

CHAPTER II

GENERAL INTRODUCTION

2.1 THE IMPORTANCE OF SOLUTION CHEMISTRY

One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation becomes predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometry, viscometry, densitometry, spectroscopy, ultrasonic interferometry and other suitable methods and to interpret the experimental data collected.¹⁻⁸

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolyte solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

In the last few decades, considerable emphasis has been placed on research in the behaviour of electrolytes in non-aqueous and mixed solvents to investigate the

ion-ion (solute-solute) and ion-solvent interactions under varied conditions. Different sequences of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry.⁹

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation,^{10,11} the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated,^{12,13} and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.¹⁴⁻¹⁶

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosities, conductances, ultrasonic velocities and spectroscopic properties of some important electrolytes in N,N-dimethylacetamide and its aqueous binary mixture. It also includes the study of excess properties of the binary mixtures of N,N-dimethylacetamide (DMA) with formamide (FA), N,N-dimethylformamide(DMF) and 2-ethoxyethanol (EE) at three different temperatures.

2.2 VISCOSITY

Although viscosity is not a thermodynamic property, together with the partial molal volume \bar{V}_2 , it gives much information regarding the ion-solvent interactions, structures of electrolytic solutions and solvation. Jones and Dole¹⁷ suggested the first quantitative empirical relation correlating the relative viscosities (η_r) of the electrolytes and their molar concentrations (c):

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (1)$$

The equation reduces to

$$(\eta_r - 1)/c^{1/2} = A + Bc^{1/2} \quad (2)$$

where A and B are constants specific to ion-ion and ion-solvent interactions respectively. The equation is equally applicable to aqueous and non-aqueous systems where there is no ion-association. The term $A c^{1/2}$, arose from the long range coulombic forces between the ions. The significance of the term has since been realized due to the development of Debye-Hückel theory¹⁸ of interionic attractions, Falkenhagen's theoretical calculations of 'A' using the equilibrium theory^{19,20} and the theory of irreversible processes in electrolytes developed by Onsager and Fuoss.²¹

For associated electrolytes the viscosity data have been analyzed by the following equation²²

$$\eta_r = 1 + A(\alpha c)^{1/2} + B\alpha c + B'(1 - \alpha)c \quad (3)$$

Here A, B and B' are the characteristic constants and α is the degree of dissociation of the ion pair.

Eq. (3) can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}] / \alpha c = B + B' (1-\alpha)/\alpha \quad (4)$$

The values of α were calculated from the conductance data using the equations described in the literature.²²

The 'A' coefficient depends on the ion-ion interactions and can be calculated using the Falkenhagen-Vernon equation.²⁰

$$A_{\text{theo}} = \frac{0.2577\Lambda^\circ}{\eta_0(\epsilon T)^{1/2} \lambda_+^\circ \lambda_-^\circ} \left[1 - 0.6863 \left(\frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda^\circ} \right)^2 \right] \quad (5)$$

where Λ° , λ_+° and λ_-° are the limiting conductances of the electrolyte, cation and anion respectively, at temperature T, ϵ is the dielectric constant and η_0 is the viscosity of the solvent. For most solutions this equation is valid upto 0.1M.^{23,24}

2.2.1 Division of B-Coefficients into Ionic Values

In order to identify the separate contributions of cations and anions to the total solute-solvent interactions, the B-coefficients as determined by Jones-Dole's equation has to be resolved into ionic components. For this Cox and Wolfenden,²⁵ Gurney,²⁶ Sacco *et al.*,²⁷ Tuan and Fuoss,²⁸ and several authors used different approximations and assumptions for different systems. For example, Sacco *et al.*²⁷

proposed the widely used 'reference electrolyte' method. Thus, for Ph_4PBPh_4 in water, we have,

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{Ph}_4\text{PBPh}_4} / 2 \quad (6)$$

$B_{\text{Ph}_4\text{PBPh}_4}$ is obtained from,

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \quad (7)$$

(since Ph_4PBPh_4 is scarcely soluble in water). These values are in good agreement with those obtained by other methods.

However, according to Krumgalz²⁹ it is impossible to select any two ions for which $\lambda^\circ_+ = \lambda^\circ_-$ in all solvents and at proper temperatures. Also, even if the mobilities of some ions are equal at infinite dilution, they are not necessarily equal at moderate concentrations. Further, equality of ionic dimensions does not necessarily imply equality of B-coefficients of these ions, as they are likely to be solvent and ion-structure dependent.

Krumgalz proposed a method³⁰ based on the fact that the large tetraalkylammonium ions are not solvated in organic solvents. So, the ionic B-values for large R_4N^+ ions (where $\text{R} \geq \text{Bu}$) in organic solvents are proportional to their ionic dimensions.

$$B_{\text{R}_4\text{NX}} = a + b r_{\text{R}_4\text{N}^+}^3 \quad (8)$$

where, $a = B_x^-$ and b is a constant independent of temperature and solvent nature. Extrapolation of the plot of B_{R_4NX} ($R > Pr$ or Bu) against $r_{R_4N^+}^3$ to zero cation dimension gives B_x^- directly in the proper solvent from which other ionic B -values can be calculated.

Ionic B -values can also be calculated from the following equations :

$$B_{R_4N^+} - B_{R_4N^+} = B_{R_4NX} - B_{R_4NX} \quad (9)$$

and

$$B_{R_4N^+} / B_{R_4N^+} = r_{R_4N^+}^3 / r_{R_4N^+}^3 \quad (10)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data.³¹

On similar reasoning, Gill and Sharma³² used Bu_4NBPh_4 as the reference electrolyte and proposed the equation.

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r_{Ph_4B^-}^3}{r_{Bu_4N^+}^3} = \left[\frac{5.35}{5.00} \right]^3 \quad (11)$$

and

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (12)$$

because the ionic radii of Bu_4N^+ (5.00 Å) and of Ph_4B^- (5.35 Å) have been found to remain constant in different non-aqueous and mixed non-aqueous solvents. Lawrence and Sacco^{33,34} used Bu_4NBBu_4 and Ph_4PBPh_4 as reference electrolytes because these cations and anions are symmetrically shaped and have almost equal van der Waals volumes. Their results and the conclusions of Thomson *et al*³⁵ agreed well with the reported values.

It is obvious that most of these methods are based on certain approximations and anomalous results may arise unless proper mathematical theories are developed to calculate B-values.

2.2.2 Thermodynamics of Viscous Flow

Feakins *et al*³⁶ suggested the following expression

$$B = \frac{\bar{V}_1^\circ - \bar{V}_2^\circ}{1000} + \frac{\bar{V}_1^\circ}{1000} \left(\frac{\Delta\mu_2^{\circ\#} - \Delta\mu_1^{\circ\#}}{RT} \right) \quad (13)$$

where \bar{V}_1° and \bar{V}_2° are the partial molal volumes of the solvent and solute respectively, $\Delta\mu_1^{\circ\#}$ is the free energy of activation for viscous flow per mole of the solvent and $\Delta\mu_2^{\circ\#}$ is the contribution per mole of solute to the free energy of activation for the viscous flow of the solution.

2.2.3 Effects of Shape and Size

Stokes and Mills²³ regarded the ions in solution as rigid spheres suspended in a continuum and proposed an equation for relative viscosity as

$$\eta/\eta_0 = 1 + 2.5 \phi \quad (14)$$

where ϕ is the volume of the fraction occupied by the particles. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cation). Thus combining the above equation with Jones-Dole equation (1), we have

$$2.5 \vartheta = Ac^{1/2} + Bc \quad (15)$$

Neglecting $Ac^{1/2}$ in comparison with Bc , and substituting $\vartheta = c\bar{V}_i$ where \bar{V}_i is the partial molal volume of the solute, we get

$$2.5 \bar{V}_i = B \quad (16)$$

Assuming that the ions behave like rigid spheres with effective radii R_{\pm} , moving in a continuum, B_{\pm} , can be equated to

$$B_{\pm} = 2.5 V_{\pm} = 2.5 \times 4/3 \pi (R_{\pm}^3 N/1000) \quad (17)$$

R_{\pm} calculated using eqn (17) should be close to crystallographic radii or corrected Stokes' radii if the ions are scarcely solvated and behave as spherical entities. But R_{\pm} values of the ions, which are higher than the crystallographic radii indicate solvation.

The number (n) of solvent molecules bound to the ion in the primary solvation shell can be calculated by comparing the Jones-Dole equation with that of Einstein³⁷

$$B_{\pm} = 2.5 (V_i + n V_s) / 1000 \quad (18)$$

Where V_i is the bare ion molar volume and V_s the molar volume of the solvent. The above equation has been used by a number of workers³⁸⁻⁴¹ to study the nature of solvation.

2.3 CONDUCTANCE

Conductance measurement is one of the most accurate and widely used physical methods for investigating the electrolytic solutions.^{42,43} Together with transference number determination, it provides an excellent method for obtaining single ion values. In conjunction with viscosity measurements, conductance data give much information regarding ion-ion and ion-solvent interaction.

Onsager⁴⁴ was the first to successfully apply Debye-Hückel theory of interionic associations. Subsequently, Pitts,⁴⁵ and Fuoss and Onsager^{46,47} independently worked to account for both long and short range interactions. As Pitts' values differed considerably from Fuoss and Onsager's values, Fuoss and Hsia⁴⁸ modified the original Fuoss-Onsager equation. The modified Fuoss-Onsager equation is of the form⁴³

$$\Lambda = \Lambda^{\circ} - \frac{\alpha \Lambda^{\circ} c^{1/2}}{(1 + \kappa a)(1 + \kappa a/z^{1/2})} - \frac{\beta c^{1/2}}{(1 + \kappa a)} + G(\kappa a) \quad (19)$$

where $G(\kappa a)$ is a complicated function of the variable. The simplified form

$$\Lambda = \Lambda^{\circ} - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} \quad (20)$$

is generally employed in the analysis of experimental results. Fuoss and Accascina⁴⁶ made further correction of equation(20) taking into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

$$\Lambda = \Lambda^{\circ} - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} - B \Lambda^{\circ} c \quad (21)$$

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In most cases, however, J_2 is made zero, but this leads to a systematic deviation of the experimental data from the theoretical equations.

2.3.1 Ion - Association

The plot Λ versus $c^{1/2}$ (limiting Onsager equation) is used to determine the dissociation or association of electrolytes. If $\Lambda^\circ_{(expt)} > \Lambda^\circ_{(theo)}$, the electrolyte may be regarded as completely dissociated but if $\Lambda^\circ_{(expt)} < \Lambda^\circ_{(theo)}$, the electrolytes may be regarded as associated. The difference between $\Lambda^\circ_{(expt)}$ and $\Lambda^\circ_{(theo)}$ would be considerable with increasing association.⁴⁹

For strongly associated electrolytes, association constants K_A and Λ° were determined using the Fuoss-Kraus equation⁵⁰ or Shedlovsky's equation.^{51,52}

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda^\circ} + \frac{K_A}{(\Lambda^\circ)^2} \times \frac{c\gamma_{\pm}^2 \Lambda}{T(z)} \quad (22)$$

where, $T(z) = F(z)$ (Fuoss-Kraus) and $1/T(z) = S(z)$ (Shedlovsky)

$$F(z) = 1 - z(1 - z(1 - z(1 - \dots)^{-1/2})^{-1/2})^{-1/2} \quad (23)$$

and

$$S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (24)$$

The plot of $T(z) / \Lambda$ against $c\gamma_{\pm}^2\Lambda / T(z)$ should be a straight line having an intercept of $1 / \Lambda^\circ$ and a slope of $K_A / (\Lambda^\circ)^2$. When K_A is large, there will be considerable uncertainty in the values of Λ° and K_A determined from equation.(22)

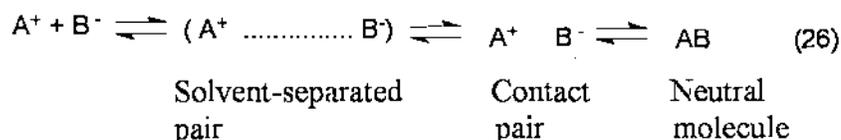
The Fuoss-Hsia conductance equation for associated electrolytes is given as

$$\Lambda = \Lambda^\circ - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (25)$$

The equation was modified by Justice.⁵³

2.3.2 Ion-size Parameter and Ionic Association

In 1978, Fuoss put forward a new conductance equation⁵⁴ replacing the one he had formulated three years earlier. He classified the ions of electrolytic solutions into three categories; (i) those which find an ion of opposite charge in the first shell of the nearest neighbours (contact pairs) with $r_{ij} = a$, (ii) those with overlapping Gurney co-spheres (solvent separated pairs); and (iii) those which find no other unpaired ion in a surrounding sphere of radius R , where R is the diameter of the co-sphere (unpaired ions). Thermal motion and forces establish a steady state, represented by the equilibria



From this equation Fuoss derived an expression for the association constant or conductometric pairing constant

$$K_A = K_R (1 + K_s) \quad (27)$$

where, K_R describes the formation and separation of solvent-separated pairs by diffusion, in and out of the spheres of diameter R around the cations (calculated using the continuum theory), K_s is a constant describing the specific short range ion-solvent and ion-ion interactions by which contact pairs form and dissociate.

The details of the calculations are presented in the 1978 paper. The shortcomings of the previous papers have been rectified in the new set of equations that are more general than the previous ones and can be used in higher concentration regions (0.1 N in aqueous solutions).

For a given set of conductivity values (c_j , Λ_j , $j = 1, \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ°), association constant (K_A), and the co-sphere diameter (R), are derived from the following set of equations :

$$\Lambda = p[\Lambda^\circ (1 + R_x) + E_L] \quad (28)$$

$$p = 1 - \alpha(1 - \gamma) \quad (29)$$

$$\gamma = 1 - K_{AC}c^2 \quad (30)$$

$$-\ln f = \beta k / 2(1 + kR) \quad (31)$$

$$\beta = e^2 / Dk_B T \quad (32)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_s) \quad (33)$$

Where R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, D is the dielectric constant of the solvent, e is the electron charge, k_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations can be performed on a computer using the programme suggested by Fuoss.

2.3.3 Limiting Ionic Equivalent Conductances

The limiting equivalent conductance (Λ°) can be divided into ionic components using the experimentally determined transport number of ions (t_\pm) as follows :

$$\lambda_{\pm}^{\circ} = t_{\pm} \Lambda^{\circ} \text{ and } \lambda_{\pm}^{\circ} = t_{\pm} \Lambda^{\circ} \quad (34)$$

However, accurate transference number determinations are limited to only a few solvents. Hence, various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance in ionic solvents for which experimental transference numbers are not yet available. These methods have been well described by Walden,⁵⁵ Fuoss,⁵⁶ and Gill.⁵⁷

Krumgalz,⁵⁸ suggested a new method based on the fact, confirmed by NMR studies, that the large tetraalkyl (aryl) onium ions are not solvated in organic solvents, in the kinetic sense, due to the extremely weak electrostatic interactions between the solvent molecules and the large ions with low surface charge density.

From the consideration of the motion of a solvated ion in an electrostatic field as a whole, it is possible to calculate the radius of the moving particle by the Stokes' equation

$$r_s = |Z| F^2 / (A\pi N\eta_0\lambda_{\pm}^{\circ}) \quad (35)$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in the case of perfect slipping). Since the r_s values, the real dimensions of the non-solvated tetraalkyl(aryl) onium ions must be constant, we have

$$\lambda_{\pm}^{\circ}\eta_0 = \text{constant} \quad (36)$$

This relation has been tested using the λ_{\pm}° values determined with precise transference numbers. The product becomes constant and independent of the

chemical nature of the organic solvents for the $I-Am_4B^-$, Ph_4As^+ , Ph_4B^- ions and for tetraalkylammonium cations starting from Et_4N^+ . The relation can also be well utilized to determine λ_{\pm}° values of ions in other organic solvents from the determined Λ° values

We have used Bu_4NBPh_4 as the 'reference electrolyte', but instead of equal division, we divided the Λ° values using a method similar to that proposed by Krumgalz²⁹ for division of B-values

$$\frac{\lambda^{\circ}(Bu_4N^+)}{\lambda^{\circ}(Ph_4B^-)} = \frac{r(Ph_4B^-)}{r(Bu_4N^+)} = \frac{5.35}{5.00} = 1.07 \quad (37)$$

The r values have been taken from the works of Gill *et al*⁵⁷

The values calculated by this method seem to be correct in different organic and mixed organic solvents. However, in aqueous binary mixtures, the solvation pattern may be different and the validity of this equation may be questioned.

Recently, Gill *et al*⁵⁹ proposed the following equation

$$\frac{\lambda^{\circ}(Bu_4N^+)}{\lambda^{\circ}(Ph_4B^-)} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (38)$$

and the ratio is close to 1.07 as used by us.

2.3.4 Solvation Number

An ion has an electric field or force around it which fades out into a negligible value after a short distance ($\sim 10 \text{ \AA}$). In other words there is an effective volume within which its influence operates. The solvent molecules within this

volume may be said to be interacting with the ion, resulting in the solvation of the ion. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number.⁶⁰

Depending upon the distance from the ion, we can classify two solvation regions : primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation

$$V_s^s = 4/3 \pi(r_s^3 - r_c^3) \quad (39)$$

Where r_c is the crystallographic radius of the ion. The solvation number n_s would then be obtained from

$$n_s = V_s^s / \bar{V}_o \quad (40)$$

Assuming Stokes' relation to hold good, the ionic solvated volume can be obtained, because of the packing effects,⁶¹ from

$$V_s^o = 4.35 r_s^3 \quad (41)$$

where V_s° is expressed in mol/mole and r_s in angstroms. However, this method is not applicable to ions of medium size though a number of empirical⁶² and theoretical corrections^{63,64} have been suggested in order to apply it to most of the ions.

2.3.5 Stokes' Law and Walden's Rule

The limiting conductance λ_i° of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^\circ = 0.819 |Z_i| / \eta_i R_i \quad (42)$$

If the radius R_i is assumed to be the same in every organic solvent, as would be the case of bulky organic ions, we get

$$\lambda_i^\circ \eta_o = 0.819 |Z_i| / R_i = \text{constant} \quad (43)$$

This is known as the Walden rule.⁶⁵ The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

2.3.6 Recent Conductivity Equations

In 1986, Papadopoulos⁶⁶ analysed some conductance data using the Lee-Wheaton⁶⁷ conductance equation and compared the values with those obtained by Kay and his co-workers.⁶⁸ From 1992 to 1995, Blum, Turq and co-workers⁶⁹⁻⁷¹ have developed a mean spherical approximation (MSA) version of conductivity

equations. Their theory starts from the same continuity and hydrodynamics equations used in the more classical treatments; however, an important difference consists in the use of the MSA expressions for the equilibrium and structural properties of the electrolyte solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem relatively small, it has been claimed that the performance of the MSA equation is good over a much wider concentration range than that covered by the classical equations. However, no thorough study of the performance of the new equations at the level of the experimental uncertainty of conductivity measurement is yet available in the literature, with the exception of a very recent study by Bianchi *et al.*⁷² They compared the results obtained, using the old and new equations in order to evaluate their capacity to describe the conductivity of different electrolyte solution. Their investigation too is limited to only three aqueous salt solutions and the picture is consistent showing a better performance for the classical equations as far as the system electrolytes are concerned.

In 2000, Chandra and Bagchi⁷³ have evolved a new microscopic approach to ionic conductance and viscosity based on mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structure factors of the charge and number densities of the electrolyte solution. They claim that their new equation is applicable at low as well as at high concentrations and it describes the crossover from low to high concentration smoothly. Debye, Hückel, Onsager and Falkenhagen expressions can be derived

from this self-consistent theory at the limiting, very low ion concentration. For conductance the agreement seems to be satisfactory up to 1 M concentration.

2.4 APPARENT AND PARTIAL MOLAR VOLUMES

Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these properties in terms of molecular phenomena is generally difficult. Sometimes, higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. For example, the partial molar volume, the pressure derivative of partial molal Gibbs energy, is a useful parameter for interpreting solute-solvent interactions. Various concepts regarding molecular processes in solutions such as, electrostriction,⁷⁴⁻⁷⁶ hydrophobic hydration,⁷⁷ micellization⁷⁸ and cosphere overlap during solute-solute interactions.^{26,79} have to a large extent been derived and interpreted from the partial molar volume data of many compounds.

The apparent molar volumes, ϕ_v , of the solutes can be calculated using the following equation

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0) / c\rho_0 \quad (44)$$

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of the solvent and solution respectively and c is the molarity of the solution. The partial molar volume, \bar{V}_2 , can be obtained from the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}(d\phi_v/dc^{1/2})} c^{1/2} \frac{d\phi_v}{dc^{1/2}} \quad (45)$$

Masson⁸⁰ found that ϕ_v varies with the square root of the molar concentration by the linear equation.

$$\phi_v = \phi_v^0 + S^*_v \sqrt{c} \quad (46)$$

where ϕ_v^0 is the apparent molar volume at infinite dilution (equal to the partial molar volume at infinite dilution) and S^*_v is the experimental slope. Redlich and Meyer⁸¹ have shown that an equation of the form of (46) cannot be any more than a limiting law where for a given solvent and temperature, the slope S^*_v should depend only upon the valence type. They suggested the equation

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (47)$$

where $S_v = Kw^{3/2}$, is the theoretical slope based on molar concentration, including the valence factor where

$$w = 0.5 \sum v_i Z_i^2 \quad (48)$$

and

$$K = N^2 e^3 (8\pi / 1000\epsilon^3 RT)^{1/2} [\partial \ln \epsilon / \partial P]_T - \beta/3 \quad (49)$$

In equation (49), β is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation⁸¹ adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies⁸² on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for poly-valent electrolytes, the more complete Owen-Brinkley equation⁸³ can be used to aid in the extrapolation to infinite dilution and to

adequately represent the concentration dependency of ϕ . The Owen-Brinkley equation⁸³ which includes the ion-size parameter, a (cm), is given by

$$\phi_v = \phi_v^0 + S_v \tau(\kappa a) \sqrt{c} + 0.5 W_v \theta(\kappa a) c + 0.5 K_v c \quad (50)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson⁸⁴ and Krumgalz *et al.*⁸⁵ to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt $M\nu_M X\nu_X$ is

$$\phi_v = \phi_v^0 + \nu \left[Z_M Z_X \left(A_w / 2b \ln(1 + b\sqrt{I}) + 2\nu_M \nu_X RT [m^{\nu} B_{MX}^{\nu} m^2 (\nu_M \nu_X)^{1/2} C_{MX}^{\nu}] \right) \right] \quad (51)$$

where the symbols have their usual significance.

2.4.1 Ionic Limiting Partial Molar Volumes

Most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions. For some time, the method of Conway *et al.*⁸⁶ was widely used. They plotted the limiting partial molar volume, $\bar{V}_{R_4NX}^0$ for a series of homologous tetraalkylammonium chlorides, bromides and iodides with a halide ion in common,

of the formula weight of the cation $M_{R_4N^+}$, and obtained straight-line graphs for each series. Their results were claimed to fit the equation.

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + b M_{R_4N^+} \quad (52)$$

and the extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, V_{x-}^0 . Uosaki *et al*⁸⁷ and later Krumgalz⁸⁸ applied the same method to non-aqueous electrolyte solutions in a wide temperature range. In our laboratory too we have used this method for the division of partial molar volumes into the ionic components in 2-methoxyethanol.^{89,90}

2.5 ULTRASONIC VELOCITY

In the last two decades there have been a number of studies on the ultrasonic velocities and isentropic compressibilities of liquids, solutions and liquid mixtures⁹¹ because these data provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic speeds in solutions. Isentropic compressibilities play a vital role in characterization of binary liquid mixtures.

2.5.1 Apparent Molal Isentropic Compressibility

The apparent molal isentropic compressibility, the second derivative of the Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information about these, particularly in cases where partial molal volume data alone fail to provide an unequivocal interpretation of the interactions.⁹²⁻⁹⁶ The isentropic compressibility (κ_s) values are calculated using the Laplace equation

$$\kappa_s = 1 / (u^2 \rho) \quad (53)$$

where u is the sound velocity in solution and ρ is the solution density. The apparent molal isentropic compressibility (κ_ϕ) of the liquid solution is calculated using the relation

$$\kappa_\phi = [(1000/m\rho\rho_0) (\kappa_s\rho_0 - \kappa_s^\circ\rho)] + \kappa_s M/\rho_0 \quad (54)$$

where m is the molality of the solution; κ_s° and κ_s are the compressibility coefficients of the solvent and solution respectively.

Plotting of κ_ϕ against the square-root of the molal concentration of solutes and extrapolation to zero molal concentration gives the limiting apparent molal isentropic compressibility (κ_ϕ°) according to the equation.^{92,96}

$$\kappa_\phi = \kappa_\phi^\circ + S_k \sqrt{m} \quad (55)$$

where S_k is the experimental slope.

The limiting molal isentropic compressibility (κ_ϕ°) and the experimental slope (S_k) can be interpreted in terms of solute-solvent and solute-solute interactions, respectively. It is well established that the solutes causing electrostriction lead to a decrease in the compressibility of the solution.^{97,98} This is reflected by the negative values of κ_ϕ° of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure.^{78,97} The compressibility of hydrogen-bonded structure, however, varies depending on the nature of H-bonds involved,⁹⁷ the poor fit of the solute

molecules⁹⁹ as well as the possibility of flexible H-bond formation causing a more compressible environment (and hence a positive κ_ϕ° value) in the aqueous medium. Positive κ_ϕ° values have been reported in aqueous non-electrolytes¹⁰⁰ and non-electrolyte – non-electrolyte solutions.¹⁰¹

2.6 SOME RECENT TRENDS IN SOLVATION MODELS

The last decade (1990-2000) witnessed some interesting trends in development of some solvation models and computer software. Based on a vast collection of experimental free energy of solvation data, Cramer, Truhlar and co-workers constructed a series of solvation models (SM1 – SM5 series) to predict and calculate the free energy of solvation of a chemical compound.¹⁰²⁻¹⁰⁶ These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and / or I. The only input data required are molecular formula, geometry, refractive index, surface tension, Abraham's α (acidity parameter) and β (basicity parameter) values, and, in the latest models, the dielectric constants. Many of these parameters for a number of compounds are available in the internet.¹⁰⁷

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 kcal/mol. They can also be used to predict the vapour pressure at 298.15K with useful accuracy. They are especially useful when other methods are not available. One can also analyse factors like, electrostatics, dispersion, hydrogen bonding, etc, using these tools. They are also relatively inexpensive and available in easy to use computer codes.

Galindo *et al*^{108,109} have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibria of electrolyte aqueous solutions. The water molecules are modeled as hard spheres with four short range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions. Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity takes values very close to unity, especially in the case in which the mean spherical approximation is used, indicating a good description of the solvent. Bosch *et al*¹¹⁰ have compared several Preferential Solvation Models especially for describing the polarity of dipolar hydrogen bond acceptor – cosolvent mixtures.

2.7 A BRIEF LITERATURE SURVEY OF THE SOLVENTS USED FOR THIS INVESTIGATION

2.7.1 N,N – Dimethylacetamide (DMA)

N,N-Dimethylacetamide has a liquid range of 253.15 to 438.15K and a dielectric constant of 37.78 at 298.15K.⁹ It is miscible with water and is generally similar in its properties to N,N-dimethylformamide (DMF). It is a dipolar aprotic solvent and due to the presence of the two methyl groups attached to the nitrogen, it is more electron donating. Its ability to solvate cations is greater than that of DMF, acetone, acetonitrile and benzonitrile.¹¹¹

Solubilities of several alkali and alkaline earth metal halides and transition metal halides in DMA were measured by Pistoia and Scrosati.¹¹² The solubilities increase in the order $\text{Cl} < \text{Br} < \text{I}$. Alexander *et al*¹¹³ reported solubility product values for numerous silver salts in DMA. The solubilities of silver halides show the same trend as in water. Cations, particularly small cations (Ag^+ and K^+) and even large ones like trans- and cis- $[\text{CoCl}_2(\text{en})_2]^+$ which possess H-bond donor sites, are substantially better solvated in strongly dipolar aprotic solvents like DMA. Sears *et al*¹¹⁴ measured the conductances of some alkali and tetraalkylammonium salts in pure DMA at 298.15K. Large polarisable anions, like picrate, perchlorate, AgCl_2^- are better solvated by the strong dipolar solvents, presumably through dipole-induced dipole interactions.¹¹⁵

Studies on binary mixtures of DMA have also been reported in the literature, mostly as a comparative study of different amides. Goma¹¹⁶ and also Pal *et al*¹¹⁷ investigated the interactions of DMF and DMA with water. Conductance measurements of some tetraalkylammonium bromides in DMA + water binary mixtures have also been reported by Ramanamurti *et al*¹¹⁸

2.7.2 Formamide

Formamide has received considerable attention as a solvent for various electrochemical study, mainly because it is an example of a solvent with a higher dielectric constant ($\epsilon = 109.5$ at 298.15K)⁹ than water and thus can dissolve many electrolytes. The oxygen and nitrogen atoms within a formamide molecule are

negatively charged and the carbon and hydrogen atoms have partially positive charges and has a dipole moment(μ) of about 3.68D at 298.15K⁹ Formamide molecules in their liquid state are strongly self-associated through extensive networks of hydrogen bonds.¹¹⁹ The molecular and liquid structures of formamide have been studied by means of X-ray diffraction.¹²⁰ From the X-ray diffraction experiment we know that liquid formamide mainly consists of chain-like hydrogen bonded structure combining through $-\text{NH}_2 \dots \text{O} = \text{CH} -$ interactions. However, the stable ring structure existing in the solid state may be rather unfavourable to give the high dielectric constant of formamide and high solubilities of electrolytes in it in the liquid phase. Spiro¹²¹ combined the value obtained for the limiting transference number, using moving boundary method with the data for the limiting equivalent conductance to generate a set of individual ionic conductances for a variety of ions in formamide.

Formamide along with other amides is also used as one of the component in the binary mixture with different alcohols and water. Ali *et al*¹¹⁹ reported the thermodynamic properties of formamide + ethanol binary mixtures as a function of concentration and temperature. Leal and co-workers¹²² investigated the thermodynamic properties of the aqueous binary mixtures of different amides including formamide also and the results were used to make a comparison with amide – alcohol mixtures. The changes in dielectric constant of formamide with respect to concentration in its aqueous binary mixture was measured by Rohdewald *et al.*¹²³

2.7.3 N,N-Dimethylformamide (DMF)

N,N-Dimethylformamide (DMF) is an aprotic, protophylic and a potentially basic medium. Owing to its easy miscibility with almost all common polar and non polar solvents and high solvating power DMF is largely utilized in analytical and electrochemical applications. DMF has a quite large dipole moment ($\mu = 3.28\text{D}$ at 25°C)⁹ and a moderately high dielectric constant ($\epsilon = 37.5$ at 25°C)⁹. The striking tendency to provide hydrogen bonds via acceptor sites $-\text{C}(=\text{O})-\text{N}=\text{}$, makes DMF a powerful breaker of polymerized structure of hydroxy compounds.¹²⁴ Raman and infrared spectra of liquid DMF have been recorded by Fini and Mirone,¹²⁵ X-ray diffraction¹²⁶ and NMR¹²⁷⁻¹³⁰ study of liquid DMF indicates that there is no significant interactions, only a weak hydrogen bonded interaction existed between DMF molecules.

Several papers have been published on the measurements of transport and thermodynamic properties in pure DMF and also its binary mixture with other organic solvents. Physicochemical Data of pure DMF and its aqueous binary mixture have been reported by Rohdewald *et al.*¹²³ Excess properties of aqueous binary mixtures of a series of amides including N,N-dimethylformamide were calculated from density and viscosity measurements.¹²²

2.7.4 2-Ethoxyethanol (EE)

2-Ethoxyethanol is a bifunctional, versatile organic liquid commonly known as 'cellosolve'¹³¹ and is widely used in chemical industries as a solvent for

lacquers, oils, resins, dyes and as an antifreeze for explosives.¹³² They can be considered to be ethylene glycol derivatives obtained by the replacement of one of the hydroxy groups by an alkoxy group. Generally the 'cellosolves' are self associated through intramolecular hydrogen bond formation and further it exists as a five membered ring monomers also.¹³³⁻¹³⁵ The physical properties of 2-ethoxyethanol are obtained from the literature.^{132,136} Thermochemical properties of aqueous binary mixture of 2-ethoxyethanol along with other alkanols have been reported in the literature.¹³¹ Density, refractive index, speed of sound and their related excess properties in the binary mixtures of 2-ethoxyethanol with a number of important industrial liquids that find applications in a variety of areas have also been reported.¹³²

In this dissertation we have devoted our attention to the study of transport and thermodynamic properties of some selected alkali-metal and tetraalkalammonium salts in DMA and aqueous binary mixture of DMA and the excess properties of non-aqueous binary mixtures of DMA with formamide, dimethylformamide and 2-ethoxy ethanol.

The results have been described in subsequent chapters.

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