PART 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 and 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 informations regarding solute-solvent interactions in aqueous solutions.

The revolutionary theory of Bernal and Fowler 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\textsuperscript{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.

In this dissertation, we are interested in the studies of solvent effects on ionogens (consisting of neutral molecules that yield ions by reacting with suitable solvents). The study would enable us to derive useful informations regarding the ion-solvent interactions, solvent-basicity and structural changes of the solvents.
The researches of Harmed and Co-workers,\textsuperscript{8} Stokes, Bates, Robinson and Co-workers,\textsuperscript{1,16,20-23} de Ligny and Co-workers,\textsuperscript{24-29} Shedlovsky\textsuperscript{30}, Grunwald\textsuperscript{31}, Peakins et al\textsuperscript{32-37} Franks,\textsuperscript{12,14,38} Hepler and co-workers\textsuperscript{39-44}, Lahiri and Co-workers,\textsuperscript{45-54} Neck,\textsuperscript{55} Strehlow\textsuperscript{56}, Das, Kundu and co-workers\textsuperscript{57-60} and others\textsuperscript{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**\textsuperscript{5,6,12-15}

The most structured liquid is water, the structure of which is 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 \textsuperscript{7}Simple alcohols\textsuperscript{7} for rings (HP).
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. Presumably, the extrema correspond to a maximum breakdown (depolymerization) of the water structure by the non-aqueous component. In case of alcohol-water mixtures, the depolymerization of water is followed by the formation of strong alcohol-water bonds at higher alcohol contents.

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.

**DISSOCIATION CONSTANTS OF LIGANDS IN MIXED SOLVENTS:**

For the reaction,

\[ HA + A^- \rightleftharpoons A^- + HA_0 \]  

\[ K = \frac{a_{A^-} X a_{HA_0}}{a_{HA} X a_{A^-}} = \frac{K_a}{K_o} \]  

\[ K_a \text{ and } K_o \text{ are the dissociation constants of the } HA \text{ and the corresponding reference acid } HA_0 \text{, in the same solvent.} \]

We have,  
\[ \Delta G_0 = -RT \ln K = \Delta G_{el} + \Delta G_{nonel} \]  

Or,  
\[ -\log K = \frac{\Delta G_{nonel}}{2.303 RT} + \frac{a}{r} \]  

Where,  
\[ a = \frac{N e^2}{2 X 2\pi \epsilon 2.303 RT} (\frac{1}{r_{A^-}} - \frac{1}{r_{A_0^-}}) \]

(according to Born 67 equation)
assuming the effective radii of the ions to remain approximately constant in series of solvents.

The plot of log $K$ against $\frac{1}{\varepsilon}$ should thus be a straight line, the intercept for $\frac{1}{\varepsilon}$ = 0, should give a measure of the dissociation constants free from electrostatic effects.

The plot of the values of $-\log \left( \frac{K_a}{K_0} \right)$ (determined in water and alcohols) against $\frac{1}{\varepsilon}$ is very close to a straight line for substituted benzoic and acetic acids, provided $\varepsilon$ is greater than 30. The slope of the line, however, varies with the nature of the acid, so that an acid which is stronger than another in one solvent may be weaker in a second solvent. Thus when comparing the dissociation constants of acids, the values employed should be extrapolated to infinite dielectric constant. In this way the electrostatic effect, at least, of the solvent should be eliminated. However, the relationship ($-\log K$ vs. $\frac{1}{\varepsilon}$) fails in dioxane-water.

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

$$ A \rightleftharpoons B + H^+ $$
\[
K = \frac{m_B + X m_B \gamma_B}{m_A} \frac{\gamma_H + X \gamma_B}{\gamma_A}
\]

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 \( \gamma_i \) approaches unity as \( m \) approaches zero.

When the composition of the solvent medium changes as well as the solute concentration (and ionic strength), it is convenient to separate each activity \( \gamma_i \) into factors \( \gamma_i^* = \frac{\gamma_i}{m_i} \gamma_i^* \)

\( \gamma_i^* \) is measured relative to the standard state in pure water and becomes unity only in infinitely dilute aqueous solution. On the contrary, the activity co-efficient \( s \gamma_i \) in equation above becomes unity when \( m = 0 \) in the solvent \( s \), where \( m \gamma_i \) has a value different from unity whenever the solvent differs from pure water.

The 'salt effect' \( s \gamma_i \) varies with the solute concentration.

Simple Debye-Hückel equation with appropriate allowance for the effect of altering the dielectric constant of the medium \( s \), can be used to estimate \( s \gamma_i \) when ionic species are involved.

The thermodynamic dissociation constant can also be determined in very dilute solution where \( s \gamma_i \rightarrow 0 \) and this is the best method for the determination of the thermodynamic dissociation.
The medium effect \( m^\gamma_i \) is a function of the free energy of the species \( 'i' \) in the two standard states.

\[
\Delta \sigma_i^0 = s_i^0 - w_i^0 = RT \ln m^\gamma_i \quad \ldots (6)
\]

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

\[
\ln m^\gamma_i = \frac{NZ_i^2 e^2}{2RT} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \quad \ldots (7)
\]

and the mass law equation for equilibrium

\[
\frac{K_s}{K_w} = \frac{m^\gamma_i}{m^\gamma_H \times m^\gamma_B} \quad \ldots (7a)
\]

Where \( s^K \) and \( w^K \) are the dissociation constants for the standard states in solvent and water respectively.

We obtain

\[
p\left(s^K\right) = p\left(w^K\right) = \frac{Ne^2}{4.5052RT} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \chi
\]

\[
\left( \frac{Z_B^2}{\gamma_B} - \frac{Z_A^2}{\gamma_A} + \frac{1}{\gamma_H} \right) \quad \ldots (8)
\]

(Charges on \( \gamma_A \), etc. omitted)

The equation has been found to be fairly satisfactory for the dissociation equilibrium of the charge type \( A^0B^- \) (e.g. \( A^0 = \) uncharged acetic acid, \( B^- = \) acetate anion, \( Z_A = 0 \)) and \( A^+B^0 \) 21,70-78...
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.\textsuperscript{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 Bernal and Fowler, various molecular approaches have been made to predict the nature of the solvation of ions. Several contributions are considered:

1. Formation of cavity in the solvent
2. Strong interaction between the ion and the solvent molecules of the first (even second) co-ordination shell.
3. Interaction between the solvent molecules in the co-ordination shell,
4. Weaker interactions between the hydration complex and the rest of the solvent molecules.
5. 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 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**:

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\textsuperscript{34}, Bockris and Sahija\textsuperscript{25,26}, Goldman and Bates\textsuperscript{37} 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\textsuperscript{38} 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\textsuperscript{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 \textsuperscript{89-95} have been made to obtain single-ion thermodynamics with moderate success. This aspect has been reviewed in details.\textsuperscript{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.\textsuperscript{15}

The free-energy changes associated with the transfer of a chemical entity (HX) from solvent (1, say water) to solvent (2, say \( \mathcal{F} \)) is known as "total medium effect"\textsuperscript{101} (\( \Delta G_{t} \)) 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

\[
\text{Pt (H}_2\text{)} \mid \text{HX (m) solvent} \mid \text{Ag X} - \text{Ag}
\]
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 electroneutral combination HX.

\[ \Delta G_t = \Delta G^o_t + 2 \text{RT} \ln \frac{\gamma^+_S}{\gamma^+_W} \]

\[ = \Delta G^o_t + 2 \text{RT} \ln \frac{\gamma^+_m}{\gamma^+_i} \quad \ldots (9) \]

\[ \Delta G^o_t = -ZF \cdot (\tilde{\delta}_{E^o} - \tilde{\psi}_{E^o}) \] 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' \( \log \gamma_i \) 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

\[ \log (\gamma_i) = \frac{s\mu^o_i - w\mu^o_i}{RT} \quad \ldots (10) \]

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-Hückel \(^92\) 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 \(s \gamma_i \to 0\) 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 significance 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; which are based on e.m.f. and conductance measurements. 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

$$H_2 (Pt) \mid a_{H^+} = 1 \mid a_{H^+} = 1 \mid H_2 (Pt)$$

Where $E = \frac{RT}{F} \ln m \gamma_{H^+} + \frac{1}{F} E F \ln J$.

In view of the limitations of having liquid junction potential of uncertain magnitude, the 'medium effect' of proton, first determined by Bjerrum and Larsson 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

$$\log m \gamma^i = \frac{N Z_i^2 e^2}{2 RT r_i} \left( \frac{1}{\varepsilon_S} - \frac{1}{\varepsilon_W} \right) \quad \cdots \quad (11)$$

It is to be noted that solvent molecules become inhomogenous due to strong influence of solute molecules near the solvent molecules. Two extreme cases are:
a) dielectric saturation in the vicinity of ions 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 Woet and successfully applied by Latimer et al., Strehlow and co-workers and Coetzee et al. 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.

\[
\Delta G^0_t = (g^0_s - g^0_w) \\
= \frac{N_2^2 e^2}{2} \left[ \frac{1 - \frac{1}{\varepsilon_s}}{r_+^s} + \frac{1 - \frac{1}{\varepsilon_w}}{r_+^w} \right] \ldots (12)
\]

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.\textsuperscript{119,126-131}

This aspect has been dealt extensively by Noyes\textsuperscript{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 $r^*$, $\varepsilon_{\text{sat}}$ and $\Delta G_0^\circ$. The equation of stokes should, therefore, be restricted to water rich solvents. The equations were utilised by Bates and co-workers\textsuperscript{1,22} to calculate $\Delta G_0^\circ$ 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 $r^{-2}$, $r^{-4}$, $r^{-5}$, $r^{-6}$ in that order where $r$ is the corresponding interaction distance which contains the ionic radius term but not always equal to it\textsuperscript{132-133}. The reliable quantitative calculation ofhydrational and solvational energies are thus very difficult.
Goldman and Bates\textsuperscript{34} used an electrostatic model to calculate $\Delta G^\circ$ ($\Delta G^\circ = \Delta G^\circ_{el} + \Delta G^\circ_{neut}$), $\Delta H^\circ$ and $\Delta S^0$ associated with the transfer of seventeen ions from the gaseous phase to water at $25^\circ C$. 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\textsuperscript{95,135,136} utilising the fundamental equation for the free energy of a dielectric continuum in an electrostatic field. Beveridge and Schnuelle\textsuperscript{137,138} gave a general expression for the free energy of an arbitrary charge distribution embedded in a spherical cavity surrounded by two dielectric continua, an extension of Kirkwood's\textsuperscript{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)

\[ \Delta \varepsilon_{el}^0 = \frac{Z^2}{2} \left( \frac{1}{\varepsilon_0^a} - \frac{1}{a} \right) \quad \ldots \quad (13) \]

(ii) The one layer model (first layer \( \rho = b \) & \( \varepsilon = \varepsilon_1 \))

\[ \Delta \varepsilon_{el}^{(1)} = \frac{Z^2}{2} \left[ \frac{1}{\varepsilon_1^a} \left( \frac{1}{a} - \frac{1}{b} \right) + \frac{1}{\varepsilon_0^b} - \frac{1}{a} \right] \quad \ldots \quad (13a) \]

(iii) The two layer model (first layer \( \rho = b \)

and \( \varepsilon = \varepsilon_1 \), second layer \( \rho = c \) and \( \varepsilon = \varepsilon_m \)).

\[ \Delta \varepsilon_{el}^{(2)} = \frac{Z^2}{2} \left[ \frac{1}{\varepsilon_m^a} \left( \frac{1}{b} - \frac{1}{c} \right) + \frac{1}{\varepsilon_1^b} \left( \frac{1}{a} - \frac{1}{b} \right) + \frac{1}{\varepsilon_0^c} - \frac{1}{a} \right] \quad \ldots \quad (14) \]

Where \( \varepsilon_i = n^2 \) and \( b = a + R \) for the first layer in both the one layer & 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\textsuperscript{140}, \( r = (\bar{V}/8n)^{1/3} \). The radius of solvent molecules have also been calculated using stearn-Eyring formula\textsuperscript{140}

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

METHODS BASED ON MEASUREMENT OF OXIDATION REDUCTION POTENTIAL AND THE E.M.F. OF DIFFERENT CELLS:

The search of a suitable reference electrode having the same e.m.f. value in all solvents thus appears imperative. Pleskov 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 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. for measurements of polarographic half wave potentials of a series of cations present as perchlorates in seven solvents.

Koepp, Wendt and Strehlow (also studied by Kuwana 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. $\Delta G^0_t$ (Foc) - $\Delta G^0_t$ (Fic) can be regarded to be solvent independent. Thus, the measurement of standard oxidation potentials in water and solvents gives the value of $\Delta G^0_t (H) - \Delta G^0_t (Fic) + \Delta G^0_t (Foc)$

According to Strehlow\textsuperscript{56}

$$\Delta G^0_t (Fic) - \Delta G^0_t (Foc) = \frac{N Z^2 e^2}{2} \left( \frac{1}{r + a_1} - \frac{1}{r + a_2} \right)$$ (15)

Where, $a_1$ and $a_2$ are constants, specific for the solvents in question. Strehlow\textsuperscript{56} used $a_1 = 0.85$, $0.72 < a_2 < 0.90$ 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.\textsuperscript{24}

In spite of the limitations, the method seems to be one of the most useful methods for the determination of the 'medium effect' of single ions and widely used by de Ligny and co-workers\textsuperscript{24-29}

They used the call of the type

$\text{Pt} (H_2) \mid HClO_4$ in water or solvents respectively $\mid KCl$ (Satd.) in $H_2O \mid Hg_2Cl_2 - Hg$

and

$\text{Pt} \mid \text{Ferrocene}(m_2)$, Ferricinium in water or solvents respectively $\mid KCl$ (Satd.) in $H_2O \mid Hg_2Cl_2 - Hg$
Due to low solubility of ferrocene and instability of ferricinium in water, the $E^0$ has been calculated from the polarographic half-wave potential of the process $\text{Foc} \rightleftharpoons \text{Fic}^+ + e$. The reaction $\text{Foc} \rightleftharpoons \text{Fic}^+ + e$ 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 $\Delta G^\circ_t$ of $H^+$ ion and other ions in different solvents. The method has been used by Kalidas et al.\textsuperscript{147} to measure $\Delta G^\circ_t(H^+)$ 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, $E^0$ - 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.\textsuperscript{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\textsuperscript{26} and specific interactions of the redox couple with water and other solvents are also known.\textsuperscript{124} There may be uncertainties in the crystal radii of ferrocene\textsuperscript{24} (3.8 \(\AA\)) and ferricinium\textsuperscript{28} (3.3 \(\AA\)) ions.

Some other redox couples were also studied with relatively little success. The couples are ferrocene/ferrocinium picrate, ferroin/ferrin couple\textsuperscript{149}, 4,7-dimethyl ferroin/ferrin couple, 4,7-dimethyl ferrin couple\textsuperscript{150}, bis diphenyl chromium (0.1) couple with relatively little success. Parker and co-workers\textsuperscript{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

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Ag(S)} & \text{AgNO}_3, 0.01 \text{ M} & \text{Satd} & \text{AgNO}_3, 0.01 \text{ M} \\
& \text{in CH}_3\text{OH} & \text{NET}_4^+ \text{ Pic.} & \text{in solvents} \\
\hline
\text{Ag(S)} & \text{AgClO}_4, 0.01 \text{ M} & 0.01 \text{ M} \text{ NET}_4^+ \text{ Pic} & \text{AgClO}_4, 0.01 \text{ M} \\
& \text{in solvents} & \text{in solvents} & \text{Ag (E)} \\
\hline
\end{array}
\]

Parker and co-workers\textsuperscript{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.
tetra ethyl ammonium 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 $\text{fic/foc}$ also couple against the $\text{Ag}^+$/Ag electrode in fifteen solvents using the cell

$$\begin{align*}
\text{Ag} & \mid 0.01 \text{ M AgClO}_4, (\text{NEt}_4)_2\text{ClO}_4, 0.1 \text{ M in solvents} \nonumber \\
(\text{NEt}_4)_2\text{ClO}_4 & \mid 0.002 \text{ M Fic/Foc, 0.02 M (NEt}_4)_2\text{ClO}_4 \mid \text{Pt} \nonumber
\end{align*}$$

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 $G^0$ of an infinitely large ion to be zero and all significant components of the solvation energy $G^0$ of an ion are functions of $1/r^n$ ($r =$ crystallographic radius,
n = 1-4 or 6. He plotted thermodynamically allowed combinations like \( (G^{0}_M - G^{0}_H) \) vs. \( 1/r_M \) and \( -(G^{0}_H + G^{0}_X) \) vs. \( 1/r_X \) (\( M= \) alkali metal ions, \( X= \) halide ions) and used extrapolations to get \( G^{0}_H \) at \( (1/r) = 0 \). The plot of \( \sqrt{-G^{0}_H + \left( \frac{G^{0}_M - G^{0}_X}{2} \right)} \) vs. \( 1/r_{av.} \) improves the value of \( G^{0}_H \). Izmarylov\textsuperscript{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 \( (G^{0}_M + G^{0}_X) \) vs. \( 1/n^2 \), \( (G^{0}_M - G^{0}_H) \) vs. \( 1/n^2 \) and \( \sqrt{-G^{0}_i + \frac{G^{0}_M - G^{0}_X}{2}} \) vs. \( 1/n^2 \), \( (n = 3, 4, 5 \text{ etc.}) \) 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, Izmarylov's assumption that \( \Delta G^{0} (\text{neut}) \) account for 1-2% of the total solvation energy was found to be erroneous from the estimates of \( \Delta G^{0} \) neut via inert gas assumption or experimental determination of \( \Delta G^{0} \) neut. Moreover, the calculations of Izmarylov\textsuperscript{155-157} 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 nonlinear and generally based on three points. Therefore, in the determination of \( \Delta G^O_t \) or 'medium effect' large errors are expected.

Peaikins and their associates used the e.m.f. methods to determine the \( \Delta G^O_t \) (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

\[
\Delta G^O_t (HX) = \Delta G^O_t (H^+^+) + arX^1
\]

and

\[
\Delta G^O_t (MCI) = \Delta G^O_t (Cl^-) + brM^2
\]

to get

\[
\Delta G^O_t (H^+) at \frac{1}{rX} = 0 \quad \text{and} \quad \Delta G^O_t (Cl^-) at \frac{1}{rM} = 0
\]

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 \( \Delta H_t \) 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 oversimplification, 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.

Inconsistent values of \( \Delta G^O_t (MCI) \) vs. \( 1/rM \) and \( \Delta G^O_t (HX) \) vs.
Das and co-workers suggested the simultaneous extrapolation to \( r_X^{-1} = 0 \) of the plots of \( \Delta G^0_t (HCl) \) and \( \Delta G^0_t (HCl = HX) \) i.e. \( \Delta G^0_t (Cl^- - X^-) \) against \( (r_X)^{-1} \) suitably aimed at having least discrepancies in the extrapolated values of \( \Delta G^0_t (H^+) = 2.303 \text{ RT } \log \frac{M_S}{M_D} \) and \( \Delta G^0_t (Cl^-) = 2.303 \text{ RT } \log \frac{M_S}{M_D} \) with respect to the experimental values of \( \Delta G^0_t (HCl) \) would lead to extra confidence to the extrapolation (error \( = \pm 0.1 \) to \( 0.2 \text{ KCal/ion} \)).

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 \( \Delta G^0_{el} \) and a neutral part \( \Delta G^0_{neut} \) i.e.

\[
\Delta G^0_t = \Delta G^0_{el} + \Delta G^0_{neut}.
\]  

The method has been elegantly put forward by Alfenaar and de Ligny and more recently by Kim, Abraham and Lissi.

In view of the difficulty in calculating \( \Delta G^0_{neut} \), it has been determined experimentally, Alfenaar and de Ligny took \( \Delta G^0_{neut} \) of very large ions to be equal to \( \Delta G^0_{neut} \) 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,

$$\Delta G^0_i (\text{ion}) = \Delta G^0_{\text{neut}} + \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + ... \quad (21)$$

The free energy of transfer of electroneutral combinations of ions have been divided by Alfencar and de Ligny into the contributions of the individual ions M and A as follows:

$$\Delta G^0_t (HA) - \Delta G^0_t, \text{neut} (A^-) = \Delta G^0_t (H^+) + \frac{a}{r_A} + \frac{b}{r_A^2} + \frac{c}{r_A^3} + ... \quad (22)$$

$$\Delta G^0_t (H^+) - \Delta G^0_t (M^+) + \Delta G^0_{t,\text{neut}, M^+} = \Delta G^0_t, H + - \frac{a}{r_M} + \frac{d}{r_M^2} + \frac{e}{r_M^3} + ... \quad (23)$$

The values of the left hand sides can be determined experimentally.

Born is calculated using the Born equation from the slope at \( \frac{1}{r} = 0 \), and \( \Delta G^0_t (H^+) \), \( a, b, c \) 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.
\( \Delta G^0_i (H^+) \). The larger the ions, the greater is the accuracy of the results.

The extrapolations, however, are non-linear. The contributions of \( \Delta G^0_i \) (neut) appear to be considerable and the reliability of the determination of \( \Delta G^0_i \) (neut) via inert gas assumption has not been proved.

de Ligny and co-workers latter slightly modified the method by incorporating ideas of Buckingham, Halliwell and Nyburg and Muirhead - Gould and Laidler.

Salomon determined the individual free energies of solvation from plot of differences in conventional free energies vs. \( \frac{1}{r_i} \) where \( r_i \) is the gas phase radius of Gouray and Adrian.\(^9\)

\[
\Delta g^0_{solv.} (H^+) \text{ is obtained from }
\]

\[
\sqrt{\Delta G^0_{conv.} (M^+) - \Delta G^0_{conv.} (X^-)} = \text{Constant} \frac{1}{r_i} - 2 \Delta g^0_{solv} (H^+) \tag{24}
\]

\[
\Delta G^0_{conv.} (M^+) = \Delta g^0_{solv} (M^+) - \Delta g^0_{solv} (H^+)
\]

\[
\Delta G^0_{conv.} (X^-) = \Delta g^0_{solv} (X^-) + \Delta g^0_{solv} (H^+)
\]

\( M^+ \) 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 $r^{-1} \cdot \Delta G^{\circ}_{\text{solv.}} (H^+)$ is found to be $-235.0$ K. Cal/mole.

Since $\Delta G^0_{\text{neut.}}$ is dependent on ionic radius, the choice of crystal radii as determined by different workers are noted. Criss and Salomon\(^\text{98}\) considered it desirable to take differences in $\Delta G^0_{t, \text{conv.}} (\text{ion})$ which automatically cancels $\Delta G^0_{t, \text{neut.}}$ 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\(^\text{15,96,167-172}\) 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 et al. proposed Tetraphenyl phosphonium tetraphenyl borate \((\text{Ph}_4\text{PB Ph}_4)\) as the reference electrolyte. Popovych proposed tri-isoamyl - n - butyl ammonium tetraphenyl borate \((\text{TABBPh}_4)\) as 'reference electrolyte' based on the equality of the stokes \(173-175\) radii of ions in water, methanol + acetonitrile. Tetraphenyl arsonium tetraphenyl borate \((\text{TATB})\) i.e. \(\text{Ph}_4\text{AsBPh}_4\) 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:
   a) formation of crystal solvates.
   b) micelle formation.
   c) formation of complex ions.
   d) ion-pair formation.

2) Insufficient evidence or no 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.\(^{124}\)

In spite of the defects, the results obtained with TABB\textsubscript{4} of Popovych and co-workers and with Ph\textsubscript{4} As BPh\textsubscript{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\textsubscript{4} As BPh\textsubscript{4} as 'reference electrolyte' to calculate single ion thermodynamics.

However, Treiner\(^{176}\) examined the Ph\textsubscript{4} AsBPh\textsubscript{4} assumption through the use of scaled particle theory outlined by Pierotti\(^{177}\) to deduce that the assumption was not valid for transfers between water, propylene carbonate, sulpholane, DMSO, \textit{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, 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: The $\Delta G^0_t (H^+)$ values, as calculated by Wells for different aquo-organic solvents, involve the use of the equation

$$\Delta G^0_t (H^+)_e = \Delta G^0_t (H^+) + \Delta G^0_t (ROH^+).$$

(25)

$\Delta G^0_t (H^+)_e$ has been calculated by the application of Born equation to the transfer of a sphere containing the tetrahedral structure $H_2O^+ (H_2O)_4$.

$$\Delta G^0_t (H^+)_e = \frac{Ne^2}{6r_{H_2O}} \left( \epsilon_p^{\lambda} - \epsilon_\lambda \right)$$

(26)

The major contribution is from $\Delta G^0_t (ROH^+)$, which covers all subsequent structural changes induced by the presence of the tetrahedral $H_2O^+ (H_2O)_4$ in the mixed solvent $\Delta G^0_t (ROH^+)$ has been calculated from the equilibrium constant $K$ of the solvent sorting equilibrium.

$$\frac{(H_2O)_{x-1} ROH_{solv} + K \sqrt{(H_2O)_{x-1} ROH} H_{solv}^{\lambda}}.$$  

(27)

The method has been criticised by Lahiri and recently by Blandamer et al.
Lahiri and co-workers have recently suggested a method for the determination of $\Delta G_t^0 (H^+)$, using the dissociation constants of the 'isoelectric reactions': \(\text{(28)}\)

$$HL^+ \rightleftharpoons L + H^+ \quad \ldots (28)$$

Where, $L = 2,2'$-dipyridyl or, $1,10$ - Phenanthroline \(\text{ as follows}\)

$$\Delta G^0_t = -2.303 \, RT \log \left( \frac{c_{L+}}{c_{H^+}} \right) \quad \ldots (29)$$

$$\Delta \Delta G^0_t = \Delta G^0_t (L) + \Delta G^0_t (H^+) - \Delta G^0_t (HL^+) \quad \ldots (30)$$

or $\Delta G^0_t (H^+) = \Delta \Delta G^0_t + \Delta G^0_{t, el} (HL^+) \quad \ldots (31)$

$\Delta G^0_{t, el} (HL^+)$ 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 eliminated and the solutions are in their respective standard states, a condition essential for the determination of 'medium effects' of ions. The $\Delta G^0_t (H^+)$ 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.

The $\Delta G^0_t (H^+)$ values calculated have been utilised to determine the 'medium effect' of other ions.

(c) METHOD OF GRUNFALD : 172

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

\[
(pK_s - pK_w)_{HA} = \log Y_{H^+} + \log \frac{Y_A^-}{Y_{HA}} = \log Y_{H^+} + m_A Y^- \quad \ldots (32)
\]

and

\[
(pK_s - pK_w)_{BH^+} = \log Y_{H^+} + m_B Y^0 \quad \ldots (32a)
\]

Where $m_A$ and $m_B$ are substituent constants independent of the nature of the solvent, $Y^-$ and $Y^0$ are the solvent parameters dependent on the solvent only.

\[
Y^- = (1 - \eta^2) \quad \ldots (33)
\]

and

\[
Y^0 = (1 - \eta^2)^2 \quad \ldots (34)
\]

($\eta$ = weight fraction of water in the solvent)

Now,

\[
(pK_s - pK_w)_{HA} - (pK_s - pK_w)_{BH^+} = m_A Y^- - m_B Y^0 \ldots (35)
\]

$m_A$ and $m_B$ are determined by multi-regression method which enables
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 \( \Delta G_t^0 \) (ions). The 'reference electrolyte' method has been advocated to be the best method though the limitations are known. The \( \Delta G_t^0 (H^+) \) 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 \( \Delta G_t^0 \) (ion-dipole) interactions in the calculation of \( \Delta G_t^0 (H^+) \) ion.\(^{53} \)

However, the recent calculation of \( \Delta G_t^0 (H^+) \) from water to methanol + water mixtures based on assumption \( (\text{Ph}_4\text{P}^+, \text{Ph}_4\text{A}^+) = \text{Ph}_4\text{B}^- \) show that the \( \Delta G_t^0 (H^+) \) values are in qualitative disagreement with the values reported in the literature.

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 Parsons \textsuperscript{180,181} for the real free energies of transfer of ions. Similar discrepancies are also apparent from the scrutiny of Tables for $\Delta G^0_t (H^+)$ (and other ions) given by Criss and Salomon\textsuperscript{96}. The results show that not too reliance should be made on a particular method.

Kolthoff \textsuperscript{182} sounds a note of warning not to accept a value of an ion medium activity co-efficient, obtained on the basis of any of the two and other assumptions with water as a reference solvent, as the true value. As pointed out by Popovych \textsuperscript{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 $\Delta H_t$ of electrolytes into single ion values from the vast collections of enthalpy of transfer of electrolytes.

According to Feakins \textsuperscript{183} and Ben Naim \textsuperscript{184} the individual ionic contributions resulting from ion-solvent interactions to $\Delta H^0_t$
and $\Delta S^0_t$ are of great importance because they reflect important structural differences in the behavior of ions in various solvents which are completely lost in the simpler free energy terms due to compensation of $\Delta H^0_t$ and $T \Delta S^0_t$ terms. It is clear that $\Delta H^0_t$ (ion) and $\Delta S^0_t$ (ion) are difficult to evaluate and any questionable assumptions regarding the physical model for the calculations could lead to large uncertainties in the resulting $\Delta H^0_t$ (ion) values. The relationship between ionic enthalpies of solvation or of transfer and structure is not clear. 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 Kcal) in the single-ion values in water have been reported. Consistent results are not given by methods such as extrapolations of enthalpy values of alkali metal halides or tetralkyl ammonium halides with respect to ionic radius or...
ii) the assumptions that the enthalpies of transfer of both
cryptates of alkali ions and the corresponding free ligands are
identical. 196

Very few determinations of $\Delta H^\circ_t$ of ions, mainly based on $\Delta H^\circ_t$
(Ph$_4$As$^+$) = $\Delta H^\circ_t$ (B Ph$_4^-$) have been made. 188,189,197 Friedman
and co-workers 197-198 recommended the use of propylene carbon­
ate (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 $\Delta H^\circ_t$ (Ph$_4$As$^+$) = $\Delta H^\circ_t$ (B Ph$_4^-$) have also been reported
though the method has been utilised by Choux and Benoit 199, Julli­
ard 188 and more recently by Abraham (who used Ph$_4$PB Ph$_4^-$ and
Ph$_4$As BPh$_4$).

Recently, Lahiri et. al. 200 determined the enthalpies of transfer
of $H^+$ ion from water to methanol + water or ethanol + water mix­
tures. The way similar to the determination of $\Delta G^\circ_t$ ($H^+$) de­
scribed before.

For the reaction $LH^+ \rightarrow L + H^+$, the relation is

$\Delta H^\circ_t$ ($H^+$) = $\Delta H^\circ_t$ (1) + $\Delta H^\circ_t$ (el) ($LH^+$)

(where L = 1, 10 - Phenanthroline).
They utilised these values to calculate the single ion values of benzoate ion and amino acid cations and anions.

We have extended the method in case of dioxane-water mixtures in the present dissertation.

It is too early to predict any thing regarding the single-ion values from these data.

However, it is desirable to acquire single ion values from different methods in order to test the applicability of the present method. The 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 enthalpy 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 dissertation is a modest attempt to understand the 'medium effects' of ions and ion-solvent interactions.

The results of our investigations are presented in subsequent chapters with the requisite description about the topics concerned.
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