CHAPTER I
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INTRODUCTION

A vast number of chemical processes occur in solution. Molecules, atoms and ions of various reactants are often completely or partially dispersed in a medium, called the solvent which is usually a liquid but may be a gas and a solid.

Among the liquid solvents, water is the most common one. Although water has a very simple chemical formula, it has a very complex structure and its understanding is far from complete. Almost all its physical and large number of chemical properties are anomalous. The distinctiveness of water among liquids is evident from its high heat capacity, dielectric constant, boiling point and freezing point, anomalous viscosity etc. All these properties suggest extensive intermolecular structure or association in water\textsuperscript{1-7}. Structure of most common form of ice i.e. ice-I has been established with certainty from X-ray and neutron scattering\textsuperscript{8} study to be of hexagonal symmetry in which each oxygen atom in the structure is hydrogen-bonded to four other oxygen atoms arranged tetrahedrally at a distance of 2.76 \AA\ from the central oxygen atom. The tetrahedral co-ordination of each
water molecule of four neighbouring molecules, as found in ice-I structure, is to a very large extent maintained in liquid water. All the models for the structure of liquid water can be grouped into two categories: mixture model and continuum model. The mixture models assume the simultaneous presence of atleast two structurally distinct species of water. Amongst these models the "interstitial model" of Samoilov\(^7\) and Forslind\(^9\), the 'flickering cluster model' of Frank and Wen\(^10\), 'gas hydrate model' of Pauling\(^11\) and the 'mixture model' of Morchi and Eyring\(^12\) based on significant structure theory of liquids, are noteworthy. In the continuum model developed by Burnal and Fowler\(^13\) and further supported by Lennard-Jones and Pople\(^14\), water is assumed to be of uniform dielectric medium. They suggest that when ice melts, the hydrogen bonds instead of breaking get distorted only. This hypothesis is based on the good agreement on the experimental results\(^14-17\) of radial distribution functions and dielectric constant with theory. This model also finds support from several infra-red and Raman spectroscopic studies\(^1,18-21\). Burnal\(^22\) extended the Pople's bent bond model and proposed a 'random network model' in which each water molecule is hydrogen bonded to four other molecules through bonds that are highly distorted,
forming an irregular network of rings. None of the models is perfect and can explain all the properties of liquid water. For reasons of space, the different models for the structure of water could not be discussed in detail.

Despite the absence of a suitable model for water tremendous efforts have been made for the complete understanding of aqueous solutions. Many books and several review articles have appeared on the influence of solutes on the structure of water and nature of aqueous solutions in general. Frank and co-workers were first to attempt the behaviour of an non-interacting ion in aqueous solution. According to them when an ion is dissolved in water, there exist around it three concentric regions (Fig.1.1). The first region (region A) contains water molecules immobilised due to strong electrostatic interactions between the water dipoles and the charge of the ion. A second region (region B) exists between the region A and the third (region C), which is the bulk water with free water molecules. In the region B, the amount of hydrogen bonding or structure is less than the bulk water. Due to the orienting influence of the central ion and the neighbouring water molecules, the water molecules in region B are slightly oriented.
FIG. 1.1
Frank-Wen zone model of the hydration sheath of a simple ion in water.
towards the central ion. According to Samoilov, regions A, B and C are classified as first hydration sphere, second hydration sphere and the bulk water. The relative size of these three regions depends on the charge, size, composition and shape of the central ion; high charge and small size increases the size of region A whereas low charge and large size increases region B.

Large non-polar molecules when put into water, are more strongly held in aqueous solutions as they have stronger Van der Waal's force fields around them. The non-polar solutes are incapable of producing or transmitting only cluster disruptive influences on water due to their feeble polarisability and electrostastic influences. An ice-like patch, therefore, is possibly formed more readily in a volume element under the sphere of influence of non-polar solute particles and once formed, should have a relatively longer half-life as a part of its boundary is protected from the high energy fluctuation that tries to dissolve it, thus increasing the net structure of the solution.

Many theoretical attempts have been made to explain effects of non-polar substances on the structure of water. There is no direct evidence on the formation of 'ice-bergs' or cages
around the solutes containing non-polar groups, but indications of solid gas hydrates\textsuperscript{37,38} and clathrates\textsuperscript{39} are available in aqueous solutions. It is argued that in aqueous solutions of non-polar solutes, the increase of structure may be the preformation of solid hydrate structure\textsuperscript{40,41}. Fluctuating cage structure in aqueous solutions of organic solutes has also been proposed from ultrasonic studies\textsuperscript{42}.

Infra-red vibrational study and other physical measurements of aqueous electrolytic solutions have been discussed in the light of structure making and structure breaking properties of ions on water.\textsuperscript{43-45} Dorosch\textsuperscript{46} has devised the following scheme of structural changes of electrolytic solutions with increasing concentration: (Solvated ion)\textsuperscript{46}→(Ion-pair solvated complex)\textsuperscript{46}→(Multilarger structure in the ion-pair solvated complex)\textsuperscript{46}→(Solvated crystal). Larger ions disrupt the water structure more. Leitzke and Stroughton\textsuperscript{47} have presented two structural models for aqueous electrolytic solutions, one being the ion atmosphere description of Debye and Huckel at low concentration and the other, a cell model for higher concentration.

Different physical methods viz. thermodynamic studies, transport properties, volumetric studies, X-ray diffraction patterns, spectroscopic
studies, NMR chemical shifts, ultrasonic studies etc. have been used to study structures of solutions with water.

Although maximum experiments have been carried out in water as the solvent in spite of the incomplete knowledge about its structure, various non-aqueous solvents offer a great scope for solution chemists to get good insight into solute-solvent interactions because of the large variation of solvent properties that can be obtained by suitable choice of solvents.

Non-aqueous solvents can be classified in various ways. One of them is on the basis of acid-base concepts. Mullikan defined acidic solvents as electron acceptors, electron being donated by a foreign species. Included in this category of compounds are acetic acid, formic acid etc. Basic solvents are those which can donate a negative charge or an electron pair. Amines, pyridines and hydrazines are included in this category. A further subdivision into amphoteric and aprotic groups is also possible. An amphoteric solvent is one which can act both as an electron donor and an electron acceptor i.e. exhibits both basic and acidic behaviours. Water and low molecular weight alcohols are examples of such classes of solvents.
Aprotic inert solvents have neither strong electron donating or strong electron accepting tendency. Such solvents principally serve as the suspending medium for solute species and do not chemically interact with them. Hydrocarbons, halogenated hydrocarbons etc. are aprotic in nature. Solvents are also classified on the basis of the behaviour exhibited by typical electrolytes in them. Two groups of solvents are conspicuous viz. (i) levelling solvents in which members of a series of electrolytes are of approximately same strength (e.g. hydrogen halides in methanol) and (ii) differentiating solvents in which the members possess markedly different strengths (e.g. hydrogen halides in acetonitrile). The extent of ionisation may also form a basis for classification and accordingly solvents may be classified as (a) ionising solvents (b) non-ionising solvents. Solvents of high dielectric constant belong to category (a) and those with low dielectric constant come under category (b).

The behaviour of an electrolyte in formamide as a solvent has been described in this thesis. It is therefore not out of place to describe some of the solvent properties of amides, in general and of formamide, in particular. Amides are, in general,
polar molecules having high dielectric constants. Formamide has a dielectric constant of 109.5 at 298.16 K. The main cause of high dielectric constant of formamide is its association through hydrogen bonding - the amino hydrogen atom being used for hydrogen bonding. The amides are moderately basic due to the presence of two functional groups, \( \equiv C = 0 \) and \(-NH_2\) which can donate electrons. In solutions of hydrogen halides in amides, salts of the type

\[
\begin{align*}
R-C-NH_2 + X^- & \quad \text{and} \quad R-C-NH_3^+ + X^- \\
\| & \quad \| \\
O^+H & \quad 0
\end{align*}
\]

(I) (II)

are possible. Which of the two forms is actually formed is of much controversy. The old view that protonation takes place on nitrogen atom has been questioned\(^\text{49}\). Recent infra-red and nmr studies show stronger evidence towards protonation on oxygen atom\(^{49-53}\), but the protonation of the nitrogen atom in smaller proportion cannot be completely ruled out. Amongst the amides, formamide has received the earliest attention as a possible non-aqueous solvent\(^5^4\). In view of the similarities of dielectric constant and viscosity of formamide with those of water and also convenient working range (m.p. 2.55°C and b.p. 210.7°C)
it offers, formamide is often used as the solvent of choice in many chemical reactions using ionic materials. Formamide easily undergoes into ionisation and the process can be represented as,

$$2\text{HCONH}_2 \rightleftharpoons \text{HCONH}^- + \text{HCONH}_2^- \text{(or HCONH}_3^-)$$

Formamide is hygroscopic and decomposes on storing to ammonia and carbon monoxide. Decomposition is often caused by traces of water as impurity and the reaction is acid-base catalysed.

In the vapour phase, the structure of formamide is as follows. The atoms of the group, $\text{N-C-H}$ is in a plane, while the group $\text{C-N-H}$ is in the form of a flattened pyramid. Costain and Dowling have shown double bond character of C-O and C=N bonds; C-O has 86% double bond character and C-N has only 25%. Although formamide forms associated species, in the liquid state its structure is not so adequate. From measurements of surface tension, Getman suggested an associated complex with six molecules in the liquid phase and the actual structure of the complex (number of molecules forming the structure) is temperature dependent. Although association may be taking place to some extent, the structure proposed by Getman is subject
to doubt. X-ray diffraction studies at 323 K has suggested some structure of formamide in solid state.

Various physico-chemical studies on mixed solvents with water as one of the components of the mixture have been made to get ideas about

(i) solute-solvent interactions

(ii) solvent-solvent interactions.

Various physical and chemical properties like dielectric constant, basicity etc. of the solvent can be varied by mixing different proportions of two liquids one of which may be water. Dioxane has a very low dielectric constant (2.02) and is a good solvent. Hence by mixing dioxane and water in various proportions one can get a series of solvents having wide variation in the dielectric constant. Moreover, presence of another liquid with water affects the structure of the latter. Franks and Ives\textsuperscript{63} and Panda\textsuperscript{163} have pointed out the change in the structural properties of water in the presence of dioxane. According to them a small proportion of dioxane in water increases the order but in larger proportions, the order is destroyed. A good review of ionic solvation in mixed aqueous solvents is made by Feakins\textsuperscript{64}.

Measurement of the electrode potential has provided a good tool for the study of the behaviour of an ion in different solvents because of high precision of
EMF measurements. For this purpose an electrode reversible with respect to the concerned ion is chosen. Silver-silver halide electrodes have been used to study the behaviour of halide ions. The data on silver-silver halide electrodes have in water are too vast to reproduce here. Janz has made a good review of all the earlier works on such electrodes. Extensive studies in mixed solvents using silver halide electrodes have been made by various workers since last several years. The cell mostly used for investigation is shown below.

\[ \text{Pt, } H_2(g) \mid H_2O(y) \mid S(x)X(y) \mid AgX(s), Ag, \]

where \( X^- \) represents \( \text{Cl}^- \), \( \text{Br}^- \) or \( \text{I}^- \); \( x \) and \( y \) represent percentage weight of organic solvents \( S \) and water respectively. The following organic solvents have been used: dioxane, methanol, ethanol, glycol, 1-propanol, glycerol, t-butanol, 1-butanol, propan-2-ol, 2-methyl-1-propanol, propylene carbonate, dimethyl formamide, 1,2-dimethoxy ethane, tetrahydrofuran, dimethyl sulfoxide, urea and N-methylpropionamide. Accurate data on the EMF of the above cell are also available in various organic solvent-water mixtures. Silver-silver chromate electrode has also been recently studied in dioxane-water.
The EMF of the above cell can be written as

\[ E = \mathcal{E}^0_m + \frac{2 \times 2.3026}{F} \log m + \frac{2 \times 2.3026 \cdot RT}{F} \gamma^+_s \]  

... (I.1)

where \( m \) is the molality and

\[ -\log \gamma^+_s = \frac{A(d_m)}{d \gamma^+_s} - b_m + \log(1+0.002 M_m) - [\text{Ext}] \]  

... (I.2)

Here \( A \) and \( B \) are Debye-Hückel constants, \( d_0 \) is the density of the solvent, \( a \) is the ion-size parameter and \( M \) is the mean molecular weight of the solvent defined by

\[ \frac{1}{M} = \frac{x}{M_{\text{water}}} + \frac{1-x}{M_{\text{solvent}}} \]  

...(I.3)

\( x \) is the weight fraction of water in the solvent mixture. \([\text{Ext}]\) denotes the extended term of the Debye-Hückel theory which can be obtained from the tables of Gronwall, LaMer and Sandved, but are generally neglected.

The activity coefficient \( \gamma^+_s \) refers to a value of unity for indefinitely dilute solution in the respective solvent. But the activity coefficients of an electrolyte in different solvents become amenable to comparison only when referred to the same standard state e.g., hypothetical ideal unimolal aqueous solution. The activity coefficient of an electrolyte at any concentration,
designated as $s\gamma$ in any solvent, referred to the aqueous standard, can be expressed as a product shown as

$$s\gamma = \gamma_m \gamma_s,$$ ... (I.4)

where $\gamma_m$ is the medium effect.

The thermodynamic properties associated with the transfer of one mole of HX from water to the solvent concerned (HX in water $\rightarrow$ HX in solvent) are found to be convenient quantities for the study of solvent effect and hence, some discussion on such transfer processes is called for. The free energy change of such a transfer process is given by the expression.

$$\Delta G^o_{t(HX)} = \bar{\tilde{G}}^o_{HX} - \bar{\tilde{G}}^o_{wHX} = s \Delta G^o_{HX(soln)} - w \Delta G^o_{HX(soln)}$$

$$= - F \left( s \bar{E}^o_m - w \bar{E}^o_N \right)$$ ... (I.5)

where $\bar{G}^o_{HX}$ denotes molar free energy of HX in solution. In the above equation, the standard electrode potentials are given in molefraction scale. The effect of solvent on free energy transfer should be more clearly reflected in such a scale, because it will eliminate free energy changes due to concentration changes. $E^o_m$, $E^o_c$ and $E^o_N$ are inter
related through the expressions

\[ E_C^0 = E_m^0 + \frac{2x2.3026 \cdot RT}{F} \log d_o \] \hspace{1cm} \ldots (I.6)

\[ E_N^0 = E_m^0 - \frac{2x2.3026 \cdot RT}{F} \log \frac{1000}{M} \] \hspace{1cm} \ldots (I.7)

The entropy change and enthalpy change of transfer process can be derived and are as follows.

\[ \Delta S_t^0 = -F \left[ \frac{\delta G_t^0}{\delta T} \right] = F \left[ \frac{\delta E_N^0}{\delta T} - \frac{\delta E_m^0}{\delta T} \right] p \] \hspace{1cm} \ldots (I.8)

\[ \Delta H_t^0 = \Delta G_t^0 + T \Delta S_t^0 = F \left[ T \frac{\delta E_N^0}{\delta T} - \frac{\delta E_m^0}{\delta T} - s \frac{E_N^0}{E_m^0} + w \frac{E_N^0}{E_m^0} \right] \] \hspace{1cm} \ldots (I.9)

Since transfer process involves transfer of charged particles from water to a solvent of different dielectric constant, the relative thermodynamic quantity will comprise of two parts, viz. electrostatic (el) and non-electrolytic or chemical (ch). Thus, the free energy change will be

\[ \Delta G_t^0 = \Delta G_{t,el}^0 + \Delta G_{t,ch}^0 \] \hspace{1cm} \ldots (I.10)

Changes of other thermodynamic quantities can also be similarly expressed. The non-electrostatic contribution reflects the chemical nature of the solvent with respect to water which includes basicity, as well as, solvating capacity of the solvent. The electrostatic contribution of free energy transfer can be calculated from the
much-used Born's equation, which for 1-1 electrolyte is

\[ \Delta G^0_t = \frac{N e^2}{2} \left[ \frac{1}{D_2} - \frac{1}{D_1} \right] \left[ \frac{1}{r_+} + \frac{1}{r_-} \right], \quad \ldots (I.10) \]

where \( r_+ \) and \( r_- \) are radii of the cation and anion respectively and \( D_1 \) and \( D_2 \) are dielectric constants of the solvent and water respectively.

From the results of the cell, \( \text{Pt}, \text{H}_2(\text{g}) \mid \text{HCl} \mid \text{AgCl}_x(\text{s}), \text{Ag} \), in mixtures of water with dioxane, alcohols, ketones, glycols, glycerols, and sugars, Feakins et al.\(^{85}\) have shown the limitation of the use of Born equation for calculation of free energy of transfer process. Obviously the treatment of the medium as a continuum with macroscopic dielectric constant, \( D \), is an over simplification. The modified equation due to Hepler\(^{86}\) which takes into account the dielectric saturation in the ionic force field may be better, but even then, the uncertain factor in the ionic radii remains.

As a corollary of equation I.10, for a series of electrolytes with a common ion (e.g. alkali metal chlorides) the free energy transfer should be invariably proportional to the radius of the variable ion. Thus,

\[ \Delta G^0_t = a + \frac{b}{r}, \quad \ldots (I.21) \]

where \( a \) and \( b \) are constants and \( r \) is the radius of the variable ion. Equation I.21 has been tested. With various
halogen acids (\(r_{\text{varied}}\)) and metal chlorides (\(r^+_{\text{varied}}\)) in water-methanol mixtures and reasonably good straight lines have been obtained\(^{64}\), particularly in solvents of low methanol content. Using these straight line plots and making some drastic assumptions, Peakins has made approximate estimate of standard free energy (also enthalpy and entropy) transfers of \(H^+, Li^+, Na^+, K^+, Cl^-, Br^-\) & \(I^-\) ions from water to water-methanol mixtures at 298.16 K. He interpreted the results on the basis of more "basic" or less "acidic" character of water-methanol mixture than pure water due to inductive effect of the methyl group. Water-dioxane mixture showed similar results as methanol-water mixture indicating that it is more "basic" than pure water. Water-acetic acid mixture, as expected, behaved entirely differently as it is more "acidic" than water.

As in the case of free energy change, the entropy and enthalpy of transfer of \(HX\) from water to mixed/non-aqueous medium can be considered to consist of electrical and chemical terms,

\[
\Delta Q^o_t = \Delta Q^o_{t,el} + \Delta Q^o_{t,ch} \quad \text{(1.22)}
\]

\((Q^o = G^o, H^o \text{ or } S^o)\). The electrical part of \(\Delta S^o_t\) can be calculated from the temperature coefficient of Born's equation.
Knowing $\Delta G^0_{t, ch}$ and $\Delta S^0_{t, ch}$, $\Delta H^0_{t, ch}$ can be calculated.

A negative value of $\Delta G^0_{t, ch}$ indicates greater affinity of the solvent (mixed/non-aqueous) for proton or in other words, a more "basic" nature of the solvent in comparison with water. Similarly, a positive value of $\Delta G^0_{t, ch}$ indicates the (mixed-non-aqueous) solvent to be more "acidic". A positive or negative value of $\Delta S^0_{t, ch}$ indicates increase or decrease in the "dis-order" associated with the transfer of the electrolyte (HX) from water to the other solvent respectively. The analysis of $\Delta S^0_{t, ch}$ in conjunction with $\Delta G^0_{t, ch}$ gives idea about the extent of solvation of ions and the state of the solvent structure in the mixed/non-aqueous solvent.

Good analysis of the chemical part of $\Delta G^0_t$ for hydrogen halides for transfer from water to other solvents in the above lines has been done by Das, Kundu & others 87.

Electrode potentials of secondary silver electrodes have also been measured in many pure non-aqueous solvents. In such works the purity of the
solvent is very important. Many earlier reported values of $E^0$ of silver-silver halide electrodes in alcohols are found to be erroneous due to impurity of water in those solvents. For lack of space we discuss only the result on electrode potentials of secondary silver electrodes in formamide, the solvent which has been used in our work. Mandel and Decroly have studied the standard potential of silver-silver chloride electrode with respect to hydrogen electrode over the temperature range of 298.16 - 318.16 K in formamide medium. The work has been reinvestigated by Agarwal and Nayak and Broadbank et al and the thermodynamic properties of HCl in formamide has been calculated. The work has also been extended to silver-silver bromide electrode. Dash and co-workers have determined the $E^0$ of various $Ag$, $Ag\_nX^{n-}$ electrodes in formamide medium by EMF or solubility measurements. The results have been explained on the basis of higher dielectric constant, lower basicity and consequently lower solvation of $H\_nX$ electrolyte, of formamide compared to water.

Study of transport properties such as viscosity, conductance, diffusion etc. give useful information about the structure of aqueous solutions relative to water mainly due to pioneering works of
Ostwald, Debye, Huckel, Onsager, Falkenhagen, Fuoss etc.

Of all transport properties, discussion will be limited here to conductivity, because only conductivity has been studied in this thesis. The equivalent conductance, $\Lambda$, the quantity most commonly used in discussing conductance data, is defined as

$$\Lambda = \frac{1000 R}{c}, \quad \ldots (I.24)$$

where $c$ is the electrolyte's equivalent concentration and $K$ is the specific conductance. Variation of equivalent conductance with concentration was first quantitatively explained by Debye-Huckel and later on Onsager put in the form of equation I.25

$$\Lambda = \Lambda_0 - SC^{1/2}, \quad \ldots (I.25)$$

where $S = B_2 + B_1 \Lambda_0$, $B_2 = \frac{82.4}{\eta (\Delta \eta)^2}$ and $B_1 = 8.20 \times 10^5 (\Delta T)^{3/2}$. $\Lambda_0$ is the equivalent conductance at infinite dilution. $S$ is the limiting slope of the curve $\Lambda$ vs. $c^{1/2}$ whose value depends on $\Lambda_0$, viscosity ($\eta$), dielectric constant ($\Delta \eta$) and temperature of the solvent. Equation I.25 was derived assuming point charges in solution ($c < 10^{-3}$ equiv dm$^{-3}$). Equation I.25 can be rearranged to give

$$\Lambda_0 = \frac{\Lambda + B_2 C^{1/2}}{1 - B_1 C^{1/2}}, \quad \ldots (I.26)$$
Shedlovsky\textsuperscript{97} observed that for 1:1 electrolytes, the quantity on the right hand side of the equation varied with concentration and he suggested the following equation which explained conductance data up to 0.1N concentration.

\[ \Lambda = \Lambda_0 - (B_1 \Lambda_0 + B_2) c^{1/2} + b c (1 - B_1 c^{1/2}) \quad \ldots (1.27) \]

Owen gave a more general equation for a variety of completely dissociated and partly associated electrolytes as

\[ \Lambda = \Lambda_0 - \frac{S c^{1/2}}{1} + A c \log c + B c \quad \ldots (1.28) \]

Owen's equation has a theoretical foundation and has been successfully applied to solutions of strength up to 0.01N.

Fuoss and Onsager\textsuperscript{99} treating the ions as finite size particles, as well as, distinguishing between those ions that are free to contribute to the conductance of the solutions and those that are not, suggested a widely used equation

\[ \Lambda = \Lambda_0 - \frac{S c^{1/2}}{1} + B c \log c + (\alpha - F \Lambda_0) c \quad \ldots (1.29) \]

where \( S = \alpha \Lambda_0 + \beta \), \( \alpha = B_1 \) and \( \beta = B_2 \) of equation 1.25,

\[ E = E_1 \Lambda_0 - E_2 ; \quad E_1 = 2.3026 \frac{k^2 a^2 b^2}{24c} \]

\[ E_2 = 2.3026 \frac{kab}{16c^{1/2}} \]

\[ k = \pi Ne^2c/125DKT \]

\[ ab = e^2/DTk \]
\[ k = \text{Boltzmann constant} \]
\[ e = \text{electronic charge} \]
\[ a = \text{ion-size parameter i.e. cation-anion distance of closest approach} \]

\[ J = \sigma_1 \Lambda_0 + \sigma_2 \]

where

\[ \sigma_1 = \left( \frac{k^2 a^2 b^2}{12c} \right) \left[ \frac{2b^2 + 2b - 1}{b^3} + 0.9074 + \ln(ka/c^2) \right] \]

\[ \sigma_2 = a(\beta + 11\beta ka/12c^2) - (kab\beta /8c^2) \left[ 1.017 + \ln(ka/c^2) \right] \]

The parameter, \( \beta \), corrects for the effect of the electrolyte on the solvent viscosity and is generally set equal to the B-coefficient of Jones-Dole viscosity equation\(^{100}\). When ionic association is taken into account, equation I.29 can be expressed as,

\[ \Lambda = \Lambda_0 - S(c \gamma)^{1/2} + E \gamma \log c \gamma + (J - f_1 \Lambda_0) c \gamma - K_a c \gamma f_1^2 \] \( \cdots \) (I.31)

where \( f_1 \) is the mean ionic activity coefficient, \( \Lambda \) is the degree of dissociation and \( K_a \) is the association constant of the process \( M^+ + A^- \rightleftharpoons MA \) (MA includes all the species that do not contribute to conductance).

Pitts\(^{101}\), through a different theoretical approach and different boundary conditions from Fuoss and Onsager, introduced a conductance equation which was rearranged in the form of equation I.31. A more generalised equation was latter developed by Onsager et al. which is similar.
to equation I.29 and I.31, and involved the calculation of the different parameters by a different method\textsuperscript{102}.

The equation is

\[ \Lambda = \Lambda_0 - \frac{Sc}{\gamma} + E_1 \ln(6E_1^'C) + Lc - \alpha f^2 \Lambda_0, \ldots (I.32) \]

where \( E_1' = E_1 - E_2' \) and \( E_1' = 2.942 \times 10^{12}/(\text{DT})^3 \)

\[ E_2' = 0.4333 \times 10^8/\eta \times (\text{DT})^2 \]

\[ L = L_1 + L_2(b) \]

\[ L_1 = 3.202 E_1' \Lambda_0 - 3.420 E_2' + \alpha \beta \]

\[ L_2(b) = 2E_1' \Lambda_0 h(b) + 44E_2'/3b - 2E \ln b \]

\[ h(b) = (2b^2 + 2b - 1)/b^3 \]

Equation I.32 can be generalised to

\[ \Lambda = \Lambda_0 - \frac{Sc}{\gamma} \gamma^\frac{1}{2} + E_1 \ln(6E_1^'C) + Lc - K_c \gamma f^2 \ldots (I.33) \]

Equation I.32 reproduces conductance data for 1:1 electrolytes in solvents of high dielectric constant and equation I.33 holds good for solvents of low dielectric constant which stabilises ion-pairs in contact. Fuoss and Hsia\textsuperscript{103} modified equation I.32 and I.33. Justice\textsuperscript{104,105} made use of Bjerrum\textsuperscript{106} critical distance, \( q \), given by

\[ q = \frac{|z_+ z_-| e^2}{2 \text{DT} R} \ldots (I.34) \]
(k stands for Boltzmann constant and other terms have their usual significance). The conductance equation of Onsager et al.\textsuperscript{102} was generalized by Chen and Onsager\textsuperscript{107} for solutions of strong electrolytes containing any number of ionic species of any valence type which requires computational method for calculation.

\[
\Lambda_j = \Lambda_j^0 - S_j \gamma^{3/2} + E_j \gamma \ln \gamma + \text{higher order terms} \quad \ldots(1.36)
\]

\[
\Lambda_j^0 = \text{limiting equivalent conductance of } j \text{ ions.}
\]

\[
S_j = \text{Onsager-Ross limiting law slope.}
\]

\[
E_j = \text{the coefficient of the 1st extended term computed.}
\]

Various terms \( c^{3/2}, c \log c \) etc. have been added to the limiting equation 1.25 (valid for \( c < 10^{-3} M \)) to make it applicable to concentrated solutions (equation 1.27 and 1.28 etc.). Equation 1.27 seems to be the best for concentrations up to 0.1N.

This empirical equation of Shedlovsky when compared with equation 1.37,

\[
\Lambda = \Lambda_0 - (B_1 \Lambda_0 + B_2) c^{3/2} + c(aBB_2 + B_1B_2 + 1.707 aBB_1)
\]

\[
\ldots(1.37)
\]

deduced by Falkenhagen\textsuperscript{108} and Stokes\textsuperscript{109}, gets some justification for 1:1 electrolytes. Stokes and Robinson\textsuperscript{10} have put forward an empirical equation,
\[ \Lambda = \Lambda_0 - \frac{B_1\Lambda_0 + B_2}{1 + ka}, \] 
\...(I.38)

in which the limiting slope of Onsager has been simply divided by \(1 + ka\) in order to allow for the finite ionic size. The authors claim this equation to be applicable upto \(c = 0.1N\) for 1:1 electrolytes.

Structural effects on the conductance of ions in aqueous solutions are derived from a comparison of their walden products (\(\Lambda \eta\)) in aqueous and non-aqueous solutions\(^{111}\). For detecting ion-solvent interaction it is essential to have ionic conductance data which can be obtained from transference number measurements.

Reliable information about the existence of ion-pairs and free ions come from ionic association theory (described later in detail). Kay\(^{94}\), on the basis of ion-solvent interactions from ionic association has classified solvents into four groups. According to Onsager\(^{102}\) solvents having dielectric constant greater than 40, ionic association does not take place and for solvents having dielectric constant less than 30, significant ionic association takes place.

In the extrapolation procedures for the determination of \(\Lambda_0\) it is often assumed that the electrolyte remains completely dissociated, but in solvents of low dielectric constant, association of
oppositely charged ions may be considerable to be neglected. Davies\textsuperscript{112} has calculated the dissociation constant, $K$, of many salts of high valence type by taking into account the deviation from a completely dissociated electrolyte. His method has, however, many defects. Fuoss and Krauss\textsuperscript{113} and Shedlovsky\textsuperscript{114} have developed graphical methods for symmetrical incompletely dissociated electrolytes in low dielectric constant medium in which both $K$ and $\Lambda_0$ can be simultaneously evaluated.

A review of the conductivity measurements of electrolytes will be an exhaustive one. For lack of space we discuss only some important papers on conductivity measurements of only 1:1 electrolytes in dioxane-water mixtures and in formamide, the solvents concerned in this thesis. James\textsuperscript{115} showed deviation from Onsager theory for certain electrolytes in many water-organic solvent (including dioxane) mixtures. Griffith and Lawrence\textsuperscript{116} measured conductance of $\text{AgNO}_3$ in dioxane-water mixtures and calculated $\Lambda_0$ and $K$ by both Fuoss and Krauss\textsuperscript{113} and Shedlovsky\textsuperscript{114} methods. Lind and Fuoss\textsuperscript{117} measured the conductivity of KCl in dioxane-water mixtures over a range of dielectric constant and according to him, association between the ions begins below dielectric constant of 40. Similar
conclusion have been drawn by Mckenzie and Fuoss\textsuperscript{118} from conductivity measurement of KN\textsubscript{O}\textsubscript{3} and AgNO\textsubscript{3} of dioxane-water mixtures of varying composition at 298.16 K. Das\textsuperscript{119} et al have studied the conductivity of KCl, NaCl, KBr, NaBr, KNO\textsubscript{3}, KIO\textsubscript{3} and NaBrO\textsubscript{3} in dioxane-water mixtures at varying temperatures and have calculated the values of $K$, $\Lambda$, and radii of ion-pairs by various methods. They have also studied a series of salts of various valence type in dioxane-water mixtures of varying composition at different temperatures for estimating the ion-solvent interaction. From the conductivity data of NaCl, KCl, NaBr, KBr, NaNO\textsubscript{3} & KNO\textsubscript{3}; they concluded that ion solvent interaction to be of order NO\textsubscript{3}$^-$ > Br$^-$ > Cl$^-$ and similarly from the conductivity of KBrO\textsubscript{3}, NaBrO\textsubscript{3}, KIO\textsubscript{3}, NaIO\textsubscript{3}, K\textsubscript{2}SO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4}, the ion solvent interaction is found to be of the order BrO\textsubscript{3} > IO\textsubscript{3} > SO\textsubscript{4}\textsuperscript{2-}

Literature data of conductivity of electrolytes in formamide is not so numerous as in water and other solvents. A recent investigation\textsuperscript{120} refers to earlier studies of conductance measurements by Davies et al. in 1915 of 1:1 electrolytes. Dawson, Sears and co-workers\textsuperscript{121} have investigated conductance phenomenon of some 1:1 electrolytes in various amides including formamide. Tewari and Johari\textsuperscript{122} have carried out conductance studies
of acetates, nitrates and higher valence electrolytes in formamide, dioxane-formamide, acetone-formamide etc. Electrolytes are invariably completely dissociated in formamide.

The association between a metal ion and a ligand (an anion or a neutral molecule with lone pair of electrons) has been a subject of interest of solution chemists since a long time. In this process of association, the water sheath around the metal ion may or may not be displaced. In the former type of association "inner-sphere complex" is formed, whereas, in the latter type of association "outer-sphere complex" results. Here the term complex, is very loosely used for all types of combination between a metal and a ligand.

Where the bonding between the metal ion and the ligand is purely due to electrostatic forces, Bjerrum's treatment can be applied to calculate the distance of approach between the ions, $a$, from the experimental value of $K$ using the formula

$$K = 4\pi \int_{a}^{\infty} \exp\left(-\frac{z_+z_-e^2}{DkT}r^2\right)dr$$  \hspace{1cm} ...(1.39)

where $q = z_+z_-e^2/2DkT$.

It is suggested that if the calculated value of 'a' is more than the sum of the radii of individual ions, ion-pair or outer-sphere complex is indicated. This
generalisation has many exceptions and classification on this basis is not advisable\textsuperscript{124}.

Bjerrum\textsuperscript{125} was the first person to point out the step-wise formation of complexes.

\begin{align*}
M + L &\rightleftharpoons ML, \\
ML + L &\rightleftharpoons ML_2 \ldots \ldots \ldots \ldots ML_{n-1} + L &\rightleftharpoons ML_n.
\end{align*}

(for simplicity charges and water molecules in the hydration sphere are omitted). Disregarding the activity coefficient terms, the stepwise formation constants,

\begin{align*}
K_1 &= \frac{[ML]}{[M][L]}, \quad K_2 = \frac{[ML_2]}{[ML][L]} \ldots \ldots \ldots \ldots K_n = \frac{[ML_n]}{[ML_{n-1}][L]},
\end{align*}

are related to the overall formation constant,

\[ \beta_n = \left( \frac{[ML_n]}{[M][L]} \right)^n, \]

through equation I.40.

\[ \beta_n = K_1 K_2 \ldots K_n = \prod_{i=1}^{n} K_i \ldots \ldots \text{(I.40)} \]

Various methods are available for the determination of stepwise and overall formation constants and some recent books by Rossotti and Rossotti\textsuperscript{126} and Beck\textsuperscript{127} describe the up to date methods of their determination.

In general, the value of \(K_i\) decreases as the number of ligand molecules attached to the metal ion increases. This is attributed to (a) statistical
Factors (b) increased steric hindrance as the number of ligands increases if they are bulkier than the water molecules they replace and (c) coulombic factors for complexes with charged ligands. However, reversal of this order can occur in the presence of specific stereochemical effects, such as, a preferred low co-ordination number or change in the ground state of the metal ion.

Any work of useful physico-chemical significance requires the determination of the thermodynamic equilibrium constant instead of equilibrium constant at arbitrary ionic strength. For a reaction of type, 

\[ M + nL = ML_n \]

the thermodynamic equilibrium constant can be written as

\[ K_t = \frac{a_{ML_n}}{a_{M^n} a_{L_n}^{n}} \cdot \frac{f_{ML_n}}{f_{M^n} f_{L_n}^{n}} = K_c \frac{f_{ML_n}}{f_{M^n} f_{L_n}^{n}} = K_c f_n \]

The terms f's stand for the molar activity coefficients of the ions, \( K_c \) stands for the concentration quotient representing the equilibrium constant at the working ionic strength. \( K_c \) can be determined by various physico-chemical means, but determination of the thermodynamic equilibrium constant requires either the
elimination or evaluation of activity coefficient terms. This can be attempted in mainly two ways\textsuperscript{127}; (a) determining $K_C$ for different ionic strengths and extrapolating to zero ionic strength where activity coefficients become unity (b) calculating activity coefficients from theoretical or empirical relationships.

The first method appears promising but extrapolations are mostly nonlinear and thus resulting in some uncertainty in the extrapolated value of $K_C$. Coming to the second method, there are a number of equations relating the activity coefficients of ions in dilute solutions with the ionic strength, but none of the equations is without any defect. Aditya and Das have recently critically discussed the scope and limitations of all the available activity equations available in a review article\textsuperscript{130}. In spite of the several objections raised, Davies equation is the most popular one due to its simplicity and wide applicability.

$$- \log f_i = A_i^2 \left( \frac{I^2}{1+I^2} - CI \right) \quad \text{(I.42)}$$

$A$ and $C$ are constants, $A$ has theoretical significance (same as Debye-Hückel constant) and is equal to 0.501 at 298.16 K for water as solvent. $C$ is an empirical constant which was originally proposed by Davies\textsuperscript{131} to be equal to 0.2 but later reassessed\textsuperscript{132} to be equal to 0.3.
Some workers prefer to work at fixed ionic strengths maintained by addition of a strong inert electrolyte like sodium perchlorate based on Bronsted's principle of constant ionic environment. A very high ionic strength, usually 1M or 3M in sodium perchlorate is maintained in this method. This method is absolutely necessary where stability constants of higher complexes are required to be determined. Formation of higher complexes requires high concentration of the ligand. The ionic strength as such becomes high where none of the known activity equations holds good. However, this approach to tackle the problem has certain disadvantages\textsuperscript{127,130} viz. (a) different results cannot be compared unless carried out at the same ionic strength (b) the assumption that ClO$_4^-$ does not associate with cations even at very high concentrations is not valid and (c) trace impurities present in sodium perchlorate, usually Cl$^-$, may amount to non-neglectable quantity in solutions containing large mole-fraction of sodium perchlorate.

Various attempts have been made to correlate stability of a complex with the property of the central metal ion. Linear plots of log $K_t$ or log $K_C$ against $\frac{1}{r_M}$, $\frac{z}{r_M}$, $\frac{z^2}{r_M}$ etc., where $r_M$ and $z$ are the radius
and charge of the central ion respectively, have been obtained. The above correlations are indicative of electrostatic bonding and deviations are attributed to covalent bonding\textsuperscript{134,135}. Correlations of complex stability with ionisation potential and electronegativity\textsuperscript{136} of the central metal ion have also been made. Van Panthaleon Van Eck\textsuperscript{137} have found that, for many ions, the relationship, $\log K_1 = p (I-q)$, is valid ($I$ is the ionisation potential and $p$ and $q$ are constants). Irving and Williams\textsuperscript{135} proposed a stability order:

\[ \text{Mn}(II) < \text{Fe}(II) < \text{Co}(II) < \text{Ni}(II) < \text{Cu}(II) < \text{Zn}(II). \]

This order is due to the combination of (a) a regular contraction leading to greater stability and (b) an irregular crystal field stability. Arhland and Larson\textsuperscript{138} and Carleson and Irving\textsuperscript{139} classified elements in the periodic table on the basis of their acceptor properties into three groups: class (a) class (b) and class (c). Class (a) ions from electrovalent complexes and class (b) ions which are more polarising form covalent complexes. A good discussion of class (a) class (b) and class (c) elements has been made in a review article by Arhland, Chatt and Davies\textsuperscript{140}. Pearson\textsuperscript{141,142} introduced the concept of "hard" and "soft" acids (acceptors) and bases (donors). The main principle behind this theory is that strong bonds are only formed between hard acids and hard
bases or soft acids and soft bases. Hard-soft bonds are either weak or non-existent. This theory has been subjected to criticism by Williams and Hale\textsuperscript{143}.

For electrostatic interactions the radius and charge of the ligands are as important as for the metal ions. Polarisability and electron affinity have also been correlated with complex stability. In case of chelate complexes, the ring size is a very important factor; five and six membered chelate rings are generally more stable. Calvin and Wilson\textsuperscript{144} have, for the first time, pointed the inter-relationship between chelate stability and base strength of ligand. There exists a linear relationship between log $K_{HL}$ and log $K_{ML}$. This relationship has been violated and even reversed in many cases\textsuperscript{145-147}. The slope of log $K_{HL}$ and log $K_{ML}$ has been the subject of discussion of some papers\textsuperscript{148,149}. Substituents on the ligands influence complex stability in various ways viz. (a) by interfering or enhancing resonance of the chelate ring (b) by steric effect and (c) by promoting or hindering $\pi$-bond formation by back donation.

It is well recognised that the standard free-energy change which is related to the stability constant by equation I.43,

$$\Delta G^\circ = -2.3026 \ RT \ \log K_t,$$  \hspace{1cm} \textit{(I.43)}
cannot fully explain all aspects of metal-ligand interactions. Standard free energy change is made up of two factors viz. standard enthalpy and entropy changes.

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]  

...(1.44)

Negative \( \Delta H^\circ \) and/or positive \( \Delta S^\circ \) favour complex formation (\( \Delta G^\circ \) becomes negative). This is why, for a more quantitative interpretation, it is necessary to determine the standard enthalpy change (or heat of reaction) along with the equilibrium constant. The former can be determined in two ways viz. (a) from the temperature coefficient of the equilibrium constant (b) by direct calorimetry. Of these, the second method is the most direct one and gives more accurate results.

The work done in the formation of an ion-pair or ion-associate from the separate ions in solution can be written as

\[
-W = \frac{\Delta G^\circ}{N} - kT \ln 55.5
\]  

...(1.44)

\( (N = \text{Avogadro number}) \)

The term \(-kT \ln 55.5\) is introduced to make the \( K_t \) values dimensionless and characteristic of a reaction in which the number of solute particles is decreased by unity. \( W \) may be regarded as being made of two parts, \( W_{\text{env}} \) and \( W_{\text{non}} \). \( W_{\text{env}} \) represents long range electrostatic forces which depend upon the environment. \( W_{\text{non}} \) represents short range quantum mechanical forces. \( W_{\text{env}} \) increases with
temperature due to change in macroscopic dielectric constant of the medium and $W_{\text{non}}$ is insensitive to it.

$$W = W_{\text{env}} + W_{\text{non}} = -kT(\ln K_t + \ln 55.5) \quad (1.45)$$

When the interaction between the metal ion and the ligand is mainly electrostatic in nature, $W_{\text{env}}$ is much greater than $W_{\text{non}}$. In such a case, the predominant effect of the rise of temperature is to decrease the mutual potential energy resulting in greater association between the ions. The reaction becomes endothermic. If, however, $W_{\text{non}}$ is more important, increase of temperature favours dissociation of the ion-pair complex due to thermal agitation. The $\Delta H^0$, in such cases, is negative.  

A similar conclusion has been drawn by Ahrland from the thermodynamic study of the formation of several complexes. According to him interactions between hard acceptors and hard donors, postulated to be mainly electrovalent, have invariably endothermic heat change but the formation of complex is almost exclusively due to increase of entropy. Conversely, the reaction between typically soft acceptors and donors are always strongly exothermic while entropy change is often negative, or, if positive, contributes only slightly to the reduction in free energy. In the former cases, there is stepwise decrease in $\Delta s^0_n$ and $\Delta H^0_n$. In the latter cases, however, virtually constant values of $\Delta H^0_n$ from step to step is often found.
We have earlier mentioned of Irving-Williams order of stability of complexes which was later rationalised on the basis of ligand field effects. According to Orgel, apart from the $\Delta H^0$ values associated with covalent and electrostatic interaction between ions, additional stabilisation occurs due to splitting of the d-levels, other than $d^0$, $d^5$, and $d^{10}$ by the electrostatic field of the ligand groups. This decrease of energy is called the "Crystal-field stabilisation energy (CFSE)". For high-spin complexes (weak-field ligands), stabilisation is maximum for $\text{Ni}^{+2}$ and $\text{Cu}^{+2}$ in the first transitional series metal ions. When the electrostatic field of the ligand is high, the energy difference between the two d-levels ($\Delta$) is more. In such cases spin-coupling occurs and consequently, low-spin complexes are formed. The Irving-Williams order is not obeyed in such complexes. George and McClure have developed a method of calculation of CFSE in complexes of first transition series from experimentally determined $\Delta H^0$ values. The method is essentially based on the deviation in the linearity of $\Delta H$ as a function of the number of d-electrons in the central metal ion.

Entropy change for the ion association in solution is usually not determined directly although, in principle, it can be calculated theoretically by
statistical methods. $\Delta S^0$ is mostly calculated from the experimentally determined values of $\Delta G^0$ and $\Delta H^0$ at a particular temperature. The errors and approximations reflected in the latter determinations are always reflected in the $\Delta S^0$ values. The accuracy of the determined value of $\Delta S^0$ is, therefore, always less than those of $\Delta G^0$ and $\Delta H^0$.

In spite of the decrease in the number of ions when a hydrated metal ion combines with a ligand in aqueous solution, generally an increase in entropy is expected due to (i) release of water molecules upon complexation and (ii) decrease in the net charge of the system resulting in decreased hydration. This is an over simplification as it disregards loss of configurational and rotational entropies in case of polyatomic ligands which accompanies the complexation process. In fact, negative values of $\Delta S^0$ are known in many cases e.g. TlCl and calcium tartarate.

One can examine the entropy change associated with complexation reaction by means of a thermodynamic cycle,

\[
\begin{align*}
\text{M}^{x+} (g) + & \quad \text{L}^- (g) \quad \xrightarrow{\Delta S^0} \quad \text{ML}^{(x-y)+} (g) \\
\Delta S^0_1 & \quad \Delta S^0_2 & \quad \Delta S^0_3 \quad \Delta S^0_4 \\
\text{M}^{x+} (aq)^+ & \quad \text{L}^- (aq) \quad \xrightarrow{\Delta S^0} \quad \text{ML}^{(x-y)+} (aq)
\end{align*}
\]
From the cycle, \( \Delta S_1^o + \Delta S_2^o + \Delta S_3^o + \Delta S_4^o = \Delta S^o \) ...(I.46)

\(- \Delta S_1^o - \Delta S_2^o\) and \( \Delta S_4^o \) are the standard entropy changes of hydration of cation, ligand and complex respectively.

For a series of related reactions, \( \Delta S_3^o \) may not change appreciably, in which case, \( \Delta S^o \) will be proportional to the difference of hydrational entropies of the complex ion \( (\Delta S_4^o) \) and the associating cations and ligands \((- \Delta S_1^o \) and \(- \Delta S_2^o\)). For a particular ligand and a series of similar cations, \( \Delta S_4^o \) may not vary considerably. In such a case, \( \Delta S^o \) will change with only hydrational entropy of the cation and will thus be proportional to only \( \frac{1}{r^+} \). Similarly for a particular metal ion and a series of similar ligands, \( \Delta S^o \) is linearly related to the entropy of hydration of the anions \(^{158,159}\). \( \Delta S_3^o \) has been calculated by statistical thermodynamics for simple monoatomic anions like halides and metal ions of first transition series. With the existing knowledge of \( \Delta S_1^o \) and \( \Delta S_2^o \) and with some approximation for the estimation of \( \Delta S_4^o \), \( \Delta S^o \) can thus be theoretically calculated for simple reactions \(^{160}\).

Arhlund \(^{161}\) has pointed out some criteria in the entropy change to distinguish between outer-sphere and inner-sphere complexes. Das and co-workers \(^{162}\) have used the entropy change to distinguish between N-bonded and S-bonded complexes of SCN\(^-\) ligand.
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