Study of Ion Association and Solvation Behaviour of Some Selected Compounds

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CERTIFICATE

This is to certify that the thesis entitled "***Study of Ion Association and Solvation Behaviour of Some Selected Compounds***" submitted to Mizoram University, Aizawl for the award of the degree of Doctor of Philosophy by ***Mrs. Olivia Lalmuanzuali*** **(Regd. No.: MZU/Ph.D./849 of 21/04/2016)**, research scholar in the Department of Chemistry, is the record of original research work carried out under my supervision. She 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 elsewhere for any degree in any other University.

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Declaration of the Candidate
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I, Olivia Lalmuanzuali, hereby declare that the subject matter of this thesis is the record of the 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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CONTENTS

1. INTRODUCTION

Electrolytic solutions is the most important topic in physical chemistry. Through thermodynamic and transport properties, behaviour of the electrolytic solutions can be achieved. The properties of the solvents such as dielectric constant or viscosity are useful for analysing the molecular interactions within the electrolytic solution. When the electrostatic interactions between two oppositely charge ions become sufficiently large for the two ions to move around as one entity, therefore ion pairing is form. The nature, charge and size of the ions, the characteristics of the solvent and the temperature mostly influenced the extent of association into ion pairs. For separating non-interacting species the ion is required to stay connected more than the time required for Brownian motion. [Lacour and Moraleda, 2009]. Therefore, only strict electrostatic interactions should take place between the ions. Coulombic attraction should be the only interaction that take place before the association of the charges-charges and remained constant in the interaction [Mac Innes, 1961].

Thermodynamic properties are classified into two classes, where extensive property depends on the size (or extent) of the system under consideration and intensive property exist at a point in space. Specifically, the interaction occur between solute-solute, solute-solvent and solvent-solvent species. Among the mixed components this properties provide important information about the nature and strength of intermolecular forces. But the real structure of the solvent molecule is not known. Since the solute molecules are already modified on addition of an ion or solute modifies the solvent structure. The behaviour of solvation and association of ions can be understood through the study of the transport properties of electrolytes in different solvent media. Various chemical processes, electrochemical processes, supercritical technology, production of energy sources, hydrometallurgical processes etc are useful for studying thermodynamic and transport properties of electrolyte solutions. [Ashwini, Rajesh and Snehal 1996]. Electrolysis and Electromotive chemistry are the two classes of electrochemistry. The conversion of electrical energy into chemical energy is term as electrolysis, whereas electromotive energy is defined as the conversion of chemical energy into electrical energy. Ionic electrochemistry are of four types i.e ion-solvent interactions, ion-ion interactions, ion transport in solution, and ionic liquids. Through the knowledge of physical chemistry of ionic solutions, ions connect actively with water as they approach the solutions. [Goodisman, 1987].

1.1. DEFINATION AND NATURE OF ION PAIRS AND TRIPLE IONS

Ion association and their interactions within a short range can be explained through Debye-Huckel theory in 1926 by Bjerrum. The neutral species formed by electrostatic attraction between oppositely charged ions in solution is termed as ion-pair [Quinanar-Guerrero *et al.,* 1997; Irwin *et al.,* 1969]. Ion-pair formation depends on the ionic size (radius of ions), solvent (dielectric constant), and temperature [Fisher, 1967]. The most important factors for the extent of association into ion pairs are the nature, charges and sizes of the ions, the characteristics of the solvent and the temperature. For separating non-interacting species the ion is required to stay connected more than the time required for Brownian motion.

Ion pairs formed by association of cations and anions can be best described from the dilute salt solutions in polar solvents such as propanone. As the permittivity of the solvent decreases, triple ion and quadruole ion are formed. [Hammet 1970; Grunwald 1997]. Two charged spheres placed symmetrically on each side of an oppositely charged sphere, with all the three being of the same size, having energy 50 % greater than that of two oppositely charged spheres are the result of simple electrostatic theory. Consequently, there is a belief that in low dielectric constant triple ion formation is formed. As the interionic effects is neglected, calculation is more simple in solvents of low dielectric constant, whereas in higher dielectric constant, the computation is not straightforward since the interionic forces are not neglible anymore. Fuoss and Kraus were able to carry the argument one stage further: by treating the approach of a the negative ion combines with the positive ion through coulomb forces only, there is a critical distance and once the ion is within this, triple ion formation is formed [Robinson *et al.* 1959]. Ion pairs and triple ions behave quite differently through the electrical conductance value. Triple ion are charged and therefore respond to the external field through the conductance contribution whereas uncharged ion-pair do not respond. The equilibrium between free ions and ion pairs is responsible for the extent of ion-pair formation and the formation of the extent of triple ion occurs between ion pairs and triple ions. Therefore, as the formation of ion-pair and triple-ion increases, greater is the stoichiometric concentration. The gibbs energies of transfer from aqueous solution into low permittivity solvents are generally positive for polar complexes and negative for non-polar species because polar species are not readily amenable to formation in low ε solvents. The formation of triple ion are at low permittivity, hence it is linear (i.e., are formed from monatomic or spherical species) as this is their most energetically stable configuration. And it will have a zero dipole moment, due to their opposite direction of the two dipoles. Consequently, the decrease in the polarization of the solution leading to an observable decrease in the dielectric permittivity explain the importance of triple-ion concentration .[Fuoss-Kraus, 1933].

1.2. DIFFERENT GROUPS OF INTERACTIONS

Three groups of interactions in the solution process are:

i). Solvent – solvent interactions

ii). Ion – ion interactions

iii). Ion – solvent interactions

The physico-chemical techniques regarding the factors associated with the ion-solvent interactions can be used qualitatively and quantitatively for understanding the thermodynamic properties such as changes of free energy, enthalpy and entropy. Theoretically, ion-ion interaction in dilute electrolytic solutions are well understood, and more stronger than ion-solvent interactions. Complete understanding of the phenomena will become a reality only when the ion-ion, ion-solvent and solvent-solvent interactions are explained, solution chemistry is completely understood. Dielectric constants, organic group types, acid base properties or association through hydrogen bonding, [Franks and Wen, 1973], donor-acceptor properties [Gutmann, 1976], hard and soft acid-base principles [Pearson, 1973] are responsible for the classification of organic solvents. The thermodynamic, transport and acoustic properties of electrolytes and non-electrolytes determined that the different solvent systems show a wide divergence of properties. The Stokes radius of the solvation ion is considerably greater than the predicted bare ion as is evidence from the presence of solvation shell. Till its solvation shell contacts the partner an ion possessing a tight solvation shell approach a counter-ion without any delay [Murray and Yeager, 1973]. Subsequently, a tight contact ion-pair is formed when the associate maintains its structure as a loose, solvent-separated ion-pair, or the solvent molecules separating the partners are squeezed out. It is understood that solvent-separated ion-pairs take place where free ions acquire tight solvation shells. Despite the presence of a solvation shell, Bjerrum's original concept of a pair of solvated ions formed by coulombic attraction in a solvent of a low dielectric constant, remain accepted.[Braunstein, 1971].

1.3. CONCEPT OF ION PAIR AND TRIPLE ION FORMATION

Most electronic states of neutral molecules appear at high energies and are quite strongly bound which is just the opposite to ion pair states. The concept of ion pair into the evaluation of the inter-ionic force in electrolytic solution and its tendency of ions to associate into ion pairs was first introduced by Bjerrum in 1926 [Bjerrum, 1926] and it depends in connection with electrostatic force and thermal energy. The association of cations and anions in solution is termed as ion pair. 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, therefore ion pair exist in this situation [Kortum, 1965]. For separating non-interacting species the ion is required to stay connected more than the time required for Brownian motion [Lacour and Moraleda, 2009].

For interpreting the behavior of ions in dilute solutions the first inter-ionic theory of electrolytic solution by Debye-Huckel was used [Debye and Huckel, 1923]. There are two effects when it is theoretically calculated for the decreased of ionic mobility with increasing concentration At first, an ion approach through the effect of an applied electric field, and disturb the surrounding ionic atmosphere and used as an opposing electric force. Next, the motion of the central ion got retarded due to the counter-current of solvent produced by the ionic atmosphere. Ions is the most random thermal motion and are in random positions as assumed by Debye-Huckel model. The ion of the pair together formed an ionic dipole on which the net charge is zero. The extents of association should not be zero and it decreases as the dielectric constant is increased therefore, anion-cation contacts will occur because a non-zero chance always occur. Using Shedlovsky equation, conductance of 1:1 electrolytes was largely studied [Das *et al*., 1996]. The chemical nature of the ions are not responsible for holding the cluster of ions. From this understanding, the associated species is an ion pair when the electrolytes of the same charge and similar size will have equilibrium constants of similar magnitude [Azzari and Kraus, 1952] as given in some salts like 2:2 sulphates, and for some cations of similar size which associated with Cl^- (aq) or I^- (aq). The electrostatic forces hold the ions together as single unit [Marcus and Hefter, 2006]. To overcome the tendency for normal thermal motion that causes the ions to move around as separate particles each with its own translational degrees of freedom, coulombic forces contribute a great amount of togetherness on the unit. Therefore, the three factors i.e the charges on the ions, the sizes of the ions and the relative permittivity of the solvent in the vicinity of the ion are responsible for physical nature of coulombic forces [Shehata and Add. El-Bary, 1996].

During the last fifty years, the study of conductance measurements were studied intensely both theoretically and experimentally. Our main focus will be on aqueous, non-aqueous, pure and mixed solvents. In deriving the Kohlrausch’s equation, Onsager made a successful application of the Debye-Huckel theory [Onsager, 1927]:

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

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

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

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

The short range interactions and the size of the ions in solution has no relation with the above equation. Ions are termed as rigid charged spheres within an electrostatic and hydrodynamic continuum [Fuoss, 1978]. Later the solution for the difficulty of electrolytic conductance accounting for both long-range and short-range interactions were studied by Pitts, Fuoss and Onsager [Fouss and Onsager, 1955] . The Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned [Pitts and Tabor, 1969] and it is considerably different from the Λ_0 values obtained for the conductance at infinite dilution using Fuoss-Onsager theory [Fouss, 1978]. Fuoss and Hsia modified the original F.O. equation [Fuoss and Hsia, 1967] by recalculating the relaxation field, absorbing important terms that are already left out.

The equation are as follow:

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

Where G (κa) is a complicated function of the variable, simple form:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1c - J_2\sqrt[3]{c} \qquad \ldots (6)$$

is mostly used for obtaining the experimental results

In spite of that the equations cannot fit in the experimental data. These are studied from Fernandez-Prini [Fernandez-Prini, 1973]. Later the equation (5) was corrected by Fuoss and Accascina [Fuoss and Accascina, 1959]. They took into consideration the change in the viscosity of the solutions and the validity of Walden's rule were taken into consideration. Therefore Λ is equal to:

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

Yet, J_2 leads to a systematic deviation of the experimental data from the theoretical equations. It is notice that Pitt's equation is more applicable in experimental data (aqueous solutions) [Fernandez *et al.*, 1980]

To determine the values of the ion-pair association constant, K_A conductance measurements is applied:

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

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

and

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

The constant, K_A and Λ_0 has been verified using Fuoss-Kraus equation [Fouss and Kraus, 1933] or Shedlovsky's equation [Shedlovsky and Franklin, 1938] for understanding strong associated electrolytes,

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

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

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

The straight line is obtained when we plot $T(Z)/\Lambda$ against $c\,\gamma_{\pm}^{2}\Lambda/T(Z)$, where $1/\Lambda_0$ are intercept and $K_A/(\Lambda_0)^2$ for its slope. In the determination of the values of Λ_0 and K_A there is a unreliability from equation (10) and K_A is large,

The Fuoss-Hsia for associated electrolytes [Fuoss and Hsia, 1967] equation is equal to:

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

Juctice changed the equation [Justice *et al.*, 1968]. In dilute solutions the conductance of symmetrical electrolytes is given as:

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

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

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

After setting a least square treatment gives the conductance parameters:

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

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

To determine the distance of closest approach, a^0, of two free ions to form an ion-pair, one can use two methods as studied through the experimental values of the association constant K_A, Fuoss proposed the equation [Fuoss and Accascina, 1959]

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

Sometimes, the calculation of a^0 is not possible as the magnitude of K_A was too small. Bjerrum contribution made the distance parameter possible for calculation [Bjerrum, 1926]

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

Except for solvation where solvated ion can be approximated by a hard sphere model, specific short-range interactions are neglected by the equations. Douheret used this method successfully.[Tissier and Douheret, 1978]

As the dielectric constant falls, conductance-concentration curves of electrolytes in solvents of dielectric constant below 15 appear at lower concentrations. The formation of triple ions + - + and - + - and even of higher aggregates are explained through Fuoss Kraus theory. Ion pairing results when in dilute solutions, simple cations and anions are present and the molar conductance decreases with rising concentration. The molar conductance rises as the triple ions are produced at higher concentrations. The conductivity data have been analyzed by the Fuoss-Krauss theory for the triple ion [Fuoss-Krauss, 1933]

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

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

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

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

$\Lambda = \Lambda_0 - S(c\Lambda/\Lambda_0)^{1/2}$, where, β' is Debye-Hückel activity coefficient S is the limiting Onsager slope coefficient. The two possible triple ions of the limiting equivalent conductivities are . $\Lambda_0\ and\ \Lambda_0^T$. From equation (1), we neglect Λ/Λ_0 = 1, and interionic attraction g(c) = 1 we have,

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

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

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

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

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

1.4. SOLVATION CONCEPTS

The process of surrounding solute with solvent is termed as solvation (dissolution). Solvation includes taking out the concentration gradient and equally scattering the ion inside the solvent. In the case of some transition metal ions, ionic solvation can lead to rather stable complexes. But with some aqueous electrolytes, more ill-defined structural effects are formed. The solvation of ions influenced the thermodynamic properties and transport properties, and are applicable for understanding ionic solvation.

The chemical potential of the species in solution are understood through the thermodynamic properties and entropies, enthalpies, heat capacities, volumes are dependent on temperature and pressure.

The forces acting between molecules, enthalpies, the statistical configuration of the solvent near the ions, volumes, the compactness of the spatial arrangement of the solvent molecules are described under free energies. Mostly strong interactions (e.q. electrostatic) between molecules will relate to free energies, and heat capacities have more impact on interactions that are temperature dependence (e.q. hydrogen-bond distribution). But in strong charge - dipole interactions of temperature independent, the property is lost. All the thermodynamic properties are required to investigate so as to understand the complete ideas of interactions. The effective size of moving particle solution can be understand through models. The size of the ions increases and the structure of the solvents are modified because the properties are sensitive to strong ion-solvent interactions and also to modification. Generally, at low concentrations reliable infinite dilution values are obtained through properties such as conductance.

It is important to understand the transition metal ions, since it is related to electrochemical systems. The main feature of solvation can be understood through systematic coverage of properties for family of typical ions and solvents.

In conclusion, in strong ion-solvent interaction the solvent is continuum and is hardly valid because the size of the solvent molecules are similar to those of solute molecules.

Therefore it is preferable to consider the solvent molecules as sphere indicated by their polarizability, dipole and quadruple moment.

1.5. THE LIMITING MOBILITIES OF IONS

When electricity is transfered fundamentally through electrolytes, and that the carriers are ions, it is found that the metallic conduction are smaller in terms of dimentions and masses. The Brownian motion of the liquid, in the ions are believed to have randomly-directed instantaneous velocities of the order of 10^4 cm sec^{-1}, although they are characterize to have an extremely short mean free path in the liquid state. The Brownian movement is completely unsystematic in the absence of an external field and therefore does not lead to a drift of ions in any one direction. The Brownian movement in a particular direction has been influenced by the presence of an electrical field (conductance), or of a concentration-gradient,(diffusion). A very small perturbation of the random ionic motions represents the average velocity of the ions and the direction of the field is of the order of 10^{-3} to 10^{-4} cm sec-1 in the field of 1V/ cm. Under an electric field of ordinary intensity the actual path of an ion is thus extremely erratic, giving a similarity of a billiard-ball sinking in water. The Brownian motion needs to be considered only in regard to its effect on the interionic forces. At least for low concentrations, experimental data on conductivity are fortunately extremely plentiful and of high accuracy. Conductivity measurements in non-aqueous solutions and in mixed solvents are far more easily made than those of activities, and provide a better knowledge of the behaviour of electrolytes. Accurate conductivity measurements are possible at concentrations down to about 0.00003 M but the electromotive forces of cells usually becomes unreliable at concentrations below about 0.001 M. At low concentrations the equivalent conductivity of strong electrolytes are in linear function of the square root of concentration and decreases as the concentration increases. The limiting equivalent conductivity Λ^{O} are obtained from the interpolation to zero concentration , at very low concentrations it is given as:

$$\Lambda = \Lambda^{O} - A\sqrt{c}$$

The theory of electrolytic conduction is qualified completely if it is able to (a)give the value of Λ^{O} through dimensions, charges and other properties of the ions and the solvent molecules, (b) give the value of the constant A in equation, (c) keep qualitatively at higher concentrations for deviations from the equation . Out of these problems, the second is solved, the third position has greatly improved and the first is far away from the solution [Robinson et. al, 2002].

1.6. THE LIMITING EQUIVALENT CONDUCTANCE AND WALDEN PRODUCT

In dilute solutions equivalent conductance Λ are measured precisely [Erdey-Grey., 1974]. Through infinite dilution value of Λo and K_A, association constant derived from the concentration dependence of Λo the knowledge of ion-solvent interactions can be obtained. By studying Bierrum equation we know that K_A is related to the distance of closest approach of the ion pair [Conway et al., 1983]. Bjerrum predicted that $\ln K_A$ is not a simple function of I/D as been studied by Kay and his co-workers [Kay et al., 1976] Simple association does not survive for vulnerability of $\ln K_A$ on ionic size. The K_A values increase, remain constant or decrease with ionic size in dependence with solvent type. Also K_A deviates significantly with solvent compositions in isodielectric mixtures.

Due to the measurement of these parameters in solute-solute interactions and a better chance of obtaining solvation information from Λo, the equilibrium constants fail to show unambiguous information of ion-solvent interactions. Through Stoke’s equation, the simplest way of relating $\lambda_0^{\pm}$ to the effective ionic size in solution $\gamma^{\pm}$ is obtained:

$$\lambda_o^{\pm} = \frac{|Z|\epsilon F}{6\pi\eta r^{\pm}} \qquad .....(37)$$

where Є = the electronic charge,

F = the Faraday

η = the viscosity of the solvent

$\gamma^{\pm}$ = interionic distance

$\lambda_0^{\pm}$ = ionic conductance

The viscous flow of water viz., 15.88kJ at 25^{0}C is nearly similar to the electrolyte conductance of activation energy [Glasstone, 1942]. The viscosity of the medium and the viscosity of water at a series of temperatures must be approximately constant since it has the possibility of associated with the ionic conductance. Usually over a range of temperature, the product of the ionic conductance, the viscosity in aqueous and non-aqueous media are almost constant.

Walden's rule is expressed as: $\Lambda_0\eta_0 \approx$ constant for a given electrolyte in solvent. Walden prominently discuss that at infinite dilution, the effect of the equivalent conductance Λ and the viscosity of the solvent were roughly constant and independent of the nature of the solvent. The Walden product $\Lambda_0\eta_0$. should be approximately constant for a given ion in all solvents because Λ_0 is the sum of the conductance of the constituent ions. The effective radius of the ions were the same in the different media therefore by Stock's law the values of $\Lambda_0\eta_0$ is constant. Since there are reasons for believing that most ions are solvated in solution, The dimension of the moving unit will undoubtedly vary to some extent and exact constancy of $\Lambda_0\eta_0$ cannot be expected because of the reasons that most ions are believed to be solvated in solution. The fundamental properties of the solvent as well as on the effective size of the ion are dependence on the value of $\Lambda_0\eta_0$ in small ions. On the other side the Walden product $\Lambda_0\eta_0$ are nearly constant with the large ions such as tetraethyl ammonium and picrate ions.

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

The concept of ion pairs and triple ion is useless when the concentration of ions is too high [Szwarc, 1972]. For instance, in a fused sodium chloride it is not possible to characterize ion-pairs and free ions. It is not possible and unprofitable to assign two oppositely charged ions to a lasting pair although each sodium ion has some chloride ions as its nearest neighbours and vice-versa. It is best understood through distribution function.

1.8. SCOPE OF THE STUDY

The neutral species formed by electrostatic interaction between oppositely charged ions in solution and that ion-pair formation depend on the ions size (radius of ions) solvent (dielectric constant) and temperature is termed as ion-pair by Bjerrum (1926). Through various methods i.e Conductance studies, U-V visible spectroscopy, IR Spectrophotometry, partition, distribution, or solvent extraction the formation of ion-pairs can be studied. The formation of ion-pair was originally studied in physical chemistry; it was later taken in colloidal chemistry, analytical chemistry, and the pharmaceutical sciences. From the numerous methods given by Higuchi et al. ions of the opposite charge are added to the aqueous phases, forming an ion-pairing between the solute ion and pairing ion by extracting ionized solutes into organic phases. The complex formed are neutral and poorly hydrated thus can be easily transferred to the organic phases. In the pharmaceutical and analytical sciences the ion-pair extraction method is widely used. The wide range temperature dependence of ion pair and triple ion formation of transition metal complexes and ionic liquids in pure and mixed solvents of comparative studies are being reported. It is also explored that the ion solvent interactions and in mixed solvents an overall view of the main aspects of solvation are given by the conductance measurements in pure solvents.

Consequently, by studying the physicochemical study on the transport properties of electrolytes in different solvent media the solvation and association behaviour of ions can be understood. In deciding the electrical conductivity in solvents, the concentration of the electrolyte and also the viscosity of the solvent play a key role. The solvation of the ions is strongly dependent on the formation of on pairs; hence the transfer of ion pairs between solvents of different solvation abilities are studied. In most non-aqueous system as well as for aqueous solutions of electrolytes at high temperature and pressure multivalent electrolytes at any temperature, ionic association is important for electrolytes. By studying limiting molar conductance (Λ_0), limiting molar conductance of triple ion (Λ_0T), at infinite dilution in different solutions and ion pair constant (K_A or K_P) and triple ion constant (K_T) at different temperatures, the work will concentrated on the knowledge of ion association and triple ion formation. Thermodynamics parameters including the activation energy has been assessed for understanding the association phenomena and that is farther assisted by spectroscopic methods i.e IR spectroscopy and for understanding the temperature effect on Λ_0,Λ_0T, K_A and K_T to obtain the Walden products ($\Lambda_0\eta_0$) for evaluating the effect of solvents composition. By applying K_A or K_P and K_T the ion pair and triple ion concentration C_P and C_T, as well as ion pair fraction (α) and triple ion fraction (αT) respectively, at the minimum molar concentration of the salt solution were also calculated.

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

Sl.No.	Salt	Solvent
1.	Bis glycinato Cu(II) Monohydrate and Cu(II) Acetate	Water
2.	[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) and [Ni (HL)(dien)](ClO_4)$_2$(H_2O) [0-100%]	Dimethylsulfoxide+ Water
3.	Pentaamminefluorocobalt(II)fluoride and Pentaamminefluoronickel (II) fluoride [0-100%]	Methanol + Water
4.	Pentaamminechloronickel (II) perchlorate [0-100%]	Methanol + Water
5.	Lithium salts (LiCl and $LiNO_3$) [100%]	Methylamine, Dichloromethane and 1,4-dioxolane
6.	Cetyl Trimethylammonium bromide ($C_{19}H_{42}NBr$)[100%]	O-Toluidine,O-Xylene and1,4 – Dioxane
7.	{1-butyl-3-methylimidazolium hexafluorophosphate $BMimPF_6$} and {1-butyl-4-methylpyridinium hexafluorophosphate $4BMimPPF_6$}[100%]	Dichloromethane,1,3-dioxolane,O-Toluidine and O-Xylene

2. REVIEW

2.1. CONDUCTOMETRIC METHOD

For studying the electrolytic solutions, conductometric measurement have been used in various organic solvents. Through conductance technique ion pairing between the metal ions and ligands are usually investigated [Bakr and Mohamed, 1999; Ue and Mori, 1995; Bakr, 2001]. Behaviour of the conductance measurement of electrolytes in mixed solvent systems are influenced because of the density, viscosity, dielectric constant of the medium, ion solvent interactions and solvent-solvent interactions. On solvation ion-solvent interactions alters the ion it. Many of the properties of electrolyte solutions [Marcus, 1985; Krestov, *et al.,*1994; Popovych and Tomkins, 1981] including their redox potential, complexation and kinetic behaviour are influenced through the solvation of dissolved ions. Ion-solvent, solvent-solvent interactions and preferential solvation of an ion are understood by studying the conductance in binary solvent mixtures [Rajasekhar Reddy, 1987]. Ion-ion and ion-solvent interactions can be better studied by enabling the variation of properties such as dielectric constant or viscosity in mixed solvents. Besides from concentration-dependence of the electrolyte conductivity different quantities strongly influenced by solvent properties can be derived. Therefore the used of high energy batteries [Aurbach, 1999] and for understanding organic reaction mechanisms are possible through a number of conductometric [Janx and Tomkins, 1973] and related studies of different electrolytes in non-aqueous solvents, specially mixed organic solvents [Krom, Petty, Streitwieser, 1993]. The mode of solvation of its ions on the nature of the solvent or solvent mixtures is responsible in the ionic association of electrolytes in solution[Das et al., 2002; Guha et al., 2003; Das et al., 2003; Roy et al., 1993]. In the determination of the extent of ion association and the solvent-solvent interactions, solvent properties such as viscosity and the relative permittivity have been taken into consideration. Hence for examining the nature and magnitude of ion-ion and ion-solvent interactions 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; Chen and Hozo, 1997; Parvatalu and Srivastava, 2003]. By studying the thermodynamic and transport properties behavior of the electrolytic solutions can be acquired. On widening the properties of the solvents such as dielectric constant or viscosity the molecular interactions within the electrolytic solution can be better studied. For thermodynamics of these processes to be better understood conductivity measurements should cover a wider temperature range. The information about electrolytes in different solvents can be obtained in the presence of relative simplicity and versatility by carrying the measurements of the conductivity of electrolyte solutions to a very high precision.

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

Inspite of the general character of H_2O in many non-aqueous solutions, and due to the ion-water interactions that determined the particular nature of the ions and solvent several may have specific result. Therefore the conductance in dimethylformamide increase with the H_2O satisfy in difference to the decrease found for dissociated salts in $AgNO_3$ and $(CH_3)_2Tl$. The conductance of perchloric acid decreases significantly upon addition of 0.3% water in methanol and ethanol [Goldenberg and Amis, 1962]. This was alloted to the change in the proton transport mechanism has been assigned.

The salts of the two first cations are dissociated for a period of time as Tl(I) salts are associated similarly to KSCN, this is defined through the conductance data of Cu(I), Ag(I) and Tl(I) salts in AN by Yeager and Kratochvil [Yeager and Kratochvil, 1969; Yeager and

Kratochvil, 1970] . The Cu(I) is a very large solvodynamic unit and is in the form $Cu(AN)^{4+}$ as observed from the limiting molar conductance values Λ_0. Through electrostatic interactions the association of $AgNO_3$ and $AgClO_4$ in AC and Cyclohexanone [Griffiths et al., 1958] are fairly considered, and if it is purely electrostatic $AgNO_3$ in benzonitrile, $AgNO_3$ and MeTl(I) in DMF would require a very small ɑ values (1.6, 1.3 and 1.1Å) .

Ion-solvent interactions of copper (ll) Perchlorate in both water-DMSO and water-Pyridine were studied by Steekumar, Rajendran and Kalidas [Steekumar et al., 1992] through conductance method. Therefore on addition of pyridine upto 20 wt% the Λo (equivalent conductance) of copper (ll) Perchlorate decreases sharply and gradually keep on decreasing upto 60 wt% pyridine and increases at the end. On addition of DSMO mixtures the Λo also decreases continuously. Also with the addition of DMSO in water-DMSO mixtures, the Walden product of copper (II) perchlorate decreases continuously. But for pyridine it is different, it decreases sharply at the beginning and later it slightly increase and with the addition of pyridine finally it decreases. The formation of water-DMSO complexes of solvent-solvent interaction compete with the ion solvent interactions and therefore complex behaviour was formed.

The conductance and ion association of bis (1-amidino-O-methylurea copper (II) acetate in aqueous medium at 5-40^oC were studied by Rajmuhon and Bag [Rajmuhon and Bag, 2001] using Shedlovsky equation. It is seen that the anion (rCH3COO-) is more or less constant with the variation of temperature as observed from the Stoke's radius. The cations become more hydrated as the temperature rises because the Stoke’s radii for the complex cations increase with temperature. Due to their polyatomic hydration the ions is most nearly constant for those of large size in walden product ($\Lambda o \eta o$). The positive value of ΔS^o and the negative value of ΔH^o indicates that the ion association process will occur spontaneously and exothermic in nature. Through the knowledge of variation of ΔG^o with temperature, at low temperature the ion association process was favoured. 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 have been studied by Singh, Rajmuhon and Manihar [Singh et al., 1995]. In order to understand the nature of ion-association the thermodynamic functions can be estimated from the association constant values at different temperatures.By using Onsagar method of extrapolation the limiting equivalent conductivities (Λo) of the complexes can be determined. From Bjerrum equation, Stokes' law and Dennison-Ramsey theory the sizes of ion pairs were evaluated. The order of the observed values of association constants (K_A) for bis 1-amidino-Omethylurea copper(ll) and bis 1 -amidino-O-ethylurea copper(II) chloride, bromide, iodide and nitrate are given as:

(i){[Cu(AMUH)2]Cl]+. > {[Cu(AMUH)2]Br] > {[Cu(AMUH)2]NO3]+ >{[Cu(AMUH)2]I]+

(ii){[Cu(AEUH)2Cl]+ > {[Cu(AEUH)2]Br]+ > {[Cu(AEUH)2]NO3]+ >{[Cu(AEUH)2]I]+

(iii){[Cu(AMUH)2]X]+ >{ [Cu(AEUH)2]X]+

For NaCl solutions in methanol, Butler, Schiff and Gordon [Butler et al., 1951] observed that by using the conductance measurement the relative decrease of Λ for 1% of added water varies with the concentration of the salt, since the concentration of salt is zero it is extrapolated precisely the decrease of the fluidity of methanol containing 1% of water. When water was added to $NaOCH_3O$ in methanol Barthel and Schwitzgebel [Barthel and Schwitzgebel, 1967] observed the same reaction. On addition of water in nitromethane [Unni et al., 1963], dimethylformamide [Prue and Sherrington, 1961], and sulpholane [Fernandez-Prini and Prue, 1960] solutions same reactions have been observed. The viscosity change introduced in the media by the addition of water can be used for understanding the change in conductance (non-specific nature). This is justified by some workers of hydrates instead of the anhydrous salts, Firstly, in more easily soluble non-aqueous solvents [Dawson et al., 1963; Parker, 1962]. D’Aprano and Fuoss [D’Aprano and Fuoss, 1963] large increase in the conductance of picric acid dissolved in acetonitrile as water was added (Λ increases ten times for 0.02% of water), since hydrates are more preferred than anhydrous salts. Due to the formation of ammonium salt (highly organized) ammonia, which is a possible degradation in acetonitrile increases the conductance of picric acid. The presence of acetates [Dawson et al., 1962] a common impurity in the solvent was the reason for abnormal variation of conductance with concentration for transition metal and aluminium salts in N-methylacetamide.

Through hydrogen bonds solvation of the anions was suggested because the mobilities and association constants of tetraalkylammonium(R_4N) halides are larger for iodides. Mostly through a minimum for R=Pr, R_4NI are more associated in ROH than in dipolar aprotic solvents. The effect is especially marked for bulky cations as been observed from the two reactions. A two step association process similar to the equilibria have been requested by Kay, Evans and coworkers [Kay et al., 1965; Evan and Gardam, 1968] for interpreting these solutions.

The protons have no excess flexibility as indicated by the conductance measurements of acids in NMA [Dawson et al., 1957] and F [Dawson et al., 1954]. The same behavior for R_4N salts in NMA was revealed by patially substituted ammonium salts [Dawson et al., 1956]. Salts were found to be dissociated in formic acid (1:1) [Wehman and Popov, 1968]. Due to the acidic nature of the solvent HCL is associated (K_A=90 mol-1l), and a proton-jump transport mechanism have been suggested through excess mobility of formate and H+ ions. By using conductance measurement the association of weak bases in acetic acid was studied

[Shkodin and Sadovnichaya, 1962]. Because of the solvent impurities Brewster, Schmid and Schaap [Brewster et al., 1959] observed an anomalous conductances in ethanolamine [Briscoe and Dirkse, 1940]. It is indicated by Λ_0 that small ions are more solvated in a solvent, and it is slightly associated in halides and more associated in nitrates, nitrites and thiocyanates. Br^- ion has a lower conductance than I^- ion and R_4NI are more associated than KI [Harstein and Windwer, 1969; Fowles and McGregor, 1964] in ethylene and propylene diamines. The change in relative permittivity ε_r has been used for considering the difference of K_A in both solvents.

Triple ion formation is formed at low dielectric constant (ε_r <12), because electrostatic ionic interactions are very large. For R_4N-p-toluenesulphonated in triaryl phosphides [French and Tomlinson, 1961], for $MeEt_3NI$ in CH_2Cl_2 [Beard and Plesch, 1964] for LiCl and bivalent chlorides in tetrahydrofuran (THF) [Strohmeier et al., 1961], and the conductance has been observed to pass through a minimum with concentration, resulting in triple ion formation.

2.3. SOLVENT MIXTURES

Almost the binary solvents of MeOH, AN and NM are constant ε_r, and are dissociated in i-Am_3BuN^+ [Coplan and Fuoss, 1964] salts. Specific ion-solvent interactions are suggested by the variation of the walden product with solvent composition. Also 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) are observed by D’Aprano and Fuoss [D’Aprano and Fuoss, 1963]. When PNA is present in the solvent mixture K_A and the Walden products of the salts are reduced, and due to anion-PNA interactions which are stronger for the bromide the effect is being largest for Br^- and least for BPh_4^-. HPic is more strongly interact with anions than PNA [D'Aprano and Fuoss, 1969]. The interactions are due to primarily on the facility with which it hydrogen bonds to the anions and not on the dipole moment of the added substance [Treiner et al., 1966].

Inspite of the small and monotonous change in ε_r with solvent composition, $CsClO_4$ and $KClO_4$ has the medium of fully dissociated 60% of AN in MeOH-AN mixtures. [Conti and Pistoia, 1968]. For in binary mixtures [Sadek and Fuoss, 1959], the association of binary mixtures for Bu_4NBr in NB, EtOH and MeOH with CCl_4 is greater studied through the electrostatic model. The order of the excess association decreases as NB>EtOH>MeOH and symphatize with the solvating power of these solvents. Anomalies are being observed in the association of Bu_4NBr with NB-MeOH mixtures of constant relative permittivity [Kay and Evans, 1964; Hyne, 1963]. When Ag^+ is added between AC and cycloalkenes specific interactions are observed [Griffiths and Pearce, 1958], and same goes with MeOH and nitroalkanes mixtures of same ion [Busby and Griffiths, 1963]. According to the predictions of the electrostatic model with contact distances of 4.01 and 5.41Å the association constants of Me_4NNO_3 and Bu_4NNO_3 in AN-CCl_4 changes respectively [Coetzee and Cunningham, 1965]. The contact pairs are favoured in dipolar aprotic solvents and solvent-separated pairs in the protic solvents through the study of $LiClO_3$ in AN-dioxan and MeOH-dioxan mixtures having α=3.70 and 5.04Å compared to 6.8Å in the water-dioxan mixture [D'Aprano and Triolo, 1967]. 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 [Hawes and Kay, 1965], for Bu_4NBPh_4 [Kay et al., 1965](α=7Å) in NB-CCl_4 and in AC-CCL_4 [Berns and Fuoss, 1960; Accascina *et al.,* 1959] have been reported to be in accordance with the electrostatic model [Treiner and Justice, 1969]. There is no evidence provided for specific interactions in alkali metal halides mixtures of NMA-DMF [Dawson and Wharton, 1960]. In ROH-H_2O

mixtures there is no abnormalities encountered as showed by Et_4NPic in MeOH-EtOH [Foster and Amis, 1956].

2.4. EFFECTS OF PRESSURE ON THE ELECTROLYTIC CONDUCTANCE

The measurements of conductance at different pressures and temperatures used for testing the predictions of the continuum model depends on the association and mechanism of ionic transport.

The conductance of i-Am_4NPic in diethylether and benzene upto 5 x 10^6 Nm^{-2} was measured by Skinner and Fuoss [Skinner and Fuoss, 1965]. Due to the ε_r value (small) ion pairs and triplets are present. The variation of Λ is expected to depend on the ratio of both associated species because of the ε_r increases with pressure. The molar conductance Λ will increase with pressure only if the pairs dominate. Distinctively the molar conductance Λ decreases when the triple ions reign and the actual variation depends on whether the concentration of the solution is smaller or bigger than that corresponding to the minimum conductance. when the triple ions reign, The molar conductance Λ is found to increase in benzene and decrease in diethylether where α = 4.9Å for the ion pairs as was predicted. The variation of Λ with pressure depends on the concentration of the solution was also experienced for Bu_4NPic in toluene [Margosian *et al.*, 1962]. The conductance of salts and HBr in MeOH with the effect of pressure has been studied [Strauss, 1966]. With pressure the mobility of H^+ decreases less than the other ions. The molar conductance Λ increase with the pressure for HPic solutions in MeOH due to the enhanced dissociation of the acid dominates the variation of mobilities. In Bu_4NBPh_4, MeOH has Walden product constant upto 5 x 10^6Nm^{-2}, NaBr shows an increase in the Walden product with pressure, and the R_4N bromides are intermediate cases [Skinner and Fuoss, 1966]. In a particular salt, variations of K_A values with pressure were also observed to be dependent.

The relationship between the activation parameters and the variations of conductance with temperature and pressure according to an activated transport mechanism were derived by Brummer and Hills [Brummer and Hills, 1961]. The importance of the isochoric activation energy in characterizing the energetic of activated transport have been emphasized. For R_4NPic in NB, E_v is similar for all R as been indicated by Barreira and Hills [Barreira and Hill, 1961] and also to the isochoric activation energy for viscous flow of the pure solvent. For all the salts the activation volume is practically the same. Due to the effective movement of the ions caused by the solvent displacement the difference in ionic mobilities occured, since the rate determining step in ionic transport is displacement of solvent molecules in the neighbourhood of the ions.

For the salts similar behavior were found in MeOH and in NB [Brummer and Hills, 1961]. The conductance of picrates [Brummer, 1965] at various pressures shows that only for large cations is activation volume independent of cationic size in DMF. The activation volume for transport is almost independent of ionic size because of the variation of conductance with temperature and pressure for R_4NI in AC [Adams, 1968]. For a number of solvents, solvent self-diffusion and viscosity is found to be similar for conductance of dilute solutions. Since it is indicated that when they move ions are not followed by their solvation sheaths. It is indicated that for determining the mobility of ions the free volume of the solvent is an important parameter.

2.5. SPECTROPHOTOMERIC METHOD

Spectrophotomeric method is the most important method for understanding the formation of outer-sphere complexes. The postulation of the concepts of ion-pair formation and complex formation is important for understanding the concentration dependence of activity coefficients. Some structural questions cannot give clear answers from these examinations. As an example, in ion association (whether the associated entities were ion pairs or complexes) it is difficult to determine if chemical forces were involved. The proposal is to suggest ion association, and to succeed the action of a particular association on the importance of activity coefficient, and ultimately to differentiate calculated and observed importance [John et.al, 2002] .

The solutions of alkali metal salts of $Co(CO)_4^-$ dissolved in tetrahydrofuran (THF) of an infrared band, from which was assigned to the cation vibrating in a solvent cage was describe in 1965 by Edgell and co-workers [Edgell and Watts, 1965]. The nature of the vibration of these monoatomic ions in several non-aqueous solvents was eventually given [Edgell *et al.*, 1970]. Broad bands of medium intensity are formed. Therefore more error are concern in measurement than the vibrational bands in these properties. The salts of BPh_4^- was also studied by French and Wood [French and Wood, 1968]. The value of 194 to 198 cm^{-1} appears to be a better value since the value of 175 cm^{-1} which they report for $NaBPh_4$ in THF was not reproduced [Kinney and Popov, 1970]. They assigned the band to contact ion pairs since the frequency was insensitive to solvent for $NaBPh_4$ in Py, D, Pip and THF. The possible ion-pair potential functions were reviewed and the change of extinction coefficient with solvent, cation and concentration, and the isotopic shift were also described.

The effect of a changing, and usually low, dielectric constant on the degree of ion pair formation and the differences assigned to a changing solvation sphere, specific solvation were discussed by electrochemistry in non- aqueous solvents. Through infrared spectroscopy the stretching vibration of an ion pair M^+ - A^- is possible for observation. The new lines with a characteristic of 'bound' species perhaps can be observed whenever A^- is a polyatomic anion. It has been given by Janz and his co-workers [Janz *et al.*, 1969] that the stretching mode of nitrate ion was determined into two Raman active components at 1041 and 1036 cm^{-1} for $AgNO_3$-CH_3CN. It was possible to follow the intensity ratio down to 0.034M since the lines are very intense. By applying Wishaw-Stokes equation, good agreement was obtained between the degree of ion-pair formation measured and the conductance value obtained [Balasubrahmanyam and Janz, 1970].

Through Evans and Lo [Evans and Lo, 1965] Raman spectral studies concluded that solvation of Zn^{2+} by acetonitrile in the system $ZnCl_2$-CH_3CN-H_2O. It was observed that in equilibrium, the bands are characteristic of two distinct forms of CH_3CN. The nature and number of other ligands attached to zinc does not influenced the complex intrigated zinc-containing species. An increase in the C-N stretching force constant was caused due to the complex formation. The salts of $ZnCl_2$, $HgCl_2$, LiCl and HCL in methanol was investigated through Raman spectra [Kecki, 1962]. There was no attempt to measure the species concentrations although a set of equilibria involving $ZnCl_2L_4$, $ZnCl_4L_2^{2-}$ and a possible $(ZnCl_2)_{2n}$ polymer were cited for $ZnCl_2$ in aqueous solution [Irish *et al.*, 1968]. The mercuric chloride salts was used in the same complex ions and ion pairs was proof and located in LiCl and $CaCl_2$ methanol solutions. The vibrational spectrum of the salts of zinc chloride in triphosphate (TBP) diluted with benzene, acetone or pyridine in the vibrational spectrum was studied [Schaarschmidt, 1968]. When TBP: $ZnCl_2$ ratio is less than 2:1, the bands at 345 cm^{-1} and 305 cm^{-1} were attributed to a $ZnCl_2$ species of symmetry(bent molecule) [Coates and Ridley, 1964]

Adams [Adams, 1967] and Nakamoto [Nakamoto, 1970] have tabulated that vibrational spectra of many inorganic crystalline compounds, in which molecules of interest to the non-aqueous solution chemist are bonded to metal ions. Due to the change of state, frequencies of similar species in solution will be displaced from those of the solids except the second one give route for the function of the first one. Fini and his groups [Fini *et al.,* 1968] studied the intensities of polarized Raman bands of binary mixtures of many solvents over a wide concentration range. In most cases, the scattering coefficient increases linearly with the refractive index of the mixture and the theoretical formula, derived from Onsager's theory of dielectric polarization was in good agreement with them [Mirone, 1966].

Consequently for studying ion-pairing phenomena and especially for the study of very complicated equilibria spectroscopic methods was extensively used. The valuable information about the binding sites of multidentate ligands, kinetics and structures of many species in solution were provided. For investigating fast equilibria between free ions and associated species in non-aqueous solution IR-Spectrometry is a powerful tool [Irish *et al.,* 1976]. The information on the vibrational and rotational energy levels of a species were provided by the IR spectroscopy and it is based on studying the light transmitted through a medium after absorption. For analysis of cation-anion interactions an internal vibration of the polyatomic anions in most cases are applied [Aroca *et al*., 2000]. To characterize ion pairs and higher aggregates the strong $IR\upsilon_3$ band of pseudo-halide anions in the 2000-2200 cm^{-1} region is most convenient.

3. METHODOLOGY

3.1 Methods

The extent of ion association and the solvent-solvent interactions can be determined with the help of viscosity and relative permittivity. Through conductance study the solvation and association behavior of ions in solutions can be obtained [Dogonadze *et al*., 1986]. Ion-solvent, ion-ion and solvent-solvent interactions explained the behaviour of the solvation ions in solutions. Due to the combination of dielectric constant and viscosity in solvents ion-ion and ion-solvent interactions can be understood. The horizon in the field of mixed solvent systems has been extended because of the used of mixed solvents in high energy batteries [Aurbach, 1999; Roy *et al*., 2006]. For the electrical conductivity of electrolytes in mixed solvent solutions the concentration of the electrolyte and the viscosity of the solvent are responsible in mixed solvent solutions [Jasinski *et al.*,1968]. At different temperatures, the electrical conductivities of pure and mixed solvent solutions of the selected salts were measured. The limiting equivalent molar conductance (Λ_o), the association constant (K_A) of ion pair were calculated using Shedlovsky [Shedlovsky, 1932] and by using Fouss Kraus method [Fouss & Krauss., 1933] the limiting equivalent of triple ion(Λ_o^T) and triple ion formation(K_T) of the selected salts were obtained. For all studied solution system the molar conductances (Λ) were calculated using the equation [El-Dossoki, 2010]

$$\Lambda = 1000\kappa/c \qquad \ldots(31)$$

3.2. Evaluation of Limiting Molar Conductance (Λ_o) and association Constant (K_A) of Electrolytic salts by Shedlovsky technique.

Shedlovsky method [Shedlovsky, 1932] was used for analysing the conductance data of the chosen simple and complex salts.

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right) \qquad \ldots(32)$$

The equivalent conductance Λ at a concentration c (g.mol.dm^{-3}), the limiting equivalent conductance Λ_o and the observed association constant K_A were given. And other signs were written as [Shedlovsky and Kay, 1956]

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

The α and β values were obtained by using Debye-Huckel-Onsager equation:

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

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

Thus,

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

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

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

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

The valence and conductance of the ions were written as Z and λ respectively, the dielectric constant of the medium is given as D and the viscosity coefficient of the medium is given as η. From the equation the degree of dissociation (τ) is related to S(Z)

$$-\log f_{\pm} = \frac{Az_{+}z_{-}\mu^{1/2}}{1+BR\mu^{1/2}} \qquad \ldots(33)$$

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

The maximum centre to centre distance between the ions in the ion-pair is given as R. There is no precise method for determining the value of R’ so far [Hogman *et al.,* 1956-1957]. The value 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, therefore R’ value can be used for treating the conductance data in the system. It is given that the distance d is equal to [Fuoss and Onsager, 1955]

$$d = 1.183\left({}^{M}/_{\rho}\right)^{1/3} \text{Å} \qquad \ldots(34)$$

The molecular weight of the solvent is given as M and the density of the solution as ρ. The value M is replaced by the mole fraction average molecular weight for a mixed solvent,

$$M_{avg} = \frac{M_1M_2}{X_1M_2 + X_2M_1} \qquad \ldots(35)$$

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

The intercept of the linear Onsager plot of Λ versus $c^{1/2}$ was used for obtaining an initial value of λ^o (Shedlovsky method), and from the literature λ^o value was obtained at 25°C and by using the following equation other values at different temperatures were obtained [Bag *et al.*, 2009]:

$$\lambda_t^0 = \lambda_{25}^0[1 + \alpha'(t - 25)] \qquad \ldots(36)$$

The value α' was sustained. The r values were calculated by using the values of Λ_o, λ^o_-, λ^o_+, z, $s(z)$. For the above chosen complex salts the mean activity coefficient f was obtained through equation (20). The value of Λ_o and K_A were evaluated from the intercept $1/\Lambda_0$ and the slope (K_A/Λ_0^2) through the linear plot of $1/\Lambda S$ (Z) versus C $\Lambda f_{\pm}^2$ S(Z). From the new values of Λ_0 and K_A obtained the procedure was repeated.

3.3. Evaluation of Limiting Molar Conductance of triple ion (Λ_o^T) and Triple ion Formation Constant (K_T) of Electrolytic salts by Fouss- Krauss technique.

The classical Fuoss-Kraus theory of triple-ion formation was used for analysing the conductance data [Fuoss-Kraus, 1933]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \qquad \ldots(37)$$

The component that lumps together all the intrinsic interaction terms is given as $g(c)$ and is equal to

$$g(c) = \frac{\exp\{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \qquad \ldots(38)$$

$$\beta' = 1.8247\ X\ 10^6/(\varepsilon T)^{1.5} \qquad \ldots(39)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204\ X\ 10^6}{(\varepsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad \ldots(40)$$

At infinite dilution the sum of the molar conductance of the simple ions is given as Λo, the sum of the conductance value of the two triple-ions as Λo^T and ion-pair and triple-ion formation constants as $K_P \approx K_A$ and K_T and S is equal to limiting Onsager coefficient(as given in the above equations).

Besides, by using the following equations the ion-pair and triple-ion concentrations, C_P and C_T, were calculated [Nandi *et al.*, 1988]

$$\alpha = 1/(K_P^{\frac{1}{2}}.c^{\frac{1}{2}}) \qquad \ldots(41)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \qquad \ldots(42)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \qquad \ldots(43)$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \qquad \ldots(44)$$

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

3.4. Evaluation of thermodynamic parameters

The values of association constants at different temperatures were used for calculating thermodynamics properties for the association, viz., changes free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for the ion-pair formation. The change in the number and strength of the bond is responsible for the enthalpy change (ΔH^o_{ass}). When we compare the association constant of some selected transition metals in pure and mixed solvents, the entropy change

(ΔS^{o}_{ass}) is measure for the change of randomness and compared for the process. The Van't hoff isothermal correlation was used for calculating ΔG^{o}_{ass}.

$$\Delta G^{0} = \Delta H^{0}_{ass} - T\Delta S^{0}_{ass} \qquad \ldots(45)$$

From the equation free energy of association process (ΔG^{o}_{ass}) was calculated

$$\Delta G^{0} = -RT\ln K_{A} \qquad \ldots(46)$$

The slope of log K_A vs 1/T was used for obtaining the entropy change of association (ΔH^{o}_{ass}), and from Gibbs Helmholtz equation the change of association entropy (ΔS^{o}_{ass}) was calculated

$$\Delta S^{o}_{ass} = \frac{\Delta H^{o}_{ass} - \Delta G^{o}_{ass}}{T} \qquad \ldots(47)$$

3.5. Calculation of Walden Product

The Walden product ($\Lambda_o\eta$) (product of the limiting molar conductance at infinite dilution and solvent viscosity) was used for discussing the tendency in limiting molar conductance Λ_o and ion-association. Since 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 therefore the above statement has been justified [Bhat and Bindu, 1995].

$$\Lambda_0\eta = \frac{1}{6\Pi r_{eff}T} \qquad ...(48)$$

Thus, the solvation of the ions has been reflected by the variation of Walden product ($\Lambda_o\eta_o$) with the change in the composition of the solvent [Conway *et al.*, 1965]. The ion is 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 because the ion in the solution is completely surrounded by solvent molecules that flows with it [Conway, 1978]. Stokes' law used as the starting point for evaluating most of the ionic conductance., states that the limiting Walden product ($\lambda_o^{\pm}\eta$) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant.

Stokes' radii (r_s) was obtained by using the $\lambda_o^{\pm}$ values and classically it is expressed as [Robinson and Stokes, 1959]

$$r_s = \frac{F^2}{6\Pi N_A \lambda_0^{\pm} r_c} \qquad \ldots(49)$$

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

Due to the development of Debye-Hückel theory of inter-ionic attractions in 1923 the importance of Stoke's law had been realized [Debye and Hückel, 1923]. The interionic attraction theory of the Falkenhagen and Vernon [Falkenhagen and Vernon, 1983] equation was used for calculating the A-coefficient that depends on the ion-ion interactions:

$$A_{Theo} = \frac{0.2577\Lambda_0}{\eta_0(\varepsilon T)^{0.5}\lambda_+^0\lambda_-^0}[1 - 0.6863(\frac{\lambda_+^0\lambda_-^0}{\Lambda_0})^2] \qquad \ldots(50)$$

and, the characters have their standard importance. The existence of the ion-ion interaction is negligible as compared to the ion-solvent interaction in the studied solvents, since *A*-coefficient is negative and very small.

3.6. Physical Measurements

3.6.1. 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 was used for measuring the conductance data.

3.6.2. Temperature Control

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

3.6.3. Measurement of Weights

METTER Balance, Model-Ae260, Delta Range was used for measuring the weights of the salts.

3.6.4. Computations

Shedlovsky and Fuoss-Krauss method were used for performing the program.

3.7. Materials

3.7.1. Ligands

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

i. Glycine
ii. 2-pyridinecarboxaldehyde
iii. Benzoylhydrazine
iv. (2-[(1)-pyridin-2-ylmethylidene]benzohydrazide)
v. Carbonatotetraamminecobalt (III) nitrate
vi. Carbonatotetraamminenickel (III) nitrate
vii. Glycine, 2-pyridinecarboxaldehyde and Benzoylhydrazine of analytical reagent grade were directly purchased from Merck Company and used as such.

viii. The ligand (2-[(1)-pyridin-2-ylmethylidene]benzohydrazide) was prepared for the following methods [R.N.Patel *et. al.*, 2012]

ix. Carbonatotetraamminecobalt (III) nitrate and Carbonatotetraamminenickel (III) nitrate were prepared for the following methods of G.G. Schlessinger [Schlessinger, 1962].

i. (2-[(1)-pyridin-2-ylmethylidine]benzohydrazide)

The condensation of 2-pyridinecarboxaldehyde and benzoylhydrazine give the Schiff base. In 10 ml ethanol, 2-pyridinecarboxaldehyde (1.07g, 10.0 mmol) with benzoylhydrazine (1.36g, 10.0 mmol) was continuously refluxed for 6 hours. Then 1-2 drops of acetic acid was added. On cooling the solution At room temperature the solution was cooled, pale yellow crystals was obtained and cleaned with methanol. They were kept in the air for drying and later stored in a $CaCl_2$ desiccator.

ii. Carbonatotetraamminecobalt (III) nitrate

A 0.208 mol of $(NH_4)_2CO_3$ was dissolved in 60 ml of H_2O in a beaker under constant stirring, 60 ml of concentrated aqueous NH_3 (ammonium hydroxide) was added. While stirring into a solution 0.0515 mol of $[Co(OH_2)_6](NO_3)_2$ in 30 ml of H_2O was added. 8 ml of a 30% H_2O_2 solution was slowly added dropwise. Then using a hot plate it is concentrated to about 90-100 ml. The temperature of the solution was maintained to 85°C and was not allowed to boil. During the course of evaporation 5g of $(NH_4)_2CO_3$ in small portions was added. Using suction filter the hot solution was filtered to see if there are any undissoved materials remain. The filtrate was cool in an ice water bath at 5°C and then isolate the red crystalline product was isolated into a clean side-arm Erlenmeyer flask by suction filtration. In a separate 250ml Erlenmeyer flask the filtrate was transferred and kept it. Wash The product with washed with a small amount of ice-cold water and later with 95% ethanol in small amount. The product was place on a watch glass and kept in a drying oven at 100°C.

iii. Carbonatotetraamminenickel (III) nitrate

A 0.208 mol of $(NH_4)_2CO_3$ was dissolved in 60 ml of H_2O in a beaker under constant stirring, 60 ml of concentrated aqueous NH_3 (ammonium hydroxide) was added. While stirring into a solution 0.0515 mol of $[Co(OH_2)_6](NO_3)_2$ in 30 ml of H_2O was added. 8 ml of a 30% H_2O_2 solution was slowly added dropwise. Then using a hot plate it is concentrated to about 90-100 ml. The temperature of the solution was maintained to 85°C and was not allowed to boil. During the course of evaporation 5g of $(NH_4)_2CO_3$ in small portions was added. Suction filter The hot solution was filtered to see if there are any undissoved materials remain. The filtrate was cool in an ice water bath at 5°C and then isolate the red crystalline product was isolated into a clean side-arm Erlenmeyer flask by suction filtration. In a separate 250ml Erlenmeyer flask the filtrate was transferred and kept it. The product was washed with a small amount of ice-cold water and later with 95% ethanol in small amount. The product was placed on a watch glass and kept in a drying oven at 100°C.

3.7.2. Preparation of the Compounds / Complexes

i. Bis(glycinato)copper (II) Monohydrate

(First isomer) In 25 ml of hot distilled water 2.0g of copper (II) acetate monohydrate was dissolved. The solution was kept hot after adding 25 ml of ethyl alcohol. And in 25 ml of hot water 1.5g of glycine was dissolved. While it is hot (70°C) the two solutions was mixed.

A needle-like precipitate of the first isomer is obtained after the solution is cool on ice. The mixture is filtered into a clean flask,and the filtrate was preserved. The solid was washed with ethanol and kept dried. **(Second isomer)** 10 ml of the filtrate from the previous preparation was placed in a small round-bottom flask along with approximately three quarters of the solid product. 1.0g of glycine was added and reflux for 1 hour under the heat. Magnetic stirrer give a gentle reflux when it is stirred under the heating mantle. The solid was filter off from the hot solution and finally kept dried.

ii.[Ni(2-](1)-pyridin-2-ylmethylidene(benzohydrazide)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)

Ni$(NO_3)_2$.6H_2O (0.29g, 1.0 mmol) in MeOH (10 ml) was added with (2-[(1)-pyridin-2-ylmethylidine]benzohydrazide) (1 mmol, 0.23g) in MeOH (10 ml),and the solution was stirred at room temperature. The solution keep on stirring for 30 mins and 2,2'-bipyridine (0.16g, 1mmol) was added in between and at room temperature it was stirred again for 45 mins. $NaClO_4$ (0.12g, 1 mmol) was added later on. With the help of methanol the green product obtained was washed and keep in the air for drying.

iii. [Ni(2-](1)-pyridin-2-ylmethylidene(benzohydrazide)(dien)]$(ClO_4)_2$(H_2O)

Ni$(NO_3)_2$.6H_2O (0.29g, 1.0 mmol) in MeOH (10 ml) was added with (2-[(1)-pyridin-2-ylmethylidine]benzohydrazide) (1 mmol, 0.23g) in MeOH (10 ml),and the solution was stirred at room temperature. The solution keep on stirring for 30 mins and diethylenetriamine (0.95g, 1mmol) was added in between and at room temperature it was stirred again for 45 mins. $NaClO_4$ (0.24g, 2.0 mmol) was added later on. The dark green crystal was obtained after the slow evaporation of the reaction mixture. With the help of methanol the dark green product obtained was washed and keep in the air for drying.

iv. Pentaammine fluorocobalt (II) fluoride

A 5.0g of $[Co(NH_3)_4CO_3]NO_3$ was dissolved in 50 ml of H_2O and slowly add concentrated HF (5-10 ml) was slowly added until all of the CO_2 gas is spread out. Neutralize the solution with concentrated ammonium hydroxide until the red litmus paper dipped in the solution become basic. The concentrated NH_3 of 5 ml was added in excess. For 20 minutes it was heated and avoid the boiling so as to form $[Co(NH_3)_5H_2O]^{3+}$. As one of the coordinated water molecules was replaced note any change in the colour. Slowly add 75 ml concentrated HF as the solution began to cool. Again it was reheated for 20-25 minutes and observed the colour change. At room temperature it was cooled and observed the formation of precipitate. With a small amount of ice-cold DI H_2O, the compound was decantated several times. The suction filtration was used to isolate the crystalline product. With cold ethanol (95%) it was washed and dried completely in the air. Cold water was used for washing the solutions so as to avoid the loss of product from dissolving again. It was dried again in an oven at 100-120°C to remove the remaining solvent, and finally $[Co(NH_3)_5F]F_2$ was obtained.

v. Pentaammine fluoronickel (II) fluoride

A 5.0g of $[Ni(NH_3)_4CO_3]NO_3$ was dissolved in 50 ml of H_2O and slowly add concentrated HF (5-10 ml) was slowly added until all of the CO_2 gas is spread out. Neutralize the solution with The concentrated ammonium hydroxide was used for neutralizing the solution until the red litmus paper dipped in the solution become basic. The concentrated NH_3 of 5 ml was added in excess. For 20 minutes it was heated and avoid the boiling so as to form $[Ni(NH_3)_5H_2O]^{3+}$. As one of the coordinated water molecules was replaced note any change in the colour. Slowly add 75 ml concentrated HF as the solution began to cool. Again it was reheated for 20-25 minutes and observed the colour change. At room temperature it was cooled and observed the formation of precipitate. With a small amount of ice-cold DI H_2O, the compound was decantated several times. The suction filtration was used to isolate the crystalline product. With cold ethanol (95%) it was washed and dried completely in the air. Cold water was used for washing the solutions so as to avoid the loss of product from dissolving again. It was dried again in an oven at 100-120°C to remove the remaining solvent, and finally $[Ni(NH_3)_5F]F_2$ was obtained.

vi. Pentaammine chloronickel (II) perchlorate

A 5.0g of $[Ni(NH_3)_4CO_3]NO_3$ was dissolved in 50 ml of H_2O and slowly add concentrated $HClO_4$ (5-10 ml) was slowly added until all of the CO_2 gas is spread out. Neutralize the solution with The concentrated ammonium hydroxide was used for neutralizing the solution until the red litmus paper dipped in the solution become basic. The concentrated NH_3 of 5 ml was added in excess. For 20 minutes it was heated and avoid the boiling so as to form $[Ni(NH_3)_5H_2O]^{3+}$. As one of the coordinated water molecules was replaced note any change in the colour. Slowly add 75 ml concentrated $HClO_4$ as the solution began to cool. Again it was reheated for 20-25 minutes and observed the colour change. At room temperature it was cooled and observed the formation of precipitate. With a small amount of ice-cold DI H_2O, the compound was decantated several times. The suction filtration was used to isolate the crystalline product. With cold ethanol (95%) it was washed and dried completely in the air. Cold water was used for washing the solutions so as to avoid the loss of product from dissolving again. It was dried again in an oven at 100-120°C to remove the remaining solvent, and finally $[Ni(NH_3)_5Cl]ClO_4$ was obtained.

vii. Lithium salts (LiCl and LiNO3)

viii. Cetyl Trimethylammonium bromide ($C_{19}H_{42}NBr$)

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

x. 1-butyl-4-methylpyridinium hexafluorophosphate[4BMimPPF$_6$]

The above three complexes and two ILs selected for the present work puriss grade were procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of the ILs was ≥ 0.95.

4. RESULTS AND DISCUSSIONS

4.1. Physico-Chemical Characterization of copper metal complexes in aqueous system at different temperature.

4.1.1. Introduction

The conductometric technique has been used for examining ion pairing between the metal ions and ligands [Bakr et.al, 1999; Ue et.al, 1995; Bakr, 2001]. Ion hydration and ion association plays an important role in aqueous electrolytic solutions. The ability of solvent, interaction of solute, and the nature of the complex ion formation are responsible for the properties of electrolytic solutions. A strong electrostatic interactions between oppositely charged ions results in the formation of ion pair [Fedova, 2006].

Bis glycinato copper (II) monohydrate and copper (II) acetate in water at different temperatures ranges 15-40^{0}C, were comparatively studied for conductometric properties and thermodynamic properties. The Shedlovsky extrapolation method was used for analyzing the conductance data. From the calculated values of standard thermodynamic parameters, the effect of temperature on limiting molar conductance and association constant for the selected compounds were also investigated. The association constant values were used for discussing these results and thermodynamic features of metal-ion complexes at various temperatures were discussed through the approach of Gibbs energy relationship [Jenkins and Monk, 1951]. From the experimental temperatures the K_{AS} and Λ_0 have been evaluated in these solvents. The values of ion association constant at various temperatures were used for studying the thermodynamic parameters viz., ΔH^0, ΔS^0 and ΔG^0.

4.1.2. Experimental

4.1.2.1. Preparation of ligands and compounds

According to the reported procedure 3.7.2. (i) [O’ Brien, 1982] the salts selected for the present work, ie., Bis glycinato copper (II) monohydrate was synthesized.

4.1.2.2. Conductivity measurements

The stock solution of an electrolyte was prepared by weighing the salts of bis glycinato Cu(II) monohydrate (METTER Balance TB-214, max=210g; d=0.1mg) and at different concentrations (1 x 10 $^{-3}$) M requisite amount of the sample were dissolved in conductivity water. From the literature all the viscosity, dielectric constant and density values were interpolated [Hodgman et al., 1956; Akhadov, 1981; Timmermanns, 1960]. The Orion Star A122 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges using a dip-type immersion conductivity cell was used for obtaining the conductance measurement. Circular- Cole-Palmer, Polystat R6L water bath and graduated thermometer were used for maintaining the temperatures. Using a basic programmed given by Shedlovsky method, all calculations were done on IBM-PC-AT/386.

Table 1(a): Molar conductivities (Λ) of Cu (II) Acetate in aqueous medium in different temperatures.

Conc.x10^{-3}	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
0.001	142.00	146.20	150.00	154.00	158.05	162.30
0.976	143.03	147.03	151.02	155.02	159.01	163.01
0.952	143.28	147.16	151.16	155.14	159.13	163.13
0.930	143.55	147.31	151.40	155.26	159.24	163.22
0.909	144.00	147.74	151.60	155.44	159.30	163.36
0.889	144.54	148.48	152.31	156.24	160.06	164.00
0.869	144.88	148.79	152.70	156.61	160.41	164.21
0.851	145.48	149.35	153.23	157.10	160.75	164.51
0.833	145.97	149.58	153.42	157.26	161.22	165.18
0.816	146.45	150.37	154.29	157.96	161.88	165.68

Table 1(b): Molar conductivities (Λ) of Bis glycinato Cu (II) Monohydrate in aqueous medium in different temperatures.

Conc.x10^{-3}	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
0.001	124.00	128.00	`132.80	136.43	140.58	144.00
0.976	125.00	129.09	133.09	137.09	141.08	145.29
0.952	125.32	129.20	133.29	137.28	141.28	145.48
0.930	125.59	129.55	133.44	137.42	141.61	145.59
0.909	125.85	129.59	133.77	137.73	141.80	145.76
0.889	126.32	130.03	134.08	138.02	141.95	145.90
0.869	126.58	130.03	134.17	138.20	142.00	146.02
0.851	126.79	130.26	134.31	138.30	142.18	146.18
0.833	127.25	131.21	134.93	138.53	142.25	146.21
0.816	127.45	131.37	135.29	139.10	143.01	146.81

4.1.3. Evaluation of limiting molar conductance and association constant

For all studied solution system the molar conductances (Λ) were calculated using the equation [El-Dossoki, 2010]

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

Where the molar concentration is given as c and the measured specific conductance of the studied solutions as k. Shedlovsky method [Shedlovsky, 1932] was used for analysing the conductance data of the chosen simple and complex salts.

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right) \qquad \ldots(50)$$

The equivalent conductance Λ at a concentration c (g.mol.dm^{-3}), the limiting equivalent conductance Λ_o and the observed association constant K_A were given. And other signs were written as [Shedlovsky and Kay, 1956]

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

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

The valence and conductance of the ions were written as Z and λ respectively, the dielectric constant of the medium is given as D and the viscosity coefficient of the medium is given as η. From the equation the degree of dissociation (τ) is related to S(Z)

$$-\log f_{\pm} = \frac{Az_+ z_- \mu^{1/2}}{1 + BR\mu^{1/2}} \qquad \ldots(51)$$

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

The maximum centre to centre distance between the ions in the ion-pair is given as R. There is no precise method for determining the value of R’ so far [Hogman *et al.*, 1956-1957]. The value 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, therefore R’ value can be used for treating the conductance data in the system. It is given that the distance d is equal to [Fuoss and Onsager, 1955]

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

The molecular weight of the solvent is given as M and the density of the solution as ρ. The value M is replaced by the mole fraction average molecular weight for a mixed solvent,

$$\mathrm{M_{avg}} = \frac{\mathrm{M_1M_2}}{\mathrm{X_1M_2 + X_2M_1}}$$

The mole fraction of methanol of molecular weight M_1 and X_2 that of water of molecular weight M_2 was given as X_1. By using least square method (Λ and concentration C was introduced as input in a computer programme) an initial value of Λ_o was obtained. For the above chosen simple and complex salts, equation (13) was used for determining the mean activity coefficient $f_\pm$ [Akhadov, 1981]. The value of Λ_o and K_A were evaluated from the intercept $1/\Lambda_0$ and the slope (K_A/Λ_0^2) through the linear plot of $1/\Lambda S$ (Z) versus C $\Lambda f_\pm^2$ S(Z) respectively [Glasstone, 1942].

The intercept of the linear Onsager plot of Λ versus $c^{1/2}$ was used for obtaining an initial value of λ^o (Shedlovsky method), and from the literature λ^o value was obtained at 25°C and by using the following equation other values at different temperatures were obtained [Bag *et al.*, 2009]:

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

The value α' was sustained. The *r* values were calculated by using the values of Λ_o, λ^o_-, λ^o_+, *z*, *s(z)*. For the above chosen complex salts the mean activity coefficient f was obtained through equation (20). The value of Λ_o and K_A were evaluated from the intercept $1/\Lambda_0$ and the slope (K_A/Λ_0^2) through the linear plot of $1/\Lambda S$ (Z) versus C $\Lambda f_\pm^2$ S(Z). From the new values of Λ_0 and K_A obtained the procedure was repeated. In Table 2(a) & Table 2(b) the results of limiting molar conductance (Λ_0) and association constant (K_A) at different temperatures are obtained.

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

	288.15K	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
Λ_0	183.11	208.72	235.52	269.95	299.48	335.12
K_A	176.39	185.23	193.42	199.00	214.06	246.12
Log K_A	2.246	2.268	2.286	2.299	2.330	2.391

Table 2(b): The value of limiting molar conductance Λ_0 (Scm^2mol^{-1}) and association constant K_A (dm^3mol^{-1}) obtained for Bis glycinato Cu(II) Monohydrate in aqueous solution at different temperatures.

	288.15K	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
Λ_0	152.56	157.30	166.57	197.07	231.59	268.11
K_A	149.39	151.23	163.13	175.08	187.00	194.19
Log K_A	2.174	2.180	2.212	2.243	2.272	2.288

Because of the increase thermal energy results in bond breaking, higher frequency and higher mobility of the ions, the value of Λ_0 for the electrolytes always increased with increase in temperature in aqueous medium resulting in less solvation or higher mobility of ions, as given in tables 2(a) & 2(b) [Das, 2008]. Since the salts are most prone to the variation in vibrational, rotational and translational energy levels with temperature the values of Λ_0 for Cu(II) acetate are always greater than those values of bis glycinato Cu(II) monohydrate [Jenkins and Monk, 1950]. With the rise in temperature the values of the K_As for the two complexes increases.

The charge density of metal ion is greater than that of the charge density of the metal ion for bis glycinato Cu(II) monohydrate, therefore the higher K_A values in case of Cu(II) acetate salt compared to bis glycinato Cu(II) monohydrate is due to the more coulombic type of interaction (specific short-range interaction) between the metal ion and sulfate ion [Pura and Atun, 2003].

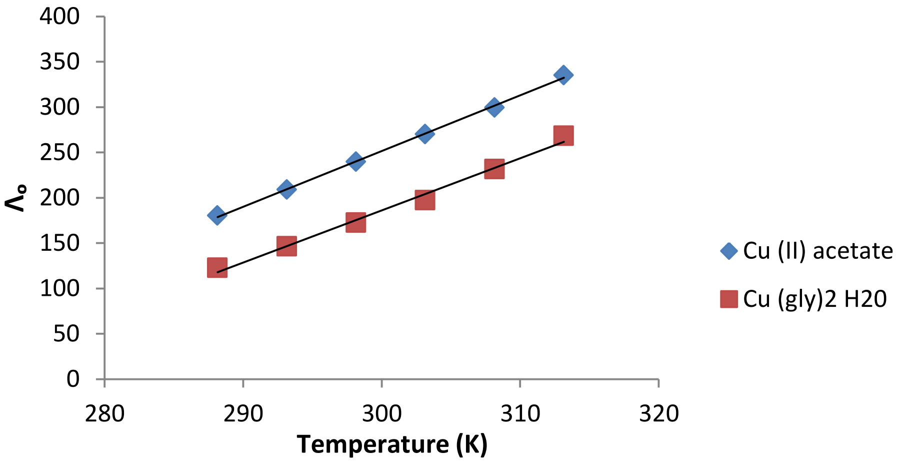

Fig 1: Plot of limiting molar conductance (Λ_o) vs temperature (K) for Cu (II) acetate and Cu $(gly)_2$ H_20

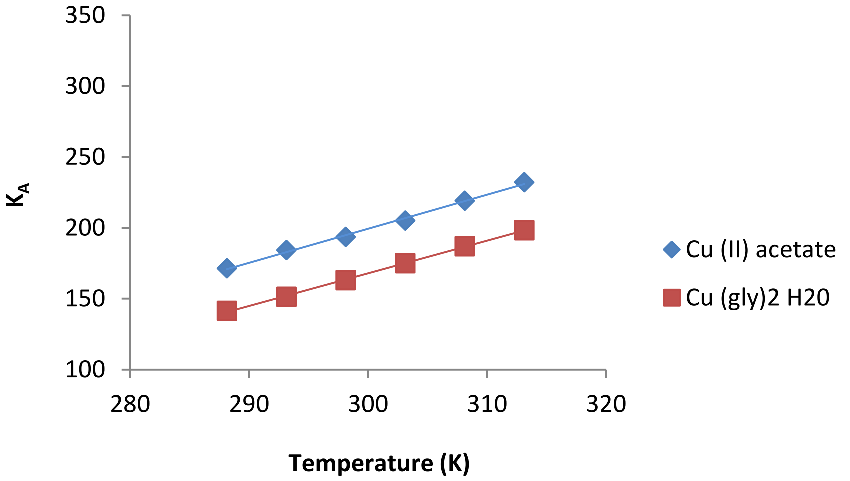

Fig 2: Plot of Association constant (K_A) vs temperature (K) for Cu (II) acetate and Cu (gly)$_2$ H_2O

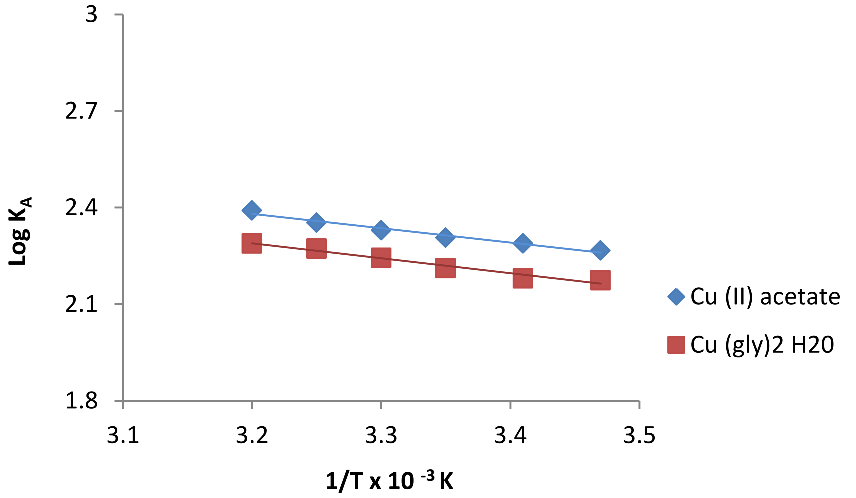

Fig 3: Plot of Log K_A vs 1/T for Cu (II) acetate and Cu (gly)$_2$ H_20

4.1.4. Evaluation of thermodynamic parameters

The values of association constants at different temperatures were used for calculating thermodynamics properties for the association, viz., changes free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for the ion-pair formation. The change in the number and strength of the bond is responsible for the enthalpy change (ΔH^o_{ass}). When we compare the association constant of some selected transition metals in pure and mixed solvents, the entropy change

(ΔS^{o}_{ass}) is measure for the change of randomness and compared for the process. The Van't hoff isothermal correlation was used for calculating ΔG^{o}_{ass}.

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

From the equation free energy of association process (ΔG^{o}_{ass}) was calculated

$$\Delta G^{0} = -RT\ln K_{A}$$

The slope of log K_A vs 1/T was used for obtaining the entropy change of association (ΔH^{o}_{ass}), and from Gibbs Helmholtz equation the change of association entropy (ΔS^{o}_{ass}) was calculated

$$\Delta S^{o}_{ass} = \frac{\Delta H^{o}_{ass} - \Delta G^{o}_{ass}}{T}$$

The values of thermodynamic functions are given in table 3(a) & 3(b).

Table 3(a): Thermodynamic parameters ΔG^{0} ($kJmol^{-1}$), ΔH^{0} ($kJmol^{-1}$), and ΔS^{0} ($kjK^{-1}mol^{-1}$) obtained by Shedlovsky technique for Cu (II) Acetate in aqueous solution at different temperatures.

	288.15K	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
ΔG^{0}	-12.392	-12.730	-13.050	-13.344	-13.747	-14.336
ΔH^{0}	-2.398					
10^{3} x ΔS^{0}	34.71	35.24	35.73	36.11	36.83	38.12

Table 3(b): Thermodynamic parameters ΔG^0 ($kJmol^{-1}$), ΔH^0 ($kJmol^{-1}$), and ΔS^0 ($kjK^{-1}mol^{-1}$) obtained by Shedlovsky technique for Bis glycinato Cu (II) Monohydrate in aqueous solution at different temperatures.

	288.15K	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
ΔG^0	-11.994	-12.236	-12.628	-13.019	-13.405	-13.719
ΔH^0	-2.304					
10^3 x ΔS^0	33.63	33.88	34.63	35.35	36.02	36.45

As the temperatures increases the limiting equivalent conductance Λ_o and the association constant K_A values also increases. The negative values of of ΔH^o determined that both the reactions are exothermic [Girolami *et al.*, 1999]. Therefore Cu(II) acetate complex is more favored in ion-pair formation because the negative values of ΔG^0 is larger.

4.2. Ion Association and Solvation Behaviour of Nickel (II) Complexes in Binary Mixtures of DMSO-H_2O at Different Temperatures

4.2.1. Introduction

Studies on electrical conductance of an electrolyte in mixed solvents is of value, as it gives information about the behavior of ions in solution, ion-solvent interaction, and solvent structural effects. Knowledge of electrolyte solution is found to be helpful for various electrochemical and technical investigations [Bockris et.al, 1998; Debye et.al, 1996; Radhika et.al, 2008; Apelblat, 2009]. Dimethylsulphoxide is a polar aprotic solvent that has applicable properties in electrochemical systems [Zamir et.al, 2008; Hamann et.al, 2009]. Attentiveness of dimethylsulfoxide is due to the broad use of DMSO-water mixtures as solvents and reaction media. Dimethylsulfoxide has a polyfunctional molecule with a highly polar S=O group and two hydrophobic methyl groups. Unfinished negative charge on the oxygen atom of a DMSO molecule approved the formation of hydrogen bonds with water molecules, whereas the non polar CH_3 groups may results in hydrophobic hydration and hydrophobic association of DMSO molecule. Research [Zijie et.al, 2009; Szmant et.al, 1975] have shown that dimethylsulfoxide gives hydrogen bonds with water molecules throughout the whole composition range. Perchlorates are applicable in electrochemical studies as an inert additive for maintaining constant ionic strength because the perchlorate anion is one of the least prone to complex formation and has no effect on chemical equilibrium. Ion association of perchlorates in non aqueous solvents with lower dielectric solvents may be significant and must be taken into consideration. Here effect of temperature on the ion association behavior of perchlorate complexes in mixed solvents were studied by measuring the electrical conductance of Ni (II) complexes at varying temperatures in 0-100 wt% dimethylsulfoxide-water solvent mixtures. The conductance data were examined by the Shedlovsky equation.

The K_A values increase on increasing the temperature and increasing the percentage of DMSO in the mixed solvent presenting endothermic character of ionic association in this system. Thermodynamic parameters (ΔH°, ΔG°, ΔS° and Ea) were obtained from the temperature dependence of K_A for these complexes. These parameters are compared according to interactions of solvent at different temperatures.

4.2.2. Experimental

4.2.2.1. Preparation of ligands and compounds

The inorganic salt selected for the present work, i.e [Ni (HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) and [Ni (HL)(dien)](ClO_4)$_2$(H_2O) were synthesized according to the literature 3.7.2. (ii) and (iii) [Patel et. al, 2012].

4.2.2.2. Conductivity measurements

The electric conductivities were measured by Eutech Instruments, PC 700 with a dip type immersion conductivity cell were used. The solutions of different concentrations (1 x10^{-3}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water of low specific conductance (< 2x10^{-6} S cm^{-1}). All the dielectric constants and viscosities were obtained from literature [Zamir et. al, 2010]. The temperature control in the ranges of 15-35^{0}C were made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a METTLER Balance, model TB-214(max=210g; d=0.1mg). 0.1MKCL solution in doubly distilled de-ionized water was prepared and used for calibrating the cell.

Table 4(a): Molar conductivities (Λ) of [Ni (HL) (dien)]$(ClO_4)_2(H_2O)$ Complex in DMSO + Water in different temperatures.

X_1=0.000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	26.38	30.40	34.00	35.40	36.80
0.976	28.90	32.20	34.43	36.96	39.05
0.952	30.20	34.30	34.90	38.06	42.02
0.930	32.52	35.20	35.81	38.66	45.19
0.909	34.01	37.21	36.15	41.20	47.84
0.889	36.12	37.60	37.00	42.38	50.22
0.869	37.57	38.42	38.21	42.50	52.00
0.851	37.84	40.54	38.90	43.40	52.72
0.833	38.09	41.51	39.70	45.16	55.58
0.816	38.54	42.74	41.60	46.46	57.24

X_1=0.0250

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	24.51	26.22	27.92	29.61	31.10
0.976	25.43	28.59	29.40	30.15	33.33
0.952	26.83	30.00	31.18	30.90	36.12
0.930	28.21	30.77	32.48	31.85	38.41
0.909	28.84	32.55	33.61	33.19	40.92
0.889	30.04	33.24	35.05	34.59	43.34
0.869	31.34	34.98	36.90	35.66	44.00
0.851	31.36	35.05	37.74	36.46	46.10
0.833	32.45	36.30	38.00	37.77	47.12
0.816	33.35	37.00	38.97	38.60	48.42

X_1=0.0900

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	21.14	21.51	21.88	22.22	23.00
0.976	22.97	23.48	23.59	23.84	24.76
0.952	23.67	24.81	24.98	25.87	26.50
0.930	24.50	25.36	25.62	26.47	27.93
0.909	25.36	26.33	26.15	28.08	28.71
0.889	26.40	26.66	27.77	28.99	29.23
0.869	27.57	27.57	28.80	30.13	29.84
0.851	28.35	28.55	29.76	30.61	31.33
0.833	28.78	29.05	30.31	31.50	32.10
0.816	29.90	30.40	30.42	32.32	32.85

X_1=0.1874

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	19.31	19.80	20.17	20.92	21.56
0.976	20.30	21.17	21.69	21.64	23.09
0.952	21.31	22.03	23.16	22.06	23.88
0.930	22.01	22.72	24.00	22.13	24.03
0.909	22.87	23.92	25.45	22.79	24.68
0.889	23.69	24.89	26.39	22.82	25.31
0.869	24.70	25.76	27.50	23.25	25.66
0.851	25.32	26.96	28.76	23.42	26.12
0.833	25.57	27.75	29.75	24.03	26.60
0.816	25.72	28.99	31.14	24.22	26.84

X_1=0.3499

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	20.50	21.80	22.00	24.75	25.46
0.976	21.78	23.33	23.95	26.57	27.68
0.952	22.93	24.55	24.33	28.52	29.62
0.930	24.45	25.50	25.36	29.93	31.48
0.909	24.51	26.61	25.83	31.96	33.07
0.889	25.70	28.11	26.31	32.98	34.71
0.869	26.34	28.30	26.77	34.69	36.54
0.851	26.51	28.57	27.60	35.31	37.81
0.833	26.62	29.19	27.72	35.65	39.32
0.816	27.07	29.52	28.52	36.39	39.62

X_1=0.6749

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	23.57	24.49	26.88	28.98	29.14
0.976	25.60	26.41	28.99	30.57	31.73
0.952	27.31	28.03	31.15	31.67	32.98
0.930	29.04	29.92	32.34	33.90	35.18
0.909	30.78	31.72	33.19	36.22	37.69
0.889	31.08	32.11	33.87	36.99	38.67
0.869	31.28	33.81	34.42	37.55	39.49
0.851	32.01	35.58	34.66	38.04	40.10
0.833	32.57	35.89	35.25	39.24	40.43
0.816	34.18	36.06	36.77	40.40	44.51

X_1=1.000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	25.83	27.93	28.18	30.02	32.77
0.976	27.14	30.37	30.15	30.64	35.53
0.952	29.07	32.68	32.32	35.51	38.15
0.930	31.00	35.32	34.56	36.83	40.48
0.909	32.86	37.58	36.85	39.13	43.23
0.889	34.74	39.78	38.56	40.80	45.56
0.869	36.43	41.84	39.54	43.00	48.08
0.851	38.33	44.01	41.61	43.62	50.83
0.833	40.20	46.00	43.56	44.24	53.15
0.816	40.91	46.40	45.89	46.42	54.49

Table 4(b): Molar conductivities (Λ) of [Ni (HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) Complex in DMSO + Water in different temperatures.

X_1=0.000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	27.94	30.80	31.30	33.32	34.53
0.976	29.57	33.24	33.92	35.75	37.40
0.952	31.54	35.11	35.17	38.25	40.53
0.930	33.65	37.35	36.71	39.91	42.37
0.909	34.33	38.42	39.28	41.29	43.63
0.889	36.10	40.22	41.32	42.79	45.35
0.869	37.68	40.77	43.38	43.84	47.20
0.851	39.40	41.62	44.66	45.48	48.72
0.833	41.06	42.72	45.86	46.85	49.73
0.816	42.09	43.27	47.55	47.87	51.52

X_1=0.0250

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	25.30	25.55	26.44	27.40	29.51
0.976	26.71	27.44	27.74	29.46	31.54
0.952	28.36	28.51	29.59	31.57	33.69
0.930	29.86	29.35	31.57	33.72	35.94
0.909	30.97	30.09	33.01	34.93	37.34
0.889	31.78	31.14	34.27	35.28	38.08
0.869	33.23	32.00	34.90	36.66	39.89
0.851	33.40	32.21	35.39	37.02	40.22
0.833	33.76	32.64	35.52	38.04	41.64
0.816	34.94	33.31	36.04	38.86	43.25

X_1=0.0900

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	23.41	24.26	25.30	25.64	27.02
0.976	25.68	25.87	26.72	27.41	28.42
0.952	27.05	26.42	28.66	29.32	30.00
0.930	27.82	27.76	30.60	31.44	31.00
0.909	29.22	29.06	31.43	32.60	31.88
0.889	29.69	30.22	32.37	34.62	32.80
0.869	30.85	30.70	33.57	36.62	33.06
0.851	31.75	31.43	34.86	37.00	34.68
0.833	32.62	31.82	35.23	37.63	35.13
0.816	33.00	33.27	36.27	39.01	37.00

X_1=0.1874

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	20.58	22.07	24.77	25.03	26.52
0.976	22.16	23.95	26.74	26.80	28.60
0.952	23.58	25.03	28.38	28.60	30.90
0.930	25.20	25.80	30.07	30.61	32.41
0.909	25.88	26.44	31.82	30.91	33.64
0.889	26.84	26.60	33.64	32.58	35.17
0.869	27.36	27.17	33.92	34.24	36.91
0.851	28.10	27.50	35.58	36.02	38.21
0.833	29.30	28.58	37.07	37.57	39.87
0.816	30.59	29.26	38.93	38.40	40.59

X_1=0.3499

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	22.66	24.98	25.32	27.76	29.68
0.976	24.55	26.63	27.64	28.93	31.25
0.952	25.90	28.40	29.45	30.52	33.82
0.930	27.53	30.21	31.61	32.68	35.76
0.909	28.85	31.57	33.77	34.68	38.30
0.889	29.28	33.33	35.38	36.36	40.63
0.869	30.56	34.77	37.18	38.61	42.77
0.851	31.84	36.33	38.26	40.00	44.42
0.833	32.93	37.23	40.00	41.55	45.56
0.816	33.40	39.01	41.50	42.93	46.84

X_1=0.6749

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	24.00	26.71	28.62	29.79	30.16
0.976	26.28	28.97	30.96	32.13	32.62
0.952	28.17	30.94	33.23	34.56	34.93
0.930	30.05	32.91	35.63	37.03	37.18
0.909	32.00	35.03	37.79	38.30	39.60
0.889	33.81	37.18	40.16	39.82	42.07
0.869	35.54	39.20	40.94	41.55	44.72
0.851	36.63	39.73	41.43	42.26	45.60
0.833	38.00	40.00	43.42	42.70	46.30
0.816	39.13	41.79	45.72	43.08	47.00

X_1=1.000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	25.92	26.77	28.81	30.59	31.40
0.976	26.96	28.98	30.99	32.45	33.91
0.952	28.67	31.09	33.47	34.36	35.68
0.930	29.40	31.92	34.81	36.76	37.97
0.909	29.52	33.78	37.14	38.68	40.35
0.889	31.18	35.41	37.69	40.72	42.34
0.869	32.66	35.81	39.92	43.10	44.78
0.851	33.60	36.85	40.41	43.79	45.42
0.833	34.08	37.37	40.61	44.37	45.74
0.816	34.86	37.76	40.86	44.62	47.15

4.2.3. Evaluation of limiting molar conductance and association constant

The limiting equivalent conductance Λ_o and the observed association constant K_A were analyzed by using Shedlovsky extrapolation technique: $\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right)$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_o the limiting equivalent conductance and K_A the observed association constant.

Table 5(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 [Ni (HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) Complex have been measured in various DMSO +water mixtures at 288.15K-308.15K

X_{DMSO}	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=288.15K				T=293.15K			
0.0000	398.40	13.26	525.25	3.51	294.61	17.06	385.34	4.70
0.0250	450.13	19.71	615.13	3.34	347.44	24.32	495.48	3.65
0.0900	542.32	25.36	789.89	2.33	486.54	30.10	676.74	2.67
0.1874	504.44	31.15	759.38	2.43	450.31	36.41	655.55	2.76
0.3499	470.36	38.36	673.02	2.74	422.71	42.23	574.19	3.15
0.6749	401.28	42.15	555.28	3.32	385.68	48.94	464.13	3.91
1.0000	354.42	48.43	433.45	4.26	290.57	53.17	349.13	5.18
T=298.15K						T=303.15K		
0.0000	266.42	21.51	354.15	5.03	237.82	26.35	324.42	5.41
0.0250	309.71	27.44	445.14	4.00	282.52	29.12	425.34	4.12
0.0900	436.52	33.17	638.37	2.80	383.31	37.80	613.23	2.86
0.1874	400.36	39.25	630.57	2.83	323.64	42.22	596.46	3.00
0.3499	382.49	46.28	540.00	3.30	268.11	49.28	517.75	3.38
0.6749	300.26	50.17	433.32	4.12	228.73	54.24	412.60	4.24
1.0000	206.49	56.29	312.98	5.68	189.60	59.10	300.04	5.85

T=308.15K

X_{DMSO}	Λ_0 dm^3mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
0.0000	195.48	29.21	260.23	6.62
0.0250	233.29	32.42	364.25	4.74
0.0900	310.67	39.37	554.39	3.11
0.1874	270.33	45.11	536.48	3.22
0.3499	211.71	51.12	464.41	3.70
0.6749	191.62	57.35	362.13	4.76
1.0000	152.20	63.32	257.68	6.67

Table 5(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 [Ni (HL) (dien)]$(ClO_4)_2(H_2O)$ Complex have been measured in various DMSO + water mixtures at 288.15K-308.15K.

X_{DMSO}	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=288.15K				T=288.15K			
0.0000	354.86	29.40	505.12	3.65	265.96	36.40	370.21	4.88
0.0250	408.20	34.67	600.00	3.10	301.20	42.89	480.35	3.77
0.0900	595.22	39.70	749.76	2.46	442.16	56.73	635.61	2.85
0.1874	480.04	45.63	706.25	2.61	419.82	59.29	605.42	3.00
0.3499	408.42	52.90	609.89	3.02	352.64	63.81	518.06	3.50
0.6749	311.36	63.12	499.15	3.70	286.32	75.91	415.00	4.00
1.0000	205.28	69.71	390.32	4.72	196.68	79.31	320.00	5.65

T=298.15K					T=303.15K			
0.0000	229.31	43.81	341.00	5.00	200.40	52.64	309.19	5.65
0.0250	275.27	49.62	390.15	4.55	249.18	64.48	410.21	4.27
0.0900	378.42	56.92	487.68	3.65	342.27	72.86	578.10	3.03
0.1874	300.26	67.77	408.95	4.35	234.53	79.40	559.33	3.13
0.3499	246.29	73.63	352.50	4.98	219.82	84.32	479.62	3.65
0.6749	200.60	82.19	278.10	6.41	184.92	87.16	375.47	4.67
1.0000	102.45	86.40	191.62	9.26	138.51	91.37	280.91	6.25

T=308.15K

X_{DMSO}	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r
0.0000	163.57	59.68	245.00	7.04
0.0250	186.71	63.20	349.02	5.00
0.0900	280.26	68.41	529.16	3.26
0.1874	222.28	71.78	513.25	3.33
0.3499	194.18	86.93	438.18	4.00
0.6749	160.36	92.86	339.90	5.10
1.0000	96.20	98.20	248.45	6.94

From Table 5(a) and Table 5(b), the values of Λ_0 decreased invariable with increase in temperature in all solvents irrespective of X_{DMSO}, indicating less solvation or higher mobility of ions (Fig.4 & 5). This is attributed to the fact that increased in thermal energy results in greater bond-breaking in vibrational, rotational and translational energies of the molecules that lead to higher frequency and hence higher mobility of ions. The dependence of viscosity on composition of the solvent is remarkable and that the maximum deviation of relative viscosity from additive behaviour (calculated under the assumption of additive behavior of both binary systems) is achieved at $X_{DMSO} = 0.09$. Therefore, it follows that the most important is to investigate the influence of gradual replacement of water by DMSO on electrical conductivity and to compare it with behavior of viscosity of the system. Values of Λ_0 of salts increase up to the mole fraction $X_{DMSO} = 0.09$ at all temperatures as expected from Walden rule {Table 5(a) and 5(b)}.If change in solvation is reflected by the variation in $\Lambda_0\eta_0$ [Singh et.al, 2008] , the increase of the Walden product indicates the weak salvation of the ions. The decrease of the product indicates an increase of the hydrophobic salvation with increasing concentration of DMSO. As the DMSO content increases, progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture [Bag et.al, 2000] .Then effective radius(r) of ion or solute can be calculated as

$$\Lambda_0\eta_0 = 1/6\ \pi r T$$

The smaller $\Lambda_0\eta_0$ values in DMSO rich region may be due to the large effective radius of the cation, whereas the maximum values of $x_{DMSO} = 0.09$ correspond to minimum values of r. The Walden products in these are solvents increase and then decrease after passing through a maximum [Bag et.al 2001 (a) and (b)] .It is thus apparent that its variation with the solvent composition is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions of the mixed solvents and temperature of the solution. 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.,

$\Lambda_o = A.e^{-E^a/RT}$ or $\ln \Lambda_o = \ln A - E^a/RT$

Where A is the frequency factor, R is 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 are shown in Table 6a and Table 6b.

4.2.4. Evaluation of thermodynamic parameters

Table 6(a) : Thermodynamic parameters ΔG° (KJ mole^{-1}), ΔH° (KJ mole^{-1}), ΔS° (KJ mole^{-1}), Ea (KJ mole^{-1}) and 10^{-3} A of Shedlovsky techniques[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) Complex have been measured in various DMSO + water mixtures at different temperatures.

	288.15K	293.15K	298.15K	303.15K	308.15K
		X_1=0.0000			
ΔG°	- 8.11	- 8.76	- 9.36	- 9.98	- 10.44
ΔH°	- 1.60	- 1.73	- 1.87	- 1.96	- 2.08
10^{-3}xΔS°	22.60	24.00	25.12	26.46	27.13
E^a	11.30				
10^{-3}A	2.88				
		X_1=0.0250			
ΔG°	- 8.50	- 9.15	- 9.70	- 10.51	- 10.62
ΔH°	- 1.78	- 1.85	- 1.94	- 2.01	- 2.15
10^{-3}xΔS°	23.32	24.90	26.03	28.04	27.50
E^a	13.21				
10^{-3}A	3.02				
		X_1=0.0900			
ΔG°	- 8.83	- 9.82	- 10.05	- 10.80	- 10.80
ΔH°	- 1.84	- 1.92	- 2.07	- 2.17	- 2.27

10^{-3}x$\Delta S°$	24.26	26.95	26.77	28.47	27.70
E^a	15.13				
$10^{-3}A$	3.16				
		X_1= 0.1874			
$\Delta G°$	- 9.16	- 9.93	- 10.45	- 11.03	- 10.97
$\Delta H°$	- 1.96	- 2.00	- 2.16	- 2.28	- 2.36
10^{-3}x$\Delta S°$	25.00	27.05	27.80	28.86	28.00
E^a	17.04				
$10^{-3}A$	3.31				
		X_1=0.3499			
$\Delta G°$	- 9.49	- 10.10	- 10.68	- 11.14	- 11.45
$\Delta H°$	- 2.05	- 2.15	- 2.24	- 2.34	- 2.49
10^{-3}x$\Delta S°$	25.82	27.12	28.31	29.03	29.08
E^a	19.00				
$10^{-3}A$	3.47				
		X_1=0.6749			
$\Delta G°$	- 9.93	- 10.55	- 10.90	- 11.26	- 11.62
$\Delta H°$	- 2.17	- 2.27	- 2.32	- 2.40	- 2.52
10^{-3}x$\Delta S°$	26.93	28.24	28.78	29.23	29.53
E^a	20.87				
$10^{-3}A$	3.63				
		X_1=1.0000			
$\Delta G°$	- 10.15	- 10.66	- 11.07	- 11.38	- 11.80
$\Delta H°$	- 2.25	- 2.30	- 2.48	-2.51	- 2.68
10^{-3}x$\Delta S°$	27.42	28.52	28.81	29.33	29.60
E^a	22.78				
$10^{-3}A$	3.80				

Table 6(b) : Thermodynamic parameters ΔG° (KJ mole^{-1}), ΔH° (KJ mole^{-1}), ΔS° (KJ mole^{-1}), Ea(KJ mole^{-1}) and 10^{-3}A of Shedlovsky techniques for $[Ni(HL)(dien)](ClO_4)_2(H_2O)$ Complex have been measured in various DMSO + water mixtures at different temperatures.

	288.15K	293.15K	298.15K	303.15K	308.15K
		X_1=0.0000			
ΔG°	- 6.18	- 6.90	- 7.59	- 8.24	- 8.61
ΔH°	- 1.30	- 1.59	- 1.78	- 1.89	- 2.06
$10^{-3}x\Delta S^\circ$	16.93	18.11	19.49	20.95	21.26
E^a	9.57				
$10^{-3}A$	4.47				
		X_1=0.0250			
ΔG°	- 7.17	- 7.74	- 8.22	- 8.47	- 8.91
ΔH°	- 1.52	- 1.73	- 1.82	- 1.96	- 2.18
$10^{-3}x\Delta S^\circ$	19.61	20.50	21.46	21.47	21.84
E^a	11.48				
$10^{-3}A$	4.68				
		X_1=0.0900			
ΔG°	- 7.62	- 8.31	- 8.68	- 9.17	- 9.44
ΔH°	- 1.73	- 1.91	- 1.97	- 2.08	- 2.28
$10^{-3}x\Delta S^\circ$	20.44	21.83	22.51	23.39	23.24
E^a	13.40				
$10^{-3}A$	4.90				
		X_1=0.1874			
ΔG°	- 8.27	- 8.76	- 9.13	- 9.40	- 9.73
ΔH°	- 1.86	- 2.08	- 2.04	- 2.15	- 2.39
$10^{-3}x\Delta S^\circ$	22.24	22.79	23.78	23.91	23.82
E^a	15.32				

10^{-3}A	5.13				
		X_1=0.3499			
ΔG°	- 8.72	- 9.09	- 9.48	- 9.87	- 10.09
ΔH°	- 1.94	- 2.23	- 2.12	- 2.27	- 2.48
10^{-3}xΔS°	23.53	23.40	24.68	25.07	24.70
E^a	17.23				
10^{-3}A	5.37				
		X_1=0.6749			
ΔG°	- 8.94	- 9.54	- 9.70	- 10.04	- 10.38
ΔH°	- 2.09	- 2.34	- 2.23	- 2.38	- 2.57
10^{-3}xΔS°	23.77	24.56	25.05	25.27	25.34
E^a	19.15				
10^{-3}A	5.62				
		X_1=1.0000			
ΔG°	- 9.27	- 9.65	- 10.0	- 10.27	- 10.62
ΔH°	- 2.15	- 2.41	- 2.35	-2.48	- 2.69
10^{-3}xΔS°	24.70	24.70	25.66	25.70	25.73
E^a	21.06				
10^{-3}A	5.89				

The values of E^a increases with increase in X_1 throughout the mole fraction. The experimentally determined of K_As of the complex are found to increase with increase in x_1 which indicate an increased association as DMSO is added to water. Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between ions which is again indicated by negative value of enthalpy change. As expected that the values of ΔG^0 become more negative at higher percentage of DMSO 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 versus $1/T$. ΔH^0 values obtained are found to increase with the composition of the mixed solvents (Fig.8 & 9) The entropy of change is calculated from Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The values of these thermodynamic in nature in all solvent mixtures at all temperature are given in Table 6(a) and Table 6(b). At all temperatures, ΔG^0 values become more negative with increase in X_1 indicating that the ion pair formation is favored with lowering of permittivity of the medium.

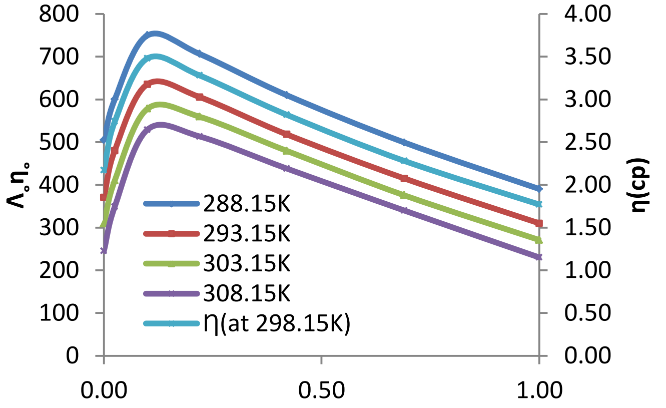

Fig 4. The value of Walden Product $\Lambda_\circ\eta_\circ$ and (η) for $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$ Complex in water + DMSO solvents

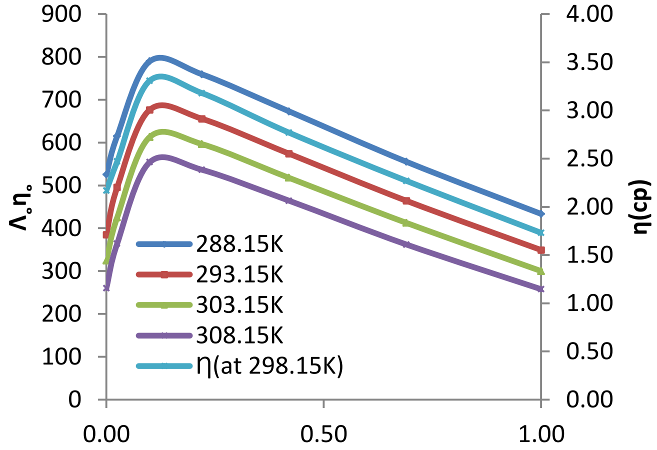

Fig 5. The value of Walden Product $\Lambda_{\circ}\eta_{\circ}$ and (η) for $[Ni(HL)(dien)](ClO_4)_2(H_2O)$ Complex in water + DMSO solvents

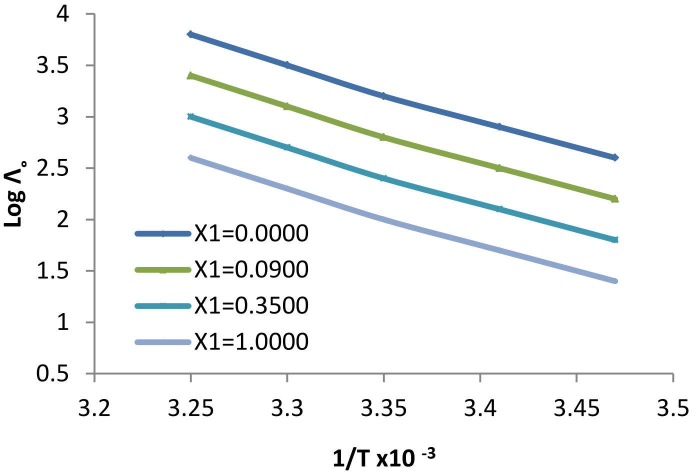

Fig 6. Log $\Lambda_{\circ}$ vs 1/T for $[Ni(HL)(bipy)(H_2O)](N0_3)(ClO_4)(H_2O)$

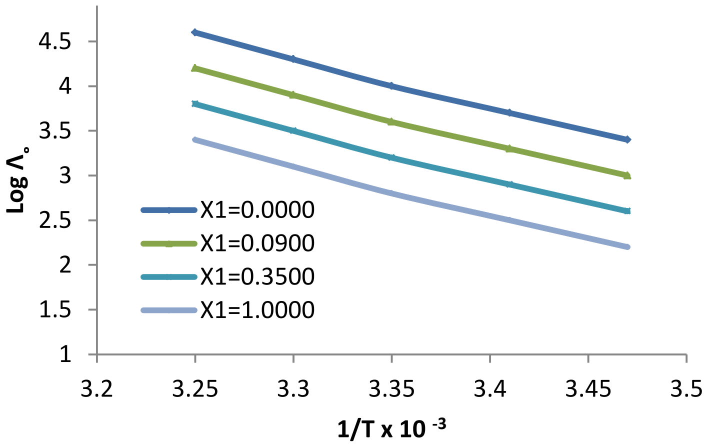

Fig 7. Log $\Lambda_{\circ}$ vs 1/T for $[Ni(HL)(dien)](ClO_4)_2(H_2O)$

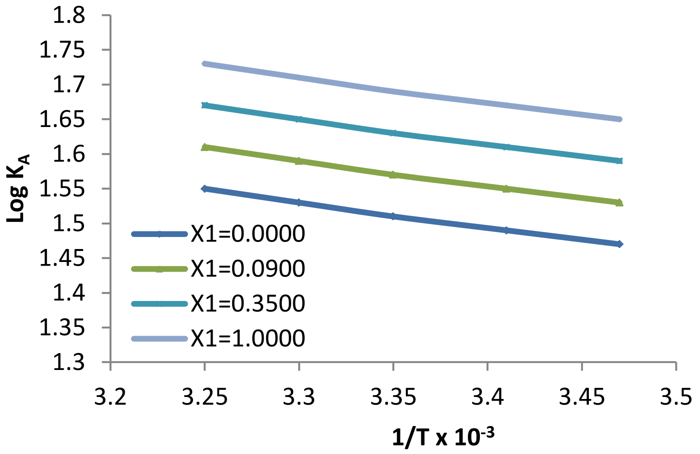

Fig 8. Log K_A vs 1/T for $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$

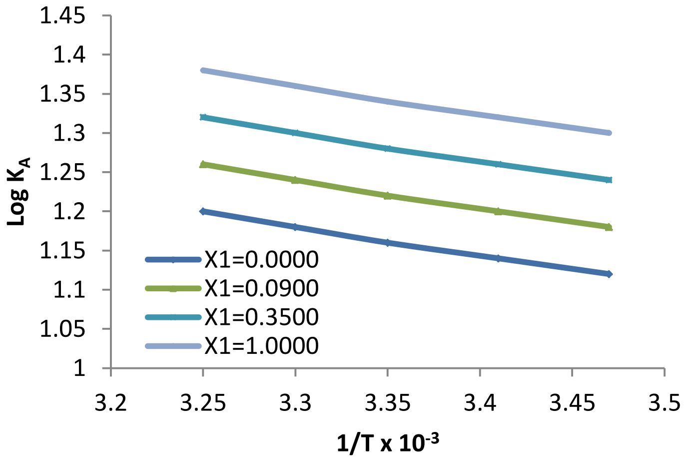

Fig 9. LogK_A vs 1/T for $[Ni(HL)(dien)](ClO_4)_2(H_2O)$

The experimentally determined of K_As of the complex are found to increase with increase in X_1 which indicate an increased association as DMSO is added to water. Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between ions which is again indicated by negative value of enthalpy change. As expected that the values of ΔG^0 become more negative at higher percentage of DMSO which indicate that ion-pair association are favored with lowering dielectric constant of the medium. The value of E^a increases with increase in X_1 indicating that there is an increased association on adding DMSO in water. Therefore, among the two complexes it shows that in DMSO rich region $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$ complex requires more higher activation energy processes as DMSO.

4.3. Study of Ion Pair Formation of Pentaammine Metal Complexes in Binary Mixtures of Water + Methanol Solution at Different Temperatures

4.3.1. Introduction

Studies of electrolytic conductance provide very important information concerning ions in solution. Mixed solvents are suitable for such studies because even a small change in solvent composition may lead to a significant difference in behavior of the dissolved electrolyte. The formation of pairs and higher aggregates of oppositely charged ions occurs in a medium of low relative electrical permittivity. Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore the ion-ion and ion-solvent interactions can be better studied .Furthermore different quantities strongly influenced by solvent properties can be derived from concentration-dependence of the electrolyte conductivity.Consequently a number of conductometric [Janx et al., 1973] and related studies of different electrolytes in non-aqueous solvents,specially mixed organic solvents,have been made for their optimal use in high energy batteries [Aurbach, 1999] and for understanding organic reaction mechanisms [Kromet et al., 1993]. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions [Das et al., 2002], [Das et al., 2003], which in its turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions.Thus extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years [Das et al., 2000] to examine the nature and magnitude of ion-ion and ion-solvent interactions. Conductivity measurements should cover a wider temperature range to make thermodynamics of these processes better understood.

Thus in this study, it was attempted to obtain some information on the association of perchlorate in methanol solutions at different temperatures ranging from 15-35^{0}C by Shedlovsky technique. The thermodynamic functions ($\Delta H°$,$\Delta G°$, $\Delta S°$ and E^a), effective radius (r) and Walden product ($\Lambda_0\eta_0$) were calculated and compared according to interactions of solvent at different temperatures.

4.3.2. Experimental

4.3.2.1. Preparation of ligands and compounds

The Metal (II) Complexes were synthesized and characterized according from the literature 3.7.2. (iv) and (v) [Schlessinger GG, 1962].

4.3.2.2. Conductivity measurements

The purity of the sample was checked through conventional analysis and spectral measurements.The electric conductivities were measured by Eutech Insruments, PC 700 with a dip type immersion conductivity cell were used. The solutions of different concentrations (1 x10^{-4}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water of low specific conductance (< $2x10^{-6}$ S cm^{-1}) and conductivity measurements were carried out over the temperature range of 15^{o}C – 35^o C. All the dielectric constants and viscosities were obtained from literature [Lalrosanga, 2011]. The temperature control in the ranges of 15-35^{0}C were made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a METLER TOLEDO Balance, model ME104E (max=210g; d=0.1mg). The observed conductivities were corrected for the conductivity of the solvent. The accuracy of the temperature of the thermostat was ± 0.01^{0}C.

Table 7(a): Molar conductivities (Λ) of Pentaammine fluoronickel(II) fluoride Complex in Methanol + Water in different temperatures.

X_1=0.000

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	275.15	282.06	294.28	307.03	319.02
0.976	275.45	282.54	294.79	307.46	319.28
0.952	275.68	283.34	295.81	308.19	320.01
0.930	276.21	283.57	296.39	309.43	321.18
0.909	277.17	284.29	297.28	309.79	321.49
0.889	277.47	284.63	298.18	310.81	322.28
0.869	277.71	285.37	299.38	310.91	322.58
0.851	278.43	285.58	299.83	311.37	323.10
0.833	279.29	286.69	300.17	312.10	324.38
0.816	280.47	287.48	301.28	312.48	324.81

X_1=0.0588

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	248.38	271.18	284.00	293.18	317.13
0.976	248.75	271.49	284.61	293.78	317.38
0.952	249.29	272.48	285.27	294.87	317.47
0.930	250.27	273.27	286.49	295.28	318.19
0.909	251.17	274.38	287.41	296.40	318.58
0.889	252.39	274.52	288.64	297.54	319.18
0.869	252.28	275.71	289.48	298.28	320.76
0.851	252.43	276.63	290.18	298.75	320.47
0.833	253.27	277.83	290.72	299.08	321.48
0.816	253.51	278.61	291.72	300.17	321.26

X_1=0.1942

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	245.00	251.00	273.39	284.00	295.00
0.976	245.61	251.78	273.79	284.61	295.75
0.952	246.24	252.64	273.61	285.26	296.79
0.930	247.48	253.97	274.49	286.34	297.21
0.909	248.42	254.38	275.17	287.23	298.43
0.889	249.39	254.76	275.29	288.10	299.23
0.869	250.18	255.86	276.58	289.05	300.17
0.851	250.29	256.41	277.29	290.79	301.72
0.833	251.69	257.89	278.19	291.93	302.76
0.816	252.82	258.09	279.72	292.47	303.31

X_1=0.3600

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	237.28	246.28	258.17	269.00	289.18
0.976	237.53	246.61	258.77	269.27	289.65
0.952	238.09	247.37	259.59	270.00	290.54
0.930	238.28	248.57	260.93	270.39	291.21
0.909	239.12	249.42	261.02	271.19	292.56
0.889	239.80	250.39	261.72	272.38	292.96
0.869	240.60	251.05	262.92	273.48	293.83
0.851	241.68	252.10	263.49	274.18	294.65
0.833	242.09	253.78	263.89	275.72	295.21
0.816	243.19	254.75	264.00	276.30	296.39

X_1=0.5676

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	315.00	328.00	337.05	341.48	357.19
0.976	315.13	328.60	337.27	342.01	358.23
0.952	316.45	329.29	338.60	343.10	359.29
0.930	316.76	330.28	339.12	344.40	360.43
0.909	317.48	331.38	339.56	345.53	361.61
0.889	317.18	331.84	340.32	346.54	362.45
0.869	318.37	332.28	340.75	347.39	363.78
0.851	319.68	333.75	340.98	348.28	364.32
0.833	319.91	334.73	341.76	349.75	365.48
0.816	320.20	335.20	342.34	350.19	366.17

X_1=0.8351

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	328.00	338.74	347.56	351.19	359.00
0.976	328.85	338.43	348.28	352.38	359.51
0.952	329.57	339.82	349.36	353.39	360.19
0.930	330.28	340.84	349.69	354.15	360.83
0.909	330.83	341.73	350.91	355.63	360.57
0.889	331.18	342.33	351.28	356.73	361.68
0.869	331.65	343.96	352.50	357.28	362.92
0.851	332.18	344.99	352.85	358.18	363.36
0.833	333.38	345.75	353.27	358.23	363.71
0.816	334.15	346.51	354.10	359.31	364.33

X_1=1.000

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	358.35	363.30	374.29	385.19	409.83
0.976	358.18	363.85	375.61	385.65	409.58
0.952	359.78	364.23	376.65	386.80	410.18
0.930	360.43	364.84	377.54	387.92	411.27
0.909	361.94	365.71	378.29	388.56	412.54
0.889	362.75	366.65	379.67	389.37	413.75
0.869	363.71	367.29	380.18	389.72	414.86
0.851	364.31	368.56	381.28	390.19	415.17
0.833	365.94	369.67	381.65	391.25	416.71
0.816	366.28	370.19	382.10	392.23	417.31

Table 7(b): Molar conductivities (Λ) of Pentaammine fluorocobalt(II) fluoride Complex in Methanol + Water in different temperatures

X_1=0.000

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	262.00	275.00	288.00	301.00	313.00
0.976	262.30	275.61	288.93	301.23	313.52
0.952	262.61	276.26	289.92	302.52	314.08
0.930	263.44	276.34	290.32	303.23	315.05
0.909	264.03	277.23	290.43	303.63	315.73
0.889	264.34	277.84	291.34	304.84	316.09
0.869	264.67	278.48	292.29	304.95	316.46
0.851	265.57	279.67	292.60	305.52	317.27
0.833	266.51	279.71	293.00	306.12	318.13
0.816	267.16	280.64	294.12	306.37	318.63

X_1=0.0588

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	241.00	263.00	276.00	288.00	301.00
0.976	241.80	263.32	276.64	288.93	301.23
0.952	242.65	263.65	277.31	289.92	302.52
0.930	243.01	264.52	277.41	290.32	303.23
0.909	243.12	265.13	278.32	290.43	303.63
0.889	244.10	265.47	278.96	291.43	304.84
0.869	245.11	265.82	279.63	292.29	304.95
0.851	245.59	266.74	280.00	292.60	305.52
0.833	246.10	267.71	280.91	293.00	306.12
0.816	246.32	268.38	281.86	294.12	306.37

X_1=0.1942

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	233.00	240.00	262.00	275.00	287.00
0.976	233.61	240.78	262.30	275.61	287.91
0.952	234.24	241.59	262.61	275.26	288.86
0.930	234.41	241.93	263.44	276.34	289.25
0.909	235.42	242.02	264.03	277.23	289.33
0.889	236.22	242.96	264.34	277.84	290.21
0.869	237.05	243.95	264.67	278.48	291.14
0.851	237.36	244.41	265.57	278.50	291.42
0.833	237.69	244.89	266.51	279.71	291.72
0.816	237.75	245.09	268.38	280.64	292.89

X_1=0.3600

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	230.00	233.00	240.00	261.00	283.00
0.976	230.53	233.61	240.77	261.27	283.81
0.952	231.09	234.24	241.59	262.00	284.66
0.930	231.18	234.41	241.93	262.36	285.00
0.909	232.12	235.42	242.02	263.00	286.13
0.889	232.84	236.22	242.96	263.22	287.96
0.869	233.60	237.05	243.95	264.00	288.83
0.851	233.84	237.36	244.41	264.39	289.07
0.833	234.09	237.69	244.89	265.31	289.31
0.816	235.29	237.75	245.00	267.16	290.44

X_1=0.5676

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	297.00	316.00	323.00	333.00	343.00
0.976	297.13	316.60	323.80	334.01	34.23
0.952	297.27	317.23	324.60	334.10	344.54
0.930	297.85	318.28	325.00	334.40	345.16
0.909	298.13	319.03	325.63	335.53	345.43
0.889	299.33	319.46	326.21	336.33	346.45
0.869	300.40	319.91	327.00	337.16	347.52
0.851	301.00	320.80	327.85	338.42	348.00
0.833	302.52	321.73	328.93	338.53	348.14
0.816	303.00	322.30	329.66	339.46	349.70

X_1=0.8351

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	315.00	324.00	334.00	344.00	354.00
0.976	315.57	324.79	335.04	344.26	354.51
0.952	316.18	325.63	335.10	345.59	355.04
0.930	317.20	325.81	335.48	346.24	355.91
0.909	317.93	326.73	336.63	346.53	356.44
0.889	318.33	327.33	337.46	347.58	357.71
0.869	318.76	327.96	338.32	348.68	357.88
0.851	319.62	328.99	339.60	349.00	358.40
0.833	320.53	329.97	339.73	349.34	358.94
0.816	322.30	330.88	340.69	350.49	360.29

X_1=1.000

Conc.x10^{-3}	283.15K	288.15K	293.15K	298.15K	303.15K
0.001	346.00	354.00	366.00	369.00	400.00
0.976	346.31	354.51	366.80	369.88	400.61
0.952	347.69	355.04	367.65	370.80	401.26
0.930	348.39	355.91	367.74	370.97	402.15
0.909	348.73	356.44	368.54	371.84	402.64
0.889	349.83	357.71	368.95	372.33	403.82
0.869	350.98	357.88	369.39	372.84	403.91
0.851	351.35	358.40	370.15	373.68	403.23
0.833	351.74	358.94	370.95	374.55	404.56
0.816	352.94	361.52	371.32	375.00	405.64

4.3.3. Evaluation of limiting molar conductance and association constant

The limiting equivalent conductance Λ_o and the observed association constant K_A were analyzed by using Shedlovsky extrapolation technique:

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

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_o the limiting equivalent conductance and K_A the observed association constant.

Table 8(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 Pentaammine fluoronickel(II) fluoride have been measured in various methanol + water mixtures at 283.15K-303.15K.

$X_{Methanol}$	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=288.15K				T=293.15K			
0.0000	329.06	475.85	394.87	4.66	356.18	420.17	356.18	5.08
0.0588	321.42	482.85	464.77	3.96	334.65	385.85	419.32	4.32
0.1942	316.03	503.43	619.10	2.97	325.33	408.95	546.55	3.02
0.3600	290.52	556.68	602.25	3.06	311.83	412.84	560.67	3.23
0.5676	309.59	585.19	522.90	3.52	315.15	470.34	476.82	3.79
0.8351	318.64	633.01	307.49	5.99	330.12	481.27	288.52	6.27
1.0000	326.11	698.43	208.06	8.85	341.90	554.64	202.06	11.16

	T=298.15K				T=303.15K			
0.0000	360.45	419.89	288.36	6.17	367.48	409.48	257.24	6.81
0.0588	335.05	389.95	367.88	4.84	351.72	351.55	442.11	3.96
0.1942	330.45	377.61	477.17	3.73	340.25	358.05	427.69	4.09
0.3600	325.48	451.04	511.65	3.48	339.76	396.83	463.09	3.78
0.5676	329.22	467.03	440.82	4.04	341.37	428.55	404.18	4.33
0.8351	330.85	486.52	266.33	6.68	358.52	452.04	260.28	6.73
1.0000	357.86	508.98	197.90	8.99	372.49	485.43	191.83	9.13

	T=308.15K			
0.0000	371.20	397.43	222.72	7.73
0.0588	358.59	379.68	313.77	5.49
0.1942	351.33	357.19	390.33	4.41
0.3600	347.44	376.30	416.23	4.14
0.5676	349.18	402.41	369.43	4.66
0.8351	354.93	409.18	238.87	7.21
1.0000	370.25	420.88	178.83	9.63

Table 8(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 Pentaammine fluorocobalt(II) fluoride have been measured in various methanol + water mixtures at 283.15K-303.15K.

$X_{Methanol}$	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=288.15K				T=293.15K			
0.0000	347.78	444.38	417.34	4.41	356.48	428.98	385.00	4.70
0.0588	338.28	470.67	489.15	3.76	347.57	447.07	435.51	4.16
0.1942	328.84	500.35	644.20	2.86	330.54	471.48	555.31	3.26
0.3600	312.55	555.92	647.92	2.84	323.13	489.41	580.98	3.12
0.5676	321.68	570.40	543.32	3.39	328.66	532.69	497.26	3.64
0.8351	336.62	590.24	324.84	5.67	345.87	556.78	302.29	5.98
1.0000	339.50	613.01	216.60	8.50	350.47	566.86	207.13	8.74
		T=298.15K				T=303.15K		
0.0000	368.89	412.37	295.11	6.03	381.63	397.52	267.14	6.55
0.0588	360.28	436.10	395.59	4.50	374.61	433.24	367.87	4.76
0.1942	347.58	467.88	501.90	3.55	350.25	459.23	440.26	3.98
0.3600	330.66	485.18	519.80	3.42	343.92	477.15	468.76	3.73
0.5676	342.77	489.65	458.97	3.88	348.03	500.52	412.07	4.25
0.8351	351.00	536.63	282.55	6.30	362.38	536.62	243.88	7.18
1.0000	367.32	560.53	203.13	8.76	376.89	598.25	182.04	9.62

		T=308.15K		
0.0000	385.13	387.79	231.08	7.45
0.0588	377.75	368.10	330.53	5.21
0.1942	367.84	445.15	408.67	4.21
0.3600	360.25	471.67	431.58	3.99
0.5676	369.63	521.90	391.07	4.40
0.8351	374.89	548.90	252.30	6.83
1.0000	380.29	562.19	183.68	9.38

Table 8(a) & 8(b) shows that for both the complex salts studied, the limiting molar conductances (Λ_0) increase as the temperature increases but decrease as the mole fraction of methanol in the solvent mixtures increases up to 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 up to 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 [Singh NM et al., 2008] . 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 .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

$$\Lambda_0\eta_0 = 1/6\ \pi r T$$

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 up to $x_{\mathrm{MeOH}} = 0.36$ 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 $x_{\mathrm{MeOH}} = 0.36$ correspond to minimum values of r [Bag GC et al., 2001] 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.,

$$\Lambda_o = A.e^{-E^a/RT} \text{ or } \ln \Lambda_o = \ln A - E^a/RT$$

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 and are shown in Fig 12 & 13

4.3.4. Evaluation of thermodynamic parameters

Table 9(a): Thermodynamic parameters ΔG°(KJ mole^{-1}), ΔH°(KJ mole^{-1}), ΔS°(KJ mole^{-1}), Ea(KJ mole^{-1}) and 10^{-3} A of Shedlovsky techniques for Pentaammine fluorocobalt(II) fluoride have been measured in various methanol + water mixtures at different temperatures.

$X_{Methanol}$	288.15K	293.15K	298.15K	303.15K	308.15K
			X_1=0.0000		
ΔG^0	-13.46	-13.34	-13.30	-13.21	-13.15
ΔH^0	-23.27				
$10^3 \Delta S^0$	-38.21	-37.97	-37.46	-37.14	-36.73
E^a	6.93				
$10^{-3}A$	1.31				
			X_1=0.0588		
ΔG^0	-13.52	-13.49	-13.36	-13.30	-13.26
ΔH^0	-23.21				
$10^3 \Delta S^0$	-37.09	-36.57	-36.39	-35.99	-35.53
E^a	7.12				
$10^{-3}A$	1.36				
			X_1=0.1942		
ΔG^0	-13.68	-13.57	-13.43	-13.38	-13.32
ΔH^0	-22.73				
$10^3 \Delta S^0$	-34.88	-34.66	-34.55	-34.14	-33.78
E^a	7.31				
$10^{-3}A$	1. 41				

			$X_1=0.3600$		
ΔG^0	-14.07	-14.03	-13.90	-13.70	-13.50
ΔH^0	-22.18				
$10^3\,\Delta S^0$	-31.61	-31.21	-31.12	-31.27	-31.41
E^a	7.50				
$10^{-3}A$	1.46				
			$X_1=0.5676$		
ΔG^0	-14.40	-14.32	-14.15	-14.03	-15.83
ΔH^0	-21.75				
$10^3\,\Delta S^0$	-28.98	-28.76	-28.84	-28.76	-28.95
E^a	7.27				
$10^{-3}A$	1.40				
			$X_1=0.8351$		
ΔG^0	-14.56	-14.48	-14.38	-14.18	-13.97
ΔH^0	-21.42				
$10^3\,\Delta S^0$	-27.28	-27.08	-26.97	-27.18	-27.42
E^a	7.08				
$10^{-3}A$	1.32				
			$X_1=1.0000$		
ΔG^0	-14.90	-14.83	-14.60	-14.36	-14.15
ΔH^0	-21.20				
$10^3\,\Delta S^0$	-25.23	-25.14	-25.50	-25.86	-26.12
E^a	6.89				
$10^{-3}A$	1.29				

Table 9(b): Thermodynamic parameters ΔG°(KJ mole^{-1}), ΔH°(KJ mole^{-1}), ΔS°(KJ mole^{-1}), Ea(KJ mole^{-1}) and 10^{-3} A of Shedlovsky techniques for Pentaammine fluoronickel(II) fluoride have been measured in various methanol + water mixtures at different temperatures.

$X_{Methanol}$	288.15K	293.15K	298.15K	303.15K	308.15K
			X_1=0.0000		
ΔG^0	-13.29	-13.16	-12.98	-12.64	-12.45
ΔH^0	-22.57				
$10^3 \Delta S^0$	-32.20	-32.10	-32.16	-32.76	-32.84
E^a	6.51				
$10^{-3}A$	1.36				
			X_1=0.0588		
ΔG^0	-13.41	-13.37	-13.26	-12.76	-12.56
ΔH^0	-22.32				
$10^3 \Delta S^0$	-30.92	-30.53	-30.39	-31.53	-31.67
E^a	6.89				
$10^{-3}A$	1.41				
			X_1=0.1942		
ΔG^0	-13.68	-13.64	-13.57	-12.98	-12.70
ΔH^0	-21.86				
$10^3 \Delta S^0$	-28.39	-28.04	-27.80	-29.29	-29.72
E^a	7.27				
$10^{-3}A$	1. 45				

			X_1=0.3600		
ΔG^0	-14.07	-14.03	-13.70	-13.16	-12.94
ΔH^0	-21.45				
$10^3\,\Delta S^0$	-25.61	-26.06	-25.99	-27.35	-27.62
E^a	7.66				
$10^{-3}A$	1.50				
			X_1=0.5676		
ΔG^0	-14.18	-14.14	-14.03	-13.39	-13.21
ΔH^0	-21.10				
$10^3\,\Delta S^0$	-24.01	-26.06	-23.71	-25.43	-25.60
E^a	8.04				
$10^{-3}A$	1.43				
			X_1=0.8351		
ΔG^0	-14.73	-14.31	-14.26	-13.68	-13.48
ΔH^0	-20.65				
$10^3\,\Delta S^0$	-20.54	-23.74	-21.43	-22.99	-23.27
E^a	8.42				
$10^{-3}A$	1.38				
			X_1=1.0000		
ΔG^0	-14.95	-14.78	-14.58	-14.09	-13.96
ΔH^0	-20.21				
$10^3\,\Delta S^0$	-18.25	-18.52	-18.88	-23.27	-20.28
E^a	8.81				
$10^{-3}A$	1.33				

The negative values of ΔG^0 and ΔH^0 from Table 9(a) and 9(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 unfavoured the ion-association process and thus favouring ion solvation process. The values of E^a increases with increase in X_1 up to about X_1=0.3600 and thereafter decreases rapidly. It follows that in water rich region up to X_1=0.36, the chosen complexes 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 $1/T$. ΔH^0 values obtained are found to increase with the composition of the mixed solvents. The entropy change is calculated from Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0$-TΔS^0. The values of these thermodynamic parameters in all solvent mixtures at all temperature are given in Table 9(a) and 9(b) .

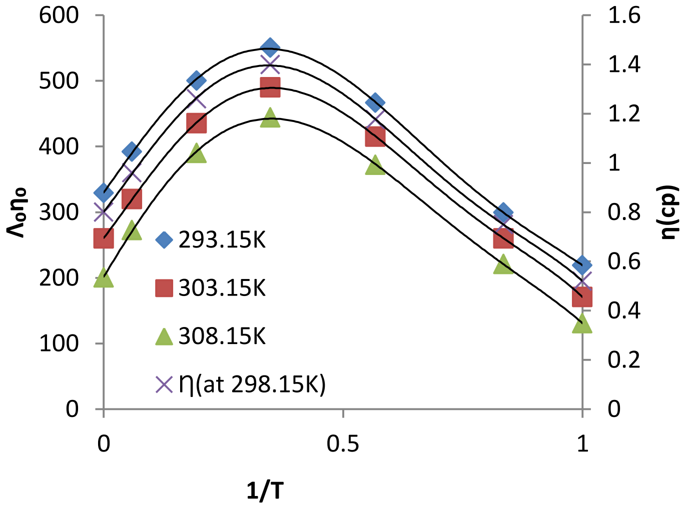

Fig10: The value of Walden product $\Lambda_o\eta_o$ and (η) for Ni (II) Complex as a function of X_{MeOH} in methanol + water solvents

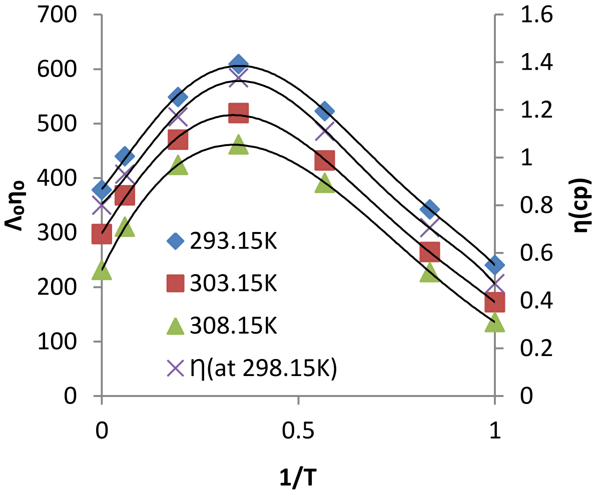

Fig 11: The value of Walden product $\Lambda_0\eta$ and (η) for Co (II) Complex as a function of XMeOH in methanol + water solvents

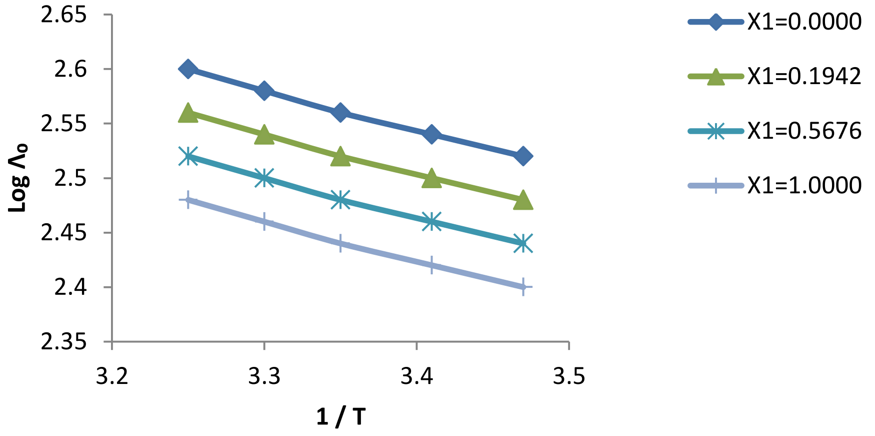

Fig 12: Plot of Log Λ_o vs 1/T for [Ni(NH3)5F]F2 Complex

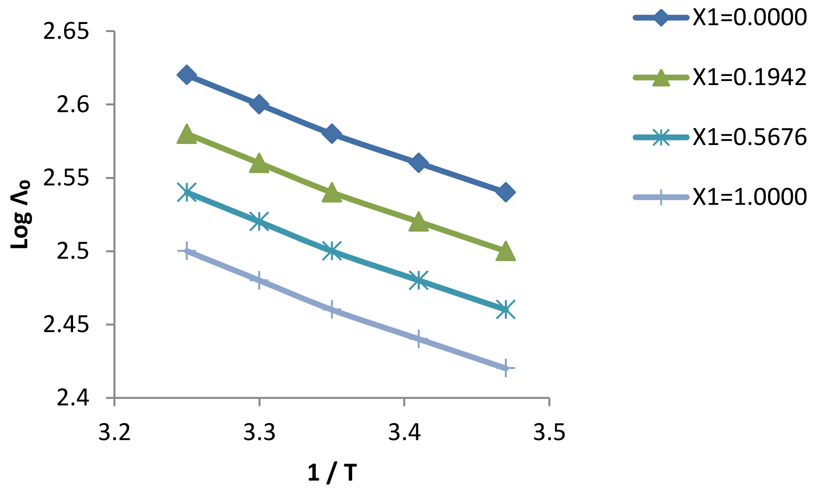

Fig 13: Plot of Log Λ_o vs 1/T for $[Co(NH_3)_5F]F_2$ Complex

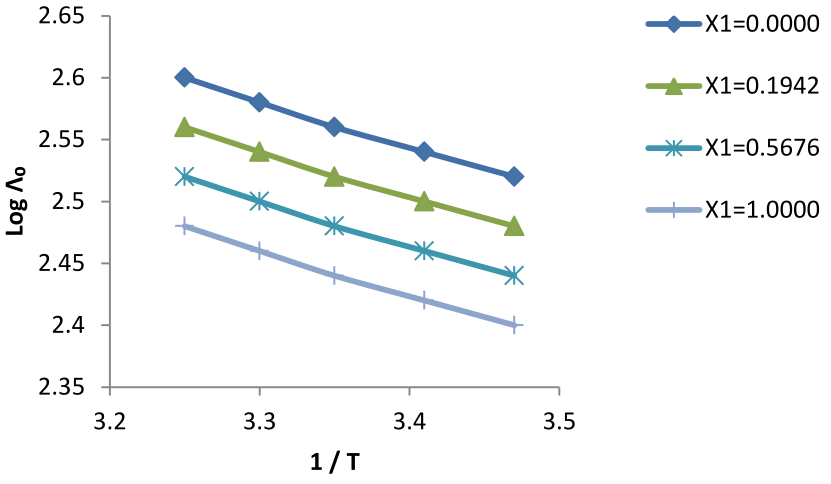

Fig 14: Plot of Log Λ_o vs 1/T for [Ni(NH3)5F]F2 Complex

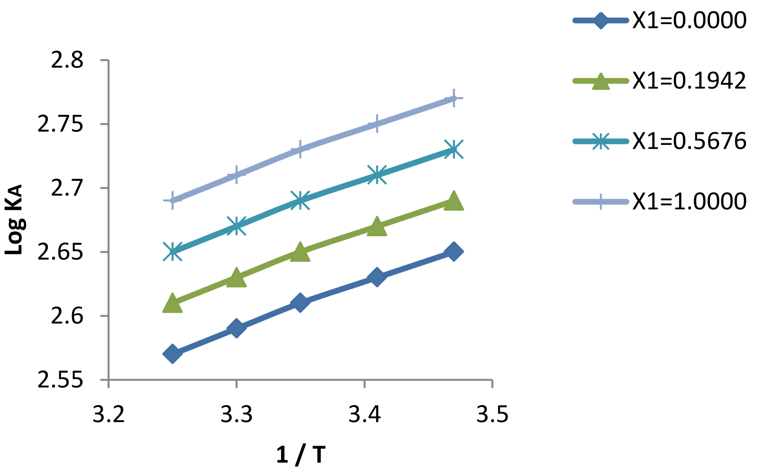

Fig 15: Plot of Log K_A vs 1/T for $[Co(NH_3)_5F]F_2$ Complex

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 favoured with lowering dielectric constant of the medium. The values of E^a increased with increase in X_1 up to about X_1=0.3600 and thereafter decreased rapidly. It follows that in water rich region up to 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. Thermodynamics studies of metal perchlorates in methanol + water mixtures at different temperatures

4.4.1. Introduction

The concept of ion association in electrolyte solutions was introduced by (Bjerrum et al ., 1926) so as to improve Debye-Huckel theory. According to this concept, electrolyte is considered to be a mixture of free ions and ion clusters which are assumed to be taken part in chemical equilibrium according to the corresponding mass action law [Debye et al ., 1923] . The phenomenon of ion association has an important effect in thermodynamic, transport, dielectric and other properties of electrolyte solutions. Several experimental techniques have been applied to study the thermodynamic and various interactions in electrolytic solutions [Yokoyama et al .,1994; Das et al ., 1995; Parmar et al ., 1996; Ue et al ., 1996; Ue et al ., 1997; Seleem et al ., 2002]. Ion pairing between the metal ions and ligands has usually investigated by means of conductance technique [Ue et al ., 1995; Bakr et al ., 1999; Bakr et al ., 2001] . The conductance behavior of many electrolytes in mixed solvent systems is reported to be influenced by number of factors like density, viscosity, dielectric constant of the medium, ion solvent interactions and solvent-solvent interactions. Ion-solvent interactions stabilizes the ion by solvating it. The solvation of dissolved ions determines many of the properties of electrolyte solutions, including their redox potential, complexation and kinetic behaviour. Conductance studies in binary solvent mixtures not only give an idea about ion-solvent and solvent-solvent interactions but also the preferential solvation of an ion .

Methanol is polar solvents and often used to dissolve salts. They have high dielectric constant and high polarity. Alcohols associate in liquids by hydrogen bond . Perchlorates are often used in electrochemical studies as an inert additive for maintaining constant ionic strength since the perchlorate anion is one of the least prone to complex formation and has no effect on chemical equilibria. The ion association of perchlorates in non aqueous solvents with lower dielectric solvents may be significant and must be taken into account. Thus in this study, it was attempted to obtain some information on the association of perchlorate in methanol solutions at different temperatures ranging from 15-35^{0}C by Shedlovsky technique. The thermodynamic functions ($\Delta H°$, $\Delta G°$, $\Delta S°$ and E^a), effective radius (r) and Walden product ($\Lambda_0\eta_0$) were calculated and compared according to interactions of solvent at different temperatures.

4.4.2. Experimental

4.4.2.1. Preparations of ligands and compounds

The Inorganic salt selected for the present work i.e., pentaammine chloronickel (II) perchlorate salt synthesized according from the literature 3.7.2. (vi) [Schlessinger et al ., 1962].

4.4.2.2. Conductivity measurements

The purity of the sample was checked through conventional analysis and spectral measurements. The electric conductivities were measured by Eutech Insruments, PC 700 with a dip type immersion conductivity cell were used. The solutions of different concentrations (1 x10^{-3}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water of low specific conductance (< 2x10^{-6} S cm^{-1}) and conductivity measurements were carried out over the temperature range of 15^{o}C – 35^o C. All the dielectric constants and viscosities were obtained from literature [Lalrosanga et al ., 2011]. The temperature control in the ranges of 15-35^{0}C were made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a

METTER Balance, model TB-214(max=210g; d=0.1mg). All calculations were done on IBM-PC-AT/386 using a basic programmed. The observed conductivities were corrected for the conductivity of the solvent. The accuracy of the temperature of the thermostat was ± 0.01-^{0}C.

Table 10: Molar conductivities (Λ) of Pentaammine chloronickel(II) perchlorate Complex in Methanol + Water in different temperatures.

X_1=0.000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	269.10	275.28	281.00	298.00	310.29
0.976	269.38	275.61	281.91	298.23	310.82
0.952	269.54	276.29	282.42	299.52	311.00
0.930	270.14	276.76	283.36	300.23	312.28
0.909	270.33	277.23	283.63	300.63	312.73
0.889	270.39	277.61	284.38	301.84	313.02
0.869	270.75	278.19	285.18	301.95	314.42
0.851	271.41	279.47	285.87	302.52	315.57
0.833	271.63	279.82	286.30	303.12	316.39
0.816	277.28	280.32	287.46	303.37	316.75

X_1=0.0588

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	251.39	260.08	266.23	278.00	300.15
0.976	251.87	260.52	266.69	278.93	300.47
0.952	252.65	261.75	267.19	279.92	301.68
0.930	253.54	262.52	267.35	280.32	302.23
0.909	253.97	263.13	268.32	280.43	302.78
0.889	254.30	264.47	268.91	281.43	303.84
0.869	255.19	265.82	269.67	282.29	304.63

0.851	255.87	266.74	270.17	282.60	305.52
0.833	256.79	267.71	270.41	283.00	306.37
0.816	256.91	268.38	271.67	284.12	306.82

X_1=0.1942

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	230.49	236.00	252.00	270.00	281.00
0.976	230.82	236.72	252.30	270.61	281.91
0.952	231.17	237.51	253.61	271.46	282.86
0.930	231.47	238.93	254.44	272.34	283.25
0.909	232.57	239.02	255.03	273.29	284.33
0.889	233.28	240.46	256.34	273.84	285.21
0.869	234.50	241.35	257.67	274.78	286.14
0.851	234.91	242.49	258.57	275.50	287.42
0.833	235.79	242.91	259.51	276.91	288.72
0.816	236.36	243.39	260.38	277.80	289.89

X_1=0.3600

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	290.20	231.38	240.00	261.40	282.00
0.976	290.58	231.69	240.71	261.87	282.81
0.952	291.29	232.28	241.59	262.06	283.61
0.930	291.79	232.71	241.96	262.38	284.20
0.909	292.47	233.70	242.22	263.20	285.23
0.889	292.89	234.36	242.78	263.62	286.90
0.869	293.50	235.48	243.92	264.17	287.57
0.851	293.92	236.39	244.31	264.46	288.46
0.833	294.38	237.64	244.89	265.79	289.63
0.816	295.29	237.83	245.50	266.32	290.58

X_1=0.5676

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	297.20	314.28	323.00	330.00	343.18
0.976	297.67	314.59	323.80	331.01	344.29
0.952	298.27	315.23	324.60	332.10	344.71
0.930	298.85	316.28	325.27	332.40	345.35
0.909	299.45	317.03	325.82	333.59	345.68
0.889	299.71	317.46	326.76	334.33	346.51
0.869	300.48	318.91	327.36	335.19	347.78
0.851	301.37	319.80	327.92	335.42	348.26
0.833	302.68	320.73	328.65	336.83	348.58
0.816	303.82	321.30	329.84	337.46	349.35

X_1=0.8351

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	315.23	321.00	332.00	340.28	354.29
0.976	315.67	321.60	333.04	340.26	354.46
0.952	316.25	322.63	334.10	341.50	355.04
0.930	317.29	322.81	334.48	342.24	355.91
0.909	317.97	323.72	335.58	343.23	356.44
0.889	318.33	324.23	336.32	344.43	357.71
0.869	318.80	324.78	337.41	344.52	357.91
0.851	319.67	325.65	337.67	345.14	358.57
0.833	320.73	326.97	338.87	345.57	358.94
0.816	321.54	327.74	339.68	346.69	359.34

X_1=1.000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K
0.001	340.30	352.00	366.10	369.00	401.26
0.976	340.71	352.51	366.80	369.88	402.49
0.952	341.69	353.04	367.21	370.80	403.26
0.930	342.39	353.71	367.44	370.89	404.15
0.909	342.73	354.44	368.50	371.93	404.52
0.889	343.83	354.51	368.95	372.45	405.82
0.869	344.68	355.28	369.32	372.84	405.86
0.851	345.35	356.40	370.15	373.72	406.23
0.833	346.14	356.14	370.29	374.79	406.48
0.816	346.94	357.52	371.12	375.21	407.64

4.4.3. Evaluation of limiting molar conductance and association constant

The limiting equivalent conductance Λ_o and the observed association constant K_A were analyzed by using Shedlovsky extrapolation technique:

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

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), $\Lambda_{o,}$ the limiting equivalent conductance and $K_{A,}$ the observed association constant.

Table 11: 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 Pentaammine chloronickel(II) perchlorate have been measured in various methanol +water mixtures at 288.15K-308.15K.

Xmethanol	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=288.15K				T=293.15K			
0.0000	260.74	420.11	344.88	5.341	279.05	350.21	317.83	5.697
0.0588	245.53	449.23	500.91	3.677	268.20	362.26	464.18	3.901
0.1942	238.64	460.41	537.83	3.244	245.00	380.00	500.03	3.621
0.3600	214.12	485.53	551.94	3.163	220.23	398.43	563.81	3.404
0.5676	221.00	521.34	462.76	3.980	238.42	400.23	445.83	4.062
0.8351	232.33	540.36	363.00	5.074	242.44	413.05	337.16	5.370
1.0000	240.23	562.21	350.11	6.974	257.70	427.32	246.97	7.331
	T=298.15K				T=303.15K			
0.0000	290.74	324.98	294.69	6.042	300.70	300.24	274.27	6.386
0.0588	279.56	394.76	420.54	4.234	282.22	315.66	380.39	4.604
0.1942	263.44	420.68	455.77	3.906	278.69	337.40	423.54	4.134
0.3600	243.16	451.57	483.69	3.303	255.30	358.08	487.43	3.719
0.5676	251.30	473.90	412.18	4.320	265.53	379.29	377.44	4.638
0.8351	267.83	498.62	319.45	5.574	274.47	385.82	293.64	5.963
1.0000	270.13	532.32	232.33	7.663	298.51	409.23	218.11	8.026

T=308.15K

0.0000	325.85	273.07	249.01	6.916
0.0588	305.25	286.56	348.36	4.945
0.1942	282.48	308.40	383.52	4.492
0.3600	263.88	322.28	439.53	4.239
0.5676	281.84	337.72	350.41	4.916
0.8351	290.41	340.82	276.21	6.238

From Table 11, the values of Λ_0 increased invariable with increase in temperature in all solvents irrespective of X_{MeOH}, indicating less solvation or higher mobility of ions (Fig.16). This is attributed to the fact that increased in thermal energy results in greater bond-breaking in vibrational, rotational and translational energies of the molecules that lead to higher frequency and hence higher mobility of ions. The viscosity of M + W mixtures increases up to $X_{MeOH} = 0.36$ and thereafter it decreases. Values of Λ_0 of salts decrease up to this mole fraction ($X_{MeOH} = 0.36$) and then increase in methanol rich region at all temperatures as expected from Walden rule (Table 11).If change in solvation is reflected by the variation in $\Lambda_0\eta_0$ [Singh et al ., 2008] , the increase of the Walden product indicates the weak solvation of the ions. The decrease of the product indicates an increase of the hydrophobic solvation with increasing concentration of methanol. As the methanol content increases, progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture.Then effective radius(r) of ion or solute can be calculated as

$$\Lambda_0\eta_0 = 1/6\ \pi r T$$

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 $x_{\mathrm{MeOH}} = 0.36$ correspond to minimum values of r. The Walden products in these are solvents increase and then decrease after passing through a maximum [Bag et al ., 2001]. It is thus apparent that its variation with the solvent composition is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions of the mixed solvents and temperature of the solution. 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.,

$$\Lambda_o = A.e^{-E^a/RT} \text{ or } \ln \Lambda_o = \ln A - E^a/RT$$

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 are shown in Table 17

4.4.4. Evaluation of Thermodynamic parameters

Table 12: Thermodynamic parameters ΔG°(KJ mole^{-1}),ΔH°(KJ mole^{-1}),ΔS°(KJ mole^{-1}), Ea (KJ mole^{-1}) and 10^{-3} A of Shedlovsky techniques for Pentaammine chloronickel(II) perchlorate have been measured in various Methanol + water mixtures at different temperatures**.**

	288.15K	293.15K	298.15K	303.15K	308.15K
			X_1=0.0000		
ΔG°	-14.47	-14.28	-14.27	-14.22	-14.16
ΔH°	-23.54				
10^{-3}xΔS°	-30.33	-31.58	-31.09	-30.74	-30.43
E^a	7.67				
10^{-3}A	2.74				
			X_1=0.0588		
ΔG°	-14.62	-14.59	-14.55	-14.51	-14.45
ΔH°	-23.25				
10^{-3}xΔS°	-29.95	-29.54	-29.18	-28.83	-28.56
E^a	7.80				
10^{-3}A	2.96				
			X_1=0.1942		
ΔG°	-14.67	-14.42	-14.27	-14.22	-14.16
ΔH°	-23.06				
10^{-3}xΔS°	-29.12	-29.47	-29.48	-29.16	-28.88
E^a	8.12				
10^{-3}A	3.16				

		X_1=0.3600			
ΔG°	-14.78	-14.59	-14.27	-14.20	-14.16
ΔH°	-22.86				
10^{-3}xΔS°	-28.04	-28.21	-28.81	-28.56	-28.23
E^a	8.38				
10^{-3}A	3.43				
		X_1=0.5676			
ΔG°	-14.89	-14.87	-14.84	-14.80	-14.75
ΔH°	-22.62				
10^{-3}xΔS°	-26.83	-26.44	-26.09	-25.79	-25.54
E^a	8.10				
10^{-3}A	3.21				
		X_1=0.8351			
ΔG°	-15.17	-15.13	-14.84	-14.51	-14.45
ΔH°	-22.31				
10^{-3}xΔS°	-24.78	-24.49	-25.05	-25.72	-25.50
E^a	7.90				
10^{-3}A	3.00				
		X_1=1.0000			
ΔG°	-15.45	-15.43	-15.41	-15.38	-15.34
ΔH°	-22.10				
10^{-3}xΔS°	-23.08	-22.75	-22.44	-22.17	-21.94
E^a	7.73				
10^{-3}A	2.81				

The values of E^a increases with increase in X_1 up to about X_1=0.36 and thereafter decreases rapidly. It follows that in water rich region up to 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 mobilities 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 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. Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between ions which is again indicated by negative value of enthalpy change. As expected that the values of ΔG^0 become more negative at higher percentage of methanol which indicate that ion-pair association are favoured with lowering dielectric constant of the medium.

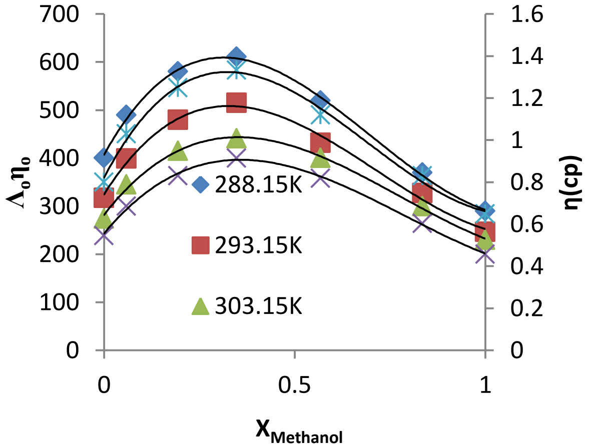

Fig.16: The value of Walden product $\Lambda_o\eta_o$ and (η) for Ni (II) Complex as a function of X_{MeOH} in methanol + water solvents

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 $1/T$. ΔH^0 values obtained are found to increase with the composition of the mixed solvents (Fig.18). The entropy of change is calculated from Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The values of these thermodynamic in nature in all solvent mixtures at all temperature are given in Table 12 . At all temperatures, ΔG^0 values become more negative with increase in X_1 indicating that the ion pair formation is favoured with lowering of permittivity of the medium.

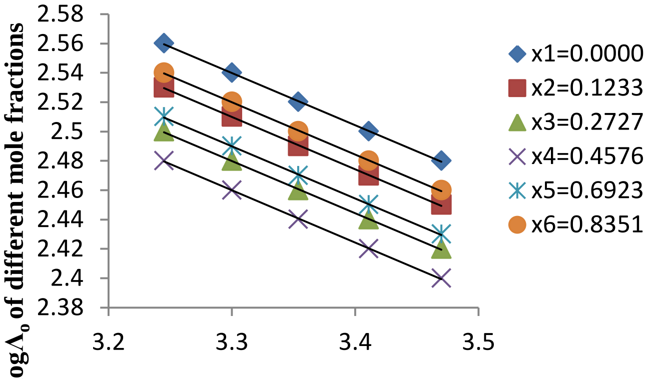

Fig 17: Log Λ_o Vs 1/T for Ni(II) complex in different mole fraction at temperature

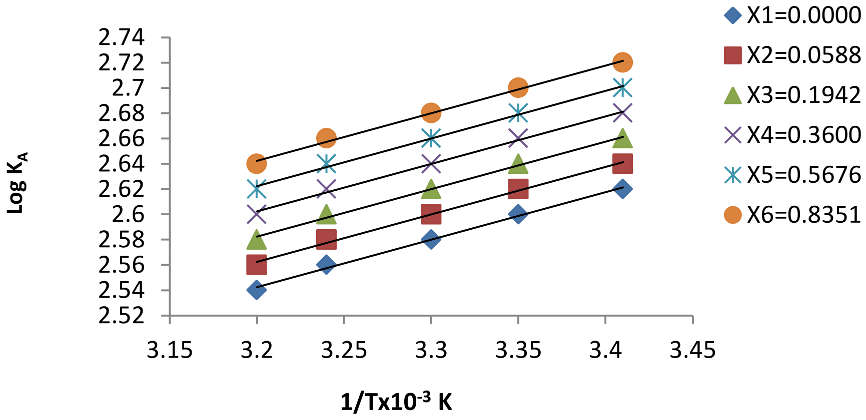

Fig 18: Log K_A vs 1/T for Ni(II) Complex in diffrent mole fractions at temperature 288.15-308.15 K

The experimentally determined of 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. Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between ions which is again indicated by negative value of enthalpy change. As expected that the values of ΔG^0 become more negative at higher percentage of methanol which indicate that ion-pair association are favoured with lowering dielectric constant of the medium. The value of E^a increases with increase in X_1 up to about X_1=0.36 and thereafter decreases rapidly. It follows that in water rich region up to 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

4.5. Ion -Pair and Triple -Ion Formation of Lithium Salts in non- aqueous solvents at 25° C

4.5.1. 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 et.al, 1997]. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. 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. Understanding the state of association of the electrolytes and their interaction with the solvent molecules is important for selecting the solvent and electrolyte. Conductometric measurement have been used for studying the electrolytic solutions in various organic solvents.

We have come out with a modern technique [Nandi et.al, 1989., Nandi et. al, 1989., Muhuri et.al, 1993., Das et.al, 1995] to study Li^+ ion solvation in various organic solvents from conductometric measurements. In this work, conductometric studies have been carried out for lithium chloride (LiCl) and lithium nitrate ($LiNO_3$) in 100% mass fraction of methylamine, dichloromethane and 1,3 dioxolane. The lithium salts used in this work when mixed with various organic solvents are very good electrolytes in lithium-ion batteries. Lithium-ion batteries are widely used in products such as portable consumer electronic devices. Therefore, by studying the behaviour of these lithium salts in various organic solvents, it will help in the production of more useful and cost effective batteries. Carefully, this would give a reasonable idea for selecting an important electrolyte in battery construction.

4.5.2. Experimental

The lithium salts selected for the present work puriss grade was procured from Sigma-Aldrich, Germany. The mass fraction purity of the lithium salts was ≥ 0.99. Methylamine, Dichloromethane (DCM) and 1,3 Dioxolane were procured from Sigma-Aldrich, Germany. The mass fraction purity of the solvent was ≥ 0.995. The solutions of different concentrations ($1\ \mathrm{x}10^{-4}$) M were carefully prepared by dissolving requisite amount of the sample in conductivity solvent of low specific conductance ($< 2\mathrm{x}10^{-6}$ S cm^{-1}) and conductivity measurements were carried out at 25^{o} C. All the dielectric constants and viscosities were obtained from literature [Ekka et.al, 2012., Ekka et.al, 2014., Bhattacharjee et. al, 2010]. The temperature control at 25^{0}C was made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg). All calculations were done on computer program using a Fouss-Kraus technique. The observed conductivities were corrected for the conductivity of the solvent. The accuracy of the temperature of the thermostat was ± 0.01^{0}C.

4.5.2.1. Conductivity measurements

The concentrations and molar conductances (Λ) of LiCl and $LiNO_3$ in 100% mass fraction of Methylamine, Dichloromethane and 1,3 Dioxolane are given in Table 13. The molar conductance (Λ) has been obtained from the specific conductance (k) value using the following equation [Lalzawnpuia et.al, 2016]

$$\Lambda = (1000\ k) / c$$

Table 13: Molar conductance (Λ) and the corresponding concentration (C) of the studied LiCl and $LiNO_3$ in different solvents at T = 298.15K.

c x 10^{-4} (S m^{2} mol^{-1})	Λ x 10^{-4} (mol mol^{-3})	c x 10^{-4} (S m^{2} mol^{-1})	Λ x 10^{-4} (mol mol^{-3})	c x 10^{-4} (S m^{2} mol^{-1})	Λ x 10^{-4} (mol mol^{-3})
LiCl					
CH_3NH_2		CH_2Cl_2		1,3 - Dioxolane	
2.988	28.41	2.512	25.48	2.405	18.92
3.486	26.75	2.669	24.42	2.491	15.89
3.652	25.67	2.826	23.54	2.580	13.35
3.818	24.58	2.983	22.72	2.666	11.41
3.984	23.79	3.140	22.00	2.752	9.82
4.150	23.24	3.297	21.40	2.838	8.59
4.316	22.87	3.454	20.82	2.924	7.87
4.482	22.67	3.611	20.41	3.010	7.94
4.648	22.71	3.768	20.10	3.096	8.56
4.814	22.81	3.925	19.77	3.182	9.86
4.980	23.08	4.082	19.81	3.268	12.08
5.146	23.45	4.239	20.24	3.354	14.62
$LiNO_3$					
CH_3NH_2		CH_2Cl_2		1,3-Dioxolane	
2.160	26.42	1.727	23.83	1.548	16.43
2.320	25.00	2.041	22.55	1.720	13.13
2.490	23.68	2.198	21.69	1.978	10.56
2.656	22.59	2.355	21.07	2.147	8.73
2.822	21.88	2.512	20.44	2.233	7.35
2.988	21.19	2.669	19.85	2.319	6.43

3.154	20.94	2.826	19.24	2.405	6.20
3.320	20.76	2.983	18.70	2.491	6.25
3.486	20.79	3.140	18.24	2.580	6.78
3.652	20.82	3.297	18.26	2.666	7.92
3.818	20.96	3.454	18.28	2.752	9.79
3.984	21.46	3.611	18.59	2.838	12.43

4.5.3. Evaluation of calculating limiting molar conductance of ion-pair (Λo), limiting molar conductance of triple-ion (Λo^T), slope and intercept.

Non linear conductance curve (Λ vs √c) was obtained for the lithium salts in pure methylamine, dichloromethane and 1,3 dioxolane which shows that, the electrolyte (Li^+…X) follows the same trend, i.e. the conductance value decreases with increasing concentration, it reach a minimum and then increases. Due to the deviation of the conductometric curves from linearity in case of lithium salts (Li^+…X) in methylamine (ε_r = 9.35), dichloromethane (ε_r = 8.93) and 1,3 dioxolane (ε_r = 7.31) the conductance data have been analyzed by the classical Fuoss-Kraus theory of triple-ion formation [Harada et.al, 1985] in the form

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right) c \qquad \ldots(52)$$

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

$$g(c) = \frac{\exp\{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1-S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1-\Lambda/\Lambda_0)^{0.5}} \qquad \ldots(53)$$

$$\beta' = 1.8247 \text{ X } 10^6/(\varepsilon T)^{1.5} \qquad \ldots(54)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \text{ X } 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad \ldots(55)$$

In the above equations, Λo is the sum of the molar conductance of the simple ions LiX at infinite dilution, Λo^T is the sum of the conductance value of the two triple-ions LiX_2^- and Li_2X^+ for the lithium salts, where X= Cl^- and NO_3^-; $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants respectively and S is the limiting Onsager coefficient. To make equation (52) applicable, the symmetrical approximation of the two possible formation constants of triple-ions equal to each other has been adopted [Fuoss et. al, 1933] and Λo values for the studied electrolyte have been calculated using the following scheme as suggested by B.Z. Krumgalz [Krumgalz 1983] . Λo^T has been calculated by setting the triple-ion conductance equal to 2/3 Λo [Delsignore et .al, 1985] .The calculated values are listed in Table 14.

The ratio Λo^T / Λo was thus set equal to 0.667 during linear regression analysis of equation (52). Table 14 shows the calculated limiting molar conductance of simple ion (Λo), limiting molar conductance of triple ion (Λo^T), slope and intercept of equation (52) for lithium salts (Li^+…X) in methylamine, dichloromethane and 1,3 dioxolane at 298.15K. The linear regression analysis of equation (52) 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 15. A perusal of Table 15 shows that the K_P is larger than K_T, indicate the major portion of the electrolytes (Li^+…X) 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 [Nandi et.al, 1993]. At very low permittivity of the solvent, i.e., ε_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 14: The calculated limiting molar conductance of ion-pair (Λo), limiting molar conductance of triple-ion (Λo^T), slope and intercept of lithium salts in methylamine, dichloromethane and 1,3 dioxolane at 298.15K

Solvents	Λ_0 x 10^{-4} (S m^2 mol^{-1})	Λ_0^T x 10^{-4} (S m^2 mol^{-1})	Slope x 10^{-2}	Intercept x 10^{-2}
		LiCl		
CH_3NH_2	139.10	93.20	1.82	0.96
CH_2Cl_2	116.51	78.06	2.05	0.75
1,3- Dioxolane	101.50	68.00	2.25	0.49
		$LiNO_3$		
CH_3NH_2	128.77	86.28	1.97	0.78
CH_2Cl_2	104.55	70.05	2.48	0.52
1,3- Dioxolane	90.01	60.31	2.88	0.38

4.5.4. 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 15: Salt concentration at the minimum conductivity (c_{min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T) for lithium salts in methylamine, dichloromethane and 1,3 dioxolane at 298.15K.

Solvents	c_{min}. 10^{-4}/ ($mol.dm^{-3}$)	log c_{min}	K_P x 10^{-4} ($(mol.dm^{-3})^{-1}$)	K_T x 10^{-4} ($(mol.dm^{-3})^{-1}$)	K_T/K_P x 10^{-4}	log K_T/K_P
			LiCl			
CH_3NH_2	4.482	-3.35	25.31	18.45	728.96	-1.14
CH_2Cl_2	3.925	-3.41	28.74	21.29	740.78	-1.13
1,3-Dioxolane	2.924	-3.53	30.67	23.68	772.09	-1.11
			$LiNO_3$			
CH_3NH_2	3.320	-3.48	23.63	15.78	667.79	-1.17
CH_2Cl_2	3.140	-3.50	26.43	20.34	769.58	-1.12
1,3-Dioxolane	2.405	-3.62	28.98	22.29	769.15	-1.10

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

$M^+ + A^- \leftrightarrow M^+ \cdots\cdots\cdots A^- \leftrightarrow MA$ (ion-pair) … (56)

$MA + M^+ \leftrightarrow MAM^+$ (triple-ion) …(57)

$MA + A^- \leftrightarrow MAA^-$ (triple-ion) …(58)

where M^+ and A^- are $[Li]^+$ and X^- (where X= Cl^- and NO_3^-) respectively. The effect of ternary association [Sinha et. al, 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 lithium salts in methylamine, dichloromethane and 1,3 dioxolane.

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, 1988]

$$\alpha = 1/(K_P^{\frac{1}{2}}.c^{\frac{1}{2}}) \qquad \ldots(59)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \qquad \ldots(60)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \qquad \ldots(61)$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \qquad \ldots(62)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions present in the salt-solutions are given in Table 16. Thus the values of C_P and C_T given in Table 16, 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 $[Li]^+$ and X^- (where X= Cl^- and NO_3^-) + methylamine, dichloromethane and 1,3 dioxolane.

Table 16: 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 methylamine, dichloromethane and 1,3 dioxolane T = 298.15 K

Solvents	c_{min} x 10^{-4} (mol dm^{-3})	Λ_{mn} x 10^{-4}	α x 10^{-2}	α_T x 10^{-2}	c_P x 10^{-5} (mol dm^{-3})	c_T x 10^{-5} (mol dm^{-3})
			LiCl			
CH_3NH_2	4.482	22.67	9.38	3.60	8.59	1.61
CH_2Cl_2	3.925	19.77	9.42	3.86	7.84	1.75
1,3-Dioxolane	2.924	7.87	10.56	4.31	6.57	2.49
			$LiNO_3$			
CH_3NH_2	3.320	20.76	11.31	3.97	7.38	2.02
CH_2Cl_2	3.140	18.24	10.99	4.08	6.98	2.25
1,4 -Dioxane	0.039	4.24	10.95	2.08	0.62	0.07

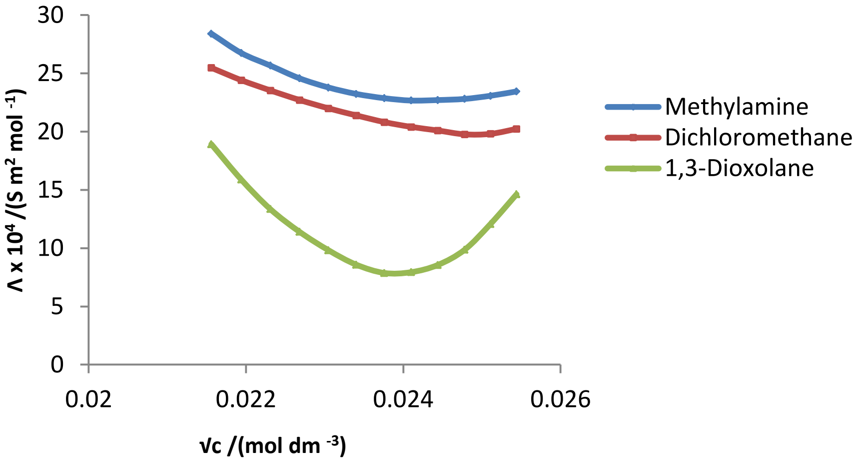

Fig.19 Plot of molar conductance (Λ) vs. the square root of molar concentration ($\sqrt{c}$) for LiCl in methylamine, dichloromethane and 1,3-dioxolane at T = 298.15K

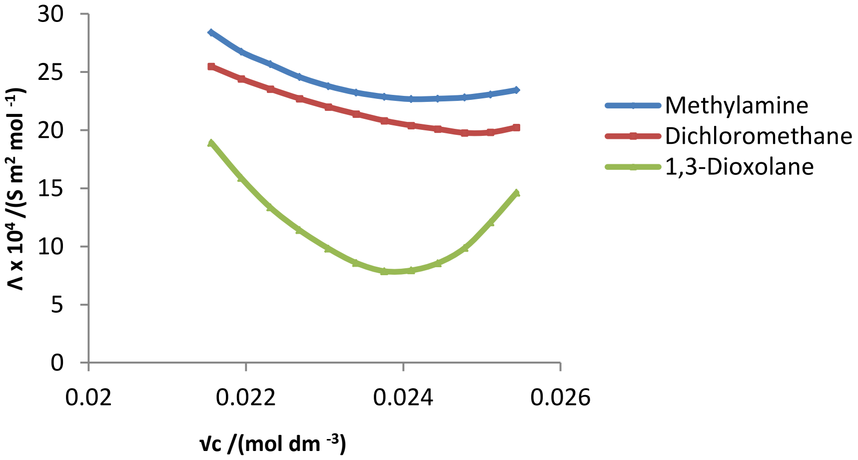

Fig.19 Plot of molar conductance (Λ) vs. the square root of molar concentration ($\sqrt{c}$) for LiCl in methylamine, dichloromethane and 1,3-dioxolane at T = 298.15K

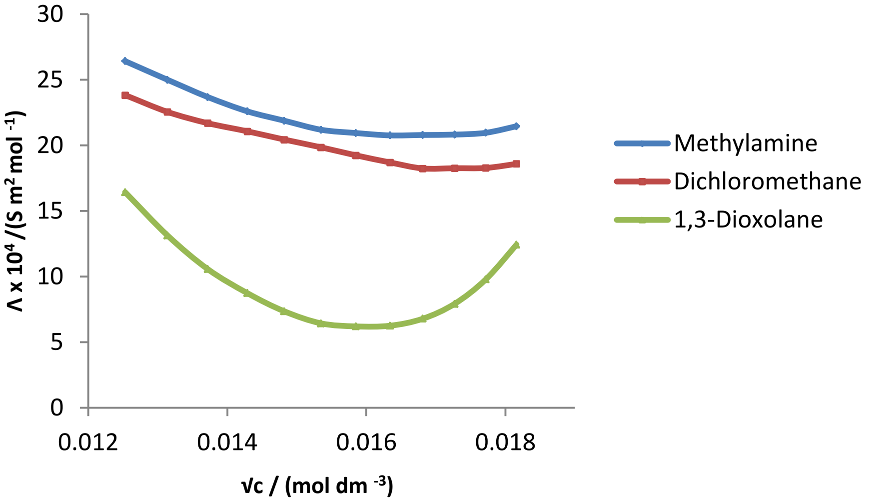

Fig. 20: Plot of molar conductance (Λ) vs. the square root of molar concentration (√c) for $LiNO_3$ in methylamine, dichloromethane and 1,3-dioxolane at T = 298.15K

The present work reveals an extensive study on the ion-solvation behaviour of the lithium salts $[Li]^+$ and X^- (where $X= Cl^-$ and NO_3^-) in 100% mass fraction of methylamine, dichloromethane and 1,3 dioxolane through the conductometric. It becomes clear that all the studied lithium salts exists as triple-ion in 100% mass fraction of methylamine, dichloromethane and 1,3 dioxolane at 298.15K. The tendency of the ion-pair and triple-ion formation depends on the size, the charge distribution of the anions (Cl^- and NO_3^-) for the common cation (Li^+), and structural aspects (functional group of the solvents).

4.6. Study of various interactions of Cetyl Trimethylammonium bromide in significant solvent systems using compensated equation of Fuoss-Kraus conductance

4.6.1. Introduction

The study of ion solvation is very useful for understanding the application of the complex in modern systems. Behaviour of the conductance measurement of electrolytes in mixed solvent systems are influenced because of the density, viscosity, dielectric constant of the medium, ion solvent interactions and solvent-solvent interactions. On solvation ion-solvent interactions alters the ion. Many of the properties of electrolyte solutions [Marcus, 1985; Krestov, *et al.*,1994; Popovych and Tomkins, 1981] including their redox potential, complexation and kinetic behaviour are influenced through the solvation of dissolved ions. Ion-solvent, solvent-solvent interactions and preferential solvation of an ion are understood by studying the conductance in binary solvent mixtures [Rajasekhar Reddy, 1987]. Ion-ion and ion-solvent interactions can be better studied by enabling the variation of properties such as dielectric constant or viscosity in mixed solvents. Besides from concentration-dependence of the electrolyte conductivity different quantities strongly influenced by solvent properties can be derived. Therefore the use of high energy batteries [Aurbach, 1999] and for understanding organic reaction mechanisms are possible through a number of conductometric [Janx and Tomkins, 1973] and related studies of different electrolytes in non-aqueous solvents, specially mixed organic solvents [Krom, Petty, Streitwieser, 1993].

4.6.2. Experimental

Cetyl Trimethylammonium bromide salt was purchased from Sigma-Aldrich, Germany. The measurement of the conductance data were carried out at temperature 25^o C. The solvents i.e O- Toluidine, O-Xylene and 1,4 Dioxane were procured from Sigma-

Aldrich, Germany. The value of dielectric constant and viscosity were obtained from the literature [Dutta and Roy, 2015]. At different concentrations (1 x10^{-4}) M the sample was dissolved in the conductivity solvent of low specific conductance. The temperature at 25^0C was controlled using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The METTER Balance, model TB-214(max=210g; d=0.1mg) was used for measuring the weight of the sample. ± 0.01^0C was the accuracy of the temperature for the thermostat.

4.6.2.1. Conductivity measurements

The concentrations and molar conductances (Λ) of Cetyl Trimethylammonium bromide in 100% mass fraction of O- Toluidine, O-Xylene and 1,4 Dioxane are given in Table 17. For all studied solution system the molar conductances (Λ) were calculated using the equation [El-Dossoki, 2010]

$$\Lambda = (1000\ k) / c$$

Table 17: Molar conductance (Λ) and the corresponding concentration (C) of the studied Cetyl Trimethylammonium bromide in different solvents at T = 298.15K.

c x 10 $^{-4}$ (mol dm^{-3})	Λ x 10 $^{-4}$ (S m^{2} mol^{-1})	c x 10 $^{-4}$ (mol dm^{-3})	Λ x 10 $^{-4}$ (S m^{2} mol^{-1})	c x 10 - ^{4} (mol dm^{-3})	Λ x 10^{4} (S m^{2} mol^{-1})
$C_{19}H_{42}NBr$					
O – Toluidine		O - Xylene		1,4 – Dioxane	
0.632	20.73	0.628	18.72	0.623	15.1
0.703	17.18	0.672	15.76	0.648	12.21
0.733	13.96	0.676	12.92	0.652	10.04
0.814	11.54	0.740	11.02	0.737	8.21
0.865	9.41	0.784	9.32	0.751	6.91
0.916	7.8	0.837	8.27	0.816	5.48
0.967	6.51	0.921	7.49	0.851	4.5
1.018	5.55	0.955	7.52	0.905	4.47
1.069	5.1	0.989	8.29	0.936	5.18
1.120	5.09	1.103	9.66	0.982	6.85
1.171	6.16	1.156	11.53	1.124	8.68
1.222	8.48	1.200	14.42	1.187	11.61

4.6.3. Evaluation of calculating limiting molar conductance of ion-pair (Λo), limiting molar conductance of triple-ion (Λo^T), slope and intercept.

In $C_{19}H_{42}NBr$ solutions (i.e O-Toluidine, O-Xylene and 1,4,Dioxane) the conductance value decreases with increasing concentration, it reach a minimum and then increase again.Therefore non linear conductance curve (Λ vs √c) was obtained. The classical Fuoss-Kraus theory of triple-ion formation was used for analysing the conductance data [Fuoss-Kraus, 1933]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right) c \qquad \ldots(63)$$

The component that lumps together all the intrinsic interaction terms is given as *g(c)* and is equal to

$$g(c) = \frac{\exp\{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1-S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1-\Lambda/\Lambda_0)^{0.5}} \qquad \ldots(64)$$

$$\beta' = 1.8247 \text{ X } 10^6/(\varepsilon T)^{1.5} \qquad \ldots(65)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \text{ X } 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad \ldots(66)$$

At infinite dilution, the sum of the molar conductance of the simple ions is given as Λo, the sum of the conductance value of the two triple-ions as Λo^T and ion-pair and triple-ion formation constants as $K_P \approx K_A$ and K_T and *S* is equal to limiting Onsager coefficient(as given in the above equations). The symmetrical approximation of the two possible formation constants of triple-ions equal to each other has been adopted for the application of equation

(63) [Fuoss et. al, 1933] and from the suggestion of B.Z. Krumgalz the Λo values for the studied electrolyte have been obtained [Krumgalz 1983]. The equations $2/3\Lambda o$ has been used for calculating Λo^T [Delsignore et .al, 1985]. The calculated values are given in Table 18.

During linear regression analysis of equation (63) the ratio $\Lambda o^T / \Lambda o$ was thus set equal to 0.667. The observed values of limiting molar conductance of simple ion (Λo), limiting molar conductance of triple ion (Λo^T), slope and intercept of equation (63) for $C_{19}H_{42}NBr$ solutions (i.e O-Toluidine, O-Xylene and 1,4,Dioxane) 298.15K were given in table 14. Intercept and slope were obtained from the linear regression analysis of equation (63) for the electrolytes with an average regression constant, $R^2 = 0.9689$. The values of other derived parameters such as K_P and K_T were calculated from the values obtained through Λo and Λo^T (Table 19). Since K_P is larger than K_T, indicate the major portion of the electrolytes exists as ion-pairs (Table 19). The K_T/K_P ratio and log (K_T/K_P) described the tendency of triple ion formation with respect to ion-pair. Therefore due to the coulombic interactions as well as to covalent forces in the solution, strong ion-association between the ions and solvent exist [Nandi et.al, 1993]. Electrostatic ionic interactions are very large in a low permittivity of the solvent, i.e., $\varepsilon_r < 10$. The distance of the closest approach of the ions becomes minimum, therefore the ion-pairs attract the free cations or anions present in the solution medium.

Table 18: The calculated ion – pair limiting molar conductance (Λ_0), triple – ion limiting molar conductance (Λ_0^T), slope and intercept obtained from Fuoss – Kraus equation for Cetyl Trimethylammonium bromide in different solvents at 298.15K.

Solvents	Λ_0 x 10 $^{-4}$ (S m^2 mol^{-1})	Λ_0^T x 10 $^{-4}$ (S m^2 mol^{-1})	Slope x 10^{-2}	Intercept x 10^{-2}
		$C_{19}H_{42}NBr$		
O – Toluidine	115.95	77.69	15.22	9.22
O – Xylene	71.34	47.80	32.57	5.48
1,4 – Dioxane	47.79	32.02	37.19	2.15

4.6.4. 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 19: Salt concentration at the minimum conductivity (c_{min}) along with the ion – pair formation constant (K_P), triple – ion formation constant (K_T) for Cetyl Trimethylammonium bromide in different solvents at 298.15K.

Solvents	c_{min}. 10 $^{-4}$/ (mol.dm^3)	log c_{min}	K_P x 10^{-4} (mol.dm^{-3})$^{-1}$	K_T x 10^{-4} (mol.dm^{-3})$^{-1}$	K_T/K_P x 10 $^{-4}$	log K_T/K_P
			$C_{19}H_{42}NBr$			
O - Toluidine	1.120	-3.95	28.59	9.04	316.08	-1.50
O – Xylene	1.103	-4.00	36.97	12.44	336.49	-1.47
1,4 Dioxane	0.982	-4.01	49.20	19.89	404.06	-1.39

The charge of the respective ions attracted from the solution bulk was acquired due to the formation of these triple-ions [Fuoss et.al, 1960] i.e.;

$M^+ + A^- \leftrightarrow M^+\cdots\cdots A^- \leftrightarrow MA$ (ion-pair) … (67)

$MA + M^+ \leftrightarrow MAM^+$ (triple-ion) … (68)

$MA + A^- \leftrightarrow MAA^-$ (triple-ion) …(69)

Besides, by using the following equations the ion-pair and triple-ion concentrations, C_P and C_T, were calculated [Nandi *et al.*, 1988]

$$\alpha = 1/(K_P^{\frac{1}{2}}.c^{\frac{1}{2}}) \quad \ldots(70)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \quad \ldots(71)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \quad \ldots(72)$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \quad \ldots(73)$$

Here, the fraction of ion-pairs and triple-ions present in the salt-solutions are given as α and α_T in Table 20. The major portion of ions are present as ion-pair even at high concentration and a small fraction exist as triple-ion as indicated by values of C_P and C_T in Table 20. In the studied solution media $[C_{19}H_{42}]^+$ and X^- (where X= NBr^-) in O-Toluidine, O-Xylene and 1,4,Dioxane, certain concentration the fraction of the triple-ions in the solution increases with the increasing concentration.

Table20: Salt concentration at the minimum conductivity (c_{min}), the ion - pair fraction (α), triple – ion fraction (α_T), ion – pair concentration (c_P) and triple – ion concentration (c_T) for Cetyl Trimethylammonium bromide in different solvents at 298.15K.

Solvents	c_{min} x 10^{-4} (mol dm^{-3})	Λ_{mn} x 10^{-4}	α x 10^{-2}	α_T x 10^{-2}	c_P x 10^{-5} (mol dm^{-3})	c_T x 10^{-5} (mol dm^{-3})
			$C_{19}H_{42}NBr$			
O - Toluidine	1.120	8.09	2.00	1.11	4.84	0.12
O - Xylene	1.103	7.49	5.49	2.86	1.19	0.10
1,4 - Dioxane	0.982	4.47	6.21	3.02	0.78	0.08

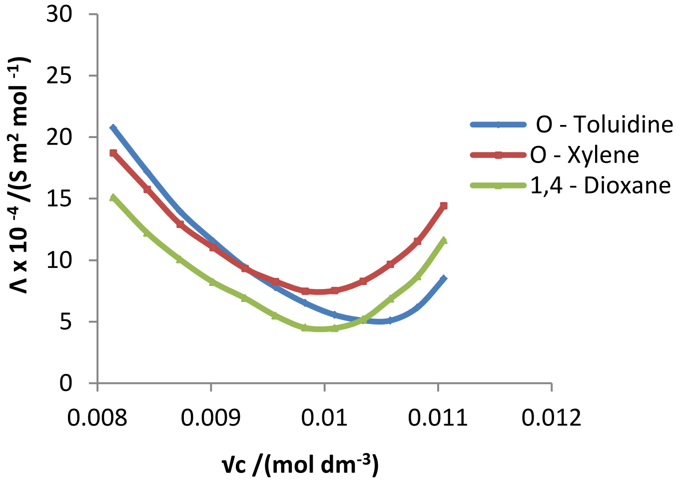

Fig.21 Plot of molar conductance (Λ) vs. the square root of molar concentration (√c) for $C_{19}H_{42}NBr$

Through the conductometric measurements an extensive study on the ion-solvation behavior of the Cetyl Trimethylammonium bromide [$C_{19}H_{42}NBr$] in O-Toluidine, O-Xylene and 1,4 Dioxane solutions were observed. Depending on the size and the charge distribution of the ions and structural aspects (functional group of the solvents) the tendency of the ion-pair and triple-ion formation are determined. Cetyl Trimethylammonium bromide salt interact through hydrogen bonding and ion-dipole interactions in all the solvents. Ion-solvent interactions dominate over ion-ion interactions as observed from the study. Therefore, Cetyl Trimethylammonium bromide has the maximum amount of triple-ions in 1,4 Dioxane.

4.7. Relationship between Triple Ion Formation and a Green Compounds {[BMimPF$_6$, 4BMimPPF$_6$]} in Low- Permittivity Solvents with the Manifestation of Solvation Consequence

4.7.1. Introduction

Ionic association provides a self-consistent method of conducting with the position that appears when ions of opposite sign are close together. In these situation a virtually new entity in the solution of sufficient stability persist through a number of collisions with solvent molecules because the energy of their mutual electrical attraction is much greater than their thermal energy. In principle, ionic liquids is defined as liquid electrolytes that is formulate of the outcome of organic-organic or organic-inorganic cations / anions. Ionic liquids have shown importance interest in a wide range of industrial uses and many academic areas because of their distinctive physicochemical nature, like the favourable solubility of organic and inorganic compounds, low vapour pressures, low melting points, high thermal stability, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical stability, non-flammability and high ionic conductivity. Through the analyzation of the ionic solvation and ion-association in the solution systems these applications were best understood. Few of them were environmentally friendly because of their less hazardous characters for human and less toxic for other living organisms, and majority of the ILs were good illustrations of neoteric solvents [Bemot et. al, 2005]. In ionic liquids, organic reactions and separation processes were tested intensively in recyclable solvents [Plechkova et. al, 2008].

Ionic level relationship of the individual electrolyte ions in the measured solution systems is the responsibility of the ion solvation therefore, determines the characteristics of the solvent or solvent mixtures. The solvent properties like viscosity and relative permittivity interpret the extent of ion-solvent interaction and ion association in the solution systems.

For understanding the nature of ion-solvent interactions of ILs {1-butyl-3-methylimidazolium hexafluorophosphate BMimPF$_6$} and {1-butyl-4-methylpyridinium hexafluorophosphate 4BMimPPF$_6$} in polar solvents (i.e pure dichloromethane, 1,3-dioxolane, O-Toluidine and O- Xylene) conductance measurement was performed [Roy et. al, 2008; Chanda et. al, 2008; Roy et.al, 2006]. The shifting of FT-IR vibrational intensity of the characteristic functional groups in acetonitrile, methanol and formamide were applied for identifying the solvation phenomena.

4.7.2. Experimental

1-butyl-3-methylimidazolium hexafluorophosphate BMimPF$_6$ and 1-butyl-4-methylpyridinium hexafluorophosphate 4BMimPPF$_6$ were purchased from Sigma-Aldrich, Germany. The measurement of the conductance data were carried out at the temperature 25^o C. The solvents i.e dichloromethane, 1,3- dioxolane, O-Toluidine and O- Xylene were procured from Sigma-Aldrich, Germany. The value of dielectric constant and viscosity were obtained from the literature [Dutta and Roy, 2015]. At different concentrations (1 x10^{-4}) M the sample was dissolved in the conductivity solvent of low specific conductance. The temperature at 25^{0}C was controlled using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The METTER Balance, model TB-214(max=210g; d=0.1mg) was used for measuring the weight of the sample. ± 0.01^{0}C was the accuracy of the temperature for the thermostat. Infrared spectra were recorded with an Horizon ABB MB-3000 FT-IR spectrometer (Quebec, Canada). The details of the instrument were discussed based on the literature [Halida et.al, 2015]. The concentration of the studied solutions used in IR study was 0.05M.

4.7.2.1. Conductivity measurements

The concentrations and molar conductances (Λ) of 1-butyl-3-methylimidazolium hexafluorophosphate $BMimPF_6$ and 1-butyl-4-methylpyridinium hexafluorophosphate $4BMimPPF_6$ in 100% mass fraction of organic solvents Table 21. For all studied solution system the molar conductances (Λ) were calculated using the equation [Lalzawnpuia et. al, 2016]

$$\Lambda = (1000\ k) / c$$

Table 21. Molar conductance (Λ) and the corresponding concentration (C) of the studied Ionic liquids in different solvents at T = 298.15K.

$C \times 10^{-4}$ (mol dm^{-3})	$\Lambda \times 10^{-4}$ (Sm^{2}mol^{-1})	$C \times 10^{-4}$ (mol dm^{-3})	$\Lambda \times 10^{-4}$ (Sm^{2}mol^{-1})	$C \times 10^{-4}$ (mol dm^{-3})	$\Lambda \times 10^{-4}$ (Sm^{2}mol^{-1})	$C \times 10^{-4}$ (mol dm^{-3})	$\Lambda \times 10^{-4}$ (Sm^{2}mol^{-1})
$BMimPF_6$							
CH_2Cl_2		1,3 - Dioxolane		O - Toluidine		O - Xylene	
1.884	31.21	1.876	28.95	1.852	27.72	1.838	24.83
2.041	29.93	1.892	25.65	1.883	24.37	1.852	21.53
2.198	28.97	1.978	23.08	1.934	20.95	1.896	18.96
2.355	28.25	2.064	21.25	1.985	19.53	1.927	17.13
2.512	27.72	2.147	19.55	2.036	18.46	1.953	15.43

2.669	27.13	2.233	18.42	2.087	17.07	1.976	14.3
2.826	26.52	2.319	17.72	2.138	16.7	2.012	13.63
2.983	26.14	2.405	17.73	2.189	15.84	2.015	13.71
3.14	25.83	2.491	18.52	2.24	15.14	2.141	14.4
3.297	25.65	2.58	19.89	2.29	15.23	2.178	15.77
3.454	25.54	2.67	22.11	2.341	16.2	2.203	17.99
3.611	25.97	2.752	24.65	2.392	17.65	2.237	20.53

4BMimPPF$_6$

CH_2Cl_2		1,3 - Dioxolane		O -Toluidine		O - Xylene	
1.884	30.69	1.872	28.73	1.85	26.1	1.838	24.23
2.041	29.41	1.892	25.43	1.883	22.83	1.852	21.1
2.198	28.45	1.978	22.86	1.934	19.31	1.896	18.76
2.355	27.63	2.064	21.03	1.982	18.89	1.927	16.53
2.512	27.09	2.147	19.33	2.036	17.72	1.953	14.83
2.652	26.61	2.233	18.2	2.087	16.53	1.974	13.7
2.809	26.13	2.315	17.5	2.136	15.16	2.011	13
2.961	25.62	2.402	17.51	2.183	15.1	2.012	13.01
3.1	25.31	2.491	18.3	2.225	14.6	2.139	13.8
3.285	24.98	2.573	19.67	2.232	14.29	2.176	15.17
3.43	25.02	2.652	21.89	2.337	15.66	2.201	17.39
3.591	25.45	2.736	24.43	2.387	16.11	2.235	19.93

4.7.3. Evaluation of calculating limiting molar conductance of ion-pair (Λo), limiting molar conductance of triple-ion (Λo^T), slope and intercepts

In ILs solutions (i.e dichloromethane (DCM, ε_r = 8.93), 1,3-dioxolane (ε_r = 7.31), O-Toluidine (ε_r =6.14) and O-Xylene (ε_r =2.60),) the conductance value decreases with increasing concentration, it reach a minimum and then increase again.Therefore non linear conductance curve (Λ vs √c) was obtained. The classical Fuoss-Kraus theory of triple-ion formation was used for analysing the conductance data [Harada et. al, 1985]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right) c \qquad \ldots(74)$$

The component that lumps together all the intrinsic interaction terms is given as *g(c)* and is equal to

$$g(c) = \frac{\exp\{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1-S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1-\Lambda/\Lambda_0)^{0.5}} \qquad \ldots(75)$$

$$\beta' = 1.8247 \text{ X } 10^6/(\varepsilon T)^{1.5} \qquad \ldots(76)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \text{ X } 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad \ldots(77)$$

At infinite dilution the sum of the molar conductance of the simple ions is given as Λo, the sum of the conductance value of the two triple-ions as Λo^T and ion-pair and triple-ion formation constants as $K_P \approx K_A$ and K_T and *S* is equal to limiting Onsager coefficient(as given in the above equations). The symmetrical approximation of the two possible formation constants of triple-ions equal to each other has been adopted for the application of equation (63) [Fuoss et. al, 1933] and from the suggestion of B.Z. Krumgalz the Λo values for the studied electrolyte have been obtained [Krumgalz 1983]. The equations 2/3Λo has been used for calculating Λo^T [Delsignore et .al, 1985]. The calculated values are given in Table 22.

During linear regression analysis of equation (63) the ratio Λo^T / Λo was thus set equal to 0.667. The observed values of limiting molar conductance of simple ion (Λo), limiting molar conductance of triple ion (Λo^T), slope and intercept of equation (63) for ILs solutions (i.e O-Toluidine, O-Xylene and 1,4,Dioxane) 298.15K were given in table 22. Intercept and slope were obtained from the linear regression analysis of equation (63) for the electrolytes with an average regression constant, $R^2 = 0.9689$. The values of other derived parameters such as K_P and K_T were calculated from the values obtained through Λo and Λo^T (Table 23). Since K_P is larger than K_T, indicate the major portion of the electrolytes exists as ion-pairs (Table 23). The K_T/K_P ratio and log (K_T/K_P) described the tendency of triple ion formation with respect to ion-pair. Therefore due to the coulombic interactions as well as to covalent forces in the solution strong ion-association between the ions and solvent exist [Nandi et.al, 1993]. Electrostatic ionic interactions are very large in a low permittivity of the solvent, i.e., $\varepsilon_r < 10$. The distance of the closest approach of the ions becomes minimum, therefore the ion-pairs attract the free cations or anions present in the solution medium.

Table 22. The calculated ion – pair limiting molar conductance (Λ_0), triple – ion limiting molar conductance (Λ_0^T), slope and intercept obtained from Fuoss – Kraus equation for Ionic liquids in different solvents at 298.15K.

Solvents	$\Lambda_0 \times 10^{-4}$ (S m^2 mol^{-1})	$\Lambda_0^T \times 10^{-4}$ (S m^2 mol^{-1})	Slope x 10^{-2}	Intercept x 10^{-2}
		BMimPF6		
CH_2Cl_2	85.45	57.25	24.12	3.39
1,3- Dioxolane	72.48	48.56	30.26	3.21
O - Toluidine	66.42	44.30	32.87	2.73
O - Xylene	56.97	38.00	35.63	2.28
		4BMimPPF6		
CH_2Cl_2	80.53	53.96	28.66	2.88
1,3- Dioxolane	65.00	43.55	34.32	2.52

O - Toluidine	57.12	38.10	36.91	2.05
O - Xylene	45.44	30.31	39.32	1.89

4.7.4. 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 23: Salt concentration at the minimum conductivity (c_{min}) along with the ion – pair formation constant (K_P), triple – ion formation constant (K_T) for Ionic liquids in different solvents at 298.15K.

Solvents	c_{min}. 10^4/ ($mol.dm^{-3}$)	log c_{min}	K_P x 10^{-4} ($(mol.dm^{-3})^{-1}$)	K_T x 10^{-4} ($(mol.dm^{-3})^{-1}$)	K_T/K_P x 10^4	log K_T/K_P
			$BMimPF_6$			
CH_2Cl_2	3.454	-3.46	63.54	37.27	586.56	-3.23
1,3-Dioxolane	2.319	-3.63	69.21	42.24	610.32	-3.21
O - Toluidine	2.240	-3.65	72.82	45.93	630.73	-3.20
O - Xylene	2.012	-3.70	75.19	49.63	660.06	-3.18
			$4BMimPPF_6$			
CH_2Cl_2	3.285	-3.48	60.03	31.99	532.90	-3.27
1,3-Dioxolane	2.315	-3.61	67.03	37.09	553.33	-3.25
O - Toluidine	2.232	-3.63	70.49	40.33	572.14	-3.24
O - Xylene	2.011	-3.68	73.62	43.91	596.44	-3.22

The charge of the respective ions attracted from the solution bulk was acquired due to the formation of these triple-ions [Fuoss et.al, 1960] i.e.;

$$M^+ + A^- \leftrightarrow M^+\cdots\cdots A^- \leftrightarrow MA \quad \text{(ion-pair)} \qquad \ldots (78)$$

$MA + M^+ \leftrightarrow MAM^+$ (triple-ion) …(79)

$MA + A^- \leftrightarrow MAA^-$ (triple-ion) …(80)

Besides, by using the following equations the ion-pair and triple-ion concentrations, C_P and C_T, were calculated [Nandi *et al.*, 1988]

$$\alpha = 1/(K_P^{\frac{1}{2}}.c^{\frac{1}{2}}) \quad \text{…(81)}$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \quad \text{…(82)}$$

$$C_P = c(1 - \alpha - 3\alpha_T) \quad \text{…(83)}$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \quad \text{…(84)}$$

Here, the fraction of ion-pairs and triple-ions present in the salt-solutions are given as α and α_T in Table 24. The major portion of ions are present as ion-pair even at high concentration and a small fraction exist as triple-ion as indicated by values of C_P and C_T in Table 24. In the studied solution media $[BMim]^+$ (or $[4BMim]^+$) and PF_6^- (where X= PF_6^- and PPF_6^-) + dichloromethane, 1,3-Dioxolane, O-Toluidine and O-Xylene.

Table 24: Salt concentration at the minimum conductivity (c_{min}), the ion - pair fraction (α), triple – ion fraction (α_T), ion – pair concentration (c_P) and triple – ion concentration (c_T) for Ionic Liquids in different solvents at 298.15K.

Solvents	c_{min} x 10^{-4} (mol dm^{-3})	Λ_{mn} x 10^{-4}	α x 10^{-2}	α_T x 10^{-2}	c_P x 10^{-5} (mol dm^{-3})	c_T x 10^{-5} (mol dm^{-3})
			$BMimPF_6$			
CH_2Cl_2	3.454	25.54	6.75	8.69	1.10	0.30
1,3 - Dioxolane	2.319	17.72	7.89	7.73	0.70	0.36
O - Toluidine	2.240	15.14	7.93	8.06	0.69	0.41
O - Xylene	2.012	13.63	8.13	8.12	0.63	0.46
			$4MBPPF_6$			
CH_2Cl_2	3.285	24.98	7.12	7.53	0.94	0.32
1,3 - Dioxolane	2.315	17.50	8.03	6.89	0.64	0.33
O - Toluidine	2.232	14.29	8.18	7.18	0.62	0.37
O - Xylene	2.011	13.00	8.22	7.25	0.58	0.43

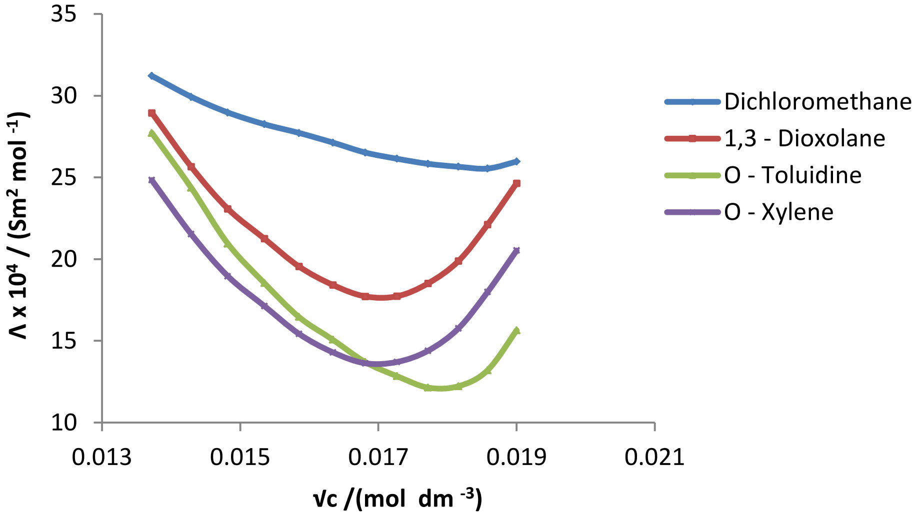

Fig.22: Plot of molar conductance (Λ) versus √c for BMimPF$_6$ in Dichloromethane, 1,3 - Dioxolane, O - Toluidine & O - Xylene at 298.15K

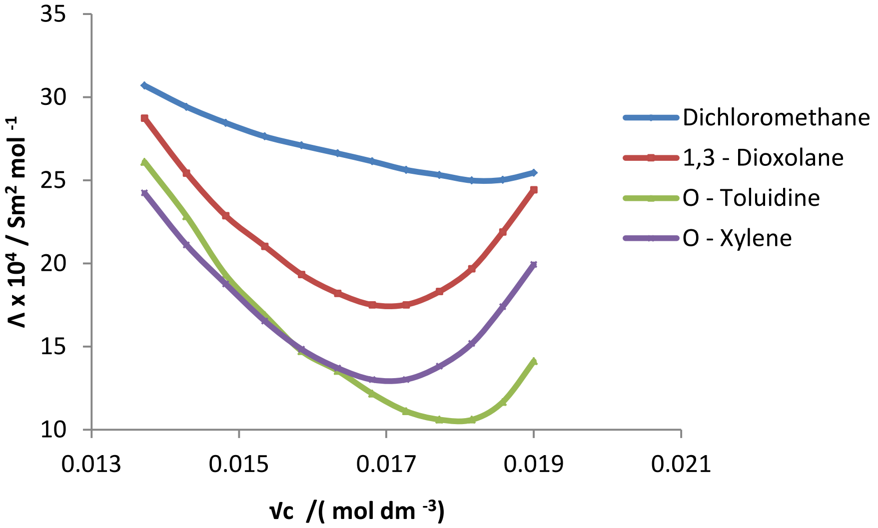

Fig.23: Plot of molar conductance (Λ) versus √c for 4BMimPPF$_6$ in Dichloromethane, 1,3 - Dioxolane, O - Toluidine & O - Xylene at 298.15K

4.7.5. FT-IR Spectroscopic Study

The studies of ion-solvent and solvent-solvent interactions were supported through FT-IR spectroscopy. Molecular interactions between the solvents and the green compounds were introduced quantitatively from this study. The stretching frequencies of the functional groups of pure solvents with BMimPF$_6$ (or 4BMimPPF$_6$) are given in Table 25.

Table 25: Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of Ionic liquids in solvents.

Solvents	Stretching frequencies (cm $^{-1}$)				
	Functional group	Range (ν cm^{-1})	Pure solvent	Solvent + [BMim]PF$_6$	Solvent + [4BMim]PF$_6$
Acetonitrile	C≡N	2210-2260	2252.69	2287.41	2295.12
Methanol	O-H	3200-3600	3321.18	3328.89	3336.61
Formamide	C=O N-H	1640-1690 3100-3500	1697.23 3309.61	1699.16 3317.32	1704.95 3326.96

The FT-IR spectra of acetonitrile give a sharp peak at ν_0 = 2259.69 cm^{-1} which is assigned as the C≡N stretching vibration range (2210-2260 cm^{-1}). Through ion-dipole interaction, – vely charged N nitrogen atom of acetonitrile and +vely charged [BMim / 4BMim]$^+$ atom of BMimPF$_6$ / 4BMimPPF$_6$ was formed. When the electrolyte (BMimPF$_6$ / 4BMimPPF$_6$) is added to acetonitrile (i.e [BMimPF$_6$ / 4BMimPPF$_6$] + CH$_3$CN) the peak shift to ν_s = 2287.41 cm^{-1}, 2295.12 cm^{-1}. The formation of ion-dipole interaction between [BMim / 4BMim]$^+$ ion with the C≡N bond results in the shifting of CN stretching frequency because of the disruption of dipole-dipole interaction in acetonitrile [Yandagni and Kebarle, 1972].

In the event of methanol, the presence of more – ve oxygen O atom give a stable order since the interaction is more stronger. A broad peak is observed at v_o = 3321.18 cm^{-1} which is alloted to H-bonded O-H stretching vibration (within the range 3200-3600 cm^{-1}). The – vely charged oxygen O atom and + vely charged $[BMim / 4BMim]^+$ atom (or + vely charged hydrogen H atom and – vely charged $[PF6 / PPF6]^-$) form stronger interaction with $BMimPF_6$ / $4BMimPPF_6$, resulting in ion-dipole interaction. The IR spectra of [$BMimPF_6$ / $4BMimPPF_6$] + CH_3OH) solution was observed and the broad peak shift to v_s = 3328.89 cm^{-1}, 3336.61 cm^{-1} . Due to the interaction of ions $[BMim / 4BMim]^+$ or $[PF6 / PPF6]^-$ with the – OH of CH3OH there is a shift in the H-bonded O-H stretching frequency, because the H-bond between the methanol molecule [Pagliai, 2003] get distorted with the addition of $BMimPF_6$ / $4BMimPPF_6$.

In the event of formamide, the peak are observed at vo = 1697.23 cm^{-1} and 3309.61 cm^{-1} for C=O (1650-1695 cm^{-1}) and N-H (3100-3500 cm^{-1}). When the electrolyte is added to formamide the peak shifts to v_s = 1699.16 cm^{-1}, 1704.95 cm^{-1} and v_s =3317.32 cm^{-1}, 3326.96 cm^{-1} for C=0 and N-H respectively. The formation of ion-dipole interaction between the ion $[BMim / 4BMim]^+$ or $[PF6 / PPF6]^-$ with C=O and N-H bond results in the shifting of the stretching frequency of these bonds because of the disruption of dipole-dipole interaction in formamide [Jasien and Stevens, 1986].

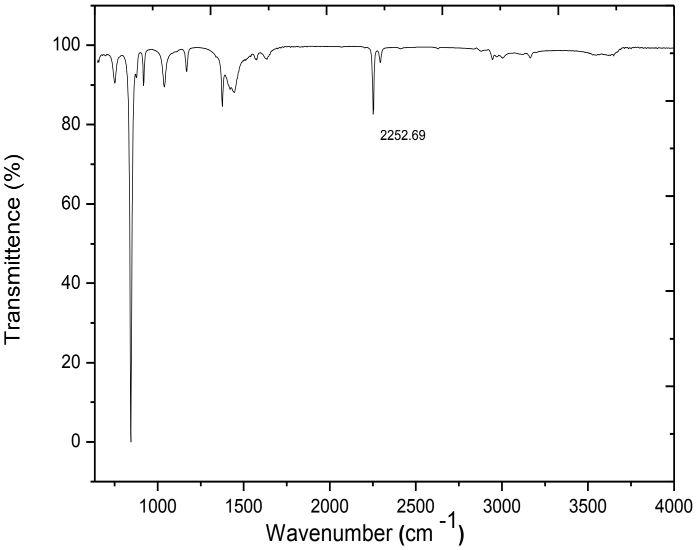

Fig. 24: IR Spectra of Pure Acetonitrile

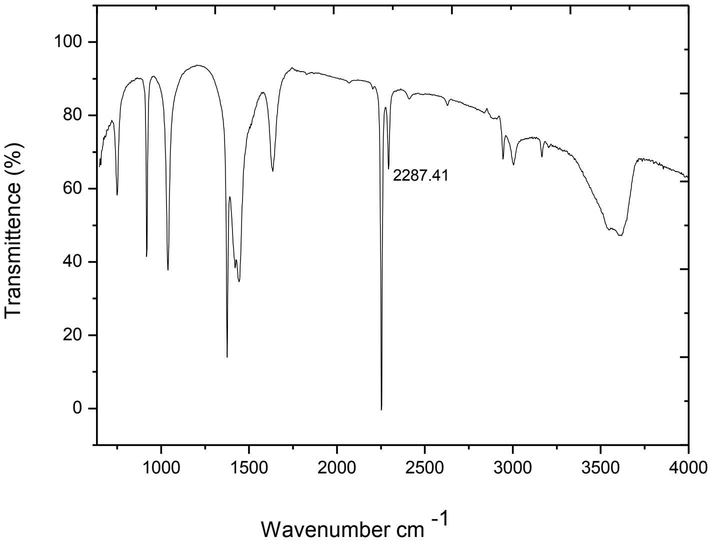

Fig.24(a):IR Spectra of 1-butyl-3-methylimidazolium hexaflorophosphate with Acetonitrile

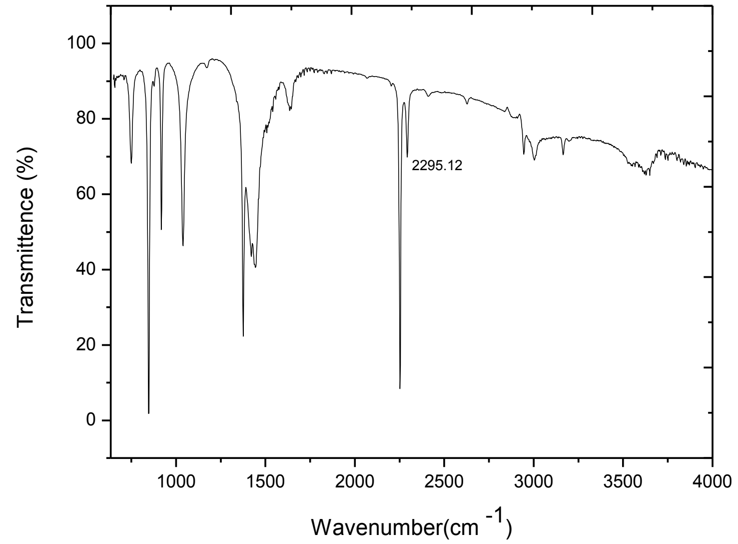

Fig. 24(b): IR Spectra of 1-butyl-4-methylpyridinium hexaflorophosphate with Acetonitrile

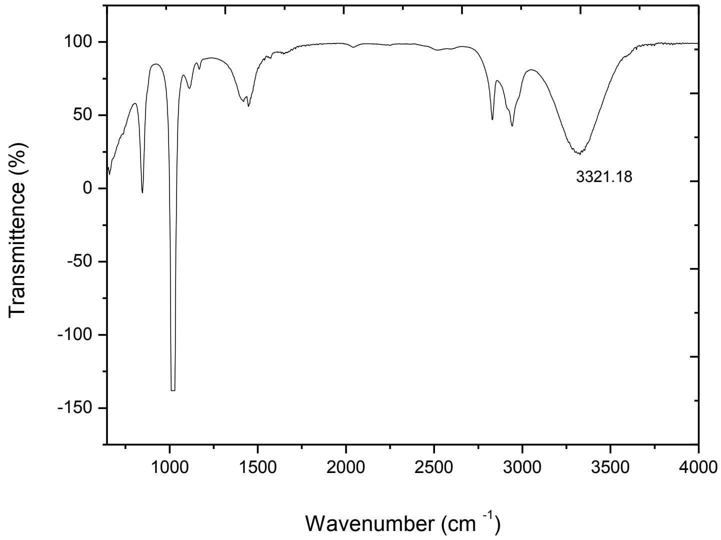

Fig. 25: IR spectra of Pure Methanol

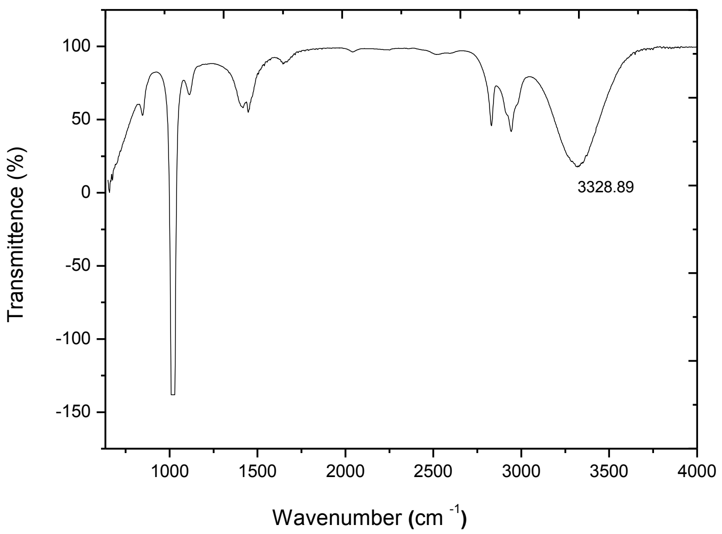

Fig. 25(a): IR spectra of 1-butyl-3-methylimidazolium hexafluorophosphate with Methanol

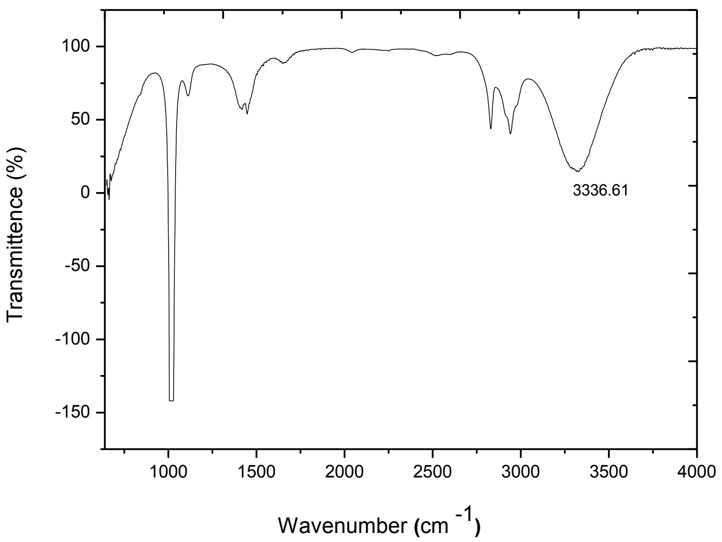

Fig. 25(b): IR spectra of 1-butyl-4-methylpyridinium hexafluorophosphate with Methanol

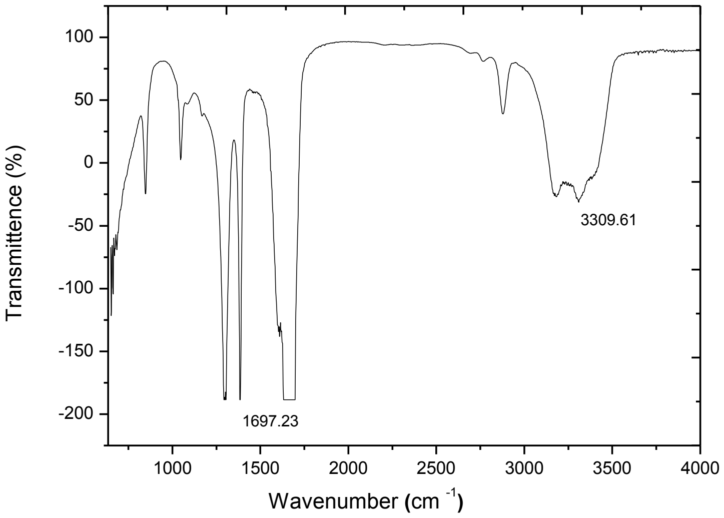

Fig. 26: IR spectra of Pure Formamide

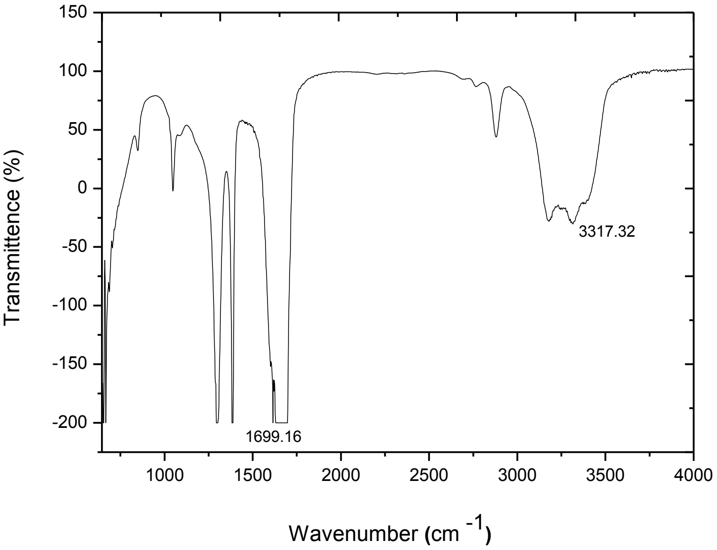

Fig.26(a):IR spectra of 1-butyl-3-methylimidazolium hexafluorophosphate with Formamide

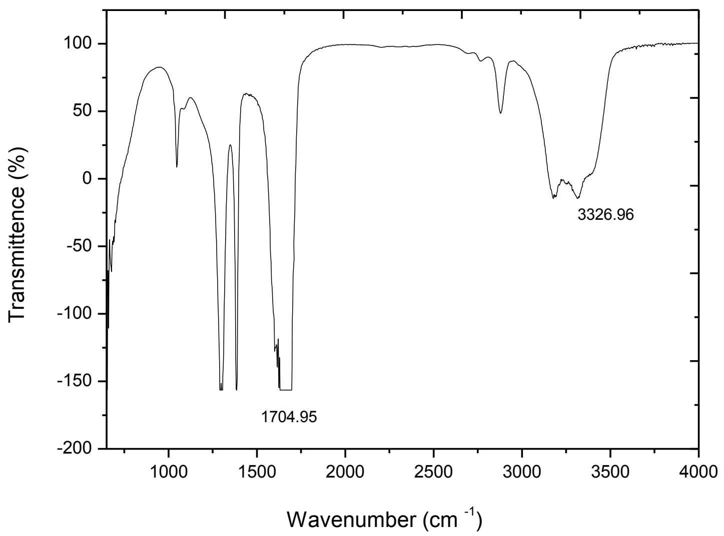

Fig. 26(b): IR spectra of 1-butyl-4-methylpyridinium hexafluorophosphate with Formamide

Through the conductometric measurements and FTIR spectroscopic measurements an extensive study on the ion-solvation behavior of the 1-butyl-3-methylimidazolium hexafluorophosphate $BMimPF_6$ and 1-butyl-4-methylpyridinium hexafluorophosphate $4BMimPPF_6$ in dichloromethane, 1,3-Dioxolane, O-Toluidine and O-Xylene solutions were observed. Depending on the size and the charge distribution of the ions and structural aspects (functional group of the solvents) the tendency of the ion-pair and triple-ion formation are determined. 1-butyl-3-methylimidazolium hexafluorophosphate $BMimPF_6$ and 1-butyl-4-methylpyridinium hexafluorophosphate $4BMimPPF_6$ interact through hydrogen bonding and ion-dipole interactions in all the solvents. Ion-solvent interactions dominate over ion-ion interactions as observed from the study. Therefore, it is found that $4BMimPPF_6$ has the maximum amount of triple-ions formed in O-Xylene.

Chapter 5

Conclusions