STUDIES ON ION PAIR FORMATION OF SOME SELECTED TRANSITION METAL AND NON-TRANSITION METAL COMPOUNDS

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By

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CERTIFICATE

This is to certify that the thesis entitled '*Studies on Ion Pair Formation of Some Selected Transition Metal and Non-Transition Metal Compounds*' submitted by ***Mr. Lalrosanga,*** for the degree of ***Doctor of Philosophy*** in the Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted for any degree in any other university.

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CONTENTS

1. INTRODUCTION

The concept of ion-pair into the evaluation of the inter-ionic force in electrolytic solution was first introduced by Bjerrum in 1926 [Bjerrum, 1926]. The tendency of ions to associate into ion pairs depends on the balance between the electrostatic force and thermal energy. Ion pair formation refers to the association of cations and anions in solution. An ion-pair is defined to exist when a cation and an anion are close enough in space with a common solvation shell, the energy associated with their electrostatic attraction being larger than the thermal energy (kT) available to separate them [Kortum, 1965]. The ions need also to stay associated longer than the time required for Brownian motion to separate non-interacting species [Lacour and Moraleda, 2009]. Key to this definition is also the fact that only strict electrostatic interactions should occur between the ions. No interactions other than the Coulombic attraction should formally exist upon the association of the charges- charges that existed prior to the interaction and remaining unchanged in the interaction [Mac Innes, 1961].

The Debye-Huckel model assumed the ions to be in almost random thermal motion and therefore, in almost random positions. The slight deviation from randomness was pictured as giving rise to an ionic cloud around a given ion, a positive ion (of charge $+Ze_0$) being surrounded by a cloud of excess negative charge ($-Ze_0$). However, the possibility was not considered that some negative ions in the cloud would get sufficiently close to the central positive ion in the course of their quasi-random solution movements so that their thermal translational energy would not be sufficient for them to continue their independent movements in the solution [Pura and Atun, 2003]. Bjerrum suggested that a pair of oppositely charged ions may get trapped in each other's coulombic field; an ion-pair may be formed. Within the ionic cloud, the locations of such ion-pairs are completely random, since, being uncharged, they are not acted upon the coulombic field of the central ion [Harned and

Owen,1958]. Furthermore, on the average, a certain fractions of the ions in the electrolytic solution will be stacked together in the form of ion-pairs [Hefter, 2006].

In solvents of low dielectric constant, where the electrostatic potential energy of an anion and a cation at contact is large as compared to mean thermal energy kT, it is expected the association of ions as a non-conducting pairs [Bag *et al.*, 2009]. As the dielectric constant is increased the extents of association should (and does) decrease, but it should never become zero because there is always a non-zero chance that anion-cation contacts will occur. Conductance of 1:1 electrolytes has been extensively studied [Das and Patnaik, 1996] by using Shedlovsky equation.

The double layer theory describes the process of ion-exchange and ion-interaction chromatography from the point view of distributed electrostatic field effect on the charged analyte retention. Other approaches have more stoichiometric characters and describe the analyte retention on the basis of the formation of ionic pairs and their subsequent retention on the adsorbent surface.

1.1. THE ION-PAIR CONCEPT

In 1926, Bjerrum used Debye-Huckel theory to describe ion association and take into account that the interaction of ions within a short range. He introduced an ion-pair concept give a definition of ion-pairs as neutral species formed by electrostatic attraction between oppositely charged ions in solution, and showed how ion-pair formation was dependent on the ionic size (radius of ions), solvent (dielectric constant), and temperature [Fisher,1967].

Neutral species formed by electrostatic attraction between oppositely charged ions in solution or the partial association of oppositely charged ions in electrolyte solution to form distinct chemical species called ion pairs [Fouss, 1978]. An ion pair is a physical entity with no specific chemical interactions between the ions. The ions of the ion pair move together as a single unit and are held together by electrostatic forces of the coulomb type acting over the short distances that the ions are apart in the ion pair [Marcus and Hefter, 2006]. These Coulombic forces impose a certain degree of cohesion on the unit and this is sufficiently great to overcome the tendency for normal thermal motion to cause the ions to move around as separate particles each with its own translational degrees of freedom. Because the forces holding the ions together are of this physical nature, they depend on three factors, the charges on the ions, the sizes of the ions and the relative permittivity of the solvent in the vicinity of the ion [Shehata and Add. El-Bary, 1996].

It is very important to realize that these forces holding the ions together are therefore independent of the chemical nature of the ions. On this basis, it would be expected that electrolytes which have ions of the same charge and are of similar size would have equilibrium constants of similar magnitude if the associated species is an ion pair [Azzari and Kraus, 1952]. This is found for some 2:2 sulphates, and for some cations of similar size which associate with Cl^- (aq) or I^- (aq).

The first inter-ionic theory of electrolytic solution was that of Debye-Huckel [Debye and Huckel, 1923] and this theory has been remarkably used in interpreting the behavior of ions in dilute solutions. The theoretical calculation for the decreased of ionic mobility with increasing concentration considered two effects [Covington and Dickinson, 1973]. Firstly, when an ion moves through under the influence of an applied electric field, it tends to disturb the surrounding ionic atmosphere which exerts an opposing electric force and, secondly, the ion comprising the ionic atmosphere produced a counter-current of solvent; which also retards the motion of the central ion [Krell *et al*, 1987]. According to the Debye-Huckel theory, in the calculation of the potential at a distance from the central ion, the exponential of the Boltzmann distribution $Z_i\ \epsilon\psi_j$ / kT is expanded in series, thereby transforming the Boltzmann distribution into the linear one.

$$n_i' = n_i\left[1 - Z_i\epsilon\psi_j / kT\right] \qquad \ldots(1)$$

Where subscript *j* refers to the central ion while *i* refers to the i^{th} ion at distance r from the central ion j, Z_i is the valence of the ion i, ϵ is the electronic charge, n_i the stoichiometric concentration, n_i' the concentration modified by the existence of the interionic field and ψ_j the potential due to the ion j and k is the Boltzmann constant. The approximations involved in the above equation are reasonable if $Z_i\epsilon\psi_j \ll kT$. Since ψ_j increases as r decreases, the situation may arise where the two ions may approach each other at such distance that the above equation and therefore, the Debye-Huckel expression become invalid [Holokov and Kapko, 2007]. This problem and the observed deviation from the Debye-Huckel theory are too large. To remove this difficulty, Bjerrum developed the concept of ion pair by postulating that a pair of oppositely charged ions may get trapped in each other's coulombic field [Bockris and Reddy, 1998].

Species are generally describe as ion pairs if two oppositely charged ions in solution stay together at a separation, r, which is smaller than some specified cutoff distance, R. Ions farther apart than are considered "free''. Various theories have been proposed for choosing the value of R and for describing the properties of the ion pairs and free ions that together produce the observed behavior of electrolyte solutions. Ion pairing describes the (partial) association of oppositely charged ions in the electrolyte solutions to form distinct chemical species called ion pairs [Baky *et al*., 1996]. However, when the ion association is weak, there is a strong correlation between these non-specific ion-ion interactions [Nelson and Essington, 2005] (characterized in terms of activity coefficients) and ion pair formation (characterized in terms of association constant). It is generally accepted that ions cannot approach each other more closely than some 'distance of closest approach,' a, due to the strong repulsive forces of the electron shells of the ions, even if polarizable [Samoilov and Ya, 1957]. The distance, a is understood to bear some relation to the sum of the (crystal ionic) radii of the oppositely charged ions, generally $a \geq r_+ + r_-$. In summary, two ions of opposite sign are considered to form an ion pair if their distance apart is between a and R for a time longer than the time needed to diffuse over such a distance. Once ions are paired, they are thought to have no tendency to associate with other ions in dilute solutions, although, at higher electrolyte concentrations, ion triplets, quadruplets, or larger aggregates may form [Marcus, 2008]. Very short- range interactions (hard or nearly-hard sphere repulsions) involve the mutual exclusion of ions at $r > a$. However at distance $a < r < R$, solvation of the constituent ions must be considered. On this basis an ion pair may be classified as (double) separated ion pair (2SIP), when the primary solvation shells of both ions remain essentially intact, as a solvent-shared ion pair (SIP), if a single solvent layer exists in the space between the ion partners of the pair, or as a contact ion pair (CIP), if no solvent exists between the partners and the ions are in direct contact [Marcus and Hefter, 2006]. The long-range electrostatic forces that keep the partners of an ion pair together are non-directional. The type of association that is involved, in most cases, is not true chemical association where a bond, complex or contact pair is formed between two ions. The electrostatic association, defined by Bjerrum mode is simply a convenient way of representing strong coulombic interactions at short interionic distances, where the limiting law approximation fail. Justice has shown that Bjerrum association model is actually consistent with statistical thermodynamics and linear reversible processes and in fact, takes into account higher terms of the limiting Debye-Huckel theory. Many modern conductance theories now incorporate the Bjerrum association concept [Barthel *et al*, 1979]. In any solution of an electrolyte there is always the possibility that the ions of the electrolyte might not be fully dissociated in solution. Ion pairing results when the electrostatic interaction between two oppositely charged ions become sufficiently large for the two ions to move around as one entity, the ion-pair [Fouss and Onsager, 1955]. The extent of association into ion-pairs depends on many factors, with the most important being the nature, charges and sizes of the ions, the characteristics of the solvent and the temperature.

1.2. DEFINITION AND NATURE OF THE ION-PAIRS

Ion-pairs may be defined as a neutral species formed by electrostatic attraction between oppositely charged ions in solution, which are often sufficiently lipophilic to dissolve in non-aqueous solvents (Quinanar-Guerrero *et al.*, 1997, Irwin *et al.*, 1969). It should be emphasized that the formation of an ion pair is due only to outer sphere interaction and even though this molecular interaction can be written according to the mass action law, no chemical bond of any kind is formed. The general notation A^+, B^- is used to describe an ion-pair product which exists as stable, thermodynamically distinct species and not as a transient, continuously exchanging association (Florence and Attwood, 1988; Szwarc, 1970; Breimerand, 1983). It is clear therefore that any charged molecule in solution, under certain conditions, can form an ion-pair, with ions of oppositely charge.

1.3. FACTORS AFFECTING THE FORMATION OF ION PAIRS

The association constant for ion pair formation (outer-sphere complex ions) increases with decreasing size of the anions [Bester-Rogae, 2008]. Association constant also depends on the size of the complex ion. Larger the size of the complex, less stable will be the ion pair. As $[Co\ (en)_3]^{3+}$ is larger in size than $[Co\ (NH_3)_6]^{3+}$, therefore it is expected to form less stable ion pair[Wright and Patterson, 1995]. When the size and charge of the complex ions are nearly the same, the tendency to form the outer-sphere complexes depends on the total number of protons possessed by the complex ions. Therefore, $[Co\ (NH_3)_6]^{3+}$ with 18 protons presents a more favorable positively charged periphery to a negative ion than does $[Cr\ (H_2O)_6]^{3+}$ with 12 protons. Cis and trans effects of complex ion plays an important role for the ion pair formation. Trans-$[Co\ (en)_2\ Cl_2]^+$ does not form a recognizable ion pair with Cl^- because it does not have any dipole moment. Against that a cis isomer favors association with a negative ion in an outer-sphere complex, as it carries a net dipole. The ion pair formation constant increases with increasing product of the charges ($-Z_1 Z_2$). Ion pair formation is easily detected for $-Z_1Z_2=3$ or greater. For 1:1 electrolyte having $-Z_1 Z_2=1$, it is not possible to find evidence for outer-sphere complexes, but it is possible by changing the medium, i.e., changing the dielectric constant of solvent. When we consider $[Co (en)_2 Cl_2]^+$ a cis complex it forms ion pair with chloride ion in methanol having dielectric constant of 32. There is no evidence of any such interaction taking place in water, having dielectric constant of 78. The charge transfer absorption region is markedly changed and shifted from intense band to longer wavelengths, depending upon the electronegativity of the anion [Evans and Noncollas, 1952]. Ion pair formation between $[Co (NH_3)_6]^{3+}$ and different halides, Cl^-, $Br^{-,}$ I^-. Spectral line shifts are more pronounced for iodide and less for chloride ion.

1.4. FORMS OF ION-PAIRS

The work of Sadek and Fous (Sadek and Fous, 1954) and that of Winstein (Winstein *et al.*, 1954), later confirmed by Robert and Szwarc [Robert and Szwarc, 1965], showed that ion pair can exist in two forms: as a tight or intimate ion pair, or as a loose or solvent separated ion-pair, depending on the nature of the solvent-ion interaction. These authors established that free ions in solution are surrounded by solvent molecules polarized by electric fields generated by the ionic charges. A sufficiently strong polarization and solvent ion interaction result in the formation around each ion, of a tight solvation shell. The presence of such a solvation shell is reflected in the fact that the Stokes radius of the solvation ion is substantially greater than that predicted for the bare ion. An ion possessing a tight solvation shell may approach a counter-ion without hindrance until its solvation shell contacts the partner [Murray and Yeager, 1973]. Thereafter, either the associate maintains its structure as a loose, solvent-separated ion-pair, or the solvent molecules separating the partners are squeezed out and a tight contact ion-pair is formed. This implies that solvent-separated ion-pairs may exist only in those media in which the free ions acquire tight solvation shells; otherwise, only tight contact ion-pair is formed. It is important to mention that Bjerrum's original concept of a pair of solvated ions that are held together by coulombic attraction, in a solvent of a low dielectric constant, remains valid without modification despite the presence of a solvation shell [Braunstein, 1971]. For example, if the solvated ion is paired with a bulky counter-ion, the gain in coulombic force arising from the approach of the partners into close proximity may not be sufficient to accomplish the destruction of the solvation shell. Therefore, such pairs exist only in the loose form.

1.5. ION PAIRS, FREE IONS AND GURNEY COSPHERE

In any solution of an electrolyte there is always the possibility that the ions of the electrolyte might not be fully dissociated in solution. Ion pairing results when the electrostatic interaction between two oppositely charged ions become sufficiently large for the two ions to move around as one entity, the ion-pair [Bockris and Reddy, 1998]. The extent of association into ion-pairs depends on many factors, with the most important being the nature, charges and sizes of the ions, the characteristics of the solvent and the temperature.

As a result of electrostatic attraction, ions of oppositely charged form a certain proportion of ion pairs. This is from purely electrostatic consideration defined by Bjerrum [Bjerrum, 1926]. The degree of association (1-α) is given by the following relations:

$$(1-\alpha) = 4\pi n_i \int_a^q \exp\left(-\frac{z_+z_-e^2}{drkT}\right) r^2\, dr \qquad \ldots(2)$$

Where, a= Distance of closest approach

$q = \frac{|z_+\ z_-|e^2}{2DkT} = \text{Critical Bjerrum distance}$

α = degree of dissociation

n_i = number of the ions of the ith kind in unit volume

For two oppositely charged ions to stick together to form an ion pair, it is necessary that they should be closed enough for the Coulombic attraction energy to overcome the thermal energy that scatters them apart [Barthel *et al.,* 1997]. Then one can say that an ion pair will form when the distance (r) between a positive and a negative ion becomes less than q. According to Bjerrum, ion pair formation occurs when an ions of one type of charge (e.g. a negative ion) enters a sphere of radius (q) drawn around a reference ion of the opposite charge (e.g. a positive ion). However, it is the ion pair parameter that defined the distance of closest approach of a pair of ion.

If $a < q$, the ion pair formation can occur (figure 1(a)).

If $a > q$, the ions remain free (figure1(b)).

Bjerrum assumed that all ions lying within a sphere of radius q should be regarded as associated to form ion pair whereas this outside this sphere may be free ions [Glasstone, 1942].

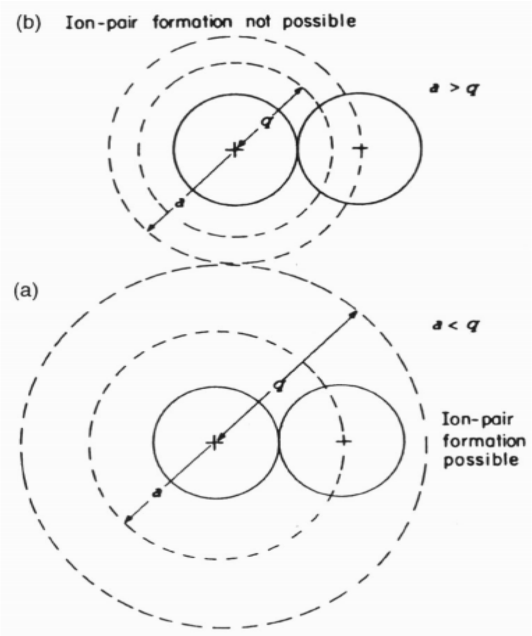


Figure 1(a): ion pair formation possible if $a < q$ and **(b):** ion pair formation not possible if $a > q$.

The ions of an electrolyte solution which find no other unpaired ion in a surrounding sphere of radius R' where R' is the diameter of the cosphere (unpaired ions) and with overlapping Gurnney Cosphere (solvent separated pairs).

Gurney Cosphere R'= Diameter of Gurney Cosphere

Figure 2: Gurney Cosphere

1.6. PROBABILITY OF FINDING OPPOSITELY CHARGED IONS NEAR EACH OTHER

The fraction dn_i/dr is a measure of probability $P(r)$ of finding an ion of charge opposite to that of the central ion at a distance r from the latter (figure 3). Then, according to the Boltzman distribution law, the number dn_i ions of the i^{th} kind in a spherical shell of radius r and thickness dr, surrounding a specified ion is given by [Bjerrum, 1926]

$$\mathrm{dn_i} = \mathrm{n_i} 4\pi \mathrm{r}^2 \mathrm{e}^{-\mathrm{w}/\mathrm{kT}} . \mathrm{dr}$$

$$\mathrm{P(r)} = \frac{\mathrm{dn_i}}{\mathrm{dr}} = \mathrm{n_i} 4\pi \mathrm{r}^2 \mathrm{e}^{-\mathrm{w}/\mathrm{kT}} \qquad \ldots(3)$$

Where, w = work required to separate one of these ions from the central ions from a distance r to infinity.

$$= \frac{\mathrm{Z_+ Z_- e_0^2}}{\mathrm{Dr}}$$

Z_+e = charge of the central ion

Z_-e = charged of the i^{th} ion.

D = dielectric constant of the medium

r = distance of i^{th} ion from the central ion

k = Boltzman constant

T = Absolute temperature

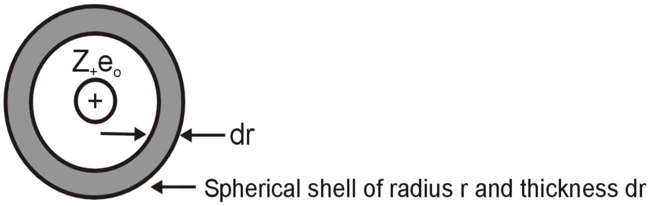


Figure 3: The probability p(r) of finding an ion of charge Z_-e_o in a dr-thickness spherical shell of radius r around a reference ion of charge Z_-e_o

Notice that in this above formula there are two competing factors varying with distance r. The volume of the shell $4\pi r^2 dr$ increased with r and exponential factor, $Z_+ Z_- e_0^2/2DkT$ decreased when Z_+ and Z_- are of opposite sign. The interionic distance r_{min} for which the probability of finding two oppositely charged ions together is minimum (figure 4), and can be obtained by differentiating P(r) with respect to r and setting the result equal to zero.

$$\therefore \frac{2r - Z_+Z_-e_0^2}{DkT} = 0 \qquad \ldots(4)$$

For substituting,

$$r_{min} \frac{Z_+Z_-e_0^2}{2DkT} = q$$

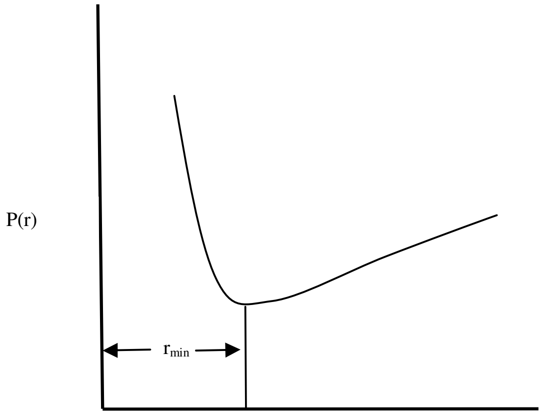


Figure 4: Distribution of oppositely charged ions about a central ion (Bjerrum)

1.7. SIZE OF AN ION AND AN ION PAIR IN SOLUTION

Most size correlations for free ions used crystallographic radii which represent the bare ion. There is no doubt that most ions are solvated in solution though it is difficult to assess precisely the extent of solvation, and hence the size of the solvated ion. Likewise, the ion pair will be solvated, and some estimate of its size is required. Furthermore, the change in solvation pattern on forming the ion pair is of crucial importance [Justice, 1983].

Three limiting situations can be envisaged, but other intermediate situations are possible:

1. An ion pair is formed with no disruption of the individual solvation sheaths of the individual ions, so that in the ion pair these solvation sheaths of the individual ions are in contact and solvent is present between the ions.
2. An ion pair is formed with total disruption of the individual solvation sheaths of the individual ions so that in the ion pair the bare ions are in contact and there is no solvent between the ions.
3. An ion pair is formed with the partial disruption of the individual solvation sheaths of the individual ions so that in the ion pairs some solvent has been squeezed out, but there is still some solvent present between the ions.

The ion pairs which can be found are thus not necessarily identical, and there is the possibility that different experimental methods may pick out and detect only one kind of ion pair, for instance, detect contact ion pairs but not solvent separated ion- pairs [Akhadov, 1981].

A further formal definition commonly used in inorganic chemistry can be proposed:

- an outer-sphere ion pair is one where one, or at most two, solvent molecules lie between the ions.
- an inner-sphere ion pair is one where the bare ions are in contact – all solvent sheaths have been eliminated between the ions.

However, both inner and outer-sphere ion pairs are still solvated as the composite unit, and are described as contact or solvent separated. Although the definitions can be quite unambiguous, experimental classification into contact or solvent separated or inner and outer sphere ion pairs most certainly is not unambiguous, and may even, at best, be only a guess. This is exactly the same problem as is encountered when discussing the formal and experimental distinctions between complexes and ion pairs [Fernandez-Prini, 1973].

Attempts to distinguish experimentally between the formations of:

(a) ion pairs from free ions

(b) complexes and chelates from free ions

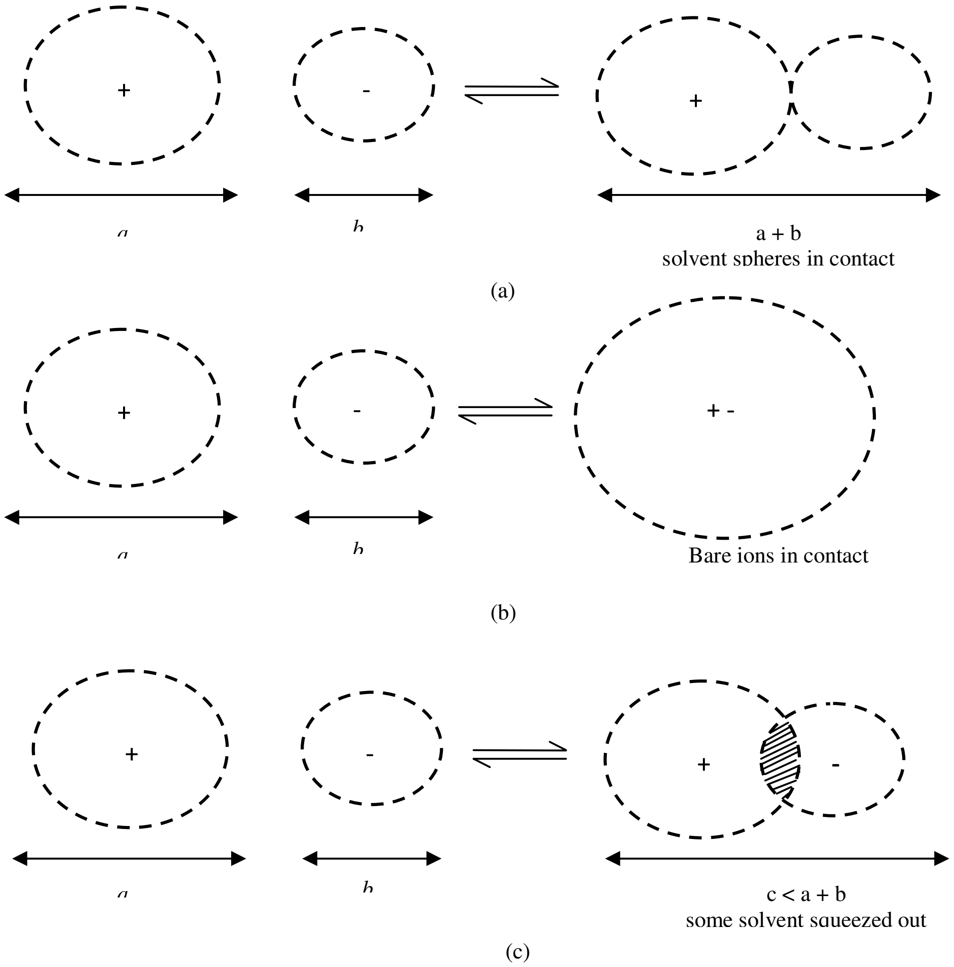


Figure 5 (a): Solvent sheaths of individual ions in contact; **(b)** bare ions in contact; **(c)** partial disruption of the solvation sheaths of ions showing some solvent being squeezed out.

1.8. MODEL FOR IONS IN SOLUTION

The model used here for aqueous solution is shown in (Figure 6). Both the cations and the anions have primarily solvation shells (A) consisting of solvent molecules interacting directly with the ions [Bockris and Reddy, 1998]. Beyond primary solvation shells, are secondary solvation shells (B), solvent molecules are not in contact with the ions, but are influenced by their proximity, mainly through interaction of their dipoles with the electrostatic fields of the ions. At a sufficient distance from the ion its perturbing effect on the solvent can be considered negligible and such solvent molecules comprise bulk solvent (D). In a specific three (3) dimensional structure, there is likely to be mismatch between the structures of the regions D and B. hence it is necessary to consider an intermediate disordered region C between regions D and B. One objective must be to attempt to estimate the number of solvent molecules in each of the shells, and really only applies to very dilute solutions.

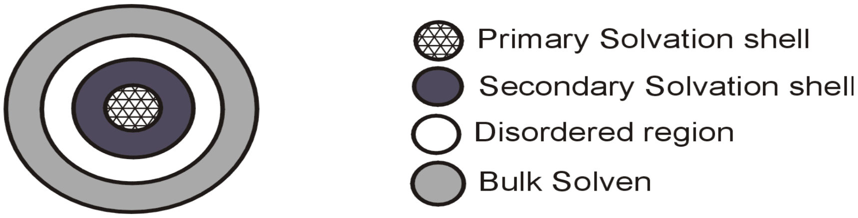


Figure 6: The Environment of an ion in aqueous solution

1.9. SUCCESSIVE STAGES AND THERMODYNAMICS OF ION PAIR

The distinction between the ion pairs and complexes is, a distinction between aggregates held together mainly by electrostatic forces or by covalent forces. Different kinds of problem arise when successive ion pair equilibria arise. This can occur in two ways [Conway *et al.*, 1983]; firstly, successive hydration may lead to distinguishable types of ion pairs, from the case where both the cation and anion remain hydrated and a loose hydrate contact pair is formed. Secondly, in some cases one or more anions may become associated with a given cation, particular if the latter is divalent or trivalent. For the equilibrium, successive ion pair involving varying degrees of solvation may be represented by,

$$M^{z+}aq \quad + \quad A^{z-}aq \;\rightleftharpoons\; [M^{z+}aq, A^{z-}aq] \;\rightleftharpoons\; [M^{z+}H_2O\,A^{z-}]aq + XH_2O$$

Loose hydrate complex solvent separated ion pair

$$\rightleftharpoons \left[MA^{(Z_+ - Z_-)}\right]_{aq} + \;(X-1)H_2O, etc$$

contact ion pair

A small distinction between the various ion pair can be made on the basis of whether they are 'outer-sphere' (one or two solvent molecules or ligands involved between the pair of ions) or 'inner-sphere' complexes corresponding to the contact situation (contact ion pair). A thermodynamic criteria for distinction between ion pair and complexes was proposed by Duncan and Kepert [Duncan and Kepert, 1959; Davies, 1962]. Given the equilibrium,

$$M^{z+}_{aq} \quad + \quad A^{z-}_{aq} \quad \leftrightharpoons \quad \left[MA^{(z_+ - z_-)}\right]_{aq} - G^o(M^{z+}) - \; G^o(A^{z-})$$

Vant't Hoff isothermal correlation.

$-RTlnK_A = \Delta G^o = \Delta H^o - T\Delta S^o$ is extremely instructive to differentiate between entropic and enthalpic effects in the association process [Petrocci,]. The measurement of ΔH^o and ΔS^o can be made by studying the association constant over the range of temperature.

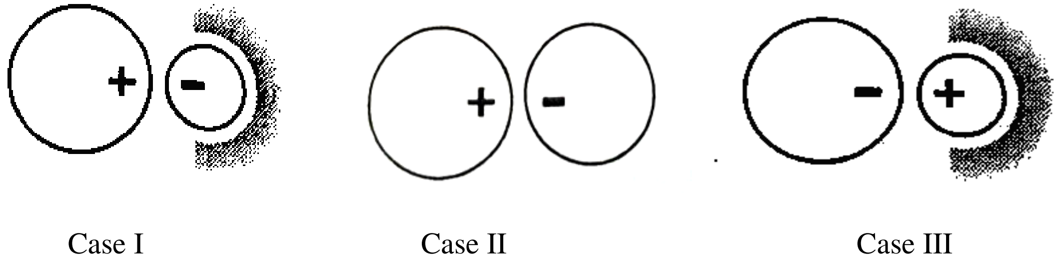
1.10. SOLVATION OF ION-PAIRS

The formation of ion-pairs is only possible if the ions approach each other and reach a critical separation distance (d) given by the Bjerrum equation:

$$D=|Z^+Z^-|e^2/2\varepsilon kT \qquad \ldots(5)$$

Where Z^+ and Z^- are the ionic charges, e is the electron charge, ε is the dielectric constant, k is Boltzmann's constant and T is the absolute temperature. The equation shows the importance of the dielectric constant (ε) in ion pair formation; accordingly a solvent with a high dielectric constant such as water ($\varepsilon=78.5$) will be unfavourable for ion pair formation, but this does not mean that this is impossible. On the other hand, the interaction becomes increasingly important solvents with $\varepsilon < 40$. Although this rule is applicable to a large number of ion-pair extraction systems (Lee and Kim, 1987; Bult, 1983; Lee *et al.*, 1987), some authors have shown that other non-coulombic contributions can be involved in the ion association, for example hydrogen bonding, lipophilicity of the ions, and other factors such as the solubility parameters would explain more satisfactorily the solvation of the ion-pair (Sadek and Fous, 1954; Freiser, 1969).

The behaviour of the solvating agent and its affinity for the ion-pair can be explained by the solvation theory proposed by Higuchi (Higuchi *et al.*, 1967). Ion-pairs can be classified according to the degree of charge accessibility, into three different categories (Figure 7). In the first case, it is assumed that the cation is large and lipophilic except for the positively charged center. The small external surface would be expected to carry a relatively a negative charge per unit area (shown by the external shadow in figure 7). This type of system may be effectively solvated by lipophilic molecules having a positively charged surface, e.g. dipolar molecules with acidic protons such as chloroform, phenols and alcohols. Since the bonded solvating molecules would have polar end buried adjacent to the anion, the appearance presented to the surrounding solvent by the solvated ion-pair would be that of a relatively non-polar aggregate.



Case I Case II Case III

Figure 7: Different types of ion pairs according to the degree of charge accessibility.

In the second case, the situation is reversed, the ion-pair having its cationic charge largely exposed. Solvating species containing nucleophilic sites may be expected to be particularly effective for this type of ion-pair, e.g. ethers, ketones, amides and phosphate esters. The third case is that of an ion pair with deeply buried charges. Having no exposed electrically unbalanced surface, it would be expected neither to require solvation in order to be readily extracted by non-polar solvents. On the other hand, Higuchi attributes ion-pair solubility to the formation of complexes involving association with a discrete number of solvent molecules, which take part in the formation of the ion pair in the organic phase. This solvation can be written as equilibrium:

$$A^{+}, B^{-} + nS \rightleftharpoons A^{+}, B^{-}.nS \quad \ldots(6)$$

Where A^+ and B^- are oppositely charged ions in solution and nS is the discrete number of solvent molecules assumed to be complexed with the ion-pair. The concept of a specific solvation for ion-pairs has been confirmed using infrared techniques, and nuclear magnetic resonance and electron spin resonance spectroscopies (Szwarc, 1972).

1.11. VISCOSITY, EQUIVALENT IONIC CONDUCTANCE AND WALDEN PRODUCT

The equivalent conductance Λ can be measured very precisely [Erdey-Gruz., 1974] in dilute solutions. Information on ion-solvent interactions can be obtained both from Λ_o, the infinite dilution value, and from K_A, association constant derived from the concentration dependence of Λ_o. Essentially K_A is related to the distance of closest approach of the ion pair through Bjerrum equation [Conway *et al.*, 1983]. Unfortunately, as Kay and his co-workers [Kay *et al.*, 1976] have shown, $\ln K_A$ is not a simple function of I/D as predicted by Bjerrum, no simple correlation exists for the dependence of $\ln K_A$ on ionic size. Depending on the type of solvent, K_A values increase, remain constant or decrease with the ionic size. Even with iso-dielectric mixtures K_A varies significantly with solvent compositions. The failure of the equilibrium constants to reveal unambiguous information of ion-solvent interactions is due to the fact that these parameters are measuring solute-solute interactions and there is better hope of obtaining solvation information from Λ_o. The simplest form of relating $\lambda_o^{\pm}$ to the effective ionic size in solution $\gamma^{\pm}$ is through the Stoke's equation:

$$\lambda_o^{\pm} = \frac{|Z|\epsilon F}{6\pi\eta r^{\pm}} \quad \ldots(7)$$

Where ϵ → the electronic charge

F→ the Faraday

η → the viscosity of the solvent

$r^{\pm}$ → interionic distance

$\lambda_o^{\pm}$ →ionic conductance

Again the activation energy for the viscous flow of water viz., 15.88kJ at 25°C [Glasstone, 1942], hence it is probable that ionic conductance is related to the viscosity of the medium and the viscosity of the water at a series of temperatures should be approximately constant. In general, the product of the ionic conductance and the viscosity in aqueous and non-aqueous media is also approximately constant over a range of temperature. Walden noted that the product of the equivalent conductance at infinite dilution and the viscosity of the solvent were approximately constant and independent of the nature of the solvent. This conclusion is known as Walden's Rule [Glasstone , 1932] and may be expressed as:

$\Lambda_o\eta_o \approx$ constant for a given electrolyte in solvent

Since Λ_o is the sum of the conductances of the constituent ions it follows that $\Lambda_o\eta_o$ should be approximately constant for a given ion in all solvents. If Stoke's law were obeyed, the values of $\Lambda_o\eta_o$ would be constant only if the effective radius of the ions were same in different media. 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 $\Lambda_o\eta_o$ not be expected. For small ions the value of $\Lambda_o\eta_o$ will depend to some extent on the fundamental properties of the solvent as well as on the effective size of the ion. And for large ions such as tetraethyl ammonium and picrate ions, the $\Lambda_o\eta_o$ are much more nearly constant than in the case of other ions.

1.12. ION-PAIR IN AQUEOUS SYSTEM

Although ion-pair formation has been considered only for solvents with a low dielectric constants (Bjerrum's ion-pair), the existence of the ion-pair in water or in other highly structured (bonded) solvents is possible when the ions involved are largely hydrophobic. In this case, ion-pairing is due to a solvent mediated effect rather than to an electrostatic interaction (Lee *et al*., 1987; Florence and Attwood, 1988). The term "water structure enforced" ion-pairing was introduced by Diamond (Diamond, 1963) in order to explain the existence of ion-pairs in aqueous systems. If both the cation and anion are large hydrophobic species, the hydrogen-bonded water structure forces them together to maximize the water-water interactions and to minimize the structural perturbation. Water structure enforced ion-pairing involves both electrostatic and hydrophobic interactions, the relative contribution of which is dependent upon both ions structures and on their immediate environment. Despite the possibility to form ion-pairs in aqueous solution, the usefulness of this phenomenon is very limited due to the low association constant; furthermore, the ion-pairs exist only at very low concentration, because of the poor solubility of the ions (Lee, 1987; Freiser, 1972; Freiser, 1969).

1.13. THE STRUCTURE-BREAKING EFFECT : IS THE IMPORTANT EFFECT OF THE SOLVATION CONCEPT

In highly structured solvents, such as water and heavy water; modification in the structure of the liquid by ions may significantly influenced the properties of the solution. For example, aqueous solutions of KCl are less viscous than pure water. These phenomena are generally attributed to structure breaking or negative hydration [Frank and Evans, 1945; Samoilov, 1965]. In bulk water, through hydrogen bonding, most water molecules are coordinated to four other molecules, two dipoles being oriented towards the central molecule and two away from it. On the other hand, near an ion, the field tends to orient all the water molecules radially. It is therefore reasonable to imagine that at some distance from the ion there will be competition between the two orienting influences and the water molecules will be more labile than in pure water, i.e., they will behave as if they were at higher temperature. While this effect should be observable in all highly structured solvents, it has been evidenced mostly in aqueous systems [Hansen and Mc. Donald, 1986].

1.14. ION MOVEMENT METHODS

There are number of methods of assessing ion solvation that are based on determining the resistance to motion through the solution. The motion may be spontaneous (e.g. diffusion), mechanically engineered (e.g. viscosity), or engendered by some electrical means (e.g. conductivity). Many of these methods give the sum of cation plus anion contributions but some do give estimates for individual ions. Conductivities and mobilities, which are closely related, are most direct relevance, as they provide a measure of the resistance to motion through the liquid of solvated ions. This resistance reflects their effective size [Burgess, 1987]. Another way of looking at ionic drift is to consider the fate of any particular ion under the field. The electric force/ field would impart to it acceleration according to Newton's second law.

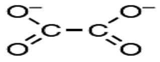
1.15. COMPLEXES FROM FREE IONS

Where a complex is formed there is an intimate chemical interaction between the ions. Some electronic rearrangement is occurring resulting in covalent interactions, in contrast to the physical coulombic electrostatic interactions involved in the formation of an ion pair [Torell, 1987]. If complexes and chelates involve intimate chemical interactions, the extent of association should reflect the chemical nature of the ions involved. Equilibrium constants should be different, and possibly even very grossly different, for equilibria which superficially seem very similar and alike, for instance, association of one species with ions of similar size and charge. The situation is reminiscent that found for the dissociation constants of weak acids and bases where the magnitude of the equilibrium constants depends on the chemical nature [Sillen and Martell, 1971] of the species involved. It is expected for the formation of ion pairs, where the magnitude of the association constant is expected to be independent of the chemical nature of the ions involved.

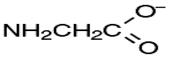
The metal ions:

$Cu^{2+}(aq)$, $Ni^{2+}(aq)$, $Co^{2+}(aq)$, $Zn^{2+}(aq)$, $Mn^{2+}(aq)$

have crystallographic radii which are very similar, and they all have the same charge,+2. When they interact with oxalate and with glycinates



oxalate



glycinate

A wide variation in the association constants is found. The glycinates, for instance, have values ranging from 2.75 x 10^3 to 4.2 x 10^8 $mol^{-1}dm^3$. Complexes are assumed to be formed. On the other hand, it is believed that the interaction of the same metal ions with SO_4^{2-} (aq) results in ion pair. Here the association constants are very similar, ranging from 1.9 x 10^2 to 2.9 x 10^2 $mol^{-1}dm^3$.

1.16. COMPLEXES FROM IONS AND UNCHARGED LIGANDS

If an associated species is formed between an ion and an uncharged ligand, it is usually assumed that a complex is formed and that electronic rearrangements of a chemical nature have occurred [Parsons, 1959]. When aqueous NH_3 is added to an aqueous solution containing Cu^{2+} ions an intense blue coloration indicating the electronic rearrangement occurs, and the main species formed is the complex:

$$\mathrm{Cu^{2+}(aq) + 4NH_3(aq) \rightleftarrows Cu(NH_3)_4^{2+}\ (aq)}$$

Formation of an intimate chemical species implies a fairly drastic alteration in the solvation sphere around the $Cu^{2+}(aq)$, with NH_3 ligands displacing the solvent molecules from around the ion. Ion pair formation is invoke as the most plausible explanation either of certain types of direct experimental evidence or of deviation observed at moderate concentrations from predictions of electrolyte theories that accurately describe the properties of very dilute electrolyte solutions [Robinson and Stokes, 1956].

1.17. LIMITATION OF THE CONCEPT OF ION PAIRS

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

1.18. SCOPE OF THE STUDY

Ion-pairing was initially investigated in the field of physical chemistry; the concept was rapidly adopted in colloidal chemistry, analytical chemistry, and the pharmaceutical sciences. Higuchi et al. have reported numerous methods for performing extraction of ionized solutes into organic phases in which ions of opposite charge are added to the aqueous phases, resulting ion-pairing between the solute ion and pairing ion. The resulting complex is neutral and poorly hydrated and can be easily transferred to the organic phases. The ion-pair extraction method is widely used in the pharmaceutical and analytical sciences. Without developments in theory in this area, there will be lingering doubts about the reality of ion pairing, at least for low charge electrolytes in high permittivity solvents.

Comparison of ionic association of simple salt and complex salt in water has not been reported so far. And little information is available about the ion association of complexes having mixed ligands, ion-ion, ion-solvent and solvent-solvent interactions of transition metal complexes. This is more so in the case of mixed solvents. Moreover, there is very little report of comparative studies for the wide range temperature dependence of ion pair formation of transition metal complexes in pure and mixed solvents. We also considered that the conductance measurements in pure solvents will give the ion solvent interactions and in mixed solvents an all over view of the main aspects of solvation.

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

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

Sl.No.	Salt	Solvent
1.	$CoCl_2$. $6H_2O$ and $[Co(NH_3)_5Cl]Cl_2$	Water
2.	N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride	Water + Methanol
3.	N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride	Water + Methanol
4.	LiCl and $LiNO_3$	Water + Acetonitrile

2. REVIEW

2.1. REVIEW OF ION PAIR FORMATION IN METALS Cu(II), Cu(I) AND Co(III) COMPLEXES

Study of outer sphere ion-association of transition metal complexes have been subjected to various workers. The concept of ion association provides relatively simple and self consistent method of dealing with the situation which arises when ions of oppositely sign are close together [Das *et al.*, 2003]. In these circumstances the energy of the mutual electrical attraction may be considerably greater than their thermal energy, so that they form a virtually new entity in the solution of sufficient stability to persist through a number of collisions with solvent molecules. The scope of this review is to survey the outer sphere ion-association of metal complexes using various methods.

2.2. CONDUCTOMETRIC METHOD

Among the various available methods the measurement of electrical conductivity of dilute solution provides valuable method of studying outer-sphere ion association of inert complexes [Bianchi *et al.*, 2000]. Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolytic solutions. Because of its relative simplicity and versatility, the measurements of the conductivity of electrolyte solutions which can be carried out to a very high precision, remains an important tool to obtain information about electrolytes in different solvents [Hugo L. Bianchi *et al.*, 2000]. Conductivity of aqueous system has recently provided valuable information about the influence of the solvent number-density in the low fluid-density regime and its effect on the ion-pairing equilibrium [Gruskiewiez *et al.,* 1997; Zimmerman *et al.,* 1997]. Data limited to the concentration range which $\kappa d < 0.1$ are usually analyzed using some of the available classical equations [Fernandez-Prini, 1973].

Electrical conductivity measurements provide, along with colligative properties, the oldest experiment evidence for the existence of ion pairs in solution [Pura and Atun, 2002]. Conductivity is a transport property. Nevertheless, such measurements can provide thermodynamic information, in the form of association constant, because there is a direct correspondence (at least for symmetrical electrolytes) between the formation of electro-neutral ion pairs [Singh *et al*., 2008] and a decrease in solution conductivity.

2.2.1. Ion Pair Formation in 3:2 and 3:1 Co (III) Complexes:

Using Conductivity method, Yokoyama, Ohta and Iida [Yakoyama *et al*.,1992] had investigated the ion-exhibiting the influence of decreasing size of the co-ordination sphere and increasing charges of the anion/cation forming the ion pair.

1. The association constant for tris (1-amidino-O-alkylurea) cobalt (III) complexes:

i). $\{[Co\ (AMUH)_3]Cl\}^{+2} > \{[Co(AEUH)_3]Cl\}^{+2}$

ii) $\{[Co\ (AMUH)_3]SO_4\}^{+} > \{[Co(AMUH)_3]Cl\}^{+2}$

iii) $\{[Co\ (AEUH)3]SO4\}^{+} > \{[Co(AEUH)_3]Cl\}^{+2}$

iv) $\{[Co\ (AMUH)_3]SO_4\}^{+} > \{[Co(AEUH)_3]Cl\}^{+2}$

AMUH = 1-amidino-O-methylurea

AEUH = 1-amidino-O-ethylurea

2. The association constants for diammine bis (1-amidino-O-alkylurea) cobalt (III) complexes:

i). $\{[Co(NH_3)_2(AMUH)_2]Cl\}^{+2} > \{[Co(NH_3)_2(AMUH)_2]Br\}^{+2} > \{[Co(NH_3)_2(AMUH)_2]I\}^{+2}$

ii). $\{[Co(NH_3)_2(AMUH)_2]SO_4\}^{+} > \{[Co(NH_3)_2(AEUH)_2]Cl\}^{+2} > \{[Co(NH_3)_2(AEUH)_2]Br\}^{+}$

$> \{[Co\ (NH_3)_2(AEUH)_2]I\}^{+2}$

iii) $\{[Co\ (NH_3)_2(AMUH)_2]X\}^{+2} > \{[Co(NH_3)_2(AEUH)_2]X\}^{+2}$ X= Cl or Br or I

3). The association constant for ethylene diamine bis (1-amidino-O-methylurea) cobalt (III) complexes.

$\{[Co\ (en)(AMUH)_2]Cl\}^{+2} > \{[Co\ (en)(AEUH)_2]Br\}^{+2} > \{[Co\ (en)(AMUH)_2]Br\}^{+2}$

$> \{[Co(en)(AMUH)_2]I\}^{+2}$ en = ethylene diammine

4). The association constants for α, α' –dipyridyl bis (1-amidino-O-methylurea) cobalt (III) complexes.

$\{[Co\ (\alpha, \alpha'–dipy)(AMUH)_2]Cl\}^{+2} > \{[Co\ (\alpha, \alpha'–dipy)(AMUH)_2]I\}^{+2}$

α, α'–dipy = α, α' –dipyridyl

5). The association constants for O-phenanthroline bis (1-amidino-O-methylurea) cobalt (III) complexes.

$\{[Co\ (O\text{-}phen)(AMUH)_2]Cl\}^{+2} > \{[Co\ (O\text{-}phen)(AMUH)_2]Cl\}^{+2}$

O-phen = O-Phenanthroline

6). The association constant for glycinato bis (1-amidino-O-methylurea) cobalt (III) complexes.

$\{[Co\ (glyH)(AMUH)_2]Cl\}^{+} > \{[Co\ (glyH)(AMUH)_2]I\}^{+}$ glyH = glycine

The order of the association constants found for the above observations, the following conclusions were made:

- With increase in size of the complex cation, the association constant of the ion pair decreases.
- Charge of the ions (cations/anions) also plays an important role in the association constant values. Outer sphere association constant decreases with decreasing charge of ions.
- The electronegativity of anion also plays an important role in the formation of outer-sphere ion-association. With increase in the electronegativity of the anion forming the ion pair, the value of association constant increases.

- The association constant of the ion pairs increase with increase in temperature. This is due to the break-down of the hydration shell of the complex cation and anion thereby favoring the association constant.

Using conductance method, Jenkins and Monk had studies the ion pair formation of $[Co(NH_3)_6]^{+3}$, $[Co(en)_3]^{+3}$ and $[Co(pn)_3]^{+3}$ (pn = propylene diamine) with chloride and sulphate ions[Jenkins and Monk., 1953]. It was observed that the increasing radii of the complex cations are found to alter systematically the limiting mobility of the ions. That is λ^o for $[Co(NH_3)_6]^{+3}$ (99.2) > $[Co(en)_3]^{+3}$ (74.7) > $[Co(pn)_3]^{+3}$ (65.06) and the sizes of the ions bring in the order : $[Co(NH_3)_6]^{+3}$ (2.77Å) < $[Co(en)_3]^{+3}$ (3.68Å) < $[Co(pn)_3]^{+3}$ (4.23 Å). Using Stoke's law and Bjerrum equation, the sizes of ion pairs of the complexes were also calculated (table.1).

Table 1: Radii of ion pair (Å) and dissociation constant (k)

Ion pair	k	Radii of ion pair (Å) Bjerrum's Method	Stokes law	Ref.
$[Co(NH_3)_6]^{3+}SO_4^{2-}$	2.77×10^{-4}	2.56	5.06	2
$[Co(en)_3]^{3+}SO_4^{2-}$	3.55×10^{-4}	4.28	5.97	2
$[Co(pn)]^{3+}SO_4^{2-}$	17.5×10^{-4}	5.76	6.52	2

Rajmuhon and Jibanlata [Rajmuhon and Jibanlata, 1997] had done the physico-chemical studies and thermodynamics of association of some cobalt (III) mixed ligand complexes containing 1-amidino-O-alkylurea as main ligand and O-phenanthroline, α, α' – dipyridyl, ethylenediamine, biguanide as secondary ligands. These complexes show outer sphere ion association within the experimental temperature range 5°C to 50°C, which is supported by negative ΔG values of ion-association. Each of the complex in the chosen set of compounds shows a minimum values of association constant K_A (min) at a particular temperatures t_{min} which is characteristic of the anion. The increasing order of t_{min} are found in the order Cl^- < Br^- < I^-. The values of ΔH^o have –ve value below t_{min} indicating that exothermic interaction exist between the ion and become dominant at different temperatures below t_{min} .The +ve and increasing value of ΔH^o_{ass} with increasing temperature after t_{min} suggests the ion association process is endothermic in nature. After, t_{min} association constant of the ion pair increases with rise in temperature. This might be due to the breakdown of the hydration shell of the complex cation and anion thereby favouring the association process. This is supported by the +ve and increasing values of entropy with rise in temperature [Austin and Mair, 1962].

The variation of equivalent conductivity with concentration for the compounds $[Co(NH_3)_6]Cl_3$ and $[Co(NO_2)(NH_3)_5]Cl_2$ had been investigated by Tamamushi, Isono and Katayama [Tamamushi *et al.*, 1967]. The plot of Λ_{exp} (equivalent conductance) vs $\sqrt{C}$ (C=concentration) were found to deviate from the theoretical Onsager line. The deviations were interpreted due to ion-pair formation between the complex cations and chloride ions. The degree of dissociation (α) from the conductivities data of the possible ion-pairs $[Co(NH_3)_6]^{3+}Cl^-$ and $[Co(NO_2)(NH_3)_5]^{2+}Cl^-$ were determined according to the successive approximation method as described by Jenkin and Monk [Jenkins and Monk, 1950]. They also calculated the thermodynamic association constant, K_A by using the activity co-efficient of the ions estimated from the Debye-Huckel limiting equation. The log K_A values of hexamine cobalt (III) and nitroso-ammine cobalt (III) with chloride ions at 25°C were found to be 1.5 and 1.2 respectively. The value of the log K_A of the former is in good agreement with that (log K_A = 1.49) reported by Jenkins and Monk. Hartley and Donalson [Hartley and Donalson, 1937] based on the conductance behavior had also studied the ion-association by hexamine cobalt (III) trimetaphosphate and tetraphosphate in aqueous solutions and obtained similar results. Pethybridge and Spiers [Pethybridge and Spiers, 1976] have measured conductivities of trans-$[Co(NO_2)_2(en)_2]X$ (where X=Cl, Br, I, NO_3, ClO_4).

Cis$[Co(NO_2)_2(en)_2]X$ (where $X=I^-$ and NO_3) and M[Co(edta)] (M=Li, Na, K and edta=ethylenediamine tetra acetic acid anion). They analyzed their experimental data by using the equation for Fouss-Hsia [Fous and Hsia, 1967] and found that each electrolyte is slightly associated in water.

The electrical conductivity and ion association of the diastereoisomeric salts, $\Delta(-)_{598}$-$[Co(NO_2)_2(en)_2]$ $\Delta(+)$-[Co(edta)] and $\Delta(+)_{598}$-$[Co(NO_3)_2(en)]$ $\Delta(+)_{546}$-[Co(edta)] in aqueous solutions at 15°, 25° and 35°C was studied by Yokoyama [Yakoyama and Nishmura, 1985]. The deviation from Onsager limiting law was suggested due to ion-association. He also evaluated the stokes radii for cis-$[Co(NO_2)_2(en)_2]^+$ and $[Co(edta)]^+$ as 3.44Å and 3.52Å respectively. He also investigated the temperature dependence of ion solvent interaction and evaluated thermodynamic functions ΔG^0, ΔH^0 and ΔS^0. The negative values of ΔH^0 were interpreted due to the existence of short-range forces almost independent of the dielectric constant of the medium and could not be explained from ion association theories. The low entropy values (ΔS^0~0) was suggested due to the ion-association occurring within the release of the hydration water molecules of the complex ions [Yakoyama *et al.*, 1994]. The comparative larger value of K_A for each salt was considered to be due to the formation of contact ion pairs. Yokoyama and Nishimura studied the electric conductivities of aqueous solution of the diastereoisomeric salts $\Delta(-)_{589}$-cis-$[Co(NO_2)_2(en)_2]$, $\Delta(-)_{589}$-$[Co(mal)_2(en)]$ and $\Delta(+)_{589}$-cis-$[Co(NO_2)_2(en)]$ $\Delta(+)_{589}$-cis-$[Co(NO_2)_2(en)]$ $\Delta(-)_{589}$-$[Co(mal)_2(en)]$ (en=ethylenediamine, mal= malonate ion) at temperature ranging from 15° to 35°C to investigate the ion pair formation.

Dash and his co-workers [Dash *et al.*, 1997] investigated viscosity and Conductometric studies of octahedral Co (III) complexes in water + mannitol, water + sorbitol and water + DMSO mixtures. They found that the Λ_0 values in any solvent increase from carbonatopentamine to aquopentamine and is replaced by a carboxylato group, remarkable changes in Λ_0 values are observed. For oxalate, the Λ_0 value becomes maximum, then decreases for the malonate and further decreases for succinato complex. The difference in Λ_0 can be interpreted as being a superposition of two effects: (1) various limiting molar conductivities of the complex cations, and (2) different extent of association in solution. Thus it follows that the difference between the values arises from the difference in the transport properties of solvated complexes which reflect factors affecting their effective sizes. The factors which influence the size of the complex can be: radii of the non-solvated cations. These factors should be of little importance in view of the fact that the central metal ion is common in all the complexes. Therefore, the factors which influence the solvodynamic radii may be the distorsion of the octahedral symmetry or the metal-ligand bond length or both. The solvodynamic radii of the complex play an important role in influencing the ionic mobilities and hence the differentiation of the conductivity of the complexes. It is convenient to consider first any information obtainable from the Walden product ($\Lambda_0\eta_0$) value, as it should be virtually free of ambiguity. Appreciable variation in the walden product as a function of the solvent is generally regarded as an index of specific ion-solvent interactions including structural effects.

Walden product of water, water + 5wt% mannitol and water + 5wt% sorbitol: A reasonable constancy of the Walden product in different solvents for carbonatopentamine cobalt (III) nitrate, and for aquopentamine cobalt (III) nitrate in water and 5 wt% mannitol indicates that there is not much change in the solvation of the corresponding ion pair with change of solvent. However, as observed, oxalatopentaamine and malonatopentaamine-Co (III) complex cations exhibit considerable variation in their Walden product with the solvent. In these cases solvation reflects are reflected in the variation of the walden products of the Co (III) complexes with change of ligand in the complex cation. The variation in the values of $\Lambda_0\eta_0$ can be interpreted in terms of the effect of the complex cation (since the anion is same in all complexes) on the structure of the solutions. A structure breaking ion, in general possesses high mobility and decreases the local viscosity leading to a high value of $\Lambda_0\eta_0$.

Walden product and Arrhenius activation energy of transport processes for water + DMSO at different temperatures: They observed that the walden product decrease in the order: oxalatopentaamine → malonatopentaamine → aquopentaamine → succinatopentaamine → carbonatopentamine-Co (III) complex. The high value of $\Lambda_0\eta_0$ for oxalatopentaamine and malonatopentaamine Co (III) complexes is attributed to their structural breaking properties. It has been observed that the effective radius *r* of the complex cations decreases with increase in DMSO content but increases with rise in temperature. The smaller $\Lambda_0\eta_0$ value may be due to the larger *r* value whereas smaller *r* value corresponds to higher $\Lambda_0\eta_0$ value. The size of the solvation sphere that is dragged along by the ion in an electric field varies with the complexing ligand. Since the conductance of an ion depends on its mobility, they have used the equation.

$$\Lambda_o = A.e^{Es/RT} \quad \ldots(8)$$

Where, A= frequency factor

R= ideal gas constant

and, Es= Arrhenius activation energy of transport processes.

With the increase in DMSO content in the solution, the Es values increase for carbonatopentamine and aquopentaamine-Co (III) complexes but decreases for carboxylatopentaamine-Co (III) complexes. They observed a larger ion pair association of succinatopentaamine Co (III) nitrate in all the solvent mixtures at all temperatures. This was attributed to the least cation-complex stability and to the lack of solvation of the complex ion; reverse was the case with oxalatopentaamine which gave smaller ion pair association. Hartley and Donaldson [Hartley and Donalson, 1937] studied the conductance behavior and the ion-association of hexamine cobalt (III) chloride in aqueous solutions. Jenkins and Monk

[Jenkins and Monk, 1951] studied the nature of associations of lanthanum sulphate and found the dissociation constant as k=2.4x10^{-4}. Later it was found that the value agrees well with the dissociation constant value obtained by the Conductometric measurement of cobalt (III) complexes containing sulphate anions.

2.2.2. Ion Pair Formation in 2:2 and 2:1 Co (III) Complexes

Using conductivity, Masterton and Bierly [Masterton and Bierly, 1970] had studied ion pairing in 2:2 complex ion electrolytes: [Co $(NH_3)_5NO_2$] SO_4. The conductivity data are reported for aqueous solutions of [Co $(NH_3)_5NO_2$] in the concentration range 10^{-4} to 10^{-3}N. The Shedlovsky method was used to calculate an ion pair dissociation constant of 2.5 x10^{-3}. The pK value (2.60) is significantly larger than those of simple 2:2 suphates, corresponding to greater association. A comparison of observed pK values with those calculated using the Fouss theory of ion-pair formation suggests the non electrostatic forces are of major importance in 2;1 and particularly in 1:1 co-ordination compounds. Preliminary experiments indicated that the conductivities of solution of [Co $(NH_3)_5NO_2$] SO_4 increased slowly when exposed to light. On the basis of electrostatic factors, which predict a decrease in ionic association with increasing ionic size. The complex cation such as [Co $(NH_3)_5NO_2]^{2+}$ can hardly be smaller than alkaline earth or transition metal cations. Non electrostatic forces must contribute significantly to the stability of the ion pairs formed by complex ion in electrolytes. The Fouss theory [Fouss, 1955] which considers only electrostatic forces, predicts that

$$pK = 21.40 + 3 \log a + b/2.3 \qquad \ldots(9)$$

where $a = 3.5\text{Å}$ = the interionic distance in the contact ion pair

$$b = \frac{|Z_1 Z_2|}{aDkT} e^2$$

z = charge of ion
e = electronic charge
D = dielectric constant of water
K= Boltzmann constant

In order to obtain a pK value of 2.60 for [Co $(NH_3)_5NO_2$] SO_4 (Z_1=Z_2=2), it is necessary to make a= 3.5Å, if it is assumed that ‘a’ remains constant. The pK values calculated for 2:1 and 1:1 complex salts on the basis of the Fouss theory are considerably smaller than those observed. The ion pair association constants are 2 to 3 times smaller than those predicted on the basis of electrostatic forces alone. It would appear that non electrostatic forces are of major importance in ion pair formation in complex ion electrolytes of lower charge types.

The equivalent conductivities of tris biguanide Cobalt (III) chloride, bromide, iodide and sulphate salts in dilute aqueous solutions at 25°C and 30°C using Onsager’s method of extrapolation Onsager, [Onsager, 1927] was investigated by De and Dutta [De and Dutta, 1973]. The association constants were found to follow the order:

$\{[Co(BigH)_3]I\}^{2+}$, (K_A=22) < $\{[Co(BigH)_3]Br\}^{2+}$, (K_A=33) < $\{[Co(BigH)_3]Cl\}^{2+}$ (K_A=55) < $\{[Co(BigH)_3]SO_4\}^{2+}$, (K_A=16x10^2)

They have also evaluated the sizes of ion pairs applying Bjerrum equation Stoke’s law. (Table 2)

Table 2: Approximate radii of $[Co(BigH)_3]^{3+}$, anions and ion-pairs.

Cation/anion	Radius from Stoke’s law	Ion -pair	Radius Stoke’s law (Å)	From Bjerrum equation
$[Co(BigH)_3]^{3+}$	4.03	$\{[Co(BigH)_3]Cl\}^{2+}$	5.23	4.28
Cl^-	1.20	$\{[Co(BigH)_3]Br\}^{2+}$	5.21	6.11
Br^-	1.18	$\{[Co(BigH)_3]I\}^{2+}$	5.22	7.38
I^-	1.19			
SO_4^{2-}	2.29			

As expected, they found that $[Co\ (BigH)_3]^{3+}$ (4.03Å) is substantially larger than $[Co\ (NH)_6]^{3+}$ (2.77Å) and is only slightly larger than the reported size of $[Co\ (P^n)_3]^{3+}$ (4.23Å). De and Dutta [De and Dutta, 1973] also investigated the effect of temperature on association constant and found that with the increase in temperature there was some slight enhancement in the association constant values indicating a somewhat favourable entropy changes in respect of outer sphere ion association had been reported in the literature [Jenkins and Monk, 1951]. According to De and Dutta, the explanation possibility lies in the breakdown of the hydration shell of the complex cation and anion, thus leading to the release of solvent molecules from an 'ordered' state to a state of 'disorder'.

Bag, Mohondas and Rajmuhon [Bag *et al*, 2000; Bag *et al*, 2001] had studied ion association of Cobalt (III) complexes in different solvent mixtures at a different temperatures. The conductance data in all the cases have been analysed by Shedlovsky method. The influence of dielectric constant on the ion-pairing process of an electrolyte has been revealed by many workers. The observed association constant values are known to be a composite quantity depending on specific and non-specific solute-solvent interactions.

I. The Association constants and Walden products of α-alanine bis (biguanide) Co (III) iodide in methanol + water mixtures at 5-40^0C, the values of the K_As of the complex decreases with rise in the temperature until the $K_{A(min)}$ is reached at $t_{(min)}$ which is characteristic of the anions. Beyond $t_{(min)}$, these values increase gradually. The presence of $t_{(min)}$ was explained due to their structure breaking properties. The increase in the value K_A beyond $t_{(min)}$ is supported by increase of entropy change. The Walden product ($\Lambda_0\eta_0$) increase upto a mole fraction of methanol (X_{CH3OH}) of 0.36 in methanol and then decreases. If change in solvation is reflected by the variation in $\Lambda_0\eta_0$, the increase of the product indicates the weak solvation of the ions. Their experimental work found that K_As are found to increase with increase in X_{MeOH} which indicates an increase association as methanol is added to water.

II. Conductance of diammine bis 1-amidino-O-methylurea Cobalt (III) monochloride has been measured in various water + Acetonitrile mixtures at 283.15-303.15K. The conductance data in all the cases have been analysed by Shedlovsky equation to obtain Λ_0 and K_A value for the electrolyte. The influence of the mixed solvent composition on the solvation of ion has been discussed based on the composition dependence of Λ_0, the thermodynamic parameters and Arrhenius activation energy (E^a) of transport processes have been determined. The results have been discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Bag, Rajen and Rajmuhon [Bag *et al.*, 2001] had determined the degree of ionic association in methanol + water mixed solvent interactions of conductance of α-alanine bis (biguanide) cobalt (III) bromide at different temperatures. The temperature dependence of ion-association constants is important because the standard enthalpies of ion association provide the interaction between the ions than the association constant at certain fixed temperature. The conductivity values were analyzed using Shedlovsky technique [Shedlovsky, 1932]. The Λ_0 value increased with increase in temperature in methanol + water mixtures. This is due to the fact that the increased thermal energy results in bond breaking and variation in vibrational, rotational and translational energy of the molecules leads to higher frequency and higher mobilities of ions. The observed association constants (K_A) are found to increase with increase in mole fraction of methanol which indicates an increased association as methanol is added to water, and dielectric constant is particularly property of the solvent that influences the association [Pura and Atun, 2003]. Lower the dielectric constant of the medium, the higher is the electrostatic attraction between the ions and hence the greater is the value of association constant (K_A). The values of ΔS^0 are negative in all solvents. This indicates that the association process is exothermic in nature and the process will occur spontaneously at all temperatures [Singh *et al.*, 2008]. The variation of Walden product with the mole fraction of methanol at different temperature, it decreases with increase in mole fraction of methanol. This indicates an increase in hydrophobic solvation. As the methanol content increases, progressive disruption of water structure occurs and ions become solvated with the other components of the solvent mixture (viz. methanol). Further, this effect will be more in case of a solution at higher temperature [Ue, 1994].

2.2.3. Ion pair Formation in 3:1 Co (III) complexes

Using electrical conductance method, Balt and Pothoff [Balt and Pathoff, 1975] had studied ion association of $Co(NH_3)_6(ClO_4)_3$, $Co(NH_3)_6(NO_3)_2$, $Co(NH_3)_5F(ClO_4)_2$, $Co(NH_3)_6F(NO_3)_2$ and $Co(NH_3)_5Cl(ClO_4)_2$ in liquid ammonia at concentration between $2x10^{-4}$ and 10^{-2} M from 40° to 70°C. They showed that in solution more concentrated than $6x10^{-4}$ M, there is evidence that the only ionic species are univalent ions. The conductance data have been fitted to the Λ_o for the univalent complexes and the association constant of the uncharged complex ion pair. The conductance behaviour of some tris-(ethylenediamine) cobalt (III) complex in dilute aqueous solution at 25°C had been investigated for the ion pair formation by Kaneko and Wada [Kaneko and Wada, 1978]. The degree of dissociation of the possible ion pairs, α, was determined from the conductivity data according to the successive approximation method of Jenkins and Monk. They calculated the thermodynamic formation constant K_A by using Debye-Huckel equation for the activity coefficient to an ion. In table 3, the thermodynamic formation constant determined from the experimental data are compared with those calculated theoretically:

Table 3: Thermodynamic formation of the ion –pair $[Co(en)_3]^{3+}X^-$ in aqueous solution at 25^0C

Complex	K_A, mole dm^3	
	Experimental	Theoretical (Bjerrum)[a]
$[Co(en)_3]Cl_3$	28	38
$[Co(en)_3]Br_3$	28	37
$[Co(en)_3](NO_3)_3$	19	31
$[Co(en)_3](ClO_4)_3$	14	28

[a]The crystallographic radii used are 3.75Å for $Co(en)_3^{3+}$, 1.81 Å for Cl^-, 1.95 Å for Br^-, 2.64 Å for NO^-_3 and 2.92 Å for ClO^-_4. The size of the anion increases with increase in the K_A values (table 3).

El-Hammamy and co-workers [El-Hammamy *et al.*, 1991] studied electrical conductance of Cobalt (III) complexes acetyl-pyridine thiosemicarbazone halide in methanol at 25°C. They used the Fuoss-Onsager equation for the analysis of K_A, the association constant and 'a' (Å) the distance of closest approach, [Table 4].

Table 4: Association constant (K_A), limiting molar conductance (Λ_0) and distance of closest approach a (Å) of Cobalt (III) complexes acetyl-pyridine thiosemicarbazone halide in methanol at 25°C

Salt	Λ_0	J	a(Å)	K_A	σ_A
$[Co(APT)_2Cl$	92.65±0.886	1923.2	5.947±0.062	73.918±2.135	0.0418
$[Co(APT)_2Br$	96.774±0.488	1880.7	5.504±0.072	40.625±10.167	0.2337
$[Co(APT)_2I$	102.60±0.408	1846.8	5.011±0.084	43.226±11.554	0.0116

In table 4, Λ_0 increases from the Cl^- complex to I^- complex. The values of 'J' and 'a' decreased with increase in the size of the solvated anions. This supports the view that for salts with a common cation, the size of the solvated anion becomes the essential factor in controlling the extent ion pairing. They found that the solvation of these anions of cobalt (III) acetylpyridine thiosemicarbazone halides increases in the order $Cl^- > Br^- > I^-$, which is in accordance with the trend of 'a'.

Pethybridge and Spiers [Pethybridge and Spiers, 1976] studied precisely the conductivity results of seven salts of trans and cis- $[Co(en)_2](NO_2)_2]^+$. They are analysed in terms of the full Pitts and the association constants for salts, although small, are found to increase with increasing radii of the ions being particularly large for cis-$[Co(en)_2](NO_2)_2]I$. Contrary to popular belief, trans-$[Co(en)_2](NO_2)_2]ClO_4$ is also appreciably associated in the dilute aqueous solution. The following anions of the association constants of the outer-sphere complexes in the order:

$Cl < Br < NO_3 < I \approx ClO_4$

Kessling and Maeyer [Kessling and Maeyer, 1995] has given the precision modeling of conductivity data of monovalent aqueous electrolytes. In their approach, the mean spherical approximation transport (MSAT) theory is combined with a chemical equilibrium model of ion pair formation, taking into account the hydration of the ions. In the macroscopic view, the hydration shell is a certain spherical volume around the ion. The number of water molecules in the hydration shell is called the hydration number of the ion. If hydrated ions of opposite charge come close to each other, an ion pair may form. Anions and cations come into close contact and form a neutral species. They will not move in an external field as long as they keep together. The strong charge-dipole interactions between an ion and water molecules in the hydration shell is weakened by a nearby charge of opposite sign. When ions form ion-pairs, the ions lose at least part of their hydration shell [Frank and Wen, 1957].

Bag, Mohondas and Rajmuhon [Bag *et al.*, 2001] had studied the association constants, walden products and Arrhenius activation energies of diammine bis(1-amidino-O-methylurea) Cobalt (III) monochloride in acetonitrile + water mixtures and in methanol + water mixtures at different temperatures. They observed that K_As are found to increase with increase in mole fraction of acetonitrile or methanol which indicates an increased association as acetonitrile or methanol is added to water. Large values of K_A and exothermic ion pair formation indicates the presence of specific short-range interaction between the ions. The variation of $\Lambda_0\eta_0$ with mole fraction is due to an electrochemical equilibrium between the cations with 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. The values of E^a increase with mole fraction of acetonitrile (X_1) upto X_1=0.07 and that of methanol (X_1) upto X_1=0.36 and thereafter both the cases decrease rapidly. A reaction which requires higher activation energy is slow at ordinary temperatures indicating the lower mobilities of the ion in solution.

2.2.4. Ion Pair Formation of 2:1 and 1:1 Copper Complexes.

Using conductance method, Steekumar, Rajendran and Kalidas [Steekumar *et al.*, 1992] had studied ion-solvent interactions of copper (II) Perchlorate in both water-DMSO and water-Pyridine. It was observed that the Λ_o (equivalent conductance) of copper (II) Perchlorate first decrease sharply on addition of pyridine upto 20 wt%, then gradually decreases upto 60wt% pyridine and finally it increases. The Λ_o also decreases continuously with the addition of DSMO mixtures. The Walden product of copper (II) perchlorate decreases continuously with the addition of DSMO in water-DSMO mixtures. In case of pyridine, it first decreases sharply with the addition of pyridine and then it increases slightly and subsequently decreases with the addition of pyridine. It may be of interest to point out that strong solvent-solvent interaction resulting in the formation of water-DSMO complexes compete with the ion solvent interactions and presumably give rise to the complex behaviour. Using Shedlovsky [Shedlovsky, 1932] method, the equivalent conductance and Walden products were calculated.

Table 5: Λ_o (ohm^{-1}cm^2 eq^{-1}) and Walden product

Composition	**Λ_o**		**$\Lambda_o\eta_o$**	
In P.C.	Wt % Py	Wt% DMSO	Wt % Py	Wt% DMSO
0	137.00	161.00	1.096	1.288
20	64.40	114.54	0.753	1.289
40	51.00	72.52	0.796	1.340
60	40.60	48.18	0.726	1.353

Recently, Rajmuhon and Bag (Rajmuhon and Bag, 2001] had studied the conductance and ion association of bis (1-amidino-O-methylurea copper (II) acetate in aqueous medium at 5-40^oC using Shedlovsky equation. As evident from experimental values of Stoke's radius of anion ($^rCH_3COO^-$) is more or less constant with the variation of temperature. The Stoke’s radii for the complex cations increase with temperature which indicates that the cations become more hydrated as the temperature rises. Walden product ($\Lambda_o\eta_o$) of the ions is most nearly constant for those of large size due to their being polyatomic or extensive hydration. The ion association process will occur spontaneously and is exothermic in nature which is supported by the positive value of ΔS^o and the negative value of ΔH^o. Then the variation of ΔG^o with temperature reveals that the ion association process is favoured at low temperature. Singh, Rajmuhon and Manihar [Singh *et al.*, 1995] had studied the electrical conductivities and ion pair-formation of bis-l-amidino-O-methylurea-, bis-l-amidino-O-ethylurea-copper (II) halides and nitrates in aqueous solution at 18°, 25°and 35°. From the values of association constants of these complexes at different temperatures, the thermodynamic functions can be estimated in order to understand the nature of ion-association. The limiting equivalent conductivities (Λ_o) of the complexes were determined by Onsagar method of extrapolation. The sizes of ion pairs were evaluated from Bjerrum equation, Stokes' law and Dennison-Ramsey theory. The observed values of association constants (K_A) for bis 1-amidino-Omethylurea copper(ll) and bis 1 -amidino-O-ethylurea copper(II) chloride, bromide, iodide and nitrate are in the following order:

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

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

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

2.2.5. Spectrophotomeric/Spectroscopic Method

Spectrophotomeric/Spectroscopic method is also one of the most convenient methods in studying the formation of outer-sphere complexes. The formation of metal complex is often accompanied by a change in the light absorption of the complex relative to that of the free metal ion or ligand. Inner-sphere complex formation of short range interaction (contact ion pair formation) is reflected by change in the visible spectrum whereas changes in the ultraviolet region are associated with outer-sphere complexes or solvent separated ion pairs [Noncollas, 1966]. Evans and Nancollas [Evans and Noncollas, 1953] had determined the association constant K_A spectroscopically at 25°C and 35°C for the ion association reactions:

$$[Co(NH_3)_6]^{3+} + X^- \leftrightharpoons [Co(NH_3)_6]^{3+}X^-$$

$$[\mathrm{Co(en)_3}]^{3+} \ + \ \mathrm{X}^- \ \leftrightarrows \ [\mathrm{Co(en)_3}]^{3+}\,\mathrm{X}^-$$

Where, X^- = Cl^-, Br^-, I^- and N_3^-, the association constant K_A was represented as:

$$\mathrm{K_A} = \frac{\mathrm{c}}{(\mathrm{a-b})(\mathrm{b-c})} \quad \ldots(10)$$

Where, a, b and c are the molar concentrations of the complex cation, the anion and the ion-pair respectively. The concentration of the ion pair c is related to the molar extinction co-efficient of the ion pair as

$c = \delta/\varepsilon$

Where, δ = the absorption due to ion pair

ε = molar extinction co-efficient of the ion pair.

The differences between the absorption spectra of the ion-pair had been discussed on the assumption that they are electron transfer spectra. In table 6, the calculated values of association constants at 25°C and 35°C are given.

Table 6: The values of association constants K_A for the reaction

$$\mathrm{M^{3+}} \ + \ \mathrm{X^-} \ \rightleftharpoons \ \mathrm{M^{3+}X^-}$$

M^{3+}	X^-	K_A I.mol^{-1} (at 25°C)	K_A I.mol^{-1} (at 35°C)	Ref.
$[Co(NH_3)_6]^{3+}$	Cl^-	74 ± 4	91 ± 4	74
	Br^-	46 ± 2	52± 2	74
	N_3^-	20 ± 2	16± 2	74
	I^-	17 ± 1	18.5 ± 0.5	74
$[Co(en)_3]^{3+}$	Br^-	21 ± 0.5	23.5 ± 1	74
	N_3^-	8.6 ± 0.4	9.2 ± 0.4	74
	I^-	11.4 ± 0.8	8.5 ± 0.7	74

They calculated the entropy of association following the methods of Evans and Uri [Evans and Uri, 1951]. The calculated thermodynamic functions ΔH^0, ΔG^0 and ΔS^0 are shown in table 7.

Table 7: Thermodynamics of ion association

Reaction	ΔG^0 at 25°C (Kcal.mol^{-1})	ΔH^0 at 25°C (Kcal.mol^{-1})	ΔS^0 (expt.) Cal.deg^{-1}.mol^{-1}	ΔS^0 (calc.) Cal.deg^{-1} .mol^{-1}
$[Co(NH_3)_6]^{3+} + Cl^- \leftrightharpoons [Co(NH_3)_6]^{3+}Cl^-$	-2.57	3.72	21	19
$[Co(NH_3)_6]^{3+} + Br^- \leftrightharpoons [Co(NH_3)_6]^{3+}Br^-$	-2.28	2.08	15	14
$[Co(NH_3)_6]^{3+} + I^- \leftrightharpoons [Co(NH_3)_6]^{3+}I^-$	-1.69	1.63	11	10
$[Co(NH_3)_6]^{3+} + N_3^- \leftrightharpoons [Co(NH_3)_6]^{3+}N_3^-$	-1.79	-3.95	-7	-
$[Co(en)_3]^{3+} + Br^- \leftrightharpoons [Co(en)_3]^{3+} Br^-$	-1.82	1.96	13	11
$[Co(en)_3]^{3+} + I^- \leftrightharpoons [Co(en)_3]^{3+} I^-$	-1.28	1.22	8	6
$[Co(en)_3]^{3+} + N_3^- \leftrightharpoons [Co(en)_3]^{3+} N_3^-$	-1.45	-5.2	.13	-

Posey and Taube [Posey and Taube, 1956] had been determined the dissociation constant of hexamine cobalt (III) sulphate ion pair

$$[Co(NH_3)_6]^{3+} + SO_4^{2-} \rightleftharpoons \{[Co(NH_3)_6]SO_4\}^+$$

Spectrophotometrically; and the value was found to be4.76x10^{-4} at zero ionic strength in aqueous medium at 24.5°C. This value corresponds reasonably well to that of Davis [Davies, 1927] 3.0 x 10^{-4} calculated from the solubility of some sparingly soluble hexamine cobalt

(III) salts in dilute K_2SO_4 and that of Jenkins and Monk 2.77×10^{-4} obtained by conductance measurements.

The outer sphere association constants of hexamine cobalt (III) ion with halide ions $[Co\ (NH_3)_6]^{3+}\ Cl^-$ and $[Co\ (NH_3)_6]^{3+}\ Br^-$ were found to be much lower than the values reported by Evans and Nancollas [Evans and Noncollas, 1953]. The discrepancies were explained on the basis of the absorbance enhancement. Charge transfer bands as indicated by complexes $[Co\ (NH_3)_6X]^{2+}$ (X=F, Cl, Br, I) was first observed by Linhard and his co-workers [Linhard *et al.*, 1955] and Becker [Becker, 1970]. The gradual shift of the charge transfer bands towards shorter wavelengths were in order $I^- > Br^- > Cl^- > F^-$. The result indicated that the share of the central ion in controlling the electron pairs coming from halide ions changes in the same order. Same phenomenon was observed with $[Co\ (NH_3)_6]^{3+}$ and halide ions which suggested that electronic interaction is transmitted by the NH_3 molecules of the inner-sphere. It has been suggested that comparative study of inert complexes containing ligands of widely different ability to mediate electronic state (e.g, ethylene diammine and α, α'-dipyridyl) is expected to throw more light on this interesting and important phenomenon. The possibility of spectroscopic distinction between inner and outer sphere complexes had also been reported by Jorgesen [Jorgensen, 1965], Taube and Posey [Taube and Posey, 1953] and Smithson and Williams [Smithson and Williams, 1958]. Hey suggested that for transition metals the outer sphere ion pair formation would be expected to have very little effect on the low intensity absorption bands in visible spectrum. These were attributed to the forbidden d-d transitions (Laporte's selection rule), the wavelength depending upon the separation of the d-d polarization of the cation by the associating cation.

Spectrophotometric studies on the ion pair formation of hexamine cobalt (III) and tris (ethylenediamine) cobalt (III) complexes with chloride, bromide, iodide and sulphate ions had been undertaken by Tanaka and his co-workers (Tanaka *et al.*, 1967]. The association constants were determined at ionic strength 0.07 ($NaClO_4$) at 235°C from the change in O.D. The values were 2.2 ± 0.5 for $[Co(NH_3)_6]^{3+}$ Cl^-, 2.2 ± 0.6 for $[Co(NH_3)_6]^{3+}$ Br^-, 0.7 ± 0.5 for $[Co(NH_3)_6]^{3+}$ I^-, 114 ± 3 for $[Co(NH_3)_6]^{3+}$ SO_4^{2-}, 2.9 ± 0.5 for $[Co(en)_3)]^{3+}$ Cl^-, and 102 ± 8 for $[Co(en)_3)]^{3+}$ SO_4^{2-} respectively. The ion-size parameters of the ion-pair were estimated to be 4.5Å for $[Co(NH_3)_6]^{3+}$ Cl^-, $[Co(NH_3)_6]^{3+}$ Br^-, $[Co(NH_3)_6]^{3+}$ I^-, and $[Co(NH_3)_6]^{3+}$ SO_4^{2-} and 5Å for $[Co(en)_3)]^{3+}$ Cl^-, and $[Co(en)_3)]^{3+}$ SO_4^{2-} from the consideration of the charge and the structure of the ion pairs. The association constant of tris (ethylenediamine) cobalt (III) ion with sulphate ion was reported by Ogino and Saito (K_A=2.93). This value is much smaller as compared to that of Tanaka and his co-workers. The partial ion association constant for contact ion pairs in aqueous $[Co (NH_3)_6]^{3+}$ I^- have been investigated spectrophotometrically by Yokoyama and Yamatera [Yakoyama and Yamatera, 1971]. The study was made of aqueous system of constant ionic strength of 0.062 containing $[Co (NH_3)_6](ClO_4)_3$, KI and $NaClO_4$. The absorption band which appeared near 37000 cm^{-1} on the addition of iodide to the aqueous solution of hexamine cobalt (III) perchlorate is known to be due to the $[Co(NH_3)_6]^{3+}$ I^- ion-pair [Evans and Noncollas, 1953; Tanaka *et al.*, 1967]. The association constant value of the ion pair was found to be 9.0 ±0.6.

NMR study of the rotational motion of $[Co (en)_3)]^{3+}$ in aqueous solution had been performed by Masuda and Yamatera [Masuda and Yamatera, 1983] with particular reference to dynamic features of ion-ion interaction. By measuring the spin-lattice relaxation times of ^{13}C and ^{1}H of the methylene group, the rotational correction times τ_c of the $[Co (en)_3)]^{3+}$ ion in D_2O solution of various salts were obtained. The τ_c values of the $[Co (en)_3)]^{3+}$ ion (extrapolated to infinite dilution) at various temperatures followed the Stokes –Einstein equation [Stokes, 1945]. Remarkable higher τ_c values with significant anisotropy were observed for the complex ion in the presence of bi-negative anions such as succinato ion, L-tartarate ion and SO_4^{2-}. These features of rotational motion of $[Co (en)_3)]^{3+}$ were explained by the ion association model. The rotational motion of the C_3-axis of [Co (en)$_3$)]$^{3+}$ was largely retarded by ion pairing with SO_4^{2-}, L-tart^{2-} and Succ^{2-}, while rotation around the C_3-axis was only slightly influenced by ion-pairing. The high τ_c value and its anisotropy for the [Co (en)$_3$)]$^{3+}$ SO_4^{2-} ion pair were reasonably explained by considering the ion pair as a rigid prelate and dealing with the rotational motion of that prolate on the basis of hydrodynamic model.

Spectroscopic methods have been employed extensively to study ion-pairing phenomena. IR-Spectrometry is a powerful tool for investigating fast equilibria between free ions and associated species in non-aqueous solution [Irish *et al.,* 1976]. IR spectroscopy resembles Raman spectroscopy in that it provides information on the vibrational and rotational energy levels of a species, but it differs from the latter techniques in that it is based on studying the light transmitted through a medium after absorption and not that scattering by light. In most cases internal vibration of the polyatomic anions are used as probes of cation-anion interactions [Aroca *et al*., 2000]. For instance the strong $IR\upsilon_3$ band of pseudo-halide anions in the 2000-2200 cm^{-1} region is most convenient to characterize ion pairs and higher aggregates. Raman scattering [Torell, 1987] and Infrared spectroscopy have been employed extensively to study the ion pairing phenomena in polyether-salt systems for the amount of ion locked in various ion-ion formations. Similarly, Raman and Li NMR studies for investigating the structures and dynamics of Li^+ ions in concentrated solutions of $LiClO_4$ (EC+PC) have been reported by Cazzanelli. Absorption in the ultraviolet and visible regions of the electromagnetic spectrum corresponds to transitions between electronic energy levels and provides useful analytical information for both inorganic and organic samples. There is no doubt that UV/Vis (electronic) and vibrational (especially Raman) spectroscopies are extremely powerful tools for studying chemical speciation in solution. Used separately or in combination, such techniques have been employed successfully to measure the stability (association) constants of hundreds of metal-ligand (including ion-ion) systems [Sillen *et al.,* 1964 & 1971; Perrin *et al.,* 1979; Hogfeldft, 1982]. Spectroscopic methods often have advantages over other techniques, especially for the study of very complicated equilibria. They have provided valuable information about the binding sites of multidentate ligands and on the kinetics and structures of many species in solution.

IR-Spectrometry is a powerful tool for investigating fast equilibria between free ions and associated species in non-aqueous solution. IR spectroscopy resembles Raman spectroscopy in that it provides information on the vibrational and rotational energy levels of a species, but it differs from the latter techniques in that it is based on studying the light transmitted through a medium after absorption and not that scattering by light [Das *et al.*, 2008]. In most cases internal vibration of the polyatomic anions are used as probes of cation-anion interactions [Debye, 1933]. The technique of Raman and IR spectroscopy are generally considered complementary in the gas and solid phases because some of the species under study may reveal themselves in only one of the techniques. Nevertheless, it must be stressed that Raman scattering is not affected by an aqueous medium, whereas the strong absorption in the infrared shown by water proves to be a troublesome interfering factor in the study of aqueous solution by the IR method [Yeager *et al.*, 1976].

3. METHODOLOGY

3.1. Methods

The conductance method is one of the most sensitive and widely used methods for the investigation of physico-chemical nature of ion pair formation of simple and complex salts in pure and mixed solvent solutions [Shehata, 1994; Harned and Owen, 1958; Singh *et al.*, 2008]. The electrical conductivities of the pure and mixed solvent solutions of the selected simple and complex salts were measured at different temperatures. The limiting equivalent molar conductance (Λ_o) and the association constant (K_A) of the complex ion with the anions were calculated by using Shedlovsky method [Shedlovsky, 1932]. A brief account on theories and equation used in our investigation are outlined below:

3.1.1. Evaluation of Limiting Molar Conductance (Λ_o) and association Constant (K_A) of Electrolytic salts.

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

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right) \qquad \ldots(11)$$

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

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

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

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

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

Therefore,

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

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

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

$$\mathrm{q} = \frac{\mathrm{Z}_+\mathrm{Z}_-}{\mathrm{Z}_+ + \mathrm{Z}_-} \frac{\lambda_+\lambda_-}{\mathrm{Z}_+\lambda_- + \mathrm{Z}_-\lambda_+}$$

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

$$-\log \mathrm{f}_\pm = \frac{\mathrm{Az}_+\mathrm{z}_-\mu^{1/2}}{1+\mathrm{BR}\mu^{1/2}} \qquad \ldots(12)$$

Where, $\mathrm{A} = \frac{1.8247\mathrm{x}10^6}{(\mathrm{DT})^{3/2}}$; $\mathrm{B} = \frac{0.5029\mathrm{x}10^{10}}{(\mathrm{DT})^{1/2}}$; $\mu = \frac{1}{2}\sum_i (\mathrm{c}_i\tau_i)\mathrm{z}_i^2$

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no precise method [Hogman *et al.,* 1956-1957] for determining the value of R'. In order to treat the data in our system, the R' value is assumed to be R' = a + d, where 'a' is the sum of crystallographic radii of the ions approximately equal to $5\mathrm{A}^0$ and 'd' is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by [Fouss and Onsager, 1955]

$$\mathrm{d} = 1.183\left(\mathrm{M}/\rho\right)^{1/3} \text{Å} \qquad \ldots(13)$$

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

$$M_{avg} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1} \qquad \ldots(14)$$

X_1 is the mole fraction of methanol of molecular weight M_1 and X_2 that of water of molecular weight M_2. An initial value of Λ_o was obtained by least square method (Λ and concentration C was introduced as input in a computer programme). The mean activity coefficient $f_\pm$ was determined by equation (13) for the above chosen simple and complex salts [Akhadov, 1981]. From the linear plot of $1/\Lambda S$ (Z) versus C $\Lambda f_\pm^2$ S(Z); Λ_o and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope (K_A/Λ_0^2) respectively [Glasstone, 1942]. The procedure was repeated using these new values of Λ_0 and K_A. All calculations were carried out by IBM-PC-AT/386.

3.1.2. Evaluation of thermodynamic parameters

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

$$-RT\ln K_A = \Delta G^o = \Delta H^o_{ass} - T\,\Delta S^o_{ass} \qquad \ldots(15)$$

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

$$\Delta G^o_{ass} = -2.303RT\log K_A \qquad \ldots(16)$$

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

$$\Delta S^o_{ass} = \frac{\Delta H^o_{ass} - \Delta G^o_{ass}}{T} \qquad \ldots(17)$$

3.1.3. Calculation of Walden Product and effective radius

Walden Product means the product of equivalent/molar conductance at infinite dilution (Λ_o) and viscosity of the medium (η_o). The relationship between viscosity and ion conductance has been interpreted in at least two ways. Some writers have suggested that the constancy of the product $\Lambda_o\eta_o$ proved that applicability of Stoke's law [Stokes, 1945] to ions in solution. According to Stoke's law

$$f = 6\pi\eta ru$$

Where, *u* is the steady velocity with a particle of radius *r* moves through a medium of viscosity *η* when a force *f* is applied. For a particular ion *r* may be regarded as constant and since the conductance is proportional to the speed of the ion under the influence of a definite applied potential, it obeyed Stoke's law (according to Stoke's law, $\Lambda_o\eta_o$ should be constant). Another suggestion that has been made to explain this fact is that the ion in solution is so completely surrounded by solvent molecules [Conway, 1978] which move with it, it is so extensively 'solvated' that its motion through the medium is virtually the same as the movement of the solvent molecules past one another in viscous flow of the solvent.

The structural properties of a solvent are characterized, among other ways, by the bulk viscosity. Solvent effects in conductance were conveniently investigated by examining the applicability of Walden's rule to conductance by an electrolyte in mixed solvent media of varying viscosity. Hydrodynamic mobilities depend on the viscosity of the solution. For the model of spherical charge particles subject to resisting forces proportional to their viscosity and moving in homogenous fluid of definite viscosity. Then, Walden's rule,

$$\Lambda_o \eta_o = \frac{0.82 \text{ x } 10^{-8}}{\mathrm{r}} = \text{Constant}$$

For given electrolyte in a series of solvents followed from Stoke's law where Λ_o is limiting conductance, η_o is the viscosity of the pure solvent, and r is the hydrodynamic radius of the ion. If Stoke's were obeyed, the value of $\Lambda_o\eta_o$ would be constant only if the effective radius of the ion were same in different media, 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 the conductance –viscosity product is not to be expected. Therefore, variation of Walden product ($\Lambda_o\eta_o$) with the change in the composition of the solvent reflects the solvation of the ions [Conway *et al.*, 1965]. The effective radius(*r*) of ion or solute can be calculated as

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

Where, $\Lambda_0\eta_0$ is walden product and T is temperature in Kelvin.

3.2. Physical Measurements

3.2.1. Conductance Measurements:

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

3.2.2. Temperature Control

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

3.2.3. Measurement of Weights

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

3.2.4. Analysis

Estimation of the metals Co, Cu and anions Cl^-, Br^-, NO_3^- and water of crystallization were carried out by using standard methods. Dehydration was studied in an oven. Carbon, Hydrogen and nitrogen estimation were done at Central Instrumentation Laboratory (CIL), Mizoram University.

3.2.5. Computations

All calculations were done on IBM-PC-AT/386 using a basic programme.

3.3. Materials

3.3.1. Ligands

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

(i) Histidine

(ii) Serine

(iii) Benzoyl isothiocyanate

(iv) N-(benzyolamino)thiozomethyl] histidine

(v) N-(benzyolamino)thiozomethyl] serine

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

i. Preparation of benzoyl isothiocyanate

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

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

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

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

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

3.3.2. Preparation of the compounds/ Complexes

i. Preparation of N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride

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

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

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

iii. Preparation of N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride

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

iv. Preparation of N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride

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

v. Preparation of Chloropentaamminecobalt (III) chloride

Chloropentaamminecobalt (III) chloride was synthesized as described by Baykut [Baykut *et al.*, 1990] and recrystallized twice from water. A solution of 5g cobalt (II) chloride hexahydrate in 5ml water was mixed with a solution of 10g ammonium chloride in 30ml concentrated ammonia solution and 5ml water in conical flask. 2ml of 30% hydrogen peroxide was added and the flask was shaken for 3minutes. This procedure was repeated three times and the reaction mixture is then poured into 250ml beaker and left at room temperature for 15 minutes with frequent stirring. From a separatory funnel 35ml concentrated hydrochloric acid was added carefully while stirring was continued. The mixture was then heated during stirring to the boiling point for 3 minutes. (Beware of bumping).

The solution was left to cool to temperature. The purple red crystals were filtered on a glass filter funnel. They were washed, first with 15 ml of 4 M hydrochloric acid (for removal of ammonium chloride), then with 10ml of 96% ethanol (for removal of hydrochloric acid). The product was dried at room temperature. The amount of the product is 5g, corresponding to a yield of 97%.

Table 8: Elemental analysis data of some N-[(benzoyl-amino)-thioxomethyl] amino acids and their metal complexes.

Compound	Stoichiometry	% C		% H		% N	
		Calc.	(Found)	Calc.	(Found)	Calc.	(Found)
N-[(benzoyl-amino)-thioxomethyl] serine + $CuCl_2$	MLCl	34.67	(34.48)	2.89	(2.63)	7.35	(7.20)
N-[(benzoyl-amino)-thioxomethyl] serine + $CoCl_2$	MLCl	34.15	(34.01)	2.69	(2.35)	6.92	(6.76)
N-[(benzoyl-amino)-thioxomethyl] histidine + $CuCl_2$	MLCl	31.86	(31.69)	2.34	(2.11)	6.53	(6.37)
N-[(benzoyl-amino)-thioxomethyl] histidine + $CoCl_2$	MLCl	31.47	(31.28)	2.22	(2.06)	6.38	(6.21)

4. RESULTS AND DISCUSSIONS

4.1. Ion pair formation of $CoCl_2.6H_2O$ and $[Co\ (NH_3)_5\ Cl]\ Cl_2$ in aqueous medium at different temperatures – A Conductance Method.

4.1.1. Introduction

Among the various methods, the conductance method is one of the most sensitive and widely used methods for investigation of ion association of simple and mixed solvents (Bjerrum, 1926]. Wide temperature range (0^o-50^oC) conductivity measurements for electrolyte solutions can give detailed information on ion-ion and ion-solvent interactions [Ue and Mori, 1994]. The formation of ion pair is a well known consequence of strong electrostatic interactions between oppositely charged ions [Jean-Francois, 1999; Atkinson and Petrucci, 1996]. Ionic association occurs in the majority of electrolytic solutions, a notable exception being aqueous solution of electrolytes with ions of low charge at ambient condition. The tendency of ions to associate into ion pairs depends on the balanced between the electrostatic force and thermal energy. Using conductivity method, Yokoyama, Ohta and Iida [Yokoyama *et al.*, 1992] had investigated the ion-pair association between tris (ethylenediamine) cobalt and monovalent anions at different temperatures ranging from 0^0 to 50^0C. The ions association constants of the complex ion with anions had minimum values at temperatures (t_{min}) characteristic of the salts. The values of t_{min} increased in the order $Cl^- < Br^- < I^- < NO_3^- < ClO_4^-$. The order of magnitude of association constants at 25^0C was $ClO_4^- < NO_3^- < I^- < Br^- < Cl^-$. The K_A and t_{min} values for the nitrate and perchlorate of $[Co\ (en)_3]^{+3}$ were smaller than those of $[Co\ (NH_3)_6]^{+3}$ and both the entropy and enthalpy changes of ion association for the former salts were more positive. This was attributed to the decrease in the fraction of the contact ion-pair [Saleem *et al.*, 2002] formed by the hydrogen bonding between the polar hydrogen atoms of the complexes and the oxygen atoms of the anions.

Here, the Conductometric technique was applied to study the association of the selected metal ions with the ligands in aqueous solution at 298.15 to 323.15 K. The conductance data were treated using Shedlovsky extrapolation method [Shedlovsky and Kay, 1956]. We have also investigated the effect of temperature on limiting molar conductance and association constant for the selected compounds which have been supported by the calculated values of standard thermodynamic parameters. These results were discussed in terms of the association constants and also approach of Gibbs energy relationship [Tanaka *et al.*, 1967] can be applied to the association process at various temperatures to discuss the thermodynamic features of metal-ion complexes. Also, the thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 were evaluated by investigating the process over a certain temperature range.

4.1.2. Experimental

Chloropentaamminecobalt (III) chloride was prepared according to chapter 3 section 3.3.2.(v).The electrical conductivities were measured by EUTECT-PC-700 digital conductivity bridges with a dip type immersion conductivity cell were used (accuracy ±1% F.S. ± 1digit). The solutions of different concentrations (8.6–3.4 x 10^{-3}) were carefully prepared by dissolving requisite amount of the sample in conductivity water (i.e., double distilled water) of specific conductance (< $3x10^{-6}$ Scm^{-1}). Conductivity measurements were carried out over the temperature range 25^0C - 50^0C. All the dielectric constants and viscosities were obtained from literature [Hodgman *et al.*, 1956-1957]. The temperature control in the ranges 25 -50^0C were made by using refrigerated Bath and Circulator - Cole-Palmer, Polystat R6L with the help of thermometer. The measurements of weights were done by using a METTER Balance, Model-Toledo, Delta Range. All calculations were done on IBM-PC-AT/386 using a basic programmed. The conductance measurement for each solution was accomplished within 5 hrs after the preparation of the solution so that the dissociation of the complex ion itself can be neglected.

Table 9(a): Molar conductivities (Λ) of Cobalt (II) chloride hexahydrate salt in aqueous solution at different temperatures.

Conc. x 10^{-3}	**298.15K**	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
8.6	132.55	136.63	138.01	140.12	142.29	145.00
7.5	133.60	137.28	139.13	141.27	143.56	146.01
6.7	134.77	138.73	140.27	143.67	145.53	147.09
6.0	135.83	139.11	141.98	144.93	146.77	149.62
5.5	136.36	140.27	142.36	145.27	147.89	150.22
5.1	137.45	141.36	143.79	146.33	148.21	151.39
4.7	138.51	142.73	144.66	147.53	149.29	152.72
4.3	139.76	143.59	145.17	148.87	150.53	153.96
4.7	140.50	144.66	146.23	149.36	151.67	154.67
3.8	141.50	145.87	147.65	150.17	152.79	155.12
3.6	142.21	146.68	148.93	151.77	153.32	156.23
3.4	143.61	147.73	149.88	152.29	155.24	157.62

Table 9(b): Molar conductivities (Λ) of Pentamminechlorocobalt (III) chloride in aqueous solution at different temperatures

Conc. x 10^{-3}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
8.6	110.13	113.12	118.45	120.87	125.58	131.39
7.5	110.56	113.89	118.67	121.78	126.65	132.13
6.7	111.67	114.97	119.78	122.53	127.91	133.73
6.0	112.00	115.66	120.33	123.83	128.83	134.66
5.5	113.09	116.18	121.81	124.90	129.45	135.45
5.1	114.11	116.66	122.74	125.49	130.19	136.47
4.7	114.25	117.44	123.19	126.80	131.91	137.44
4.3	115.34	118.83	124.18	127.20	132.09	138.60
4.7	116.25	119.75	125.25	128.75	133.50	139.50
3.8	117.10	120.00	126.31	129.47	134.47	140.78
3.6	117.77	121.66	126.77	129.68	135.27	141.11
3.4	118.23	122.64	127.56	130.00	136.47	142.94

4.1.3. Calculation of Limiting Molar Conductance and Association Constant

From the observed molar conductivities of the salts Cobalt (II) chloride hexahydrate and Pentamminechlorocobalt (III) chloride at various concentrations, the limiting molar conductivity (Λ_0) of the salts were determined by Shedlovsky extrapolation method [Shedlovsky, 1932]

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda \int_{\pm}^{2} S(z)\right) \qquad \ldots(18)$$

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. The other symbols are given by [Shedlovsky and Kay, 1956]

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

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

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

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

$$-\log f_\pm = \frac{A z_+ z_- \mu^{1/2}}{1 + BR\mu^{1/2}} \qquad \ldots(19)$$

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

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

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

Where M is the molecular weight of the solvent and ρ is the density of the solution

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

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

α' is constant. Using these values of Λ_o, λ^o_-, λ^o_+, z, $s(z)$ and r values were calculated. The mean activity coefficient f was determined by equation (20) for the above chosen complex salts. From the linear plot of $1/\Lambda S$ (Z) versus C $\Lambda f_\pm^2$ S(Z); Λ_o and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope K_A $/\Lambda_0^2$ respectively [Nelson and Errington, 2005] . The procedure was repeated using these new values of Λ_0 and K_A. All calculations were carried out by IBM-PC-AT/386. The results of Limiting molar conductance (Λ_0) and association constant (K_A) at different temperatures are summarized in table 10(a) & Table 10(b).

Table 10(a): The value of limiting molar conductance Λ_0 (Scm^2mol^{-1}) and association constants K_A (dm^3 mol^{-1}) obtained for cobalt (II) chloride hexahydrate in aqueous solution at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
Λ_0	155.83	160.62	163.21	167.03	169.64	173.10
K_A	28.96	29.54	30.40	31.89	32.46	33.16

Table 10(b): The value of limiting molar conductance Λ_0 (Scm^2mol^{-1}) and association constants K_A (dm^3 mol^{-1}) obtained for pentaamminechlorocobalt (III) chloride in aqueous solution at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
Λ_0	128.84	132.38	138.77	142.38	148.70	155.78
K_A	26.66	27.90	28.93	29.32	30.76	31.51

4.1.4. Calculation of thermodynamic parameters

The free energy change (ΔG^0) for association is calculated from the relation $\Delta G^0 = -RT \ln K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A vs 1/T (figure 10). The entropy change (ΔS^0) is calculated from the Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - \Delta S^0 T$. The values of thermodynamic functions are given in table 11(a) & 11(b).

Table 11(a): Thermodynamic parameters ΔG^0 (KJ mol^{-1}), ΔH^0 (KJ mol^{-1}) and ΔS^0 (KJ K^{-1} mol^{-1}) obtained by Shedlovsky technique for cobalt (II) chloride hexahydrate in aqueous solutions at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
ΔG^0	-8.34	-8.53	-8.74	-9.01	-9.20	-9.40
ΔH^0	-251.00					
ΔS^0	-242.66	-242.47	-242.26	-241.99	-241.80	-241.60

Table 11(b): Thermodynamic parameters ΔG^0 (KJ mol^{-1}), ΔH^0 (KJ mol^{-1}) and ΔS^0 (KJ K^{-1} mol^{-1}) obtained for pentaamminechlorocobalt (III) chloride in aqueous solutions at different temperatures.

	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
ΔG^0	-8.14	-8.34	-8.60	-8.93	-9.05	-9.26
ΔH^0	-285.00					
ΔS^0	-276.86	-276.62	-276.40	-276.07	-275.95	-275.74

From Tables 10(a) & 10(b), the value of Λ_0 for the electrolytes increased invariably with increase in temperature in aqueous medium indicating less solvation or higher mobility of ions [Das, 2008]. This is due to the fact that the increase thermal energy results in bond breaking and leads to higher frequency and higher mobility of the ions. Values of Λ_0 for Cu

$Cl_2.6H_2O$ are always greater than those values of complex [Co $(NH_3)_5Cl$] Cl_2 is most prone to the variation in vibrational, rotational and translational energy levels with temperature [Jenkins and Monk, 1950]. The values of the K_As for these two complexes increase with rise in temperature.

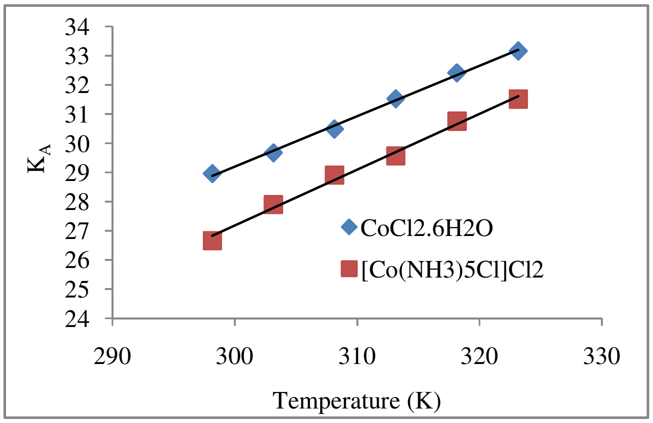


Figure 8: Temperature dependence of ion association constant for Cobalt (II) chloride hexahydrate and Pentaamminechlorocobalt (III) chloride in aqueous solution.

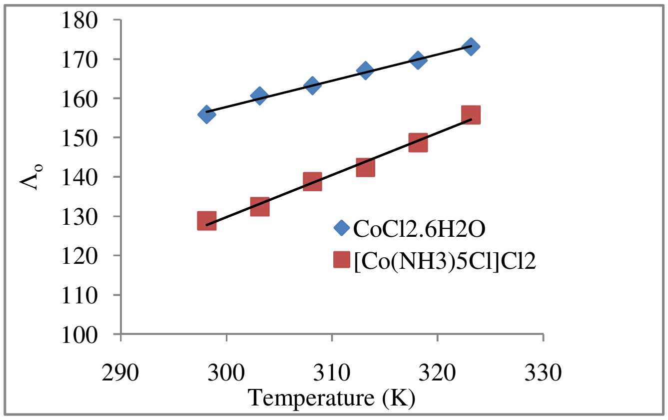


Figure 9: Plot of Λ_o vs T (K) for Cobalt (II) chloride hexahydrate and Pentaamminechloro cobalt (III) chloride in aqueous solution.

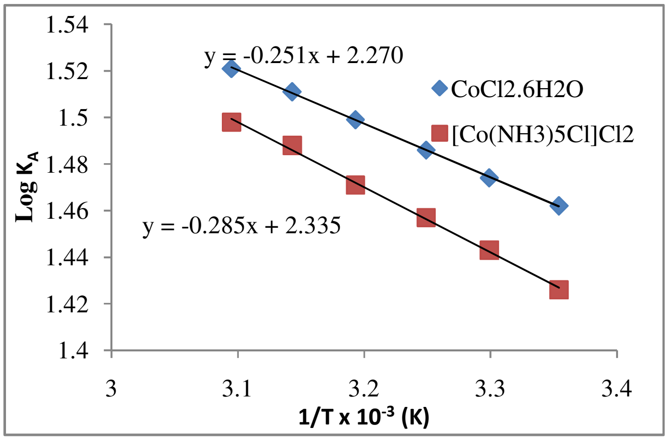


Figure 10: Plot of log K_A vs 1/T for Cobalt (II) chloride hexahydrate and Pentaamminechloro cobalt (III) chloride in aqueous solution.

The higher K_A values in the case of simple salt compared to complexes salt may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the cobalt ion and chloride ion [Pura and Atun, 2003]. This is so because the charge density of Co^{+2} ion is greater than that of the charge density of $[Co\ (NH_3)_5Cl]^{+2}$ ion. Out of these two complexes, negative values of ΔG^0 is more in cobalt (II) chloride hexahydrate and this complex is more favored in ion – pair formation. The positive values of ΔS^0 and negative values of ΔH^0 indicate that ion association process will occur spontaneously at all temperatures [Marusak and Lappin., 1989]. A positive entropy change is broken when association takes place leading to an increase in the degree of disorderliness [Ue and Mori, 1995]. The negative value of ΔH^0 indicates that ion association processes are exothermic at all temperatures [Singh *et al.*, 2008].

4.2. Conductance Studies of the Ion association of N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride in Methanol + Water Solutions at Different Temperatures.

4.2.1. Introduction

Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore the ion-ion and ion-solvent interactions can be better studied [Roy *et al.*, 2009]. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration-dependence of the electrolyte conductivity. The theories of conductance have revealed one feature in common that the solvent is assumed as a continuum of permittivity D and viscosity η. This assumption is hardly valid when discussing strong ion-solvent interaction, since the size of solvent molecules are comparable to those of solute molecules, since the size of solvent molecules are also considered as rigid uniformity charged unpolarizable sphere [Fouss, 1978; De *et al.*, 2006]. Mohondas *et al* had evaluated the thermodynamic parameters, Walden Products of different complexes, effective radius, Arrhenius activation energy and the comparison of transition metal complexes like Co^{III}, Ni^{II} and Cu^{II} among the halide groups in aqueous, methanol-water and acetonitrile mixed solutions at different temperatures for ion-ion, ion-solvent and solvent-solvent interactions [Bag *et al.,* 2000; Bag *et al.*, 2001; Singh *et al.*, 2001; Singh *et al.*, 2008]. The present work aims at determining the molar conductance values of the solutions of the title electrolyte in methanol + water mixtures at 283.15-313.15 K to examine the validity of Shedlovsky technique. The K_A and Walden products for Cu^{II} and Co^{II} complexes have been evaluated in these solvents at experimental temperatures. The limiting molar conductance (Λ_o) and association constant (K_A) for different mole fractions, i.e., 0.0000, 0.0588, 0.1233, 0.1942, 0.2727, 0.3600, 0.4576, 0.5676, 0.6923, 0.8351 and 1.0000 have been calculated using Shedlovsky method. These computed values have been discussed qualitatively the nature of ion-ion, ion-solvent and solvent-solvent interactions of the Cu^{II} and Co^{II} complexes in M-W mixed solvents. Temperature dependence of the K_A has also been studied to get the thermodynamic parameters, viz. ΔG^0, ΔS^0, ΔH^0 and E^a as a function of the solvent composition.

4.2.2. Experimental

N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride were prepared according to chapter-3, section 3.3.2(i) & 3.3.2(ii). The purity of the sample was determined by conventional chemical analysis and spectral measurements and the values are in good agreement with the literature values [Kabbani *et al.,* 2005]. Methanol was treated by the standard procedure [Wiesberger, 1995]. All the solutions were prepared by dissolving weighed samples of the electrolyte in solvent mixtures. All the viscosity, dielectric constant and density values were interpolated from literature values [Pura and Atun, 2003; Shedlovsky and Kay, 1956]. The experiment was performed between 10-40 ºC. The equivalent conductivities are shown in tables.12 (a) & 12(b).

4.2.3. Calculation of Limiting Molar Conductance, Association Constant, Walden product and effective radius

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

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

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_o is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are same as given in chapter 3, section 3.1.1. The effective radius(r) of ion or solute can be calculated as described in chapter-3, section-3.1.3.

Table 12(a): The values of molar conductance (Λ) obtained for N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride in methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	264.01	288.01	304.01	315.01	329.61	352.41	369.21
0.9091	265.61	289.24	305.59	316.10	330.24	353.36	370.46
0.8333	266.02	290.35	305.85	316.78	330.58	353.82	370.79
0.7692	267.12	290.61	306.36	317.44	331.44	354.42	371.88
0.7143	268.41	291.46	306.68	317.68	331.68	354.57	372.35
0.6667	269.00	292.46	308.54	318.36	332.38	355.28	372.58
0.6250	269.21	292.68	308.77	318.87	332.86	355.69	372.92
0.5882	269.33	293.31	309.28	319.37	333.37	356.39	373.09
0.5556	270.31	293.69	309.58	319.93	333.90	356.82	373.46
0.5263	271.57	295.24	310.03	320.68	334.77	357.03	373.69

X_1=0.0588

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	235.61	251.01	260.87	279.21	288.61	300.41	321.01
0.9091	236.57	252.25	261.64	280.35	289.53	300.90	321.88
0.8333	237.01	252.46	262.45	280.68	289.62	301.47	322.35
0.7692	237.68	253.35	263.38	281.24	290.13	301.94	322.79
0.7143	238.01	253.90	263.56	281.75	290.46	302.32	323.07
0.6667	238.90	254.24	264.14	282.44	291.38	302.77	323.68
0.6250	239.57	254.68	264.39	282.66	291.66	303.10	323.99
0.5882	240.24	255.61	265.29	283.57	292.43	303.65	324.30
0.5556	241.68	256.88	265.92	283.88	292.69	304.24	324.66
0.5263	242.46	257.59	266.96	284.68	293.13	304.57	325.13

X_1=0.1233

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	217.81	231.01	239.12	255.91	267.21	279.91	300.01
0.9091	218.81	231.81	239.88	256.60	268.11	280.24	300.84
0.8333	219.33	232.46	240.50	257.00	268.26	280.68	301.23
0.7692	220.28	233.01	241.23	257.45	268.76	281.15	301.64
0.7143	220.62	233.66	241.68	258.09	269.09	281.50	301.97
0.6667	221.29	233.96	242.09	258.60	269.51	282.10	302.51
0.6250	221.96	234.56	242.38	258.95	270.20	282.40	302.84
0.5882	222.41	235.15	242.99	259.70	270.77	283.00	303.21
0.5556	223.40	236.26	243.90	260.21	271.12	283.44	303.40
0.5263	224.03	237.05	245.03	260.87	271.70	283.83	303.98

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	200.01	211.00	217.21	232.61	245.81	259.41	279.01
0.9091	201.04	211.36	217.87	232.86	246.69	259.58	279.80
0.8333	201.64	212.46	218.36	233.32	246.91	259.89	280.10
0.7692	202.88	212.68	218.97	233.65	247.39	260.36	280.48
0.7143	203.22	213.42	219.62	234.44	247.73	260.68	280.87
0.6667	203.69	213.68	219.84	234.76	248.25	261.43	281.33
0.6250	204.35	214.44	220.19	235.24	248.73	261.70	281.68
0.5882	204.57	214.69	220.76	235.83	249.11	262.35	282.13
0.5556	205.13	215.64	221.43	236.54	249.56	262.364	282.39
0.5263	205.59	216.51	222.51	237.05	250.27	263.09	282.83

X_1=0.2727

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	188.31	202.01	213.61	227.01	239.71	255.01	276.01
0.9091	189.35	202.84	214.55	227.33	240.61	255.21	276.74
0.8333	189.77	203.56	215.12	227.89	240.92	255.67	277.08
0.7692	190.72	204.01	215.60	228.17	241.41	256.02	277.52
0.7143	191.02	204.62	216.14	228.88	241.71	256.52	277.83
0.6667	191.52	205.06	216.58	229.26	242.34	257.14	278.45
0.6250	192.02	205.60	216.87	229.82	242.66	257.58	278.78
0.5882	192.57	206.05	217.44	230.27	243.15	258.06	279.19
0.5556	193.30	206.76	218.08	230.96	243.49	250.37	279.76
0.5263	193.98	207.45	219.05	231.72	244.16	258.76	279.94

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	176.61	193.01	210.00	221.41	233.61	250.61	273.01
0.9091	177.66	194.32	211.24	221.80	234.54	250.84	273.68
0.8333	177.90	194.65	211.87	222.46	234.93	251.46	274.06
0.7692	178.57	195.35	212.43	222.68	235.43	251.68	274.55
0.7143	178.81	195.82	212.76	223.33	235.68	252.44	274.79
0.6667	179.35	196.43	213.33	223.75	236.43	252.86	275.57
0.6250	179.68	196.75	213.65	224.39	236.59	253.46	275.87
0.5882	180.57	197.42	214.22	224.70	237.19	253.77	276.24
0.5556	181.46	197.88	214.84	225.38	237.42	254.09	276.68
0.5263	182.37	198.39	215.77	226.39	238.05	254.43	277.05

X_1=0.4576

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	183.31	198.01	216.01	228.61	237.81	258.01	274.71
0.9091	184.18	199.25	217.06	228.88	239.09	258.26	275.62
0.8333	184.79	199.53	217.77	229.49	239.34	258.95	276.42
0.7692	185.63	200.31	218.43	229.76	239.89	259.27	276.74
0.7143	186.03	200.75	218.77	230.38	240.17	259.94	277.02
0.6667	186.53	201.39	219.34	230.76	240.94	260.32	277.60
0.6250	187.12	201.65	219.63	231.86	241.21	260.78	277.88
0.5882	187.33	202.48	220.35	232.32	241.73	261.09	278.41
0.5556	188.25	203.13	221.09	232.91	242.15	261.74	278.74
0.5263	189.21	203.91	222.05	233.60	242.71	262.43	279.41

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	190.01	203.01	222.01	235.81	242.01	265.41	276.41
0.9091	190.71	204.19	222.87	235.96	243.64	265.68	277.57
0.8333	191.67	204.42	223.66	236.53	243.75	266.44	278.79
0.7692	192.69	205.27	224.43	236.84	244.35	266.85	278.93
0.7143	193.24	205.68	224.77	237.43	244.66	267.43	279.24
0.6667	193.70	206.35	225.35	237.77	245.45	267.77	279.63
0.6250	194.57	206.54	225.60	239.34	245.83	268.09	279.88
0.5882	194.88	207.53	226.48	239.94	246.27	268.94	280.57
0.5556	195.03	208.37	227.35	240.44	246.88	269.38	280.80
0.5263	196.05	209.43	228.33	240.81	247.37	270.43	281.77

X_1=0.6923

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	200.58	213.02	232.02	245.80	252.00	275.42	286.42
0.9091	201.34	213.78	232.98	246.79	252.66	275.81	286.88
0.8333	202.12	214.71	233.87	247.60	253.09	276.30	287.31
0.7692	202.71	215.75	234.74	248.01	253.58	276.80	287.84
0.7143	203.56	216.35	235.32	248.77	254.23	277.46	289.25
0.6667	204.35	216.79	235.76	249.41	254.88	278.11	289.84
0.6250	204.87	217.58	235.51	249.82	255.37	278.72	290.31
0.5882	205.62	217.98	236.89	250.46	255.84	279.52	290.78
0.5556	206.62	218.48	237.36	251.09	256.61	280.28	291.26
0.5263	208.94	219.44	238.34	252.15	257.71	280.81	291.78

X_1=0.8351

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	211.14	223.02	242.01	255.70	262.02	285.42	296.40
0.9091	212.18	223.91	242.91	255.97	263.08	285.69	297.57
0.8333	212.81	224.46	243.76	256.58	263.55	286.45	298.79
0.7692	213.86	224.99	244.62	257.25	264.24	286.86	299.13
0.7143	214.48	225.73	245.31	257.82	264.62	287.44	299.55
0.6667	215.16	226.61	245.94	258.64	265.39	287.78	299.98
0.6250	215.91	227.42	246.46	259.56	266.03	288.10	300.38
0.5882	216.76	228.24	247.22	260.41	266.56	288.95	301.21
0.5556	217.36	228.89	247.99	261.04	267.35	289.39	301.58
0.5263	218.28	228.77	248.94	261.99	268.16	290.44	302.39

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	231.16	243.04	262.05	275.72	282.04	305.44	316.44
0.9091	231.91	243.84	262.86	276.62	282.87	305.96	317.26
0.8333	232.82	244.78	263.74	277.42	283.63	306.68	317.92
0.7692	233.64	245.56	264.62	277.94	284.51	307.47	318.61
0.7143	234.46	246.39	265.34	278.76	285.26	307.97	319.27
0.6667	235.32	246.94	265.96	279.59	285.84	308.78	319.73
0.6250	235.96	247.65	266.64	280.38	286.52	309.56	320.46
0.5882	236.68	248.51	267.63	280.96	287.25	310.32	320.88
0.5556	237.67	249.43	268.46	281.89	287.87	310.84	321.71
0.5263	238.54	250.36	269.31	282.92	288.54	311.71	322.52

Table 12(b): The values of molar conductance (Λ) obtained for N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride in methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	243.76	267.97	283.00	294.00	308.60.	327.00	345.00
0.9091	244.60	269.15	284.58	295.09	309.23	327.70	345.55
0.8333	245.01	270.14	284.84	295.77	309.57	328.53	346.03
0.7692	246.11	270.21	285.35	296.43	310.43	328.93	346.42
0.7143	247.40	270.59	285.67	296.67	310.67	329.23	346.86
0.6667	247.99	271.16	287.53	297.35	311.31	329.56	347.11
0.6250	248.20	271.70	287.76	297.86	311.85	330.34	347.57
0.5882	248.32	272.41	288.27	298.36	312.36	330.75	348.20
0.5556	249.42	273.62	288.57	298.92	312.89	331.01	348.53
0.5263	250.26	275.92	289.02	299.67	313.76	331.75	349.31

X_1=0.0588

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	214.60	239.00	239.86	258.20	267.60	279.40	300.00
0.9091	215.56	231.24	240.63	259.34	268.52	279.89	300.87
0.8333	216.00	231.45	241.44	259.67	268.61	280.46	301.34
0.7692	216.67	232.34	24.37	260.23	269.12	280.93	301.78
0.7143	217.00	232.89	242.55	260.74	269.45	281.31	302.06
0.6667	217.89	233.23	243.13	261.43	270.37	281.76	302.67
0.6250	218.56	233.67	243.38	261.65	270.65	282.09	302.98
0.5882	219.23	234.60	244.28	262.56	271.42	282.64	303.29
0.5556	220.67	235.87	244.91	262.87	271.68	283.23	303.65
0.5263	221.45	236.58	245.95	263.67	272.12	283.56	304.12

X_1=0.1233

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	196.80	210.00	218.11	234.90	246.20	258.90	279.00
0.9091	197.81	210.80	218.87	235.59	247.10	259.23	279.83
0.8333	198.32	211.45	219.49	236.00	247.25	259.67	280.22
0.7692	199.27	212.10	220.22	236.45	247.75	260.14	280.63
0.7143	199.61	212.65	220.67	237.08	248.08	260.49	280.96
0.6667	200.28	212.95	221.08	237.59	248.80	261.09	281.50
0.6250	200.95	213.55	221.37	237.94	249.09	261.39	281.83
0.5882	201.40	214.14	221.98	238.69	249.76	262.00	282.20
0.5556	202.39	215.25	222.89	239.20	250.11	262.43	282.39
0.5263	203.02	216.04	224.02	239.86	250.69	262.82	282.97

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	179.00	190.00	196.20	211.60	224.80	238.40	258.00
0.9091	180.03	190.35	196.86	211.86	225.68	238.57	258.79
0.8333	180.63	191.45	197.35	212.31	225.90	238.89	259.09
0.7692	181.87	191.67	197.76	212.64	226.38	239.35	259.47
0.7143	182.21	192.41	198.51	213.43	226.72	239.67	259.86
0.6667	182.68	192.67	198.83	213.75	227.24	240.42	260.32
0.6250	183.34	193.43	199.08	214.23	227.72	240.69	260.67
0.5882	183.56	193.68	199.65	214.82	228.10	241.34	261.12
0.5556	184.12	194.63	200.32	215.53	228.55	241.63	261.38
0.5263	184.59	195.50	201.38	216.04	229.26	242.08	261.82

X_1=0.2727

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	167.30	181.00	192.60	206.00	218.70	234.00	255.00
0.9091	168.34	181.83	193.54	206.32	219.60	234.20	255.73
0.8333	168.76	182.55	194.11	206.88	219.91	234.66	256.07
0.7692	169.71	183.00	194.59	207.18	220.40	235.01	256.51
0.7143	170.01	183.61	195.13	207.87	220.70	235.51	256.82
0.6667	170.51	184.05	195.57	208.25	221.33	236.13	257.44
0.6250	171.01	184.59	195.86	208.81	221.65	236.57	257.77
0.5882	171.56	185.04	196.43	209.26	222.14	237.05	258.18
0.5556	172.29	185.75	197.07	209.95	222.48	237.36	258.75
0.5263	172.97	186.44	198.04	210.71	223.15	237.75	258.93

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	155.60	172.00	189.00	200.40	212.60	229.60	252.00
0.9091	156.65	173.31	190.23	200.79	213.53	229.83	252.67
0.8333	156.89	173.64	190.86	201.45	213.92	230.45	253.05
0.7692	157.56	174.34	191.42	201.67	214.42	230.67	253.54
0.7143	157.80	174.81	191.75	202.32	214.67	231.43	253.78
0.6667	158.34	175.42	192.32	202.74	215.42	231.85	254.56
0.6250	158.67	175.74	192.64	203.38	215.58	232.45	254.86
0.5882	159.56	176.41	193.21	203.69	216.18	232.76	255.23
0.5556	160.45	176.87	193.83	204.37	216.41	233.08	255.67
0.5263	161.36	177.38	194.76	205.38	217.05	233.42	256.04

X_1=0.4576

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	162.30	177.00	195.00	207.60	216.80	237.00	253.70
0.9091	163.17	178.24	196.05	207.87	218.08	237.25	254.61
0.8333	163.78	178.52	196.76	208.48	218.33	237.94	255.41
0.7692	164.62	179.30	197.42	208.75	218.88	238.26	255.73
0.7143	165.02	179.74	197.76	209.37	219.16	238.93	256.01
0.6667	165.52	180.38	198.35	209.75	219.93	239.31	256.59
0.6250	166.11	180.64	198.62	210.85	220.20	239.77	256.87
0.5882	166.72	181.47	199.34	211.31	220.72	240.08	257.40
0.5556	167.24	182.12	200.08	211.90	221.14	240.73	257.73
0.5263	168.20	182.90	201.04	212.59	221.70	241.42	258.40

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	169.00	182.00	201.00	214.80	221.00	244.40	255.40
0.9091	169.76	183.18	201.86	214.95	222.63	244.67	256.56
0.8333	170.66	183.41	202.65	215.52	222.74	245.43	257.78
0.7692	171.68	184.26	203.42	215.83	223.34	245.84	257.92
0.7143	172.23	184.67	203.76	216.42	223.65	246.42	258.23
0.6667	172.69	185.34	204.34	216.76	224.44	246.76	258.62
0.6250	173.56	185.53	204.59	218.33	224.82	247.08	258.87
0.5882	173.87	186.52	205.47	218.93	225.26	247.93	259.56
0.5556	174.04	187.36	206.34	219.43	225.87	248.37	259.79
0.5263	175.04	188.42	207.32	219.80	226.36	249.92	260.76

X_1=0.6923

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	179.57	192.01	211.01	224.79	231.00	254.41	265.41
0.9091	180.33	192.77	211.97	225.78	231.65	254.80	265.87
0.8333	181.11	193.70	212.86	226.59	232.08	255.29	266.30
0.7692	181.70	194.74	213.73	227.00	232.57	255.79	266.83
0.7143	182.55	195.34	214.31	227.76	233.22	256.45	267.56
0.6667	183.34	195.78	214.85	228.40	233.87	257.10	268.11
0.6250	183.86	196.57	215.70	228.81	234.36	257.71	268.64
0.5882	184.61	196.97	215.98	229.45	234.83	258.51	269.42
0.5556	185.61	197.47	216.55	230.08	235.60	259.27	269.92
0.5263	185.93	198.43	217.63	231.14	236.70	259.80	270.75

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	190.13	202.01	221.00	234.69	241.01	264.41	275.39
0.9091	191.17	202.90	221.90	234.96	242.07	264.68	276.56
0.8333	191.80	203.45	222.75	235.57	242.54	265.44	277.78
0.7692	192.85	203.98	223.61	236.24	243.23	265.85	278.12
0.7143	193.47	204.72	224.30	236.81	243.61	266.43	278.54
0.6667	194.15	205.60	224.93	237.63	244.38	266.47	278.97
0.6250	194.90	206.41	225.45	238.55	245.02	267.09	279.37
0.5882	195.75	207.23	226.21	239.40	245.55	267.94	280.20
0.5556	196.35	207.88	226.98	240.03	246.34	268.38	280.57
0.5263	197.27	208.76	227.93	240.98	247.15	269.43	281.38

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	210.15	222.03	241.04	254.71	261.03	284.43	295.43
0.9091	210.90	222.83	241.85	255.61	261.86	284.95	296.25
0.8333	211.81	223.77	242.73	256.41	262.62	285.67	296.91
0.7692	212.63	224.55	243.61	256.93	263.50	286.46	297.60
0.7143	213.45	225.38	244.33	257.75	264.25	286.96	298.26
0.6667	214.31	225.93	244.95	258.58	264.83	287.77	298.72
0.6250	214.95	226.64	245.63	259.37	265.51	288.55	299.45
0.5882	215.67	227.50	246.62	259.95	266.24	289.31	299.87
0.5556	216.66	228.42	247.45	260.88	266.86	289.83	300.70
0.5263	217.23	229.35	248.30	261.91	267.53	290.70	301.51

Table 13(b): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) for N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride in methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0	K_A	$\Lambda_0\eta_0$	r	Λ_0	K_A	$\Lambda_0\eta_0$	r
	Scm^2mol^{-1}	dm^3mol^{-1}			Scm^2mol^{-1}	dm^3mol^{-1}		
		T=283.15K				**T=288.15K**		
0.0000	258.41	645.48	336.71	5.567	282.37	567.35	321.34	5.732
0.0588	229.32	740.45	370.81	5.055	244.01	630.26	352.84	5.221
0.1233	210.85	759.95	413.90	4.529	223.07	653.12	388.03	4.747
0.1942	192.38	779.24	419.39	4.470	202.13	675.61	391.97	4.699
0.2727	180.16	813.09	421.57	4.447	193.36	709.58	393.93	4.676
0.3600	167.92	850.92	423.27	4.429	184.59	747.69	395.47	4.658
0.4576	175.88	899.58	376.38	4.981	190.45	788.88	371.18	4.963
0.5676	183.81	939.74	363.94	5.151	196.32	827.36	331.58	5.555
0.6923	195.79	990.70	306.77	6.111	207.86	865.83	271.67	6.780
0.8351	207.84	1044.46	221.14	8.477	218.69	908.48	211.03	8.729
1.0000	228.95	1074.41	157.06	11.935	240.32	962.72	153.32	12.014
		T=293.15K				**T=298.15K**		
0.0000	297.04	503.75	297.63	6.083	306.32	435.36	272.93	6.523
0.0588	252.93	550.97	316.92	5.713	270.25	452.02	296.73	6.000
0.1233	230.46	580.84	349.38	5.182	246.05	472.42	312.53	5.696
0.1942	207.18	602.76	351.42	5.152	221.84	492.41	320.29	5.558
0.2727	204.37	620.99	361.73	5.005	216.62	522.10	325.36	5.472
0.3600	201.65	668.99	362.93	4.989	211.42	553.88	332.35	5.357
0.4576	208.48	699.57	350.45	5.167	219.51	584.44	320.70	5.551
0.5676	215.38	731.50	325.88	5.556	227.65	613.87	304.82	5.840
0.6923	227.03	770.26	270.62	6.691	239.84	651.74	259.27	6.866
0.8351	238.01	812.33	208.02	8.704	250.47	710.37	201.63	7.610
1.0000	259.32	864.87	153.25	11.185	271.45	773.94	150.11	11.860

$X_{Methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
		T=303.15K				**T=308.15K**		
0.0000	319.80	363.39	255.20	6.861	336.48	313.86	242.27	7.110
0.0588	278.09	370.17	273.08	6.412	289.10	338.51	252.96	6.809
0.1233	256.34	389.74	293.51	5.965	268.20	356.83	270.61	6.365
0.1942	234.68	414.32	295.02	5.935	247.20	378.26	274.75	6.269
0.2727	227.81	431.13	302.76	5.783	243.35	392.46	281.56	6.118
0.3600	222.97	448.81	304.02	5.759	239.42	418.75	286.83	6.005
0.4576	228.33	485.43	289.75	6.043	247.59	442.76	285.72	6.029
0.5676	233.75	522.36	276.76	6.326	256.13	476.50	270.99	6.356
0.6923	244.40	547.98	235.60	7.432	268.19	504.47	233.86	7.365
0.8351	277.82	604.29	201.70	8.681	289.59	547.82	194.89	8.838
1.0000	278.81	649.23	148.59	11.783	300.45	589.56	145.12	11.869
		T=313.15K						
0.0000	354.29	260.03	248.44	6.823				
0.0588	309.53	302.61	262.16	6.465				
0.1233	288.18	323.30	278.93	6.077				
0.1942	267.02	344.06	284.91	5.949				
0.2727	264.64	366.32	287.57	5.894				
0.3600	261.98	381.04	295.80	5.730				
0.4576	264.86	415.84	285.09	5.945				
0.5676	267.78	439.41	273.27	6.203				
0.6923	278.64	475.18	234.71	7.222				
0.8351	302.83	517.73	193.51	8.759				
1.0000	310.57	544.26	149.59	11.331				

Table 13(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 for N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride in methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
		T=283.15K				**T=288.15K**		
0.0000	280.10	633.93	364.97	5.1308	303.19	543.58	345.03	5.3331
0.0588	250.29	662.26	407.72	4.5928	265.01	567.94	383.20	4.8019
0.1233	231.83	673.00	455.08	4.1148	244.07	582.62	430.05	4.2788
0.1942	213.34	680.17	465.08	4.0264	223.14	595.90	437.13	4.2095
0.2727	201.13	703.35	470.64	3.9788	214.36	620.37	440.15	4.1806
0.3600	188.91	727.62	483.04	3.8767	205.59	648.31	446.81	4.1183
0.4576	196.86	772.72	421.28	4.4450	211.46	688.37	412.14	4.4647
0.5676	204.80	809.14	405.50	4.6180	217.33	729.95	367.07	5.0133
0.6923	216.58	842.92	319.67	5.8579	228.62	764.05	298.81	6.1581
0.8351	228.82	911.03	242.78	7.7131	240.68	816.34	232.26	7.9226
1.0000	249.96	951.52	171.47	9.9208	261.26	852.58	166.68	10.0397
		293.15K				**298.15K**		
0.0000	318.04	463.72	318.68	5.6756	327.34	383.42	291.66	6.0974
0.0588	273.77	491.52	343.03	5.2727	291.28	411.65	319.83	5.5604
0.1233	251.48	516.32	381.24	4.7443	267.09	426.53	351.49	5.0595
0.1942	233.20	528.67	391.78	4.6166	242.88	439.32	354.06	5.0229
0.2727	225.39	542.75	398.94	4.5333	237.66	463.55	358.26	4.9639
0.3600	222.68	588.01	400.38	4.5179	232.46	489.01	365.43	4.8665
0.4576	229.51	615.01	385.81	4.6881	240.56	517.17	351.46	5.0600
0.5676	236.41	644.20	357.69	4.7989	248.71	544.05	330.02	5.3887
0.6923	247.84	666.59	295.43	1.2229	260.82	582.42	281.95	6.3074
0.8351	259.21	721.40	226.55	7.9837	271.48	628.29	218.54	8.1375
1.0000	280.38	777.45	165.70	10.1489	293.53	699.35	162.32	10.9560

$X_{Methanol}$	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=303.15K				**T=308.15K**		
0.0000	340.99	343.07	272.11	6.4277	363.16	284.92	261.48	6.5805
0.0588	299.14	337.98	293.76	5.9544	310.15	291.57	271.38	6.3404
0.1233	277.43	355.06	317.66	5.5060	289.25	305.84	291.85	5.8957
0.1942	255.73	371.29	321.45	5.4411	268.36	319.18	298.15	5.7711
0.2727	249.87	384.54	330.08	5.2988	264.41	335.84	305.92	5.6246
0.3600	244.02	397.70	334.01	5.2365	260.49	352.61	312.07	5.5149
0.4576	249.40	430.79	316.49	5.5264	268.67	363.71	310.05	5.5496
0.5676	254.82	463.61	301.71	5.7971	277.22	389.31	293.30	5.8666
0.6923	265.68	495.69	256.12	6.8290	289.20	418.13	252.18	6.8232
0.8351	277.13	539.20	201.20	8.6931	300.01	456.28	200.56	8.5793
1.0000	298.90	623.51	153.93	11.3626	321.56	536.49	151.02	11.3936
		313.15K						
0.0000	379.88	253.71	248.44	6.8153				
0.0588	330.59	250.73	262.16	6.4586				
0.1233	309.23	258.65	278.93	6.0703				
0.1942	288.08	273.43	284.91	5.9429				
0.2727	285.71	298.35	287.57	5.8879				
0.3600	283.06	307.92	295.80	5.7241				
0.4576	285.95	333.40	285.09	5.9391				
0.5676	288.87	357.41	273.27	6.1960				
0.6923	299.38	385.73	234.71	7.2140				
0.8351	312.11	418.00	193.51	8.7499				
1.0000	331.68	460.03	149.59	11.3189				

From the experimental data, the values of Λ_0 are found to increase with increase in temperature in all solvents irrespective of X_{MeOH}, indicating less solvation or higher mobility of ions (Tables 13(a) & 13(b).).This is attributed to the fact that increase 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 [Yakoyama *et al.*, 1994]. The variation of $\Lambda_0\eta_0$ and η with mole fraction of methanol is shown in Fig. 4.2.1(a) & Fig.4.2.1 (b). The viscosity of M + W mixtures increases upto $X_{MeOH} = 0.3600$ in both cases and thereafter it decreases. Values of Λ_0 of salts decrease upto this mole fraction and then increase in methanol rich region at all temperatures as expected from Walden rule which was supported by the work of Singh and his co-workers [Singh *et al.*, 2008] (Table 13(a) & 13(b)). The maximum in η versus mole fraction indicates maximum interaction between water and methanol in such solvent mixtures. $\Lambda_0\eta_0$ increases upto mole fraction of 0.3600 in methanol and then decreases. If change in solvation is reflected by the variation in $\Lambda_0\eta_0$ [Bag *et al.*, 2000], 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 [Pura and Atun, 2003]. The effective radius(r) of ion or solute can be calculated as

$$\Lambda_0\eta_0 = 1/6\ \pi r T \qquad \ldots(20)$$

It has been possible to derive the values of r for the cation of the octahedral Cu^{II} and Co^{II} complexes. The calculated values of r decrease with increase in methanol content upto $x_{MeOH} = 0.3600$ and thereafter increase in methanol rich regions. The smaller $\Lambda_0\eta_0$ values in methanol rich region may be due to the large effective radius of the cation, whereas the maximum values of $x_{MeOH} = 0.3600$ correspond to minimum values of r. The Walden product in these solvents increases, and then decreases 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., [Bag *et al.*, 2000]

$$\Lambda_o = A.e^{-E^a/RT} \text{ or } \ln \Lambda_o = \ln A - E^a/RT \qquad \ldots(21)$$

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 Tables 14(a) & 14(b).

4.2.4. Calculation of Thermodynamic parameters

For the calculation of thermodynamic parameters, all the equations involved are same as given in chapter-3, section 3.1.2.

Table 14(a): Thermodynamic parameters ΔG^0 ($kJmole^{-1}$), ΔH^0 ($kJmol^{-1}$), ΔS^0 ($kJK^{-1}mol^{-1}$), E^a ($kJmol^{-1}$) and $10^{-3}A$ for N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.0000			
ΔG^0	-14.54	-14.35	-14.26	-13.92	-13.83	-13.64	-13.48
ΔH^0	-24.65						
$10^3 \Delta S^0$	-35.78	-35.75	-35.48	-35.93	-35.72	-35.74	-35.62
E^a	7.01						
$10^{-3}A$	5.66						

	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
				X_1=0.0588			
ΔG^0	-14.70	-14.47	-14.44	-14.12	-14.00	-13.82	-13.68
ΔH^0	-24.44						
10^3 ΔS^0	-34.41	-34.59	-34.12	-34.64	-34.43	-34.45	-34.37
E^a	7.29						
10^{-3}A	4.10						
				X_1=0.1233			
ΔG^0	-14.86	-14.67	-14.55	-14.34	-14.17	-13.93	-13.91
ΔH^0	-23.91						
103 ΔS0	-31.97	-31.99	-31.92	-32.07	-32.11	-32.38	-31.89
E^a	7.48						
10^{-3}A	3.79						
				X_1=0.1942			
ΔG^0	-15.04	-14.85	-14.77	-14.62	-14.41	-14.23	-14.12
ΔH^0	-23.52						
10^3 ΔS^0	-29.99	-30.08	-29.83	-29.84	-30.03	-30.13	-30.19
E^a	7.78						
$10^{-3}A$	4.48						
				X_1=0.2727			
ΔG^0	-15.15	-15.02	-14.94	-14.73	-14.59	-14.47	-14.23
ΔH^0	-23.29						
10^3 ΔS^0	-28.79	-28.71	-28.49	-28.69	-28.72	-28.63	-28.94
E^a	8.29						
10^{-3}A	6.76						

				X_1=0.3600			
ΔG^0	-15.24	-15.18	-15.00	-14.86	-14.75	-14.64	-14.47
ΔH^0	-23.02						
103 ΔS^0	-27.46	-27.18	-27.33	-27.35	-27.24	-27.18	-27.28
E^a	8.79						
$10^{-3}A$	8.09						
				X_1=0.4576			
ΔG^0	-15.36	-15.24	-15.11	-14.98	-14.93	-14.77	-14.52
ΔH^0	-22.76						
103 ΔS^0	-26.18	-25.74	-26.13	-26.12	-25.84	-25.95	-26.30
E^a	8.51						
$10^{-3}A$	8.73						
				X_1=0.5676			
ΔG^0	-15.46	-15.35	-15.31	-15.14	-15.05	-14.94	-14.57
ΔH^0	-22.49						
103 ΔS^0	-24.85	-24.79	-24.44	-24.63	-24.57	-24.51	-24.67
E^a	8.43						
$10^{-3}A$	7.36						
				X_1=0.6923			
ΔG^0	15.63	-15.57	-15.45	-15.32	-15.17	-15.01	-14.94
ΔH^0	-22.31						
$10^3 \Delta S^0$	-24.00	-23.37	-23.65	-23.45	-23.56	-23.68	-23.51
E^a	8.29						
$10^{-3}A$	7.24						

	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
				X_1=0.8351			
ΔG^0	-15.73	-15.68	-15.56	-15.42	-15.29	-15.11	-15.06
ΔH^0	-22.02						
$10^3 \Delta S^0$	-22.18	-21.98	-21.99	-22.18	-22.37	-22.21	-22.04
E^a	7.69						
$10^{-3}A$	5.93						
				X_1=1.0000			
ΔG^0	-15.89	-15.74	-15.67	-15.57	-15.45	-15.30	-15.19
ΔH^0	-21.76						
$10^3 \Delta S^0$	-20.75	-20.91	-20.39	-21.40	-20.80	-20.98	-20.51
E^a	7.09						
$10^{-3}A$	5.07						

Table 14(b): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A for N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
				X_1=0.0000			
ΔG^0	-14.07	-13.91	-13.81	-13.63	-13.46	-13.27	-12.94
ΔH^0	-34.02						
$10^3 \Delta S^0$	-35.14	-35.08	-34.82	-34.84	-34.83	-34.88	-35.38
E^a	8.68						
$10^{-3}A$	5.35						

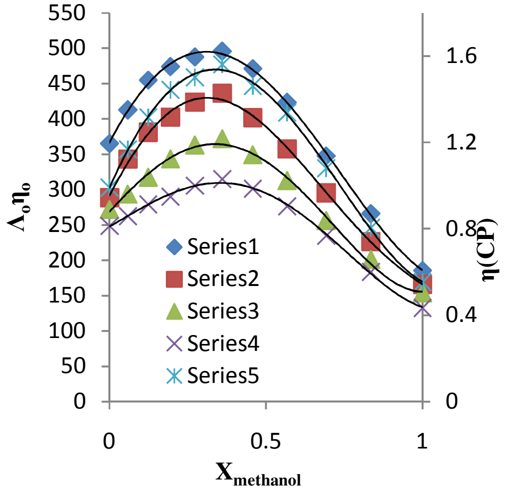
	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
X_1=0.0588							
ΔG^0	-14.11	-13.96	-13.84	-13.86	-13.49	-13.32	-13.06
ΔH^0	-27.74						
$10^3\,\Delta S^0$	-34.01	-33.94	-33.77	-33.62	-33.57	-33.56	-33.57
E^a	8.93						
$10^{-3}A$	5.56						
X_1=0.1233							
ΔG^0	-14.33	-14.16	-13.92	-13.73	-13.56	-13.39	-13.21
ΔH^0	-23.06						
$10^3\,\Delta S^0$	-32.65	-31.51	-31.31	-31.29	-31.27	-31.21	-31.31
E^a	9.21						
$10^{-3}A$	5. 77						
X_1=0.1942							
ΔG^0	-14.52	-14.35	-14.16	-14.94	-13.96	-13.67	-13.45
ΔH^0	-22.84						
$10^3\,\Delta S^0$	-29.72	-29.61	-29.47	-29.32	-29.54	-29.31	-29.34
E^a	9.40						
$10^{-3}A$	5.94						
X_1=0.2727							
ΔG^0	-14.71	-14.56	-14.39	**-14.15**	-14.02	-13.87	-13.63
ΔH^0	-21.96						
$10^3\,\Delta S^0$	-27.02	-27.89	-27.71	-27.60	-27.58	-27.46	-27.32
E^a	9.63						
$10^{-3}A$	6.25						

	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
				X_1=0.3600			
ΔG^0	-14.98	-14.81	-14.64	-14.42	-14.25	-14.07	-13.85
ΔH^0	-21.23						
$10^3\,\Delta S^0$	-26.31	-26.16	-26.87	-26.67	-26.59	-26.45	-26.36
E^a	9.83						
$10^{-3}A$	6.54						
				X_1=0.4576			
ΔG^0	-15.38	-15.16	-14.92	-14.77	-14.53	-14.31	-14.06
ΔH^0	-20.57						
$10^3\,\Delta S^0$	-25.21	-25.06	-24.98	-24.76	-24.64	-24.42	-24.35
E^a	8.97						
$10^{-3}A$	6.14						
				X_1=0.5676			
ΔG^0	-15.43	-15.25	-15.06	-14.84	-14.62	-14.43	-14.23
ΔH^0	-20.12						
$10^3\,\Delta S^0$	-23.68	-23.47	-23.41	-23.25	-23.27	-23.23	-23.17
E^a	8.71						
$10^{-3}A$	5.84						
				X_1=0.6923			
ΔG^0	-14.90	-14.78	-14.51	-14.35	-13.96	-13.77	-13.49
ΔH^0	-19.73						
$10^3\,\Delta S^0$	-20.96	-20.84	-20.67	-20.53	-20.38	-20.21	-20.04
E^a	8.53						
$10^{-3}A$	5.64						

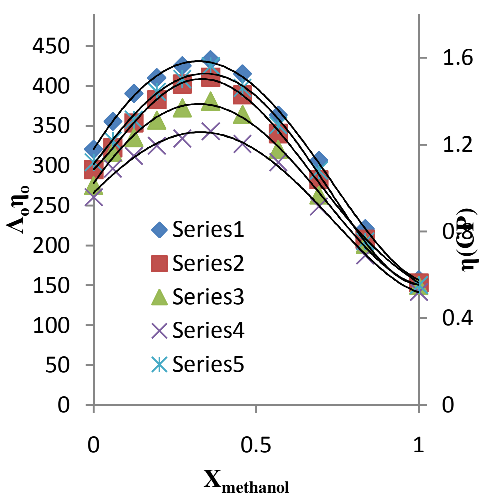
	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
X_1=0.8351							
ΔG^0	-13.81	-13.64	-13.46	-13.32	-13.14	-13.03	-12.87
ΔH^0	-19.21						
$10^3 \Delta S^0$	-19.07	-18.92	-18.77	-18.59	-18.41	-18.25	-18.08
E^a	8.16						
$10^{-3}A$	5.45						
X_1=1.0000							
ΔG^0	-12.62	-12.46	-12.23	-12.07	-11.91	-11.76	-11.62
ΔH^0	-17.69						
$10^3 \Delta S^0$	-17.90	-17.75	-17.63	-17.47	-17.32	-17.08	-16.87
E^a	7.87						
$10^{-3}A$	5.21						

Tables 14(a) & 14(b) showed that the values of E^a increases with increase in X_1 upto about X_1=0.36 and thereafter decreases rapidly. It follows that in water rich region upto X_1=0.36, the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond X_1=0.3600. 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=0.3600, as the activation energy decreases the Λ_0 values increases with X_1 (Tables 14(a) & 14(b)). The experimentally determined K_As (tables 13(a) & 13(b)) of the complex 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 values 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 heat of association (ΔH^0) is obtained from the slope of the plot of log K_A versus $1/T$ (Figures 12(a) & 12(b)). ΔH^0 values obtained are found to increase with the composition of the mixed solvents. The values of these thermodynamic parameters in all solvent mixtures at all temperature are given in Tables 14(a) &14(b).



Series1→283.15K, series2→288.1 K series3→293.15, series4→303.15 K, series4→313.15K,series5→η(at 25°C)



(Series1→283.15K, series2→293.15K, series3→288.15,series4→303.15K,series4→313.15K

Figure 11(a): The value of Walden product ($\Lambda_o\eta_o$) and viscosity (η) for Cu^{II} complex as a function of X_{MeOH} in methanol + water solvents

Figure 11(b): The value of Walden product ($\Lambda_o\eta_o$) and viscosity (η) for Co^{II} complex as a function of X_{MeOH} in methanol + water solvents

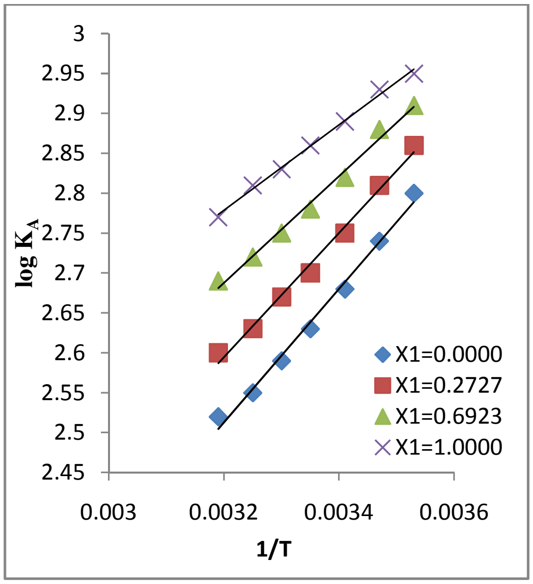


Figure 12(a): Plot of log K_A vs 1/T for Cu^{II} complex in different mole fractions at 283.15-313.15K

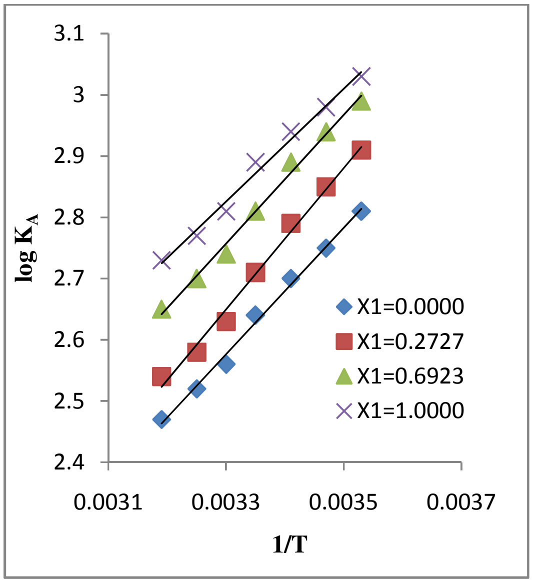


Figure 12(b): Plot of log K_A vs 1/T for Co^{II} complex in different mole fractions at 283.15-313.15K

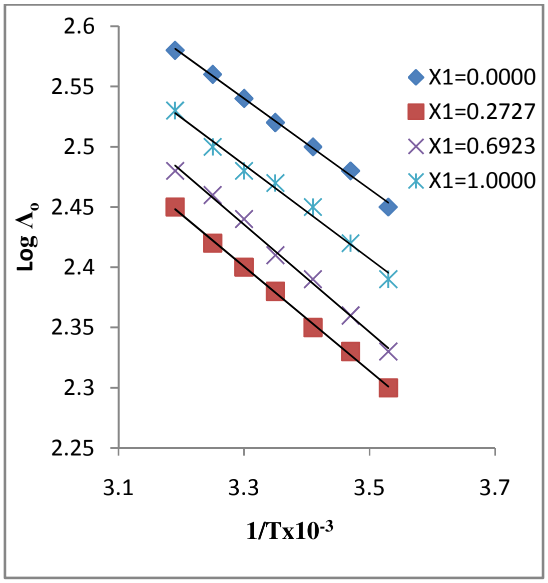


Figure 13(a): Plot of log Λ_o vs 1/T for Cu^{II} complex in different mole fractions at 283.15-313.15K

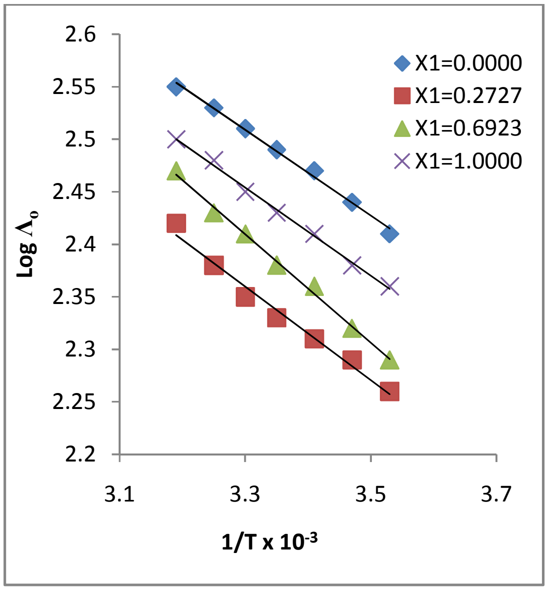


Figure 13(b): Plot of log Λ_o vs 1/T for Co^{II} complex in different mole fractions at 283.15-313.15K

For the two complexes, the values of $\Lambda_o\eta_o$ increase with increase in X_1 upto about 0.3600 and thereafter it decreases rapidly. The viscosity of water + methanol mixtures also passes through maximum about $X_1 = 0.3600$. It is interesting to note that the Λ_o values of the solute decrease upto the mole fraction of methanol and then increase in methanol rich region at temperatures from 10 to 40^0C, indicating maximum methanol-water interaction in the region $X_1 = 0.3600$.

4.3. Ion-Pair Formation and Thermodynamics of N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride in Methanol + Water Solutions at Different Temperatures.

4.3.1. Introduction

The conductivity method is well suited to investigate the ion-ion and ion-solvent interactions in electrolytic solutions [De *et al.*, 2006]. The measurement of electrical conductivities of dilute solution of salts or complexes are considered to be one of the important methods for studying the ion-pair or multiple ion-association not only in aqueous solutions but also in non-aqueous or mixed ones [Zimmerman *et al.*, 1997; Marusak and Lappin, 1989].Also conductivity measurements were used to evaluate the hydration free energy of some electrolytic solutions and to study the nature of the solute-solvent interaction[El-Hammamy *et al.*, 2010].The conductance and viscosity measurements provide valuable information regarding the ion-ion and ion-solvent interactions [Singh, 2002]. The present works reports the comparative studies of conductometric properties, thermodynamic behaviour and Walden product of N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride in water and water + methanol mixed solvent at temperatures between 10°C -40°C to examine the validity of Shedlovsky equation [Shedlovsky and Kay,1956].The limiting equivalent conductance (Λ_o), the association constant (K_A) and the solvation for complex have been evaluated. These values have been used to discuss the nature of the ion-ion, ion-solvent and solvent-solvent interaction of the complex. Temperature variation of (K_A) has been studied to get the thermodynamic parameters as a function of the solvent structure.

4.3.2. Experimental

N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride and N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride were prepared according to chapter-3, section 3.3.2(iii) & 3.3.2(iv). All the detailed processes/methods are same as given in chapter-4, section-4.2.2.The equivalent conductivities are shown in the following tables (table. 4.3.1(a) and 4.3.1(b)).

4.3.3. Calculation of limiting molar conductance, association constants, Walden products and effective radius

The experimental values of conductance measurements of Cu^{II} and Co^{II} complexes in water-methanol mixtures 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 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are same as given in chapter 3, section 3.1.1. The effective radius(*r*) of ion or solute can be calculated as described in chapter-3, section-3.1.3.

The variation of Walden product ($\Lambda_o\eta_o$) for three salts with X_1 at 10, 15, 20, 25, 30, 35 and 40^0C are shown in Figure 14.(a) and Figure 14(b). For the two complexes, the values of $\Lambda_o\eta_o$ increase with increase in X_1 upto about 0.3600 and thereafter it decreases rapidly. The viscosity of water + methanol mixtures also passes through maximum about $X_1 = 0.3600$. It is interesting to note that the Λ_o values of the solute decrease upto the mole fraction of methanol and then increase in methanol rich region at temperatures from 10 to 40^0C, indicating maximum methanol-water interaction in the region $X_1 = 0.3600$.

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, solvent-solvent interactions become stronger and in turn producing maximum Walden product [Das *et al.*, 2004]. Further addition of methanol results in progressive disruption of water structure and the ions become solvated with the other component of the solvent mixture (viz, methanol). The effect would be more in case of a solution at a higher temperature. As expected, Λ_o, values increase with rise in temperature linearly irrespective of the nature of the solvent. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A Vs 1/T. (Figure15 (a), and Figure 15(b)). The ΔH^0 values obtained are found to increase systematically with the composition of the mixed solvent. The Values of these thermodynamic functions are given in Table 17(a) & Table 17(b). The negative values of ΔH^0 indicate that ion association processes are exothermic in nature in all solvents at all temperatures.

Table: 15(a). The values of molar conductance (Λ) obtained for N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride in various methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	248.43	272.84	288.03	298.98	313.49	329.02	348.02
0.9091	249.34	274.01	289.47	300.03	314.12	329.69	348.54
0.8333	250.28	275.16	289.73	300.65	314.46	330.42	349.02
0.7692	251.06	275.68	290.24	301.32	315.32	330.82	349.31
0.7143	252.24	275.96	290.56	301.56	315.56	331.12	349.75
0.6667	252.85	276.38	292.42	302.24	316.20	331.45	350.00
0.6250	253.18	276.81	292.65	302.75	316.74	332.23	350.46
0.5882	253.55	277.38	293.16	303.25	317.25	332.64	351.19
0.5556	254.37	278.43	293.46	303.81	317.78	333.00	351.42
0.5263	255.09	280.52	293.91	304.56	318.65	333.64	352.20

X_1=0.0588

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	219.58	235.01	244.75	263.08	272.49	284.39	305.01
0.9091	220.45	236.13	245.52	264.23	273.41	284.78	305.76
0.8333	220.98	236.34	246.34	264.56	273.50	285.35	306.23
0.7692	221.56	237.23	247.26	265.12	274.01	285.82	306.67
0.7143	221.98	237.78	247.45	265.63	274.34	286.20	307.01
0.6667	222.78	238.12	248.02	266.32	275.26	286.65	307.56
0.6250	223.45	238.56	248.27	266.54	275.54	287.01	307.87
0.5882	224.12	239.47	249.17	267.45	276.31	287.53	308.18
0.5556	225.56	240.76	249.80	267.76	276.57	288.12	308.54
0.5263	226.34	241.47	250.84	268.76	277.01	288.45	309.01

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	183.89	194.98	201.09	216.49	229.69	243.29	261.01
0.9091	184.92	195.24	201.75	216.75	230.57	243.46	261.68
0.8333	185.52	196.34	202.24	217.20	230.80	243.78	262.01
0.7692	186.76	196.56	202.65	217.53	231.27	244.24	262.36
0.7143	187.10	197.30	203.40	218.32	231.61	244.56	262.75
0.6667	187.57	197.56	203.72	218.64	232.13	245.31	263.21
0.6250	188.23	198.32	204.01	219.12	232.61	245.58	263.56
0.5882	188.45	198.57	204.54	219.71	233.01	246.23	264.01
0.5556	189.01	199.52	205.21	220.42	233.45	246.56	264.27
0.5263	189.48	200.01	206.27	221.01	234.15	247.01	264.71

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	160.49	176.81	194.01	205.29	217.49	234.48	254.98
0.9091	161.54	178.20	195.12	205.68	218.42	234.72	255.56
0.8333	161.78	178.53	195.75	206.34	218.81	235.34	256.01
0.7692	162.45	179.23	196.31	206.56	219.31	235.56	256.43
0.7143	162.69	179.70	196.64	207.21	219.56	236.32	256.67
0.6667	163.23	180.31	197.21	207.63	220.31	236.74	257.45
0.6250	163.56	180.63	197.53	208.27	220.47	237.34	257.75
0.5882	164.45	181.30	198.10	208.58	221.07	237.65	258.12
0.5556	165.34	181.76	198.72	209.26	221.30	238.01	258.56
0.5263	166.25	182.27	199.65	210.27	222.01	238.32	259.01

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	173.98	187.01	205.97	219.69	225.98	246.29	260.29
0.9091	174.65	188.07	206.75	219.84	227.32	246.56	261.35
0.8333	175.54	188.30	207.54	220.41	227.63	247.32	262.67
0.7692	176.57	189.15	208.31	220.72	228.23	247.73	262.81
0.7143	177.12	189.56	208.65	221.31	228.54	248.31	263.12
0.6667	177.58	190.23	209.23	222.65	229.33	248.65	263.51
0.6250	178.45	190.42	209.48	223.21	229.71	249.01	263.76
0.5882	178.76	191.41	210.36	223.82	230.17	249.82	264.45
0.5556	179.01	192.25	211.23	224.32	230.76	250.26	264.68
0.5263	180.00	193.31	212.21	224.69	231.25	251.81	265.65

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	195.02	206.90	225.98	239.58	245.90	269.30	280.28
0.9091	196.06	207.79	226.79	239.85	246.96	269.57	281.45
0.8333	196.69	208.34	227.64	240.46	247.43	270.32	282.67
0.7692	197.74	208.87	228.50	241.13	248.12	270.74	283.01
0.7143	198.36	209.61	229.19	241.70	248.50	271.32	283.43
0.6667	199.04	210.49	229.82	242.52	249.27	271.36	283.86
0.6250	199.79	211.30	230.34	243.44	249.91	272.01	284.26
0.5882	200.64	212.12	231.10	244.29	250.45	272.83	285.09
0.5556	201.24	212.76	231.87	244.92	251.23	273.27	285.46
0.5263	202.16	213.65	232.82	245.87	252.04	274.32	286.27

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	215.04	226.92	245.93	259.60	270.92	289.32	300.32
0.9091	215.79	227.72	246.74	260.51	271.75	289.84	301.14
0.8333	216.70	228.67	247.62	261.30	272.51	290.56	301.80
0.7692	217.52	229.43	248.50	261.82	273.39	291.35	302.49
0.7143	218.34	230.27	249.21	262.64	274.14	291.85	303.15
0.6667	219.20	230.82	249.84	263.47	274.72	292.67	303.61
0.6250	219.84	231.53	250.52	264.26	275.40	293.43	304.34
0.5882	220.56	232.39	251.51	264.84	276.13	294.20	304.76
0.5556	221.55	233.31	252.34	265.78	276.75	294.72	305.59
0.5263	222.12	234.24	253.19	266.80	277.42	295.51	306.40

Table 15(b): The values of molar conductance (Λ) obtained for N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride in various methanol+ water mixtures at 283.15-313.15K.

X_1=0.0000

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	268.90	289.92	308.91	320.00	334.50	354.30	374.10
0.9091	270.50	291.13	310.48	320.98	335.13	355.25	375.35
0.8333	270.91	292.24	310.74	321.67	335.47	355.71	375.68
0.7692	272.01	292.50	311.25	322.34	336.43	356.31	376.78
0.7143	273.30	293.35	311.57	322.57	336.62	356.46	377.24
0.6667	273.89	294.35	313.24	323.25	337.27	357.17	377.47
0.6250	274.10	294.57	313.67	323.76	337.75	357.58	377.81
0.5882	274.23	295.20	314.17	324.26	338.26	358.28	378.00
0.5556	275.20	295.58	314.47	324.82	338.79	358.71	378.35
0.5263	276.46	296.89	315.00	325.57	339.67	359.00	378.58

X_1=0.0588

Conc.x10^{-4}	**283.15K**	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	240.50	253.90	265.76	282.10	293.50	305.30	322.90
0.9091	241.46	255.14	266.53	283.24	294.42	305.79	323.78
0.8333	241.90	255.35	267.34	283.57	294.51	306.36	324.24
0.7692	242.57	256.24	268.27	284.13	295.02	306.83	324.68
0.7143	242.90	256.79	268.45	284.64	295.35	307.21	325.00
0.6667	243.79	257.13	269.03	285.34	296.27	307.67	325.57
0.6250	244.46	257.59	269.28	285.54	296.56	308.00	325.87
0.5882	245.13	258.50	270.18	286.46	297.32	308.54	326.19
0.5556	246.57	259.76	270.81	286.78	297.58	309.13	326.56
0.5263	247.35	260.48	271.85	287.57	298.02	309.46	327.02

X_1=0.1942

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	204.90	214.89	222.10	237.50	250.70	264.30	280.90
0.9091	206.00	216.25	222.76	237.75	251.58	264.47	281.69
0.8333	206.53	217.35	223.25	238.21	251.80	264.78	282.00
0.7692	207.78	217.57	223.86	238.54	252.28	265.25	282.37
0.7143	208.12	218.31	224.51	239.34	252.62	265.57	282.76
0.6667	208.58	218.57	224.73	239.65	253.14	266.32	288.23
0.6250	209.24	219.34	225.08	240.13	253.62	266.59	283.57
0.5882	209.46	219.58	225.65	240.72	254.00	267.24	284.02
0.5556	210.02	220.53	226.32	241.43	254.45	267.53	284.28
0.5263	210.48	221.40	227.40	242.00	255.16	268.00	284.72

X_1=0.3600

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	181.50	194.90	212.99	226.30	238.50	253.52	274.90
0.9091	182.56	196.21	214.13	226.69	239.43	253.73	275.57
0.8333	182.79	196.54	214.76	227.35	239.82	254.35	276.00
0.7692	183.46	197024	215.32	227.57	240.32	254.57	276.45
0.7143	183.70	197.71	215.65	228.23	240.57	255.34	276.68
0.6667	184.24	198.32	216.23	228.64	241.32	255.75	277.46
0.6250	184.57	198.64	216.54	229.28	241.48	256.35	277.76
0.5882	185.46	199.31	217.12	229.59	242.08	256.67	278.13
0.5556	186.35	199.78	217.73	230.27	242.31	257.00	278.57
0.5263	187.26	200.28	218.67	231.28	243.00	257.32	279.00

X_1=0.5676

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	194.91	208.00	224.90	240.70	251.90	268.30	281.32
0.9091	195.60	209.08	225.76	240.85	253.53	268.57	282.46
0.8333	196.56	209.31	226.56	241.42	253.64	269.34	283.68
0.7692	197.58	210.16	227.32	241.73	254.24	269.74	283.82
0.7143	198.13	210.57	227.67	242.32	254.56	270.32	284.13
0.6667	198.59	211.24	228.24	242.67	255.34	270.67	284.52
0.6250	199.46	211.43	228.49	244.23	255.72	271.00	284.78
0.5882	199.78	212.42	229.37	244.83	256.16	271.83	285.46
0.5556	200.00	213.26	230.24	245.34	256.78	272.27	285.69
0.5263	201.01	214.32	231.23	245.70	257.26	273.32	286.67

X_1=0.8351

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	216.03	227.91	244.90	260.59	271.91	288.31	299.29
0.9091	217.07	228.80	245.80	260.86	273.00	288.58	300.46
0.8333	217.70	229.35	246.65	261.47	273.45	289.34	301.68
0.7692	218.75	229.89	247.51	262.14	274.13	289.75	302.02
0.7143	219.37	230.62	248.20	262.71	274.51	290.34	302.45
0.6667	220.05	231.50	248.83	263.53	275.28	290.67	302.87
0.6250	220.80	232.31	249.35	264.45	275.92	291.00	303.27
0.5882	221.65	233.13	250.12	265.30	276.45	291.84	304.10
0.5556	222.25	233.78	250.89	266.00	277.24	292.28	304.47
0.5263	223.17	234.67	251.83	266.89	278.05	293.34	305.28

X_1=1.0000

Conc.x10^{-4}	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	236.05	247.93	264.94	278.61	286.93	308.34	321.34
0.9091	236.80	248.83	265.75	279.51	287.76	308.85	322.15
0.8333	237.71	249.67	266.63	280.31	288.52	309.57	322.81
0.7692	238.53	250.45	267.51	280.83	289.40	310.36	323.50
0.7143	239.35	251.28	268.23	281.65	290.15	310.86	324.16
0.6667	240.21	251.83	268.85	282.48	290.73	311.67	324.62
0.6250	240.85	252.54	269.53	283.27	291.41	312.45	325.35
0.5882	241.57	253.40	270.52	283.85	292.14	313.21	325.78
0.5556	242.56	254.32	271.35	284.78	292.76	313.73	326.60
0.5263	243.43	255.25	272.20	285.81	293.43	314.60	327.41

Table 16(a): The values of limiting molar conductance (Λ_o), association constant (K_A), Walden product (Λ_o) and effective radius r $(\Lambda_o\eta_o)$ for N-[(benzoyl-amino)thioxomethyl] serine cobalt (II) chloride in methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r
		T=283.15K				**T=288.15K**		
0.0000	293.71	594.36	405.42	4.624	309.52	501.86	363.07	5.074
0.0588	255.18	686.25	412.63	4.543	267.87	588.86	387.34	4.756
0.1942	218.18	742.17	455.63	4.114	229.06	674.40	418.73	4.399
0.3600	193.79	802.90	482.74	3.883	207.51	721.91	430.17	4.282
0.5676	209.84	896.57	415.48	4.512	222.12	768.95	375.16	4.910
0.8351	233.71	984.27	247.97	7.559	244.62	856.70	236.06	7.803

$X_{Methanol}$	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=293.15K				**T=298.15K**		
0.0000	325.38	408.64	325.93	5.555	337.88	325.76	268.28	6.636
0.0588	278.83	487.67	349.37	5.183	294.18	406.85	323.01	5.511
0.1942	233.37	585.49	392.06	4.618	247.83	481.25	357.87	4.975
0.3600	225.49	640.60	405.43	4.466	237.36	556.89	373.13	4.947
0.5676	239.31	701.90	362.08	5.001	253.62	620.36	339.60	5.242
0.8351	261.97	790.98	228.96	7.908	276.51	721.84	222.59	7.998
1.0000	286.58	847.72	175.28	10.330	299.44	776.29	171.12	10.404
		T=303.15K				**T=308.15K**		
0.0000	353.08	262.93	221.03	7.922	370.29	232.76	195.51	8.810
0.0588	304.04	331.36	298.57	5.864	315.05	285.99	275.67	6.248
0.1942	260.62	372.35	327.60	5.345	273.38	320.00	303.73	5.671
0.3600	248.97	480.30	339.35	5.160	263.39	387.17	315.54	5.459
0.5676	264.76	560.08	313.48	5.585	280.13	483.87	296.38	5.812
0.8351	287.03	630.64	208.38	8.402	300.75	553.24	202.40	8.510
1.0000	310.70	715.36	168.25	10.406	326.57	637.68	163.53	10.533
		T=308.15K						
0.0000	387.62	206.17	185.28	9.148				
0.0588	332.48	248.64	263.66	6.429				
0.1942	289.97	270.99	286.78	5.910				
0.3600	284.98	326.21	297.80	5.692				
0.5676	293.78	398.23	277.92	6.099				
0.8351	314.28	471.58	194.85	8.699				
1.0000	338.12	549.43	158.36	10.703				

Table 16(b). The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) for N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride in methanol+ water mixtures at 283.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
		T=283.15K				**T=288.15K**		
0.0000	253.07	662.74	361.38	5.187	268.32	531.26	331.57	5.393
0.0588	224.08	710.34	372.34	5.174	238.86	610.92	345.39	5.333
0.1942	197.25	753.92	420.01	4.359	206.61	683.57	374.75	4.551
0.3600	172.79	818.69	450.42	4.355	189.56	738.89	402.96	4.508
0.5676	188.74	908.02	373.71	5.016	201.08	786.75	339.62	5.424
0.8351	212.72	1010.45	225.70	8.305	223.58	880.13	215.75	8.538
1.0000	233.08	1098.27	159.89	11.724	245.74	996.46	156.78	11.749
		T=293.15K				**T=298.15K**		
0.0000	325.38	408.64	325.93	5.555	337.88	325.76	268.28	6.636
0.0588	278.83	487.67	349.37	5.183	294.18	406.85	323.01	5.511
0.1942	212.09	615.27	356.31	5.082	226.79	513.09	327.48	5.436
0.3600	206.42	667.50	381.14	4.879	216.31	587.48	340.04	5.235
0.5676	220.19	731.59	294.83	6.141	232.87	652.93	295.51	6.024
0.8351	242.80	790.74	212.21	8.532	255.37	731.28	205.57	8.660
1.0000	257.26	881.90	152.04	11.809	271.87	812.88	150.34	11.842

$X_{Methanol}$	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=303.15K				**T=308.15K**		
0.0000	321.92	321.09	233.71	7.491	339.08	277.81	212.94	8.089
0.0588	283.08	364.15	272.98	6.299	294.01	307.72	257.26	6.696
0.1942	239.60	424.39	301.18	5.813	252.26	368.77	280.26	6.146
0.3600	227.92	499.74	320.65	5.636	244.37	437.17	292.76	5.884
0.5676	241.71	572.35	286.18	6.118	258.46	496.27	273.45	6.299
0.8351	268.96	658.00	195.63	8.950	281.55	572.39	189.48	9.091
1.0000	286.44	736.20	147.90	11.838	298.29	658.71	144.07	11.956
		T=313.15K						
0.0000	357.29	206.17	170.78	9.925				
0.0588	314.94	248.64	249.75	6.787				
0.1942	279.79	270.99	266.82	6.353				
0.3600	264.84	326.21	246.76	6.124				
0.5676	272.75	398.23	258.02	6.569				
0.8351	295.48	471.58	183.19	9.253				
1.0000	315.83	549.43	141.44	11.983				

4.3.4. Calculation of thermodynamic parameters

The equations involved for the calculation of thermodynamic parameters are same as given in chapter-3, section 3.1.2.

Table 17(a): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A for N-[(benzoyl-amino) thioxomethyl] serine cobalt (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.0000			
ΔG^0	-15.039	-14.902	-14.655	-14.346	14.046	-13.965	-13.880
ΔH^0	-26.052						
$10^3\Delta S^0$	-38.895	-38.695	-38.877	-39.262	-39.604	-39.254	-38.869
E^a	9.70						
$10^{-3}A$	6.48						
				X_1=0.0588			
ΔG^0	-15.378	-15.282	-15.087	-14.844	-14.627	-14.490	-14.366
ΔH^0	-25.772						
$10^3\Delta S^0$	-36.708	-36.405	-36.449	-36.485	36.764	-36.612	-36.423
E^a	9.95						
$10^{-3}A$	6.81						
				X_1=0.1942			
ΔG^0	-15.662	-15.608	-15.536	-15.308	-15.056	-14.779	-14.588
ΔH^0	-25.225						
$10^3\Delta S^0$	-33.774	-33.375	-33.051	-33.262	-33.544	-33.899	-33.968
E^a	10.60						
$10^{-3}A$	8.15						

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
X_1=0.3600							
ΔG^0	-15.849	-15.801	-15.795	-15.756	-15.567	-15.269	-15.067
ΔH^0	-24.845						
$10^3 \Delta S^0$	-31.771	-31.386	-30.872	-30.485	-30.605	-31.076	-31.225
E^a	10.87						
$10^{-3}A$	8.54						
X_1=0.5676							
ΔG^0	-16.009	-15.983	-15.902	-15.846	-15.750	-15.642	-15.589
ΔH^0	-24.336						
$10^3 \Delta S^0$	-29.408	-28.988	-28.770	-28.476	-28.323	-28.213	-27.932
E^a	9.76						
$10^{-3}A$	5.68						
X_1=0.8351							
ΔG^0	-16.226	-16.182	-16.106	-16.015	-15.952	-15.784	-15.693
ΔH^0	-23.843						
$10^3 \Delta S^0$	-26.901	26.587	-26.393	-26.255	-26.030	-26.153	-26.026
E^a	8.71						
$10^{-3}A$	4.01						
X_1=1.0000							
ΔG^0	-16.416	-16.410	-16.404	-16.388	-16.271	-16.150	-16.028
ΔH^0	-23.547						
$10^3 \Delta S^0$	-25.185	-24.768	-24.366	-24.011	-24.001	-24.005	-24.011
E^a	8.42						
$10^{-3}A$	3.65						

Table 17(b): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A of N-[(benzoyl-amino) thioxomethyl] serine copper (II) chloride in methanol+ water mixtures at different temperatures.

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.0000			
ΔG^0	-15.039	-14.902	-14.655	-14.346	14.046	-13.965	-13.880
ΔH^0	-26.052						
$10^3 \Delta S^0$	-38.895	-38.695	-38.877	-39.262	-39.604	-39.254	-38.869
E^a	9.70						
$10^{-3}A$	6.48						
				X_1=0.0588			
ΔG^0	-15.378	-15.282	-15.087	-14.844	-14.627	-14.490	-14.366
ΔH^0	-25.772						
$10^3 \Delta S^0$	-36.708	-36.405	-36.449	-36.485	36.764	-36.612	-36.423
E^a	9.95						
$10^{-3}A$	6.81						
				X_1=0.1942			
ΔG^0	-15.662	-15.608	-15.536	-15.308	-15.056	-14.779	-14.588
ΔH^0	-25.225						
$10^3 \Delta S^0$	-33.774	-33.375	-33.051	-33.262	-33.544	-33.899	-33.968
E^a	10.60						
$10^{-3}A$	8.15						

	283.15K	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
				X_1=0.3600			
ΔG^0	-15.849	-15.801	-15.795	-15.756	-15.567	-15.269	-15.067
ΔH^0	-24.845						
$10^3\,\Delta S^0$	-31.771	-31.386	-30.872	-30.485	-30.605	-31.076	-31.225
E^a	10.87						
$10^{-3}A$	8.54						
				X_1=0.5676			
ΔG^0	-16.009	-15.983	-15.902	-15.846	-15.750	-15.642	-15.589
ΔH^0	-24.336						
$10^3\,\Delta S^0$	-29.408	-28.988	-28.770	-28.476	-28.323	-28.213	-27.932
E^a	9.76						
$10^{-3}A$	5.68						
				X_1=0.8351			
ΔG^0	-16.226	-16.182	-16.106	-16.015	-15.952	-15.784	-15.693
ΔH^0	-23.843						
$10^3\,\Delta S^0$	-26.901	26.587	-26.393	-26.255	-26.030	-26.153	-26.026
E^a	8.71						
$10^{-3}A$	4.01						
				X_1=1.0000			
ΔG^0	-16.416	-16.410	-16.404	-16.388	-16.271	-16.150	-16.028
ΔH^0	-23.547						
$10^3\,\Delta S^0$	-25.185	-24.768	-24.366	-24.011	-24.001	-24.005	-24.011
E^a	8.42						
$10^{-3}A$	3.65						

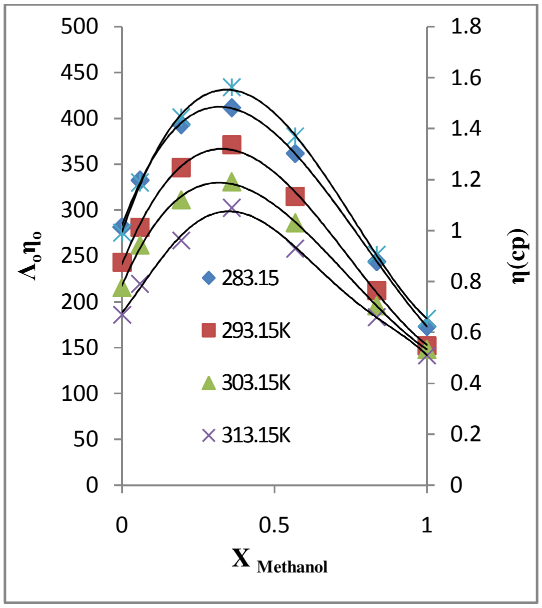


Figure 14(a): The value of Walden product $\Lambda_o\eta_o$ and (η) for Co^{II} complex as a function of X_{MeOH} in methanol + water solvents

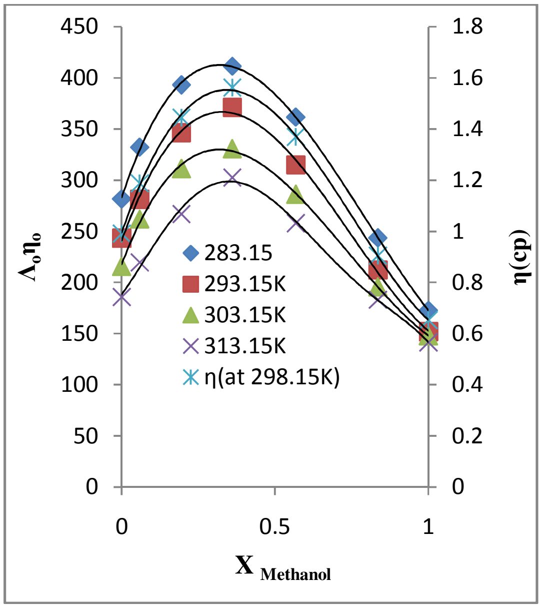


Figure 14(b): The value of Walden product $\Lambda_o\eta_o$ and (η) for Cu^{II} complex as a function of X_{MeOH} in methanol + water solvents

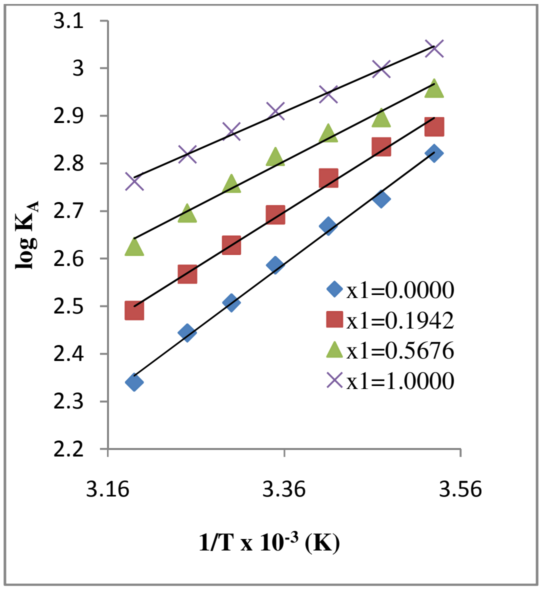


Figure 15(a): Plot of log K_A vs 1/T for Co^{II} complex in different mole fractions at 283.15-313.15K

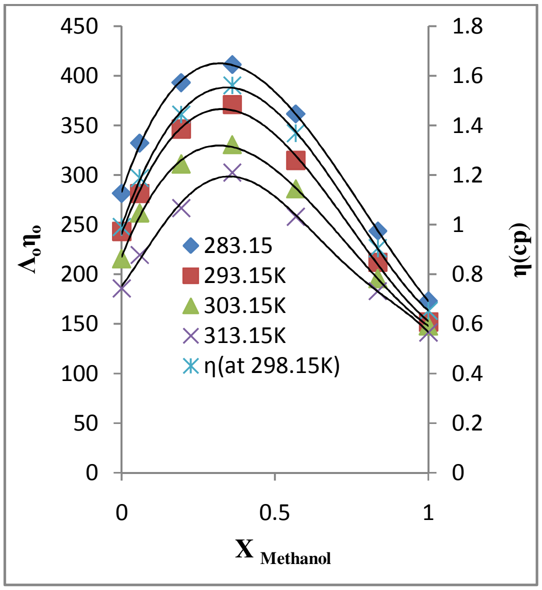


Figure 15(b): Plot of log K_A vs 1/T for Cu^{II} complex in different mole fractions at 283.15-313.15K

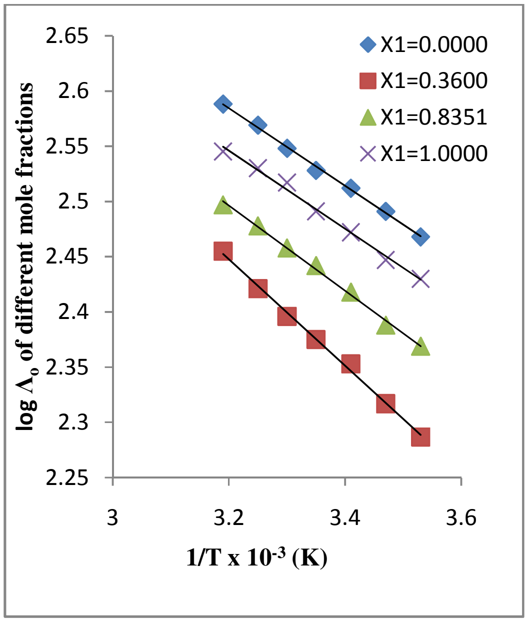


Figure 16(a): Plot of log Λ_o vs 1/T for Co^{II} complex in different mole fractions at 283.15-313.15K

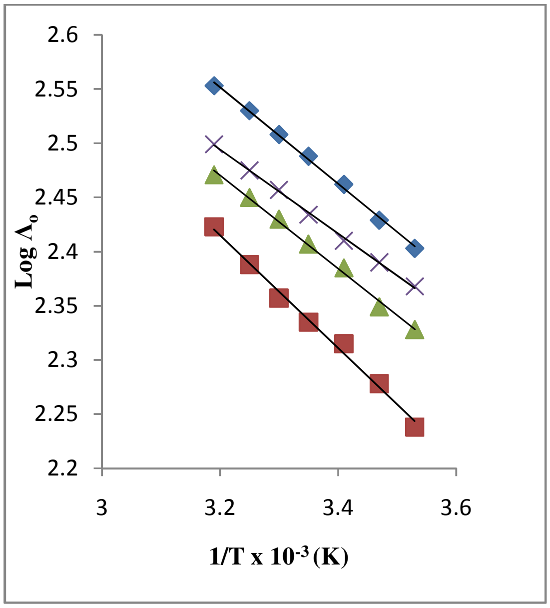


Figure 16(b): Plot of log Λ_o vs 1/T for Cu^{II} complex in different mole fractions at 283.15-313.15K

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, solvent-solvent interactions become stronger and in turn producing maximum Walden product [Das *et al.*, 2004]. Further addition of methanol results in progressive disruption of water structure and the ions become solvated with the other component of the solvent mixture (viz, methanol). The effect would be more in case of a solution at a higher temperature.

4.4. Ion Pair Formation of LiCl and $LiNO_3$ in water + Acetonitrile solution at different temperatures.

4.4.1. Introduction

Lithium has been studied for many years as an anode material for non-aqueous solution batteries [Das, 2008; Ue, 1997]. In such systems, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte possessing high specific conductivity, and hence with minimal ion-ion interactions, is required to maintain low internal resistance in the cell [Mohoney *et al.*, 2001; Guggenheim, 1935]. Knowledge of the state of association of the electrolytes and their interaction with the solvent molecules is essential for making an optimal choice of solvent and electrolyte in such systems [Ue and Mori, 1995; El-Arab *et al.*, 1995].

Ion pair formation in solution of alkali metal halides of small metal ions have been extensively investigated [Sillen and Martell, 1971] both in aqueous and aquo-organic solvent mixtures. The present work reports determination of the molar conductance values of the solutions of the title electrolyte in acetonitrile + water mixtures at 283.15K to 313.15 K to examine the validity of Shedlovsky technique. The K_A and Walden products for NiCl and $NiNO_3$ compounds have been evaluated in these solvents at experimental temperatures. The limiting molar conductance (Λ_o) and association constant (K_A) for different mole fractions, i.e., 0.0000, 0.0588, 0.1233, 0.1942, 0.2727, 0.3600, 0.4576, 0.5676, 0.6923, 0.8351 and 1.0000 have been calculated using Shedlovsky method [Shedlovsky, 1932]. These computed values have been discussed qualitatively the nature of ion-ion, ion-solvent and solvent-solvent interactions of the two selected compounds in M-W mixed solvents. Temperature dependence of the K_A has also been studied to get the thermodynamic parameters, viz. ΔG^0, ΔS^0, ΔH^0 and E^a as a function of the solvent composition.

4.4.2. Experimental

Lithium Chloride (BDH 99% minimum purity) and Lithium nitrate (BDH 99.8% minimum purity) were used after crystallization (these had purity >99.9 % for LiCl and 99.8% for $LiNO_3$). Acetonitrile (BDH) was purified as described by Vogel [Vogel, 1955) and had a specific conductance < 1.0 x10^{-7} S-cm. Water with a specific conductance1.0 x 10^{-6}S-cm was used. The overall accuracy of the measured molar conductances was better than ±0.07%. All the viscosity, dielectric constant and density values were interpolated from literature values [Raju *et al*., 1990; Zarei *et al*., 2008; Saleh *et al*., 2007]. The experiment was performed between 15-40 ºC.

4.4.3. Calculation of limiting molar conductance, association constants, Walden products and effective radius

The experimental data of conductance measurements of LiCl and $LiNO_3$ in water – Acetonitrile mixtures after solvent corrections were analyzed using Shedlovsky equation.

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

$$\propto = \frac{0.8204x10^6}{(DT)^{3/2}}$$

For 1:1 electrolytes.

$$\beta = \frac{82.501}{\eta (DT)^{1/2}}$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_o is the limiting equivalent conductance and K_A is the observed association constant. Other symbols are same as discussed in chapter 3, section 3.3.1. The effective radius(*r*) of ion or solute can be calculated as described in chapter-3, section-3.1.3.

Table 17(a): The values of molar conductance (Λ) obtained for Lithium chloride in Acetonitrile + water mixtures at 288.15-313.15K.

X_1=0.0000

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	81.63	95.91	112.18	128.73	142.19	157.27
0.9091	82.81	97.09	113.97	129.36	148.89	157.82
0.8333	83.80	97.35	114.65	129.70	143.72	158.30
0.7692	83.87	97.86	115.31	130.56	144.12	158.69
0.7143	84.25	98.18	115.55	130.80	144.42	159.13
0.6667	84.82	100.04	116.23	131.44	144.75	159.38
0.6250	85.36	100.27	116.74	131.98	145.53	159.84
0.5882	86.07	100.78	117.24	132.49	145.94	160.47
0.5556	87.28	101.08	117.80	133.02	146.20	160.80
0.5263	88.85	101.53	118.55	139.89	146.94	161.58

X_1= 0.0464

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	70.36	82.61	91.48	102.68	111.36	123.81
0.9091	71.60	83.38	92.62	103.60	111.85	124.68
0.8333	71.81	84.19	92.95	103.69	112.42	125.15
0.7692	72.70	85.12	93.51	104.20	112.89	125.59
0.7143	73.25	85.30	94.02	104.53	113.27	125.87
0.6667	73.59	85.88	94.71	105.45	113.72	126.48
0.6250	74.03	86.13	94.93	105.73	114.05	126.79
0.5882	74.96	87.03	95.84	106.50	114.60	127.10
0.5556	76.23	87.66	96.15	106.76	115.19	127.93
0.5263	76.94	88.70	96.95	107.20	115.52	128.48

X_1=0.1582

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	61.94	70.26	78.98	89.24	101.75	109.46
0.9091	62.29	70.92	79.24	90.12	101.92	110.25
0.8333	63.39	71.41	79.69	90.34	102.24	110.55
0.7692	63.61	71.82	80.02	90.82	102.70	110.93
0.7143	64.35	72.57	80.81	91.16	103.02	111.32
0.6667	64.61	72.89	81.13	91.68	103.77	111.78
0.6250	65.37	73.14	81.61	92.16	104.04	112.13
0.5882	65.62	73.71	82.20	92.54	104.69	112.58
0.5556	66.57	74.38	82.91	92.99	104.98	112.84
0.5263	67.44	75.44	83.42	93.70	105.43	113.28

X_1=0.3048

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	52.73	61.91	69.07	78.46	89.16	97.53
0.9091	54.04	63.14	69.46	79.39	89.39	98.20
0.8333	54.37	63.77	70.12	79.78	90.01	98.58
0.7692	55.07	64.33	70.34	80.28	90.23	99.07
0.7143	55.54	64.66	70.99	80.53	90.99	99.31
0.6667	56.15	65.23	71.41	81.28	91.41	100.09
0.6250	56.47	65.55	72.05	81.44	92.01	100.39
0.5882	57.14	66.12	72.36	82.04	92.32	100.76
0.5556	57.60	66.74	73.04	82.27	92.64	101.20
0.5263	58.11	67.67	74.05	82.91	92.98	101.57

X_1=0.5057

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	57.93	66.08	74.24	84.46	96.20	104.84
0.9091	59.11	66.94	74.39	86.09	96.47	106.00
0.8333	59.34	67.73	74.96	86.20	97.23	107.22
0.7692	60.19	68.50	75.27	86.80	97.64	107.36
0.7143	60.60	68.84	75.86	87.11	98.22	107.67
0.6667	61.27	69.42	76.20	89.90	98.56	108.06
0.6250	61.46	69.67	77.77	88.28	98.88	108.31
0.5882	62.45	70.55	78.37	88.72	99.73	109.00
0.5556	63.29	71.42	78.87	89.33	100.17	109.23
0.5263	64.35	72.40	79.24	89.82	101.72	110.20

X_1=0.6369

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	65.17	75.04	86.46	95.81	108.31	116.44
0.9091	66.06	75.94	86.73	96.87	108.58	117.61
0.8333	66.61	76.79	87.34	97.34	109.34	118.83
0.7692	67.14	77.65	88.01	98.03	109.75	119.17
0.7143	67.88	78.34	88.58	98.41	110.33	119.59
0.6667	68.76	78.97	89.40	99.18	110.37	120.02
0.6250	69.57	79.49	90.32	99.82	110.99	120.42
0.5882	70.39	80.25	91.17	100.35	111.84	121.25
0.5556	71.04	81.02	91.80	101.14	112.28	121.62
0.5263	71.92	81.97	92.75	101.95	113.33	122.43

Table 17(b): The values of molar conductance (Λ) obtained for Lithium nitrate in Acetonitrile + water mixtures at 288.15-313.15K.

X_1=0.0000

Conc.x10^{-3}	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	76.52	90.40	107.07	123.62	137.08	152.16
0.9091	77.70	91.98	108.86	124.25	137.78	152.71
0.8333	78.69	92.24	109.54	124.59	138.61	153.19
0.7692	78.76	92.75	110.20	125.45	139.01	153.58
0.7143	79.14	93.07	110.44	125.69	139.31	154.02
0.6667	79.71	94.93	111.12	126.34	139.64	154.27
0.6250	80.25	95.16	111.63	126.87	140.42	154.73
0.5882	81.96	95.67	112.13	127.38	140.83	155.36
0.5556	82.17	95.97	112.69	127.91	141.09	155.69
0.5263	83.74	96.42	113.45	127.78	141.83	156.47

X_1=0.0464

Conc.x10^{-3}	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	66.25	78.50	87.37	98.57	107.25	119.70
0.9091	67.49	79.27	88.51	99.49	107.74	120.57
0.8333	67.70	80.80	88.84	99.58	108.31	121.04
0.7692	68.59	81.01	89.40	100.09	108.78	121.48
0.7143	69.14	81.19	89.91	100.42	109.16	121.76
0.6667	69.48	81.77	90.60	101.34	109.61	122.37
0.6250	70.00	82.02	90.82	101.62	109.94	122.68
0.5882	70.85	82.92	91.73	102.39	110.49	122.99
0.5556	71.62	83.56	91.04	102.65	111.08	123.82
0.5263	72.83	84.59	92.84	103.09	112.41	124.37

X_1=0.1582

Conc.x10^{-3}	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	56.83	65.15	73.87	84.13	96.64	104.35
0.9091	57.18	65.81	74.13	85.01	96.81	105.14
0.8333	58.28	66.30	74.58	85.23	97.13	105.44
0.7692	58.50	66.71	74.91	85.71	97.59	105.82
0.7143	59.24	67.46	75.70	86.05	97.91	106.21
0.6667	59.50	67.78	76.02	86.57	98.66	106.67
0.6250	60.26	68.03	76.50	87.05	98.93	107.02
0.5882	60.51	68.60	77.09	87.43	99.58	107.47
0.5556	61.46	69.27	77.80	87.88	99.87	107.73
0.5263	62.34	70.33	78.31	88.59	100.32	103.17

X_1=0.3048

Conc.x10^{-3}	**288.15K**	**293.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
1.0000	47.62	56.80	63.96	73.35	84.05	92.42
0.9091	48.93	58.03	64.35	74.28	84.28	93.09
0.8333	49.26	58.66	65.01	74.67	84.90	93.47
0.7692	49.96	59.22	65.23	75.17	85.12	94.00
0.7143	50.43	59.56	65.89	75.42	85.89	94.20
0.6667	57.04	60.12	66.30	76.17	86.30	94.98
0.6250	57.36	60.45	66.94	76.34	86.90	95.28
0.5882	52.03	61.01	67.25	76.93	87.21	95.65
0.5556	52.47	61.63	67.93	77.16	87.53	96.09
0.5263	53.00	62.56	68.94	77.80	87.87	96.46

X_1=0.5057

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	53.82	61.97	70.13	80.35	92.09	100.73
0.9091	55.00	62.83	70.28	81.98	92.36	101.99
0.8333	55.23	63.62	70.85	82.09	93.12	103.11
0.7692	56.08	64.39	71.16	82.69	93.03	103.25
0.7143	56.49	64.73	71.75	83.00	94.11	103.56
0.6667	57.16	65.31	72.09	83.79	94.45	103.95
0.6250	57.35	65.56	73.66	84.17	94.77	104.20
0.5882	58.34	66.44	74.26	84.61	95.62	104.99
0.5556	59.18	67.31	74.76	85.23	96.06	105.12
0.5263	60.24	68.29	75.13	85.71	97.61	106.09

X_1=0.6369

Conc.x10^{-3}	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
1.0000	60.06	69.93	81.35	90.70	103.20	111.34
0.9091	60.95	70.83	81.62	91.76	103.47	112.50
0.8333	61.50	71.68	82.23	92.23	104.23	113.72
0.7692	62.03	72.54	82.90	92.92	104.64	114.06
0.7143	62.77	73.23	83.47	93.30	105.22	114.48
0.6667	63.65	73.86	84.29	94.07	105.26	114.91
0.6250	64.46	74.38	85.21	94.71	105.88	115.31
0.5882	65.28	75.14	86.06	95.24	106.73	116.14
0.5556	65.93	75.91	86.69	96.03	107.17	116.51
0.5263	66.81	76.86	87.64	96.84	108.23	117.32

Table 18(a): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) for Lithium Chloride in Acetonitrile + water mixtures at 288.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
		T=288.15K				**T=293.15K**		
0.0000	97.92	368.39	120.54	1.528	111.75	316.71	117.84	1.537
0.0464	87.32	430.77	131.48	1.401	97.88	376.42	124.32	1.456
0.1582	76.64	487.37	108.59	1.696	83.02	428.16	94.68	1.912
0.3048	68.53	542.13	80.99	2.274	77.18	484.26	75.85	2.387
0.5057	76.13	600.91	67.20	2.741	83.83	537.92	57.62	3.142
0.6369	87.08	688.35	59.41	3.101	96.60	618.07	48.64	3.723
		T=298.15K				**T=303.15K**		
0.0000	127.63	262.07	114.60	1.553	141.18	212.19	112.56	1.556
0.0464	105.27	320.31	120.25	1.480	114.44	268.02	116.98	1.497
0.1582	90.68	389.32	96.75	1.840	100.31	322.70	93.56	1.871
0.3048	81.97	434.13	74.68	2.383	90.09	380.84	71.48	2.449
0.5057	88.25	470.79	57.54	3.094	99.16	426.81	54.72	3.200
0.6369	105.83	547.19	46.72	3.180	113.72	483.40	42.31	4.138
		T=308.15K				**T=313.15K**		
0.0000	153.77	157.21	109.15	1.578	167.53	106.06	106.23	1.596
0.0464	122.16	202.79	114.21	1.508	135.23	153.73	111.51	1.520
0.1582	111.66	268.62	90.47	1.904	119.40	211.75	87.42	1.939
0.3048	100.22	326.04	67.54	2.550	108.66	265.29	65.45	2.590
0.5057	110.09	370.33	51.29	3.358	118.79	314.13	46.58	3.639
0.6369	122.45	427.50	40.05	4.301	133.76	368.97	37.05	4.575

Table 18(b): The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) for Lithium Nitrate in Acetonitrile + water mixtures at 288.15-313.15K.

$X_{Methanol}$	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r
		T=288.15K				**T=293.15K**		
0.0000	105.34	315.88	129.67	1.421	118.73	252.62	123.18	1.600
0.0464	94.93	378.08	140.58	1.310	105.81	319.74	132.88	1.363
0.1582	82.93	421.22	121.57	1.515	94.39	363.71	114.25	1.584
0.3048	72.58	485.34	105.89	1.740	83.55	419.79	96.56	1.875
0.5057	81.74	538.21	87.67	2.101	91.84	467.37	80.47	2.250
0.6369	92.88	594.67	68.41	2.666	101.56	519.92	63.43	2.855
		T=298.15K				**T=303.15K**		
0.0000	131.38	201.47	119.55	1.489	144.79	156.38	115.62	1.514
0.0464	117.42	255.96	125.49	1.419	129.07	207.52	120.57	1.452
0.1582	106.08	307.05	107.52	1.656	115.91	254.46	102.05	1.716
0.3048	93.93	356.29	91.27	1.951	104.09	304.73	87.27	2.006
0.5057	102.27	402.52	75.41	3.920	113.55	350.29	72.51	2.415
0.6369	113.77	461.25	58.46	3.045	125.06	408.86	56.94	3.075
		T=30815K				**T=313.15K**		
0.0000	156.27	104.34	112.73	1.528	167.58	62.45	107.91	1.571
0.0464	138.65	147.71	116.98	1.473	147.44	103.82	112.66	1.505
0.1582	125.73	198.79	100.06	1.721	134.78	142.58	96.59	1.755
0.3048	116.37	252.05	85.61	2.012	126.06	198.71	82.36	2.058
0.5057	124.52	297.71	70.61	2.439	135.38	241.62	67.24	2.521
0.6369	135.91	353.28	53.61	3.213	144.28	301.72	48.55	3.491

The experimentally determined K_As (Table 18(a) and table 18(b)) values are found to increase with increase in X_1 (linear plot). Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between the ions. The value of $\Lambda_o\eta_o$ would be constant only if the effective radius of the ions were same in the different media [Glasstone, 1942]. Since most ions are solvated in solution of the constancy of $\Lambda_o\eta_o$ is not expected. $\Lambda_o\eta_o$ is inversely proportional to the effective radius of ion in a given solvent or solvent mixture [Hodgman *et al*., 1956-57]. Using the relation

$$\Lambda_o\eta_o = \frac{1}{6\pi r T}$$

Where, r is the effective radius of the concern ion. It has been possible to derive the values of r for the cation of LiCl and $LiNO_3$ salts. As evidence from table 18(a) and table 18(b), the value of r decreases with increase in Acetonitrile upto X_1=0.046 and thereafter increases in Acetonitrile rich region. The smaller $\Lambda_o\eta_o$ in water rich region may be due to the large effective radius of the cation whereas maximum value of r. The variation of $\Lambda_o\eta_o$ with X_1 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 the composition of the mixed solvents and the 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 the rate processes taking place with change of temperature [Dash and Pasupalak, 1997] i.e,

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

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 plot of log Λ_o versus 1/T (Fig.19 (a) & fig.19 (b)), are recorded in table 19(a) and table 19(b).

As observed from table 19(a) and table 19(b), the values of E^a increase with increase in X_1 upto x_1=0.07 and thereafter decrease rapidly. It follows that, in water rich region upto x_1=0.07 both the chosen salts required activation energy for the transport process as Acetonitrile content in the mixed solvent increases but reverse is the case beyond x_1=0.07. A reaction which required higher activation energy is slow at ordinary temperatures indicating the lower Λ_o values. Beyond x_1=0.07, as the activation energy decreases, the Λ_o values increase with x_1.

4.4.4. Calculation of thermodynamic parameters

The equations involved for the calculation of thermodynamic parameters are same as given in chapter-3, section 3.1.2.

The free energy change (ΔG^0) for association process is calculated from the relation [Coetzee and Ritchie, 1976]. ΔG^0=-RTlnK_A. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A versus 1/T. The enthalpy of association values obtained are found to increase with the composition of the mixed solvent. The entropy change (ΔS^0) is calculated from the Gibbs- Helmholz equation, ΔG^0= ΔG^0 -T ΔS^0; the values of these thermodynamics functions are given in table 19(a) and table 19(b). The negative value of ΔH^0 indicates that ion-association processes are exothermic in nature at all temperatures (288.15K-313.15K). At a particular temperature, ΔG^0 becomes more negative with the increase in x_1 indicating that the ion pair association is favored with lowering of permittivity of the medium.

Table 19 (a): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3}A for LiCl in Acetonitrile+ water mixtures at different temperatures.

	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
			X_1=0.0000			
ΔG^0	-14.16	-14.04	-13.80	-13.52	-12.96	-12.15
ΔH^0	-36.81					
$10^3\,\Delta S^0$	-76.35	-77.67	-77.18	-76.83	-77.40	-78.75
E^a	9.726					
			X_1=0.0465			
ΔG^0	-14.53	-14.46	-14.31	-14.10	-13.61	-13.11
ΔH^0	-32.81					
$10^3\,\Delta S^0$	-63.43	-63.77	-63.34	-63.12	-63.82	-66.52
E^a	10.927					
$10^{-3}A$	9.516					
			X_1=0.1518			
ΔG^0	-14.83	-14.80	-14.78	-14.57	-14.50	-13.95
ΔH^0	-29.57					
$10^3\,\Delta S^0$	-51.15	-51.78	-51.32	-51.51	-51.25	-52.52
E^a	9.882					
$10^{-3}A$	7.361					
			X_1=0.3048			
ΔG^0	-15.13	-15.09	-15.05	-14.99	-14.83	-14.53
ΔH^0	-27.06					
$10^3\,\Delta S^0$	-41.40	-41.72	-41.47	-41.30	-41.46	-42.06
E^a	9.327					
$10^{-3}A$	5.919					
			X_1=0.5057			
ΔG^0	-15.43	-15.33	-15.26	-15.16	-15.09	-14.97
ΔH^0	-24.53					
$10^3\,\Delta S^0$	-31.58	-31.62	-31.79	-31.82	-31.63	-31.94
E^a	8.536					
$10^{-3}A$	4.096					

	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
			X_1=0.6369			
ΔG^0	-15.66	-15.57	-15.63	-15.59	-15.52	-15.39
ΔH^0	-21.47					
$10^3\,\Delta S^0$	-20.16	-2033	-20.35	-20.24	-20.18	-20.28
E^a	7.947					
$10^{-3}A$	3.662					

Table 19(b): Thermodynamic parameters ΔG^0 (kJmole^{-1}), ΔH^0 (kJmol^{-1}), ΔS^0 (kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3} A for $LiNO_3$ in Acetonitrile + water mixtures at different temperatures.

	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
			X_1=0.0000			
ΔG^0	-13.79	-13.48	-13.15	-12.73	-11.91	-11.03
ΔH^0	-43.66					
$10^3\,\Delta S^0$	-103.66	-102.29	-102.33	-102.03	-103.03	-104.20
E^a	9.501					
$10^{-3}A$	6.626					
			X_1=0.0465			
ΔG^0	-14.22	-14.06	-13.75	-13.45	-12.80	-12.09
ΔH^0	-39.79					
$10^3\,\Delta S^0$	-88.74	-87.67	-87.64	-87.43	-87.45	-87.37
E^a	10.679					
$10^{-3}A$	9.217					
			X_1=0.1518			
ΔG^0	-14.48	-14.37	-14.20	-13.97	-13.56	-12.92
ΔH^0	-35.71					
$10^3\,\Delta S^0$	-60.39	-59.92	-60.07	-60.11	-60.38	-59.89
E^a	9.671					
$10^{-3}A$	7.013					

	288.15K	293.15K	298.15K	303.15K	308.15K	313.15K
			X_1=0.3048			
ΔG^0	-14.82	-14.72	-14.57	-14.42	-14.17	-13.78
ΔH^0	-30.95					
$10^3\,\Delta S^0$	-55.98	-55.36	-55.41	-54.52	-55.13	-55.19
E^a	9.111					
$10^{-3}A$	5.726					
			X_1=0.5057			
ΔG^0	-15.07	-14.99	-14.87	-14.77	-14.60	-14.25
ΔH^0	-25.83					
$10^3\,\Delta S^0$	-37.34	-37.49	-37.69	-37.72	-37.63	-37.94
E^a	8.154					
$10^{-3}A$	3.899					
			X_1=0.6369			
ΔG^0	-15.30	-15.24	-15.21	-15.16	-15.03	-14.87
ΔH^0	-23.31					
$10^3\,\Delta S^0$	-27.80	-27.91	-27.96	-27.82	-27.77	-27.86
E^a	7.721					
$10^{-3}A$	3.420					

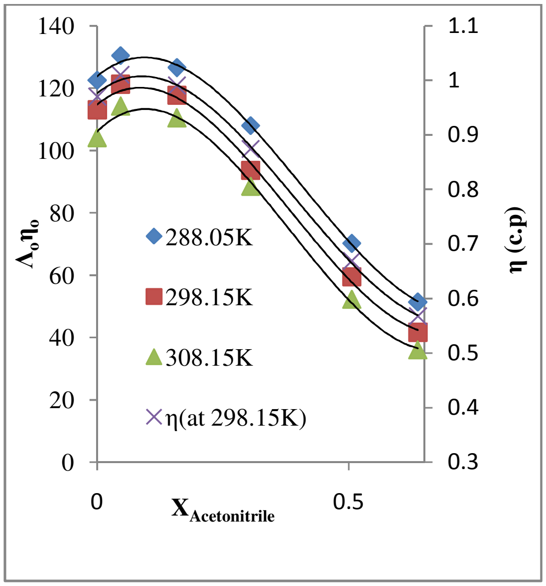


Figure 18(a): The value of $\Lambda_o\eta_o$ and η for $NiCl_2$ as a function of $X_{Acetonitrile}$ in acetonitrile + water solvent

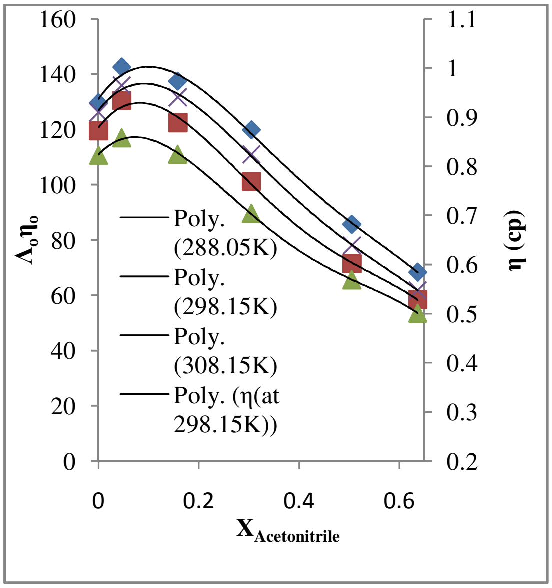


Figure 18(b): The value of $\Lambda_o\eta_o$ and η for $NiNO_3$ as a function of $X_{Acetonitrile}$ in acetonitrile + water solvent

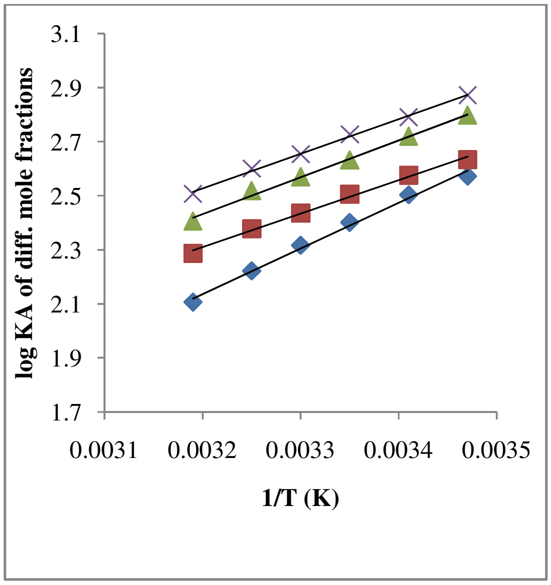


Figure 19(a): Plot of log K_A vs 1/T for LiCl in different mole fractions at 288.15-313.15K.

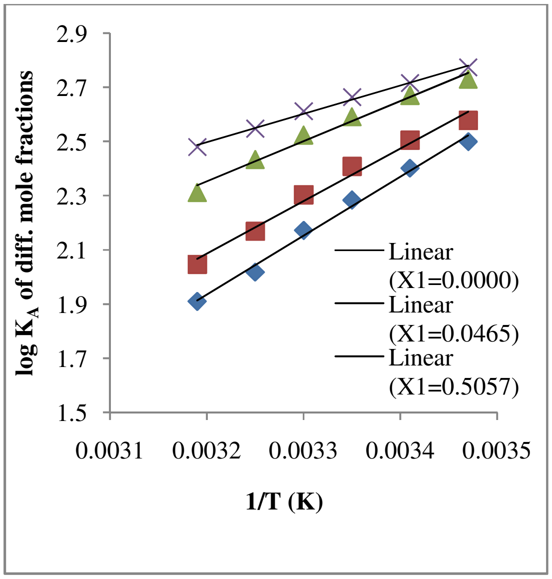


Figure 19(b): Plot of log K_A vs 1/T for $LiNO_3$ in different mole fractions at 288.15-313.15K.

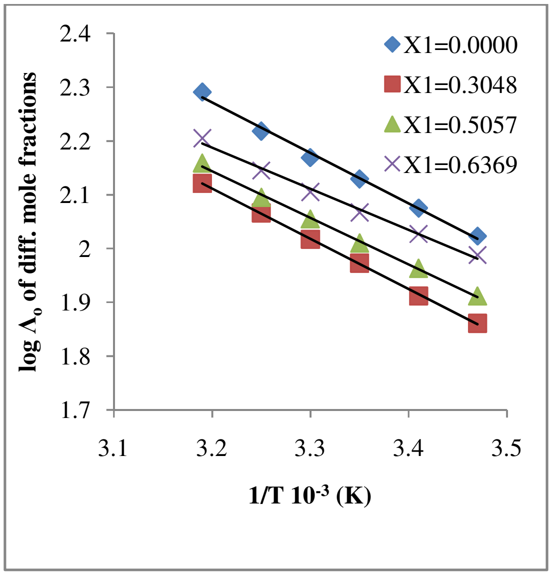


Figure 20(a): Plot of log Λ_o vs 1/T for LiCl in different mole fractions at 288.15-313.15K

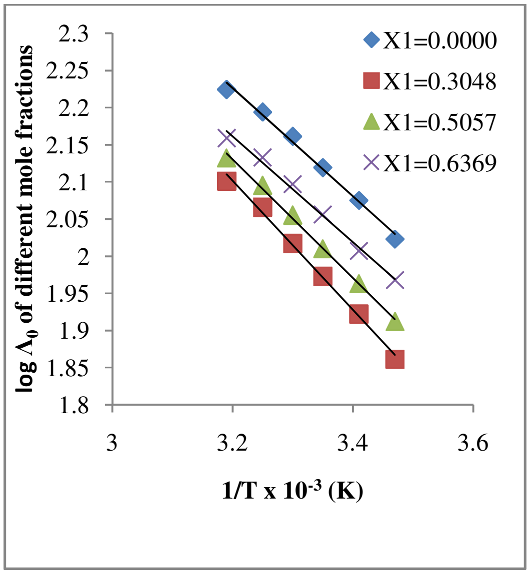


Figure 20(b): Plot of log Λ_o vs 1/T for LiCl in different mole fractions at 288.15-313.15K

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The variation of Walden product ($\Lambda_o\eta_o$) with X_1 at 288.15K, 298.15K and 303.15K are shown in figure 18(a) and figure 18(b). In all the cases, the values of $\Lambda_o\eta_o$ increases with increase in the X_1 upto about 0.07 and thereafter it decreases rapidly which reflects the change of total solvation [Bag *et al.*, 2001]. The viscosity of W-AN mixtures also passes through a maximum at about X_1=0.07 (figure 18(a) and Figure 18(b)). It is interesting to note that the Λ_o values of the solute decreases upto this mole fraction of Acetonitrile and then decreases in Acetonitrile rich region at all temperatures (288.15-313.15K) indicating maximum Acetonitrile-water interaction in the region X_1=0.07.

The increase in amount of product indicates weak solvation of ions which attains a maximum value at X_1=0.07. The decrease in product indicates an increase in hydrophobic solvation with increase in concentration of Acetonitrile. On the water rich side, there exists a region, where water structure remains more or less intact as Acetonitrile molecules enter into the interstitial cavities. As more and more Acetonitrile is added, cavities are filling up progressively; W-AN interactions become stronger and in turn produced maximum Walden Product. The maximum solvent-solvent interactions thus may cause hydrophobic dehydration of cations. Further addition of Acetonitrile results in progressive disruption of water structure and the ions become solvated with the other component of the solvent mixture (i.e., Acetonitrile). The effect should be more in case of a solution at higher temperature. As expected, Λ_o values increase linearly with rise in temperature irrespective of the nature of the solvent [Parmer and Gupta, 1996].

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A. Research Journals:

1. **Lalrosanga** and N. Mohondas Singh. Ion Pair formation of $CoCl_2$.6H2O and [Co $(NH_3)_5$Cl]Cl_2 in Aqueous Medium at Different Temperatures – A Conductance Method. *Asian Journal of Chemistry*, 23(3) (2011)1120. [IF=0.355]
2. **Lalrosanga** and N. Mohondas Singh, Ion pair formation and thermodynamic parameters of N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride in water + methanol mixtures at different temperatures-A conductance study, *Der Chemica Sinica*, 2015, 6(4): 5-10. ISSN: 0976-8505. [IF(G)= 0.516]
3. **Lalrosanga** and N. Mohondas Singh, Ion pair formation and thermodynamic parameters of N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride in water + methanol mixtures -A conductance study, *Science and Technology Journal*, Vol. 3 Issue: I, ISSN: 2321-3388
4. N. Mohondas Singh, M. Kiranjit Singh and **Lalrosanga**. Ion Pair Formation of 1-Amidino-O-ethylurea Nickel (II) Chloride and 1-Amidino-O-ethylurea Nickel (II) Bromide in Aqueous Medium at Different Temperatures- A Conductance Method. *Asian Journal of Chemistry*, 24(5) (2012) 2317-2320. [IF=0.355]
5. N. Mohondas Singh, **Lalrosanga** and Michael Lalhruaitluanga. Ion Pair Formation of Hexamine Nickel (II) Chloride and Tris-Ethylene Diamine Nickel (II) Chloride in Aqueous Medium at Different Temperatures. *Res J Pharm Biol Chem Sci,* 3(3) (2012) 1-7.
6. N. Mohondas Singh, N.C. Lalnunchami and **Lalrosanga**. Calculation of Ion Association Constants of $CuCl_2.2H_2O$ and [Cu $(Me\text{-}AMUH)_2$]Cl_2. *Indian Journal of Science and Technology,* 6(S3) (2013) 122-125.

7. N. Mohondas Singh, Bendangsenla. N and **Lalrosanga**. Ion Pair Formation of $[Co(gly)(AMUH)_2]Br_2$ and $[Co(\beta\text{-ala})(BigH)_2]I_2$. *Indian Journal of Science and Technology,* 6(S3) (2013) 126-129.
8. N. Mohondas Singh, S. Khenglawt and **Lalrosanga**. Calculation of oscillator strength for praseodymium and praseodymium mixed with L-histidine in different solvents using 4f-4f transition spectra as Probe. *Res J Pharm Biol Chem Sci,* 3(3) (2012) 8-15.
9. N. Mohondas Singh, Lanuwapang Jamir, and **Lalrosanga**. Calculation of Thermodynamic Parameters of Copper Complexes Using Shedlovsky Technique, *RRJC* 2 (3) (2013) 23-27.
10. N. Mohondas Singh and **Lalrosanga**. Evaluation of Ion Association and Thermodynamic Parameters of Methyl Bis-1-Amidino-O-Methylurea Nickel (II) Halides in Water at Different Temperatures, *International Journal of Researches in Biosciences Agriculture and Technology*, 1(2) (2014) 1020-1029.

B. Book form/Proceedings (Full Length Paper):

1. N. Mohondas Singh, Watinaro and **Lalrosanga**. Study on Ion Pair of Copper(II) Acetate and Bis-1-Amidino- Ethylurea Copper(II) Acetate in Aqueous Medium at Different Temperatures. Recent Advances in Natural Products Reseach, ISBN 987-81-924321-0, Pp165-170, (2012).
2. Geetashree Sarmah, **Lalrosanga** and N. Mohondas Singh. “Association constant and thermodynamic parameters for simple and complex salt of cobalt ions in aqueous medium - A comparative study, International Conference on Advances in Environmental Chemistry, Excel India Publishers, Pp 212-215, November (2011); ISBN No. 93-8161-53-3.
3. N. Mohondas Singh, T. Moaienla Ao and **Lalrosanga**. Ion Pair Formation of bis-1-amidino-O-Methylurea Copper(II) Thiocynide and bis-1-amidino-O-Methylurea Copper(II)

Nitrate in Aqueous Medium at different Temperatures, Environment, Biodiversity and Traditional System, Biotech Books, New Delhi. Pp 419-426; ISBN 978-81-7622-307-2 (2014).

C. Conferences/Workshops/seminar attended

1. Presented a paper entitled, "Calculation of Thermodynamic Parameters of Copper Complexes by using Shedlovsky Technique" in UGC sponsored national seminar in Advances in Research in Physical Sciences organized by Cachar College, Silchar on 25 & 26 March 2013.
2. Presented a paper entitled, "Study on Ion Pair Formation of Copper (II) acetate and Bis-1-Amidino-Copper (II) Acetate in Aqueous Medium at Different Temperatures" in National seminar on Recent Advances in Natural Product Research (RANPR) organized by Department of Zoology, Pachhunga University College on 29th November to 1st December, 2012.
3. Presented a paper entitled, "Association Constant and Thermodynamic Parameters for Simple and Complex Salt Of Cobalt Ions in Aqueous Medium - A Comparative Study" in International Conference on Advances in Environmental Chemistry organized by Department of Chemistry, Mizoram University on November 16-18, 2011.
4. Attended 74th BRNS - IANCAS National Workshop on "RADIOCHEMISTRY AND APPLICATIONS OF RADIOISOTOPES" organized by Department of Chemistry, Mizoram University on October 25 - November 02, 2010.
5. Presented paper in one day National seminar cum Training Programme on 'Green Environmental Chemistry' held on March 30, 2012, organized by Department of Chemistry, Mizoram University.
6. Participated in the National Workshop on "Structure Determination of Macromolecules" sponsored by Department of Biotechnology (DBT), Ministry of Science & Technology, Government of India, New Delhi, held from 26-28 March 2013.
7. Attended for One Day Workshop on University Level Awareness and Communication Campaign for National e-Governance Plan (NeGP) on 4th November, 2011(Friday) organized by Computer Centre, Mizoram University and Department of Information Technology, New Delhi (Govt. of India).

8. Participated in the “Training Course on Bioinformatics-Structure and Determination of Macromolecules” organized by the Bioinformatics Infrastructure Facility, Mizoram University on March 28-29, 2011.
9. Participated in the “National Workshop on Computational Physics” organized by Department of Physics, Mizoram University in collaboration with University of Hyderabad on 14-19 February 2011.
10. Attended Two Days National Workshop on “Dynamical Systems” organized by Department of Mathematics and Computer Sciences on 26-27 November 2013.