	5.05						

Table 10(b): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3} A for N-[(benzoyl-amino)-thioxomethyl]-serine Mn (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
			X_1=0.0000				
ΔG^0	-15.13	-15.03	-15.02	-14.98	-14.94	-14.91	-14.87
ΔH^0	-26.83						
$10^3\,\Delta S^0$	-41.33	-40.94	-40.27	-39.75	-39.23	-38.70	-38.18
E^a	7.06						
10^{-3}A	5.46						
			X_1=0.0588				
ΔG^0	-15.38	-15.32	-15.31	-15.25	-15.16	-15.13	-15.07
ΔH^0	-26.13						
$10^3\,\Delta S^0$	-37.96	-37.50	-36.91	-36.50	-36.18	-35.68	-35.31
E^a	7.19						
10^{-3}A	4.01						

			X_1=0.1942				
ΔG^0	-15.58	-15.57	-15.56	-15.51	-15.44	-15.39	-15.33
ΔH^0	-25.45						
$10^3\ \Delta S^0$	-34.85	-34.15	-33.75	-33.75	-33.02	-32.65	-32.31
E^a	7.55						
$10^{-3}A$	4.28						
			X_1=0.3600				
ΔG^0	-15.77	-15.75	-15.74	-15.73	-15.72	-15.69	-15.65
ΔH^0	-24.75						
$10^3\ \Delta S^0$	-31.72	-31.11	-30.52	30.21	-29.75	-29.42	-29.07
E^a	8.79						
$10^{-3}A$	7.85						
			X_1=0.5676				
ΔG^0	-16.02	-15.97	-16.00	-15.99	-15.98	-15.97	-15.91
ΔH^0	-24.11						
$10^3\ \Delta S^0$	-28.56	-28.24	-27.66	-27.23	-26.77	-26.37	-26.20
E^a	8.23						
$10^{-3}A$	7.26						
			X_1=0.8351				
ΔG^0	-16.23	-16.21	-16.20	-16.19	-16.17	-16.16	-16.14
ΔH^0	-23.73						
$10^3\ \Delta S^0$	-26.48	-25.99	-25.54	-25.01	-24.57	-24.20	-23.73
E^a	7.69						
$10^{-3}A$	5.73						

			X_1=1.0000				
ΔG^0	-16.43	-16.42	-16.40	-16.39	-16.37	-16.34	-16.31
ΔH^0	-23.21						
$10^3\,\Delta S^0$	-23.95	-23.45	-22.95	-22.41	-21.90	-21.61	-23.21
E^a	7.09						
$10^{-3}A$	5.02						

The negative values of ΔG^0 and ΔH^0 from Table 10 (a) & 10 (b) can be explained by considering the participation of specific covalent interaction in the ion-association process. But the binding entropy (ΔS^0) between the ions was found to be negative to unfavored the ion-association process and thus favoring ion solvation process. The value of E^a increases with increase in X_1 upto about X_1=0.3600 and thereafter decreases rapidly. It follows that in water rich region upto X_1=0.36, the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond X_1=0.36. A reaction which requires higher activation energy is slow at ordinary temperatures indicating the lower mobility of the ions in the solutions and hence lower Λ_0 values. Beyond X_1=0.36, as the activation energy decreases the Λ_0 values increases with X_1. The free energy change (ΔG^0) for association processes is evaluated from the relation, $\Delta G^0 = -RT \ln K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A versus 1/T (Fig.11 & 12). ΔH^0 values obtained are found to increase with the composition of the mixed solvents. The entropy change is calculated from Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The values of these thermodynamic parameters in all solvent mixtures at all temperature are given in Table 10 (a) & (b).

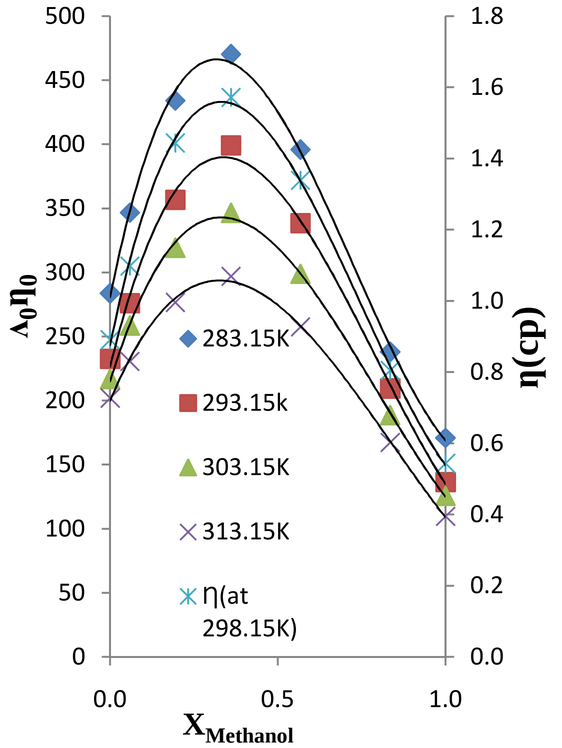


Fig 7: The value of Walden product and viscosity for Ni^{II} as afunction of X_{MeOH} in methanol+water solvent

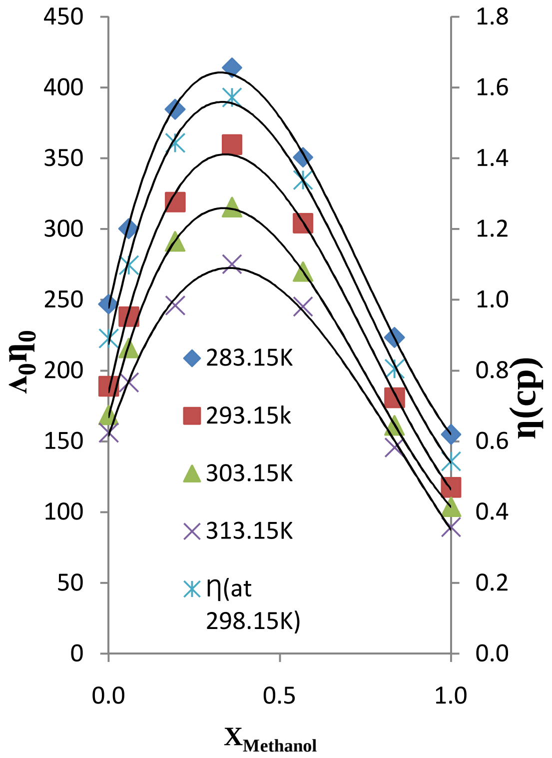


Fig 8: The value of Walden product and viscosity for Mn^{II} as a function of X_{MeOH} in methanol+water solvent

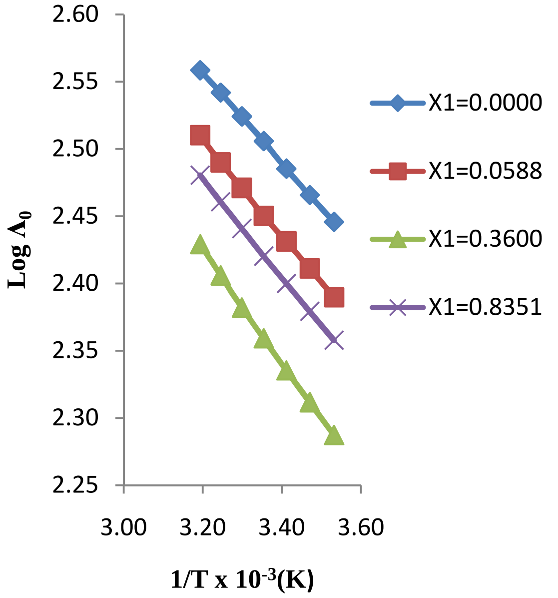


Fig 9: Plot of Log Λ_0 vs 1/T for Ni^{II} complex in different mole fractions at 283.15 -313.15K

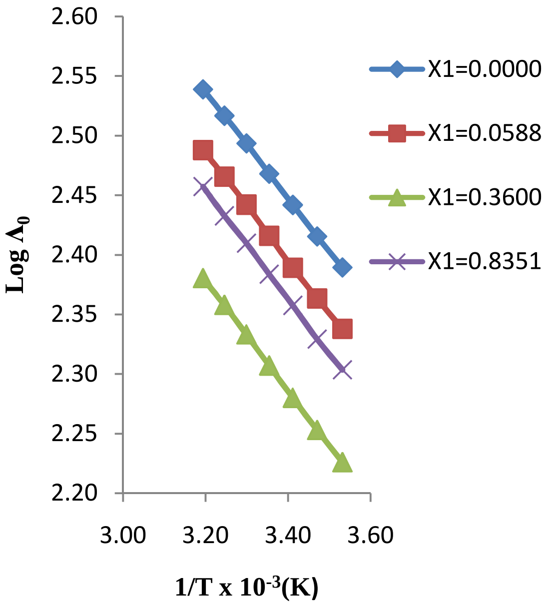


Fig 10: Plot of Log Λ_0 vs 1/T for Mn^{II} complex in different mole fractions at 283.15 - 313.15K

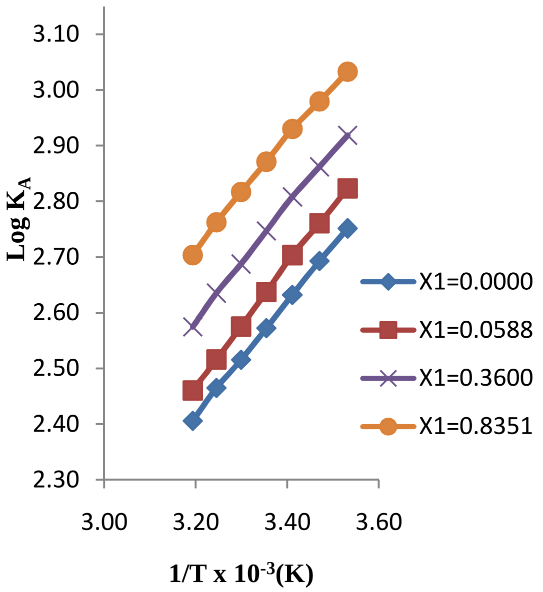


Fig 11: Log K_A vs 1/T for Ni^{II} complex in different mole fractions at 283.15 -313.15K

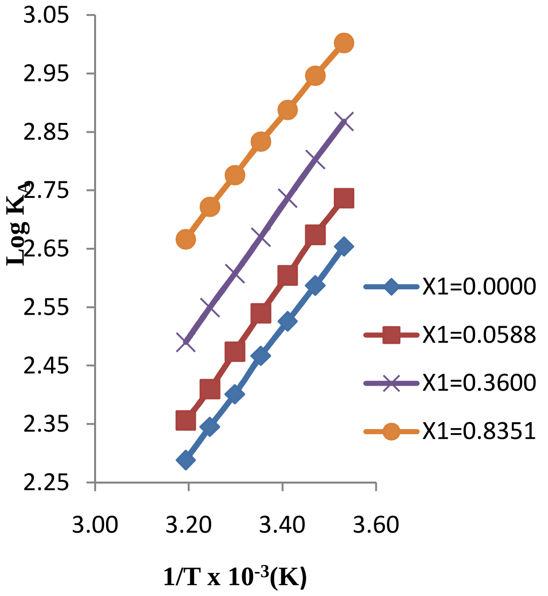


Fig 12: Log K_A vs 1/T for Mn^{II} complex in different mole fractions at 283.15 -313.15K

The extensive conductometric study of the two complex salts in methanol-water solvent mixtures have been reported at T= (283.15 to 313.15)K. The conductivity data have been analyzed using Shedlovsky equation. The experimentally determined K_As of the complex are found to increase with increase in X_1 which indicate an increased association as methanol is added to water. The negative values ΔH^0 indicates ion-pairing process is exothermic. As expected that the values of ΔG^0 become more negative at higher percentage of methanol which indicate that ion-pair association are favored with lowering dielectric constant of the medium. The values of E^a increased with increase in X_1upto about X_1=0.3600 and thereafter decreased rapidly. It follows that in water rich region upto X_1=0.36, the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond X_1=0.3600.

4.4. Ion association and solvation behavior of metal (II) chlorides in binary mixtures of methanol + water: A conductance method

4.4.1. Introduction

Behavior of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity which can be attained by using mixed solvent systems. The influence of the solvent mixtures on the ionic association of the electrolytes is due to the mode of solvation of the ions [Das *et al.*, 2004; Guha *et al.*, 2003; Roy *et al.*, 2006]. Solvent properties such 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. Conductance study is a very important tool in obtaining the information regarding the solvation and association behavior of ions in solutions [Dogonadze *et al.*, 1986]. Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent [Saito *et al.*, 1976]. Here, we have investigated the conductance behavior of two inorganic salts(transition metal salt) with common anion ie., N-[Benzoylamino)-thioxomethyl]-histidine Ni (II) chloride and N-[Benzoylamino)-thioxomethyl]-histidine Mn (II) chloride in different mass fraction (0.0000, 0.0588, 0.1233, 0.1942, 0.2727, 0.3600, 0.4576, 0.5676, 0.6923, 0.8351 and 1.0000) of methanol (CH_3OH) in water (H_2O) at different temperatures ranging from 283.15, 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15K. Experimental results were treated by Shedlovsky equation to obtain the limiting molar conductance (Λ_0) and the association constant (K_A) which served further to calculate Walden product ($\Lambda_0\eta_0$) and other thermodynamic quantities of the ion association reaction (ΔG^0, ΔH^0, ΔS^0). The calculation was further extended to derive Arrhenius activation energy (E^a) for ion-association reaction and described accordingly.

4.4.2. Experimental

4.4.2.1. Preparation of ligands and compounds

The salts selected for the present work, ie N-[(benzoyl-amino)-thioxomethyl]- histidine manganese (II) chloride and N-[(benzoyl-amino)- thioxomethyl]- histidine nickel (II) chloride were prepared according to chapter-3, section 3.8.2 (vii) & 3.8.2 (viii). The purity of the sample was determined by conventional chemical analysis and spectral measurements and the values are in good agreement with the literature values [Kabbani *et al*., 2005].

4.4.2.2. Conductivity measurements

Water was distilled twice (specific conductivity ≈ 10^{-6} S cm^{-1}) and KCL (Merck, India) was dried for six hours at 393.15K before use. Methanol (Merck, India, absolutely, 99.8% pure) was used without further purification. The solutions of different concentrations (1 x10^{-4}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water. All the viscosity, dielectric constant and density values were interpolated from literature values [Pura and Atun, 2003; Shedlovsky and Kay, 1956]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used. Conductivity measurements were carried out over the temperature range of $10^oC – 40^o C$. The temperature control in the ranges of 10-40^0C were made by using refrigerated water bath and circulator Model D8-G of HAAKE Mess-Technik) and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg).

Table 11(a): The values of molar conductance (Λ) obtained for N-[(benzoyl-amino)-thioxomethyl]- histidine nickel (II) chloride in methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	253.89	277.99	293.51	304.51	319.11	339.71	357.11
0.9091	254.99	279.11	294.53	305.42	320.00	340.53	357.82
0.8333	255.97	280.04	295.40	306.23	320.75	341.22	358.50
0.7692	256.81	280.85	296.19	306.94	321.40	341.79	359.06
0.7143	257.50	281.61	296.86	307.54	321.95	342.35	359.54
0.6667	258.26	282.30	297.52	308.08	322.51	342.83	359.97
0.6250	258.85	282.82	298.05	308.57	322.93	343.24	360.36
0.5882	259.46	283.41	298.59	309.06	323.34	343.62	360.72
0.5556	259.98	283.94	299.04	309.52	323.76	343.99	361.05
0.5263	260.47	284.38	299.48	309.95	324.11	344.31	361.34

X_1=0.0588

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	225.11	240.51	250.37	268.71	278.11	289.91	310.51
0.9091	226.19	241.58	251.35	269.59	278.88	290.64	311.20
0.8333	227.11	242.43	252.23	270.35	279.53	291.25	311.82
0.7692	227.97	243.25	252.95	271.00	280.11	291.79	312.36
0.7143	228.70	243.90	253.59	271.61	280.62	292.28	312.84
0.6667	229.38	244.56	254.20	272.18	281.09	292.73	313.25
0.6250	229.96	245.12	254.65	272.60	281.50	293.14	313.60
0.5882	230.45	245.61	255.12	273.02	281.88	293.51	313.96
0.5556	230.98	246.07	255.57	273.47	282.25	293.83	314.28
0.5263	231.46	246.49	255.94	273.82	282.57	294.17	314.61

X_1=0.1233

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	207.31	219.51	227.62	244.41	255.71	268.41	288.51
0.9091	208.34	220.54	228.53	245.25	256.45	269.15	289.20
0.8333	209.23	221.35	229.30	245.97	257.09	269.75	289.76
0.7692	210.01	222.07	229.96	246.55	257.64	270.27	290.31
0.7143	210.72	222.71	230.61	247.12	258.15	270.76	290.75
0.6667	211.33	223.34	231.15	247.64	258.62	271.19	291.14
0.6250	211.84	223.81	231.60	248.08	259.00	271.56	291.51
0.5882	212.38	224.32	232.06	248.50	259.36	271.89	291.85
0.5556	212.86	224.73	232.49	248.87	259.70	272.22	292.16
0.5263	213.28	225.15	232.92	249.21	260.01	272.53	292.46

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	189.51	200.50	206.70	222.10	235.30	248.90	268.50
0.9091	190.44	201.44	207.56	222.87	236.01	249.61	269.13
0.8333	191.23	202.17	208.28	223.54	236.64	250.20	269.67
0.7692	192.00	202.88	208.91	224.08	237.13	250.71	270.21
0.7143	192.65	203.43	209.46	224.61	237.60	251.18	270.66
0.6667	193.22	204.01	209.99	225.09	238.04	251.60	271.08
0.6250	193.73	204.49	210.41	225.51	238.42	251.94	271.42
0.5882	194.20	204.93	210.87	225.90	238.80	252.28	271.74
0.5556	194.62	205.32	211.29	226.24	239.13	252.57	272.00
0.5263	195.01	205.71	211.64	226.58	239.44	252.84	272.32

X_1=0.2727

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	177.81	191.51	203.11	216.51	229.21	244.51	265.45
0.9091	178.67	192.40	203.98	217.30	229.87	245.20	266.17
0.8333	179.46	193.15	204.73	217.98	230.50	245.78	266.76
0.7692	180.18	193.82	205.37	218.56	231.04	246.29	267.28
0.7143	180.78	194.43	205.89	219.11	231.49	246.77	267.75
0.6667	181.37	195.00	206.42	219.58	231.91	247.18	268.17
0.6250	181.83	195.45	206.83	220.02	232.30	247.54	268.52
0.5882	182.31	195.91	207.28	220.38	232.68	247.89	268.89
0.5556	182.77	196.37	207.69	220.76	233.03	248.25	269.22
0.5263	183.18	196.71	208.08	221.09	233.34	248.54	269.53

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	166.11	182.51	199.51	210.91	223.11	240.11	262.51
0.9091	166.98	183.41	200.42	211.75	223.78	240.87	263.19
0.8333	167.75	184.20	201.18	212.43	224.37	241.50	263.82
0.7692	168.46	184.86	201.85	213.00	224.92	242.03	264.33
0.7143	169.07	185.48	202.46	213.57	225.42	242.50	264.81
0.6667	169.56	186.00	202.97	214.08	225.86	242.91	265.25
0.6250	170.03	186.44	203.43	214.50	226.27	243.28	265.64
0.5882	170.49	186.88	203.92	214.89	226.60	243.65	265.98
0.5556	170.90	187.31	204.34	215.24	226.92	243.97	266.35
0.5263	171.31	187.69	204.73	215.62	227.25	244.30	266.65

X_1=0.4576

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	172.81	187.51	205.51	218.11	227.31	247.51	264.21
0.9091	173.75	188.43	206.53	219.00	228.02	248.28	264.93
0.8333	174.58	189.25	207.34	219.72	228.70	248.93	265.57
0.7692	175.37	189.98	208.07	220.41	229.31	249.52	266.15
0.7143	176.03	190.63	208.69	220.96	229.83	250.04	266.67
0.6667	176.61	191.20	209.28	221.52	230.30	250.49	267.13
0.6250	177.14	191.69	209.75	221.96	230.71	250.87	267.54
0.5882	177.63	192.18	210.23	222.41	231.12	251.87	267.95
0.5556	178.07	192.66	210.64	222.79	231.47	251.64	268.31
0.5263	178.44	193.03	211.08	223.20	231.81	251.93	268.68

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	179.51	192.51	211.51	225.31	231.51	254.91	265.91
0.9091	180.49	193.54	212.52	226.23	232.32	255.72	266.76
0.8333	181.37	194.42	213.39	227.02	233.03	256.41	267.41
0.7692	182.15	195.18	214.17	227.75	233.70	257.05	268.03
0.7143	182.88	195.89	214.83	228.36	234.26	257.62	268.61
0.6667	183.52	196.54	215.48	228.94	234.80	258.13	269.12
0.6250	184.08	197.09	215.99	229.43	235.21	258.58	269.53
0.5882	184.60	197.57	216.53	229.92	235.63	259.00	269.90
0.5556	185.11	198.05	216.97	230.36	236.02	259.36	270.28
0.5263	185.62	198.48	217.38	230.80	236.38	259.73	270.61

X_1=0.6923

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	190.08	202.52	221.52	235.30	241.51	264.92	275.92
0.9091	191.19	203.57	222.58	236.37	242.39	265.79	276.83
0.8333	192.17	204.55	223.53	237.25	243.15	266.58	277.61
0.7692	193.12	205.38	224.36	238.06	243.83	267.31	278.26
0.7143	193.87	206.16	225.15	238.77	244.44	267.90	278.94
0.6667	194.56	206.83	225.84	239.38	245.04	268.47	279.47
0.6250	195.18	207.42	226.37	239.89	245.52	268.96	279.91
0.5882	195.74	207.98	226.93	240.42	246.03	269.40	280.38
0.5556	196.29	208.55	227.44	240.91	246.45	269.82	280.77
0.5263	196.80	209.04	227.96	241.35	246.84	270.22	281.16

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	200.64	212.52	231.51	245.52	251.52	274.92	285.90
0.9091	201.89	213.68	232.67	246.67	252.60	275.97	286.81
0.8333	202.93	214.73	233.68	247.64	253.48	276.84	287.65
0.7692	203.92	215.64	234.67	248.48	254.27	277.67	288.41
0.7143	204.77	216.50	235.46	249.29	254.94	278.36	289.10
0.6667	205.59	217.27	236.21	249.94	255.55	278.95	289.72
0.6250	206.30	217.89	236.85	250.55	256.10	279.43	290.26
0.5882	206.93	218.58	237.46	251.13	256.64	279.92	290.77
0.5556	207.54	219.19	238.02	251.68	257.13	280.39	291.20
0.5263	208.13	219.67	238.57	252.21	257.56	280.84	291.60

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	220.66	232.54	251.55	265.22	271.54	294.94	305.94
0.9091	222.09	233.95	252.98	266.60	272.81	296.23	307.09
0.8333	223.35	235.12	254.19	267.75	273.83	297.25	308.12
0.7692	224.51	236.15	255.23	268.74	274.72	298.20	308.93
0.7143	225.54	237.14	256.16	269.67	275.56	299.01	309.71
0.6667	226.40	238.03	256.99	270.52	276.33	299.72	310.39
0.6250	227.12	238.72	257.74	271.21	276.95	300.33	310.97
0.5882	227.84	239.45	258.43	271.87	277.58	300.90	311.54
0.5556	228.48	240.11	259.14	272.49	278.16	301.46	312.08
0.5263	229.13	240.76	259.72	273.04	278.69	302.01	312.56

Table 11(b): The values of molar conductance (Λ) obtained for N-[(benzoyl-amino)-thioxomethyl]-histidine manganese (II) chloride in methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	233.63	257.87	272.85	283.85	298.45	314.65	333.25
0.9091	234.62	259.33	273.81	284.79	299.31	315.49	333.90
0.8333	235.50	260.56	274.76	285.66	300.05	316.20	334.49
0.7692	236.26	261.68	275.59	286.42	300.72	316.82	334.98
0.7143	236.92	262.59	276.26	287.07	301.29	317.36	335.40
0.6667	237.54	263.48	276.90	287.64	301.88	317.88	335.81
0.6250	238.10	264.21	277.43	288.16	302.37	318.30	336.15
0.5882	238.59	265.02	278.00	288.63	302.84	318.74	336.48
0.5556	239.08	265.60	278.44	289.08	303.26	319.13	336.79
0.5263	239.53	266.18	278.87	289.52	303.61	319.46	337.07

X_1=0.0588

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	204.09	219.49	229.35	247.69	257.09	268.89	289.49
0.9091	205.03	220.62	230.37	248.64	257.87	269.62	290.08
0.8333	205.79	221.53	231.23	249.45	258.55	270.25	290.57
0.7692	206.50	222.38	232.04	250.10	259.16	270.76	291.00
0.7143	207.13	223.19	232.78	250.76	259.64	271.22	291.39
0.6667	207.74	223.85	233.39	251.31	260.09	271.67	291.72
0.6250	208.22	224.44	233.97	251.82	260.53	272.08	292.04
0.5882	208.68	225.00	234.56	252.30	260.90	272.46	292.35
0.5556	208.06	225.51	235.00	252.75	261.27	272.79	292.62
0.5263	209.40	226.07	235.44	253.16	261.61	273.05	292.89

X_1=0.1233

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	186.29	196.49	204.60	221.39	232.69	245.39	265.49
0.9091	287.07	197.43	205.58	222.23	233.43	246.00	266.03
0.8333	187.85	198.37	206.43	223.00	234.10	246.56	266.48
0.7692	188.46	199.15	207.25	223.65	234.72	247.13	266.90
0.7143	189.05	199.88	207.93	224.20	235.21	247.58	267.31
0.6667	189.60	200.50	208.54	224.71	235.68	248.00	267.63
0.6250	190.02	201.05	209.10	225.19	236.10	248.37	267.92
0.5882	190.48	201.59	209.62	225.62	236.47	248.71	268.24
0.5556	190.88	202.04	210.10	225.98	236.86	249.00	268.51
0.5263	191.26	202.53	210.51	226.35	237.18	249.31	268.72

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	168.49	179.59	185.79	201.19	214.39	227.99	247.59
0.9091	169.31	180.54	186.68	201.95	215.14	228.65	248.10
0.8333	169.99	181.30	187.40	202.60	215.75	229.18	248.57
0.7692	170.58	182.05	188.06	203.18	216.32	229.65	248.98
0.7143	171.11	182.68	188.67	203.67	216.87	230.07	249.35
0.6667	171.57	183.27	189.25	204.13	217.36	230.46	249.68
0.6250	171.96	183.79	189.70	204.52	217.78	230.78	249.94
0.5882	172.35	184.21	190.13	204.96	218.19	231.13	250.23
0.5556	172.73	184.70	190.52	205.31	218.56	231.42	250.46
0.5263	173.10	185.09	190.95	205.63	218.85	231.67	250.71

X_1=0.2727

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	156.79	170.49	182.09	195.49	208.19	223.49	244.49
0.9091	157.48	171.37	183.00	196.30	208.94	224.15	245.02
0.8333	158.13	172.18	183.78	197.00	209.58	224.66	245.47
0.7692	158.70	172.90	184.47	197.65	210.17	225.17	245.88
0.7143	159.21	173.52	185.15	198.18	210.68	225.58	246.26
0.6667	159.65	174.10	185.71	198.66	211.14	226.00	246.62
0.6250	160.04	174.58	186.19	199.07	211.55	226.31	246.91
0.5882	160.42	175.06	186.64	199.48	211.99	226.62	247.22
0.5556	160.78	175.55	187.10	199.85	212.31	226.93	247.46
0.5263	161.12	175.93	187.53	200.20	212.64	227.24	247.72

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	145.09	161.49	178.49	189.89	202.09	219.09	241.49
0.9091	145.77	162.44	179.45	190.70	202.83	219.75	242.05
0.8333	146.39	163.25	180.32	191.43	203.47	220.33	242.53
0.7692	146.88	163.92	181.08	192.12	204.10	220.82	242.97
0.7143	147.40	164.52	181.73	192.67	204.56	221.22	243.36
0.6667	147.84	165.09	182.34	193.20	205.08	221.66	243.70
0.6250	148.20	165.61	182.89	193.65	205.47	222.00	244.02
0.5882	148.56	166.06	183.40	194.10	205.89	222.33	244.29
0.5556	148.90	166.45	183.81	194.53	206.22	222.63	244.56
0.5263	149.20	166.87	184.25	194.87	206.54	222.91	244.83

X_1=0.4576

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	151.79	166.49	184.49	197.09	206.29	226.49	243.19
0.9091	152.61	167.51	185.51	197.93	207.10	227.21	243.78
0.8333	153.26	168.34	186.37	198.65	207.78	227.86	244.29
0.7692	153.85	169.10	187.19	199.30	208.46	228.45	244.72
0.7143	154.35	169.79	187.86	199.87	209.00	229.00	245.17
0.6667	154.81	170.45	188.45	200.42	209.56	229.44	245.54
0.6250	154.23	170.98	189.02	200.89	210.00	229.82	245.87
0.5882	155.62	171.46	189.55	201.27	210.47	230.25	246.14
0.5556	156.01	171.94	190.02	201.66	210.85	230.57	246.45
0.5263	156.42	172.39	190.53	202.08	211.19	230.91	246.69

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	158.49	171.49	190.49	204.29	210.49	233.89	244.89
0.9091	159.31	172.61	191.61	205.10	211.41	234.83	245.58
0.8333	160.06	173.58	192.56	205.81	212.18	235.61	246.12
0.7692	160.72	174.40	193.32	206.46	212.87	236.32	246.57
0.7143	161.30	175.10	194.06	207.06	213.49	236.94	246.99
0.6667	161.79	175.78	194.70	207.59	214.07	237.53	247.42
0.6250	162.21	176.34	195.28	208.07	214.57	238.07	247.75
0.5882	162.65	176.90	195.87	208.53	215.00	238.56	248.08
0.5556	163.04	177.43	196.35	208.88	215.44	239.05	248.41
0.5263	163.41	177.91	196.81	209.29	215.85	239.41	248.72

X_1=0.6923

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	169.06	181.50	200.50	214.28	220.49	243.90	254.90
0.9091	170.00	182.55	201.63	215.40	221.45	244.74	255.56
0.8333	170.74	183.43	202.58	215.40	222.30	245.56	256.14
0.7692	171.47	184.32	203.42	216.32	222.98	246.30	256.70
0.7143	172.09	185.06	204.17	217.10	223.68	246.91	257.17
0.6667	172.64	185.71	204.88	217.76	224.26	247.45	257.61
0.6250	173.12	186.29	205.47	218.43	224.77	247.98	257.99
0.5882	173.65	186.87	206.03	219.00	225.25	248.44	258.36
0.5556	174.08	187.45	206.63	220.10	225.77	248.86	258.72
0.5263	174.52	187.92	207.12	220.63	226.19	249.29	259.04

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	179.62	191.50	210.49	224.18	230.50	253.90	264.88
0.9091	180.63	192.63	211.63	225.27	231.51	254.73	265.67
0.8333	181.55	193.57	212.56	226.20	232.40	255.46	266.32
0.7692	182.34	194.48	213.48	227.03	233.22	256.12	266.89
0.7143	183.03	195.29	214.30	227.74	233.89	256.69	267.40
0.6667	183.67	195.93	215.03	228.38	234.50	257.17	267.91
0.6250	184.22	196.57	215.64	228.96	235.12	257.60	268.33
0.5882	184.78	197.19	216.31	229.47	235.64	258.08	268.69
0.5556	185.26	197.77	216.89	229.99	236.20	258.49	269.08
0.5263	185.74	198.25	217.42	230.47	236.64	258.92	269.44

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	199.64	211.52	230.79	244.20	250.52	273.92	284.92
0.9091	200.78	212.70	231.95	245.38	251.60	274.94	285.89
0.8333	201.83	213.75	232.97	246.43	252.56	275.87	286.70
0.7692	202.71	214.76	233.93	247.32	253.41	276.70	287.42
0.7143	203.60	215.56	234.86	248.19	254.20	277.43	287.98
0.6667	204.33	216.41	235.60	249.00	254.84	278.10	288.59
0.6250	204.94	217.04	236.23	249.68	255.45	278.66	289.10
0.5882	205.62	217.76	236.91	250.32	256.06	279.20	289.57
0.5556	206.20	218.33	237.54	250.85	256.55	279.74	290.00
0.5263	206.74	218.84	238.05	251.40	257.02	280.19	290.43

4.4.3. Evaluation of limiting molar conductance, association constant, walden product and effective radius

The limiting molar conductances (Λ_0) and ion association constants (K_A) have been computed using Shedlovsky method [Shedlovsky, 1932].

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are same as given in chapter 3, section 3.1.1.1.

Table 12(a): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) for N-[(benzoyl-amino)-thioxomethyl]-histidine nickel (II) chloride in methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	**Λ_0** Scm^{2}mol^{-1}	**K_A** dm^{3}mol^{-1}	**$\Lambda_0\eta_0$**	**r**	**Λ_0** Scm^{2}mol^{-1}	**K_A** dm^{3}mol^{-1}	**$\Lambda_0\eta_0$**	**r**
		T=283.15K				**T=288.15K**		
0.0000	260.33	589.12	339.21	5.53	284.97	507.75	324.30	5.68
0.0588	240.24	628.14	388.47	4.83	252.49	545.63	365.10	5.05
0.1233	223.63	671.55	438.99	4.27	235.08	576.41	414.21	4.45
0.1942	212.29	704.79	462.79	4.05	222.96	609.04	436.78	4.22
0.2727	203.28	739.11	475.68	3.94	213.54	638.55	439.47	4.19
0.3600	191.73	771.45	477.60	3.93	202.16	670.62	459.51	4.01
0.4576	197.34	813.75	422.31	4.44	207.78	703.34	404.96	4.55
0.5676	207.98	862.33	411.80	4.55	218.04	738.03	368.27	5.00
0.6923	216.46	899.84	318.20	5.89	228.42	771.45	298.54	6.17
0.8351	231.10	938.66	245.20	7.65	242.81	809.77	234.31	7.86
1.0000	247.95	998.02	171.58	10.93	262.46	851.74	163.51	11.27

$X_{Methanol}$	Λ_0	K_A	$\Lambda_0\eta_0$	r	Λ_0	K_A	$\Lambda_0\eta_0$	r
	Scm^2mol^{-1}	dm^3mol^{-1}			Scm^2mol^{-1}	dm^3mol^{-1}		
		T=293.15K				**T=298.15K**		
0.0000	300.52	434.14	301.12	6.01	317.32	377.32	282.73	6.30
0.0588	264.89	467.49	331.91	5.46	279.03	409.01	306.37	5.81
0.1233	246.86	495.05	374.24	4.84	258.78	428.73	340.55	5.23
0.1942	230.03	524.23	386.45	4.69	245.77	451.55	354.89	5.02
0.2727	219.15	551.16	387.90	4.67	236.52	478.39	355.25	5.01
0.3600	216.32	580.64	388.94	4.66	227.09	502.14	356.99	4.99
0.4576	218.73	609.15	367.69	4.92	229.65	526.93	335.52	5.31
0.5676	225.58	637.37	341.30	5.31	240.53	555.51	322.07	5.53
0.6923	236.88	667.66	282.36	6.41	251.41	581.38	271.77	6.55
0.8351	248.41	696.91	217.11	8.34	268.69	607.77	216.30	8.23
1.0000	273.10	735.62	163.04	11.11	287.98	643.24	156.66	11.36
		T=303.15K				**T=308.15K**		
0.0000	333.14	329.73	265.85	6.59	350.59	290.62	252.42	6.82
0.0588	292.62	356.37	287.35	6.09	307.16	311.69	268.77	6.41
0.1233	272.18	376.36	311.65	5.62	284.79	331.46	287.35	5.99
0.1942	253.57	397.04	323.30	5.42	270.58	349.43	300.61	5.73
0.2727	245.06	418.68	325.68	5.38	260.66	367.65	301.58	5.71
0.3600	240.65	439.73	328.01	5.34	253.08	388.52	303.19	5.68
0.4576	242.08	462.00	307.20	5.70	256.04	409.15	295.47	5.83
0.5676	251.96	487.95	298.32	5.87	265.23	429.32	280.61	6.14
0.6923	265.24	512.44	255.69	6.85	276.31	452.64	240.94	7.15
0.8351	281.62	535.76	204.46	8.56	295.03	473.68	198.56	8.68
1.0000	302.74	568.18	154.40	11.44	314.74	498.97	154.22	11.69
		T=313.15K						
0.0000	356.22	254.64	232.97	7.28				
0.0588	324.14	273.23	257.04	6.59				
0.1233	298.07	292.73	268.86	6.30				
0.1942	277.77	309.12	274.71	6.17				
0.2727	275.24	328.03	276.07	6.14				
0.3600	266.47	345.76	278.46	6.09				
0.4576	270.89	364.01	270.08	6.28				
0.5676	277.87	383.62	262.87	6.45				
0.6923	288.46	401.84	226.15	7.50				
0.8351	308.75	417.46	191.43	8.86				
1.0000	330.51	441.84	150.71	12.74				

Table 12(b): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) for N-[(benzoyl-amino)-thioxomethyl]-histidine manganese (II) chloride in methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r
		T=283.15K				**T=288.15K**		
0.0000	228.82	603.41	298.15	6.29	242.83	519.36	276.34	6.67
0.0588	213.24	634.34	344.81	5.44	227.35	552.22	328.75	5.60
0.1233	192.81	681.22	378.49	4.95	205.26	592.63	361.67	5.09
0.1942	181.34	712.01	395.32	4.74	192.58	621.77	377.26	4.88
0.2727	170.87	742.52	399.84	4.68	184.15	649.29	378.98	4.86
0.3600	162.05	776.62	403.67	4.64	172.38	688.51	391.82	4.70
0.4576	166.35	833.75	355.99	5.27	177.04	731.42	345.05	5.34
0.5676	174.11	871.04	344.74	4.43	185.39	769.44	313.12	5.88
0.6923	186.16	915.46	273.66	6.85	198.42	809.83	259.33	7.10
0.8351	200.54	955.24	212.77	8.81	214.09	842.69	206.60	8.92
1.0000	221.62	1019.15	153.36	12.22	240.32	892.81	149.72	12.30
		T=293.15K				**T=298.15K**		
0.0000	258.65	451.76	259.17	6.99	274.67	394.78	244.73	7.27
0.0588	241.45	484.91	302.54	5.98	257.55	421.57	282.79	6.30
0.1233	212.53	513.85	322.20	5.62	231.81	449.08	305.06	5.84
0.1942	198.26	540.45	333.08	5.44	217.06	473.96	313.43	5.68
0.2727	192.67	563.79	341.03	5.31	209.67	495.57	314.92	5.65
0.3600	190.68	604.54	342.84	5.28	201.53	535.38	316.81	5.62
0.4576	187.41	649.67	315.04	5.75	198.76	578.15	290.39	6.13
0.5676	196.80	682.85	297.76	6.08	208.61	605.84	279.33	6.37
0.6923	210.89	718.03	251.38	7.20	223.59	632.71	241.70	7.37
0.8351	227.71	749.05	199.02	9.10	242.71	664.72	195.38	9.11
1.0000	249.23	797.62	148.79	12.35	270.05	705.87	146.91	12.46

$X_{Methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
		T=303.15K				**T=308.15K**		
0.0000	289.93	348.43	231.36	7.57	308.44	309.31	222.08	7.76
0.0588	272.62	374.82	267.71	6.54	287.89	332.42	251.90	6.84
0.1233	240.64	399.73	275.53	6.36	257.31	357.32	259.63	6.64
0.1942	221.94	420.62	282.97	6.19	234.82	373.83	260.89	6.60
0.2727	213.08	441.81	283.18	6.18	225.78	395.72	261.23	6.59
0.3600	209.23	475.47	285.18	6.14	219.08	422.75	262.46	6.56
0.4576	210.12	515.71	266.64	6.57	222.74	457.43	257.04	6.70
0.5676	220.17	540.86	260.68	6.72	232.86	482.19	246.37	6.99
0.6923	236.72	567.18	228.20	7.67	251.43	505.41	219.25	7.86
0.8351	257.16	590.48	186.70	9.38	272.96	527.61	183.70	9.40
1.0000	286.06	624.63	145.89	12.55	296.04	562.15	145.06	12.62
		T=313.15K						
0.0000	325.44	275.85	212.84	7.96				
0.0588	295.04	296.71	233.97	7.24				
0.1233	265.75	317.88	239.71	7.07				
0.1942	244.33	336.16	241.64	7.01				
0.2727	242.76	353.28	243.49	6.96				
0.3600	234.39	379.62	244.94	6.92				
0.4576	237.68	411.62	236.97	7.15				
0.5676	243.02	431.81	229.90	7.37				
0.6923	261.84	453.67	205.28	8.27				
0.8351	289.21	473.59	179.31	9.45				
1.0000	317.09	504.15	144.59	12.76				

The results showed that the limiting molar conductances (Λ_0) increase as the temperature increases but decrease as the mass fraction of methanol in the solvent mixtures increases up to 50% of methanol. This trend in limiting molar conductances can be well described by the viscosity behavior of the solvent media. The viscosity of methanol-water mixtures passes through a maximum at about 50% of methanol. It is interesting to note that the Λ_0 values of salts decrease up to this mole fraction and then increase in methanol rich region at all temperatures. The limiting molar conductances (Λ_0) follow the order: $Ni^{II}>Mn^{II}$ complexes suggesting that solvation increases the ionic sizes of cations in such a way that the sizes of the solvated cations follows the crystallographic radii of the transition metal ions in aqueous methanol solutions. The values of K_A follows the order: $Ni^{II}<Mn^{II}$ complexes for all the solvent composition and experimental temperature, i.e., with increasing methanol content the association equilibrium shifts to the right of the above order as a result of decrease in mixture permittivity.

Walden products ($\Lambda_0\eta_0$) for the transition metal (II) chlorides are given Table 12 (a) & (b). The variations of Walden products with concentration are common and they can be attributed to change in ion-solvation and ion-solvent interaction. The value of $\Lambda_0\eta_0$ would be constant only if the effective radius of the ions were the same in different media. The increase of Walden product indicates the weak solvation of ions which attains a maximum value at 50% of methanol and decrease of Walden product indicates an increase of the hydrophobic solvation with increasing concentration of methanol. The variation of Walden product with X_{MeOH} is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions on the other with the change in composition of the mixed solvents and the temperature of the solution.

On the water-rich side there exists a region, where water structure remains more or less intact as methanol molecules are added interstitially into cavities in the structure. As more and more methanol is added the cavities are progressively filled, water-methanol interactions become stronger and in turn producing maximum Walden product. As the methanol content increases, progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture.

The effective radius(r) of ion or solute can be calculated as

$$\Lambda_0 n_0 = \frac{1}{6\pi r T}$$

It has been possible to derive the values of r for the cations of Ni^{II} complexes. The calculated values of r decrease with increase in methanol content upto $X_{MeOH} = 0.36$ and thereafter increase in methanol rich regions. The smaller $\Lambda_0\eta_0$ values in methanol rich region may be due to the large effective radius of the cations, whereas the maximum values of $X_{MeOH} = 0.36$ correspond to minimum values of r. Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employed for rate processes taking place with change of temperature, i.e.,

$$\Lambda_0 = \mathrm{A}e^{-\mathrm{E^a}/\mathrm{RT}} \text{or} \qquad \ln\Lambda_0 = \ln \mathrm{A} - \mathrm{E^a}/\mathrm{RT}$$

Where A is the frequency factor, R the ideal gas constant and E^a is Arrhenius activation energy of transport processes. E^a values can be computed from the slope of the plot of log Λ_o vs 1/T (fig 15 & 16) and are shown in Table 13 (a) & (b).

4.4.4. Evaluation of thermodynamic parameters:

Table 13(a): Thermodynamic parameters ΔG^0 ($kJmole^{-1}$), ΔH^0 ($kJmol^{-1}$), ΔS^0 ($kJK^{-1}mol^{-1}$), E^a ($kJmol^{-1}$) and 10^{-3}A for N-[(benzoyl-amino)-thioxomethyl]-histidine nickel (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
			X_1=0.0000				
ΔG^0	-15.02	-14.93	-14.81	-14.71	-14.62	-14.53	-14.43
ΔH^0	-24.25						
$10^3\ \Delta S^0$	-32.60	-32.35	-32.22	-32.00	-31.78	-31.53	-31.37
E^a	7.07						
10^{-3}A	5.46						

			X_1=0.0588				
ΔG^0	-15.17	-15.10	-14.99	-14.91	-14.81	-14.71	-14.61
ΔH^0	-24.04						
$10^3 \Delta S^0$	-31.33	-31.02	-30.89	-30.62	-30.44	-30.27	-30.12
E^a	7.21						
$10^{-3}A$	3.90						
			X_1=0.1233				
ΔG^0	-15.33	-15.23	-15.13	-15.03	-14.95	-14.87	-14.79
ΔH^0	-23.51						
$10^3 \Delta S^0$	-28.90	-28.73	-28.60	-28.45	-28.24	-28.03	-27.85
E^a	7.48						
$10^{-3}A$	3.59						
			X_1=0.1942				
ΔG^0	-15.44	-15.36	-15.27	-15.16	-15.09	-15.00	-14.93
ΔH^0	-23.12						
$10^3 \Delta S^0$	-27.12	-26.92	-26.80	-26.71	-26.51	-26.33	-26.15
E^a	7.75						
$10^{-3}A$	4.28						
			X_1=0.2727				
ΔG^0	-15.55	-15.48	-15.39	-15.30	-15.22	-15.14	-15.09
ΔH^0	-22.89						
$10^3 \Delta S^0$	-25.91	-25.73	-25.60	-25.46	-25.31	-25.16	-24.92
E^a	7.99						
$10^{-3}A$	6.56						

			X_1=0.3600				
ΔG^0	-15.65	-15.59	-15.51	-15.42	-15.34	-15.28	-15.22
ΔH^0	-21.62						
$10^3\,\Delta S^0$	-21.07	-20.91	-20.83	-20.80	-20.71	-20.58	-20.43
E^a	8.29						
$10^{-3}A$	7.89						
			X_1=0.4576				
ΔG^0	-15.78	-15.71	-15.63	-15.54	-15.47	-15.41	-15.36
ΔH^0	-20.36						
$10^3\,\Delta S^0$	-16.18	-16.14	-16.13	-16.17	-16.14	-16.06	-15.98
E^a	8.11						
$10^{-3}A$	8.53						
			X_1=0.5676				
ΔG^0	-15.92	-15.82	-15.74	-15.67	-15.61	-15.53	-15.49
ΔH^0	-19.09						
$10^3\,\Delta S^0$	-11.21	-11.33	-11.42	-11.48	-11.50	-11.54	-11.49
E^a	8.03						
$10^{-3}A$	7.16						
			X_1=0.6923				
ΔG^0	-16.02	-15.93	-15.85	-15.78	-15.73	-15.67	-15.61
ΔH^0	-14.81						
$10^3\,\Delta S^0$	4.26	3.89	3.56	3.26	3.03	2.79	2.57
E^a	7.89						
$10^{-3}A$	7.04						

			X_1=0.8351				
ΔG^0	-16.12	-16.05	-15.96	-15.89	-15.84	-15.78	-15.71
ΔH^0	-12.62						
$10^3\ \Delta S^0$	12.35	11.89	11.39	10.97	10.62	10.27	9.88
E^a	7.39						
$10^{-3}A$	5.73						
			X_1=1.0000				
ΔG^0	-16.26	-16.17	-16.09	-16.03	-15.99	-15.92	-15.86
ΔH^0	-21.26						
$10^3\ \Delta S^0$	21.19	20.50	19.89	19.36	18.90	18.36	17.89
E^a	6.91						
$10^{-3}A$	4.87						

Table 13(b): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A for N-[(benzoyl-amino)-thioxomethyl]-histidine manganese (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
			X_1=0.0000				
ΔG^0	-15.08	-14.98	-14.90	-14.82	-14.76	-14.69	-14.63
ΔH^0	-26.22						
$10^3\ \Delta S^0$	-39.36	-39.00	-38.61	-38.23	-37.82	-37.40	-37.00
E^a	8.18						
$10^{-3}A$	5.15						

			X_1=0.0588				
ΔG^0	-15.19	-15.13	-15.08	-14.99	-14.94	-14.88	-14.82
ΔH^0	-25.84						
$10^3\ \Delta S^0$	-37.60	-37.17	-36.72	-36.41	-35.96	-35.57	-35.18
E^a	8.43						
$10^{-3}A$	5.36						
			X_1=0.1233				
ΔG^0	-15.36	-15.30	-15.22	-15.14	-15.10	-15.06	-15.00
ΔH^0	-25.46						
$10^3\ \Delta S^0$	-35.67	-35.27	-34.94	-34.61	-34.17	-33.74	-33.39
E^a	8.81						
$10^{-3}A$	5. 57						
			X_1=0.1942				
ΔG^0	-15.47	-15.41	-15.34	-15.28	-15.23	-15.18	-15.15
ΔH^0	-24.84						
$10^3\ \Delta S^0$	-33.11	-32.72	-32.41	-32.08	-31.70	-31.35	-30.95
E^a	9.10						
$10^{-3}A$	5.74						
			X_1=0.2727				
ΔG^0	-15.56	-15.52	-15.44	-15.39	-15.35	-15.33	-15.28
ΔH^0	-23.96						
$10^3\ \Delta S^0$	-29.65	-29.30	-29.06	-28.76	-28.39	-28.02	-27.72
E^a	9.33						
$10^{-3}A$	6.05						

X_1=0.3600							
ΔG^0	-15.67	-15.66	-15.61	-15.58	-15.54	-15.49	-15.47
ΔH^0	-23.23						
$10^3\ \Delta S^0$	-26.70	-26.28	-25.99	-25.67	-25.37	-25.10	-24.79
E^a	9.53						
$10^{-3}A$	6.54						
X_1=0.4576							
ΔG^0	-15.84	-15.80	-15.79	-15.77	-15.74	-15.70	-15.68
ΔH^0	-22.57						
$10^3\ \Delta S^0$	-23.78	-23.49	-23.14	-22.81	-22.52	-22.31	-22.01
E^a	9.20						
$10^{-3}A$	5.94						
X_1=0.5676							
ΔG^0	-15.94	-15.92	-15.91	-15.88	-15.86	-15.83	-15.80
ΔH^0	-20.12						
$10^3\ \Delta S^0$	-14.77	-14.56	-14.36	-14.21	-14.04	-13.92	-13.79
E^a	8.95						
$10^{-3}A$	5.64						
X_1=0.6923							
ΔG^0	-16.06	-16.05	-16.03	-15.99	-15.98	-15.95	-15.93
ΔH^0	-14.73						
$10^3\ \Delta S^0$	4.69	4.57	4.44	4.23	4.14	3.97	3.83
E^a	8.63						
$10^{-3}A$	5.44						

			X_1=0.8351				
ΔG^0	-16.16	-16.14	-16.13	-16.11	-16.08	-16.06	-16.05
ΔH^0	-12.21						
$10^3\ \Delta S^0$	13.94	13.64	13.39	13.09	12.78	12.50	12.24
E^a	8.26						
$10^{-3}A$	5.25						
			X_1=1.0000				
ΔG^0	-16.31	-16.28	-16.23	-16.21	-16.20	-16.18	-16.15
ΔH^0	-10.09						
$10^3\ \Delta S^0$	21.96	21.48	21.14	20.70	20.24	19.91	19.53
E^a	7.97						
$10^{-3}A$	5.01						

The negative values of ΔG^0 and ΔH^0 from Table 13 (a) & (b) can be explained by considering the participation of specific covalent interaction in the ion-association process. But the binding entropy (ΔS^0) between the ions was found to be negative to unfavored the ion-association process and thus favoring ion solvation process. The value of E^a increases with increase in X_1upto about X_1=0.3600 and thereafter decreases rapidly. It follows that in water rich region upto X_1=0.36, the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond X_1=0.36. A reaction which requires higher activation energy is slow at ordinary temperatures indicating the lower mobility of the ions in the solutions and hence lower Λ_0 values. Beyond X_1=0.36, as the activation energy decreases the Λ_0 values increases with X_1 from Table 12 (a) & (b). The values of these thermodynamic parameters in all solvent mixtures at all temperature are given in Table 13 (a) & (b). As expected that the values of

ΔG^0 become more negative at higher percentage of methanol which indicate that ion-pair association are favored with lowering dielectric constant of the medium.

The free energy change (ΔG^0) for association processes is evaluated from the relation, $\Delta G^0 = -RT \ln K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A vs 1/T. The entropy change is calculated from Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$.

ΔH^0 values obtained are found to increase with the composition of the mixed solvents. The negative values of ΔH^0 indicate that ion association processes are exothermic in nature in all solvents at all temperatures. A positive entropy change is explained on the assumption that iceberg structure around the cations is broken when assumption takes place leading to an increase in the degree of disorderliness.

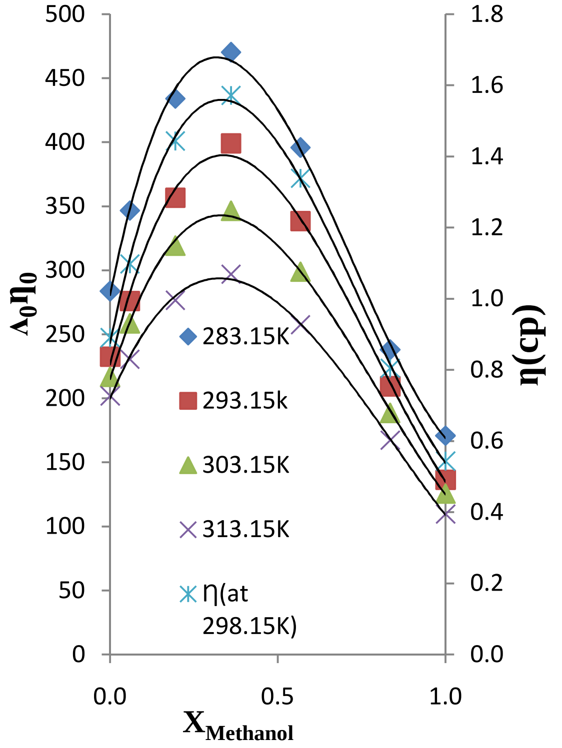


Fig 13: The value of Walden product and viscosity for Ni^{II} as afunction of X_{MeOH} in methanol+water solvent

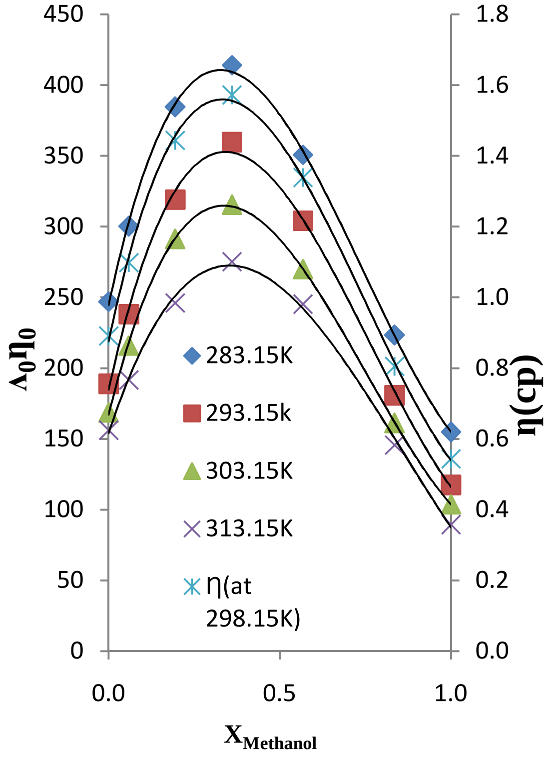


Fig 14: The value of Walden product and viscosity for Mn^{II} as a function of X_{MeOH} in methanol+water solvent

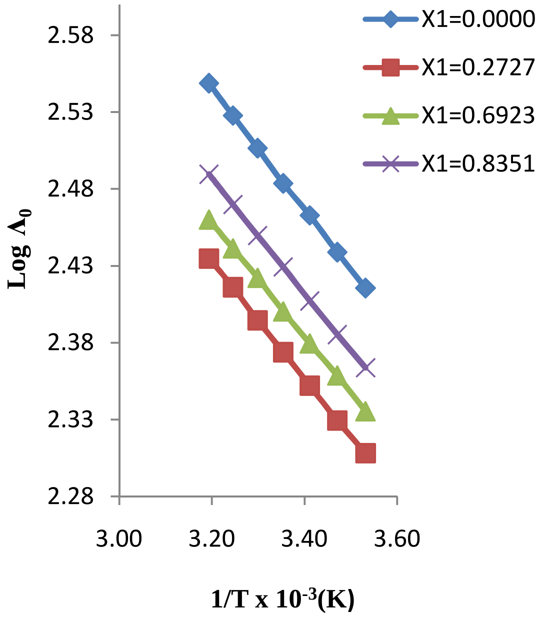


Fig 15: Plot of Log Λ_0 vs 1/T for Ni^{II} complex in different mole fractions at 283.15 - 313.15K

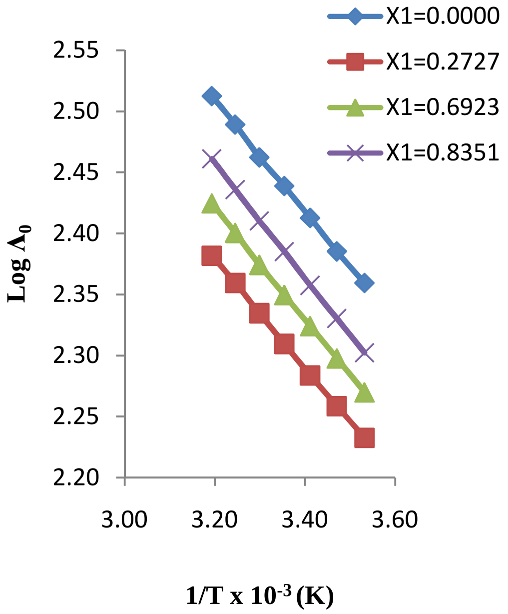


Fig 16: Plot of Log Λ_0 vs 1/T for Mn^{II} complex in different mole fractions at 283.15 - 313.15K

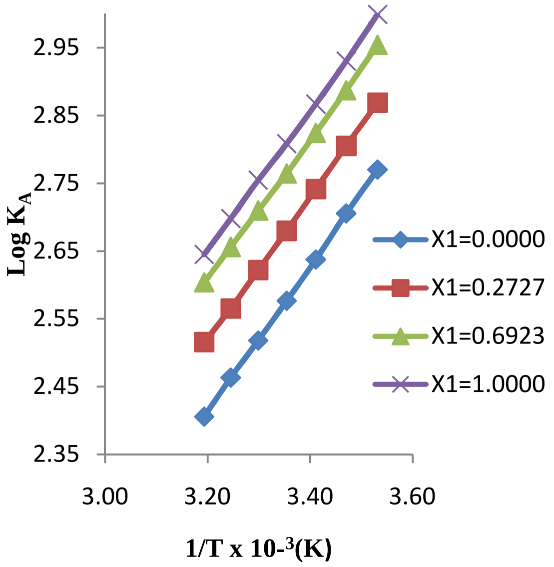


Fig 17: Plot of Log K_A vs 1/T for Ni^{II} complex in different mole fractions at 283.15 - 313.15K

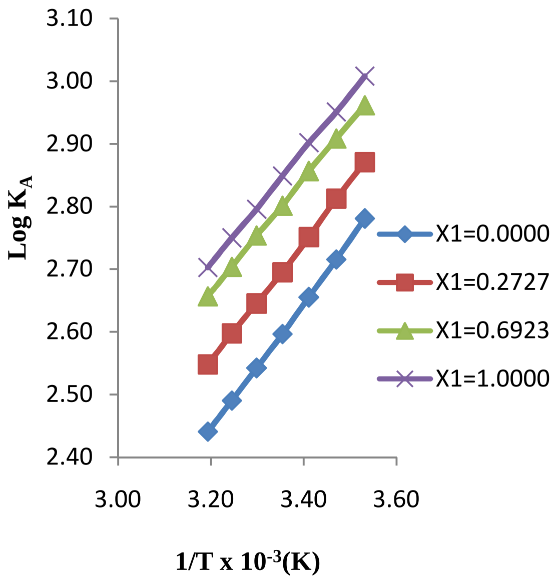


Fig 18: Plot of Log K_A vs 1/T for Mn^{II} complex in different mole fractions at 283.15 - 313.15K

Conductivity measurement of Ni^{II} and Mn^{II} complexes in 0-100% MeOH-water mixtures at 283.15-313.15K have been reported. The conductivity data have been analyzed using Shedlovsky equation. As the composition of MeOH in mixed solvents increased, the K_As for both the complex are found to increase. As expected that the values of ΔG^0 become more negative at higher percentage of methanol which indicate that ion-pair association are favored with lowering dielectric constant of the medium. The values of E^a increased with increase in X_1upto about X_1=0.3600(50% of methanol) and thereafter decreased rapidly. It follows that in water rich region upto X_1=0.36, the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond X_1=0.3600.

4.5. Association constant of 1-butyl-4-methylpyridinium hexafluorophosphate in binary solvent of methanol, acetonitrile and dimethylsulphoxide at different temperatures.

4.5.1. Introduction

Ionic liquids (ILs) have been actively tested as innovative nonvolatile solvents and they are used in many academic and industrial research areas. Ionic liquids are good examples of neoteric solvents (new types of solvents, or older materials that are finding new applications as solvents), which is environmentally friendly (or eco-friendly) because they are not hazardous for human body as well as non-toxic for living organism. Recently ionic liquids have been considered attractive compounds due to their unique intrinsic properties, such as negligible vapor pressure, large liquid range, ability of dissolving a variety of chemicals non-volatility, high thermal stability, large electrochemical window and their potential as ‘designer solvents’ and ‘green’ replacements for volatile organic solvents [Welton,1999] they have been intensively investigated for various applications such as recyclable solvents for organic reactions and separation processes [Plechkov and Seddon, 2008], lubricating fluids [Ye *et al.*, 2001], heat transfer fluids for processing biomass and electrically conductive liquids as electrochemical device in electrochemistry (batteries and solar cells)[Endres and Abedin., 2006; Wang *et al.*, 2003]mand so forth. By modifying the cations and anions, the physical properties (such as the melting point, viscosity, density, hydrophobicity, or hydrophilicity) of ionic liquids can be customized [Dupont *et al.*, 2002]. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions which in turn depends on the nature of the solvent/solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties helps in determining the extent of ion association and the ion-solvent interactions. The non-aqueous solution systems have been of immense importance [Popvych and Tomkins, 1981] to the technologist and theoretician as many chemical processes occur in these systems to examine the nature and magnitude of ion-ion and ion-solvent interactions. In continuation of our investigations on electrical conductance, an attempt has been made in the present study, to ascertain the nature of ion-association of 1-butyl-4-methylpyridinium hexafluorophosphate in methanol, acetonitrile, dimethylsulfoxide and their binary solutions at different temperatures as literature survey reveals that very scarce work has been carried out in studied binary solution systems.

4.5.2. Experimental

The IL selected for the present work, 1-butyl-4-methylpyridinium hexafluorophosphate [$4MBPPF_6$] of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of 1-butyl-4-methylpyridinium hexafluorophosphate was 97%. Doubly distilled de-ionized water with a specific conductance $<1\times10^{-6}$ S cm^{-1} at 298.15K was used for the experimental work. All the solvents of spectroscopic grade were procured from Sigma-Aldrich, Germany and were used as procured. The purities of acetonitrile is 98%, methanol is ≥99.8%, and dimethylsulfoxide is ≥99.6%. All the viscosity, dielectric constant and density values were interpolated from literature values [Mikhail and Kimel, 1961; Grande *et al.*, 2006-2007]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used. Conductivity measurements were carried out over the temperature range of 25^{o}C – 40^{o} C. The temperature control in the ranges of 25-40^{0}C were made by using refrigerated water bath and Circulator - Cole-Palmer, Polystat R6L and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg).

Table 14(a): The values of molar conductance (Λ) obtained for 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in methanol+ water mixtures at 298.15-313.15K.

X_1=0.0588

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
121.00	100.68	106.58	111.49	116.62
169.00	96.95	102.76	107.69	113.39
207.36	94.56	100.45	105.53	110.23
243.36	92.51	98.32	103.27	108.37
272.25	90.63	96.54	101.38	106.48
299.29	88.82	94.71	99.91	104.65
345.96	86.29	92.18	97.18	102.71
380.25	84.37	90.25	95.24	100.34
412.09	82.18	88.67	93.76	98.67
449.44	80.43	86.79	91.82	96.83
506.25	78.19	84.11	88.95	94.79
538.24	76.77	82.68	87.62	92.52

X_1=0.1233

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
79.21	92.83	98.12	103.31	108.61
136.89	88.47	94.02	98.47	104.47
158.76	86.79	92.18	96.53	102.45
179.56	85.52	91.12	95.42	101.21
196.00	83.88	89.77	93.99	99.73
237.16	81.59	87.48	91.67	97.23
259.21	79.94	85.79	89.95	95.53
299.29	77.65	83.84	87.85	93.78
331.24	75.75	81.93	86.07	91.47
376.36	73.85	79.78	84.16	89.29
424.36	71.78	77.81	82.51	87.71
466.56	70.31	75.73	80.94	85.71

X_1=0.1942

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
49.00	87.56	91.70	96.41	101.79
67.24	85.33	89.23	93.92	98.82
82.81	83.21	87.14	91.85	96.75
96.04	81.43	85.55	90.43	94.84
118.81	78.96	83.11	88.00	92.06
136.89	76.78	81.32	86.28	90.17
158.76	75.53	79.42	84.35	88.26
182.25	73.37	77.29	81.97	86.47
204.49	71.49	75.68	80.63	84.52
231.04	69.68	73.77	78.78	82.65
265.69	67.87	71.98	76.69	80.31
292.41	66.18	70.53	75.26	78.55

X_1=0.2727

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
27.04	75.21	87.72	91.59	96.83
37.21	73.55	85.64	89.87	94.72
53.29	71.33	83.53	87.33	92.14
65.61	69.86	81.85	85.56	90.61
81.00	67.77	79.91	83.94	88.46
96.04	66.29	78.79	82.71	86.38
114.49	64.87	77.17	80.98	84.17
129.96	63.56	75.91	79.46	82.51
148.84	62.44	74.35	77.96	80.75
179.56	60.13	72.77	75.67	78.38
196.00	58.99	71.39	74.98	77.17
234.09	56.61	69.15	72.83	74.83

Table 14(b): The values of molar conductance (Λ) obtained for 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in acetonitrile + water mixtures at 298.15-313.15K.

X_1=0.0465

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
171.61	134.51	140.83	147.04	154.02
213.16	132.04	138.42	144.82	151.43
249.64	130.09	136.39	142.74	149.44
282.24	128.53	134.92	141.27	147.72
309.76	127.22	133.56	140.06	146.46
353.44	125.34	131.63	138.03	144.39
392.04	123.55	130.05	136.45	142.74
436.81	121.73	128.07	134.63	140.91
470.89	120.42	127.00	133.25	139.54
519.84	118.63	125.11	131.43	137.63
561.69	117.35	123.78	130.04	136.24
605.16	116.16	122.22	128.45	134.58

X_1=0.0989

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
116.64	129.52	133.62	141.86	146.31
144.00	127.42	131.34	139.55	144.05
169.00	125.61	129.43	137.71	142.11
190.44	124.03	127.94	136.18	140.48
210.25	122.54	126.65	134.76	139.16
240.25	120.62	124.87	133.03	137.33
265.69	119.21	123.28	131.46	135.66
295.84	117.43	121.58	129.88	134.00
320.41	116.03	120.24	128.53	132.73
353.44	114.31	118.66	126.76	131.00
372.49	113.42	117.72	125.89	129.99
420.25	111.23	115.43	123.65	127.65

X_1=0.1583

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
75.69	115.11	126.19	132.72	139.04
94.09	113.27	124.24	130.98	137.28
108.16	112.01	122.86	129.75	136.05
123.21	110.87	121.71	128.46	134.86
153.76	108.78	119.45	126.35	132.65
171.61	107.65	118.27	125.16	131.36
201.64	105.96	116.43	123.31	129.41
231.04	104.18	114.73	121.72	127.72
265.69	102.34	112.95	119.85	125.85
295.84	100.98	111.46	118.28	124.28
338.56	99.13	109.52	116.46	122.06
380.25	97.42	107.69	114.54	120.00

X_1=0.2264

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
44.89	113.00	121.07	123.64	131.76
54.76	111.71	119.73	122.35	130.45
72.25	109.86	117.89	120.46	128.66
86.49	108.52	116.34	119.23	127.23
108.16	106.73	114.67	117.46	125.26
125.44	105.42	113.26	116.05	123.85
151.29	103.57	111.38	114.14	121.74
174.24	102.20	109.83	112.65	120.25
198.81	100.71	108.29	111.11	118.61
237.16	98.72	106.02	108.92	116.22
272.25	97.01	104.10	107.03	114.13
299.29	95.67	102.60	105.49	112.79

Table 14(c): The values of molar conductance (Λ) obtained for 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in dimethylsulfoxide + water mixtures at 298.15-313.15K.

X_1=0.0250

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
190.44	66.92	71.38	76.99	82.40
234.09	64.75	69.05	75.01	80.07
275.56	62.76	67.24	73.04	78.13
309.76	61.43	66.34	71.25	76.86
338.56	60.26	64.86	70.16	75.76
364.81	59.25	63.87	68.82	74.37
412.09	57.33	62.03	67.53	72.78
449.44	55.95	60.86	66.05	71.46
492.84	54.81	59.22	64.52	69.76
533.61	53.62	57.85	63.05	68.34
580.81	52.43	56.13	61.71	66.93
635.04	51.01	54.53	60.04	65.19

X_1=0.0545

Conc.x10^{-4}	**298.15K**	**303.15K**	**308.15K**	**313.15K**
144.00	62.52	66.88	72.50	77.89
179.56	60.55	65.05	70.35	76.15
210.25	59.06	63.43	69.06	74.36
237.16	57.53	61.66	67.63	72.83
259.21	56.66	60.64	66.46	71.66
299.29	55.21	58.87	64.75	69.85
342.25	53.45	57.25	63.14	68.34
368.64	52.42	56.12	61.85	67.05
404.01	51.11	54.74	60.11	65.41
441.00	49.82	53.47	58.92	64.02
488.41	48.03	52.04	57.03	62.33
538.24	46.74	50.09	55.58	60.70

X_1=0.0899

Conc.x10^{-4}	298.15K	303.15K	308.15K	313.15K
108.16	58.24	62.67	68.21	73.49
134.56	56.35	60.71	66.05	72.05
156.25	55.06	59.51	64.96	70.43
174.24	54.13	58.36	63.73	69.26
207.36	52.44	56.37	61.56	67.12
234.09	51.35	54.93	60.25	65.34
262.44	50.04	53.75	59.14	64.47
292.41	48.75	52.46	57.45	62.95
331.24	47.11	50.56	55.81	61.27
361.00	45.91	49.45	54.62	59.82
412.09	43.83	47.53	52.53	57.73
449.44	42.53	46.12	51.34	56.32

X_1=0.1333

Conc.x10^{-4}	298.15K	303.15K	308.15K	313.15K
77.44	54.03	58.39	63.84	69.43
96.04	52.51	56.55	61.93	67.53
112.36	51.28	55.36	60.74	66.07
125.44	50.32	54.43	59.85	65.11
148.84	48.83	53.06	58.17	63.46
169.00	47.73	51.75	56.98	61.94
201.64	46.21	50.04	55.12	59.84
225.00	44.92	48.85	53.84	58.43
259.21	43.01	47.01	52.13	56.91
299.29	41.22	45.22	50.03	54.93
324.00	40.13	43.93	48.92	53.86
364.81	38.36	41.68	47.05	52.28

4.5.3. Evaluation of Limiting Molar Conductance and Association Constant

The specific conductance (κ, mS cm^{-1}) of the electrolytes (ILs) solutions under investigation with a molar concentrations in different solvents were measured. The molar conductances (Λ) for all studied solution system have been calculated using following equation [El-Dossoki, 2010]

$$\Lambda = 1000\boldsymbol{\kappa}/\boldsymbol{c}$$

Where c is the molar concentration and κ is the measured specific conductance of the studied solutions. For all solvents mixtures (conc range from 0.1-0.4), for aqueous acetonitrile, aqueous methanol and aqueous dimethylsulfoxide at different temperatures, the conductance curves (Λ versus √c) were linear. As for the studied ionic liquids (ILs) in solvents (aqueous acetonitrile, aqueous methanol, aqueous dimethylsulfoxide), no significant minima were observed in the δ versus R curves, whereas the R values were arbitrarily preset at the centre to centre distance of solvent-separated ion pair. Thus, R values are assumed to be

$$R = a + d$$

where a = (r_+ + r_-)is the sum of the crystallographic radii of the cation (r_+)and anion (r_-)and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by [Fuoss and Accascina, 1959].

$$d(\text{Å}) = 1.183(M/\rho)^{1/3}$$

Where M is the molecular weight of the solvent and ρ is the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{avg} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1}$$

X_1 is the mole fraction of methanol of molecular weight M_1 and X_2 that of water of molecular weight M_2. 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, Λ_j, j=1,…n), n, ε, n, T, initial values of Λ_0, and an instruction to cover a pre-selected range of R values.

Fuoss Technique

Thus the conductance data, in studied solvents systems have been analyzed using the Fuoss conductance equation [Fuoss, 1978]. For a given set of conductivity values (c_j, Λ_j, j=1,…n), three adjustable parameters, the limiting molar conductance (Λ_0), the association constant (K_A) and the distance of closest approach of ions (R) are derived from the following set of equations

$$\Lambda = P\Lambda_0[(1 + R_X) + E_L) \qquad \ldots(81)$$

$$P = 1 - \alpha(1 - \gamma) \qquad \ldots(82)$$

$$\gamma = 1 - K_A c\gamma^2 f^2 \qquad \ldots(83)$$

$$-lnf = \beta\kappa/2(1 + \kappa R) \qquad \ldots(84)$$

$$\beta = e^2/(\varepsilon_r k_B T) \qquad \ldots(85)$$

$$K_A = K_R/(1 - \alpha) = K_R/(1 + K_S) \qquad \ldots(86)$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current, k^{-1} is the radius of the ion atmosphere, ε_r is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall paring constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance. The computations were performed using a program suggested by Fuoss.

Shedlovsky technique

The limiting molar conductances (Λ_0) and ion association constants (K_A) have been computed using Shedlovsky method [Shedlovsky, 1932].

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are same as given in chapter 3, section 3.1.1.1.

Table 15(a): The value of limiting molar conductance (Λ_0) and association constant (K_A) of 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in methanol +water solvent at different temperatures by three different methods of analysis.

$X_{Methanol}$	Λ vs $c^{1/2}$	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}
	T=298.15K	**Shedlovsky**		**Fuoss**	
0.0588	123.10	123.07	38.06	121.75	37.33
0.1233	109.15	116.15	43.71	112.62	42.74
0.1942	104.50	109.11	51.27	105.71	49.97
0.2727	101.62	105.43	59.19	101.99	57.76
	T=303.15K				
0.0588	128.70	128.72	33.38	126.13	32.57
0.1233	114.70	121.01	38.48	116.46	37.54
0.1942	108.90	113.45	45.05	110.03	43.68
0.2727	104.85	109.45	51.31	106.75	50.54
	T=308.15K				
0.0588	133.60	134.58	29.17	130.33	28.29
0.1233	125.57	125.57	33.37	121.18	32.52
0.1942	118.36	118.36	38.83	114.16	37.70
0.2727	107.20	114.32	44.65	111.02	43.54
	T=313.15K				
0.0588	138.70	139.76	25.45	134.41	24.57
0.1233	128.70	131.37	29.01	124.72	28.39
0.1942	119.70	123.78	33.48	118.49	33.02
0.2727	116.50	119.02	38.76	115.70	37.46

Table 15(b): The value of limiting molar conductance (Λ_0) and association constant (K_A) of 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in acetonitrile +water solvent at different temperatures by three different methods of analysis.

X_{AN}	Λ vs $c^{1/2}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}
	T=298.15K	**Shedlovsky**		**Fuoss**	
0.0465	155.6	153.46	12.18	150.75	11.88
0.0989	150.20	142.02	14.81	139.79	14.75
0.1583	129.00	131.45	17.81	130.10	17.48
0.2264	123.60	121.94	21.29	121.26	20.06
	T=303.15K				
0.0465	162.00	159.55	11.51	156.74	11.13
0.0989	153.70	148.23	13.90	145.64	13.76
0.1583	140.60	138.50	16.62	137.02	16.30
0.2264	132.50	127.94	20.02	126.91	18.71
	T=308.15K				
0.0465	168.40	165.78	10.77	162.86	10.53
0.0989	162.00	154.84	13.02	152.56	12.83
0.1583	147.10	144.92	15.49	142.62	15.22
0.2264	134.90	135.12	18.67	132.99	17.48
	T=313.15K				
0.0465	176.00	173.18	10.10	169.05	9.91
0.0989	167.00	161.39	12.27	157.68	11.93
0.1583	154.30	151.99	14.57	149.43	14.28
0.2264	143.80	141.87	17.31	139.55	16.41

Table 15(c): The value of limiting molar conductance (Λ_0) and association constant (K_A) of 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in dimethylsulfoxide +water solvent at different temperatures by three different methods of analysis.

X_{DMSO}	Λ vs $c^{1/2}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}
	T=298.15K	**Shedlovsky**		**Fuoss**	
0.0250	86.17	94.84	51.86	86.94	50.49
0.0545	79.50	88.62	61.08	81.02	60.23
0.0899	73.14	82.65	75.41	74.31	73.36
0.1333	67.31	75.74	89.14	68.69	88.37
	T=303.15K				
0.0250	91.86	99.28	45.58	92.01	44.02
0.0545	84.92	92.87	53.92	86.02	53.03
0.0899	78.50	86.39	66.04	79.65	64.65
0.1333	72.10	79.53	77.73	73.13	77.47

X_{DMSO}	Λ vs $c^{1/2}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}
	T=308.15K	**Shedlovsky**		**Fuoss**	
0.0250	97.72	103.68	39.34	96.95	38.67
0.0545	91.05	97.29	46.83	91.01	46.45
0.0899	84.92	90.22	57.41	84.39	56.71
0.1333	77.82	83.73	68.48	78.15	67.67
	T=313.15K				
0.0250	103.20	107.94	34.55	102.50	33.76
0.0545	96.84	101.62	41.21	96.02	40.81
0.0899	90.42	95.23	50.79	89.58	49.72
0.1333	83.79	88.18	60.82	82.85	59.71

The limiting molar conductance (Λ_0) of 1-butyl-4-methylpyridinium hexafluorophosphate [$4MBPPF_6$] is highest in CH_3CN and lowest in case of DMSO among the studied solvents [Table 15(a), (b) & (c)]. The trend in the Λ_0 of [$4MBPPF_6$] in different solvents is as follows: CH_3CN > CH_3OH > DMSO. This shows that [[$4MBPPF_6$] is solvated more by DMSO, which has the highest viscosity value among the studied solvents and is evident from the K_A values given in Table 15(a), (b) & (c). The weakest solvation is seen in the case of the CH_3CN, which has the lowest viscosity value. As the viscosity of DMSO is high, the mobility of the ions decreases resulting in decrease in conductance values but, CH_3CN has a low viscosity leading to increase in mobility of the ions resulting in increase in conductance value.

Table 15 (a), (b) & (c) also reveals that the association constant (K_A) of the ionic liquid is just reverse of the limiting molar conductance, lower in acetonitrile and higher in dimethylsulfoxide, which is in following order;

DMSO > CH_3OH > CH_3CN

Hence the ion-solvent interaction or ion-association increases from acetonitrile to dimethylsulfoxide among the chosen solvents, leading to a lower conductance of ionic liquids. From the Table 15 (a), (b) & (c), we can see that the association constant values follow the same trend as viscosity value of the solvents, thus the viscosity values also support the above facts, i.e; the electrolytes (ILs) in the lower viscous solvent the Λ_0 value should increase.

4.5.4. Calculation of walden product

Table 16(a): The value of limiting Walden product ($\Lambda_0\eta_0$) of 1-butyl-4-methylpyridinium hexafluorophosphate[4MBPPF$_6$] in methanol + water solvents at different temperatures by Shedlovsky and Fuoss techniques.

$X_{Methanol}$	$\Lambda_0\eta_0$	$\Lambda_0\eta_0$		$\Lambda_0\eta_0$	$\Lambda_0\eta_0$
T=298.15K	**Shedlovsky**	**Fuoss**	**T=303.15K**	**Shedlovsky**	**Fuoss**
0.0588	135.13	133.68		126.40	123.86
0.1233	152.85	148.21		138.56	133.35
0.1942	157.55	152.65		144.65	140.29
0.2727	158.36	153.19		145.46	141.87
T=308.15K			**T=313.15K**		
0.0588	117.76	114.04		110.83	106.59
0.1233	126.70	122.27		118.50	112.50
0.1942	131.50	126.83		122.42	117.19
0.2727	132.27	128.45		125.33	121.83

Table 16(b): The value of limiting Walden product ($\Lambda_0\eta_0$) of 1-butyl-4-methylpyridinium hexafluorophosphate[4MBPPF$_6$] in acetonitrile + water solvents at different temperatures by Shedlovsky and Fuoss techniques.

X_{AN}	$\Lambda_0\eta_0$	$\Lambda_0\eta_0$		$\Lambda_0\eta_0$	$\Lambda_0\eta_0$
T=298.15K	**Shedlovsky**	**Fuoss**	**T=303.15K**	**Shedlovsky**	**Fuoss**
0.0465	146.82	144.22		137.66	135.24
0.0989	124.17	122.22		117.56	115.51
0.1583	103.73	103.10		99.06	98.00
0.2264	84.78	84.31		80.58	79.93
T=308.15K			**T=313.15K**		
0.0465	130.00	127.71		123.91	120.96
0.0989	111.76	110.12		106.97	104.51
0.1583	94.23	92.73		90.45	88.93
0.2264	77.52	76.30		74.71	73.49

Table 16(c): The value of limiting Walden product ($\Lambda_0\eta_0$) of 1-butyl-4-methylpyridinium hexafluorophosphate[4MBPPF$_6$] in dimethylsulfoxide + water solvents at different temperatures by Shedlovsky and Fuoss techniques.

X_{DMSO}	$\Lambda_0\eta_0$	$\Lambda_0\eta_0$		$\Lambda_0\eta_0$	$\Lambda_0\eta_0$
T=298.15K	**Shedlovsky**	**Fuoss**	**T=303.15K**	**Shedlovsky**	**Fuoss**
0.0250	119.27	109.34		113.97	105.63
0.0545	183.22	167.51		173.82	161.00
0.0899	272.84	245.30		255.16	235.25
0.1333	276.94	251.16		259.96	239.04
T=308.15K			**T=313.15K**		
0.0250	107.95	100.94		101.15	96.05
0.0545	162.62	152.12		149.50	141.26
0.0899	234.95	219.77		215.05	202.29
0.1333	241.21	225.13		220.06	206.76

Ion-solvation can also be explained with the help of another characteristics property called the Walden product ($\Lambda_o\eta_0$). Walden product of the electrolytes, have been calculated in various binary solvent mixtures CH_3OH, CH_3CN and DMSO at different temperatures and given in Table 16(a), (b) & (c). Aqueous CH_3OH and DMSO at different temperatures, the $\Lambda_0\eta_0$ values increases as the content of methanol and dimethylsulfoxide (w_1) increases in the binary mixtures but in case of acetonitrile, as the content of acetonitrile increase, the $\Lambda_0\eta_0$ decreases [Bocris and Reddy, 1998] due to viscosity behavior of the solvent effect. However, the decreasing trend of walden product with increasing temperature can be attributed to thermal expansion of the solvent sheath due to the activation of the solvent molecules. Similar observation was described earlier by Roy and his groups [Roy *et al.*, 2005]. The results of molar conductance and the Walden product reflect strong electrostatic ion-solvent interactions. Though the variation of the Walden product with solvent composition is difficult to interpret quantitatively, its variation with solvent composition can still be explained by preferential solvation [Janz and Tomkins, 1973; Inove *et al.*, 1987] of the electrolyte by CH_3OH, CH_3CN and DMSO molecules. Changes in the Walden product with concentration are common and they can be attributed to changes in ion-solvation i.e., ion-solvent interactions. The Gibb's energy change of solvation, ΔG^0, is given by the following equation [Fuoss and Kraus, 1933] and given in Table 17(a), (b) & (c).

$$\Delta G^0 = -RT ln K_A$$

It is observed from the Table 17(a), (b) & (c).that the values of the Gibb's free energy are all negative entire all over the solutions and the negativity increases from CH_3CN to DMSO. This result indicates the extent of solvation enhanced by the following order:

DMSO > CH_3OH > CH_3CN

The negative values of ΔG^0 and ΔH^0 [Table 17(a), (b) & (c)] can be explained by considering the participation of specific covalent interaction in the ion-association process. But the binding entropy (ΔS^0) between the ions was found to be negative to unfavored the ion-association process and thus favoring ion solvation process. Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employed for rate processes taking place with change of temperature [Dash and Pasupalak, 1997] i.e.,

$$\Lambda_0 = Ae^{-E^a/RT} \text{or} \qquad ln\,\Lambda_0 = ln\,A - E^a/RT$$

Where A is the frequency factor, R the ideal gas constant and E^a is Arrhenius activation energy of transport processes. E^a values can be computed from the slope [Corradini *et al.*, 1994] of the plot of log Λ_o versus 1/T and are shown in Table 17(a), (b) and (c). The enthalpy change of association (ΔH^0) was obtained from the slope of log K_A vs. 1/T. The change of association entropy (ΔS^0) was calculated from the Gibbs- Helmholtz equation:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

Table 17(a), (b) and (c) shows that, the values of E^a increase with increase in mole fraction of CH_3OH, CH_3CN and DMSO. The chosen complex ion requires higher activation energy for transport processes as methanol, acetonitrile & dimethylsulfoxide content in the mixed solvent increases. The values of these thermodynamic parameters in all solvent mixtures at different temperature are given in Table 17 (a), (b) & (c). As expected that the values of ΔG^0 become more negative at higher percentage of methanol, acetonitrile & dimethylsulfoxide which indicate that ion-pair association are favored with lowering dielectric constant of the medium.

4.5.5. Evaluation of thermodynamic parameters:

Table 17(a): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A for 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in methanol+ water mixtures at different temperatures.

	Shedlovsky				**Fuoss**			
	298.15K	**303.15K**	**308.15K**	**313.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.0588				
ΔG^0	-8.56	-8.26	-7.94	-7.62	-8.52	-8.20	-7.87	-7.54
ΔH^0	-20.83				-21.67			
$10^3\,\Delta S^0$	-41.13	-41.47	-41.82	-42.18	-44.10	-44.43	-44.78	-45.13
E^a	6.319				5.055			
10^{-3}A	3.129				2.971			
				X_1=0.1233				
ΔG^0	-8.89	-8.60	-8.26	-7.93	-8.84	-8.54	-8.20	-7.88
ΔH^0	-21.29				-21.27			
$10^3\,\Delta S^0$	-41.57	-41.88	-42.29	-42.67	-41.69	-42.01	-42.42	-42.76
E^a	6.414				5.323			
10^{-3}A	3.180				2.985			
				X_1=0.1942				
ΔG^0	-9.27	-8.97	-8.62	-8.27	-9.21	-8.89	-8.55	-8.23
ΔH^0	-22.15				-21.60			
$10^3\Delta S^0$	-43.20	-43.49	-43.92	-44.33	-41.56	-41.92	-42.36	-42.68
E^a	6.510				5.840			
10^{-3}A	3.187				3.049			

	Shedlovsky				**Fuoss**			
	298.15K	**303.15K**	**308.15K**	**313.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.2727				
ΔG^0	-9.61	-9.27	-8.95	-8.61	-9.55	-9.24	-8.89	-8.53
ΔH^0	-21.87				-22.48			
$10^3\,\Delta S^0$	-41.13	-41.56	-41.95	-42.34	-43.37	-43.69	-44.12	-44.54
E^a	6.568				6.472			
$10^{-3}A$	3.243				3.145			

Table 17(b): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A for 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in acetonitrile + water mixtures at different temperatures.

	Shedlovsky				**Fuoss**			
	298.15K	**303.15K**	**308.15K**	**313.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.0465				
ΔG^0	-5.89	-5.75	-5.60	-5.45	-5.83	-5.67	-5.54	-5.40
ΔH^0	-9.75				-9.34			
$10^3\,\Delta S^0$	-12.96	-13.19	-13.48	-13.75	-11.78	-12.09	-12.32	-12.58
E^a	6.338				5.821			
$10^{-3}A$	3.296				3.200			
				X_1=0.0989				
ΔG^0	-6.35	-6.20	-6.04	-5.90	-6.34	-6.17	-6.01	-5.84
ΔH^0	-9.80				-10.97			
$10^3\,\Delta S^0$	-11.58	-11.89	-12.19	-12.44	-15.44	-15.72	-16.00	-16.30
E^a	6.702				6.261			
$10^{-3}A$	3.328				3.242			
				X_1=0.1583				
ΔG^0	-6.78	-6.62	-6.45	-6.31	-6.74	-6.57	-6.41	-6.26
ΔH^0	-10.42				-10.47			
$10^3\Delta S^0$	-12.21	-12.54	-12.88	-13.13	-12.52	-12.86	-13.17	-13.44
E^a	7.448				6.893			
$10^{-3}A$	3.429				3.324			
				X_1=0.2264				
ΔG^0	-7.20	-7.06	-6.89	-6.71	-7.06	-6.89	-6.74	-6.59
ΔH^0	-10.70				-10.44			
$10^3\,\Delta S^0$	-11.74	-12.02	-12.36	-12.73	-11.33	-11.69	-12.02	-12.30
E^a	7.467				7.353			
$10^{-3}A$	3.462				3.373			

Table 17(c): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and $10^{-3}A$ for 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] in dimethylsulfoxide + water mixtures at different temperatures.

	Shedlovsky				**Fuoss**			
	298.15K	**303.15K**	**308.15K**	**313.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.0250				
ΔG^0	-9.30	-8.99	-8.65	-8.34	-9.23	-8.91	-8.61	-8.29
ΔH^0	-21.22				-20.76			
$10^3\ \Delta S^0$	-39.99	-40.33	-40.80	-41.13	-38.66	-39.09	-39.44	-39.83
E^a	6.682				8.521			
$10^{-3}A$	3.149				3.432			
				X_1=0.0545				
ΔG^0	-9.68	-9.39	-9.06	-8.76	-9.65	-9.35	-9.04	-8.73
ΔH^0	-20.51				-20.20			
$10^3\ \Delta S^0$	-36.32	-36.69	-37.17	-37.54	-35.39	-35.79	-36.22	-36.62
E^a	7.046				8.942			
$10^{-3}A$	3.184				3.474			
				X_1=0.0899				
ΔG^0	-10.18	-9.87	-9.54	-9.25	-10.11	-9.82	-9.51	-9.20
ΔH^0	-20.58				-20.14			
$10^3\ \Delta S0$	-34.89	-35.34	-35.84	-36.19	-33.63	-34.06	-34.50	-34.94
E^a	7.544				9.631			
$10^{-3}A$	3.237				3.545			
				X_1=0.1333				
ΔG^0	-10.57	-10.25	-9.95	-9.67	-10.55	-10.24	-9.92	-9.63
ΔH^0	-19.78				-20.35			
$10^3\ \Delta S^0$	-30.88	-31.44	-31.90	-32.28	-32.86	-33.34	-33.84	-34.24
E^a	7.850				9.746			
$10^{-3}A$	3.254				3.561			

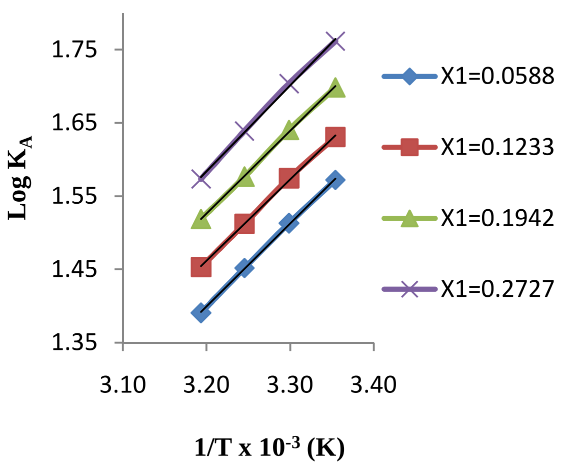


Fig 19: Log K_A vs 1/T for IL in different mole fractions of methanol at 298.15 -313.15K (Fouss)

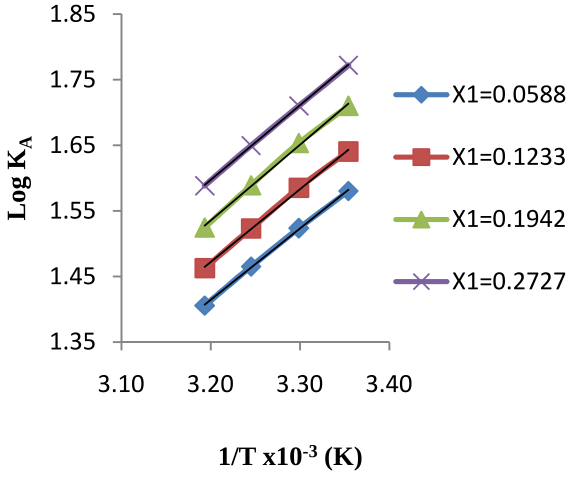


Fig 20: Log K_A vs 1/T for IL in different mole fractions of methanol at 298.15-313.15K(Shedlovsky)

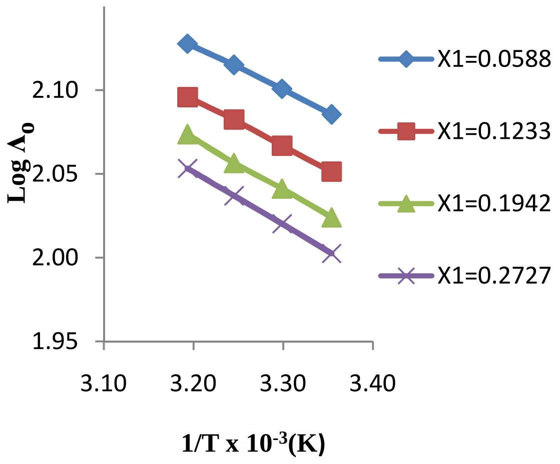


Fig 21: Log Λ_0 vs 1/T of IL in different mole fractions of methanol at 298.15 - 313.15K(Fouss)

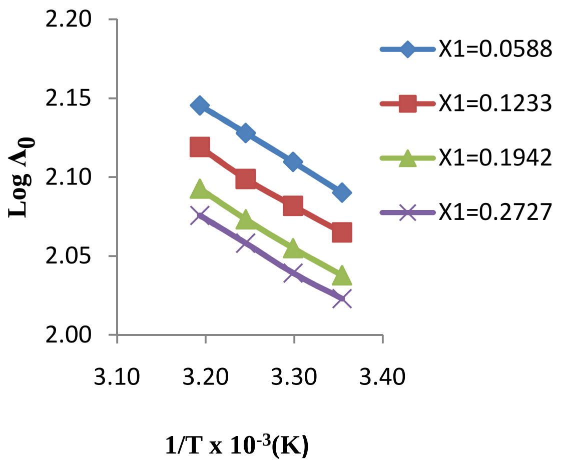


Fig 22: Log Λ_0 vs 1/T of IL in different mole fractions of methanol at 298.15 - 313.15K(Shedlovsky)

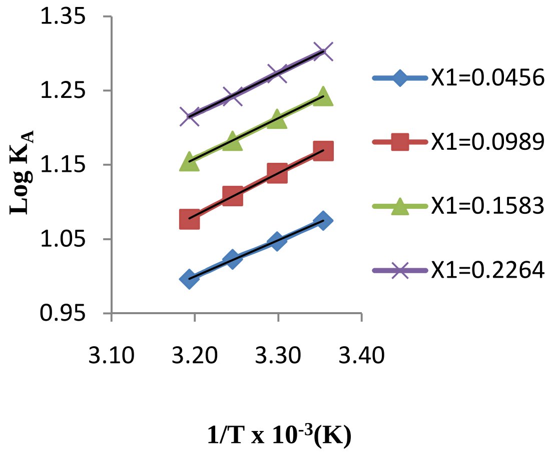


Fig 23: Log K_A Vs 1/T for IL in different mole fractions of acetonitrile at 298.15 - 313.15K(Fouss)

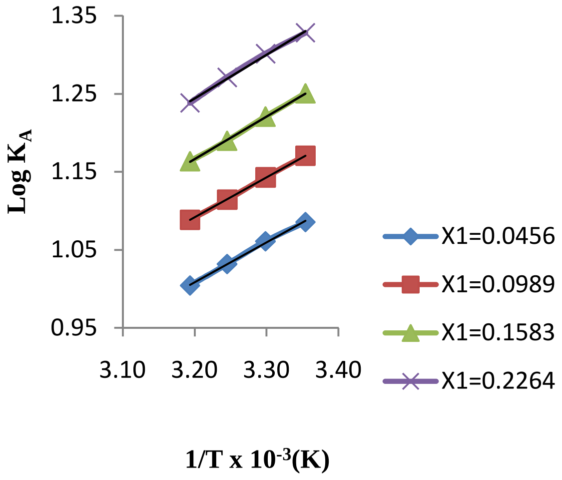


Fig 24: Log K_A Vs 1/T for IL in different mole fractions of acetonitrile at 298.15-313.15K(Shedlovsky)

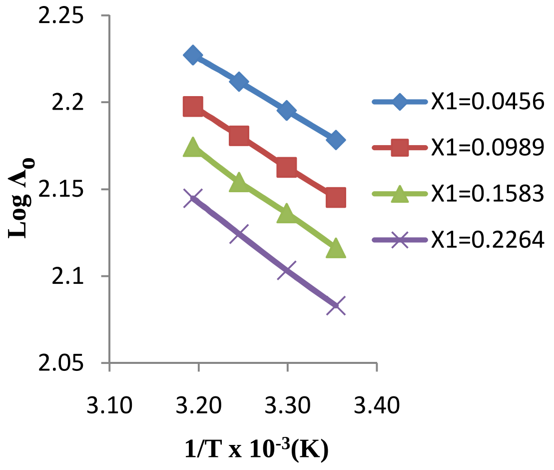


Fig 25: Log Λ_o vs 1/T for IL in different mole fractions of acetonitrile at 298.15-313.15K(Fouss)

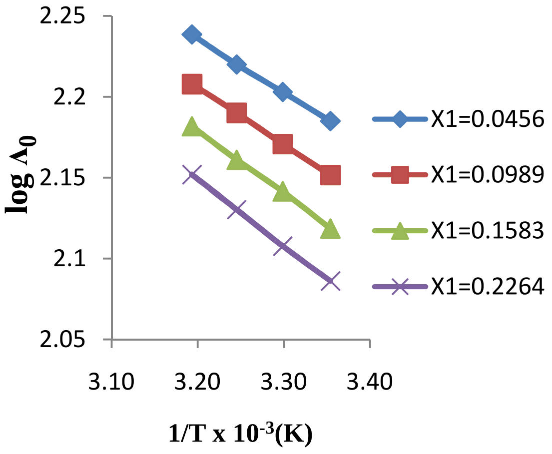


Fig 26: Log Λ_0 vs 1/T for IL in different mole fractions of acetonitrile at 298.15 - 313.15K(Shedlovsky)

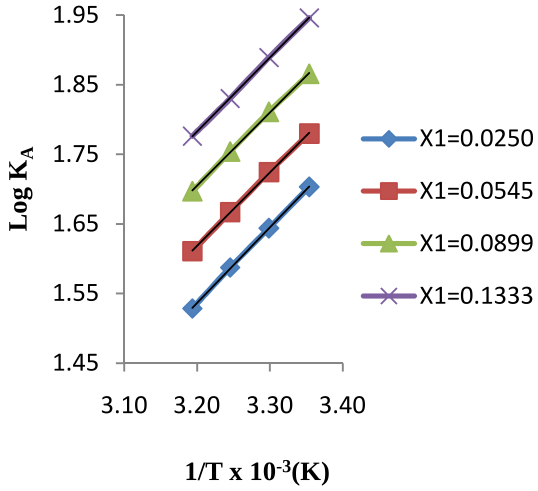


Fig 27: Log K_A vs 1/T for IL in different mole fractions of dimethylsulfoxide at 298.15-313.15K(Fouss)

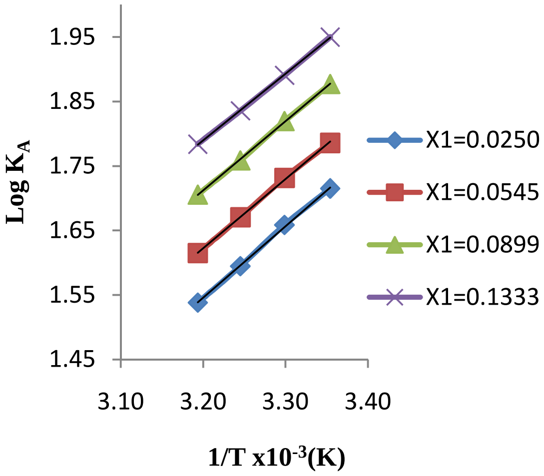


Fig 28: Log K_A Vs 1/T for IL in different mole fractions of dimethylsulfoxide at 298.15-313.15K(Shedlovsky)

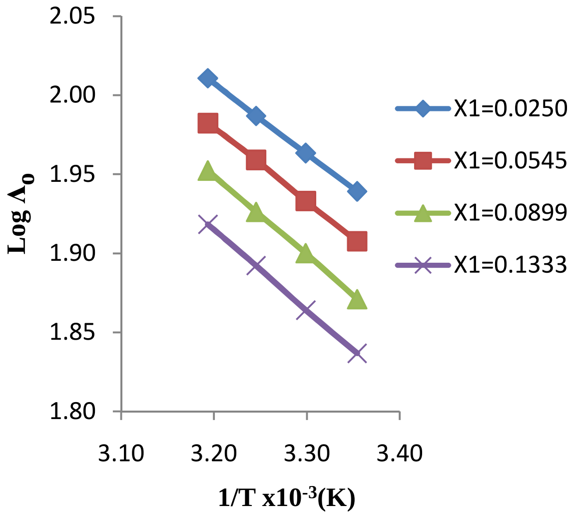


Fig 29: Log Λ_0 Vs 1/T for different mole fractions of dimethylsulfoxide at 298.15-313.15K(Fouss)

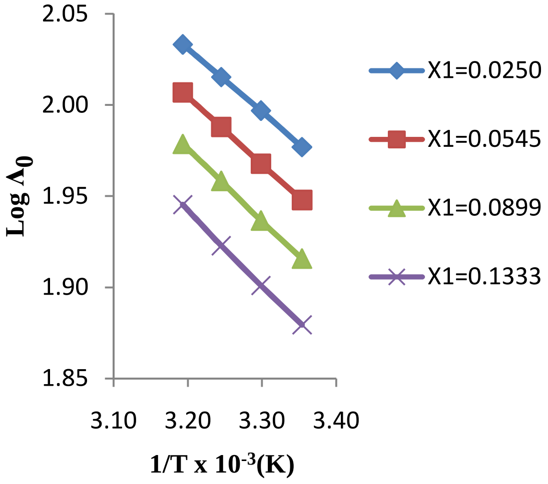


Fig 30 : LogΛ_0 vs 1/T for IL in different mole fractions of dimethylsulfoxide at 298.15 - 313.15K(Shedlovsky)

4.5.1. Evaluation of bond length, surface of electron density and electrostatic potential by using a computational software Gaussian 09W, Revision A.02:

Gaussian 09W, Revision A.02, program package (Gaussian Inc.) is computational software with which **Gauss View 5.0.9** is used for graphical interface which is necessary for input and output analysis. In Gaussian calculation, the geometrical optimization and harmonic vibrational frequencies of the complexes are calculated under gas phase using the Density Functional Theory (DFT) with B3LYP three- parameter hybrid functional proposed by Becke [Becke, 1993]. The B3LYP functional comprises an exchange-correlation functional that mixes the nonlocal Fock exchange with the gradient-corrected form of Becke [Becke, 1988] and adds the correlation functional proposed by Lee et al. [Lee *et al.*, 1988]. Unrestricted calculations are needed for processes such as bond dissociation which requires the separation of an electron pair [Foresman *et al.*, 1996] and diffuse functions are necessary for describing the weak bond interaction. Therefore, for all calculation u6-311++G basis set is used. Gauss View 5.0.9 is a graphical user interface designed to help me prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. Gauss View 5.0.9 is not integrated with the computational module of Gaussian, but rather is a front-end/back-end processor to aid in the use of Gaussian. Gauss View 5.0.9 provides me three main benefits as Gaussian users (Gaussian.com, 2016).

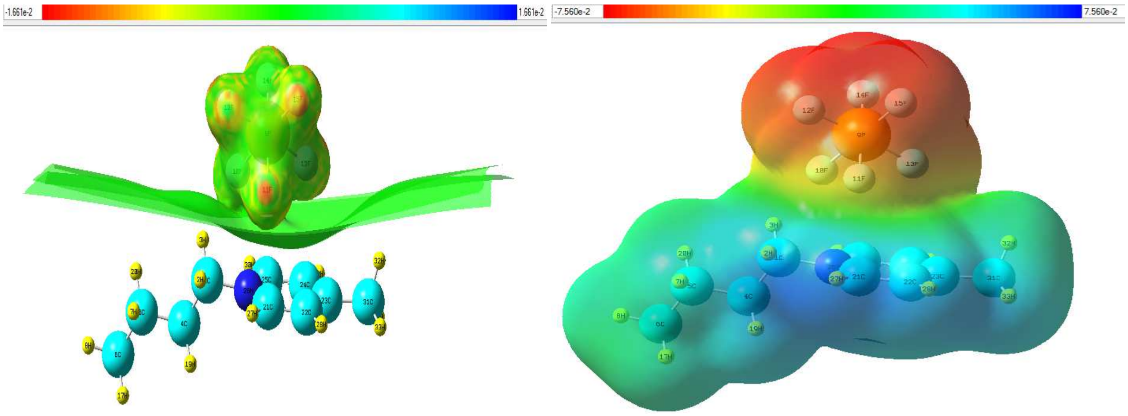


Figure 31: Surfaces of Electron Density (from -7.560e-2 to 7.560e-2) and Electrostatic Potential (from -1.661e-2 to 1.661e-2) generated from Total SCF Density and mapped with ESP in 1-butyl-4-methylpyridinium hexafluorophosphate.

Ion association occurs from the red region which is shown in figure 31 (surface of electron density is rich in red region), which is supported by electrostatic potential generated from total SCF density. Ion association occurs from 10F of anion and 3H of cation sites of 1-butyl-4-methylpyridinium hexafluorophosphate as shown in figure 32.

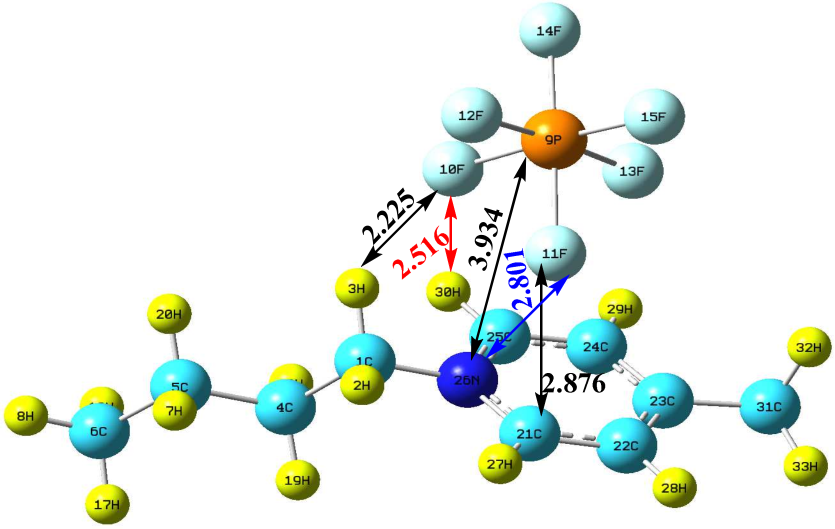


Figure 32: Bond lengths of 1-butyl-4-methylpyridinium hexafluorophosphate

The present work reveals an extensive study on the ion-solvation behavior of the [4BMPPF$_6$] in CH$_3$OH +H$_2$O, CH$_3$CN +H$_2$O and DMSO+H$_2$O mixtures at different temperatures through the conductometric measurements. The limiting molar conductance (Λ_0) and the association constant (K$_A$) in mixed solvent systems have been evaluated by using Shedlovsky equation and Fuoss conductance equation (1978). K$_A$s increases with increase in mole fraction of CH$_3$OH, CH$_3$CN and DMSO, Λ_0 values increase linearly with increase in temperatures. Ion association process is exothermic in nature. The thermodynamic functions of association such as Gibbs energy (ΔG^0), enthalpy (ΔH^0), entropy (ΔS^0) and Arrhenius activation energy (E^a) for ion-association reaction were evaluated. Based on the composition dependence of Walden product and different thermodynamic properties, the influence of the solvent composition on ion-association and solvation behavior of ions were discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions in the mixed solvent media. By using computational software, surface of electron density, electrostatic potential and bond lengths were evaluated.

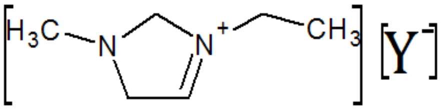
4.6. Association and solvation behavior of some ionic liquids ([emim]NO_3, [emim]CH_3SO_3, [emim]Tos) in pure and aqueous- tetrahydrofuran solutions at T = 298.15, 303.15 and 308.15K by Physicochemical approach.

4.6.1. Introduction

Recently ionic liquids (ILs) have been considered attractive compounds due to their unique intrinsic properties, such as negligible vapor pressure, large liquid range, ability of dissolving a variety of chemicals non-volatility, high thermal stability, large electrochemical window and their potential as 'designer solvents' and 'green' replacements for volatile organic solvents [Welton, 1999; Earlie and Seddon, 2000; Dupont *et al.*, 2002], used in reactions involving inorganic and bio-catalysis etc. They are used as recyclable solvents for organic reactions and separation process, lubricating fluids, pharmaceuticals, cellulose processing, gas handling, gas treatment, solar thermal energy, nuclear fuel processing, food and bi-products, waste recycling, heat transfer fluids for processing biomass and electrically conductive liquids as electrochemical device in electrochemistry (batteries and solar cells) [Plechkova and Seddon, 2008; Reich *et al.*, 2003; Macfarlane *et al.*, 2007; Endres and Zein, 2006]. In the modern technology, the application of the ILs is well understood by studying the ionic solvation or ion association. Conductance study is a very important tool in obtaining the information regarding ion association and solvation behavior of ions in solution. The solvation behavior of ions in solutions can well understand in terms of ion-solvent, ion-ion and solvent-solvent interactions. Variation in the dielectric constant and viscosity in solvents due to mixing, leads to a better understanding of ion-ion and ion-solvent interactions. The use of mixed solvents in high energy batteries has also extended the horizon in the field of mixed solvent systems [Dogonadze *et al.*, 1986; Roy *et al.*, 2006; Aurbach, 1999].

The solvents used in this study find wide industrial usage. Tetrahydrofuran (THF) is used as a precursor to polymers, industrial solvent for PVC and in varnishes. Water is a universal solvent. A greater number of substances dissolve in it than in any other liquid, a good solvent for dissolving many solids, serving as an excellent coolant both mechanically and biologically, and acting as a reactant in many chemical reactions [Ekka and Roy, 2013; Debenedetti and Stanley, 2003].

In this paper, an attempt has been made to ascertain the nature of ion-solvent interactions of some imidazolium based ionic liquids ([emim] Y, where Y = NO_3, CH_3SO_3 and Tos) in aqueous-tetrahydrofuran solutions at 298.15, 303.15 and 308.15K, as literature survey reveals that very little work has been carried out with the binary mixtures.



Scheme 1: 1-ethyl-3-methylimidazolium based ionic liquids; (where Y= NO_3^-, $CH_3SO_3^-$ and Tos^-)

4.6.2. Experimental

The RTILs selected for the present work puriss grade was procured from Sigma-Aldrich, Germany. The mass fraction purity of the ILs was ≥ 0.99. Tetrahydrofuran(THF) was procured from Sigma-Aldrich, Germany and the mass fraction purity of the solvent was ≥ 0.995. Doubly distilled de-ionized water with a specific conductance $< 1 \times 10^{-6}$ Scm^{-1} at 298.15K was used for preparing the mixed solvents by mass.

Table 18(a): Molar conductance (Λ) and the corresponding concentration (c) of the studied [emim]NO_3 in aqueous-tetrahydrofuran solutions with different tetrahydrofuran mass fraction (w_2) at different temperatures.

[emim]NO_3(w_2=0.70)

$c\times10^4$ $(\mathrm{mol\ dm^{-3}})$	**$\Lambda\times10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$**	**$c\times10^4$ $(\mathrm{mol\ dm^{-3}})$**	**$\Lambda\times10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$**	**$c\times10^4$ $(\mathrm{mol\ dm^{-3}})$**	**$\Lambda\times10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$**
298.15K		**303.15K**		**308.15K**	
4.78	37.50	4.52	41.23	4.27	44.37
8.76	36.27	8.29	40.16	7.83	43.36
12.12	35.44	11.48	39.45	10.84	42.61
15.02	34.88	14.21	38.92	13.42	42.08
19.70	34.11	18.65	38.12	15.67	41.64
21.64	33.76	20.48	37.85	17.62	41.25
24.90	33.32	23.55	37.38	19.35	40.97
27.53	32.78	26.05	37.05	22.26	40.56
31.53	32.23	29.83	36.51	25.63	40.06
35.59	31.72	34.66	35.92	30.79	39.41
39.73	31.25	37.60	35.56	34.29	38.96
42.99	30.87	40.69	35.26	38.45	38.43

[emim]NO_3(w_2=0.80)

$c\times10^4$ $(\mathrm{mol\ dm^{-3}})$	**$\Lambda\times10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$**	**$c\times10^4$ $(\mathrm{mol\ dm^{-3}})$**	**$\Lambda\times10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$**	**$c\times10^4$ $(\mathrm{mol\ dm^{-3}})$**	**$\Lambda\times10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$**
298.15K		**303.15K**		**308.15K**	
2.05	34.32	1.95	38.12	1.86	40.34
3.76	33.10	3.58	37.08	3.41	39.38
5.21	32.32	4.96	36.43	4.72	38.77
6.45	31.75	6.14	35.91	5.84	38.28
7.52	31.31	7.16	35.52	6.81	37.85
8.46	31.02	8.06	35.20	7.67	37.53
9.29	30.81	8.85	34.91	8.42	37.28
10.69	30.15	10.18	34.45	9.68	36.86
11.82	29.84	11.26	34.11	11.15	36.39
14.78	29.05	12.90	33.66	12.26	36.10
16.11	28.64	15.35	33.02	14.24	35.54
18.46	27.87	17.58	32.45	16.72	34.91

[emim]NO_3(w_2=0.90)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
0.63	31.59	0.61	35.84	0.59	34.54
1.15	30.73	1.11	35.00	1.07	33.86
1.60	30.16	1.54	34.45	1.49	33.39
1.98	29.71	1.91	34.06	1.84	33.02
2.85	28.81	2.23	33.72	2.15	32.74
3.08	28.62	2.75	33.24	2.65	32.26
3.46	28.31	3.16	32.87	3.05	31.95
3.91	27.99	3.50	32.61	3.37	31.72
4.15	27.80	4.01	32.22	3.87	31.37
4.53	27.54	4.52	31.78	4.22	31.15
5.14	27.11	4.97	31.46	4.87	30.77
5.66	26.79	5.47	31.14	5.27	30.54

[emim]NO_3(w_2=1.00)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
0.09	12.25	0.09	15.67	0.09	18.45
0.16	10.97	0.16	14.51	0.16	17.12
0.22	10.11	0.22	13.75	0.22	16.25
0.27	9.49	0.27	13.24	0.27	15.58
0.36	8.56	0.36	12.47	0.36	14.68
0.39	8.17	0.39	12.19	0.39	14.37
0.43	7.86	0.43	11.93	0.43	14.05
0.50	7.18	0.50	11.41	0.50	13.46
0.54	6.87	0.54	11.15	0.54	13.15
0.60	6.54	0.60	10.88	0.60	12.87
0.65	6.58	0.65	10.95	0.65	12.92
0.72	7.01	0.72	11.34	0.72	13.41

Table 18(b): Molar conductance (Λ) and the corresponding concentration (c) of the studied [emim]CH_3SO_3 in aqueous-tetrahydrofuran solutions with different tetrahydrofuran mass fraction (w_2) at different temperatures.

emim]CH_3SO_3(w_2=0.70)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
4.78	34.21	4.52	36.76	4.27	40.22
8.76	33.02	8.29	35.65	7.83	39.18
12.12	32.15	11.48	34.94	10.84	38.50
15.02	31.54	14.21	34.43	13.42	37.96
19.70	30.82	18.65	33.61	15.67	37.54
21.64	30.57	20.48	33.32	17.62	37.20
24.90	30.05	23.55	32.84	19.35	36.92
27.53	29.73	26.05	32.45	22.26	36.46
31.53	29.04	29.83	31.86	25.63	35.97
35.59	28.48	34.66	31.24	30.79	35.29
39.73	28.09	37.60	30.86	34.29	34.85
42.99	27.61	40.69	30.46	38.45	34.40

emim]CH_3SO_3(w_2=0.80)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
2.05	30.32	1.95	32.41	1.86	35.37
3.76	29.05	3.58	31.31	3.41	34.26
5.21	28.35	4.96	30.67	4.72	33.42
6.45	27.83	6.14	30.21	5.84	32.96
7.52	27.37	7.16	29.78	6.81	32.53
8.46	27.01	8.06	29.42	7.67	32.10
9.29	26.75	8.85	29.00	8.42	31.79
10.69	26.31	10.18	28.56	9.68	31.24
11.82	26.00	11.26	28.21	11.15	30.81
14.78	25.01	12.90	27.62	12.26	30.50
16.11	24.62	15.35	26.81	14.24	29.89
18.46	23.97	17.58	26.23	16.72	29.42

emim]CH_3SO_3(w_2=0.90)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
0.63	26.34	0.61	28.12	0.59	29.53
1.15	25.45	1.11	27.33	1.07	28.79
1.60	24.88	1.54	26.75	1.49	28.26
1.98	24.35	1.91	26.33	1.84	27.87
2.85	23.42	2.23	25.99	2.15	27.55
3.08	23.23	2.75	25.48	2.65	27.08
3.46	22.89	3.16	25.15	3.05	26.72
3.91	22.61	3.50	24.89	3.37	26.46
4.15	22.48	4.01	24.48	3.87	26.11
4.53	22.24	4.52	24.15	4.22	25.84
5.14	21.79	4.97	23.87	4.87	25.38
5.66	21.54	5.47	23.54	5.27	25.14

emim]CH_3SO_3(w_2=1.00)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
0.09	9.25	0.09	12.21	0.09	15.14
0.16	8.38	0.16	10.75	0.16	13.92
0.22	7.76	0.22	9.73	0.22	13.17
0.27	7.35	0.27	9.01	0.27	12.56
0.36	6.74	0.36	8.05	0.36	11.68
0.39	6.55	0.39	7.69	0.39	11.35
0.43	6.36	0.43	7.33	0.43	11.16
0.50	6.05	0.50	6.65	0.50	10.61
0.54	5.93	0.54	6.43	0.54	10.39
0.60	6.02	0.60	6.52	0.60	10.48
0.65	6.18	0.65	6.68	0.65	10.67
0.72	6.56	0.72	7.06	0.72	11.36

Table 18(c): Molar conductance (Λ) and the corresponding concentration (c) of the studied [emim]Tos in aqueous-tetrahydrofuran solutions with different tetrahydrofuran mass fraction (w_2) at different temperatures.

[emim]Tos(w_2=0.70)

$c\times10^4$ (mol dm^{-3})	**$\Lambda\times10^4$ (S m^2 mol^{-1})**	**$c\times10^4$ (mol dm^{-3})**	**$\Lambda\times10^4$ (S m^2 mol^{-1})**	**$c\times10^4$ (mol dm^{-3})**	**$\Lambda\times10^4$ (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
4.78	28.32	4.52	30.48	4.27	32.53
8.76	27.21	8.29	29.29	7.83	31.48
12.12	26.54	11.48	28.56	10.84	30.72
15.02	26.03	14.21	28.04	13.42	30.31
19.70	25.18	18.65	27.39	15.67	29.81
21.64	24.87	20.48	27.08	17.62	29.33
24.90	24.48	23.55	26.60	19.35	29.10
27.53	24.04	26.05	26.15	22.26	28.63
31.53	23.44	29.83	25.65	25.63	28.11
35.59	22.93	34.66	25.01	30.79	27.41
39.73	22.51	37.60	24.65	34.29	27.05
42.99	22.12	40.69	24.20	38.45	26.61

[emim]Tos(w_2=0.80)

$c\times10^4$ (mol dm^{-3})	**$\Lambda\times10^4$ (S m^2 mol^{-1})**	**$c\times10^4$ (mol dm^{-3})**	**$\Lambda\times10^4$ (S m^2 mol^{-1})**	**$c\times10^4$ (mol dm^{-3})**	**$\Lambda\times10^4$ (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
2.05	24.34	1.95	26.23	1.86	28.24
3.76	23.41	3.58	25.18	3.41	27.27
5.21	22.75	4.96	24.52	4.72	26.65
6.45	22.20	6.14	24.00	5.84	26.14
7.52	21.83	7.16	23.51	6.81	25.68
8.46	21.45	8.06	23.23	7.67	25.34
9.29	21.17	8.85	22.94	8.42	25.07
10.69	20.65	10.18	22.56	9.68	24.66
11.82	20.32	11.26	22.26	11.15	24.22
14.78	19.64	12.90	21.75	12.26	23.83
16.11	19.36	15.35	21.15	14.24	23.41
18.46	18.85	17.58	20.62	16.72	22.82

[emim]Tos(w_2=0.90)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
0.63	20.43	0.61	21.65	0.59	22.76
1.15	19.67	1.11	20.82	1.07	21.96
1.60	19.22	1.54	20.28	1.49	21.55
1.98	18.78	1.91	19.92	1.84	21.10
2.85	18.12	2.23	19.62	2.15	20.78
3.08	17.90	2.75	19.18	2.65	20.41
3.46	17.64	3.16	18.79	3.05	20.07
3.91	17.32	3.50	18.61	3.37	19.87
4.15	17.16	4.01	18.27	3.87	19.53
4.53	16.92	4.52	17.93	4.22	19.31
5.14	16.56	4.97	17.71	4.87	18.86
5.66	16.22	5.47	17.46	5.27	18.59

[emim]Tos(w_2=1.00)

c×10^4 (mol dm^{-3})	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**	**c×10^4 (mol dm^{-3})**	**Λ×10^4 (S m^2 mol^{-1})**
298.15K		**303.15K**		**308.15K**	
0.09	7.57	0.09	10.72	0.09	13.61
0.16	6.32	0.16	9.27	0.16	11.97
0.22	5.44	0.22	8.36	0.22	10.85
0.27	4.77	0.27	7.60	0.27	9.95
0.36	3.92	0.36	6.63	0.36	8.70
0.39	3.58	0.39	6.29	0.39	8.22
0.43	3.34	0.43	5.98	0.43	7.86
0.50	2.92	0.50	5.64	0.50	7.23
0.54	3.00	0.54	5.73	0.54	7.35
0.60	3.24	0.60	6.04	0.60	7.70
0.65	3.47	0.65	6.25	0.65	8.07
0.72	3.86	0.72	6.63	0.72	8.48

4.6.3. Evaluation of limiting molar conductivity (Λ_0), the association constant (K_A) of Ion-Pair Formation, The distance of closest approach of ions (R), Walden product ($\Lambda_0\eta_0$) and Gibb's energy change (ΔG^o).

The electrolyte was freely soluble in all proportions of pure solvent and solvent mixtures. The specific conductance (κ, mS cm^{-1}) of the electrolytes (ILs) solutions under investigation with a molar concentrations in different solvents were measured. The molar conductances (Λ) for all studied solution system have been calculated using following equation [El-Dossoki, 2010]

$$\Lambda = 1000\boldsymbol{\kappa}/\boldsymbol{c}$$

Where c is the molar concentration and κ is the measured specific conductance of the studied solutions. The molar conductances (Λ) of the studied ionic liquids were studied in different mass fraction (0.70, 0.80, 0.90 and 1.00) of tetrahydrofuran (C_4H_8O) in water (H_2O) at 298.15, 303.15 and 308.15K. For mixed solvents (0.70, 0.80 and 0.90), the conductance curves (Λ) versus √c) were linear and extrapolation of √c = 0 was used to evaluate the starting limiting molar conductance for the electrolytes; however, in pure tetrahydrofuran, non-linearity was observed in conductance curves, showing a decrease value in conductance values up to a certain concentration, reaching a minimum and then increasing, indicating triple-ion formation. Thus, the conductance data in mixed solvents have been analyzed in terms of the limiting molar conductance (Λ_0) and the ion-association constant ($K_{A,c}$) of the electrolytes using Fuoss conductance-concentration equation, resolved by an iterative procedure programmed in a computer as suggested by Fuoss [Fuoss, 1978]

For such an analysis initial Λ_0 values for the iterative procedure were obtained from Shedlovsky extrapolation [Fuoss and Shedlovsky, 1949] of the experimental data using least square treatment. Shedlovsky method involves a linear extrapolation of conductance data given by the relation,

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_{A,c}}{\Lambda_0^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right)$$

Where Λ_o is the limiting molar conductivity and other symbols have their usual meaning.

So with a given set of conductivity values (c_j, Λ_j, j=1,…n), three adjustable parameters, the limiting molar conductance (Λ_0), the association constant ($K_{A,c}$) and the distance of closest approach of ions (R) are derived from the Fuoss conductance equation. Since there is no precise method [Per, 1977] for determining the R-value and for the electrolytes studied no significant minima were observed obtained in the σ_Λ versus R- curves and thus in order to treat the data in our system, R-values were preset at the centre-to centre distance of solvent separated ion-pairs, i.e., Thus, R values are assumed to be

$$R = a + d$$

where a = (r_+ + r_-)is the sum of the crystallographic radii of the cation (r_+)and anion (r_-)and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by [Fuoss and Accascina, 1959].

$$d(\text{Å}) = 1.183(M/\rho)^{1/3}$$

Where M is the molecular weight of the solvent and ρ is the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{avg} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1}$$

where w_1 is the weight fraction of the first component of molar mass M_1. Thus, the Fuoss conductance equation and other symbols are same as given in 3.1.2. The computations were performed using a program suggested by Fuoss.

Table 19(a): Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ, Walden product ($\Lambda_0\eta_0$) and Gibb's energy change (ΔG^0) of [emim]NO_3 in aqueous-tetrahydrofuran solutions at different temperatures from Fuoss conductance –concentration equation.

Temp(K)	**$\Lambda_0\times10^4$ (S m^2 mol^{-1})**	**K_A (dm^2 mol^{-1})**	**R (Å)**	**δ**	**$\Lambda_0\eta_0\times10^4$ (S m^2 mol^{-1} mPa s)**	**Log(K_A)**	**ΔG^0 (kJ mol^{-1})**
[emim]NO_3(w_2=0.70)							
298.15K	39.92	102.58	7.28	0.08	48.85	2.01	-1.15
303.15K	43.09	76.57	7.28	0.03	47.68	1.88	-1.09
308.15K	46.49	69.49	7.29	0.03	45.99	1.84	-1.08
[emim]NO_3(w_2=0.80)							
298.15K	36.61	247.56	7.19	0.10	33.82	2.39	-1.37
303.15K	39.17	174.69	7.20	0.03	33.45	2.24	-1.30
308.15K	42.32	152.52	7.20	0.02	33.18	2.18	-1.29
[emim]NO_3(w_2=0.90)							
298.15K	33.35	520.60	7.12	0.02	21.89	2.72	-1.54
303.15K	34.24	392.70	7.12	0.05	21.03	2.59	-1.50
308.15K	36.06	323.13	7.13	0.02	20.63	2.51	-1.48

Table 19(b): Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ, Walden product ($\Lambda_0\eta_0$) and Gibb's energy change (ΔG^0) of [emim]CH_3SO_3 in aqueous-tetrahydrofuran solutions at different temperatures from Fuoss conductance –concentration equation.

Temp(K)	**$\Lambda_0\times10^4$ ($S\ m^2\ mol^{-1}$)**	**K_A ($dm^2\ mol^{-1}$)**	**R (Å)**	**δ**	**$\Lambda_0\eta_0\times10^4$ ($S\ m^2\ mol^{-1}$ mPa s)**	**Log(K_A)**	**ΔG^0 ($kJ\ mol^{-1}$)**
[[emim]CH_3SO_3 (w_2=0.70)							
298.15K	36.61	117.28	7.12	0.10	44.80	2.07	-1.18
303.15K	39.08	102.20	7..12	0.09	43.24	2.01	-1.17
308.15K	42.29	81.43	7.13	0.02	41.84	1.91	-1.13
[[emim]CH_3SO_3 (w_2=0.80)							
298.15K	32.65	306.66	7.03	0.11	30.16	2.49	-1.42
303.15K	34.80	278.99	7.04	0.14	29.71	2.45	-1.41
308.15K	37.50	243.93	7.04	0.07	29.40	2.39	-1.40
[emim]CH_3SO_3 (w_2=0.90)							
298.15K	28.69	786.51	6.96	0.05	18.83	2.90	-1.65
303.15K	29.79	636.20	6.96	0.02	18.30	2.80	-1.63
308.15K	31.15	552.90	6.97	0.03	17.82	2.74	-1.62

Table 19(c): Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ, Walden product ($\Lambda_0\eta_0$) and Gibb's energy change (ΔG^0)of [emim]Tos in aqueous-tetrahydrofuran solutions at different temperatures from Fuoss conductance –concentration equation.

Temp(K)	**$\Lambda_0 \times 10^4$ ($S\ m^2\ mol^{-1}$)**	**K_A ($dm^2\ mol^{-1}$)**	**R (Å)**	**δ**	**$\Lambda_0\eta_0 \times 10^4$ ($S\ m^2\ mol^{-1}\ mPa\ s$)**	**Log(K_A)**	**ΔG^0 ($kJ\ mol^{-1}$)**
[emim]Tos(w_2=0.70)							
298.15K	30.77	153.03	8.45	0.12	37.66	2.19	-1.25
303.15K	32.25	138.07	8.45	0.12	36.25	2.14	-1.24
308.15K	34.70	123.70	8.46	0.06	34.33	2.09	-1.23
[emim]Tos(w_2=0.80)							
298.15K	26.62	385.78	8.36	0.08	24.59	2.59	-1.47
303.15K	28.34	349.92	8.37	0.04	24.20	2.54	-1.46
308.15K	30.27	305.81	8.37	0.04	23.73	2.49	-1.45
[emim]Tos(w_2=0.90)							
298.15K	22.04	955.75	8.29	0.07	14.47	2.98	-1.70
303.15K	23.15	898.05	8.29	0.03	14.22	2.95	-1.69
308.15K	24.76	802.76	8.30	0.05	14.17	2.90	-1.68

Table 19 (a), (b) and (c) shows that for all ILs, the limiting molar conductances (Λ_0) increases as the temperature increases but decrease as the mass fraction of tetrahydrofuran in the solvent mixtures increase. This trend in limiting molar conductances (Λ_0) can be well described by the viscosity behavior of the solvent media.

Thus, the observed trend of the limiting molar conductances (Λ_0) values as:

[EMIm]NO_3 > [EMIm]CH_3SO_3) > [EMIm]Tos)

But the values of $K_{A,C}$follow the order:

[EMIm]NO_3 < [EMIm]CH_3SO_3) < [EMIm]Tos)

For all solvent composition and experimental temperature, i.e., with increasing tetrahydrofuran content the association equilibrium shifts to the right of the above order as a result of decreasing in mixture permittivity as the Tos^- anion significantly enhances the ion-solvent interaction relative to $CH_3SO_3^-$ and NO_3^- in molecular solvents.

The trend in Λ_0 and ion-association can be discussed through another characteristic function called the Walden product ($\Lambda_0\eta_0$) (product of the limiting molar conduactance and solvent viscosity) This is justified as the Walden product of an ion or solute is inversely proportional to the effective solvated radius (r_{eff}) of the ion or solute in a particular solvent/solvent mixtures [Bhat and Bindu, 1995].

$$\Lambda_0\eta_0 = \frac{1}{6\pi r_{eff}T}$$

The variation of the Walden products with solvent composition and temperature reflects the change of ion- solvation and ion-solvent interactions [Janz and Tomkins, 1973]. Walden product either varies slightly with temperature or is almost independent of temperature for the ILs studied with the experimental results but decreases with increasing mass fraction of tetrahydrofuran.

4.6.4. Evaluation of limiting ionic conductance ($\lambda_o^{\pm}$), ionic walden product ($\lambda_o^{\pm}n_0$), stokes' radii (r_S) and crystallographic radii (r_c) of ionic liquids.

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting ionic Walden product ($\lambda_o^{\pm}\eta_0$), (the product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function of the ionic radius (crystallographic radius) and thus under normal condition, is a constant. The ionic conductances $\lambda_o^{\pm}$ for the $[emim]^+$ cation and NO_3^-, $CH_3SO_3^-$, Tos^- anion in different mass fraction of tetrahydrofuran, were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' using the following scheme as suggested by Bijan Das [Das *et al*., 2003]. We have calculated the ionic limiting molar conductances$\lambda_o^{\pm}$, in studied solvents by interpolation of conductance data from the literature[Fuoss and Hirsch, 1960] using cubic spline fitting. The ionic conductance values given in Table 20, the degree of ionic conductance is higher for $[emim]^+$ ion than for NO_3^-, $CH_3SO_3^-$, Tos^-, suggesting that the anions (NO_3^-, $CH_3SO_3^-$, Tos^-) are responsible for a greater share of ionic association than the common imidazoliumcation$[emim]^+$.

Table 20: Limiting ionic conductance ($\lambda_o^{\pm}$), ionic Walden product ($\lambda_o^{\pm}n_0$), Stokes' radii(r_S) and crystallographic radii (r_c) of imidazolium based ionic liquids in different studied mass fraction of tetrahydrofuran (w_2) at T = 298.15 K

Mass fraction of THF(w_2)	$\lambda_o^{\pm}\times10^4$ (S m^2 mol^{-1})		$\lambda_o^{\pm}\eta_0\times10^4$ (S m^2 mol^{-1} mPas)		r_s (Å)		r_c (Å)		$t_\pm$	
	[emim]$^+$	NO_3^-	[emim]$^+$	NO_3^-	[emim]$^+$	NO_3^-	[emim]$^+$	NO_3^-	[emim]$^+$	NO_3^-
0.70	23.93	15.99	29.28	19.57	2.79	4.19	1.33	1.99	0.599	0.401
0.80	21.94	14.67	20.27	13.55	4.04	6.05	1.33	1.99	0.599	0.401
0.90	19.99	13.36	13.12	8.77	6.24	9.34	1.33	1.99	0.599	0.401
	[emim]$^+$	$CH_3SO_3^-$	[emim]$^+$	$CH_3SO_3^-$	[emim]$^+$	$CH_3SO_3^-$	[emim]$^+$	$CH_3SO_3^-$	[emim]$^+$	$CH_3SO_3^-$
0.70	24.91	11.70	30.48	14.32	2.69	5.72	1.33	2.83	0.680	0.320
0.80	22.21	10.44	20.52	9.64	3.99	8.49	1.33	2.83	0.680	0.320
0.90	19.52	9.17	12.81	6.02	6.40	13.61	1.33	2.83	0.680	0.320
	[emim]$^+$	Tos$^-$	[emim]$^+$	Tos$^-$	[emim]$^+$	Tos$^-$	[emim]$^+$	Tos$^-$	[emim]$^+$	Tos$^-$
0.70	21.66	9.11	26.50	11.15	3.09	7.35	1.33	3.16	0.704	0.296
0.80	18.73	7.89	17.31	7.28	4.73	11.25	1.33	3.16	0.704	0.296
0.90	15.51	6.53	10.18	4.29	8.05	19.12	1.33	3.16	0.704	0.296

The $\lambda_o^{\pm}$ values were in turn utilized for the calculation of Stokes' radii (r_s) according to the classical expression [Robinson and Stokes, 1959]

$$r_S = \frac{F^2}{6\pi N_A \lambda_0^{\pm} r_c} \qquad \ldots(87)$$

Ionic Walden products ($\lambda_o^{\pm}\eta_0$), Stokes' radii (r_s), and crystallographic radii (r_c) are presented in Table 20. For the [emim]$^+$, NO_3^-, $CH_3SO_3^-$, and Tos$^-$ ions, the Stokes' radii (r_s) are higher than their crystallographic radii (r_c), this suggests that the ion are comparatively more solvated due to its intrinsic surface charge density. These results also support the fact of higher association of the ions by the solvent molecules in the experimental solutions. The distance parameter R is the least distance that two free ions can approach before they merge into an ion-pair in the studied media. The nature of the curve for the Gibb's energy changes for ion-pair formation, ΔG^0, clearly predicts the tendency for ion-pair formation. The Gibb's energy change ΔG^0 is given by the following relationship [Fuoss and Kraus, 1933] and is given in Table 19 (a), (b) and (c).

$$\Delta G^0 = -RTlnK_A$$

The negative values of ΔG^0 can be explained by considering the participation of specific interaction in the ion-association process. It is observed from the Table 19 (a), (b) and (c) that the values of the Gibb's free energy for all ILs are negative at different temperatures and the negativity increases as the mass fraction of tetrahydrofuran increases which leads to the increase in the ion-solvent interaction. This result indicates the extent of solvation enhanced by the following order: [EMIm]NO_3 < [EMIm]CH_3SO_3) < [EMIm]Tos)

4.6.5. Evaluation of A-coefficient and solvation number.

The significance of the term had since then been realized due to the development Debye-Hückel theory [Debye-huckel, 1923] of inter-ionic attractions in 1923. The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory and is given by the Falkenhagen and Vernon [Falkenhagen and Vernon, 1983] equation:

$$A_{Theo} = \frac{0.2577\Lambda_0}{\eta_0(\varepsilon T)^{0.5}\lambda_+^0\lambda_-^0}[1 - 0.6863(\frac{\lambda_+^0\lambda_-^0}{\Lambda_0})^2] \qquad \ldots(88)$$

where the symbols have their usual significance. A-coefficient suggesting that should be calculated from conductivity measurements and given in the Table 21. From the table, A-coefficient is negative and very small, shows that the existence of the ion-ion interaction negligible, as compared to the ion-solvent interaction for all the chosen ionic liquids in the studied solvents. 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 (n_S). 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 as well as the ILs.

If the limiting conductance of the ions ($\lambda_o^{\pm}$) of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law and the volume of the solvation shell is given by the equation.

$$V_s = \left(\frac{4\pi}{3}\right)(r_s^3 - r_c^3) \qquad \ldots(89)$$

where r_c and r_s is the crystallographic and Stokes' radius of the ions. The solvation number n_s would then be obtained from

$$n_s = \frac{V_s}{V_0} \qquad \ldots(90)$$

where V_0 is the volume of the solvent molecules. The solvation number n_S is given in the Table 21. The solvation number increases as mass fractions of tetrahydrofuran increases which suggested that the number of solvent molecules which are aligned in the force field of the ions increases, which leads to the increasing trend of ion-solvent interaction as the mass fractions of tetrahydrofuran increases.

Table 21: A-coefficient and solvation number (n_S) of ionic liquids in different studied aqueous-tetrahydrofuran solutions at 298.15K

w_2	A-coefficient /(mPas $K^{1/2}$ S m^2 mol^{-1})$^{-1}$	n_S	A-coefficient /(mPas $K^{1/2}$ S m^2 mol^{-1})$^{-1}$	n_S	A-coefficient /(mPas $K^{1/2}$ S m^2 mol^{-1})$^{-1}$	n_S
	[emim]NO_3		[emim]CH_3SO_3		[emim]Tos	
0.70	-0.015	8.31	-0.012	9.14	-0.010	11.56
0.80	-0.021	27.08	-0.016	28.23	-0.013	44.12
0.90	-0.032	102.51	-0.025	130.20	-0.017	220.55

4.6.6. Evaluation of diffusion coefficient ($D_\pm$) and ionic mobility ($i_\pm$)

The diffusion coefficient (D) is obtained using the Stokes-Einstein Relation:

$$D = \frac{K_B T}{6\pi\eta_0 r_s} \quad \text{...(91)}$$

Where k_B is the Boltzmann's constant, T is the temperature, η_o is the solvent viscosity and r_s is the Stoke's radius.

The ionic mobility was obtained using the following equation

$$i_\pm = \frac{z_\pm F}{R_g T} D \quad \text{…(92)}$$

where $z_\pm$, F, R_g, T and D is the ionic charge, Faraday constant, universal gas constant, temperature and diffusion co-efficient respectively.

Table 22: Diffusion coefficient ($D_{\pm}$) and ionic mobility ($i_{\pm}$) of ionic liquids in different studied solvents at 298.15K

w_2	$D_{\pm}\cdot 10^{16}/(m^2 s^{-1})$		$i_{\pm}\cdot 10^{14}/(m^2\ s^{-1}\ volt^{-1})$	
	$[emim]^+$	NO_3^-	$[emim]^+$	NO_3^-
0.70	6.39	4.26	2.49	1.66
0.80	5.85	3.91	2.28	1.52
0.90	5.33	3.56	2.08	1.39
	$[emim]^+$	$CH_3SO_3^-$	$[emim]^+$	$CH_3SO_3^-$
0.70	6.63	3.12	2.58	1.21
0.80	5.92	2.78	2.30	1.08
0.90	5.20	2.45	2.02	0.95
	$[emim]^+$	Tos^-	$[emim]^+$	Tos^-
0.70	5.77	2.43	2.25	0.94
0.80	4.99	2.10	1.94	0.82
0.90	4.13	1.74	1.61	0.68

Diffusion co-efficient ($D_{\pm}$) and ionic mobility ($i_{\pm}$) for the ions $[emim]^+$, NO_3^-, $CH_3SO_3^-$, and Tos^- in the studied solvents is given in Table 22. The contribution of diffusion coefficient of the anions (NO_3^-, $CH_3SO_3^-$, Tos^-) is less than the cation $[emim]^+$ in all the studied solvents, which indicates that $[emim]^+$ ions diffuses more through in the studied solvents. The diffusion coefficient decrease as the mass fraction of tetrahydrofuran increases. The ionic mobility value ($i_{\pm}$) given in Table 22, also shows that the mobility of anions (NO_3^-, $CH_3SO_3^-$, and Tos^-) is lower than $[emim]^+$ in the studied solvents, indicating greater share of conductance by $[emim]^+$ ions. The observation indicates the diffusion coefficient ($D_{\pm}$) is directly proportional to the ionic mobility ($i_{\pm}$) and these are the driving force to conduct electricity by ILs or ions in solutions. The results are inversed to the density and viscosity of the solvents. Lower the diffusivity and mobility higher the ion-solvent interaction or ion-solvation, which is evident from the association constant values, reported in Table 19 (a), (b) and (c).

4.6.7. Evaluation of calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductance of triple-ion (Λ_0^T), slope and intercept.

Non linear conductance curve (Λ vs $\sqrt{c}$) was obtained for the ionic liquids in pure tetrahydrofuran which shows that, the electrolyte (ILs) follows the same trend, i.e. the conductance value decreases with increasing concentration, reach a minimum and then increases. Due to the deviation of the conductometric curves from linearity in case of ionic liquids (ILs) in tetrahydrofuran (ε_r = 7.58), the conductance data have been analyzed by the classical Fuoss-Kraus theory of triple-ion formation [Fuoss and Kraus, 1933] in the form

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \qquad \ldots(93)$$

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

$$g(c) = \frac{exp\{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \qquad \ldots(94)$$

$$\beta' = 1.8247\, X 10^6/(\varepsilon T)^{1.5} \qquad \ldots(95)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204\, X\, 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad \ldots(96)$$

In the above equations, $\Lambda_0$is the sum of the molar conductance of the simple ions at infinite dilution, $\Lambda_0^T$is the sum of the conductance value of the two triple-ions $[(emim)_2]^+[Y]$ and $[emim][Y_2]^-$ for the imidazolium ionic liquids, [emim][Y] (where Y= NO_3^-, $CH_3SO_3^-$ and Tos^-). $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants respectively and S is the limiting Onsager coefficient. To make equation (93) applicable, the symmetrical approximation of the two possible formation constants of triple-ions,

K_{T1} = $[(emim)_2]^+[Y]/\{[(emim)^+][emim][Y]\}$ and K_{T2} = $[emim][Y_2]^- /\{[Y^-][emim][Y]\}$ equal to each other has been adopted, i.e. $K_{T1} = K_{T2} = K_T$ and Λ_0 values for the studied electrolyte have been calculated using the following scheme as suggested by B.Z. Krumgalz [Krumgalz, 1983]. Λ_0^T has been calculated by setting the triple-ion conductance equal to 2/3 Λ_0 [Harada *et al*., 1985].The calculated values are listed in Table 23.

The ratio Λ_0^T/ Λ_0were thus set equal to 0.667 during linear regression analysis of equation (92). Table 23 shows the calculated limiting molar conductance of simple ion (Λ_0), limiting molar conductance of triple ion (Λ_0^T), slope and intercept of equation (92) for ionic liquids (ILs) in tetrahydrofuran at298.15, 303.15 and 308.15K. The linear regression analysis of equation (92) for the electrolytes with an average regression constant, R^2 = 0.9689, gives intercept and slope. These values permit the calculation of other derived parameters such as K_P and K_T listed in Table 24 (a), (b) and (c). A perusal of Table 24 (a), (b) and (c) shows that the K_P is larger than K_T, indicate the major portion of the electrolytes (ILs) exists as ion-pairs with a minor portion as triple-ions. The tendency of triple ion formation with respect to ion-pair, can be judged from the K_T/K_P ratio and log (K_T/K_P). The ratios suggest that strong ion-association between the ions and solvent is due to the coulombic interactions as well as to covalent forces in the solution. These results are in good agreement with those of Hazra and his groups [Das *et al*., 1999]. At very low permittivity of the solvent, i.e., $\varepsilon_r < 10$, electrostatic ionic interactions are very large. So the ion-pairs attract the free cations or anions present in the solution medium as the distance of the closest approach of the ions becomes minimum.

Table 23: The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductance of triple-ion (Λ_0^T), slope and intercept of equation 92of ionic liquids in tetrahydrofuran at different temperatures.

Ionic liquids	Temp(K)	$\Lambda_0 \times 10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$	$\Lambda_0^T \times 10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$	Slope x 10^{-2}	Intercept x 10^{-2}
[emim]NO_3	298.15	20.91	13.95	2.56	4.58
[emim]NO_3	303.15	25.25	16.84	6.74	5.21
[emim]NO_3	308.15	31.57	21.06	10.19	6.33

Ionic liquids	Temp(K)	$\Lambda_0 \times 10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$	$\Lambda_0^T \times 10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$	Slope x 10^{-2}	Intercept x 10^{-2}
[emim]CH_3SO_3	298.15	17.17	11.45	0.63	3.96
[emim]CH_3SO_3	303.15	20.43	13.63	4.92	4.51
[emim]CH_3SO_3	308.15	25.91	17.28	7.51	5.54

Ionic liquids	Temp(K)	$\Lambda_0 \times 10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$	$\Lambda_0^T \times 10^4$ $(\mathrm{S\ m^2\ mol^{-1}})$	Slope x 10^{-2}	Intercept x 10^{-2}
[emim]Tos	298.15	12.82	8.55	1.32	0.09
[emim]Tos	303.15	17.26	11.51	4.08	0.04
[emim]Tos	308.15	21.52	14.35	6.34	0.05

4.6.8. Calculation of salt concentration at the minimum conductivity (c_{min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T)

Table 24(a): Salt concentration at the minimum conductivity (c_{min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T) for [emim]NO_3 in tetrahydrofuran at different temperatures.

Temperature	$c_{min}\times10^4$ (mol dm^{-3})	log c_{min}	$K_P\times10^{-4}$ (mol $m^{-3})^{-1}$	$K_T\times10^{-3}$ (mol $m^{-3})^{-1}$	$(K_T/K_P)\times10^4$	$\log(K_T/K_P)$
298.15K	0.60	-4.22	20.88	8.38	401.42	-1.40
303.15K	0.60	-4.22	23.40	19.40	825.54	-1.08
308.15K	0.60	-4.22	24.89	24.13	965.53	-1.01

Table 24(b): Salt concentration at the minimum conductivity (c_{min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T) for [emim]CH_3SO_3 in tetrahydrofuran at different temperatures

Temperature	$c_{min}\times10^4$ (mol dm^{-3})	log c_{min}	$K_P\times10^{-3}$ (mol $m^{-3})^{-1}$	$K_T\times10^{-3}$ (mol $m^{-3})^{-1}$	$(K_T/K_P)\times10^4$	$\log(K_T/K_P)$
298.15K	0.54	-4.27	18.76	7.39	394.06	-1.40
303.15K	0.54	-4.27	20.56	16.36	795.37	-1.10
308.15K	0.54	-4.27	21.91	20.34	928.19	-1.03

Table 24(c): Salt concentration at the minimum conductivity (c_{min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T) for [emim]Tos in tetrahydrofuran at different temperatures

Temperature	$c_{min}\times10^4$ (mol dm^{-3})	log c_{min}	$K_P\times10^{-4}$ (mol m^{-3})$^{-1}$	$K_T\times10^{-3}$ (mol m^{-3})$^{-1}$	$(K_T/K_P)\times10^4$	$\log(K_T/K_P)$
298.15K	0.50	-4.30	16.81	6.33	376.81	-1.42
303.15K	0.50	-4.30	18.27	15.16	829.68	-1.08
308.15K	0.50	-4.30	19.92	19.70	989.01	-1.00

These results in the formation of triple-ions, which acquires the charge of the respective ions, attracted from the solution bulk [Fuoss and Hirsch, 1960] i.e.;

$M^+ + A^- \leftrightarrow M^+\cdots\cdots A^- \leftrightarrow MA$ (ion-pair)

$MA + M^+ \leftrightarrow MAM^+$ (triple-ion)

$MA + A^- \leftrightarrow MAA^-$ (triple-ion)

where M^+ and A^- are $[emim]^+$ and Y^- (where Y= NO_3^-, $CH_3SO_3^-$ and Tos^-) respectively. The effect of ternary association [Sinha and Roy, 2007] thus removes some non-conducting species, MA, from solution and replaces them with triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the ionic liquids in tetrahydrofuran. Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T, respectively, have also been calculated using the following equations [Harada *et al.*, 1985]

$$\alpha = 1/(K_P^{\frac{1}{2}}.c^{\frac{1}{2}}) \quad \ldots(97)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \quad \ldots(98)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \qquad \ldots(99)$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \qquad \ldots(100)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions present in the salt-solutions are given in Table 25. Thus the values of C_P and C_T given in Table 25, indicates that the major portion ions are present as ion-pair even at high concentration and a small fraction exist as triple-ion. It is also observed that after a certain concentration the fraction of the triple-ions in the solution increases with the increasing concentration, in the studied solution media {[emim][Y]+tetrahydrofuran}.

Table 25: Salt concentration (c_{min}) at the minimum conductivity (Λ_{min}), the ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) of ionic liquids in tetrahydrofuran at T = 298.15 K

Ionic liquids	$c_{min}\times10^4$ (mol dm^{-3})	$\Lambda_{min}\times10^4$	$\alpha\times10^2$	$\alpha_T\times10^2$	$C_P\times10^5$ (mol dm^{-3})	$C_T\times10^5$ (mol dm^{-3})
[emim]NO_3	0.60	6.54	28.25	10.92	6.86	0.55
[emim]CH_3SO_3	0.54	4.93	31.42	12.54	5.73	0.68
[emim]Tos	0.50	4.11	34.50	14.21	4.91	0.85

4.6.1. Evaluation of bond length, surface of electron density and electrostatic potential by using a computational software Gaussian 09W, Revision A.02 :

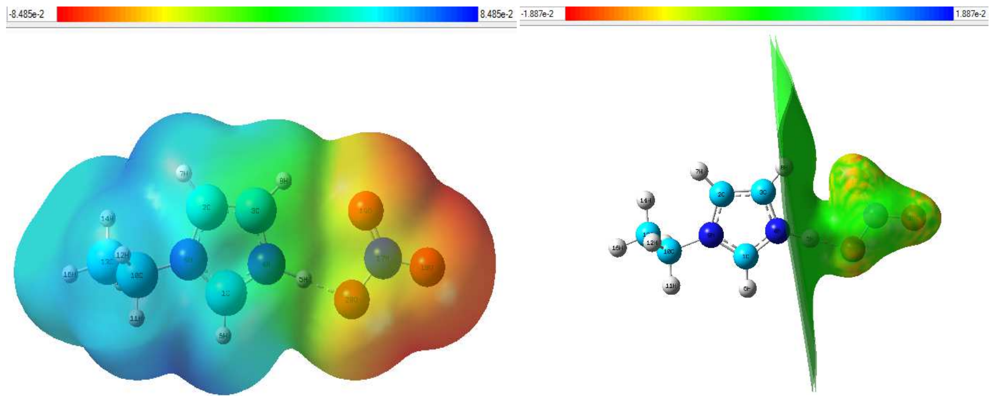


Figure 33: Surfaces of Electron Density (from -8.455e-2 to 8.455e-2) and Electrostatic Potential (from -1.887e-2 to 1.887e-2) generated from Total SCF Density and mapped with ESP in 1-ethyl-3-methylimidazolium nitrate.

Ion association occurs from the red region which is shown in figure 33 (surface of electron density is rich in red region), supported by electrostatic potential generated from total SCF density and association occurs from 20O of anion and 5H of cation sites of 1-ethyl-3-methylimidazolium nitrate as shown in the following figure 34.

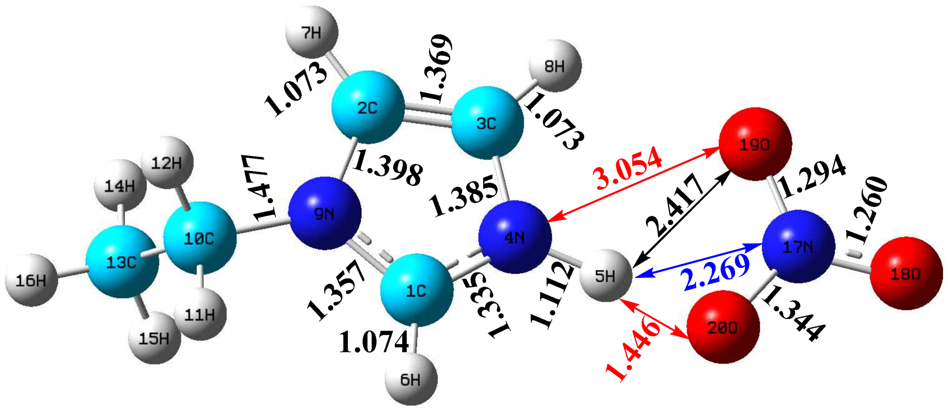


Figure 34: Bond lengths of 1-ethyl-3-methylimidazolium nitrate

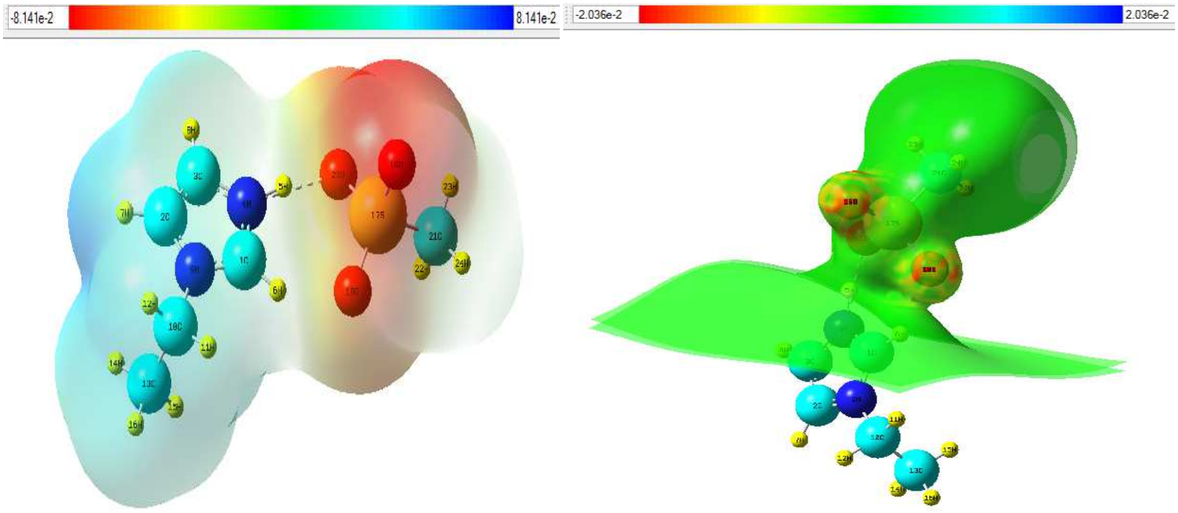


Figure 35: Surfaces of Electron Density (from -8.141e-2 to 8.141e-2) and Electrostatic Potential (from -2.036e-2 to 2.036e-2) generated from Total SCF Density and mapped with ESP in 1-ethyl-3-methylimidazolium methane sulfonate.

Ion association occurs from the red region which is shown in figure 35 (surface of electron density is rich in red region), supported by electrostatic potential generated from total SCF density and ion-ion interaction from 20O of anion and 5H of cation sites of 1-ethyl-3-methylimidazolium methane sulfonate as shown in the following figure 36.

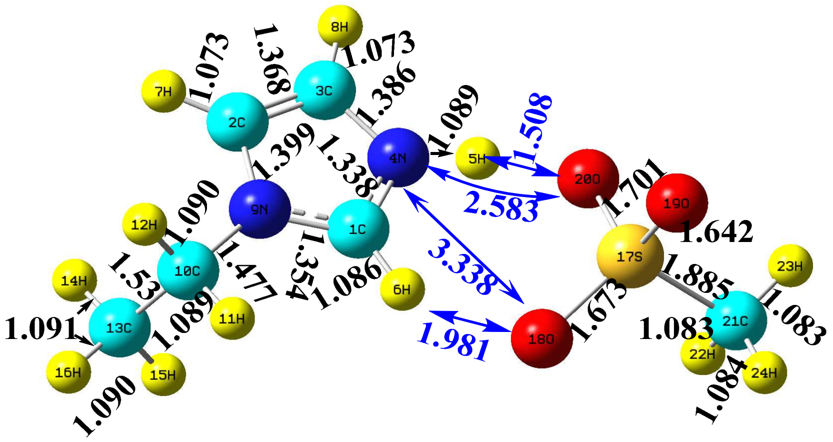


Figure 36: Bond lengths of 1-ethyl-3-methylimidazolium methane sulfonate

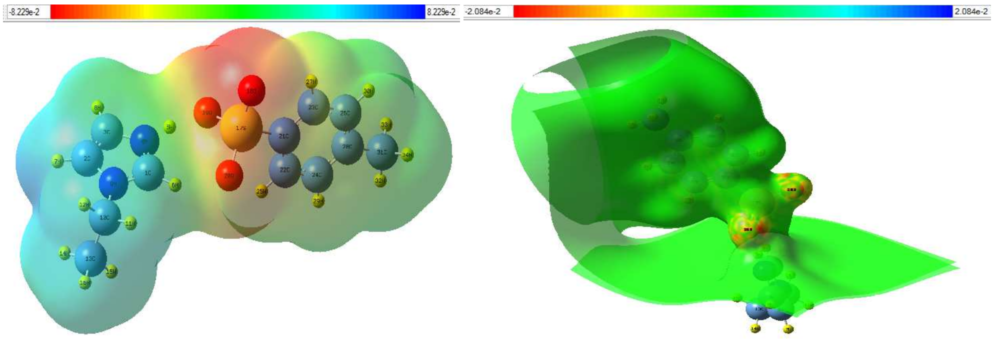


Figure 37: Surfaces of Electron Density (from -8.229e^{-2} to 8.229e-2) and Electrostatic Potential (from -2.084e-2 to 2.084e-2) generated from Total SCF Density and mapped with ESP in 1-ethyl-3-methylimidazolium tosylate.

Ion association occurs from the red region which is shown in figure 37 (surface of electron density is rich in red region), supported by electrostatic potential generated from total SCF density and ion interaction come from 19O of anion and 5H of cation sites of 1-ethyl-3-methylimidazolium tosylate as shown in the following figure 38.

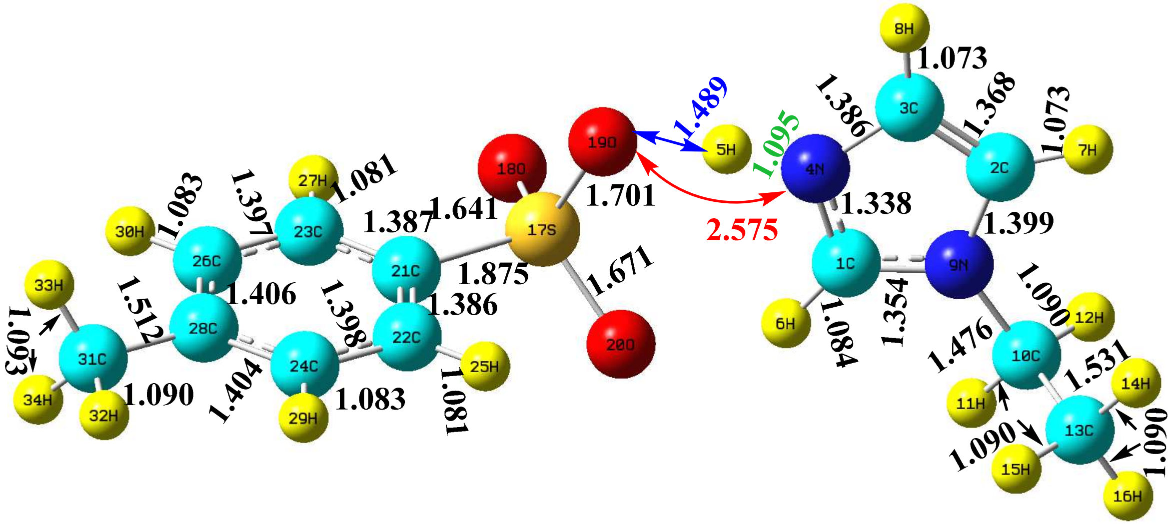


Figure 38: Bond lengths of 1-ethyl-3-methylimidazolium tosylate

The present work reveals an extensive study on the ion-solvation behavior of the 1-ethyl-3-methylimidazolium based ionic liquids {[emim][Y]; where Y= NO_3^-, $CH_3SO_3^-$ and Tos^-}in pure and different mass fractions of tetrahydrofuran through the conductometric. It becomes clear that the all the studied ionic liquids (ILs) exists as ion-pair in mass fraction of tetrahydrofuran, and as triple-ion in pure tetrahydrofuran at different temperatures. The tendency of the ion-pair and triple-ion formation depends on the size the charge distribution of the anions (NO_3^-, $CH_3SO_3^-$ and Tos^-) for the common cation ($[emim]^+$), and structural aspects (functional group of the solvents).The diffusion coefficient ($D_\pm$) and the ionic mobility ($i_\pm$) decrease as the mass fraction of tetrahydrofuran increases.

1-ehyl-3-methylimidazolium based ionic c liquids	: [emim][Y]
	(Where Y= NO_3^-, $CH_3SO_3^-$ and Tos^-
1-ehyl-3-methylimidazolium nitrate	: [emim]NO_3
1-ehyl-3-methylimidazolium methanesulfonate	: [emim]CH_3SO_3
1-ehyl-3-methylimidazolium tosylate	: [emim]Tos
Tetrahydrofuran	: C_4H_8O
Water	: H_2O

4.7. Theoretical and experimental study of 1-Butyl-3-Methylimidazolium Hexafluorophosphate and 1-Benzyl-3-Methylimidazolium Hexafluorophosphate by using Fuoss and Gaussian 09W, Revision A.02, program package (Gaussian Inc.)

4.7.1. Introduction

Ionic liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering, their molecular interaction with the industrially important organic solvents would be of utmost importance for the chemical formulations in these industries. Ionic liquids (ILs) have been actively tested as innovative non volatile solvents and they are used in many academic and industrial research areas. Recently ionic liquids (ILs) have been considered as attractive compounds due to their unique intrinsic properties, such as negligible vapor pressure, large liquid range, ability of dissolving a variety of chemicals non-volatility, high thermal stability, large electrochemical window and their potential as ‘designer solvents’ and ‘green’ replacements for volatile organic solvents [Welton, 1999], used in reactions involving inorganic and bio-catalysis etc. They are also used as heat transfer fluids for processing biomass and electrically conductive liquids as electrochemical device in electrochemistry (batteries and solar cells) [Endres and Zein El Abedin, 2006]. In the modern technology, the application of the ILs is well understood by studying the solvation ion or ion association. These solvents are often fluid at room temperature, and consist entirely of ionic species. As they are made up of at least two components which can be varied (the anion and cation), the solvents can be designed with a particular end use in mind, or to possess a particular set of properties. Hence, the term “designer solvents” has come into common use [Plechkov and Seddon, 2008]. Another useful aspect of some ionic liquids is their broad window of electrochemical stability, which can be as large as 6.0V. This window makes these ionic liquids promising candidates for use as electrolytes for electrochemistry. They are also used as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) [Wang *et al.*, 2003].

Keeping in mind the use of ionic liquids in battery industries we have here studied the the thermodynamic, optical and the transport properties of ionic liquids in industrially important solvents. These properties provide important information about the nature and strength of intermolecular forces operating among mixed components. FT-IR measurements have also been done as it is one of the most convenient methods for investigating the molecular interactions in electrolytic solutions [Dogonadze *et al.*, 1986].

4.7.2. Experimental Section

1-Butyl-3-methylimidazolium hexafluorophosphate and 1-Benzyl-3-methylimidazolium hexafluorophosphate of puriss grade was procured from Aldrich, Germany. It was used as purchased as the purity assay of the salt was ≥98.5%. All the solvents of spectroscopic grade were procured from Thomas Baker, India. The purities of the solvents were >98.5%. All the viscosity, dielectric constant and density values were interpolated from literature values [Mikhailand Kimel., 1961; Grande *et al.*, 2006-2007; Borun and Bald, 2012]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used. Conductivity measurements were carried out over the temperature range of 25^{o}C – 30^{o} C. The temperature control in the ranges of 25-30^{0}C were made by using refrigerated water bath and Circulator - Cole-Palmer, Polystat R6L and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg).

Table 28: The concentration (c) and molar conductance (Λ) of [BMIM]PF_6^- in different solvents at 298.15 – 308.15K.

$c\cdot 10^4$/ $mol\cdot dm^{-3}$	$\Lambda\cdot 10^4$/ $S\cdot m^2\cdot mol^{-1}$	$c\cdot 10^4$/ $mol\cdot dm^{-3}$	$\Lambda\cdot 10^4$/ $S\cdot m^2\cdot mol^{-1}$	$c\cdot 10^4$/ $mol\cdot dm^{-3}$	$\Lambda\cdot 10^4$/ $S\cdot m^2\cdot mol^{-1}$
AN	298.15K	303.15K		308.15K	
9.21	114.32	9.33	119.72	9.39	125.02
16.97	111.07	17.14	117.27	17.22	122.07
24.11	108.56	24.31	115.76	24.40	119.66
29.92	106.92	30.14	113.92	30.25	117.62
33.52	106.03	33.76	111.23	33.87	115.73
43.69	103.39	43.96	109.59	44.09	113.09
49.14	102.11	49.42	108.01	49.56	110.51
54.61	100.97	54.91	106.27	55.06	108.27
60.68	99.71	60.99	104.61	61.15	106.11
67.40	98.52	67.73	102.92	67.90	103.72
73.27	97.42	73.62	100.22	73.79	101.42
79.39	96.31	79.75	98.01	79.92	98.61

$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$
MeOH	298.15K	303.15K		308.15K	
9.30	89.13	9.43	93.03	9.49	98.53
13.54	87.03	13.69	90.93	13.76	96.43
18.66	85.34	18.84	89.24	18.92	94.74
23.33	83.91	23.52	87.81	23.62	92.31
30.03	82.22	30.25	86.12	30.36	90.62
37.09	80.00	37.33	83.90	37.45	88.43
43.17	78.75	43.43	82.65	43.56	85.45
48.72	77.62	49.00	80.52	49.14	83.02
55.21	76.51	55.21	78.71	55.65	81.51
65.45	74.77	65.77	77.17	65.93	79.87
76.74	73.01	77.09	75.21	77.26	77.91
86.86	71.68	87.24	73.58	87.42	75.88

$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$
DMF	298.15K	303.15K		308.15K	
18.31	62.57	18.48	66.07	18.57	70.97
25.40	60.43	25.60	64.53	25.71	69.43
31.36	59.19	31.58	62.69	31.70	67.79
36.60	58.16	36.84	61.66	36.97	65.86
42.64	56.9	42.90	60.20	43.03	64.29
50.84	55.26	51.12	58.76	51.27	62.66
61.31	53.33	61.62	57.43	61.78	60.73
68.89	51.97	69.22	56.05	69.39	59.07
73.27	51.50	73.62	54.35	73.79	57.75
80.64	50.29	81.00	52.99	81.18	56.29
85.58	49.41	85.95	51.71	86.14	54.71
91.59	48.85	91.97	50.05	92.16	53.05

$c\cdot 10^4$/ mol·dm^{-3}	$\Lambda\cdot 10^4$/ S·m^2·mol^{-1}	$c\cdot 10^4$/ mol·dm^{-3}	$\Lambda\cdot 10^4$/ S·m^2·mol^{-1}	$c\cdot 10^4$/ mol·dm^{-3}	$\Lambda\cdot 10^4$/ S·m^2·mol^{-1}
DMA	298.15K	303.15K		308.15K	
19.01	42.90	19.18	46.43	19.27	50.50
26.42	41.24	26.63	45.04	26.73	49.14
32.61	40.19	32.83	43.78	32.95	47.99
38.07	39.34	38.44	42.94	38.44	46.71
44.09	38.29	44.36	41.62	44.49	45.29
52.27	37.23	52.56	40.93	52.71	44.03
58.83	36.37	59.14	39.67	59.29	42.97
68.56	35.18	68.89	38.48	69.06	41.46
78.15	34.27	78.50	37.67	78.68	40.47
85.01	33.62	85.38	36.42	85.56	39.22
90.82	33.11	91.20	35.22	91.40	38.11
95.65	32.59	96.04	34.09	96.24	36.79

$c\cdot 10^4$/ mol·dm^{-3}	$\Lambda\cdot 10^4$/ S·m^2·mol^{-1}	$c\cdot 10^4$/ mol·dm^{-3}	$\Lambda\cdot 10^4$/ S·m^2·mol^{-1}	$c\cdot 10^4$/ mol·dm^{-3}	$\Lambda\cdot 10^4$/ S·m^2·mol^{-1}
DMSO	298.15K	303.15K		308.15K	
21.02	23.79	21.21	27.29	21.30	30.79
38.44	21.64	38.69	25.67	38.81	29.34
53.29	20.51	53.58	24.51	53.73	28.21
66.10	19.35	66.42	23.36	66.59	26.85
77.09	18.66	77.44	22.20	77.62	25.26
85.75	18.00	86.12	21.05	86.30	24.11
109.20	16.62	109.62	19.89	109.83	22.67
119.90	16.03	120.34	18.63	120.56	21.18
134.56	15.37	135.02	17.57	135.26	19.86
160.02	14.11	160.53	16.51	160.78	18.27
180.63	13.29	181.17	15.31	181.44	16.96
189.06	12.89	189.61	14.12	189.89	15.54

Table 29: The concentration (c) and molar conductance (Λ) of [BZMIM]PF_6^- in different solvents at 298.15 – 308.15K.

$c\cdot 10^4$/ $mol\cdot dm^{-3}$	$\Lambda\cdot 10^4$/ $S\cdot m^2\cdot mol^{-1}$	$c\cdot 10^4$/ $mol\cdot dm^{-3}$	$\Lambda\cdot 10^4$/ $S\cdot m^2\cdot mol^{-1}$	$c\cdot 10^4$/ $mol\cdot dm^{-3}$	$\Lambda\cdot 10^4$/ $S\cdot m^2\cdot mol^{-1}$
AN	298.15K	303.15K		308.15K	
9.15	108.70	9.27	112.40	9.33	115.59
16.81	105.04	16.97	110.25	17.06	112.64
23.91	102.21	24.11	107.91	24.21	110.11
29.70	100.37	29.92	106.07	30.03	107.87
33.29	99.45	33.52	104.05	33.64	105.65
43.43	96.79	43.69	102.19	43.82	103.59
48.86	95.23	49.14	99.93	49.28	101.43
53.29	94.18	53.58	97.88	53.73	99.08
60.37	92.65	60.68	96.15	60.84	96.85
67.080	91.09	67.40	94.29	67.57	94.29
72.93	89.64	73.27	92.04	73.44	92.84
79.03	88.58	79.39	89.98	79.57	90.08

$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$
MeOH	298.15K	303.15K		308.15K	
9.00	84.51	9.120	87.91	9.18	90.41
13.18	82.48	13.32	85.88	13.39	87.78
18.23	80.41	18.40	83.81	18.49	85.61
22.85	79.06	23.04	82.46	23.14	83.76
29.49	77.27	29.70	80.67	29.81	81.67
36.36	75.15	36.60	78.55	36.72	79.75
42.51	73.67	42.77	77.07	42.90	78.07
48.03	72.44	48.30	74.84	48.44	76.04
54.46	71.08	54.76	72.68	54.91	74.18
64.64	69.43	64.96	71.23	65.12	72.33
75.86	67.00	76.21	69.40	76.39	70.21
85.93	65.30	86.30	67.70	86.49	68.54

$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$	$c\cdot 10^4$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^4$/ $\mathrm{S\cdot m^2\cdot mol^{-1}}$
DMF	298.15K	303.15K		308.15K	
18.34	58.70	18.51	62.70	18.59	63.20
25.60	57.96	25.81	61.82	25.91	62.46
31.58	57.39	31.81	60.99	31.92	61.89
36.85	56.95	37.09	60.21	37.21	61.45
42.90	56.51	43.17	59.51	43.30	61.01
51.41	55.87	51.70	58.87	51.84	60.37
61.78	55.19	62.10	58.19	62.25	59.69
69.72	54.71	70.06	57.41	70.22	59.21
74.13	54.45	74.48	56.77	74.65	58.95
81.18	54.06	81.54	56.07	81.72	58.56
86.14	53.78	86.51	55.28	86.70	58.28
91.78	53.50	92.16	54.50	92.35	58.00

$c\cdot 10^{4}$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^{4}$/ $\mathrm{S\cdot m^{2}\cdot mol^{-1}}$	$c\cdot 10^{4}$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^{4}$/ $\mathrm{S\cdot m^{2}\cdot mol^{-1}}$	$c\cdot 10^{4}$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^{4}$/ $\mathrm{S\cdot m^{2}\cdot mol^{-1}}$
DMA	298.15K	303.15K		308.15K	
19.27	40.72	19.45	43.42	19.54	45.92
26.73	39.05	26.94	41.75	27.04	44.25
32.95	37.87	32.9476	40.57	33.30	43.07
38.32	37.04	38.18	39.74	38.69	41.89
44.49	36.12	44.75	38.82	44.89	40.52
52.71	34.93	52.99	37.63	53.14	39.63
59.14	34.02	59.44	36.72	59.60	38.52
68.89	33.00	69.22	35.27	69.39	37.2
78.68	31.76	79.03	34.36	79.21	35.96
85.75	31.07	86.12	33.28	86.30	35.27
91.39	30.56	91.77	32.36	91.97	34.05
96.04	30.08	96.43	31.15	96.63	32.68

$c\cdot 10^{4}$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^{4}$/ $\mathrm{S\cdot m^{2}\cdot mol^{-1}}$	$c\cdot 10^{4}$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^{4}$/ $\mathrm{S\cdot m^{2}\cdot mol^{-1}}$	$c\cdot 10^{4}$/ $\mathrm{mol\cdot dm^{-3}}$	$\Lambda\cdot 10^{4}$/ $\mathrm{S\cdot m^{2}\cdot mol^{-1}}$
DMSO	298.15K	303.15K		308.15K	
20.98	20.98	21.160	23.38	21.25	25.78
38.32	19.12	38.564	22.02	38.69	24.32
53.14	17.87	53.436	20.97	53.58	23.07
65.93	17.00	66.260	19.84	66.42	22.08
76.91	16.28	77.264	18.68	77.44	20.78
85.56	15.75	85.933	17.95	86.12	19.64
108.16	14.46	108.58	16.56	108.79	18.34
118.81	13.89	119.25	15.65	119.47	17.22
132.25	13.25	132.71	14.65	132.94	16.12
158.76	12.04	159.26	13.74	159.52	15.14
179.56	11.12	180.09	12.66	180.37	13.82
187.69	10.72	188.24	11.52	188.51	12.53

4.7.3. Evaluation of limiting molar conductivity (Λ_0), the association constant (K_A), The distance of closest approach of ions (R) and standard deviations of experimental Λ (δ) by Fuoss conductance equation.

The concentrations and molar conductances $\mathit{\Lambda}$ of 1-Butyl-3-methylimidazolium hexafluorophosphate and 1-Benzyl-3-methylimidazolium hexafluorophosphate in different solvents at different temperatures are given in Table 28 & 29. The molar conductances (Λ) have been obtained from the specific conductance (κ) value using the following equation [El-Dossoki, 2010].

$$\Lambda = 1000\boldsymbol{\kappa}/\mathbf{c}$$

Where c is the molar concentration and κ is the measured specific conductance of the studied solutions.

Linear conductance curves ($\mathit{\Lambda}$ versus $\sqrt{c}$) were obtained and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolyte. The conductance data for ion-pair formation have been analysed using the Fuoss conductance equation [Fuoss, 1978].

For such an analysis initial Λ_0 values for the iterative procedure were obtained from Shedlovsky extrapolation [Fuoss and Shedlovsky, 1949] of the experimental data using least square treatment. Shedlovsky method involves a linear extrapolation of conductance data given by the relation,

$$\frac{1}{\mathit{\Lambda} S(z)} = \frac{1}{\mathit{\Lambda}_o} + \left(\frac{K_{A,c}}{\mathit{\Lambda}_o^2}\right)\left(C\mathit{\Lambda}\int_{\pm}^{2} S(z)\right)$$

Where Λ_o is the limiting molar conductivity and other symbols have their usual meaning.

So with a given set of conductivity values (c_j, Λ_j, j=1,…n), three adjustable parameters, the limiting molar conductance (Λ_0), the association constant ($K_{A,c}$) and the distance of closest approach of ions (R) are derived from the Fuoss conductance equation. Since there is no precise method [Per, 1977] for determining the R-value and for the electrolytes studied no significant minima were observed obtained in the σ_Λ versus R- curves and thus in order to treat the data in our system, R-values were preset at the centre-to centre distance of solvent separated ion-pairs, i.e., Thus, R values are assumed to be

$$R = a + d$$

where a = (r_+ + r_-)is the sum of the crystallographic radii of the cation (r_+)and anion (r_-)and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by [Fuoss and Accascina, 1959].

$$d(\text{Å}) = 1.183(M/\rho)^{1/3}$$

Where M is the molecular weight of the solvent and ρ is the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{avg} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1}$$

where w_1 is the weight fraction of the first component of molar mass $M_{1.}$ Thus, the Fuoss conductance equation and other symbols are same as given in 3.1.2. The computations were performed using a program suggested by Fuoss.

Table 30: Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) of [BMIm]PF_6^- in different solvents at different temperatures.

Solutions	Temp	$\Lambda_o \cdot 10^4/S \cdot m^2 \cdot mol^{-1}$	K_A/ $dm^3 \cdot mol^{-1}$	R/Å	δ
[BMIm]PF_6^- in AN	298.15K	120.97	47.42	8.60	0.07
	303.15K	129.38	56.36	8.61	0.79
	308.15K	137.16	73.54	8.62	0.87
[BMIm]PF_6^- in MeOH	298.15K	95.64	65.80	8.23	0.14
	303.15K	100.93	73.95	8.24	0.49
	308.15K	108.44	90.79	8.25	0.62
[BMIm]PF_6^- in DMF	298.15K	72.96	101.89	9.20	0.42
	303.15K	78.27	108.51	9.21	1.48
	308.15K	85.69	123.67	9.22	1.24
[BMIm]PF_6^- in DMA	298.15K	50.76	115.10	9.52	0.23
	303.15K	56.12	124.99	9.53	1.93
	308.15K	62.04	136.56	9.53	1.64
[BMIm]PF_6^- in DMSO	298.15K	32.21	215.57	9.07	1.64
	303.15K	38.15	221.41	9.07	7.41
	308.15K	44.11	234.01	9.08	7.74

Table 31: Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) of [BZMIm]PF_6^- in different solvents at different temperatures .

Solutions	Temp	$\Lambda_o \cdot 10^4 / S \cdot m^2 \cdot mol^{-1}$	K_A/ $dm^3 \cdot mol^{-1}$	R/Å	δ
[BZMIm]PF_6^- in AN	298.15K	116.18	61.96	8.97	0.21
	303.15K	122.83	69.22	8.98	0.87
	308.15K	127.18	80.76	8.99	0.86
[BZMIm]PF_6^- in MeOH	298.15K	91.81	83.68	8.60	0.34
	303.15K	96.21	89.02	8.61	0.63
	308.15K	98.85	95.20	8.62	0.37
[BZMIm]PF_6^- in DMF	298.15K	68.69	108.96	9.57	0.35
	303.15K	72.39	123.09	9.58	0.52
	308.15K	77.91	128.31	9.59	0.43
[[BZMIm]PF_6^- in DMA	298.15K	49.56	139.94	9.89	0.40
	303.15K	53.49	144.62	9.90	0.19
	308.15K	56.99	150.92	9.90	0.17
[BZMIm]PF_6^- in DMSO	298.15K	29.80	265.69	9.44	2.06
	303.15K	34.15	268.63	9.44	8.79
	308.15K	37.93	273.23	9.45	8.38

A perusal of Table 30 & 31 shows that the limiting molar conductance (Λ_0) and association constant (K_A) of 1-Butyl-3-methylimidazolium hexafluorophosphate and 1-Benzyl-3-methylimidazolium hexafluorophosphate increase with increase in temperature in different solvent indicating less solvation or higher mobility of ions due to the fact that the increase thermal energy results in bond breaking and leads to higher frequency and higher mobility of the ions. The limiting molar conductance (Λ_0) of 1-Butyl-3-methylimidazolium hexafluorophosphate and 1-Benzyl-3-methylimidazolium hexafluorophosphate is highest in AN (which shows that weakest solvation due to lowest viscosity value) and lowest in case of DMSO (which shows that strongest solvation due to highest viscosity value) among the studied solvents and is evident from the K_A values. As the viscosity of DMSO is high, the mobility of the ions decreases resulting in decrease in conductance values but AN has a low viscosity leading to increase in mobility of the ions resulting in increase in conductance value.

The trend in the Λ_0 of 1-Butyl-3-methylimidazolium hexafluorophosphate and 1-Benzyl-3-methylimidazolium hexafluorophosphate in different solvents is as follows:
AN > MeOH > DMF > DMA > DMSO

Among the two ionic liquids, the higher K_A values in the case of 1-Benzyl-3-methylimidazolium hexafluorophosphate compared to 1-Butyl-3-methylimidazolium hexafluorophosphate may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the complex ion and hexafluorophosphate ion.

4.7.4. Evaluation of Walden product ($\Lambda_o \cdot \eta_0$) and Gibb's energy change (ΔG°)

The variation of the Walden products with solvent composition and temperature reflects the change of ion- solvation and ion-solvent interactions [Janz and Tomkins, 1973]. The Walden product, $\Lambda_0\eta_0$, of ILs is also calculated and the values are given in Table 39 & 40. Even though the Λ_0 decreases from AN to DMSO, the $\Lambda_0\eta_0$ is highest for DMSO which shows the predominance of η_0 over Λ_0.

Table 32: Walden product ($\Lambda_o \cdot \eta_0$) and Gibb's energy change (ΔG°) of $[BMIm]PF_6^-$ in different solventsat 298.15K

Solutions	$\Lambda_o \cdot \eta_0 \cdot 10^4$/ $S \cdot m^2 \cdot mol^{-1} mPa \cdot s$	$\Delta G^\circ/kJ \cdot mol^{-1}$
$[BMIm]PF_6^-$ in AN	41.66	-0.96
$[BMIm]PF_6^-$in MeOH	52.08	-1.04
$[BMIm]PF_6^-$in DMF	58.08	-1.15
$[BMIm]PF_6^-$in DMA	46.85	-1.17
$[BMIm]PF_6^-$in DMSO	62.68	-1.19

Table 33: Walden product ($\Lambda_o \cdot \eta_0$) and Gibb's energy change (ΔG°) of $[BZMIm]PF_6^-$ in different solventsat 298.15K.

Solutions	$\Lambda_o \cdot \eta_0 \cdot 10^4$/ $S \cdot m^2 \cdot mol^{-1} mPa \cdot s$	$\Delta G^\circ/kJ \cdot mol^{-1}$
$[BZMIm]PF_6^-$ in AN	40.01	-1.02
$[BZMIm]PF_6^-$in MeOH	49.99	-1.09
$[BZMIm]PF_6^-$in DMF	54.68	-1.16
$[BZMIm]PF_6^-$in DMA	45.74	-1.22
$[BZMIm]PF_6^-$in DMSO	57.99	-1.38

It is observed from the Table 32 & 33, the values of the Gibb's free energy are all negative entire all over the solutions and the negativity increases from AN to DMSO. This result indicates the extent of solvation enhanced by the following order:

DMSO > DMA > DMF > MeOH > AN

4.7.5. Evaluation of limiting ionic conductance ($\lambda_0^{\pm}$), ionic walden product ($\lambda_0^{\pm}n_0$), stokes' radii (r_S) and crystallographic radii (r_c) of ionic liquids.

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting ionic Walden product ($\lambda_0^{\pm}\eta_0$), (the product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function of the ionic radius (crystallographic radius) and thus under normal condition, is a constant. The ionic conductances $\lambda_o^{\pm}$ for the $[BMim]^+$ or $[BZMim]^+$ cation and PF_6^- anion in different solvent, were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' using the following scheme as suggested by Bijan Das [Das *et al*., 2003]. We have calculated the ionic limiting molar conductances $\lambda_0^{\pm}$, in studied solvents by interpolation of conductance data from the literature [Fuoss and Hirsch, 1960] using cubic spline fitting. The ionic conductance values given in Table 34 & 35, the degree of ionic conductance is higher for $[BMim]^+$ & $[BZMim]^+$ ion than for PF_6^-, suggesting that the anion (PF_6^-) are responsible for a greater share of ionic association than the common imidazolium cations {$[BMim]^+$ or $[BZMim]^+$.}

Table 34: Ionic limiting molar conductance ($\lambda^{\pm}_{0}$), ionic Walden product ($\lambda^{\pm}_{0}\eta_{0}$), crystallographic radii (r_c) and Stoke's radii (r_s)of $[BMIm]^+$ and PF_6^- in different solvents at 298.15K.

Solvents	$\lambda^{\pm}_{0}\cdot 10^{4}$/ $S\cdot m^{2}\cdot mol^{-1}$		$\lambda^{\pm}_{0}\eta_{0}\cdot 10^{4}$/ $S\cdot m^{2}\cdot mol^{-1} mPa\cdot s$		r_c/Å		r_s/Å	
	$[BMIm]^+$	PF_6^-	$[BMIm]^+$	PF_6^-	$[BMIm]^+$	PF_6^-	$[BMIm]^+$	PF_6^-
AN	97.50	23.47	33.58	8.08	0.71	2.95	2.44	10.14
MeOH	77.09	18.55	41.97	10.10	0.71	2.95	1.95	8.11
DMF	58.81	14.15	46.81	11.27	0.71	2.95	1.75	7.27
DMA	40.91	9.85	37.76	9.09	0.71	2.95	2.17	9.02
DMSO	25.96	6.25	50.52	12.16	0.71	2.95	1.62	6.74

Table 35: Ionic limiting molar conductance ($\lambda^{\pm}_{0}$), ionic Walden product ($\lambda^{\pm}_{0}\eta_{0}$), crystallographic radii (r_c) and Stoke's radii (r_s) of $[BZMIm]^+$ and PF_6^- in different solvents at 298.15K.

Solvents	$\lambda^{\pm}_{0}\cdot 10^{4}$/ $S\cdot m^{2}\cdot mol^{-1}$		$\lambda^{\pm}_{0}\eta_{0}\cdot 10^{4}$/ $S\cdot m^{2}\cdot mol^{-1} mPa\cdot s$		r_c/Å		r_s/Å	
	$[BZMIm]^+$	PF_6^-	$[BZMIm]^+$	PF_6^-	$[BZMIm]^+$	PF_6^-	$[BZMIm]^+$	PF_6^-
AN	85.04	31.14	29.29	10.72	1.08	2.95	2.80	7.64
MeOH	67.21	24.60	36.59	13.40	1.08	2.95	2.24	6.12
DMF	50.28	18.41	40.02	14.65	1.08	2.95	2.05	5.59
DMA	36.28	13.28	33.48	12.26	1.08	2.95	2.45	6.68
DMSO	21.81	7.99	42.45	15.54	1.08	2.95	1.93	5.27

Ionic Walden products ($\lambda_0^{\pm}\eta_0$), Stokes' radii (r_s), and crystallographic radii (r_c)are presented in Table 34 & 35. For the $[BMim]^+$, $[BZMim]^+$, PF_6^- ions, the Stokes' radii (r_s) are higher than their crystallographic radii (r_c), this suggests that the ion are comparatively more solvated due to its intrinsic surface charge density. These results also support the fact of higher association of the ions by the solvent molecules in the experimental solutions.

4.7.6. Evaluation of A-coefficient and solvation number.

The significance of the term had since then been realized due to the development Debye-Hückel theory [Debye-huckel, 1923] of inter-ionic attractions in 1923. The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory and is given by the Falkenhagen and Vernon [Falkenhagen and Vernon, 1983] equation:

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

where the symbols have their usual significance. A-coefficient suggesting that should be calculated from conductivity measurements and given in the Table 36. From the table, A-coefficient is negative and very small, shows that the existence of the ion-ion interaction negligible, as compared to the ion-solvent interaction for all the chosen ionic liquids in the studied solvents. If the limiting conductance of the ions ($\lambda_o^{\pm}$) of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law and the volume of the solvation shell is given by the equation.

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

where r_c and r_s is the crystallographic and Stokes' radius of the ions.

The solvation number n_s would then be obtained from

$$n_s = \frac{V_s}{V_0}$$

where V_0 is the volume of the solvent molecules.

Table 36: A-coefficient and solvation number (n_S) of ionic liquids in different solvents at 298.15K.

Solvent	**A-coefficient /(mPas $K^{1/2}$ S m^2 $mol^{-1})^{-1}$**	**n_S**	**A-coefficient /(mPas $K^{1/2}$ S m^2 $mol^{-1})^{-1}$**	**n_S**
	[BMIm]PF_6		[BZMIm]PF_6	
AN	-0.093	10.92	-0.113	4.71
MeOH	-0.049	13.99	-0.059	5.81
DMF	-0.037	19.79	-0.028	7.91
DMA	-0.024	27.54	-0.017	10.63
DMSO	-0.014	39.59	-0.004	16.38

From the table 36, we see that the order of solvation is DMSO > DMA > DMF > MeOH >AN meaning that the number of solvent molecules which are aligned in the force field is increasing, leading to increasing ion-solvent interaction.

4.7.7. Evaluation of diffusion coefficient ($D_\pm$) and ionic mobility ($i_\pm$)

The diffusion coefficient (D) is obtained using the Stokes-Einstein Relation:

$$D = \frac{K_B T}{6\pi\eta_0 r_s}$$

Where k_B is the Boltzmann's constant, T is the temperature, η_o is the solvent viscosity and r_s is the Stoke's radius.The ionic mobility was obtained using the following equation

$$i_{\pm} = \frac{z_{\pm}F}{R_g T} D$$

where $z_{\pm}$, F, Rg, T and D is the ionic charge, Faraday constant, universal gas constant, temperature and diffusion co-efficient respectively.

Table 37: Diffusion coefficient ($D_{\pm}$) and ionic mobility ($i_{\pm}$) of $[BMIm]^+$ and PF_6^- in different solvents at 298.15K.

Solvents	$D_{\pm}\cdot 10^{15}/(m^2\cdot s^{-1})$		$i_{\pm}\cdot 10^{15}/(m^2\ s^{-1} volt^{-1})$	
	$[BMIm]^+$	PF_6^-	$[BMIm]^+$	PF_6^-
AN	2.59	0.62	10.07	2.42
MeOH	2.05	0.49	7.98	1.92
DMF	1.57	0.38	6.10	1.47
DMA	1.09	0.26	4.24	1.02
DMSO	0.69	0.16	2.67	0.64

Table 38: Diffusion coefficient ($D_{\pm}$) and ionic mobility ($i_{\pm}$) of $[BZMIm]^+$ and PF_6^- in different solvents at 298.15K.

Solvents	$D\cdot 10^{15}/(m^2\cdot s^{-1})$		$i_{\pm}\cdot 10^{14}/(m^2\ s^{-1} volt^{-1})$	
	$[BZMIm]^+$	PF_6^-	$[BZMIm]^+$	PF_6^-
AN	2.25	0.83	8.77	3.21
MeOH	1.78	0.65	6.95	2.54
DMF	1.34	0.49	5.21	1.91
DMA	0.97	0.35	3.76	1.38
DMSO	0.58	0.21	2.24	0.82

Table 37 & 38 shows that the diffusion coefficient of $[BMIm]^+$ and $[BZMIm]^+$ is more than PF_6^- ion in all the solvents which indicates that $[BMIm]^+$ and $[BZMIm]^+$ ion diffuses more through the solvents. The diffusion coefficient decrease from AN to DMSO as indicated in Table 37 & 38for $[BMIm]^+$, $[BZMIm]^+$ and PF_6^- ions, showing greater diffusion of the ions in AN. At the same time the ionic mobility value given in Table 37 & 38 also shows that the mobility of $[BMIm]^+$ and $[BZMIm]^+$ is higher than PF_6^- in all the cases indicating greater share of conductance by $[BMIm]^+$ and $[BZMIm]^+$. The mobility of both the ions decrease from AN to DMSO given in Table 37 & 38. This is due to the fact that the increase in the viscosity of the solvent as well as due to the increase in the ion-solvent interaction which is evident from the association constant values reported in Table 30 & 31.

4.7.8. Evaluation of bond length, surface of electron density and electrostatic potential by using a computational software Gaussian 09W, Revision A.02 :

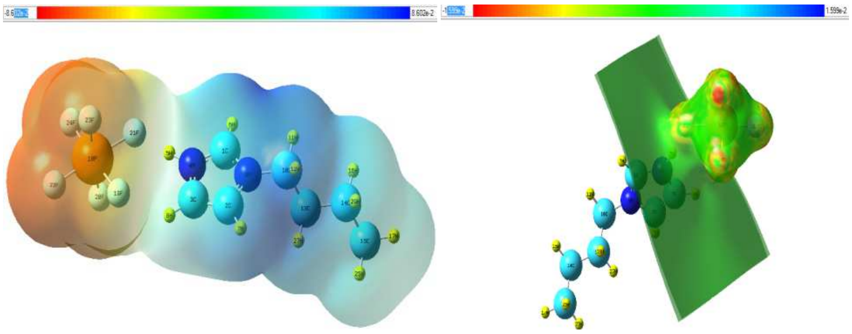


Figure 39: Surfaces of Electron Density (from -8.602e-2 to 8.602e-2) and Electrostatic Potential (from -1.599e-2 to 1.599e-2) generated from Total SCF Density and mapped with ESP in 1-butyl-3-methylimidazolium hexafluorophosphate.

Ion association occurs from the red region which is shown in figure 39 (surface of electron density is rich in red region), supported by electrostatic potential generated from total SCF density. Again, figure 40 shows the formation of ion association between 21F of anion and 5H of cation sites of 1-butyl-3-methylimidazolium hexafluorophosphate.

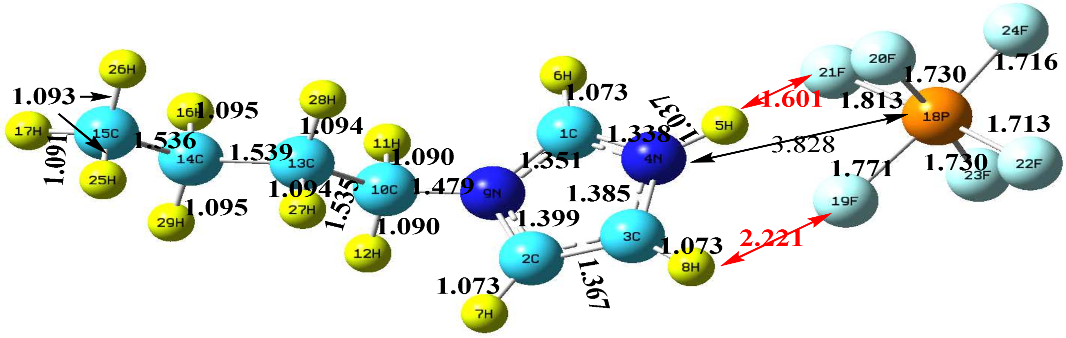


Figure 40: Bond lengths of 1-butyl-3-methylimidazolium hexafluorophosphate

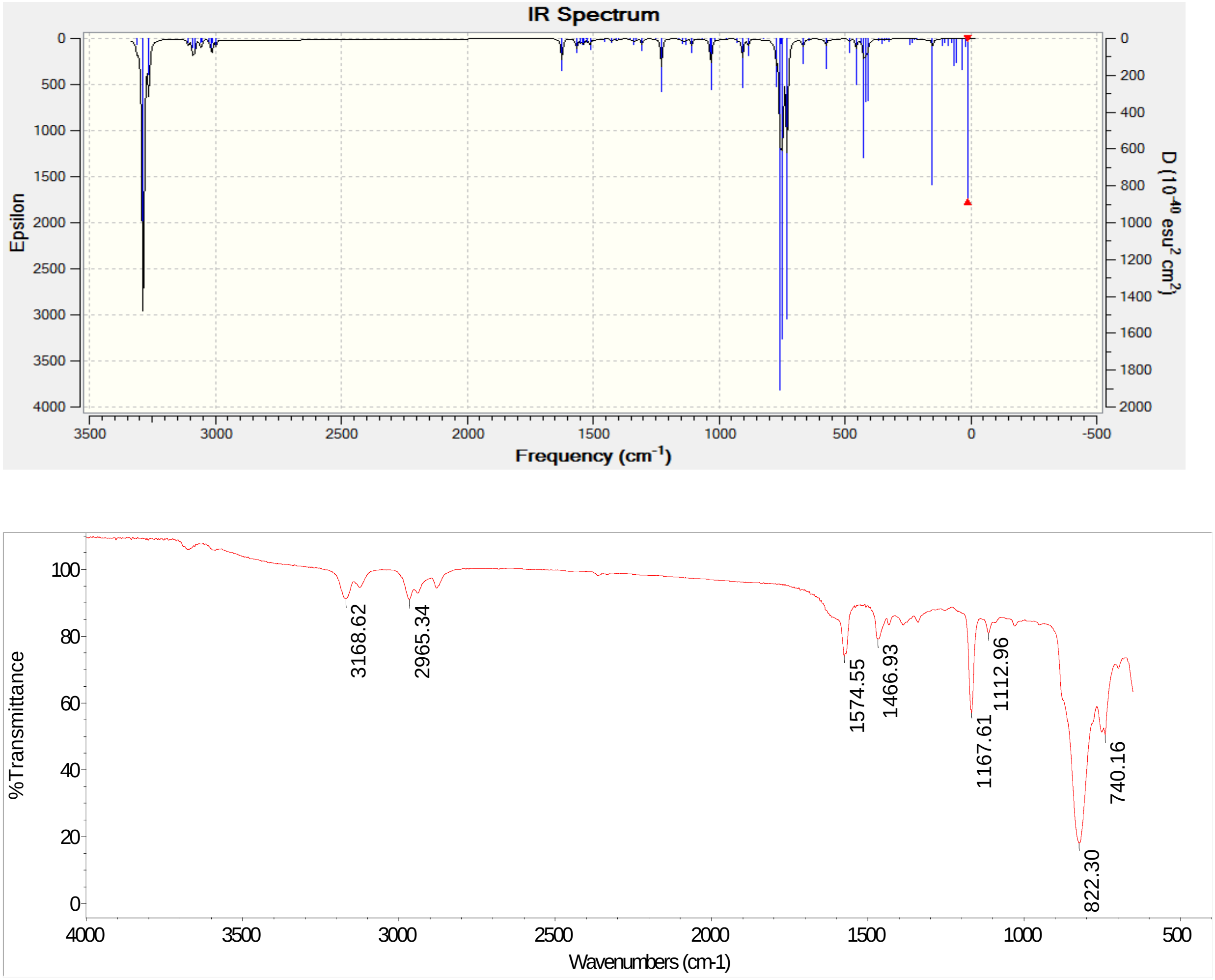


Figure 41: Computational and experimental IR spectra of 1-butyl-3-methylimidazolium hexafluorophosphate

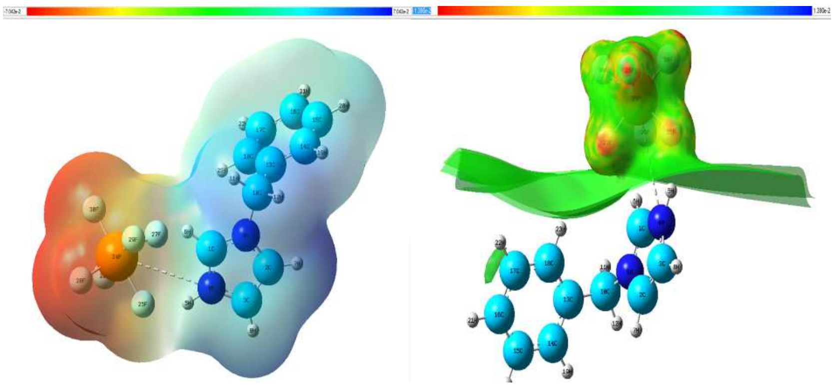


Figure 42: Surfaces of Electron Density (from -8.602e-2 to 8.602e-2) and Electrostatic Potential (from -1.599e-2 to 1.599e-2) generated from Total SCF Density and mapped with ESP in 1-benzyl-3-methylimidazolium hexafluorophosphate.

Ion association occurs from the red region which is shown in figure 42 (surface of electron density is rich in red region), supported by electrostatic potential generated from total SCF density and association occurs from 25F of anion and 5H of cation portions of their shortest bond length of1-benzyl-3-methylimidazolium hexafluorophosphate as shown in the following figure 43.

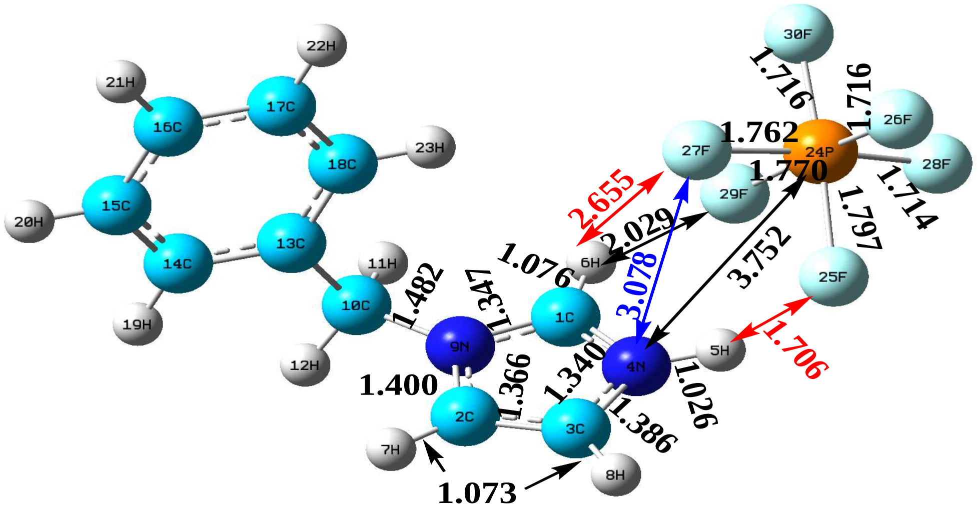


Figure 43: Bond lengths of 1-benzyl-3-methylimidazolium hexafluorophosphate

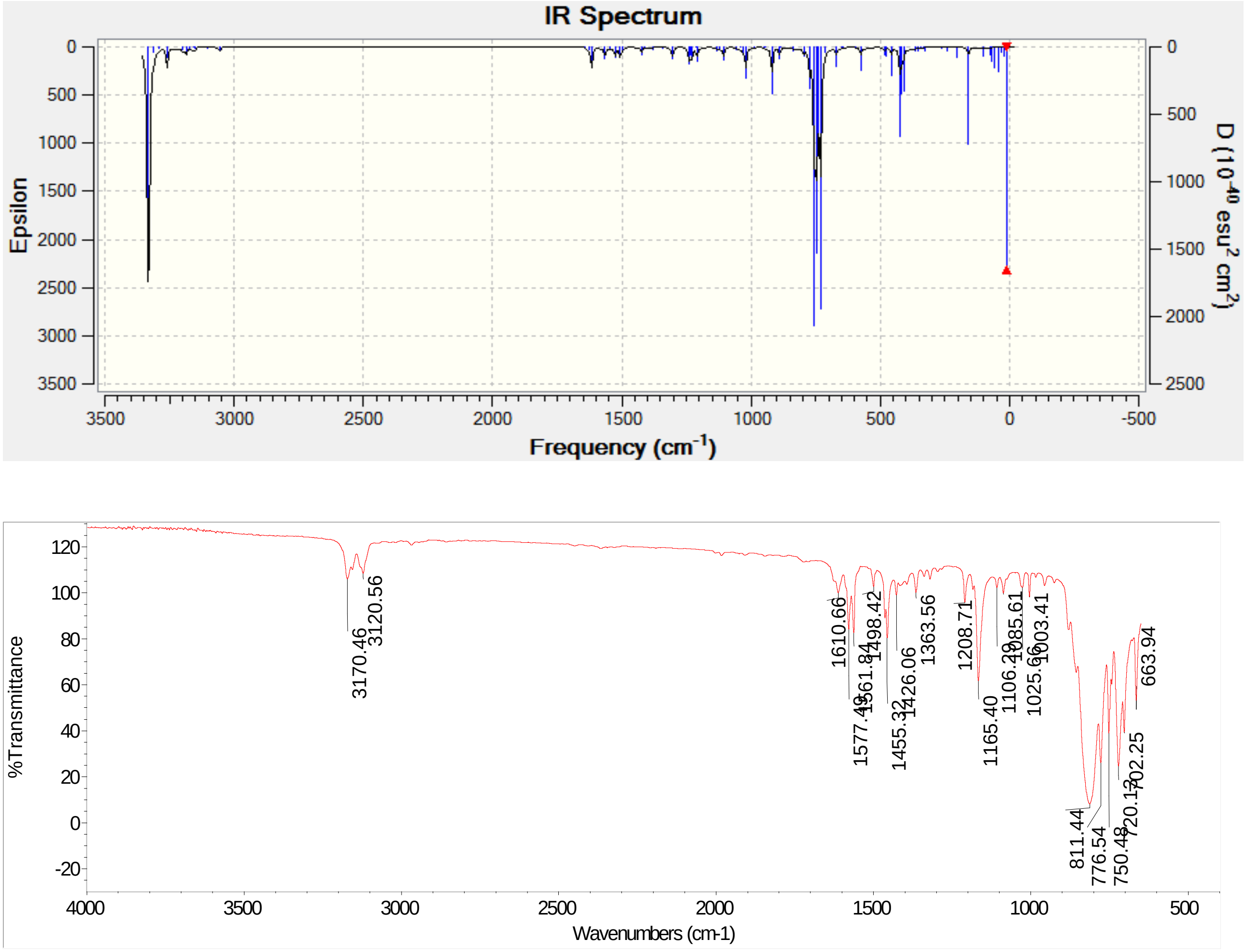


Figure 43: Computational and experimental IR spectra of 1-benzyl-3-methylimidazolium hexafluorophosphate

IR spectrums of ILs obtained from NICOLET iS10 FT-IR spectrometer agree with the IR spectrums obtained from **Gaussian 09W.Gaussian 09W, Revision A.02**, program package (Gaussian Inc.) is a computational software with which **Gauss View 5.0.9** is used for graphical interface which is necessary for input and output analysis. Small deviation occurs which may be due to standard orientation of ILs in computational IR spectra.

Table 39: Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of ILs in solvents.

Solvents	Stretching frequencies (cm^{-1})		
	Pure solvent	Solvent + [BMim]PF_6	Solvent + [BZMim]PF_6
AN	2252.84	2252.98	2252.90
MeOH	3284.54	3319.11	3316.84
DMF	1659.21	1660.05	1659.92
DMA	1732.08	1732.90	1732.83
DMSO	1016.37	1020.43	1018.95

With the help of FT-IR spectroscopy the molecular interaction existing between the solute and the solvent can be studied. The solvents under consideration are highly polar hence they interact through dipole-dipole intermolecular forces and hydrogen bonds. The IR spectra of the pure solvents at first and then ILs + solvents were studied.

In case of acetonitrile (CH_3CN), the interaction is between negatively charged nitrogen atom of acetonitrile and positively charged P atom of $[X]^+$occurs through ion-dipole interaction. When acetonitrile is dimerized, most of the positive charge in $CH_3C^+N^-$ is on the nitrile carbon, *i.e.,* "inside" the molecule, so the acetonitrile tends to associates and forms the antiparallel dimer [Yandagni and Kebarle, 1972]. The existence of antiparallel dimerization in acetonitrile, leads to the formation of less ion-solvent interaction. When ILs ($[X]^+PF_6^-$) is added to AN, small peak shifted occur due to disruption of dipole-dipole interaction present in AN leading to the formation of ion-dipole interaction between $[X]^+$ with C≡N leading to the shift in the C ≡N stretching frequency.

In case of solvent methanol, where the interaction is more intense due to the presence of more negative oxygen atom generating electrostatic and ion-dipole interactions between the negatively charged oxygen atom and the positively charged nitrogen atom of the $[X]^+$ or hydrogen bond interaction of methanol and PF_6^- making stronger interaction with IL. When ILs ($[X]^+$ PF_6^-) is added to MeOH, small peak shifted occur due to H-bonding existing between the MeOH molecule [Pagliai, 2003] and disrupted due to the interaction of $[X]^+$ with the -OH of MeOH leading to the shift in the O-H stretching frequency.

From the structure of formamide there are three possibilities of interaction i.e. with N-H, C=O, C-H bonds. Thus in the solution of ILs + formamide, the formamide strongly interact with the ionic liquid with H-bond/ion-dipole. When ILs ($[X]^+$ PF_6^-) is added to DMF, small shifted occur due to the interaction of $[X]^+$ with the C=O dipole showing ion-dipole interaction which is formed due to the disruption of H-bonding interaction in DMF molecules [Desfrancois, 1998]. In case of DMA, small sharp peak shifted occur due to the addition of Ionic liquid leading to ion-dipole interaction between $[X]^+$ and C=O dipole.

Greatest interaction is seen in DMSO among the chosen solvents, when ILs ($[X]^+$ PF_6^-) is added to DMSO, shifted occur leading to the disruption of weak H-bonding interaction the two DMSO molecules [Shun-Li *et al*., 2010] and formation of ion-dipole interaction between $[X]^+$ and S=O dipole. As the polarity of DMSO is highest it interacts strongly with the ions through ion-dipole interaction leading to strongly ion-solvent interaction resulting in decrease in conductivity values.

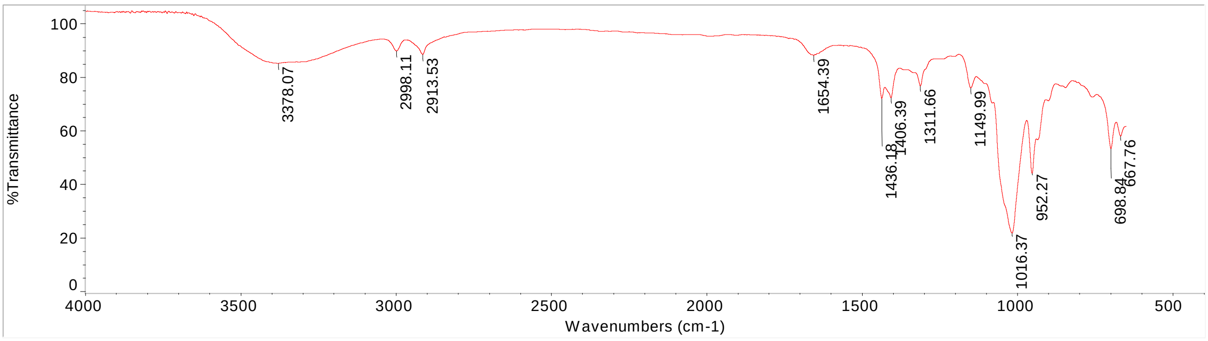


Figure 44: IR spectra of Pure DMSO

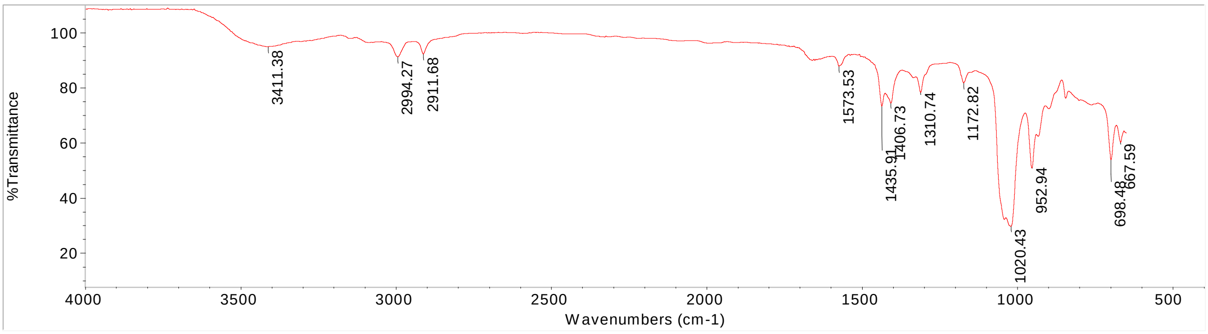


Figure 45: IR spectra of 1-butyl-3-methylimidazolium hexafluorophosphate with DMSO

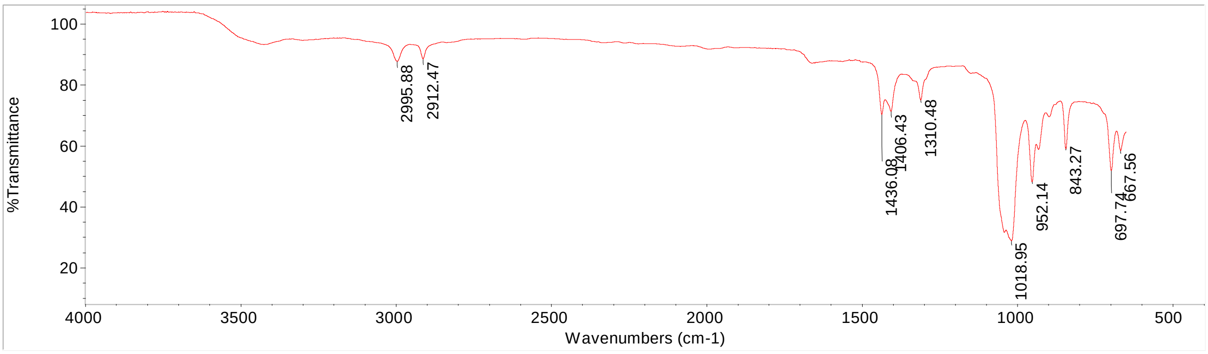


Fig. 46: IR spectra of 1-benzyl-3-methylimidazolium hexafluorophosphate with DMSO

From the above spectra, small peak shifted occurs in each sample (ILs + different solvents), water molecules play a major role in interfering in each solvent from the IR spectra. Since water has a largest dipole moment as compare to the chosen solvents like DMSO, MeOH, DMF, DMA and AN, ion-solvent interactions are very weak and distarted due to the presence of modest amount of dipolar impurities (water molecule are predominant one).

5. CONCLUSIONS

Main findings of our study:

i) The limiting equivalent conductance (Λ_0) increased linearly with the increase in temperature and the association constant K_A values increase with rise in temperature in aqueous medium.

ii) The positive values of ΔS^0 and negative values of ΔH^0 indicate that ion association process will occur spontaneously at all temperatures. The negative value of ΔH^0 indicates that ion association processes are exothermic at all temperatures.

iii) A positive entropy change ΔS^0 is broken when association takes place leading to increase in the degree of disorderliness. Negative value of ΔG^0_{ass} indicates that the ion pair association is favorable.

iv) The association constant K_A values of complexes salts of Cu (II) are determined at different temperatures and are found in the order:

Tetraammine Cu (II) sulfate > tris(ethylenediamine) Cu (II) sulfate

v) The association constant K_A values of different transition metal(II) complexes with same ligands are determined at different temperatures and are found in the order:

N-[(Benzoyl-amino)-thioxomethyl]-cystein Cu (II) chloride > N-[(Benzoyl-amino)-thioxomethyl]-cystein Ni (II) chloride > N-[(Benzoyl-amino)-thioxomethyl]-cystein Co (II) chloride > N-[(Benzoyl-amino)-thioxomethyl]-cystein Mn (II) chloride.

vi) The limiting molar conductances (Λ_0) increase as the temperature increases but decrease as the mass fraction of methanol in the solvent mixtures increases upto $X_{MeOH} = 0.3600(50\%)$

vii) The increase of Walden product indicates the weak solvation of ions which attains a maximum value at X_{MeOH} = 0.3600 (50%) and decrease of Walden product indicates an increase of the hydrophobic solvation with increasing concentration of methanol

viii) The variation of Walden product with X_{MeOH} is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions on the other with the change in composition of the mixed solvents and the temperature of the solution.

ix) The values of E^a increased with increase upto X_{MeOH}=0.3600(50%) and thereafter decreased rapidly. It follows that in water rich region upto X_1=0.3600 (50%), the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond X_1=0.3600 (50%).

x) The limiting molar conductances (Λ_0) follow the order: $Ni^{II}>Mn^{II}$ complexes (for N-[Benzoylamino)-thioxomethyl]-serine Ni (II) chloride and N-[Benzoylamino)-thioxomethyl]-serine Mn (II) chloride/also for N-[Benzoylamino)-thioxomethyl]-histidine Ni (II) chloride and N-[Benzoylamino)-thioxomethyl]-histidine Mn (II) chloride) suggesting that solvation increases the ionic sizes of cations in such a way that the sizes of the solvated cations follows the crystallographic radii of the transition metal ions in aqueous methanol solutions.

xi) The values of K_A follows the order: $Ni^{II}<Mn^{II}$ complexes for all the solvent composition and experimental temperature, i.e., with increasing methanol content the association equilibrium shifts to the right of the above order as a result of decrease in mixture permittivity.

xii) The limiting molar conductance (Λ_0) of 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF$_6$] is highest in CH_3CN (which shows that weakest solvation due to lowest viscosity value leading to increase in mobility of the ions resulting increase in conductance value) and lowest in case of DMSO (which shows that strongest solvation due to highest viscosity value leading to the mobility of the ions decreases resulting decrease in conductance values) among the studied solvents.

xiii) The association constant (K_A) of the ionic liquid is just reverse of the limiting molar conductance, lower in acetonitrile and higher in dimethylsulfoxide, which is in following order: DMSO > CH_3OH > CH_3CN

xiv) The $\Lambda_0\eta_0$ values of aqueous CH_3OH and DMSO increases as the content of methanol and dimethylsulfoxide (w_1) increases in the binary mixtures at different temperatures but in case of acetonitrile, as the content of acetonitrile increase, the $\Lambda_0\eta_0$ decreases due to viscosity behavior of the solvent effect.

xv) The results of molar conductance and the Walden product reflect strong electrostatic ion-solvent interactions. The values of the Gibb’s free energy are all negative entire all over the solutions and the negativity increases from CH_3CN to DMSO. This result indicates the extent of solvation enhanced by the following order: DMSO > CH_3OH > CH_3CN.

xvi) The limiting molar conductances (Λ_0) increases as the temperature increases but decrease as the mass fraction of tetrahydrofuran in the solvent mixtures increase. This trend in limiting molar conductances (Λ_0) can be well described by the viscosity behavior of the solvent media. Thus, the observed trend of the limiting molar conductances (Λ_0) values as: [EMIm]NO_3>[EMIm]CH_3SO_3)>[EMIm]Tos) and the values of $K_{A,C}$ follow: [EMIm]NO_3<[EMIm]CH_3SO_3)< [EMIm]Tos)

xvii) The ionic conductance values, the degree of ionic conductance is higher for $[emim]^+$ ion than for NO_3^-, $CH_3SO_3^-$, Tos^-, suggesting that the anions (NO_3^-, $CH_3SO_3^-$, Tos^-) are responsible for a greater share of ionic association than the common imidazolium cation $[emim]^+$.

xviii) The values of the Gibb's free energy for all ILs are negative at different temperatures and the negativity increases as the mass fraction of tetrahydrofuran increases which leads to the increase in the ion-solvent interaction. This result indicates the extent of solvation enhanced by the following order:

$[EMIm]NO_3$ < $[EMIm]CH_3SO_3$) < [EMIm]Tos)

xix) A-coefficient is negative and very small, shows that the existence of the ion-ion interaction negligible, as compared to the ion-solvent interaction for all the chosen ionic liquids in the studied solvents.

xx) The contribution of diffusion coefficient of the anions (NO_3^-, $CH_3SO_3^-$, Tos^-) is less than the cation $[emim]^+$ in all the studied solvents, which indicates that $[emim]^+$ ions diffuses more through in the studied solvents. The diffusion coefficient decrease as the mass fraction of tetrahydrofuran increases. The mobility of anions (NO_3^-, $CH_3SO_3^-$, and Tos^-) is lower than $[emim]^+$ in the studied solvents, indicating greater share of conductance by $[emim]^+$ ions.

xxi) Lower the diffusivity and mobility higher the ion-solvent interaction or ion-solvation, which is evident from the association constant values, The K_P is larger than K_T, indicate the major portion of the electrolytes (ILs) exists as ion-pairs with a minor portion as triple-ions.

xxii) The trend in the Λ_0 of 1-Butyl-3-methylimidazolium hexafluorophosphate and 1-Benzyl-3-methylimidazolium hexafluorophosphate in different solvents is as follows: AN > MeOH > DMF > DMA > DMSO

xxiii) The values of the Gibb's free energy are all negative entire all over the solutions and the negativity increases from AN to DMSO. This result indicates the extent of solvation enhanced by the following: DMSO > DMA > DMF > MeOH > AN

xxiv) The diffusion coefficient of $[BMIm]^+$ and $[BZMIm]^+$ is more than PF_6^- ion in all the solvents which indicates that $[BMIm]^+$ and $[BZMIm]^+$ ion diffuses more through the solvents. The diffusion coefficient decrease from AN to DMSO for $[BMIm]^+$, $[BZMIm]^+$ and PF_6^- ions, showing greater diffusion of the ions in AN. The ionic mobility value of $[BMIm]^+$ and $[BZMIm]^+$ is higher than PF_6^- in all the cases indicating greater share of conductance by $[BMIm]^+$ and $[BZMIm]^+$.

xxv) IR spectrums of ILs obtained from NICOLET iS10 FT-IR spectrometer agree with the IR spectrums obtained from **Gaussian 09W.Gaussian 09W, Revision A.02**, program package (Gaussian Inc.) is a computational software with which **Gauss View 5.0.9** is used for graphical interface which is necessary for input and output analysis.

xxvi) From the spectra, small shifted occurs in each sample (ILs + different solvents), water molecules play a major role in interfering in each solvent from the IR spectra. Since water has a largest dipole moment as compare to the chosen solvents (AN, MeOH, DMF, DMA and DMSO), ion-solvent interactions are very weak and distarted due to the presence of modest amount of dipolar impurities (water molecule are predominant one).

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Research Journals:

1. **Lalzawnpuia** and N.Mohondas Singh. Ion association and solvation behaviour of Metal (II) chlorides in binary mixtures of methanol + water: A conductance Method. *Asian Journal of Chemistry*, Vol.28, No.4 (2016), 910-916. [IF=0.355]
2. **Lalzawnpuia**and N.Mohondas Singh. Study of N-[(Benzoyl-amino)-thioxomethyl]-cystein Metal (II) chloride Complexes in Aqueous Medium at Different Temperatures. *Der Chemica Sinica*, 2015, 6(4): 104-109. ISSN: 0976-8505. [IF(G)=0.516]
3. **Lalzawnpuia** and N.Mohondas Singh. Physico-chemical Studies of Some Transition Metal (II) Chlorides in Methanol-Water Mixture at different temperatures. *Science and Technology Journal*, Vol. 4(1): 48-55. ISSN: 2321-3388.
4. N.Mohondas Singh, Reuben Lalnuntluanga and **Lalzawnpuia**. Evaluation of association constant and thermodynamic parameters of $[Cu(Me\text{-}AAUH)_2]Cl_2$ complexes in aqueous medium. *Der Chemica Sinica*, 2013, 4(4): 82-86. ISSN: 0976-8505. [IF(G)=0.516]

Conferences/Workshops/Seminar attended

1) Participate in International conference on "Advances in Environmental Chemistry(AEC 2011)" Which is organised by Department of Chemistry, Mizoram University, Aizawl – 796004, Mizoram, India. During 16th – 18th November,2011.
2) Poster presentation in National conference on "Frontiers in Chemical Sciences(NCFCS-2012)" 20 – 21th March, 2012, Organized by Department of Chemistry, Manipur University, Canchipur, Manipur.
3) Participate in National seminar on "Recent Advances in Natural Product Research(RANPR)" Which is organised by Department of Zoology, Pachhunga University College & Department of Pharmacy, Regional institute of Paramedical and Nursing Sciences(RIPANS), Zemabawk at Life Sciences Seminar Hall, Pachhunga University College, Aizawl, India. During 29th November – 1stDecember,2012.
4) Participate in National conference on " Thematic Orientation workshop on Trace element Analysis and Radiological Sciences" Organized by Manipur University, Imphal in collaboration with UGC – DAE Consortium for Scientific Research, Kolkata Centre during March 12 – 14, 2013 at Manipur University, Canchipur, Imphal– 795003.
5) Participate in UGC Sponsored National Seminar on "Advances in Research in Physical Sciences", Organized by Cachar College, Silchar – 788001 in collaboration with Assam College Teachers' Association held at Cachar College, Silchar on 25 & 26thMarch,2013.
6) Participate in "National Workshop on Dynamical Systems'' held from 26-27th November, 2013 at the Department of Mathematics and Computer Science, Mizoram University.

7) Participate in “International Conference cum Exhibition on Drugs Discovery and Development from Natural Resources” organized by the Department of Pharmacy, RIPANS under the sponsorship of the Ministry of Health & Family Welfare, Government of India on 5-6th February, 2014 at Art & Culture Auditorium, Berawtlang, AIzawl.
8) Participate in “One Day State Level Acquaintance Programme”, on March 28, 2014 held at the Department of Physics, Mizoram University, Aizawl, Mizoram.
9) Participate in Science Academies Sponsored Workshop on “Recent Advances in Chemistry” organized by Department of Chemistry, Mizoram University, Aizawl during June 2-4, 2014 at Conference Hall, Guest House, Mizoram University.
10) Presented a paper entitled, “Thermodynamic and Ion Association of Copper Complexes in Aqueous Medium” in Orientation Workshop on Radiation- Its Applications in Chemical Physical, and Life Sciences organized jointly by UGC-DAE Consortium for Scientific Research, Kolkata Centre and Department of Chemistry, Mizoram University, Aizawl during October 29-31, 2014 at Conference Hall, Guest House, Mizoram University.
11) Participate in national Seminar “Frontiers in Chemistry-2015” organized by the Department of Chemistry, University of North Bengal, held at the University of North Bengal during February 17-18, 2015.