

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 become 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.¹⁻⁷

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.⁸

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;⁹ 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,¹⁰ and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.¹¹

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 2-methoxyethanol (ME), and 1,2-dimethoxyethane (DME), and in the binary mixtures of ME with N-methylacetamide (NMA) and N,N-dimethylacetamide (DMA).

2.2 THERMODYNAMICS OF ION-PAIR FORMATION

The standard Gibbs energy changes for the ion association process, ΔG^0 , can be calculated from the equation:

$$\Delta G^0 = -RT \ln K_A \quad (1)$$

The values of the standard enthalpy change, ΔH^0 , and the standard entropy change, ΔS^0 , can be evaluated from the temperature dependence of ΔG^0 values as follows:

$$\Delta H^0 = -T^2 \left[\frac{d(\Delta G^0 / T)}{dT} \right]_p \quad (2)$$

$$\Delta S^0 = - \left(\frac{d\Delta G^0}{dT} \right)_p \quad (3)$$

The ΔG^0 values can be fitted with the help of a polynomial of the type:

$$\Delta G^0 = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (4)$$

and the coefficients of the fits can be compiled together with the $\sigma\%$ values of the fits.

The standard values at 298.15 K are then:

$$\Delta G_{298.15}^0 = c_0 \quad (5)$$

$$\Delta S_{298.15}^0 = c_1 \quad (6)$$

$$\Delta H_{298.15}^0 = c_0 + 298.15c_1 \quad (7)$$

The main factors which govern the standard entropy of ion association of electrolytes are: i) the size and shape of the ions, ii) charge density on the ions, iii) electrostriction of the solvent molecules around the ions, and iv) penetration of the solvent

molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-Coulombic part of the Gibbs energy, ΔG^* , can also be calculated using the following equation¹²

$$\Delta G^* = N_A W_{\pm}^* \quad (8)$$

$$K_A = (4\pi N_A / 1000) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}^*}{kT}\right) dr \quad (9)$$

where the symbols have their usual significance. The quantity $2q/r$ is the Coulombic part of the interionic mean force potential and W_{\pm}^* is its non-Coulombic part.

The procedure for the evaluation of the non-Coulombic part of the entropy and enthalpy (and ΔS^* and ΔH^* respectively) is the same as that used for obtaining ΔS^0 and ΔH^0 .

The ΔG^* values at different temperatures can be fitted to the polynomial:

$$\Delta G^* = c_0^* + c_1^*(298.15 - T) + c_2^*(298.15 - T)^2 \quad (10)$$

and the coefficients of the fits along with the $\sigma\%$ values can be determined.

The values of ΔG^* , ΔS^* , and ΔH^* at 298.15 K are then easily obtained from the following equations:

$$\Delta G_{298.15}^* = c_0^* \quad (11)$$

$$\Delta S_{298.15}^* = c_1^* \quad (12)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (13)$$

2.3 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 Dole¹³ suggested the first quantitative empirical relation correlating the relative viscosities (η_r) of the electrolytes and their molar concentrations (c):

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (14)$$

The equation reduces to

$$(\eta_r - 1)/c^{1/2} = A + Bc^{1/2} \quad (15)$$

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 $Ac^{1/2}$, 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 theory^{14(a)} of interionic attractions, Falkenhagen's theoretical calculations of 'A' using the equilibrium theory^{14(b),(c)} and the theory of irreversible processes in electrolytes developed by Onsagar and Fuoss.^{14(d)}

The 'A' coefficient depends on the ion-ion interactions and can be calculated using the Falkenhagen-Vernon equation^{14(e)}

$$A_{\text{theo}} = \frac{0.2577 \Lambda^0}{\eta_0 (\epsilon T)^{1/2} \lambda_+^0 \lambda_-^0} \left[1 - 0.6863 \left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0} \right)^2 \right] \quad (16)$$

where Λ^0 , λ_+^0 and λ_-^0 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 up to 0.1 M.^{15, 16}

2.3.1 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,¹⁷ Gurney,¹⁸ Sacco *et al.*,¹⁹ Tuan and Fuoss,²⁰ and several authors used different approximations and assumptions for different systems. For example, Sacco *et al.*¹⁹ proposed the widely used 'reference electrolyte' method. Thus, for Ph_4PBPh_4 in water, we have,

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{Ph}_4\text{PBPh}_4} / 2 \quad (17)$$

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

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \quad (18)$$

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

However, according to Krumgalz²¹ it is impossible to select any two ions for which $\lambda_+^0 = \lambda_-^0$ 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 method²² 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.

$$B_{\text{R}_4\text{NX}} = a + b r_{\text{R}_4\text{N}^+}^3 \quad (19)$$

where, $a = B_{\text{X}^-}$ and b is a constant independent of temperature and solvent nature.

Extrapolation of the plot of $B_{\text{R}_4\text{NX}}$ ($\text{R} > \text{Pr}$ or Bu) against $r_{\text{R}_4\text{N}^+}^3$ 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:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (20)$$

and

$$B_{R_4N^+}/B_{R'_4N^+} = \Gamma_{R_4N^+}^3 / \Gamma_{R'_4N^+}^3 \quad (21)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data.²³

On similar reasoning, Gill and Sharma²⁴ used Bu_4NBPh_4 as the reference electrolyte and proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{\Gamma_{Ph_4B^-}^3}{\Gamma_{Bu_4N^+}^3} = \left[\frac{5.35}{5.00} \right]^3 \quad (22)$$

and

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (23)$$

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^{25, 26} 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*²⁷ 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.

2.3.2 Thermodynamics of Viscous Flow

Feakins *et al*²⁸ suggested the following expression

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left[\frac{\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}}{RT} \right] \quad (24)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molal volumes of the solvent and solute respectively, $\Delta\mu_1^{0\#}$ is the free energy of activation for viscous flow per mole of the solvent and $\Delta\mu_2^{0\#}$ is the contribution per mole of solute to the free energy of activation for the viscous flow of the solution.

2.3.3 Effects of Shape and Size

Stokes and Mills¹⁵ regarded the ions in solution as rigid spheres suspended in a continuum and proposed an equation for relative viscosity as

$$\eta/\eta_0 = 1 + 2.5 \varnothing \quad (25)$$

where \varnothing 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 (14), we have

$$2.5 \varnothing = A c^{1/2} + B c \quad (26)$$

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

$$2.5 \bar{V}_i = B \quad (27)$$

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

$$B_{\pm} = 2.5 V_{\pm} = 2.5 \times 4/3 \pi (R_{\pm}^3 N/1000) \quad (28)$$

R_{\pm} calculated using (28) 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 Einstein.²⁹

$$B_{\pm} = 2.5 (V_i + n V_s) / 1000 \quad (29)$$

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 workers³⁰⁻³³ to study the nature of solvation.

2.4 CONDUCTANCE

Conductance measurement is one of the most accurate and widely used physical methods for investigating the electrolytic solutions.^{8,34, 35} 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.

Onsagar³⁶ was the first to successfully apply Debye-Hückel theory of interionic associations. Subsequently, Pitts,³⁷ and Fuoss and Onsagar^{38, 39} independently worked to account for both long and short range interactions. As Pitts' values differed considerably from Fuoss and Onsagar's values, Fuoss and Hsia⁴⁰ modified the original Fuoss-Onsagar equation. The modified Fuoss-Onsagar equation is of the form³⁵

$$\Lambda = \Lambda^0 - \frac{\alpha \Lambda^0 c^{1/2}}{(1+\kappa a)(1+\kappa a/z^{1/2})} - \frac{\beta c^{1/2}}{(1+\kappa a)} + G(\kappa a) \quad (30)$$

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

$$\Lambda = \Lambda^0 - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} \quad (31)$$

is generally employed in the analysis of experimental results. Fuoss and Accascina³⁸ made further correction of equation (31) taking into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

$$\Lambda = \Lambda^0 - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} - B \Lambda^0 c \quad (32)$$

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

2.4.1 Ion – Association

The plot of Λ versus $c^{1/2}$ (limiting Onsagar equation) is used to determine the dissociation or association of electrolytes. If $\Lambda^0_{(\text{expt})} > \Lambda^0_{(\text{theo})}$, the electrolyte may be regarded as completely dissociated but if $\Lambda^0_{(\text{expt})} < \Lambda^0_{(\text{theo})}$, the electrolytes may be regarded as associated. The difference between $\Lambda^0_{(\text{expt})}$ and $\Lambda^0_{(\text{theo})}$ would be considerable with increasing association.⁴¹

For strongly associated electrolytes, association constants K_A and Λ^0 were determined using the Fuoss-Kraus equation⁴² or Shedlovsky's equation.⁴³

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda^0} + \frac{K_A}{(\Lambda^0)^2} \times \frac{c\gamma_{\pm}^2 \Lambda}{T(z)} \quad (33)$$

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

$$F(z) = 1 - z (1 - z (1 - z (1 - \dots)^{-1/2})^{-1/2})^{-1/2} \quad (34)$$

and
$$S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (35)$$

The plot of $T(z) / \Lambda$ against $c\gamma_{\pm}^2 \Lambda / T(z)$ should be a straight line having an intercept of $1/\Lambda^0$ and a slope of $K_A / (\Lambda^0)^2$. When K_A is large, there will be considerable uncertainty in the values of Λ^0 and K_A determined from the equation (33).

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

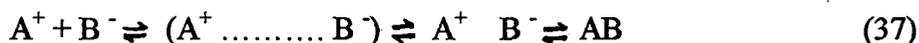
$$\Lambda = \Lambda^0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (36)$$

This equation was modified by Justice.⁴⁴

2.4.2 Ion-Size Parameter and Ionic Association

In 1978, Fuoss put forward a new conductance equation⁴⁵ 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



Solvent-separated pair	Contact pair	Neutral molecule
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From this equation Fuoss derived an expression for the association constant or conductometric pairing constant

$$K_A = K_R (1 + K_s) \quad (38)$$

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 present 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 ($c_j, \Lambda_j; j = 1, \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ^0), association constant (K_A), and the co-sphere diameter (R), are derived from the following set of equations:

$$\Lambda = p[\Lambda^0(1 + R_X) + E_L] \quad (39)$$

$$p = 1 - \alpha(1 - \gamma) \quad (40)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (41)$$

$$-\ln f = \beta k / 2(1 + kR) \quad (42)$$

$$\beta = e^2 / Dk_B T \quad (43)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (44)$$

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.

2.4.3 Limiting Ionic Equivalent Conductances

The limiting equivalent conductance (Λ^0) can be divided into ionic components using the experimentally determined transport number of ions (t_{\pm}) as follows:

$$\lambda_{+}^0 = t_{+} \Lambda^0 \text{ and } \lambda_{-}^0 = t_{-} \Lambda^0 \quad (45)$$

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,⁴⁶ Fuoss,⁴⁷ and Gill.⁴⁸

Krumgalz,⁴⁹ 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

$$r_s = |Z| F^2 / (A \pi N \eta_0 \lambda_{\pm}^0) \quad (46)$$

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

$$\lambda_{\pm}^0 \eta_0 = \text{constant} \quad (47)$$

This relation has been tested using the λ_{\pm}^0 values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^-$, Ph_4As^+ and Ph_4B^- ions and for tetraalkylammonium cations starting from Et_4N^+ . The relation can also be well utilised to determine λ_{\pm}^0 values of ions in other organic solvents from the determined Λ^0 values.

We have used Bu_4NBPh_4 as the 'reference electrolyte', but instead of equal division, we divided the Λ^0 values using a method similar to that proposed by Krumgalz²¹ for division of B-values

$$\frac{\lambda^0(\text{Bu}_4\text{N}^+)}{\lambda^0(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (48)$$

The r values have been taken from the works of Gill *et al.*⁴⁸

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*⁵⁰ proposed the following equation

$$\frac{\lambda^0(\text{Bu}_4\text{N}^+)}{\lambda^0(\text{Ph}_4\text{B}^-)} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (49)$$

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

2.4.4 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.⁵¹

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

$$V_s^s = 4/3 \pi (r_s^3 - r_c^3) \quad (50)$$

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

$$n_s = V_s^s / \bar{V}_0 \quad (51)$$

Assuming Stokes' relation to hold good, the ionic solvated volume can be obtained, because of the packing effects,⁵² from

$$V_s^0 = 4.35 r_s^3 \quad (52)$$

where V_s^0 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 empirical⁵³ and theoretical corrections^{54,55} have been suggested in order to apply it to most of the ions.

2.4.5 Stokes' Law and Walden's Rule

The limiting conductance λ_i^0 of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^0 = 0.819 |Z_i| / \eta_i R_i \quad (53)$$

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

$$\lambda_i^0 \eta_0 = 0.819 |Z_i| / R_i = \text{constant} \quad (54)$$

This is known as the Walden rule.⁵⁶ 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.

2.4.6 Recent Conductivity Equations

From 1992 to 1995, Blum, Turq and co-workers⁵⁷⁻⁵⁹ 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.*^{60(a)} 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, A. Chandra and B. Bagchi^{60(b)} 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, Onsagar 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.

2.5 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,⁶¹ hydrophobic hydration,⁶² micellization⁶³ and cosphere overlap during solute-solute interactions^{18, 64} 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

$$\phi_v = M/\rho_0 - 1000 (\rho - \rho_0)/c\rho_0 \quad (55)$$

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

$$\bar{V}_2 = \phi_v + \frac{1000 - c \phi_v}{2000 + c^{3/2} (d \phi_v / d c^{1/2})} c^{1/2} \frac{d \phi_v}{d c^{1/2}} \quad (56)$$

Masson⁶⁵ found that ϕ_v varies with the square root of the molar concentration by the linear equation

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \quad (57)$$

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 Meyer⁶⁶ have shown that an equation of the form of (57) 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

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (58)$$

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

$$w = 0.5 \sum v_i Z_i^2 \quad (59)$$

and

$$K = N^2 e^3 (8\pi / 1000 \epsilon^3 RT)^{1/2} [(\partial \ln \epsilon / \partial P)_T - \beta/3] \quad (60)$$

In equation (60), β is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation⁶⁶ adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies⁶⁷ 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 equation⁶⁸ can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of ϕ_v . The Owen-Brinkley equation⁶⁸ which includes the ion-size parameter, a (cm), is given by

$$\phi_v = \phi_v^0 + S_v \tau (\kappa a) \sqrt{c} + 0.5 W_v \theta (\kappa a) c + 0.5 K_v c \quad (61)$$

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 Atkinson⁶⁹ 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

$$\phi_v = \phi_v^0 + \nu |Z_M Z_X| A_v / 2b \ln(1+b\sqrt{I}) + 2\nu_M \nu_X RT [m B_{MX}^v + m^2 (\nu_M \nu_X)^{1/2} C_{MX}^v] \quad (62)$$

where the symbols have their usual significance.

2.5.1 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*⁷⁰ 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, as a function 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

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + b M_{R_4N^+} \quad (63)$$

and the extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, $\bar{V}_{X^-}^0$. Uosaki *et al*⁷¹ and later Krungalz⁷² 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.⁷³

2.6 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 mixtures⁷⁴ 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.

2.6.1 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.⁷⁵⁻⁷⁸ The isentropic compressibility (κ_s) values are calculated using the Laplace equation

$$\kappa_s = 1/(u^2\rho) \quad (64)$$

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

$$\kappa_\phi = [(1000/m\rho\rho_o)(\kappa_s\rho_o - \kappa_s^\circ\rho)] + \kappa_s M/\rho_o \quad (65)$$

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 the solutes and extrapolation to zero molal concentration gives the limiting apparent molal isentropic compressibility (κ_ϕ^0) according to the equation^{75, 78}

$$\kappa_\phi = \kappa_\phi^0 + S_K \sqrt{m} \quad (66)$$

where S_K is the experimental slope.

The limiting molal isentropic compressibility (κ_ϕ^0) 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.^{79, 80} This is reflected by the negative values of κ_ϕ^0 of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure.^{63, 79} The compressibility of hydrogen-bonded structure, however, varies depending on the nature of H-bonds involved,⁷⁹ the poor fit of the solute molecules⁸¹ as well as the possibility of flexible H-bond formation causing a more compressible environment (and hence a positive κ_ϕ^0 value) in the aqueous medium. Positive κ_ϕ^0 values have been reported in aqueous non-electrolytes⁸² and non-electrolyte – non-electrolyte solutions.⁸³

2.7 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, C. J. Cramer, D. G. Truhlar and co-workers from the University of Minnesota, U.S.A., constructed a series of solvation models (SM1 – SM5 series) to predict and calculate the free energy of solvation of a chemical compound.⁸⁴⁻⁸⁸ 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 at <http://comp.chem.umn.edu/solvation>.⁸⁹

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 298.15 K 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.

A. Galindo *et al.*,^{90, 91} 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 modelled as hard spheres with four short range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modelled 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. E. Bosch *et al.*,⁹² of the University of Barcelona, Spain, have compared several Preferential Solvation Models especially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixtures.

2.8 A BRIEF LITERATURE SURVEY OF THE SOLVENTS USED FOR INVESTIGATION

2.8.1 2-Methoxyethanol (ME)

n-Alkoxyethanols, commonly known as cellosolves, are good industrial solvents. However, the study of alkoxyethanols is interesting not only because of their wide use as industrial solvents, but also from the theoretical point of investigating the effect of the simultaneous presence of etheric and hydroxyl groups on the interaction of such molecules. Microwave spectroscopic,⁹³⁻⁹⁵ calorimetric^{96, 97} and infrared spectral studies⁹⁸ indicate that the molecules of n-alkoxyethanols are self-associated and form intermolecular and intramolecular hydrogen bonds.

2-Methoxyethanol (ME), commonly known as methyl cellosolve, has drawn much attention in recent years, as a solvent medium for various electrochemical studies as well as for various industrial processes.⁹⁹⁻¹⁰¹ It is an amphiprotic dipolar solvent of low dielectric constant ($\epsilon = 16.94$ at 298.15 K)¹⁰² with large dipole moment ($\mu = 2.36$ D).⁹⁴ But, unfortunately, it is hygroscopic, fairly toxic, a weak narcotic and a systemic poison,

and for these reasons, careful handling of this solvent is essential.¹⁰³ ME could be considered as a moderate Lewis acid ($pK_{\text{autoprot}} = 20.5$ at 298.15 K),¹⁰⁴ and is a probable solvent for anions through its hydrogen - bonding network, and dipole induced interactions.

IR studies⁹³ indicate that the predominant configuration of ME molecules is the gauche form to facilitate intramolecular hydrogen bonding as shown in structure I. Simple consideration of the molecular structure indicates that due to the presence of the electron repelling CH_3 group, ME is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H atom of the OH group makes ME molecules less acidic than ethylene glycol and water, thus imparting a 'quasi-aprotic' character to it. Moreover, the basicity and proticity are likely to be relayed through the co-operative structure of H-bonding¹⁰⁵ between the cosolvent and water molecules in aqueous solutions. It has unique solvating properties associated with its quasiaprotic character.¹⁰⁶ Hence, it is of much interest to study the behaviour of electrolytes in such a solvent medium.

A lot of work has been reported on pure ME. Of these, studies on dielectric properties at various temperatures of ME,¹⁰⁷ solubility studies on alkali metal chlorides, electrolytic conductance studies of salts in ME,^{33,106,108-110} measurement of various thermodynamic properties in pure ME,^{73,100,111-114} viscosity measurements,^{32,115} ultrasonic velocity studies in ME,^{33,116} spectroscopic studies¹¹⁰ etc., are noteworthy. Nandi *et al*¹⁰⁹ found strong association in a number of alkali-metal chlorides and bromides in ME and

the limiting conductances were reported to be in the order $\text{Li} > \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ and $\text{Cl} > \text{Br}$. Evaluation of Stokes radii indicates that NaCl and NaBr form ion pairs with fully solvated ions while in the other cases some solvent molecules are perhaps included in the ion pair. From their viscosity measurements the authors reported³² that Na^+ behaves as a structure-maker whereas the other ions are structure-breakers in ME. Douheret and his co-worker,¹¹⁷ and Richard *et al*,¹¹⁸ made extensive investigations on ME + water mixtures, at different temperatures. Desnoyers *et al*¹¹⁹ have reported apparent molar volumes and heat capacities of aqueous ME in water-rich compositions at 298.15 K and showed that ME behaves as a fairly typical polar non-electrolyte in water.

In recent years, several conductance,¹²⁰⁻¹²² viscosimetric,¹²³⁻¹²⁶ thermodynamic,^{123,127} and ultrasonic interferometric studies¹²⁸ have been reported on aqueous mixtures of ME, besides some research on solvent effects of these mixtures.^{129,130} A few investigations on non-aqueous binary mixtures of ME are also available.^{131,132}

ME is used extensively as a solvating agent for cellulose. It is utilized in various chemical reactions and in analytical practice,¹⁰⁰ in acid-base conductometric titrations,¹⁰¹ and as a solvent for electrolytes in high voltage capacitors and anti-icing additive for aircraft fuels. Consequently, the knowledge of ion-solvent interactions of different solutes in this solvent is capable of indicating the potential usefulness of ME in various technologies, e.g., high energy non-aqueous batteries, ion-exchangers, etc. Transport parameters of electrolytic solutions such as ionic conductance and viscosity can provide information concerning the nature of the kinetic entities from which the ion-solvent

interaction can be inferred. Information on these interactions can also be had from such thermodynamic properties as apparent molal volumes and isentropic compressibilities.

Even though ME has drawn much focus in recent years as a solvent for electroanalytical investigations,^{118,133-135} still more studies on its electrolytic behaviour in this non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on 2-methoxyethanol to study the chemical nature of the structure of ions and their mutual and specific interactions with solvent molecules by studying the transport and thermodynamic properties of some selected electrolytes in ME.

2.8.2 N-Methylacetamide (NMA)

Amides, in general, have high dielectric constants, are highly structured and are usually good solvents for both electrolytes and organic species.

Notable for its very high dielectric constant ($\epsilon = 191.3$ at 305.15 K),⁸ N-methylacetamide has a liquid range of 303.65 to 479.15 K. Hence the many salts which are soluble are completely ionized in it. The high dielectric constant is attributed to the liquid being highly structured with polymeric chains linked by hydrogen bonding.¹³⁶ It is a protic, polar and basic solvent where ion pairing is minimal even in dilute solutions.

Due to its high degree of association, NMA has received considerable interest from chemists. Wood and De Laney¹³⁷ measured the solubility of He, N₂, Ar and ethane in

NMA (at 35 to 70°C range). Non-polar solutes appear to be much more soluble in NMA than in water. The change in heat capacity on dissolution is much more negative than in water which indicates the structural effects of non-polar solutes on NMA. Activity coefficients for a large number of 1:1 electrolytes in NMA, obtained from freezing point depressions, were reported at concentrations up to 1 M by Wood *et al.*¹³⁸ Gopal and Siddiqi¹³⁹ measured several tetraalkylammonium iodides, KI, and LiCl in NMA from 35 to 80 °C and evaluated apparent molal volumes. The experimental slope S_v (using Masson's equation) was positive for salts of smaller cations but negative for larger tetraalkylammonium ions. The latter salts exhibit a positive temperature dependence over the whole range.

In NMA, alkali metal halides give slopes which are 5 – 10 % more negative than that predicted by Onsager's equation ($\Lambda = \Lambda^0 - S c^{1/2}$). Even when viscosity corrections were applied no satisfactory interpretation was found for KCl in NMA.¹⁴⁰ R_4N salts in NMA give larger negative deviations than alkali metal halides¹⁴¹ and there is evidence^{142,143} that these salts disrupt the structure of the solvent. Bøje and Hvidt¹⁴⁴ measured the excess molar volumes of NMA + water at 298.15 K.

2.8.3 N,N-Dimethylacetamide (DMA)

N,N-Dimethylacetamide has a liquid range of 253.15 to 438.15 K and a dielectric constant of 37.78 at 298.15 K.⁸ 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 electron-donating. Its ability to solvate cations is greater than that of DMF, acetone, acetonitrile and benzonitrile.¹⁴⁵

Alkali metal salts are dissociated in DMA.¹⁴⁶ Solubilities of several alkali and alkaline earth metal halides and transition metal halides in DMA were measured by Pistoia and Scrosati.¹⁴⁷ The solubilities increase in the order $\text{Cl} < \text{Br} < \text{I}$. Alexander *et al*¹⁴⁸ 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 $\text{cis-}[\text{CoCl}_2(\text{en})_2]^+$ which possess H-bond donor sites, are substantially better solvated in strongly dipolar aprotic solvents like DMA. Large polarisable anions, like picrate, perchlorate, AgCl_2^- are better solvated by the strong dipolar solvents, presumably through dipole-induced dipole interactions.¹⁴⁹

Studies on binary mixtures of DMA are also considerable in the literature, mostly as a comparative study of different amides. Goma¹⁵⁰ investigated the interactions of DMF and DMA with water.

2.8.4 1,2- Dimethoxyethane (DME)

1,2-Dimethoxyethane (DME), also commercially known as 'cellosolve', is used as a solvating agent for cellulose and as a solvent in non-aqueous batteries, and in the preparation of organo-alkaline earth compounds.^{99,151} Transport properties of electrolyte

solutions such as ionic conductance, viscosity, etc., can produce information about the nature of kinetic entities from which ion-solvent interaction can be inferred. Consequently, the knowledge of ion-solvent interactions of solutes in DME may indicate its effective usefulness in high energy non-aqueous batteries, ion-exchangers, etc.

DME has a dielectric constant of 7.08 at 298.15 K.¹⁵² Since no intramolecular hydrogen bonding is feasible in pure DME, the predominant configuration of DME is the trans form as shown in structure II. A simple consideration of the molecular structure indicates that, due to the inductive effect of two methyl groups, the O-centres of DME molecules are more basic than that of water, ethylene glycol and ME. But, due to the absence of any acidic hydrogen atom, DME is typically an aprotic solvent.

Several conductance studies in DME have compared the conductance properties of DME and tetrahydrofuran.¹⁵²⁻¹⁵⁴ Renard and Justice¹⁵² studied the conductance behaviour of CsCl in DME-water mixtures compared to dioxane-water and tetrahydrofuran-water and the differences observed in the ion-association were interpreted in terms of difference in aprotic nature of the organic molecule and that of water. Spectroscopic and conductance measurements of alkali metal salts of fluorenyl radicals indicate that DME is a better solvating medium than tetrahydrofuran and that solvent-separated and contact ion-pairs are formed in the solutions.¹⁵⁴ Solvent effects of DME on sodium salts have been investigated from NMR spectra by Detellier *et al.*¹⁵⁵ Nandi *et al.*¹⁵⁶ studied the conductance of tetraalkylammonium bromides in DME at 298.15 K and showed that a major portion of the electrolytes exists as ion pairs and only a minor portion as triple ions.

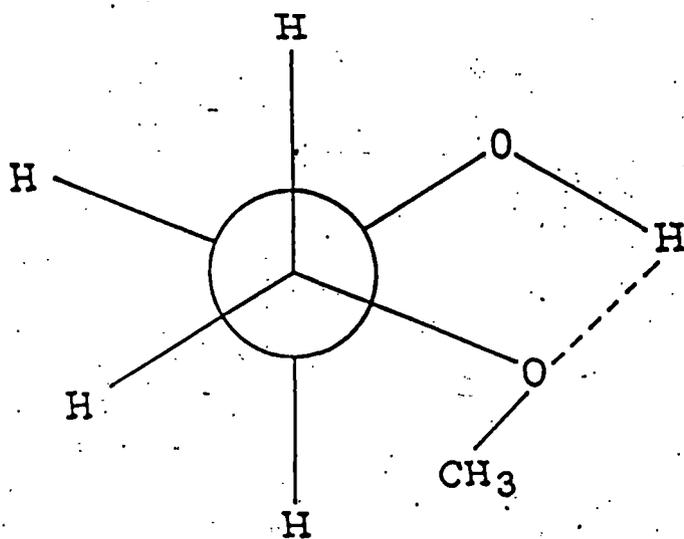
Among the other significant earlier studies on DME are the calculations of ionic solvation, free energies and entropies of transfer of gaseous univalent ions using the continuum model.¹⁵⁷ Studies on the rate of formation and stability of some organometallic complexes in DME⁹⁹ are very useful as they provide sufficient evidence of the existence of specific cation solvating effect of the solvent. Such studies, earlier, led to the prediction of tetra-coordinated DME-alkali metal ion complexes,¹⁵⁸ a view still considered as valid and very useful in studies of ion-solvation of DME.

Recently, excess volumes and the viscosity deviations of binary aqueous mixtures of DME and tetrahydrofuran were studied by Das *et al.*,¹⁵⁹ while Muhuri *et al.*,¹⁶⁰ measured the apparent molar volume and apparent molar isentropic compressibility of some symmetric tetraalkylammonium bromides in DME. Through Laser Raman spectral studies and conductance data on five lithium salts in DME, Muhuri *et al.*¹⁶¹ concluded that solvation in lithium occurs through the ethereal oxygen atom of DME.

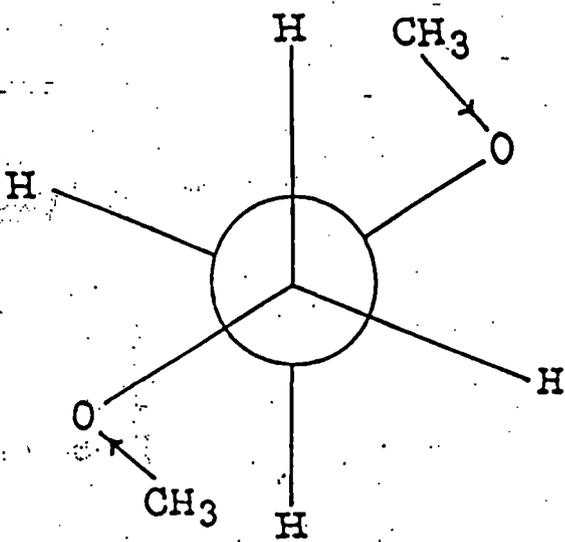
Chemically, ME and DME are mono and dimethyl ethers of ethylene glycol – a solvent well studied with regard to ion-solvent interactions. Therefore, the study of the ion-solvation of ME, and DME is likely to show the effect of increasing the number of methyl groups (electron releasing inductive effect) and decreasing the number of OH-groups.

We have, therefore, devoted our attention to the study of transport and thermodynamic properties of some selected electrolytes in ME, and DME, and, the excess properties of aqueous binary mixtures of NMA and DMA, and the non-aqueous binary mixtures of ME + NMA and ME + DMA.

The results have been described in the subsequent chapters.



Structure I: 2-methoxyethanol



Structure II: 1,2-dimethoxyethane

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