CHAPTER - I

INTRODUCTION

The majority of reactions that are of chemical or biological interest occur in solutions. Solvent is believed to provide an inert medium for chemical reactions. The significance of solute-solvent interactions was realised only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents[1-10].

It has been well-recognised that the solvent water used its structural interactions with solute play a fundamental role in the observed thermodynamic properties of the solutions. It is quite obvious that the proper understanding of the structural interactions and their implications necessitate a thorough knowledge of the structure of water which can give more information regarding solute-solvent interactions in aqueous solutions.

The revolutionary theory of Bernal and Fowler[11] regarding the structure of water and the subsequent works paved the way for the proper understanding of the properties of water and aqueous solutions.

The current models of water-structure are divided into different categories[12].

(A) UNIFORMIST AVERAGE MODEL

(B) MIXTURE MODELS

- i) Broken-down ice-lattice model
- ii) Cluster models
- iii) Clathrate cage model.

(C) CONTINUUM MODEL

Unfortunately none of the models is capable of explaining fully and sometimes even partially the different thermodynamic, transport and volumetric properties in aqueous solutions. The proper understanding and the elaborate description of the structure of water is beyond the scope of the present dissertation.

However, the uniqueness of water as solvent has been questioned in recent years[13-15] and it has been realized that the studies in other solvent media (non-aqueous and mixed solvents) would be of great help in understanding different molecular interactions and a host of complicated phenomena. The determinations of thermodynamic and transport properties of different electrolytes in various solvents would provide important steps in elucidating the structural changes associated with the dissolution of electrolytes and non-electrolytes.

In solutions containing an electrolyte, there are broadly three-types of interactions viz.

- i) ion-ion interactions
- ii) ion-solvent interactions
- iii) solvent-solvent interactions.

The strength of their interactions decreases in the order : ion-ion interactions > ion-solvent interactions > solvent-solvent interactions. In dilute solutions, ion-ion interactions can be assumed to be absent whereas the ion-solvent and solvent-solvent interactions are inseparable and can be collectively called as ion-solvent interactions and their effects lead to the phenomena of 'solvation'.

Ion-solvent interactions are the 'controlling forces' in infinitely dilute solutions and manifest themselves in all thermodynamic and transport properties of electrolytes (like lowering of vapour pressure of solvents by solutes, ionic mobilities[16,17], variation of solubilities[18], standard electrode potentials[18], viscosity B-coefficients[19] etc.) generally obtained by extrapolation to infinite dilutions.

The researches of Harned and co-workers[8], Stokes, Bates, Robinson and co-workers[1,16,20-23], De Ligny and co-workers[24-29] Shedlovsky[30], Grunwald[31], Feakins et al[32-37], Franks[12,14,38], Hepler and co-workers[39-44], Lahiri and co-workers[45-54], Meck[55], Strehlow[56], Das, Kundu and co-workers[57-60] and others[61-67] inspired us to undertake further investigations in this direction.

A brief survey of the investigations in aqueous and mixed solvents and the problems associated with such studies are presented to highlight the importance of such studies.

Structural Properties of Aqueous and Mixed Solvents[5,6,12-15]

The most structured liquid is water, the structure of which has been thoroughly investigated. It is generally accepted that liquid water has the short range order of hydrogen bonded, tetrahedrally co-ordinated structure of slightly expanded ice, with interstitial cavities filled by monomeric water. That order is believed to persist on a time-scale of about 10^{-11} sec. Water and di and polyhydric alcohols have three-dimensional hydrogen-bonded structural net-works. Other amphiprotic solvents are associated via hydrogen bonds but they form either linear polymeric chains (simple alcohols or rings (HF)).

The structure of mixed solvents are more complex when small amounts (below 10 wt%) of alcohols, acetone, dioxane etc. are added to water, the water structure becomes actually reinforced, as in the case when non-polar solutes (solid, liquid or gaseous) are dissolved. Structure formation can be inferred from the maxima of properties like viscosities, Walden product and heats of solution, excess entropy of mixing etc. Additional quantities of the organic liquid, however, cause gradual destruction of water structure until a minima is reached somewhere in the vicinity of the equimolar region for the two components. A variety of physico-chemical properties such as the Gibbs free energy of mixing and the Hammett acidity functions, exhibit maxima or minima in the vicinity of that composition.

It is apparent that the effectiveness of a liquid solvent must be evaluated in terms of superimposition of its macroscopic parameters (dielectric constants, equilibrium constants) and the microscopic properties of the individual solvent molecules (dipole moment, quadrupole moment, polarizability, H-bonding, co-ordination ability) as well as structure.

These aspects have been reviewed briefly in the subsequent pages.

Studies on the Thermodynamic Properties of Electrolytes and Non-Electrolytes:

Extensive works on the determination of the thermodynamic properties of electrolytes in various solvents have been made. The works paved the way for a proper understanding of the different aspects of the ion-solvent interactions.

Solubility and Dissociation constants of Ligands in Mixed Solvents:

The relative solubilities of electrolytes in protic and dipolar aprotic solvents and in their aqueous mixtures are influenced by the extent of solvation of the ions, solvent-solvent interactions, and other specific effects, such as volume energy. Solubility products, and dissociation constants of salts in non aqueous solvents can give insights into ionic solvation. It is normally found that solubilities of salts do not lie in the order of the dielectric constants of the solvents, but depend more on specific interations. For the case when the solute is in equilibrium with its ions, $\Delta G = 0$ and the standard free energy of solution is given by

$$\Delta G^{o}_{Soln} = -RT \ln K_{sp} \qquad \ldots (1)$$

where K_{sp} is the solubility product (or the solubility in case of uncharged molecules).

The magnitude of the solvation energy and the solubility of a substance as well as the nature of the resulting solution are determined by the properties of the solute and the solvent. Free energies and entropies of solvation can be determined from solubility data[68] and this approach was used by Criss and Luksha[69] for some alkali-metal halides in N,N-dimethyl formamide. The free energies of formation of the salts were obtained from a combination of the standard free energies of solution and the free energies of formation of the crystalline salts[70,29]. In the solubility method, the dissociation constant for the reaction

$$HA \rightleftharpoons H^{+} + A^{-} \qquad \ldots (2a)$$

can be written as

$$K_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} \times \frac{\gamma_{\pm}^{2}}{\gamma_{HA}} \qquad \ldots (2b)$$

$$= \frac{C_{H^+}^{2}}{[C]_T - C_{H^+}} \times \gamma_{\pm}^{2} \qquad \cdots (2c)$$

where $[C]_T$ is the concentration of the saturated solution determined from its solubility and C_{H^+} is the concentration of $[H^+]$ in the saturated experimental solutions determined pH-metrically[71,72]. The mean molar activity coefficients of the ions at different concentrations in aqueous and mixed solvents can be determined using Davies[73] equation

$$-\log \gamma_{\pm} = AZ_{+}Z_{-}\sqrt{k}/(1+\sqrt{k}) - 0.2\,k \qquad \cdots (3)$$

and also from Debye-Huckel limiting law with appropriate A values in mixed solvents calculated from the dielectric constant data.

The Gibbs transfer energies of different electrolytes is given by the expression

$$\Delta G_t^{o} = 2.303\ RT\ \log \frac{K_{sp(w)}}{K_{sp(s)}} \qquad \cdots (4a)$$

where $K_{sp(w)}$ and $K_{sp(s)}$ represent the thermodynamic solubility products of the electrolyte in water and water-solvent mixtures respectively in which

$$K_{sp} = m_{M^+} \cdot m_{X^-} \cdot \gamma_{M^+} \cdot \gamma_{X^-} = S^2 \gamma_{\pm}^{2} \qquad \cdots (4b)$$

In equation (4b) M^+ and X^- stand for cation and anion, S and $\gamma_\pm$ represent the molal (molar) solubility and mean molal (molar) activity coefficient of the electrolyte respectively in saturated solution. The activity coefficient ($\gamma_\pm$) can be evaluated either from the extended Debye-Huckel equation or from the Davies equation.

The thermodynamic formulation for the dissociation constant of the acid-base equilibrium

$$A \rightleftharpoons B + H^+$$

on the molal scale is given by

$$K = \frac{m_{H^+} \times m_B}{m_A} \times \frac{\gamma_{H^+} \times \gamma_B}{\gamma_A} \qquad \ldots (5)$$

The numerical value is fixed by the choice of a standard state in which the activity coefficients are assigned values of unity. In aqueous solutions, the customary standard state is so chosen that γ_i approaches unity as m approaches zero.

When the compsotion of the solvent medium changes as well as the solute concentration (and ionic strength), it is convenient to separate each activity γ_i into factors $\gamma_i = m^{\gamma_i} \times s^{\gamma_i}$ [21,74-76] γ_i is measured relative to the standard state in pure water and become unity only in infinitely dilute aqueous solution. On the contrary, the activity coefficient s^{γ_i} in equation above becomes unity when m = 0 in the solvent s, where m^{γ_i} has a value different from unity whenever the solvent differs from pure water.

The 'salt effect' s^{γ_1} varies with the solute concentration. Simple Debye-Huckel equation with appropriate allowance for the effect of altering the dielectric constant of the medium s, can be used to estimate s^{γ_1} when ionic species are involved. The thermodynamic dissociation constant can also be determined in very dilute solution where $s^{\gamma_1} \longrightarrow 0$ and this is the best method for the determination of the thermodynamic dissociation constant as it involves no error in estimating s^{γ_1}.

The medium effect m^{γ_i} is a function of the free energy of the species 'i' in the two standard states.

$$\Delta G^o_t = {}_sG^o_1 - {}_wG^o_1 = RT \ln m^{\gamma_1} \qquad \cdots (6)$$

combining the electrostatic contribution to the free energy using Born equation,

$$\ln m\gamma_i = \frac{N Z_i^2 e^2}{2RTr}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right) \qquad \cdots (7)$$

and the mass law equation for equilibrium

$$S^K = W^K \times \frac{m\gamma_i}{m\gamma_{H^+} \times m\gamma_B} \qquad \cdots (7a)$$

where ${}_sK$ and ${}_wK$ are the dissociation constants for the standard states in solvent and water respectively.

We obtain

$$p({}_sK) - p({}_wK) = \frac{Ne^2}{4{\cdot}6052\,RT}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right) \times \left(\frac{Z_B^2}{r_B} - \frac{Z_A^2}{r_A} + \frac{1}{r_H}\right) \quad \cdots (8)$$

(charges on r_A etc. omitted)

The equation has been found to be fairly satisfactory for the dissociation equilibrium of the charge type A^oB^- (e.g. A^o = uncharged acetic acid, B^- = acetate anion, z_A = 0) and A^+B^o [21,70-78] (e.g. A^+ = anilinium cation, B^o = uncharged aniline, z_B = 0). There is evidence, however, that the pK of amines decreases when methanol is added to water, passes through a minimum at a solvent composition in the 60-80% (wt. percent) of methanol[22d,79].

Physico-Chemical Properties and Ion-Solvent Interactions:

Extensive studies on the physical properties of the solvent systems have been made but a lamentable gap still exists; several classifications of organic solvent systems based on their dielectric constants, organic group type, acid-base properties or association with hydrogen bonding, donor-acceptor properties, hard and soft acid-base principles etc. have been made. The properties of the different solvent systems have been found to show wide structural modifications with the addition of electrolytes and non-electrolytes.

Naturally for the development of theories dealing with electrolytic solutions, much attention has been devoted to ion (solute) - solvent interactions. However, it is difficult to suggest quantitatively sometimes even qualitatively the forces or factors involved in the solute (ion) - solvent interactions.

Theoretical Predictions of Solvation Energies of Ions:

Various models have been proposed to predict theoretically the thermodynamic and other behaviours of electrolytes in solution[2,3,11-15].

Classical Model : In Born's continuum model[67] the ions are represented as charged incompressible hard-spheres and the solvent is considered as a structureless dielectric continuum with dielectric constant and unaffected even in presence of ionic fields. The free energy of solvation is equivalent to the difference in the electrostatic energy of a gaseous ion and that of an ion in the medium of dielectric constant.

Various modifications of the model is proposed.

Structural Model of Frank and Wen[80]:

Frank and Wen proposed that surrounding a solute molecule there are three regions that can be fairly well distinguished from each other.

Primary solvation zone around the solute molecule, where there is enhancement of solvent structure, the nature of enhancement is different for polar and non-polar molecules. Ions usually form ice-like structure in the primary zone where the secondary zone is a discorded zone arising from the opposing effects of the ion and of the surrounding solvent molecules. The third region comprises the essentially unperturbed solvent molecule. The model is simple and provide useful insight into the nature of solvation but not successful for the quantitative prediction of the solvation energy of electrolytes.

Molecular Models:

Following the classical theory of water structure by Bernel and Fowler[11,12,80-86], various molecular approaches[12,80-86] have been made to predict the nature of the solvation of ions. Several contributions are considered:

i) formation of cavity in the solvent
ii) strong interaction between the ion and the solvent molecules of the first (even second) coordination shell.
iii) interaction between the solvent molecules in the co-ordination shell,
iv) weaker interactions between the hydration complex and the rest of the solvent molecules.
v) further changes in the structure of water.

However, it is difficult to calculate the interactions identified above in view of the uncertainty in the true ionic radii, in the co-ordination number of the ions and in the orientation of the solvent molecules in the co-ordination shell. In view of the continuous exchange of solvent molecules in the co-ordination shell and free solvent molecules, a time average process is usually taken. The solvent molecules[82] may be considered as a sphere containing a certain number of point charges or the solvent molecule may be characterized by its radius, dielectric constant, polarisability, dipole and quadrupole moments.

Hamiltonian Models[83]:

In these models, the medium is represented by an assembly of a large number of identical particles representing the solvent molecules. The statistical model is highly complex and mathematical However, the possibility of accurate evaluation of the thermodynamic properties from such a model is too much complicated and difficult .

Hybrid Models:

A number of hybrid models have been proposed which combine more than one of the above concepts for solving some particular parts of the problem by one model and some other by a different model. In such models, the interaction of an ion and its first nearest neighbour solvent molecules (primary solvation sheath) is calculated in terms of inter-molecular forces (like a Hamiltonian model) while the interaction of this complex with the remaining solvent is calculated as in the theory of the Born model. Some of the models are due to Muirhead-Gould-Laidler[84], Bockris and Sahija[85,86], Goldman and Bates[87] etc. But none of the models are capable of giving the reliable information regarding the ion-solvent interactions, thermodynamic parameters and the solvation phenomena.

Sen[88] considers that the continuum theory is capable of an accurate description of the thermodynamic properties of electrolytes when allowance is made for proper standard states and structural properties of ion-solvent interactions.

Solvation and The Free-Energy of Transfer of Single-Ions:

The transfer of solutes from one solvent to another usually lead to enormous changes in both equilibrium and rate constants of chemical reactions (as manifested in the variation of solubility of a solute as a function of solvent).

The usefulness of thermodynamic transfer functions for electrolytes is rather limited. The experimental methods yield the transfer thermodynamic changes of neutral electrolytes but offer no means of separating them into single-ion characteristics.

According to Strehlow[56] "division of thermodynamic functions of electrolytes into single ion values may reveal correlation between measurable but from a thermodynamic point of view unrelated quantities".

Various theoretical and semiempirical extra thermodynamic attempts[89-95] have been made to obtain single-ion thermodynamics with moderate success. This aspect has been reviewed in details[95-100].

Obviously, it is a contentious subject and the validity of single-ion values can be questioned but the most important questions in solution chemistry is supposed to lie in the knowledge of transfer free energy changes for single ions[15].

The free-energy changes associated with the transfer of a chemical entity (HX) from solvent (1, say water) to solvent (2, say S) is known as "total medium effect"[101] (ΔG_t) which is splitted into primary medium effect or 'medium effect' and secondary medium effect or 'salt effect' as exemplified from the consideration of the cell of the type

$$Pt(H_2) \mid HX(m)\ \text{solvent} \mid AgX - Ag$$

The measurement of e.m.f. of cells of the type in two different solvents namely water (W) and solvent (S) gives the total medium effect of any electro-neutral combination HX.

$$\Delta G_t = \Delta G_t^o + 2\ RT\ \ln\ s^{\gamma_\pm} / w^{\gamma_\pm}$$

$$= \Delta G_t^o + 2\ RT\ \ln\ m^{\gamma_\pm} \qquad \cdots (9)$$

$\Delta G_t^o = -ZF\ ({}^{s}E^{o} - {}^{w}E^{o})$ is the primary medium effect and measures ion-solvent interactions, whereas the logarithmic term is known as secondary medium effect denoting ion-ion interactions and solvation.

The 'medium effect' log m^{γ_i} of an ion is the reversible work of transfer of one mole of ion i from the standard state in solvent 1 (water) to the standard state in solvent 2(s) by the expression

$$\log(m^{\gamma_i}) = \frac{{}_s\mu_i^\circ - {}_W\mu_i^\circ}{RT} \qquad \cdots (10)$$

Obviously, the primary medium effect is independent of molality but the exact value of 'medium effect' could only be determined in absence of appreciable concentrations of electrolytes which changes not only the structure of the solvent molecules but also the solvent concentration due to the solvation of ions. The secondary medium effect (salt effect) is a function of solute-concentration and can be determined with the help of theoretical equations like Debye-Huckel[92] or Davies[93] equations with appropriate values of A and B arising from the changed values of dielectric constants of the solvents. The equation fails at higher concentrations. Thus, it is desirable to work in dilute solutions so that ${}_s\gamma_i \rightarrow 0$ and the measurements account for the 'primary medium effect' only.

Determination of the Medium Effect

Thermodynamic properties of single ions in aqueous and non-aqueous solvents and thermodynamics of transfer have been presented by a number of workers[102-117].

The medium effect or the standard free energy of transfer of an electrolyte on neutral species from water to a given solvent has exact thermodynamic singificance and can be calculated from suitable experimental data without any assumptions. Generally, two methods are employed to determine medium effects of various substances. They are (1) solubility method and (2) Electrochemical methods. For weak electrolytes, spectrophotometric methods are also used to determine the medium effects.

The determination of 'medium effect' of H^+ ions ($\log {}_m\gamma_{H^+}$) evoked considerable interest as it determined directly the relative basicities of two solvents and can be obtained from the direct measurement of the cell

$$H_2(Pt) \,\Big|\, a_{H^+} = 1 \,\Big\vdots\, a_{H^+} = 1 \,\Big|\, H_2\ (Pt)$$

where $E = \frac{RT}{F} \ln {}_m\gamma_{H^+} + E \ln J.$

In view of the limitations of having liquid junction potential of uncertain magnitude, the 'medium effect' of proton, first determined by Bjerrum and Larsson[118] from e.m.f. measurements can be neglected.

The systematic efforts to determine the 'medium effect' are given as what follows.

Models Based on Modification of Born Equation

The 'medium effect' of an ion can be obtained from the simple Born equation

$$\log {}_m\gamma_i = \frac{N z_i^2 e^2}{2\,RT\,r_i}\left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_W}\right) \quad \cdots(11)$$

It is to be noted that solvent molecules become inhomogeneous due to strong influence of solute molecules near the solvent molecules. Two extreme cases are : (a) dielectric saturation in the vicinity of ions[119] in case of electrolytic solutions, and (b) formation of a clathrate by water molecules in the vicinity of a non-polar solute due to hydrophobic bonding effects in case of non-electrolytic solute.

The equation consists of two variable parameters like radius and dielectric constant. Refinements are based on (1) Increase in crystallographic radii due to solvation.

The model is due to Voet[120] and successfully applied by Latimer[121-122] et al, Strehlow[123] and co-workers and Coetzee et al[124-125] in non-aqueous solvents where ionic radii are adjusted to account for the differences between the free energies of transfer of pairs of alkali metal ions

$$\Delta G_t^{\circ} = \left({}_S G_t^{\circ} - {}_W G_t^{\circ}\right)$$

$$= \frac{N z^2 e^2}{2}\left[\frac{1-\frac{1}{\epsilon_S}}{r_+ + R_+(s)} - \frac{1-\frac{1}{\epsilon_W}}{r_+ + R_+(W)}\right] \quad \cdots(12)$$

However, the equation lacks theoretical significance and is restricted to differences between very similar cations and similar solvents.

(2) Dielectric saturation in the vicinity of the ion reducing the effective dielectric constant of the solvent[119,126-131].

This aspect has been dealt extensively by Noyes[119] Hepler et al, Stokes and others.

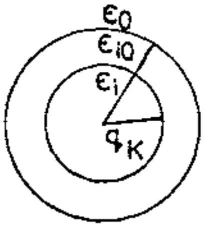
It is likely that partial or complete solvation of ions by other non-aqueous solvents may occur leading to changed values of r, $\epsilon_{sat.}$ and ΔG_t^o. The equation of Stokes should, therefore, be restricted to water rich solvents. The equations were utilised by Bates and co-workers[1,22] to calculate ΔG_{el}^o values and the basicities of different methanol + water mixtures.

All the treatments consider the interactions of the ions with solvents to be predominantly electrostatic and neglect specific solute-solvent interactions and non-specific 'neutral' component of the solvation energies of ions. Complete understanding requires the knowledge of ion-dipole, ion - (induced) dipole, ion-quadrupole, dipole-dipole and London dispersion forces which are functions of r^{-2}, r^{-4}, r^{-3}, r^{-5} and r^{-6} in that order where r is the corresponding interaction distance which contains the ionic radius term but not always equal to it[132-133]. The reliable quantitative calculation of hydrational and solvational energies are thus very difficult.

Goldman and Bates[134] used an electrostatic model to calculate ΔG° ($\Delta G^\circ = \Delta G^\circ_{el} + \Delta G^\circ_{neut.}$), ΔH° and ΔS° associated with the transfer of seventeen ions from the gaseous phase to water at 25°C. However, the model has not been extended to calculate the thermodynamic properties of transfer in other solvents.

A rigorous theoretical approach has been given by Padova[95,135,136] utilising the fundamental equation for the free energy of a dielectric continuum in an electrostatic field.

Beveridge and Schnuelle[137,138] gave a general expression for the free energy of an arbitrary charge distribution embedded in a spherical cavity surrounded by two dielectric continuum, an extension of Kirkwood's[139] treatment of reaction potential



The model has been extended to give a complete general solution for the electrostatic free energy of an ion surrounded by any number of layers, each with a given relative permittivity, immersed in the bulk solvent.

The equations are written as

(i) Born Model (zero layer)

$$\Delta G^\circ_{el} = \frac{z^2}{2}\left(\frac{1}{\epsilon_0^{a}} - \frac{1}{a}\right) \qquad \cdots (13)$$

(ii) The one layer model (first layer $r = b$ & $\epsilon = \epsilon_1$)

$$\Delta G^{o}_{i(el)1} = \frac{z^2}{2}\left[\frac{1}{\epsilon_i}\left(\frac{1}{a}-\frac{1}{b}\right)+\frac{1}{\epsilon_o^{b}}-\frac{1}{a}\right] \qquad \cdots (13A)$$

(iii) The two layer model (first layer $r = b$ and $\epsilon = \epsilon_i$,
second layer $r = c$ and $\epsilon = \epsilon_m$)

$$\Delta G^{o}_{el(2)} = \frac{z^2}{2}\left[\frac{1}{\epsilon_m}\left(\frac{1}{b}-\frac{1}{c}\right)+\frac{1}{\epsilon_i}\left(\frac{1}{a}-\frac{1}{b}\right)+\frac{1}{\epsilon_o^{c}}-\frac{1}{a}\right] \qquad \cdots (14)$$

where $\epsilon_i = n^2$ and $b = a + R$ for the first layer in both the one-layer and two-layer models (R = radius of the solvent molecule).

The values of 'a' have been taken from ionic crystal radii of Goldschmidt and Pauling, where available, or calculated from liquid molar volumes $\bar{V}$ of solutes using the Stearn-Eyring formula[140], $r = (\bar{V}/8n)^{1/3}$. The radius of solvent molecules have also been calculated using Stearn-Eyring formula[140].

Good agreement has been claimed by Abraham et al[115,141-142] between the theoretical and experimental results for ionic solvation using this model.

<u>Methods Based on Measurement of Oxidation - Reduction Potential and the E.M.F. of Different Cells:</u>

The search of a suitable reference electrode having the same e.m.f. value in all solvents thus appears imperative. Pleskov[143] proposed that the potential of Rb/Rb^+ couple, should be equal in all solvents, because of low polarizability and large radius of ions. However, both electrostatic considerations and experimental free energy of transfer values of halides (having larger radii), Rb^+ and Cs^+ in different solvents point the inherent limitations of the assumption. Strehlow and co-workers[56,123,144] made appropriate allowances for the changed dielectric constants in different solvents and for the residual electrostatic free energy terms and developed a modified Rb-scale which was utilised by Coetzee et al[145] for measurements of polarographic half wave potentials of a series of cations present as perchlorates in seven solvents.

Koepp, Wendt and Strehlow[56,123,144] (also studied by Kuwana[146] et al) selected the redox systems of large symmetrical complexes Ferricinium/Ferrocene and Cobalticinium/Cobaltocene, having very little residual charges on the surface, so that the standard e.m.f. of the Fic/Foc or Cic/Coc i.e., $\Delta G_t^o(\mathrm{Foc}) - \Delta G_t^o(\mathrm{Fic})$ can be regarded to be solvent independent. Thus, the measurement of standard oxidation potentials in water and solvents gives the value of $\Delta G_t^o(\mathrm{H}) - \Delta G_t^o(\mathrm{Fic}) + \Delta G_t^o(\mathrm{Foc})$.

According to Strehlow[56]

$$\Delta G_t^o(\mathrm{Fic}) - \Delta G_t^o(\mathrm{Foc}) = \frac{N z^2 e^2}{2}\left[\left(\frac{1-\frac{1}{\epsilon_1}}{r+a_1}\right)-\left(\frac{1-\frac{1}{\epsilon_2}}{r+a_2}\right)\right] \quad \cdots (15)$$

where, a_1 and a_2 are constants, specific for the solvents in question. Strehlow[56] used $a_1 = 0.85$, $0.72 \leq a_2 \leq 0.90$ based on the data of alkali metal ions. In addition to the inherent limitations due to liquid-junction potentials, the contributions due to surface potentials in measuring the real free energies of transfer have been neglected[24].

In spite of the limitations, the method seems to be one of the most useful method for the determination of the 'medium effect' of single ions and widely used by De Ligny and co-workers.[24-29] They used the cell of the type

$$\mathrm{Pt(H_2)}\;\left|\;\begin{array}{l}\mathrm{HClO_4}\text{ in water or}\\ \text{solvents respectively}\end{array}\;\right|\;\mathrm{KCl(satd.)}\text{ in }\mathrm{H_2O}\;\left|\;\mathrm{Hg_2Cl_2 - Hg}\right.$$

and

$$\mathrm{Pt}\;\left|\;\begin{array}{l}\text{Ferrocene}(m_2),\\ \text{Ferricinium in}\\ \text{water or solvents}\\ \text{respectively}\end{array}\;\right|\;\mathrm{KCl(satd)}\text{ in }\mathrm{H_2O}\;\left|\;\mathrm{Hg_2Cl_2 - Hg}\right.$$

to get

$$E^\circ_S(\mathrm{Fic}) - E^\circ_W(\mathrm{Fic}) = -\frac{1}{F}\left[\Delta G^\circ_t(\mathrm{H}) - \Delta G^\circ_t(\mathrm{Fic}) + \Delta G^\circ_t(\mathrm{Foc})\right]$$

$$= -\frac{1}{F}\left[\Delta G^\circ_t(\mathrm{H}) - \Delta G^\circ_t(\mathrm{Fic}) + \Delta G^\circ_t(\text{neut. Fic})\right] \qquad \cdots (16)$$

Due to low solubility of ferrocene and instability of ferricinium in water the E^o has been calculated from the polarographic half-wave potential of the process $Foc \rightleftharpoons Fic^+ + e$. The reaction $Foc \rightleftharpoons Fic^+ + e$ has been proved to be diffusion controlled and the ratio of diffusion constants of ferrocene and the ferricinium ion appeared to be independent of solvent composition. The method has been used to determine the ΔG_t^o of H^+ ion and other ions in different solvents. The method has been used by Kalidas et al[147] to measure $\Delta G_t^o (H^+)$ in different methanol-water, propylene glycol-water and methanol-propylene glycol mixtures.

However, the presence of considerable amount of indifferent electrolytes should change the solvent structure, E^o-values and thus the medium effects. The diffusion constants of ferrocene and ferricinium ions may also be unequal. It has been shown by Alfenaar et al[148] that the contribution of the solvent molecules to the diffusion potential can not be neglected and is a function of solvent composition and the nature of electrolyte. The primary medium effect is the most important contribution to the diffusion potential. The diffusion potential between electrolyte solutions in methanol-water mixtures can not be suppressed by salt-bridge. Ferrocene may have residual electrostatic component of the ion[96] and specific interactions of the redox couple with water and other solvents are also known[124]. There may be uncertainties in the crystal radii of ferrocene[24] (3.8A°) and ferricinium[28] (3.3A°) ions.

Some other redox couples were also studied with relatively little success. The couples are ferrocene/ferrocinium picrate, ferroin/ferriin couple[149], 4,7-dimethyl ferroin/4,7-dimethyl ferriin couple[150], bis diphenyl chromium (0.1) couple[151-152] with relatively little success.

Parker and co-workers[102-106,153,154] feel that the ferrocene assumption is not valid when water is one of the solvents. Parker and Alexander recommended the cells of the type

$$\begin{array}{l|l||l||l|l} \mathrm{Ag(S)} & \mathrm{AgNO_3,\ 0.01M} & \text{Satd.} & \mathrm{AgNO_3,\ 0.01\ M} & \mathrm{Ag} \\ & \text{in } \mathrm{CH_3OH} & \mathrm{NEt_4,Pic} & \text{in solvents} & \end{array}$$

$$\begin{array}{l|l|l|l|l} \mathrm{Ag(S)} & \mathrm{AgClO_4,\ 0.01\ M} & \mathrm{0.01\ M\ NEt_4Pic} & \mathrm{AgClO_4,0.01M} & \mathrm{Ag} \\ & \text{solvents} & \text{in solvent} & \text{in solvent O} & \\ & & \text{S or O} & & \end{array}$$

to determine medium effects. The bridge electrolyte contains tetraethylammonium picrate having large and comparable anion and cation size with no specific interactions with the solvents, as apparent from roughly equal molar conductances in all solvents studied. Thus the liquid-junction potential E_J can be neglected.

Parker and co-workers[153,154] also measured the potential of fic/foc couple against the Ag^+/Ag electrode in fifteen solvents using the cell

$$\begin{array}{l|l|l|l|l} \mathrm{Ag} & \mathrm{0.01M\ AgClO_4} & \mathrm{(NEt_4)ClO_4,0.01M} & \mathrm{0.002M\ Fic/Foc} & \mathrm{Pt(G)} \\ & \mathrm{(NEt_4)ClO_4} & \text{solvents} & \mathrm{0.02M(NEt_4)ClO_4} & \\ & \text{in solvents S} & & \text{in solvent S} & \end{array}$$

Thus the values based on the ferrocene assumption can be readily converted to the negligible E_j assumption.

However, the suppression of E_j by means of a salt bridge is impossible as the liquid-junction potential E_j at an interface of two different media is itself primarily a function of the medium effects for the single ion transported across it[148].

Extrapolation Methods:

The extrapolation method has its origin in the works of Izmaylov[155,157] who assumed G^{o} or an infinitely large ion to be zero and all significant components of the solvation energy G^{o} of an ion are functions of $1/r^{n}$ (r = crystallographic radius, $n = 1$–4 or 6). He plotted thermodynamically allowed combinations like $(G^{o}_{M} - G^{o}_{H})$ vs $1/r_{M}$ and $-(G^{o}_{H} + G^{o}_{X})$ vs $1/r_{X}$ (M = alkali metal ions, X = halide ions) and used extrapolations to get $-G^{o}_{H}$ at $(1/r) = 0$. The plot of $\left[-G^{o}_{H} + \left(\frac{G^{o}_{M} - G^{o}_{X}}{2}\right)\right]$ vs $1/r_{av} = \frac{1}{2} \times \left(\frac{1}{r_{M}} + \frac{1}{r_{X}}\right)$ improves the value of G^{o}_{H}. Izmaylov[155-157] also considered solvation of ions as complex formation between solvent molecules (donors) and ions with vacant orbitals as acceptors.

He determined the solvation energies of anions and cations from the plots of $(G^{o}_{M} + G^{o}_{X})$ vs $1/n^{2}$, $(G^{o}_{M} - G^{o}_{H})$ vs $1/n^{2}$ and $\left[-G^{o}_{1} + \frac{G^{o}_{M} - G^{o}_{X}}{2}\right]$ vs $1/n^{2}$, ($n = 3,4,5$ etc) for different isoelectric pairs like (Na^{+}, F^{-}), (K^{+}, Cl^{-}), (Rb^{+}, Br^{-}) and (Cs^{+}, I^{-}) where n is the principal quantum number of the lowest vacant orbital of the ion. He considered the second method to be more reliable. However, Izmaylov's assumption that $\Delta G^{o}(\text{neut})$ account for 1-2% of the total solvation energy was found to be erroneous from the estimates of $\Delta G^{o}_{\text{neut}}$ via inert gas assumption or experimental determination of $\Delta G^{o}_{\text{neut.}}$. Moreover, the calculations of Izmaylov were dependent on the large errors involved in the determination of the dissociation energies of molecular hydrogen, the sublimation energies of the metal and of atomic hydrogen in the gas phase and crystal lattice energies of silver halides. The extrapolations are non-linear and generally based on three points. Therefore, in the determination of ΔG^{o}_{t} or 'medium effect' large errors are expected.

Feakins and their associates[32-37,158-159] used the e.m.f. methods to determine the ΔG^{o}_{t} (free energies of transfer from water to different solvents) values of HCl, HBr and HI on one hand and LiCl, NaCl and KCl on the other and utilized the extrapolations

$$\Delta G^{o}_{t}\ (HX) = \Delta G^{o}_{t}(H^{+}) + a r_{X}^{-1} \qquad \cdots (17)$$

$$\text{and}\ \ \Delta G^{o}_{t}(MCl) = \Delta G^{o}_{t}(Cl^{-}) + b r_{M}^{-1} \qquad \cdots (18)$$

$$\text{to get, } \Delta G^{o}_{t}(H^{+})\ \text{at}\ \frac{1}{r_{X}} = 0\ \text{and} \qquad \cdots (19)$$

$$\Delta G^{o}_{t}(Cl^{-})\ \text{at}\ \frac{1}{r_{M}} = 0 \qquad \cdots (19a)$$

Cations are found to be in lower free energy states in the mixed solvents compared to water, while the anions show the reverse trend. However, linearity is poor in most cases due to incomplete compensation of ΔH_t and $T\Delta S_t$ terms which are complex functions of radius and the estimates based on the dependence of 1/r appear to be over simplification, the major contributions to free energy of solvation arises from ion-dipole interaction term $ze\mu/r^2$ in addition to Born charging energy beyond the solvation shell[160]. Inconsistent values of $\Delta G_t^o(MCl)$ vs. $1/r_M$ and $\Delta G_t^o(HX)$ vs. $1/r_X$ and other inconsistencies are also noted. Das and co-workers[57] suggested the 'simultaneous extrapolation' to $(r_X)^{-1} = 0$ of the plots of $\Delta G_t^o(HX)$ and $\Delta G_t^o(HCl-HX)$ i.e. $\Delta G_t^o(Cl^- - X^-)$ against $(r_X)^{-1}$ suitably aimed at having least discrepancies in the extrapolated values of $\Delta G_t^o(H^+) - 2.303\ RT\log\frac{M_s}{M_w}$ and $\Delta G_t^o(Cl^-) + 2.303\ RT\log\frac{M_s}{M_w}$ with respect to the experimental values of $\Delta G_t^o(HCl)$ would lead to extra confidence to the extrapolation (error = ± 0.1 to 0.2 K cal/ion).

The extrapolation method has been extensively used by Kundu and co-workers to determine the free energy of transfer of ions in various solvents.

However, it has been recognized that the solvation energy of an ion is composed of an electrostatic part ΔG_{el}^o and a neutral part $\Delta G_{neut.}^o$ i.e.

$$\Delta G_t^o = \Delta G_{el}^o + \Delta G_{neut.}^o \qquad \cdots (20)$$

The method has been elegantly put forward by Alfenaar and De Ligny and more recently by Kim[161], Abraham and Liszi[115].

In view of the difficulty in calculating $\Delta G^{o}_{neut.}$, Alfenaar and De Ligny took $\Delta G^{o}_{neut.}$ of very large ions to be equal to $\Delta G^{o}_{neut.}$ of the corresponding uncharged particle of equal radius but for small ions, a difference arises from the changed solvent structure around the ions of the solvent molecule.

The free energy of transfer of ions between two solvents including ion-ion, ion-dipole, ion-quadrupole interactions etc. is given by,

$$\Delta G^{o}_{i}\ (\text{ion}) = \Delta G^{o}_{neut.} + \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r3} + \cdots\cdots \qquad \ldots(21)$$

The free energy of transfer of electro-neutral combinations of ions have been divided by Alfenaar and De Ligny into the contributions of the individual ions M and A as follows:

$$\Delta G^{o}_{t}\ (\text{HA}) - \Delta G^{o}_{t,neut.}(A^-) = \Delta G^{o}_{t}(H^+) + \frac{a}{r_A} + \frac{b}{r^2_A} + \frac{c}{r^3_A} \qquad \ldots(22)$$

$$\Delta G^{o}_{t}(H^+) - G^{o}_{t}(M^+) + \Delta G^{o}_{t,neut,M^+}$$
$$= \Delta G^{o}_{t,H^+} - \frac{a}{r_M} + \frac{d}{r^2_M} + \frac{e}{r^3_M} \qquad \ldots(23)$$

The values of the left hand sides can be determined experimentally. 'a' is calculated using the Born equation from the slope at $\frac{1}{r} = 0$, and $\Delta G^{o}_{t}(H^+)$, b,c etc. can be estimated by the method of least square.

When the left hand side of the two equations (22) and (23) are plotted against $\frac{1}{r}$, two curves will have a common intercept $\Delta G^{o}_{t(H^{+})}$. The larger the ions, the greater is the accuracy of the results.

The extrapolations, however, are non-linear. The contributions of $\Delta G^{o}_{t(\text{neut})}$ appear to be considerable and the reliability of the determination of $\Delta G^{o}_{t(\text{neut})}$ via 'inert gas assumption' has not been proved.

De Ligny and co-workers latter slightly modified the method by incorporating ideas of Buckingham[82], Halliwell and Nyburg[162] and Muirhead-Gould and Laidler[84].

Salomon[163-166] determined the individual free energies of solvation from plot of differences in conventional free energies vs. $\frac{1}{r_1}$ where r_1 is the gas-phase radius of Gouray and Adrian[98]. $\Delta G^{o}_{\text{solv.}}(H^{+})$ is obtained from

$$\left[\Delta G^{o}_{\text{conv.}}(M^{+}) - \Delta G^{o}_{\text{conv.}}(X^{-})\right] = \frac{\text{Constant}}{r_1} - 2\Delta G^{o}_{\text{solv.}}(H^{+}) \qquad \cdots (24)$$

$$\left[\begin{aligned} \Delta G^{o}_{\text{conv.}}(M^{+}) &= \Delta G^{o}_{\text{solv.}}(M^{+}) - \Delta G^{o}_{\text{solv.}}(H^{+}) \\ \Delta G^{o}_{\text{conv}}(X^{-}) &= \Delta G^{o}_{\text{solv.}}(X^{-}) + \Delta G^{o}_{\text{solv.}}(H^{+}) \end{aligned}\right]$$

M^{+} and X^{-} are ions of equal charge and radius.

It is known that the enthalpy and entropy terms are complex functions of r, but due to compensation of the enthalpy and entropy of solvation, the free energy term is relatively independent of terms higher than r^{-1} . $\Delta G^{o}_{solv\ (H^{+})}$ is found to be -235.0 K cal/mole.

Since $\Delta G^{o}_{neut.}$ is dependent on ionic radius, the choice of crystal radii as determined by different workers are noted. Criss and Salomon[98] considered it desirable to take differences in $\Delta G^{o}_{t,conv.}$(ion) which automatically cancels $\Delta G^{o}_{t,neut.}$ for anions and cations of equal charge and radius. The choice of crystal radius thus becomes less important.

Method Based on 'Reference Electrolytes'

The most widely recommended and promising approach to the estimation of 'medium effects' for single ions (and also for the estimation of partial molar volume), the solvation enthalpies and other thermodynamic properties of single ions) are those based on 'reference electrolytes'. The reference electrolytes[15,96,167-172] should be composed of large symmetrical counter ions of equal size and solvation properties, so that the 'medium effects' should be equally divided between the cations and anions. The central atom and the charge of such counter ions should be shielded by large organic residues to minimize both the charge density and specific interactions with the solvent.

Grunwald[172] et al proposed Tetraphenyl phosphonium tetraphenyl borate (Ph_4PBPh_4) as the reference electrolyte.

Popovych[96] proposed tri-isoamyl-n-butyl ammonium tetraphenyl borate ($TABBPh_4$) as reference electrolyte based on the equqlity of the Stokes[173-175] radii of ions in water, methanol + acetonitrile. Tetraphenyl arsonium tetraphenyl borate [TATB i.e. Ph_4AsBPh_4] has been proposed by Parker and co-workers.

Because of their low solubility in different solvents, reference electrolytes are suitable for determining free energies of solvation without uncertain activity corrections.

The limitations of the method can be summarised as follows:

1) The results are based on solubility data and errors may arise from the possible[98]

   a) formation of crystal solvates

   b) micelle formation

   c) formation of complex ions

   d) ion-pair formation.

2) Insufficient evidence or so direct experimental evidence for the equality of radii of counter ions.

3) Approximate equality of Stokes' radii or calculated radii from models are not real indices of ion-sizes or imply a direct correlation between transport or thermodynamic properties. Dielectric relaxation, size of secondary solvation effects must be taken into account to determine free energies of solvation[95].

4) The method should not be applied to dipolar aprotic solvent, which differentiates strongly between the relative solvation of anions and cations[124].

Inspite of the defects, the results obtained with $TABBPh_4$ of Popovych and co-workers and with Ph_4AsBPh_4 assumption of Alexander and Parker are in good agreement. Discrepancies between two methods arises from Parker's use of formal solubility product rather than thermodynamic ion activity product used by Popovych[96].

Recently, Kim[161] after a critical and extensive study strongly recommends Ph_4AsBPh_4 as 'reference electrolyte' to calculate single ion thermodynamics.

However, Treiner[176] examined the Ph_4AsBPh_4 assumption through the use of scaled particle theory outlined by Pierotti[177] to deduce that the assumption was not valid for transfer between water, propylene carbonate, sulpholane, DMSO, N-Me-2-pyrrolidone and perhaps also dimethyl formamide, a conclusion different from the observations of Parker et al and Abraham et al. Abraham and Nasehzadeh[178] however, pointed out the limitations of the scaled particle theory in the calculations of the free energies of transfer.

Other Methods :

(a) Method of Wells[66]

The $\Delta G_t^o(H^+)$ values, as calculated by Wells for different aquo-organic solvents, involve the use of the equation

$$\Delta G_t^o(H^+) = \Delta G_t^o(H^+)_e + \Delta G_t^o(ROH_2^+) \qquad \cdots (25)$$

$\Delta G_t^o(H^+)_e$ has been calculated by the application of Born equation to the transfer of a sphere containing the tetrahedral structure $H_3O^+(H_2O)_4$

$$\Delta G_t^o(H^+)_e = \frac{Ne^2}{6\, r_{H_2O}} \left(\epsilon_s^{-1} - \epsilon_w^{-1} \right) \qquad \cdots (26)$$

The major contribution is from $\Delta G_t^o(ROH_2^+)$, which covers all subsequent structural changes induced by the presence of the tetrahedral $H_3O^+(H_2O)_4$ in the mixed solvent. $\Delta G_t^o(ROH_2^+)$ has been calculated from the equilibrium constant K of the solvent sorting equilibrium.

$$(H_2O)_X H^+_{solv} + ROH_{solv} \underset{}{\overset{K}{\rightleftharpoons}} \left[(H_2O)_{X-1} ROH\right] H^+_{solv} + H_2O_{solv} \cdots (27)$$

The method has been criticised by Lahiri[50-53] and recently by Blandamer et al.

(b) Method of Lahiri and co-workers[50-53]:

Lahiri and co-workers have recently suggested a method for the determination of $\Delta G_t^o(H^+)$, using the dissociation constants of the 'isoelectric reactions'

$$LH^+ \rightleftharpoons L + H^+ \qquad \cdots (28)$$

[Where L = 2,2'-dipyridyl or 1, 10-Phenanthroline] as follows

$$\Delta G_t^o = -2.303\ RT \log \left(\frac{C_s}{C_w} \right) \qquad \cdots (29)$$

$$\Delta\Delta G_t^o = \Delta G_t^o(L) + \Delta G_t^o(H^+) - \Delta G_t^o(LH^+)$$
$$\approx \Delta G_t^o(L) + \Delta G_t^o(H^+) - \left[\Delta G_t^o(L) + \Delta G_{t,el}^o(LH^+)\right] \quad \cdots (30)$$

$$\text{or } \Delta G_t^o(H^+) = \Delta\Delta G_t^o + \Delta G_{t,el}^o(LH^+) \quad \cdots (31)$$

$\Delta G_{t,el}^o$ (LH^+) has been calculated using Born equation.

The utility of the method lies in the fact that we can work in very dilute solutions so that 'salt effects' can be estimated and the solutions are in their respective standard states, a condition essential for the determination 'medium effects' of ions. The $\Delta G_t^o(H^+)$ values calculated by this method have been found to be in close agreement with the values obtained using the 'reference electrolyte' method.

The method is simple and can be utilised over the whole composition range of aquo + organic solvent mixtures.

In the present dissertation the $\Delta G_t^o(H^+)$ values were calculated by this method and also utilised to determine the 'medium effect' of other ions.

(c) Method of Grunwald[172] :

For the ionisation of acids HA (aliphatic acids, benzoic acid) and BH^+ (anilinium ion, toludinium ions etc) in alcohol + water mixtures and water, we have

$$(pK_s - pK_w)_{HA} = \log Y_{H^+} + \log \frac{Y_A^-}{Y_{HA}}$$

$$= \log Y_{H^+} + m_A Y^- \qquad \cdots (32)$$

$$\text{and} \quad (pK_s - pK_w)_{BH^+} = \log Y_{H^+} + m_B Y^o \qquad \cdots (32a)$$

where m_A and m_B are substituent constants independent of the nature of the solvent, Y^- and Y^o are the solvent parameters dependent on the solvent only.

$$Y^- = (1 - W^2) \qquad \cdots (33)$$

$$\text{and} \quad Y^o = (1 - W)^2 \qquad \cdots (34)$$

(W = weight fraction of water in the solvent)

Now,

$$(pK_s - pK_w)_{HA} - (pK_s - pK_w)_{BH^+} = m_A Y^- - m_B Y^o \qquad \cdots (35)$$

m_A and m_B are determined by multi-regression method which enables one to calculate $\log Y_{H^+}$.

The method, however, is of little value due to the inherent limitations regarding the assumptions of m_A, Y as pointed out by Wynne-Jones[179], Popovych[168] and Maity and Lahiri[49].

Kundu and co-workers[57] recently compared the different methods and found that 'extrapolation method' always give more negative values of ΔG_t^o(ions). The 'reference electrolyte' method has been advocated to be the best method though the limitations are known. The $\Delta G_t^o(H^+)$ values in ethanol + water mixtures determined by Lahiri and co-workers show qualitative and almost quantitative agreement with the values determined using 'reference electrolyte' method.

Recently, Lahiri et al has taken into consideration the calculation of ΔG_t^o(ion-dipole) interactions in the calculation of $\Delta G_t^o(H^+)$ ion[53].

Padova[95] has listed the values for the ionic free energy of transfer from water to methanol obtained by various methods used by different workers and compared their results with those of Case and Parson's[180,181] for the real free energies of transfer of ions. Similar discrepancies are also apparent from the scrutiny of Tables for $\Delta G_t^o(H^+)$ (and other ions) given by Criss and Salomon[98]. The results show that not too reliance should be made on a particular method.

Koltnoff[182] sounds a note of warning not to accept a value of an activity coefficient, obtained on the basis of the above assumptions with water as a reference solvent, as the true value. As pointed out by Popovych[96] the ultimate goal will be to compare the results of the various empirical methods with those calculated from statistical-mechanical models for solvation energies on the theoretical side and with measured simple electrode potentials on the experimental side.

Enthalpy and Entropy of Transfer:

From the discussions, it is apparent that inspite of limitations, reasonable estimates of single ion free energies can be made.

However, there has been only few attempts to divide ΔH_t of electrolytes into single ion values from the vast collections of enthalpy of transfer of electrolytes.

According to Feakins[183] and Ben Naim[184] the individual ionic contributions resulting from ion-solvent interactions to ΔH_t^o and ΔS_t^o are of great importance because they reflect important structural differences in the behaviour of ions in various solvents which are completely lost in the simpler free energy terms due to compensation of ΔH_t^o and $T\Delta S_t^o$ terms. It is clear that ΔH_t^o (ion) and ΔS_t^o(ion) are difficult to evaluate and any questionable assumptions regarding the physical model for the calculations could lead to large uncertainties in the resulting ΔH_t (ion) values[185].

The relationship between ionic enthalpies of solvation or of transfer and structure is not clear[186-193]. The enthalpy of solvation is dependent not only on the degree of increase or decrease in the structure of a solution but also upon the energy of each bond. So, there may be some relationship between enthalpies and structural properties of solution, surely it will not be simple one. Moreover, there is little agreement on how to divide enthalpies of transfer into ionic components and there are lack of fundamental data in most cases. The ionic solvation enthalpies are only rarely available as the enthalpies of formation of the gaseous are either not known or impossible to obtain. Considerable disagreements (as high as 50 K cal)[98,194] in the single-ion values in water have been reported. Consistent results are not given by methods such as[195-198]

i) extrapolations of enthalpy values of alkali metal halides or tetraalkylammonium halides with respect to ionic radius or ionic volume to zero reciprocal radius or,

ii) the assumption that the enthalpies of transfer of both cryptates of alkali ions and the corresponding free ligands are identical[196].

Very few determinations of ΔH_t^o of ions, mainly based on $\Delta H_t^o(Ph_4As^+) = \Delta H_t^o(BPh_4^-)$ have been made[188,189,197]. Friedman and co-workers[197,198] recommended the use of propylene carbonate (pc) as an ideal solvent for ions and transfer enthalpies from pc to other solvents have been evaluated and explained in terms of structural effects. However, serious deficiencies of the model $\Delta H_t^o\ (Ph_4As^+) = \Delta H_t^o\ (BPh_4^-)$ have also been reported though the method has been utilised by Choux and Benoit[199], Julliard[188] and more recently by Abraham (who used Ph_4PBPh_4 and Ph_4AsBPh_4). Single ion values would definitely be of great help in elucidating the solvent structure and the different aspects of the ion-solvent interactions.

From the discussions, it is apparent that the proper understanding of the solution chemistry and the 'medium effect' is yet a challenging task. It is necessary to have a collection of accurate data for the free energy and enthalpy of transfer of large number of electrolytes together with the free energy and ethalpy of transfer of neutral electrolytes of comparable size to understand the 'medium effects' of single ions. Comparisons of the results with the values reported for "reference electrolytes" would be of great help in the proper elucidation of solution chemistry. The different methods of knowing the ion-solvent interactions should be properly explored.

The present thesis embodies some thermodynamic studies based on solubility, spectrophotometric and conductometric measurements, on ion-solvent interactions in some non-aqueous and mixed aqueous co-solvents. The co-solvent chosen for such studies are two cello solves viz. methyl cellosolve (2-methoxy ethanol, ME) and dimethyl cellosolve (1,2-dimethoxyethane, DME).

2-Methoxy ethanol (ME) and 1,2-Dimethoxy ethane(DME)

Chemically these solvents are mono- and dimethyl ethers of ethylene glycol (EG) - a solvent well studied with regard to ion-solvent interactions. The study on ion-solvent interactions in these cosolvent systems are likely to reflect the effect of increasing number of methyl groups (electron releasing inductive effect) and decreasing number of OH groups.

IR studies[200] indicate that the prominent configurations of ME molecule is the gauch form to facile intramolecular hydrogen bonding as shown in structure IA. Since no intramolecular hydrogen bonding is feasible in pure DME, the predominentconfiguration of DME is the trans of IB.

Simple consideration of molecular structure indicates that due to the presence of electron repelling inductive effect of CH_3 group in methoxy group, ME is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H-atom of OH group makes ME molecules less acidic than ethylene glycol and water, thus imparting a 'quasi-aprotic' character to it. On the other hand, due to the inductive effect of two CH_3 groups, the two O-centres of DME molecules are more basic as compared to that of water, EG and ME. But due to the absence of any acidic hydrogen atom DME is a typically aprotic solvent.

Moreover, the basicity and proticity are likely to be related through co-operative structure of H-bonding[201] between the co-solvent and water molecules in aqueous solutions. Thus in ME + H_2O system, the possible H-bonded co-solvent water complex of the type IIA is also more basic and less acidic than water and EG-water mixtures. In DME water system the possible H-bonded aquo-DME complexes are of the type IIB and IIC, in equilibrium with each other, the former predominant at water rich composition, the later at water deficient compositions. It is to be noted that since a gauche form around $-CH_2-CH_2-$ group is likely to be more favourable for association, it may influence the equilibrium between trans and gauche forms in favour of gauche form as shown in IIC. In aqueous solutions of DME both IIB and IIC are more basic and less acidic than water, hence the mixed solvents as a whole are likely to be increasingly more basic and at the same time less acidic than not only to water but also to ME. Thus the order of basicity to be : Water < ME < DME. Also the relative acidities would increase in the reverse order.

Studies on fundamental physico-chemical properties like density[202], dielectric constants[203] for ME water mixtures have been reported at different temperatures throughout the composition range. Both properties are found to decrease monotonically with composition. For DME-water system also these values at different temperatures are available[200]. Desnoyers and co-workers[203] have reported apparent molar volume and heat capacities of aqueous ME at water rich compositions at 25 °C and showed that ME behaves as a fairly typical polar non electrolyte in water. Heat capacity and heat of solution of ME and DME[204] have been reported by number of workers. Partial molar volume[205] of ME and DME have been studied with water. The change in free energy, entropy and enthalpy associated with transfer of ME and DME from ideal gas phase to dilute aqueous solution at 25 °C[206] have also been reported.

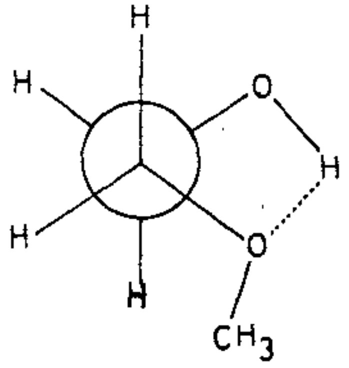
Notably enough, relatively few studies have been reported with aqueous 2-methoxy ethanol, and 1,2-dimethoxy ethane as solvent media. Renard and Justice[207] studied the conductometric behaviour of CsCl in DME-water mixtures as compared to dioxane-water and

THF-water mixtures and the differences observed for the ion-association were interpreted in terms of difference in aprotic nature of the organic molecule and that of H_2O. Solvent effect of DME, on sodium salt ion-pairs, as compared to THF and other solvents were studied[208] from NMR spectra. Conductance behaviour of ion pair formation of tetrabutylammonium bromide in aquo-ME[209] at 25 °C was interpreted on the basis of modification of water structure, depending on the nature of the system. Saits[210] studied the relation between the structure of water mixtures of organic solvents, their solvation and cation exchange selectivity of metal ions in aqueous-ME. Morel and co-workers[211] also predicted the relation between free energy of transfer and selectivity of an ion exchanger. Activity coefficients of NaCl in water mixtures of ME and DME at 25 °C were studied by Richard et al[212]. The dissociation constants of certain acids and bases have also been reported in ME + H_2O[213] and DME + H_2O[214] mixtures.

Works involving pure ME and DME are comparatively large in number. Of these, studies on dielectric properties at various temperatures of ME and DME[215], solubility studies on alkali metal chlorides, temperature dependence of electrolytic conductance of salts in ME[216], calculation of ionic solvation, free energies and entropies of transfer of gaseous univalent ions using continuum model in DME[217], dissociation constant studies of pure ME[218] and various thermodynamic studies, density, dielectric properties, viscosity etc are noteworthy. Studies on the rate of formation and stability of some organometallic complexes[219] in DME are also very much useful as they provide sufficient evidence for the existence of specific cation solvating effect of the solvent and such studies first led to the prediction of tetra-coordinated DME-alkali metal ion complexes[220], a view still considered as valid and is very much useful in studies of ion-solvation of DME.

Again ME and DME are commercially known as 'cellosolves' being used extensively as a solvating agents for cellulose. ME finds its use in various chemical reactions, and in analytical practice[221], in acid base conductometric titrations[222], electrolytes for high voltage capacitors and anti-icing additive for air-craft fuels. DME is used, now-a-days extensively as an electrochemical solvent in non-aqueous battery electrolyte, and also as solvents for the preparation and reaction of organo-alkali and organo-alkaline earth compounds[219a]. Consequently, the knowledge of ion-solvent interactions of different solutes in these solvents are, therefore capable of indicating the potential usefulness in various technologies, e.g. high energy non-aqueous batteries, ion exchangers etc. Transport parameters of electrolytic solutions such as ionic conductance[223] and viscosity, thermodynamic parameters such as solubility, dissociation constant can provide information concerning the nature of the kinetic entities from which the ion-solvent interactions can be inferred.

We have, therefore, devoted our attention to the study of thermodynamic properties in ME,DME and their aqueous mixtures.



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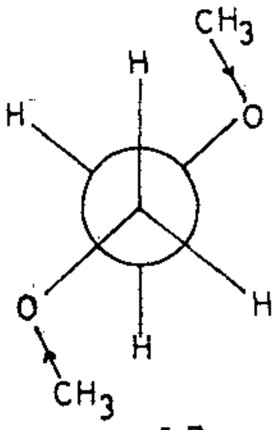

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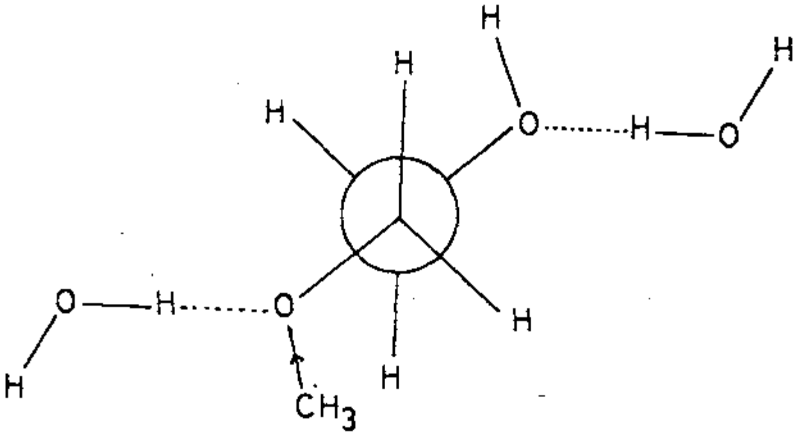
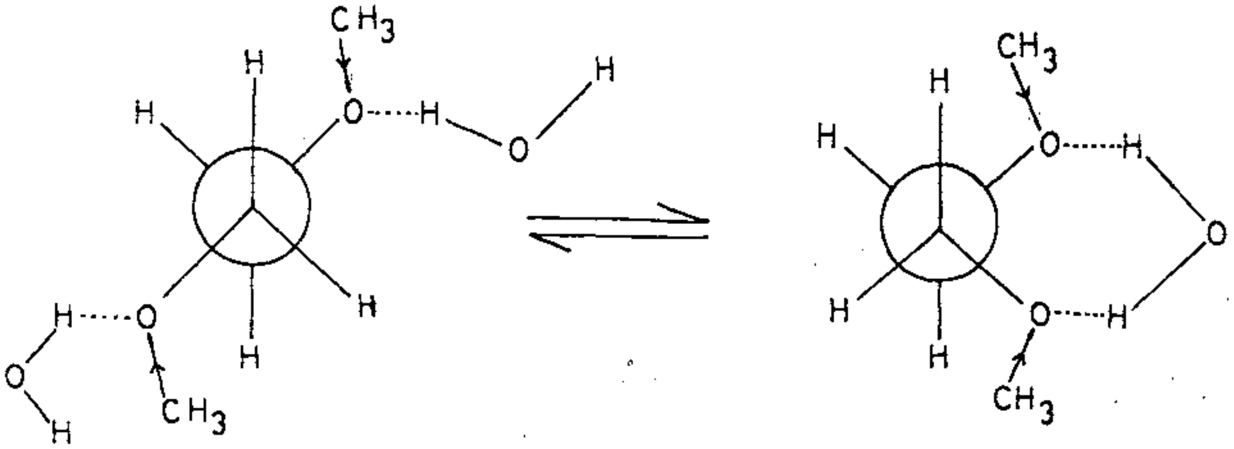


II A Hydrogen bonded ME-H_2O complex



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II B Hydrogen bonded DME-H_2O complexes

REFERENCES

1. R.G. Bates, J. Electroanal. Chem., 29, 1, (1971).
2. G.S. Kell, C.M. Davies and J. Tarynski in Water and Aqueous Solutions, Structures, Thermodynamics and Transport processes, Ed., R.A. Horne, Wiley-Interscience, 1972, Chapters 9 and 10.
3. J.S. Muirhead-Gould and K.J. Laidler, in Chemical Physics of Ionic Solutions, Ed. B.E. Conway and R.G. Barradas, John Wiley and Sons., Inc., New York, 1966, pp. 75-86.
4. J.F. Coetzee and C.D. Ritchie, Solute-Solvent Interactions, Marcel Dekker, New York, 1969.
5. J.J. Lagowski, The Chemistry of Non-aqueous Solvents, Academic Press, New York, 1966.
6. F.S. Amis and J.E. Histon, Solvent Affects on Chemical Phenomena, Academic Press, New York, 1966.
7. J.E. Gordson, The Organic Chemistry of Electrolyte Solutions, Wiley-Interscience, New York, 1975.
8. H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold Publishing Corporation, New York, Third Ed. 1958.
9. B.E. Conway and R.G. Barrads, Chemical Physics of Ionic Solutions, Ed., Wiley, New York, 1966.

10. A.K. Covington and T. Dickinson, Physical Chemistry of Organic Solvent Systems, Ed., Plenum Press, London and New York, 1973.

11. J. Bernal and R.H. Fowler, J. Chem. Phys. <u>1</u>, 515, (1933).

12. F. Franks, "Water - A Comprehensive Treatise" - Ed., Vol. I-VII, Plenum Press, New York, 1973-79.

13. O. Ya. Samoilov, Structure of Electrolyte Solutions and the Hydration of Ions, Consultant Bureau, Inc. New York, N.Y., 1965.

14. F. Franks, Physico-Chemical Processes in Mixed Aqueous Solvents, Ed. F. Franks, Heinemann Educational Books Ltd., 1967.

15. O. Popovych and R.P.T. Tomkins, Non-aqueous Solution Chemistry, John Wiley and Sons., New York, 1981.

16. R.A. Robinson and R.H. Stokes, Electrolyte Solution, Butter Worths, London, 1965.

17. H. Ulich, Trans. Faraday Soc., <u>23</u>, 388, (1977).

18. Same as 15, Chapter - 4,

19. B.S. Krumgalz, J. Chem. Soc. Faraday I, <u>76</u>, 1275, 1980.

20. R.H. Stokes and R.A. Robinson, Trans. Faraday Soc., <u>53</u>, 301, (1957)

21. R.G. Bates, Determination of pH - John Wiley and Sons Inc. New York, Second Ed. 1973 Chapter 8 and references cited therein.

22. M. Pabo, R.A. Robinson and R.G. Bates,

a) Anal. Chem., <u>38</u>, 1573 (1966).

b) J. Phys. Chem., <u>70</u>, 247, (1966)

c) Anal. Chem., <u>37</u>, 462, (1965)

d) M. Woodhead, M. Paabo, R.A. Robinson and R.G. Bates, J. Res. N.B.S. (Phys + Chem), 69A, 263, (1965)

23. L.N. Mukherjee and R.G. Bates, J. Electroanal. Chem., 187, 73, (1985).

24. M. Alfenaar and C.L. DeLigny, Rec. Trav. Chim., 86, 929, (1967).

25. C.L. deLigny, Miss H.J.M. Denessen and M. Alfenaar, Rec. Trav. Chim., 90, 1265, (1971).

26. D. Bax, M. Alfenaar and C.L. deLigny, Rec. Trav. Chim., 90, 1002, (1971); 91, 452, (1972).

27. D. Bax, C.L. DeLigny, M. Alfenaar and N.J. Mohr, Rec. Trav. Chim., 91, 601, (1972).

28. D. Bax, C.L. DeLigny and A.G. Remijnese, Rec. Trav. Chim., 91, 965, (1972); 91, 1225, (1972).

29. C.L. DeLigny, D. Bax, M. Alfenaar and M.G.L. Elferink, Rec. Trav. Chim., 88, 1183, (1969).

30. T. Shedlovsky, The Teckniques of Organic Chemistry, Vol. I, Part 4 (Ed. A. Weisberger) 3rd Ed., Wiley, New York, 1959, pp. 3011-3048.

31. E. Grunwald, G. Banghan and G. Kohnst, J. Am. Chem. Soc., 82, 5801, (1960).

32. D. Feakins and D.J. Turner, J. Chem. Soc., 4986, (1965).

33. D. Feakins and K.G. Lawrence, J. Chem. Soc., 212, (1966).

34. D. Feakins and K.H. Khoo, J. Chem. Soc., (A), 361, (1968).

35. D. Feakins, B.E. Hickeny and P.S. Voice, Trans. Faraday I, 75, 707, (1979).

36. D. Feakins, Physico-Chemical Process in Mixed Aqueous Solvents, Ed., F. Franks, Heinemann Educational Book Ltd., London, 1967, p. 71-90 and 141-151.

37. D. Feakins and C.T. Allan, J. Chem. Soc., Faraday I, 72, 314, (1976).

38. F. Franks and D.J.G. Ives, Quart. Rev. (London), 1, 20, (1966).

39. E.M. Woolley, J. Hawkins and L.G. Hepler, J. Soln. Chem., 1, 342, (1972).

40. E.M. Woolley, D.G. Hurkot and L.G. Hepler, J. Phys. Chem., 74, 3908, (1970).

41. E.M. Woolley and L.G. Hepler, Anal. Chem., 44, 1520, (1972)

42. T. Matsui, L.G. Hepler and E.M. Woolley, Can. J. Chem., 52, 1910, (1974).

43. T. Matsui and L.G. Hepler, Can. J. Chem., 51, 1941, 3789, (1973).

44. F.J. Millero, C.M. Wu, L.G. Hepler, J. Phys. Chem., 73, 2453, (1969).

45. S.K. Pal and S.C. Lahiri, Z. Physik. Chem. (Leipzig), 246, 89, (1971), 252, 177, (1973).

46. D.K. Hazra and S.C. Lahiri, J. Ind. Chem. Soc., 53, 567, (1976).

47. S.K. Maity, A.K. Chottopadhyay and S.C. Lahiri, Electrochim. Acta., 25, 1487, (1980).

48. A.K. Chottopadhyay and S.C. Lahiri, Electrochim. Acta, 27, 269, (1982).

49. S.K. Maity and S.C. Lahiri, Z. Physik. Chem. (Leipzig), 263, 183-187, (1982).

50. D. Sengupta, A. Pal and S.C. Lahiri, J. Chem. Soc. Dalton, 2685, (1983)

51. C.C. Deb, D.K. Hazra and S.C. Lahiri, Bull. Chim. Soc. Belges., 93, 421, (1984).

52. A.K. Bhattacharya, D. Sengupta and S.C. Lahiri, Z. Physik. Chem. (Leipzig), 265, 372, (1984).

53. S.K. Chakravorty, D. Sengupta and S.C. Lahiri, Z. Phys. Chem. (Leipzig), 267, 969, (1986).

54. D.K. Ram, D. Sengupta and S.C. Lahiri, J. Ind. Chem. Soc., 64, 101, (1987).

55. D.K. Meck, The Chemistry of Non-aqueous Solvents, Vol. I, Ed., J.J. Lagowski, Academic Press, New York, London, 1966, Part I, Chapter I.

56. H. Strehlow, same as 55 Chapter 4.

57. A.K.Das and K.K. Kundu, Ind. J. Chem., 16A, 467, (1978)

58. K.K. Kundu and A.K. Das, J. Soln. Chem., 8, 259, (1979)

59. K. Bose and K.K. Kundu, Can. J. Chem., 55, 3961, (1977)

60. J. Dutta and K.K. Kundu, J. Phys. Chem., 61, 625, (1987).

61. A.J. Parker, Chem. Rev., 69, 1, (1969).

62. B. Sen, D.A. Johnson and R.N. Ray, J. Phys. Chem., 71, 1523, (1971).

63. R.N. Roy, E.E. Swensson and G. Laccross (Jr), J. Chem. Thermyn. 7, 1015, (1975)

64. R.N. Roy, W. Vernon, J.J. Gibbons and A.L.M. Bothwell, J. Electroanal. Chem., 34, 101, (1972).

65. R.N. Roy and W. Vernon, J. Chem. Soc. Faraday Trans. I, 68, 2047, (1972).

66. C.F. Wells, J. Chem. Soc. Faraday I, 69, 984, (1973), 70, 694, (1974), 71, 1868, (1975), 72, 601, (1976)etc. A.K. Cavington and P. Jones, In Hydrogen-bonded Solvent Systems, Ed. (Tayler and Francis, London, 1968) p. 323-334, Adv. Chem. Ser., 177, 53, (1977)

67. M. Born, Z. Physik., I, 45, 222, (1920)

68. O. Popovych and R.P.T. Tomkins, Non-aqueous Solution Chemistry, John Wiley and Sons, New York, (1981), Chapter 2, 4 & 5.

69. C.M. Criss and E. Luksha, J. Phys. Chem., 72, 2966, (1968).

70. W.M. Latimer, "The oxidation states of the Elements and Their Potentials in Aqueous Solutions", 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., (1952)

71. R. Reynaud, C.R. Acad. Sci., 269(14), 777, (1969)

72. S.K. Ghosh and D.K. Hazra, J. Indian Chem. Soc., 65, 620, (1988)

73. C.W. Davies, J. Chem. Soc., 2093, (1938)

74. E.C. Sager, R.A. Robinson and R.G. Bates, J. Res. NBS (Phys. and Chem.), 68A, 305, (1964)

75. P.S. Gentile, M. Cefela and A.V. Celians, J. Phys. Chem., 67, 1083, (1963).

76. I.M. Kolthoff and S. Burchenstein, Treatise on Analytical Chemistry, Ed. I.M. Kolthoff and P.J. Elving Part I,

Vol. I, Chapter 13 (The Interscience Encyclopaedia, Inc., New York, N.Y. 1959).

77. T. Shedlovsky and R.L. Kay, J. Phys. Chem., 60, 151, (1956).

78. I.M. Kolthoff, J.J. Lingane and W.D. Larson, J. Am. Chem. Soc., 60, 2512, (1938).

79. C.L. DeLigny, Rec. Tran. Chim., 79, 731, (1960)

80. H.S. Frank and W.Y. Wen, Faraday Discuss. Chem. Soc., 24, 133, (1957).

81. J.E. Desnoyers and C. Jolicoeur, in Modern Aspects in Electrochemistry, Ed. J.O'M. Bockris and B.E. Conway, Plenum Press, New York, 1969, Vol. 5.

82. A.D. Buckingham, Faraday Discuss. Chem. Soc., 24, 157, (1957).

83. O. Hirschfelder, C.F. Curtise and R.B. Bird, Molecular Theory of gas and Liquids, Wiley, New York, 1954, Chapter 4.

84. J.S. Muirhead-Gould and K.J. Laidler, Trans. Faraday Soc., 63, 944, (1967).

85. J.O'M. Bockris and Sahija, J. Phys. Chem., 76, 2298, (1972)

86. P.P.S. Sahija, in International Review , J.O'M. Bockris, 1976, Serial, Vol. 6.

87. S. Goldman and R.G. Bates, J. Am. Chem. Soc., 94, 1476, (1972).

88. U. Sen, J. Ind. Chem. Soc., 63, 547, (1986)
J. Am. Chem. Soc., 101, 2531, (1979).

89. P. Debye, Z. Physik. Chem., 130, 56, (1927).

90. P. Debye and E. Huckel, Physik. Z., 24, 185, (1923)

91. C.W. Davies, Prog. React. Kinet., 1, 161, (1961).

92. E. Glueckauf, Trans. Faraday Soc., 51, 1235, (1955).

93. R.M. Stokes and R.A. Robinson, J. Am. Chem. Soc., 70, 1870, (1945).

94. B.D. Struck, Electrochim. Acta, 22, 1057, (1977).

95. J. Padova, Water and aqueous Solutions, Structure, Thermodynamics and Transport Process, Ed. 6, R.A. Horne, Wiley Interscience, 1972, Chapter 4.

96. O. Popovych, Crit. Rev. Anal. Chem., 1, 75, (1970).

97. E.J. King,
    a) Acid-Base Equilibria, Pergamon Press, 1965.
    b) in Physical Chemistry of Organic Solvent System, Ed., A.K. Covington and T. Dickinson, Plenum Press, London, 1973.

98. C.M. Criss and M. Salomon, Same as 97(b).
    J. Chem. Educ., 53, 763, (1976).

99. S.C. Lahiri and S. Aditya, J. Ind. Chem. Soc., 56, 1112, (1979).

100. H. Schneider, Topics in CurrentChemistry, 68, 105, (1976).

101. B.B. Owen, J. Am. Chem. Soc., 54, 1758, (1932).

102. A.J. Parker, Quart. Rev., 16, 163, (1962).

103. A.J. Parker and R. Alexander, J. Am. Chem. Soc., 90, 3313, (1968).

104. B.G.Cox, G.R. Hedwig, A.J. Parker and D.W. Watts, Aust. J. Chem., 27, 477, (1974).

105. R. Alexander, E.C.F. Ko. Y.C. Mac and A.J. Parker, J. Am. Chem. Soc., 89, 3703, (1967).

106. R. Alexander and A.J. Parker, J. Am. Chem. Soc., 89, 5549, (1967).

107. R. Alexander, D.A. Owensley, A.J. Parker and W.E. Waghorene, Aust. J. Chem., 27, 933, (1974).

108. D.A. Owensley, A.J. Parker and J.W. Diggle, J. Am. Chem. Soc., 96, 2682, (1974).

109. G.R. Hedwig, A.J. Parker, J. Am. Chem. Soc., 96, 6589, (1974).

110. G.R. Hedwig, D.A. Owensley and A.J. Parker, J. Am. Chem. Soc., 97, 3888, (1975).

111. M. Salomon, J. Phys. Chem., 74, 2519, (1970); 79, 429, 2000, (1975).

112. M.H. Abraham, J. Chem. Soc. Faraday I, 69, 1375, (1973).

113. M.H. Abraham and A.F. Daniel de Namor, J. Chem. Soc. Faraday I, 72, 955, (1976); 74, 2101, (1978).

114. M.H. Abraham, E. Ah-Sing, A.F. Daniel de Namor, T. Hitt, A. Nasehzadeh and R.A. Schulz., J. Chem. Soc. Faraday I, 74, 359, (1978).

115. M.H. Abraham and J. Liszi, J. Chem. Soc. Faraday I, 74, 1604, 2858, (1978).

116. C.M. Criss, J. Phys. Chem., 78, 1000, (1974).

117. C.M. Criss and E. Luksha, J. Phys. Chem., 72, 2966, (1968).

118. N. Bjerrum and E. Larsson, Z. Physik. Chem., 127, 358, (1927).

119. R.M. Noyes, J. Am. Chem. Soc., 84, 513, (1962); 86, 971, (1964).

120. A. Voet, Trans. Faraday Soc., 32, 1301, (1936).

121. W.W. Latimer, K.S. Pitzer and C.M. Slansky, J. Chem. Phys., <u>7</u>, 108, (1939).

122. R.E. Powell and W.M. Latimer, J. Chem. Phys., <u>19</u>, 1139, (1951).

123. H.M. Koepp, H. Wendt and H. Strehlow, Z. Electrochem., <u>64</u>, 483, (1960).

124. J.F. Coetzee and J.J. Campion, J. Am. Chem. Soc., <u>89</u>, 2513, (1967).

125. J.F. Coetzee, J.F. Simon and R.J. Bertozzi, Anal. Chem., <u>41</u>, 766, (1969).

126. E. Glueckanf, Trans. Faraday Soc., <u>60</u>, 572, (1964).

127. D.C. Graham, J. Chem. Phys., <u>18</u>, 903, (1950).

128. L.G. Hepler, Aust. J. Chem., <u>17</u>, 587, (1964).

129. J.B. Hasted, D.M. Ritson and C.H. Collie, J. Chem. Phys., <u>16</u>, 1, (1948).

130. R.H. Stokes, J. Am. Chem. Soc., <u>86</u>, 971, (1964).

131. W.A. Millen and D.W. Watts, J. Am. Chem. Soc., <u>89</u>, 6501, (1967).

132. J.S. Muirhead-Gould and K.J. Laidler, in Chemical Physics of Ionic Solutions, Ed., B.E. Conway and R.G. Barradas, John Wiley and Sons, Inc., New York, 1966, pp. 75-86.

133. D.R. Rosseinsky, Chem. Rev., <u>65</u>, 467, (1965).

134. S. Goldman and R.G. Bates, J. Am. Chem. Soc., <u>94</u>, 1476, (1972).

135. J. Padova, J. Phys. Chem., <u>72</u>, 692, (1968).

136. J. Padova, J. Chem. Phys., <u>39</u>, 1552, (1963).

137. D.L. Beveridge and G.W. Schnuelle, J. Phys. Chem., 79, 2562, (1975).

138. G.W. Schnuelle and D.L. Beveridge, J. Phys. Chem., 79, 2566, (1975).

139. J.G. Kirkwood, J. Chem. Phys., 2, 351, (1934).

140. A.E. Stearn and H. Eyring, J. Chem. Phys., 5, 113, (1937).

141. M.H. Abraham, J. Liszi and L. Meszaros, J. Chem.Phys., 70, 249, (1979).

142. M.H. Abraham and J. Liszi, J. Chem. Soc. Faraday I, 76, 1219, (1980).

143. V.A. Pleskov, Usp. Khim., 16, 254, (1947).

144. H. Strehlow, Z. Electrochim., 56, 827, (1952).

145. J.F. Coetzee, D.K. McGouire and J.L. Hedrick, J. Phys. Chem., 67, 1814, (1963).

146. T. Kuwana, D.E. Bublitz and G. Hoh, J. Am. Chem. Soc., 82, 5811, (1960).

147. C. Kalidas, P. Sivaprasad and U.V. Venkataram, Z. Naturforsch, 32a, 791, (1977).

148. M. Alfenaar, C.L. De Ligny and A.G. Remijnese, Rec. Trav. Chim., 86, 986, (1967).

149. I.M. Kolthoff and F.G. Thomas, J. Phys. Chem., 69, 3049, (1965).

150. J.V. Nelson and R.T. Iwamoto, Anal. Chem., 33, 1795, (1961); 35, 867, (1963).

151. H.P. Schroer and A.A. Vleck, Z. Inorg. Chem., 334, 205, (1964).

152. V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Letters, 2, 257, (1966).

153. J.H. Sharpand and A.J. Parker, Proc. Roy. Aust. Chem. Inst., 39, 89, (1972).

154. A.J. Parker, Electrochim. Acta, 21, 671, (1976).

155. N.A. Izamaylov, Electrochemistry of Solution, Kharkov University, 1959.

156. N.A. Izamaylov, Zh. Fiz. Khim., 34, 2414, (1960).

157. N.A. Izamaylov, Dokl. Akad. Nank. U.S.S.R., 126, 1033, (1959).

158. D. Feakins andD.J. Turner, J. Chem. Soc., 4986, (1965).

159. A.L. Andrews, H.P. Benneto, D. Feakins, K.G. Lawrence and R.P.J. Tomkins, J. Chem. Soc. (A), 1486, (1968).

160. B.E. Conway, Ann. Rev. Phys. Chem., 17, 481, (1966).

161. J.I. Kim, J. Phys. Chem., 82, 191, (1978).

162. H.F. Halliwell and S.C. Nyburg, Trans. Faraday Soc., 59, 1126, (1963).

163. M. Salomon, J. Electrochem. Soc., 118, 1609, (1971).

164. M. Salomon, J. Soln. Chem., 15, 237, (1986).

165. E. Plichta, M. Salomon, S. Slane and M. Uchiyama, J. Soln. Chem., 15, 662, (1986).

166. M. Salomon and M. Uchiyama, J. Soln. Chem., 16, 21, (1987).

167. O. Popovych, Anal. Chem., 38, 558, (1966).

168. O. Popovych and A.J. Dill, Anal. Chem., 41, 456, (1969).

169. O. Popovych and R.M. Friedman, J. Phys. Chem., 70, 1671, (1966).

170. O. Popovych, J. Phys. Chem., 88, 4167, (1984).

171. A.J. Dill and O. Popovych, J. Chem. Eng. Data, 14, 240, (1969).

172. E. Grunwald, G. Bangham and G. Kohnsten, J. Am. Chem. Soc., 82, 5801, (1960).

173. J.F. Skinner and R.M. Fuoss, J. Phys. Chem., 68, 1882, (1964).

174. J.F. Coetzee and G.P. Cunningham, J. Am. Chem. Soc., 87, 2529, (1965).

175. M.A. Coplan and R.M. Fuoss, J. Phys. Chem., 68, 1177, (1964).

176. C. Treiner, Can. J. Chem., 55, 682, (1977).

177. R.A. Pierotti, Chem. Rev., 76, 717, (1976).

178. M.H. Abraham and A. Nasehzadeh, Can. J. Chem., 57, 71, (1979).

179. Lord Wynne-Jones, in Hydrogen-Bonded Solvent Systems, Ed. A.K. Covington and P. Jones (Taylor and Francis, London, 1968).

180. B. Case and R. Parsons, Trans. Faraday Soc., 63, 1224, (1967).

181. R. Parsons and B.T. Rubin, J. Chem. Soc. Faraday I, 70, 1636, (1974).

182. I.M. Kolthoff, Anal. Chem., 51, IR, (1979).

183. D. Feakins and P. Watsons, J. Chem. Soc., 4734, (1963).

184. A. Ben Naim, Water and Aqueous Solution, An introduction to Molecular Theory, Plenum Press, New York and London, 1974.

185. Same as 98.

186. R.K. Mahanti, J.S. Sarma, S. Subramanian and J.C. Ahluwalia, Trans. Faraday Soc., 67, 305, (1971).

187. R.K. Mahanti, S. Sunder and J.C. Ahluwalia, J. Phys. Chem., 76, 577, (1973).

188. J. Juillard, J. Chem. Soc. Faraday Trans I, 78, 37, 43, (1982).

189. Y. Pointud and J. Juillard, J. Chem. Soc. Faraday I, 73, 1907, (1977).

190. G. Biswas, S. Aditya, A. Bhattacharyya and S.C. Lahiri, J. Ind. Chem. Soc., 54, 1137, (1977).

191. G. Biswas, S. Aditya and S.C. Lahiri, J. Inorg. Nucl. Chem., 40, 1069, (1978).

192. S.C. Lahiri, A.K. Ray and S. Aditya, Thermochim. Acta, 16, 277, (1976).

193. S. Bandyopadhyay, A.K. Mandal and S. Aditya, J. Ind. Chem. Soc., 55, 1286, (1978).

194. Same as 36, p.77.

195. B.E. Conway, J. Soln. Chem., 7, 721, (1978).

196. M.H. Abraham, A.F. Daniel de Naumor and R.A. Schulz, J. Chem. Soc. Faraday Trans. I, 76, 869, (1980).

197. C.V. Krishnan and H.L. Friedman, J. Phys. Chem., 73, 3934, (1969), 75, 388, 3606, (1971).

198. H.L. Friedman, J. Phys. Chem., 71, 1723, (1967).

199. G. Choux and R.L. Benoit, J. Am. Chem. Soc., 91, 6221, (1969).

200. a) R. Iwamoto, Spectrochim Acta., Part A,
27, 2385, (1971).

b) Poda, France et al, Mol. Phys., 27, 521, (1974).

201. a) K.K. Kundu, A.K. Rakshit and M.N. Das, Electrochim
Acta., 17, 1921, (1972).

b) D. Feakins in ref. 36, p. 71.

c) K.H. Khoo, J. Chem. Soc. (B), 2932, (1971).

202. H. Sadek, Th. F. Tadros and A.A. El-Harakany,
Electrochim Acta., 16, 339, (1971).

203. a) J.E. Desnoyers, Can. J. Chem., 56(22), 2808, (1978).

b) G. Roux, G. Perron and J.E. Desnoyers, J. Soln.
Chem., 7(9), 639, (1978).

204. a) Kusano, J. Suurkuusk, I. Wadso, J. Chem. Thermod,
5, 757, (1973).

b) J. Peter Onthrie, Can. J. Chem., 55, 3700, (1977).

c) B.M. Arnett, E.J. Mitchell, T.S.S.R. Murthy,
J. Am. Chem. Soc., 96, 3875, (1974).

205. a) S. Terasawa, R. Itsuki, S. Arakawa, J. Phys. Chem.,
79, 2345, (1975).

b) J.T. Edward, P.G. Farrel and F. Sahidi, J. Chem. Soc.,
Part I, 73, 705, (1977).

206. S. Cabani and V. Mollica, J. Chem. Soc. Faraday I,
74, 2667, (1978).

207. E. Renard, C.J. Justice, J. Soln. Chem., 3(8), 633, (1974).

208. C. Detellier, P. Laszlo, Bull. Soc. Chim. Belg., 84, 1081.,(1975).

209. S. Schiavo, B. Scrasati, Z. Phy. Chem., 102(1-4), 9,(1976).

210. R. Saits, Verh. K. Acad. West. Lett. Schone. Kunsten. Belg. Klwel., 40, 136, (1978).

211. J.P. Morel, J. Juillard, D.L. Massart, R. Smits, Anal. Chem., 48, 458, (1976).

212. J. Richard, Radidon, A. Kurt, Kraus (a) J. Chem. Eng. Data, 16, 241, (1971); (b) U.S. Office of Saline Water Res. Develop. Progr. Rep. 52-4, No. 685 (1971).

213. a) G. Franchini, E. Ori, C. Preti, L. Tassi and G. Tosi, Can. J. Chem., 65(4), 722, (1987).

b) C.A. Vega and S. Delgado, J. Chem. Eng. Data, 32, 218, (1987).

c) W. Simon and E. Heilbronner, Helv. Chim. Acta., 38, 508, (1955).

214. R. Reynaud, Bull. Soc. Chim. Fr., 12, 4597, (1967).

215. V. Viti, P. Zampetti, Chem. Phys., 2(2), 233, (1973).

216. A.D. Pethybridge, M.J. Blandamer and J. Barthel, Proc. 7th Int. Conf. on Non-aq. Solns. I.U.P.A.C. Resenberg, 11-15 Aug. (1980), P.D - 20.

217. a) M.H. Abraham and J. Liszi, in ref. 142.

b) J. Strong and T.R. Tuttle, Jr., J. Phys. Chem., 77(4), 533, (1973).

218. A.P. Kreshkov, N.T. Smolova, A. Ya. Veveris and B.A. Spintse, Zh. Fiz. Khim., 51(7), 1827, (1977)[Russian Journal of Phys. Chem. 1072, 7 (1977) Eng.]

219. a) J.F. Garst in "Solute-Solvent interactions" — Ed. J.F. Coetzee and C.D. Ritchie, Marcel Dekker, New York (1969) Chapter 8, p. 541.

b) A.F. Garito and B.B. Wayland, J. Phys. Chem., 71(12), 4062, (1967).

c) W.A.G. Fowles, D.A. Rice, W.A. Richard, J. Inorg. Nucl. Chem., 31(10), 3119, (1969).

220. A. Jeans and R. Adams, J. Am. Chem. Soc., 59, 2608, (1937).

221. A.P. Kreshkov, "Osnovy Analiticheskoi Khimii (Fundamentals of Analytical Chemistry)" Izd. Khimiya, Moscow (1970) Vol. 5.

222. A.G. Schwartz, J.B. Barker, Talanta, 22(9), 773, (1975).

223. D. Dasgupta, S. Das and D.K. Hazra, J. Chem. Soc., Faraday Trans. I, 84(4), 1057, (1988).