

## **CHAPTER II**

### **Physico-Chemical Parameters Studied in Solution Chemistry**

The development of our knowledge about solutions goes hand in hand with the developments in chemistry since times unknown. The alchemist's search for so-called universal solvent "Alkahest" provided ancient chemists experiences that gave us the first chemical rule: "like dissolves like".<sup>1</sup> Raoult systematically observed that boiling and freezing points of liquids are vastly affected by the dissolved nonionic substances and he concluded that the vapour pressure of a solvent above a solution is directly proportional to the mole fraction of pure solvent in solution (Raoult's law).<sup>2</sup> The difficulty in determining the amazing effects of various ionic solutes on the physical parameters of solutions has led to Arrhenius's theory of dissociation of ionic solutes into cations and anions in solution. Arrhenius established his theory of complete and incomplete dissociation by a comparison of the obtained results from measurements of osmotic pressure and conductivity of dilute electrolyte solutions.<sup>3</sup> The solution chemistry was further developed by many pioneers, *viz.*, Ostwald (1853-1932), Nernst (1864-1941), Lewis (1875-1946), Debye (1884-1966), Bjerrum (1879-1958), E. Huckel (1896-1980) and the likes.<sup>1</sup>

Anyway solution chemistry stands as an important branch of chemistry wherein studies deal with the change in particular solution parameters that arise when a solute is dissolved in a solvent or a solvent mixture. It elucidates how the chemical nature of both the solvent and the solute affect the solubility of the substances. When different solute or solvent is mixed with another solvent or solvent mixtures, the resulting solution most frequently manifests non-ideal behavior, *i.e.*, it does not obey Raoult's law. This disobedience or deviation from ideal behavior can be expressed by different thermodynamic parameters of the solutions. While such situations for liquid-liquid systems can be expressed by various excess or deviation properties, for solid-liquid systems apparent molar properties or partial molar properties can be used for the same purpose. These thermodynamic parameters are helpful in the study of molecular arrangements and interactions. Particularly, they reflect the interaction occurring between solute-solute, solute-cosolute and solvent-solvent species. However, the exact molecular structure of a solvent in solution is often known with certainty.

## Theoretical background

The solvent structure is modified by in presence of a solute or an ion often to an extent that can also perturb the solute molecules. The extent of solute (ion)-solvation depend on the degree of interactions amongst the solvent molecules themselves and the solute molecules themselves or that between the solute and cosolutes molecules if any, *etc.* The solute-solvent or ion-solvent interactions can be studied from a thermodynamic point of view where the free energy change, enthalpy change and entropy changes, *etc.*, associated with a particular reaction are determined using various physico-chemical techniques like viscometry, densitometry, ultrasonic interferometry, conductometry, refractometry, *etc.*, and thereafter the analysis of the data on physico-chemical properties help to understand the factors associated with the solute-solvent or ion-solvent interactions. Spectroscopic methods like UV-Visible, infrared and NMR spectroscopy are also helpful in this regard. Hence the present dissertation presents research works on the solution properties of some biologically important compounds in various aqueous media.

### 2.1. Density

Many fields of research need quantitative density data of solute-solvent and solvent-solvent systems. Important information regarding the nature and degree of the molecular interactions in such mixed systems can be studied from various volumetric properties. The volumetric information includes 'Density' as a mass function, volume and mole fraction and excess volumes of mixing. One of the well-recognized approaches to study the molecular interactions in fluids is the use of thermodynamic properties. Thermodynamic properties are proved to be convenient parameters for explaining solute-solute and solute-solvent interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs free energy represent the macroscopic state as an average of numerous microscopic states of the system at a particular temperature and pressure. An interpretation of these macroscopic properties in light of molecular phenomena is difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. Various ideas about the molecular processes in solutions like electrostriction,<sup>4</sup> hydrophobic hydration,<sup>5</sup> micellization<sup>6</sup> and co-sphere overlap during the solute-solvent interactions<sup>7</sup> can be explained from the partial molar volumes of many compounds to a wide extent.

## Theoretical background

### 2.1.1. Partial Molar Volumes

As per the phase rule:  $F = C - P + 2$ . For a one component and single phase system,  $F = 2$ . This implies that at least two properties of a ‘one phase one component’ must be known to define its state. These parameters are normally pressure and temperature as these variables can be easily controlled or manipulated. The thermodynamic approach, governed by the ideas of partial properties was proposed in order to measure each component's effect and their concentration on thermodynamic state properties like volume, enthalpy, entropy, Gibb's free energy, *etc.* They are extensive properties and depend upon the mass (number of moles). In a closed system, these parameters being a state dependent function depends upon any two of the state variables, *viz.*, pressure, temperature and volume of a system of fixed composition. But in an open system of variable composition (*e.g.*, liquid system) that contains two or even more components and the interchange of matter occurs with its surroundings undergo a change in composition (number of moles). Therefore, the total extensive property is not only a function of  $P$  and  $T$  but also of the actual mole numbers of each species present in the system. Thus for a multi-component system a thermodynamic state function ( $Y$ ) can be represented as follows:<sup>8,9</sup>

$$Y = f(T, P, n_1, n_2, n_3, \dots) \quad (1)$$

The net change in this property ( $dY$ ) at constant pressure and temperature is given by:

$$dY = \left( \frac{dY}{dn_1} \right)_{T, P, n_2, n_3, \dots} dn_1 + \left( \frac{dY}{dn_2} \right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \quad (2)$$

The term  $(dY/dn_1)_{T, P, n_{j \neq i}}$  is called the partial molar parameter of the  $i^{\text{th}}$  component and is denoted by  $\bar{Y}_{m,i} = (dY/dn_1)_{T, P, n_2, n_3, \dots}$ . Thus it is the rate at which the property  $Y$  changes with the amount of the  $i^{\text{th}}$  species added to the mixture at constant temperature, pressure and the amount of all other species. Partial molar quantities are intensive properties related to the changes in extensive properties of the solution (such as  $V$ ,  $G$ ,  $H$ ,  $S$  and  $A$ ) to the concentration changes. Of all the extensive thermodynamic properties, the volume is easiest to visualize. Taking  $Y$  as volume rearrangement of Eq. (2) gives:

$$dV = \left( \frac{dV}{dn_1} \right)_{T, P, n_2, n_3, \dots} dn_1 + \left( \frac{dV}{dn_2} \right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \quad (3)$$

## Theoretical background

$$\text{or } dV = \bar{V}_{m,1}dn_1 + \bar{V}_{m,2}dn_2 + \dots \quad (4)$$

where  $\bar{V}_{m,1}$  and  $\bar{V}_{m,2}$  are the partial molar volume of component 1 and 2, respectively.

In the molecular level, the solute-solvent interaction or solvation has some influence on partial molar volume, *e.g.*, the partial molar volume of  $\text{Li}^+$  ion is negative and such strange negative volume is a clear indication of electrostriction,<sup>10</sup> *i.e.*, strong electrostatic interaction between  $\text{Li}^+$  ion and the water molecules. Thus the partial molar volume provides valuable information about the solute-solvent interactions in solution. The partial molar quantities are additive and integration of Eq. (4) yields:

$$V = \bar{V}_{m,1}n_1 + \bar{V}_{m,2}n_2 + \dots \quad (5)$$

For an ideal solution, the total volume is the sum of the molar volumes of the components in a mixture as given by:

$$V = V_{m,1}^*n_1 + V_{m,2}^*n_2 + \dots \quad (6)$$

where  $V_{m,1}^*$  and  $V_{m,2}^*$  are the molar volumes of components 1 and 2, respectively. For ideal solutions, the partial molar volume of each component is identical to their respective molar volumes. However, for non-ideal solutions the presence of the second component (solute) influences the molar volume of the first component and *vice versa*, *i.e.*,  $\bar{V}_{m,1} \neq V_{m,1}^*$  and  $\bar{V}_{m,2} \neq V_{m,2}^*$ . So for non-ideal mixtures total volumes are either smaller (volumetric contraction) or larger (volumetric dilatation) than that for

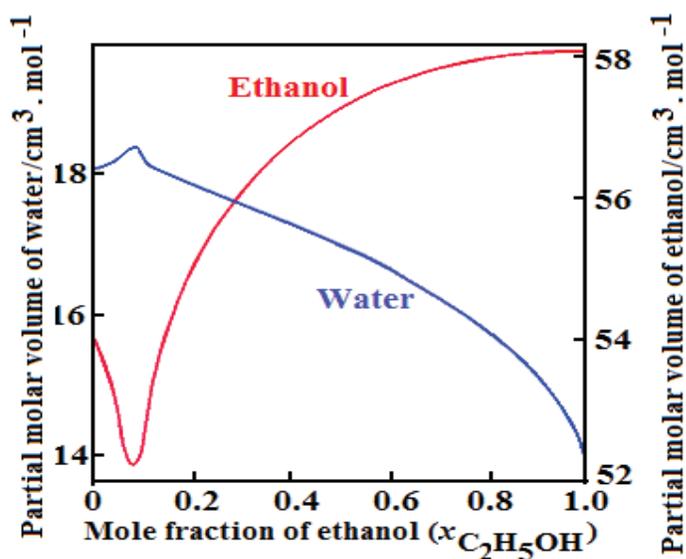


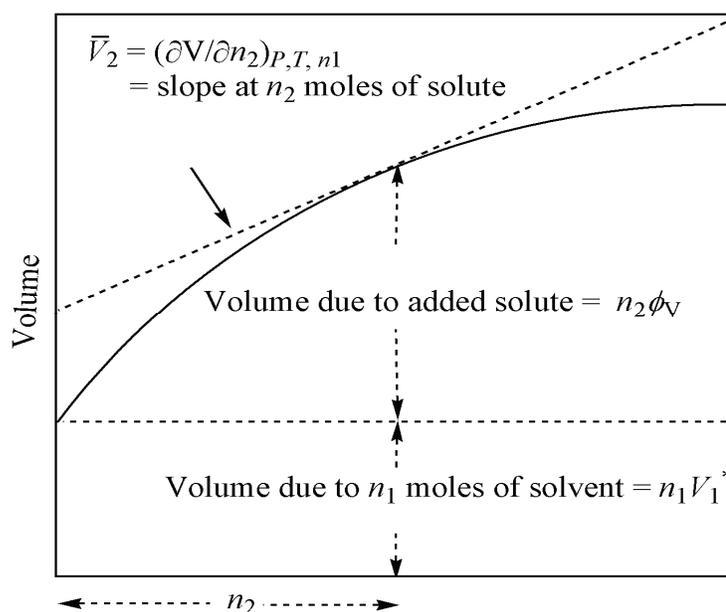
Fig 2.1. Partial molar volumes of ethanol and water in aqueous ethanol at 20 °C.

## Theoretical background

the ideal solution, *i.e.*, partial molar volumes of the components do not equal to their molar volumes but vary with the composition of the mixture due to changes in the molecular environment of each molecule (*i.e.*, packing, solvation, *etc.*). This is illustrated below in Figure 2.1 for water-ethanol system<sup>11</sup> at 20 °C at the entire composition range.

### 2.1.2. Apparent Molar Volume

Partial molar volume can be obtained by carefully measuring the solution densities of known concentrations. The determination is further simplified by apparent molar volume, a related quantity ( $\phi_V$ ). It is the volume in the solution due to addition of the solute per mole.



**Fig 2.2.** Dependence of the total solution volume on the pure solvent volume and the apparent molar volume ( $\phi_V$ ) of the solute.

From Figure 2.2 it is clear that when  $n_2$  moles of a solute are added to a solution containing a fixed  $n_1$  moles of a solvent the solution volume changes and the apparent molar volume ( $\phi_V$ ) is given by,

$$\phi_V = \frac{V_{\text{solution}} - V_{\text{solvent}}}{\text{moles of solute}} = \frac{V - n_1 V_1^*}{n_2} \quad (7)$$

and the solution volume when  $n_2$  moles of the solute are added is given by:

## Theoretical background

$$V = n_1 V_1^* + n_2 \phi_V \quad (8)$$

As mole numbers of both the solute and solvent can't be held constant simultaneously, it is useless to define apparent molar volume of the solvent. The apparent molar volume can provide estimates of the partial molar volumes of both the solute and solvent. Partial differentiation of Eq. (8) with respect to  $n_2$  at constant  $n_1$  provides the partial molar volume of the solute,

$$\bar{V}_2 = (\partial V / \partial n_2)_{n_1} = \phi_V + n_2 (\partial \phi_V / \partial n_2)_{n_1} \quad (9)$$

When determining the apparent molar volume ( $\phi_V$ ) from experimental data it is better to use the molarity scale ( $c$ ) for the solute concentration<sup>4</sup> and densities ( $\rho$ ). The apparent molar volumes ( $\phi_V$ ) of solutes can be had from the following relation:<sup>4</sup>

$$\phi_V = M / \rho_1 - 1000(\rho - \rho_1) / (c \rho_1) \quad (10)$$

where  $\rho_1$  and  $\rho$  denotes the densities of solvent and solution, respectively and  $M$  denotes the molecular weight of the solute. If concentrations are expressed in molalities ( $m$ ) of the solute, Eq. (10) converts into the following expression:<sup>4</sup>

$$\phi_V = M / \rho - 1000(\rho - \rho_1) / (m \rho \rho_1) \quad (11)$$

Four major equations, viz., the Masson equation,<sup>12</sup> the Redlich-Meyer equation,<sup>13</sup> the Owen-Brinkley equation<sup>14</sup> and the Pitzer equation<sup>15</sup> are generally used to extrapolate the apparent molar volume of an electrolyte or a solute to infinite dilution. In Masson equation the apparent molar volume of electrolytes or solutes ( $\phi_V$ ) follows a linear relation with the square root of the solute molalities ( $c$ ) as given below:

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \quad (12)$$

where  $\phi_V^0$  denotes the limiting apparent molar volume or standard partial molar volume (equal to the partial molar volume at infinite dilution,  $\bar{V}_2^0$ ) and  $S_V^*$  is the slope of the linear fit. Eq. (12) has been used for a majority of  $\phi_V$  data in water<sup>16</sup> and nearly all  $\phi_V$  data in non-aqueous<sup>17-21</sup> solvents. But according to Redlich and Meyer,<sup>13</sup> Eq. (12) is a limiting law and for a particular solvent and temperature, the slope  $S_V^*$  should depend on the valence type. They suggested the following expression for representing  $\phi_V$ :

## Theoretical background

$$\phi_V = \phi_V^0 + A_V \sqrt{c} + b_V c \quad (13)$$

$$\text{where } A_V = kw^{3/2} \quad (14)$$

Here the theoretical slope ( $A_V$ ), based on molar concentration, includes the valence factor:

$$w = 0.5 \sum_i^j \nu_i z_i^2 \quad (15)$$

$$\text{and, } k = N_A^2 e^2 (8\pi/1000 \epsilon_r^3 RT)^{1/2} [(\partial \ln \epsilon_r / \partial P)_T - \beta/3] \quad (16)$$

where  $\beta$  denotes the compressibility of the solvent. However, the variation of dielectric constant ( $\epsilon_r$ ) with pressure is not known accurately, even in water, to determine the theoretical limiting slope ( $A_V$ ) accurately. Anyway, Redlich-Meyer<sup>13</sup> equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions, although it showed discrepancies when applied for some 2:1, 3:1 and 4:1 electrolytes.<sup>22-24</sup> Actually, the volume contributed to a solvent by the addition of 1 mole of an ion is difficult to determine, because upon entry into the solvent the ion may breakup of the solvent structure and thereby changes the volume of the solution and the compression of the solvent under the influence of the ion's electric field is called electrostriction.<sup>25</sup> It is a general phenomenon that may occur whenever the electric fields is of the order of  $10^9$ - $10^{10}$  V m<sup>-1</sup>. However, for polyvalent electrolytes, the Owen-Brinkley<sup>14</sup> equation is more accurate for such extrapolation and to adequately represent the concentration dependency of  $\phi_V$ . The Owen-Brinkley equation includes the ion-size parameter ( $a$ ) and is given by:

$$\phi_V = \phi_V^0 + A_V \tau(\kappa a) \sqrt{c} + 0.5 w_V \theta(\kappa a) + 0.5 K_V c \quad (17)$$

where the symbols have their usual significance.<sup>14</sup> Pogue and Atkinson<sup>26</sup> used the Pitzer formalism to fit the apparent molar volumes. The Pitzer equation for the apparent molal volume of a single salt  $M_{\nu_M} X_{\nu_X}$  is given by:

$$\phi_V = \phi_V^0 + V |z_M z_X| A_V [2b \ln(I + bI^{1/2}) + 2\nu_M \nu_X RT [m B_{MX}^V + m^2 (\gamma_M \gamma_X)^{1/2} C_{MX}^V]] \quad (18)$$

where

$$B_{MX}^V = (\partial \beta^0 / \partial P)_T + (\partial \beta^1 / \partial P)_T (2 / \alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (19)$$

$$C_{MX}^V = (\partial C^\phi / \partial P)_T / 2 \quad (20)$$

## Theoretical background

$$V = V_M + V_X \quad (21)$$

$$\alpha = 2.0(\text{kg/mol})^{1/2} \quad (22)$$

$$b = 1.2(\text{kg/mol})^{1/2} \quad (23)$$

and other symbols have their usual significance.<sup>26</sup>

### 2.1.3. Ionic Partial Molar Volume

The individual ionic partial molar volumes often provide information about the solution structure around an ion, *i.e.*, its solvation. Although it is difficult to calculate the ionic limiting partial molar volumes in non-aqueous electrolyte solutions, most of the existing ionic limiting partial molar volumes for such systems were obtained by following the methods actually developed for aqueous solutions.<sup>27</sup> One of the most frequently used methods was suggested by Conway *et al.*<sup>27</sup> These authors determined the limiting partial molar volumes of the chlorides, bromides and iodides for a series of homologous tetraalkylammonium salts in aqueous solution and then plotted the limiting partial molar volume ( $\phi_{V,R_4NX}^0$ ) for such a series of salts with a common halide ion ( $X^-$ ) as a function of the formula weight of the cation ( $M_{R_4N^+}$ ) and obtained straight lines for each series as suggested by the following equation:

$$\phi_{V,R_4NX}^0 = \phi_{V,X^-}^0 + bM_{R_4N^+} \quad (24)$$

Eq. (24) when extrapolated to zero cationic formula weight provides the limiting partial molar volumes ( $\phi_{V,X^-}^0$ ) of the halide ions and  $\phi_V^0$  for an ion in a solution can be expressed as:<sup>28</sup>

$$\phi_{V,\text{ion}}^0 = \phi_{V,\text{int}}^0 + \Delta V \quad (25)$$

where  $\phi_{V,\text{int}}^0$  and  $\Delta V$  stand for the intrinsic volume of the ion and the volume change of the system due to ion-solvent interactions. Some authors<sup>29</sup> considered the anion solvation to be negligible for the electrolyte solutions and suggested the solvation number at infinite dilution to be associated with the extent of the cation solvation. Therefore, Eq. (25) can also be expressed as:

$$\phi_{V,\text{ion}}^0 = \phi_{V,\text{int}}^0(R_4N^+) + \Delta V \quad (26)$$

and the term  $\phi_{V,\text{int}}^0(R_4N^+)$  can be had from the following relation:<sup>30</sup>

$$\phi_{V,\text{int}}^0(R_4N^+) = 2.52r_{R_4N^+}^3 \quad (27)$$

## Theoretical background

where  $r_{R_4N^+}$  is the crystallographic radii of the  $R_4N^+$  ion. Uosaki *et al.*<sup>31</sup> used this approach for separating  $\phi_{V,R_4NX}^0$  values into ionic contributions in organic electrolyte solutions. Krumgalz<sup>30</sup> also applied the same method for a large set of partial molar volume data for non-aqueous electrolyte solutions. Based on Frank and Wen model,<sup>32</sup> Millero<sup>33</sup> has given the relation for the standard partial molar volume ( $\phi_{V,ion}^0$ ) of an ion:

$$\phi_{V,ion}^0 = \phi_{V,int}^0 + \phi_{V,elect}^0 + \phi_{V,disord}^0 + \phi_{V,caged}^0 \quad (28)$$

where  $\phi_{V,elect}^0$  is the partial molar volume due to electrostriction,  $\phi_{V,disord}^0$  is the partial molar volume due to void space and  $\phi_{V,caged}^0$  is the caged partial molar volume for the caged water structure around ions. Although it is difficult to determine thevarious contributions to  $\phi_{V,ion}^0$ , Millero<sup>33</sup> has examined  $\phi_{V,ion}^0$  values in water and methanol using the relations relations:<sup>34</sup>

$$\phi_{V,ion}^0 = 2.52r^3 + A' r^2 - B' z^2 / r \quad (29)$$

$$\phi_{V,ion}^0 = 2.52(r+a)^3 - B'' z^2 / r \quad (30)$$

where  $r$  is the crystallographic radii of the ion,  $z$  is ionic charge,  $a$ ,  $A'$ ,  $B'$  and  $B''$  are constants. The electrostriction of an ion can be estimated, when dielectric saturation is negligible, by the Drude-Nernst equation:<sup>35</sup>

$$\phi_{V,elect}^0 = -\frac{N_A z^2 e^2}{2 \epsilon_r r} (\partial \ln \epsilon_r / \partial P) = -\frac{B''' z^2}{r} \quad (31)$$

where  $\epsilon_r$  and  $B'''$  denote the dielectric constant of the solvent and a solvent dependent constant, respectively. Other symbols have their usual significance.<sup>35</sup> For highly ordered solvents there is strong competition between ion and the solvent molecules to increase the order. While ions attempts to orient solvent molecules around themselves, the solvent molecules try to retain the highly ordered bulk structure and thus a relatively large perturbed region around the solvated ions is formed resulting into large values for  $\phi_{V,disord}^0$  and  $S_{ion}^0$  (partial molar entropy of the ion). For less structured solvents, the solvent molecules are influenced by ion-solvent interactions that leads to a smaller voids space around the ion with smaller  $\phi_{V,disord}^0$ ,

## Theoretical background

negative  $\phi_{V,\text{elect}}^0$  and  $S_{\text{ion}}^0$  values. Thus the degree of the solvent structure and the dielectric constant of the solvent have crucial role for ion-solvent interactions.

### 2.1.4. Standard Partial Molar Volume of Transfer

Partial molar volume of solutes at infinite dilution can be used to explore the solute (or ion)-solvent and solvent-solvent interactions in different solvent systems.<sup>16,30,36,37</sup> Transfer volume ( $\Delta_t\phi_V^0$ ) is defined as the difference between the partial molar volumes of the solute in a particular solvent from that in a reference solvent at infinite dilution. Therefore  $\Delta_t\phi_V^0$  is given by:

$$\Delta_t\phi_V^0 = \phi_V^0(\text{solute} + \text{cosolute} + \text{solvent}) - \phi_V^0(\text{solute} + \text{solvent}) \quad (32)$$

It reflects the extent and nature of solute-solvent or ion-solvent and solute-cosolute interactions, because at infinite dilution the solute-solute or ion-ion interactions are negligible. According to Franks *et al.*<sup>38</sup> the partial molar volume of a non-electrolyte can be expressed by a combination of its intrinsic volume ( $\phi_{V,\text{int}}^0$ ) and the volume ( $\phi_{V,\text{solv}}^0$ ) for its interactions with the solvent. The intrinsic volume ( $\phi_{V,\text{int}}^0$ ) is a sum of two types of contributions, *i.e.*,  $\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}}$ ; where  $\phi_{V,\text{vw}}$  and  $\phi_{V,\text{void}}$  denote the van der Waals volume and voids in the solution, respectively. According to Shahidi *et al.*<sup>39</sup> the intrinsic volume ( $\phi_{V,\text{int}}^0$ ) of a non-electrolyte solute in solution is given by:

$$\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}} - n\sigma_s \quad (33)$$

where  $\sigma_s$  denotes the shrinkage volume due to the interactions of hydrogen bonding groups present in the solute with solvent molecules and  $n$  denotes the number of hydrogen bonding sites in the solute. For electrolytes and zwitterionic solutes, the shrinkage arises from the electrostriction and Eq. (33) can be expressed as:

$$\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}} - \phi_{V,\text{shrinkage}} \quad (34)$$

Generally  $\phi_{V,\text{vw}}$  and  $\phi_{V,\text{void}}$  are assumed<sup>40</sup> to have same magnitude in water and in mixed solvent for the same type of solutes. Thus,  $\phi_{V,\text{int}}^0$  depends on  $\phi_{V,\text{shrinkage}}^0$ , that is actually caused by the electrostriction in the solution. In this regard the cosphere overlap model<sup>41,42</sup> helps to analyze  $\Delta_t\phi_V^0$  values in terms of solute-cosolute interactions. According to this model properties of water molecules in the hydration

## Theoretical background

cosphere depend on the nature of the solute molecules. When two solute particles approach close enough so that their cospheres overlap, some of the molecules in the cosphere are displaced and thus the thermodynamic properties of the solution may change. Various interactions are possible: (i) polar-ionic and polar-polar group interactions (*e.g.*, ion-dipole, ion-quadrupole, ion-induced dipole interactions), (ii) polar-non-polar and non-polar-non-polar group interactions (*e.g.*, hydrophobic-hydrophilic interactions, hydrophobic-hydrophobic interactions), *etc.*, depending on the nature of the solvent and solute. Interactions of type (i) contribute positive values to transfer volumes ( $\Delta_t\phi_V^0$ ), while the interactions of types (ii) and (iii) contribute negative values to transfer volumes ( $\Delta_t\phi_V^0$ ). The overlap of hydration cospheres of charged species reduces the electrostriction leading to a decrease in  $\phi_{V,\text{shrinkage}}^0$  and thus positive  $\Delta_t\phi_V^0$  values result.<sup>41</sup> Kozak *et al.*<sup>43</sup> proposed a theory based on the McMillan-Mayer theory of solutions that permit the formal separation of the various effects due to pair-wise interactions of solute molecules as well as those due to interactions amongst three or more solvent molecules. Further Friedman and Krishnan<sup>44</sup> as well as Franks and Evans<sup>38</sup> developed this approach to incorporate the solute-cosolute interactions in the solvation sphere. Thus the transfer volume ( $\Delta_t\phi_V^0$ ) is given by:

$$\Delta_t\phi_V^0 = 2Z_{12}m_2 + 3Z_{122}m_2^2 + 4Z_{1222}m_2^3 \quad (35)$$

where  $Z_{12}$ ,  $Z_{122}$  and  $Z_{1222}$  are the pair, triplet and quartet interaction coefficients, respectively and  $m_2$  is the molality of the cosolute in the solution.

However, it is difficult to obtain individual ionic transfer volumes ( $\Delta_t\phi_V^0$ ) and the method used adopts some extra-thermodynamic assumptions (similar to the partial molar volume in section 2.1.3 above) in order to split the transfer volume ( $\Delta_t\phi_V^0$ ) into ionic components. Maestre *et al.*<sup>45</sup> used the method of reference electrolyte ( $\text{Ph}_4\text{AsBPh}_4$ ) for this purpose as reflected by the relations:

$$\Delta_t\phi_V^0(\text{Ph}_4\text{AsBPh}_4) = 2\Delta_t\phi_V^0(\text{Ph}_4\text{As}^+) = 2\Delta_t\phi_V^0(\text{BPh}_4^-) \quad (36)$$

$$\Delta_t\phi_V^0(\text{Ph}_4\text{AsBPh}_4) = \Delta_t\phi_V^0(\text{Ph}_4\text{AsCl}) + \Delta_t\phi_V^0(\text{NaBPh}_4) - \Delta_t\phi_V^0(\text{NaCl}) \quad (37)$$

## Theoretical background

Once  $\Delta_t \phi_V^0(\text{Ph}_4\text{As}^+)$  or  $\Delta_t \phi_V^0(\text{BPh}_4^-)$  has been determined, other single ion transfer volumes can be obtained from the transfer volume of the electrolyte. Conway<sup>46</sup> expressed the partial molar volume of an ion at infinite dilution as follows:

$$\phi_{V,\text{ion}}^0 = \phi_{V,\text{int}}^0 + \phi_{V,\text{elect}}^0 + \phi_{V,\text{struc}}^0 \quad (38)$$

where  $\phi_{V,\text{int}}^0$ ,  $\phi_{V,\text{elect}}^0$  and  $\phi_{V,\text{struc}}^0$  denote the molar volume of the ion itself (a positive term), the partial molar volume due to electrostriction of the solvent (a negative term) and the structural contribution to the volume, respectively. The last term can be split into two parts: one due to the accommodation of the ion in a cavity of the solvent (a negative term) and the other due to a local reinforcement of the solvent structure (a positive term). So Eq. (38) becomes:

$$\Delta_t \phi_{V,\text{ion}}^0 = \Delta_t \phi_{V,\text{elect}}^0 + \Delta_t \phi_{V,\text{struc}}^0 \quad (39)$$

The term  $\Delta_t \phi_{V,\text{int}}^0$  vanishes because  $\phi_{V,\text{int}}^0$  is the crystallographic volume of the ion and  $\Delta_t \phi_{V,\text{ion}}^0$  will depend on a balance between the electrostriction and the structural contributions.

### 2.1.5. Apparent Molar Expansibility

The apparent molar expansibility ( $\phi_E$ ) of a solution is given by  $\phi_E = (\partial \phi_V / \partial T)_p$  and therefore from Eq. (7):

$$\phi_E = \frac{\alpha V - \alpha_1 n_1 V_1^*}{n_2} \quad (40)$$

where  $\alpha$  and  $\alpha_1$  are the thermal expansion coefficients of the solution and the solvent, respectively; *i.e.*,  $\alpha = -\rho^{-1}(\partial \rho / \partial T)_p$  and  $\alpha_1 = -\rho_1^{-1}(\partial \rho_1 / \partial T)_p$ . The apparent molar expansibility ( $\phi_E$ ) can be determined using the densities and their temperature coefficients as follows:

$$\phi_E = \alpha_1 \phi_V + \frac{1000(\alpha - \alpha_1)}{c} \quad (41)$$

$$\phi_E = \alpha \phi_V + \frac{1000(\alpha - \alpha_1)}{m \rho_1} \quad (42)$$

## Theoretical background

### 2.1.6. Standard Partial Molar Expansibility

The standard partial molar expansibilities ( $\phi_E^0$ ) is given by:<sup>4</sup>

$$\phi_E = \phi_E^0 + S_E \sqrt{c} \quad (43)$$

When solute concentrations are expressed in molalities ( $m$ ), Eq. (43) becomes:

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \quad (44)$$

and the value  $(\partial\phi_E^0/\partial T)_P$  is given by the slope when  $\phi_E^0$  values are linearly regressed against the experimental temperatures ( $T$ ). Again, the temperature dependence of  $\phi_V^0$  for various solutes can be also expressed as:

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (45)$$

where  $a_0$ ,  $a_1$  and  $a_2$  denotes the regression coefficients for the solute and  $T$  is the absolute temperature. Eq. (45) when differentiated with respect to  $T$  at constant pressure  $P$  yields the partial molar expansibilities ( $\phi_E^0$ ) of the solute:

$$\phi_E^0 = (\partial\phi_V^0/\partial T)_P = a_1 + 2a_2 T \quad (46)$$

The partial molar heat capacities for most of the electrolytes are negative and the fact that  $(\partial C_P^0/\partial P)_T$  should be positive for the structure breaking solutes/electrolytes as per the structural model<sup>47</sup> gives the following thermodynamic relation:

$$(\partial C_P^0/\partial P)_T = -T(\partial^2\phi_V^0/\partial T^2)_P \quad (47)$$

Therefore the structure breaking solutes have negative  $(\partial^2\phi_V^0/\partial T^2)_P$  values. Similarly the structure-making solutes should have positive  $(\partial^2\phi_V^0/\partial T^2)_P$  values. According to Hepler<sup>47</sup> the sign of  $(\partial\phi_E^0/\partial T)_P$  reveals the long-range structure-making and breaking capacity of the electrolytes/solutes in different solvent systems. The general thermodynamic expression for  $(\partial\phi_E^0/\partial T)_P$  is as follows:

$$(\partial\phi_E^0/\partial T)_P = (\partial^2\phi_V^0/\partial T^2)_P = 2a_2 \quad (48)$$

If the sign of  $(\partial\phi_E^0/\partial T)_P$  is positive the electrolyte/solute is a structure maker and if the sign of  $(\partial\phi_E^0/\partial T)_P$  is negative, it is a structure breaker.

## Theoretical background

### 2.1.7. Ionic Partial Molar Expansibility

When  $\phi_{V,\text{ion}}^0$  values are plotted against the experimental temperatures ( $T$ ), the slope provides the partial molar expansibilities ( $\phi_{E,\text{ion}}^0$ ) of the ions, so the partial molar expansibilities of the electrolytes ( $\phi_E^0$ ) can further be split into ionic contributions:

$$\phi_E^0 = \phi_{E,+}^0 + \phi_{E,-}^0 \quad (49)$$

where  $\phi_{E,+}^0$  and  $\phi_{E,-}^0$  are the partial molar expansibility of the cation and anion, respectively. Similar to  $\phi_{V,\text{ion}}^0$ ,  $\phi_{E,\text{ion}}^0$  can be resolved into different contributions as per Frank and Wen model<sup>33</sup> for the hydration of ions:

$$\phi_{E,\text{ion}}^0 = \phi_{E,\text{int}}^0 + \phi_{E,\text{elect}}^0 + \phi_{E,\text{disord}}^0 + \phi_{E,\text{caged}}^0 \quad (50)$$

Here the intrinsic expansibility ( $\phi_{E,\text{int}}^0$ ) is the volume change due to expansion of the ion and is negligible for monovalent ions. This term in Eq. (50) incorporates the expansibility of covalent bonds in the ions with hydrocarbon portion. The electrostriction expansibility ( $\phi_{E,\text{elect}}^0$ ) is associated with the volume changes due to electrostriction. It is negative and proportional to  $z^2/r$ ; where  $z$  and  $r$  are the charge and the crystal radius of the ion. The disordered expansibility ( $\phi_{E,\text{disord}}^0$ ) is due to changes in a disordered region and it is different for cations and anions of similar size but different orientation of water molecules around them in the first electrostricted region. This term depends on the temperature and magnitude of  $z^2/r$ . Thus for ions with a large electrostricted region (*i.e.*, large  $z^2/r$ ), the disordered region is very small or even nonexistent. However, for ions with a small electrostricted region (*i.e.*, small  $z^2/r$ ), the disordered region has an important contribution. The caged expansion ( $\phi_{E,\text{caged}}^0$ ) is due to the changes in highly structured water around the hydrocarbon portion of an ion. It is positive and its magnitude increases with the size of the hydrocarbon portion of the ion.

### 2.1.8. Apparent specific volumes and taste quality

Taste behavior of a solute in presence of a cosolute in a solution can be interpreted from the apparent specific volumes ( $\phi_{ASV}$ ). It can differentiate the four basic tastes: salty, sour, sweet and bitter. It reflects the degree of packing

## Theoretical background

compatibility of a solute within the water structure and can be had from the apparent molar volumes ( $\phi_V$ ) at the experimental temperatures using the relation:

$$\phi_{Vsp} = \frac{\phi_V}{M} \quad (51).$$

Apparent specific volume gives an idea about its relationship with taste quality in the order salty < sour < sweet < bitter.<sup>48-50</sup> The whole human taste range lies with apparent specific volumes ( $\phi_{Vsp}$ ) between 0.1 and 0.95 cm<sup>3</sup>.g<sup>-1</sup>; for salty the range is  $\phi_{Vsp} < 0.33$  cm<sup>3</sup>.g<sup>-1</sup>, for sour the range is  $\phi_{Vsp} = 0.33-0.52$  cm<sup>3</sup>.g<sup>-1</sup>, for sweet the range is  $\phi_{Vsp} = 0.52-0.71$  cm<sup>3</sup>.g<sup>-1</sup> and for bitter the range is  $\phi_{Vsp} = 0.71-0.93$  cm<sup>3</sup>.g<sup>-1</sup>).<sup>51</sup> When the extent of solute-solvent interaction is large, the solute molecules reach the taste receptors lying much deeper in the lingual epithelium easily. Thus solvation or hydration of solutes can help to understand why a particular solute tastes characteristically sour, bitter or salty, *etc.*

### 2.2. Viscosity

Viscosity is an important non-thermodynamic transport property of liquids. It represents the force required to produce unit shear rate between two layers of the molecules in question separated by unit distance. It is often used as a tool for the determination of solute-solvent or ion-solvent interactions. Viscosities of an electrolytic solution can provide valuable information about the solute-solvent or ion-solvent interactions and thereby the structural nature of the electrolytic solutions.

#### 2.2.1. Viscosity of Electrolyte Solution

The viscosity relationships of electrolytic solutions are highly complicated, because of various interactions like ion-ion and ion-solvent interactions occurring in the solution and separation of these forces is really a difficult task. Since viscosity is related to the friction between adjacent, relatively moving parallel planes of the liquid, anything that may affect the interaction between the planes will have a concomitant effect on the viscosity. If large spheres are placed in the liquid, the planes will be stacked together and viscosity will increase. Similarly, hydrogen bonding between the planes will increase the friction between the planes and will increase viscosity. An ion with a large rigid co-sphere will behave as a rigid sphere and it can increase the inter-planar friction. Similarly, an ion that can increase the degree of hydrogen bonding

## Theoretical background

between the adjacent solvent molecules will increase the viscosity. On the contrary, ions that destroy above-mentioned effect will decrease the viscosity. In 1929, Jones and Dole<sup>52</sup> suggested an empirical equation to correlate the relative viscosities of the electrolytes with molar concentrations ( $c$ ):

$$\eta/\eta_1 = \eta_r = 1 + A\sqrt{c} + Bc \quad (52)$$

The above equation can be rearranged as:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (53)$$

where the coefficients  $A$  and  $B$  signify the ion-ion and ion-solvent interactions. Eq. (53) is equally applicable to aqueous and non-aqueous solutions with negligible ionic association. The term  $A\sqrt{c}$  in Eq. (52) due to Grüneisen effect (*i.e.*, the long-range coulombic forces between the ions) can be interpreted in terms of Debye-Hückel theory<sup>53</sup> of inter-ionic attractions. The ion-ion interaction coefficient  $A$  can be calculated from interionic attraction theory<sup>54, 55</sup> through the Falkenhagen Vernon<sup>55</sup> equation:

$$A_{\text{Theo}} = \frac{0.2577\Lambda_0}{\eta_1(\epsilon_r T)^{0.5} \lambda_+^0 \lambda_-^0} [1 - 0.6863(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0})^2] \quad (54)$$

where  $\Lambda_0$ ,  $\lambda_+^0$  and  $\lambda_-^0$  are the limiting molar conductances of the electrolyte as a whole and its cation and anion, respectively; other symbols have their usual significance. When the  $A$ -coefficients obtained by fitting  $\eta_r$  values to Eq. (53) for aqueous solutions<sup>56</sup> were compared with the values calculated from Eq. (54), good agreement was observed. But the accuracy was poor with partially aqueous solutions.<sup>57</sup> Crudden *et al.*<sup>58</sup> suggested that if association of the ions occurs to form an ion pair, the viscosity should be analyzed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha_{\text{IP}}c}}{\alpha_{\text{IP}}c} = B_i + B_p \left( \frac{1 - \alpha_{\text{IP}}}{\alpha_{\text{IP}}} \right) \quad (55)$$

where  $A$ ,  $B_i$  and  $B_p$  are characteristic constants and  $\alpha_{\text{IP}}$  is the degree of dissociation of ion pair. Thus an extrapolation of the  $(\eta_r - 1 - A\sqrt{\alpha_{\text{IP}}c})/\alpha_{\text{IP}}c$  versus  $(1 - \alpha_{\text{IP}})/\alpha_{\text{IP}}$  plot to  $(1 - \alpha_{\text{IP}})/\alpha_{\text{IP}} = 0$  gave the intercept  $B_i$ . However for the most of the electrolytic solutions both in aqueous and non-aqueous media, the Eq. (53) is valid up to 0.1 (M)<sup>4, 59, 60</sup> within experimental errors. However, for higher concentrations the extended

## Theoretical background

Jones-Dole equation, with an additional coefficient  $D$ , originally used by Kaminsky,<sup>61</sup> is used:

$$\eta/\eta_1 = 1 + A\sqrt{c} + Bc + Dc^2 \quad (56)$$

The significance of the coefficient  $D$  is not always meaningful and therefore, Eq. (53) is the most popular. The  $A$ -coefficients, obtained from the  $(\eta/\eta_1 - 1)/\sqrt{c}$  versus  $\sqrt{c}$  plots for the electrolytes, are sometimes negative, scattered and deviate from linearity.<sup>4, 62, 63</sup> In such cases the  $A$ -coefficients should be determined using Eq. (54). According to the inter-ionic attraction theory of electrolytes the ions tend to build and maintain a space lattice structure in solution and opposes any influence or force that tend to disturb this space lattice structure; thus the inter-ionic forces tend to stiffen or increase the viscosity of the solution. Thus it is expected that  $A$ -coefficient will have a negative value for all strong electrolytes and a value of zero for non-electrolytes.<sup>52</sup> The  $B$ -coefficient may be either positive or negative. The effect of solute size on the  $B$ -coefficient is apparent from hydrodynamic theories applicable to particles in a fluid continuum. When penetration between the solute and solvent occurs, the steric effect may contribute to the  $B$ -coefficient and thus  $B$ -coefficient is greatly sensitive to the “rigidity” or “flexibility” of the solute. Thus the  $B$ -coefficient is determined by the solute/ion size and the nature of the solvent. The  $B$ -coefficients are obtained as slopes of the straight lines using the least square method and intercepts equal to the  $A$  values. The factors influencing the  $B$ -coefficients are:<sup>64, 65</sup> (i) ionic solvation and the action of the field of the ion produces long-range order in solvent molecules and thereby increase  $\eta$  or  $B$ -values, (ii) destruction of the three dimensional bulk structure of solvent molecules that decreases  $\eta$  values, (iii) high molar volume and low dielectric constant yield high  $B$ -values for similar solvents and (iv) steric hindrance of the primary solvation of ions due to high molar volume solvents or poor solvation of either ion of the binary electrolyte yield reduced  $B$ -values.

In structured solvents like water, a solute with or without a primary solvation sheath can apparently affect the degree of ‘structure’ of the solvent molecules at relatively long distances. A ‘structure-making’ solute lowers the average effective temperature of the solvent molecules and thus increases the viscosity of the solution and leads to a high  $B$ -coefficient values. Because of the exponential relationship between viscosity and temperature,<sup>59</sup> a rise in temperature of the solution causes  $B$ -

## Theoretical background

coefficients to fall, this fall is greater at low than at high temperatures. Such behavior can be used to identify ‘structure-making’ solutes.<sup>66</sup> However, ‘structure-breaking’ solutes have rather low  $B$ -coefficients that may increase with rise in temperatures.<sup>54</sup> If solvation decreases with increasing temperature, the  $B$ -coefficient of a solvated species also fall and consequently both primary solvation and structure making should have high  $B$ -coefficient at low temperature and negative  $\partial B/\partial T$  values.

### 2.2.2. Ionic Viscosity $B$ -Coefficients

The separation of viscosity  $B$ -coefficients into ionic components is based on some extra-thermodynamic assumptions. The following methods are used for separating the  $B$ -coefficients in the ionic contributions:

(1) Cox and Wolfenden<sup>67</sup> used the assumption that  $B_{\text{ion}}$  values of  $\text{Li}^+$  and  $\text{IO}_3^-$  in  $\text{LiIO}_3$  are proportional to their respective ionic volumes, which are further proportional to the third power of the respective ionic mobilities. The method of Gurney<sup>41</sup> and Kaminsky<sup>61</sup> are based on:

$$B_{\text{K}^+} = B_{\text{Cl}^-} \text{ (in water)} \quad (57)$$

The argument in favor of this assignment is based on the fact that the  $B$ -coefficients for  $\text{KCl}$  is very small and that the mobilities of  $\text{K}^+$  and  $\text{Cl}^-$  are very similar over the temperature range 15-45 °C. The assignment is supported by other thermodynamic properties.

(2) The Desnoyers and Perron method<sup>68</sup> is based on the assumption that the  $\text{Et}_4\text{N}^+$  ion in water is closest to be neither structure breaker nor a structure maker. They suggest the application of the Einstein’s equation<sup>69</sup> with a high degree of accuracy:

$$B = 0.0025 \phi_{V, \text{ion}}^0 \quad (58)$$

and with an accurate value of the partial molar volume ( $\phi_{V, \text{ion}}^0$ ) of the ion, it is possible to calculate a value of 0.359 for  $B_{\text{Et}_4\text{N}^+}$  in water at 25 °C. Sacco *et al.*<sup>70</sup> proposed the “reference electrolytic” method for the separation of the  $B$ -values, *e.g.*, for tetraphenyl phosphonium tetraphenyl borate ( $\text{Ph}_4\text{PBPh}_4$ ) in water:

$$B_{\text{Ph}_4\text{B}^-} = B_{\text{Ph}_4\text{P}^+} = B_{\text{Ph}_4\text{PBPh}_4}/2 \quad (59)$$

As  $\text{Ph}_4\text{PBPh}_4$  is sparingly soluble in water,  $B_{\text{Ph}_4\text{PBPh}_4}$  can be taken as:

## Theoretical background

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \quad (60)$$

The criteria adopted for the separation of the  $B$ -coefficients in non-aqueous solvents differ from those used for aqueous solutions, although these methods<sup>63, 64, 71, 72</sup> are based on the equality of equivalent conductance of the counter ions at infinite dilution.

According to Krumgalz<sup>73, 74</sup> the method for the separation of the  $B$ -coefficients into ionic components is based on the fact that the large tetraalkylammonium cations ( $\text{R}_4\text{N}^+$ ) are not solvated<sup>75, 76</sup> in organic solvents. Thus, the ionic  $B$ -values for large tetraalkylammonium ions,  $\text{R}_4\text{N}^+$  (where  $\text{R} > \text{Bu}$ ) in organic solvents, are proportional to their ionic dimensions, *i. e.*,

$$B_{\text{R}_4\text{NX}} = a + br_{\text{R}_4\text{N}^+}^3 \quad (61)$$

where  $a = B_{\text{X}^-}$  and  $b$  is a constant dependent on temperature and solvent nature. The extrapolation of the plot of  $B_{\text{R}_4\text{NX}}$  ( $\text{R} > \text{Pr}$  or  $\text{Bu}$ ) versus  $r_{\text{R}_4\text{N}^+}^3$  to zero cation dimension gives directly  $B_{\text{X}^-}$  in the proper solvent and thus  $B$ -ion values can be had.

The  $B$ -ion values can also be calculated from the relations:

$$B_{\text{R}_4\text{N}^+} - B_{\text{R}'_4\text{N}^+} = B_{\text{R}_4\text{NX}} - B_{\text{R}'_4\text{NX}} \quad (62)$$

$$B_{\text{R}_4\text{N}^+} / B_{\text{R}'_4\text{N}^+} = r_{\text{R}_4\text{N}^+}^3 / r_{\text{R}'_4\text{N}^+}^3 \quad (63)$$

using the radii of the tetraalkylammonium ions ( $r_{\text{R}_4\text{N}^+}^3$  and  $r_{\text{R}'_4\text{N}^+}^3$ ) obtained from the conductance data.<sup>77</sup>

Gill and Sharma<sup>78</sup> used  $\text{Bu}_4\text{NBPh}_4$  as a reference electrolyte. The method of resolution is based on the assumption that  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of  $\text{Bu}_4\text{N}^+$  (5.00 Å) and  $\text{Ph}_4\text{B}^-$  (5.35 Å) were found to remain constant in different non-aqueous and mixed non-aqueous solvents used by Gill and co-workers. They proposed the equations:

$$B_{\text{Ph}_4\text{B}^-} / B_{\text{Bu}_4\text{N}^+} = r_{\text{Ph}_4\text{B}^-}^3 / r_{\text{Bu}_4\text{N}^+}^3 = (5.35/5.00)^3 \quad (64)$$

$$\text{and, } B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{Ph}_4\text{B}^-} \quad (65)$$

The method requires only the  $B$ -values of  $\text{Bu}_4\text{NBPh}_4$  and is equally applicable to non-aqueous solvents. The  $B$ -ion values obtained by this method agree well with

## Theoretical background

those reported by Lawrence *et al.*<sup>70</sup> in different organic solvents using the assumption as given below:

$$B_{[(i-Am)_3BuN^+]} = B_{Ph_4B^-} = 1/2B_{[(i-Am)_3BuNPh_4B]} \quad (66)$$

Lawrence *et al.*<sup>70</sup> used tetrabutylammonium tetrabutylborate ( $Bu_4NBBu_4$ ) as ‘reference electrolyte’ because the cation and anion are symmetrical in shape and have almost equal van der Waals volumes. Thus,

$$B_{Bu_4N^+} / B_{Bu_4B^-} = V_{W(Bu_4N^+)} / V_{W(Bu_4B^-)} \quad (67)$$

$$\text{or, } B_{Bu_4N^+} = B_{Bu_4NBBu_4} / [1 + V_{W(Bu_4B^-)} / V_{W(Bu_4N^+)}] \quad (68)$$

A similar separation can be made for  $Ph_4PBPh_4$  system and Lawrence *et al.*<sup>70</sup> made the viscosity measurements of tetraalkylammonium bromides (from Pr to Hept.) in DMSO and HMPT. The  $B$ -coefficients,  $B_{R_4NBr} = B_{Br^-} + a[f(r_{R_4N^+})]$ , were plotted as functions of the van der Waals volumes. The  $B_{Br^-}$  values thus obtained were compared with the accurately determined  $B_{Br^-}$  value using  $Bu_4NBBu_4$  and  $Ph_4PBPh_4$  as ‘reference electrolyte’. They concluded that the ‘reference electrolyte’ method is the best available method for division into ionic contributions. Anyway, all these methods are based on certain approximations and anomalous results may arise unless proper mathematical theory is developed to calculate  $B$ -values.

### 2.2.3. Temperature Dependence of Ionic Viscosity $B$ - Coefficients

A regularity in the behavior of  $B_{\pm}$  and  $\partial B_{\pm} / \partial T$  has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminsky.<sup>79</sup> He observed that (i) within a group of the periodic table the  $B$ -ion values decrease as the crystal ionic radii increase, (ii) within a group of periodic table, the temperature co-efficient of  $B_{ion}$  values increase as the ionic radius increases. The results can be summarized as follows:

For structure breaking ions-

$$(i) A \text{ and } \partial A / \partial T > 0 \quad (69)$$

$$(ii) B_{ion} < 0 \text{ and } \partial B_{ion} / \partial T > 0 \quad (70)$$

For structure making ions-

$$(iii) B_{ion} > 0 \text{ and } \partial B_{ion} / \partial T < 0 \quad (71)$$

## Theoretical background

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvation layer may be different from those present in the bulk structure. This is well reflected in the ‘Co-sphere’ model of Gurney,<sup>41</sup> A, B, C zones of Frank and Wen<sup>32</sup> and hydrated radius of Nightingale.<sup>80</sup> The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent ( $\eta_1$ ) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation becomes,

$$\eta = \eta_1 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_1 + \eta(A\sqrt{c} + Bc) \quad (72)$$

where  $\eta^*$ , the positive increment in viscosity, is caused by coulombic interaction. The  $B$ -coefficient can then be interpreted in terms of the competitive viscosity effects. Following Stokes, Mills and Krumgalz<sup>73</sup> the  $B_{\text{ion}}$  is given by:

$$B_{\text{ion}} = B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} + B_{\text{ion}}^{\text{Str}} + B_{\text{ion}}^{\text{Reinf}} \quad (73)$$

whereas according to Lawrence and Sacco:<sup>70</sup>

$$B_{\text{ion}} = B_w + B_{\text{solv}} + B_{\text{shape}} + B_{\text{ord}} + B_{\text{disord}} \quad (74)$$

$B_{\text{ion}}^{\text{Einst}}$  is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to  $\eta^E$  or  $B_{\text{shape}}$ ).

$B_{\text{ion}}^{\text{Orient}}$  is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to  $\eta^A$  or  $B_{\text{ord}}$ ).

$B_{\text{ion}}^{\text{Str}}$  is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymmetrically and solvent to keep its own structure (this corresponds to  $\eta^D$  or  $B_{\text{disord}}$ ).

$B_{\text{disord}}$  is the positive increment conditioned by the effect of ‘reinforcement of the water structure’ by large tetraalkylammonium ions ( $R_4N^+$ ) due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents.

$B_w$  and  $B_{\text{solv}}$  account for viscosity increases and attributed to the van der Waals volume and the volume of the solvation of ions. Thus, small and highly charged cations like  $Li^+$  and  $Mg^{2+}$  form a firmly attached primary solvation sheath around these ions ( $B_{\text{ion}}^{\text{Einst}}$  or  $\eta^E$  positive). At ordinary temperature, alignment of the solvent

## Theoretical background

molecules around the inner layer also cause increase in  $B_{\text{ion}}^{\text{Orient}} (\eta^A)$ ,  $B_{\text{ion}}^{\text{Str}} (\eta^D)$  is small for these ions. Thus,  $B_{\text{ion}}$  will be large and positive as  $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} > B_{\text{ion}}^{\text{Str}}$ . However,  $B_{\text{ion}}^{\text{Einst}}$  and  $B_{\text{ion}}^{\text{Orient}}$  would be small for ions of greatest crystal radii (within a group) like  $\text{Cs}^+$  or  $\text{I}^-$  due to small surface charge densities resulting in weak orienting and structure forming effect.  $B_{\text{ion}}^{\text{Str}}$  would be large due to structural disorder in the immediate neighborhood of the ion due to competition between the ionic field and the bulk structure. Thus  $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} < B_{\text{ion}}^{\text{Str}}$  and  $B_{\text{ion}}$  is negative. Ions of intermediate size (*e.g.*,  $\text{K}^+$  and  $\text{Cl}^-$ ) have a close balance of viscous forces in their vicinity, *i.e.*,  $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} = B_{\text{ion}}^{\text{Str}}$ , so that  $B_{\text{ion}}$  is close to zero. Large molecular ions like tetraalkylammonium ions ( $\text{R}_4\text{N}^+$ ) have large  $B_{\text{ion}}^{\text{Einst}}$  because of large size but  $B_{\text{ion}}^{\text{Orient}}$  and  $B_{\text{ion}}^{\text{Str}}$  would be small, *i.e.*,  $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} \gg B_{\text{ion}}^{\text{Str}}$  and  $B_{\text{ion}}$  would be positive and large. The value would be further reinforced in water arising from  $B_{\text{ion}}^{\text{Reinf}}$  due to hydrophobic hydrations. The increase in temperature will have no effect on  $B_{\text{ion}}^{\text{Einst}}$ . But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in  $B_{\text{ion}}^{\text{Str}}$ .  $B_{\text{ion}}^{\text{Orient}}$  will decrease slowly with temperature as there will be less competition between the ionic field and reduced solvent structure. The positive or negative temperature co-efficient will thus depend on the change of the relative magnitudes of  $B_{\text{ion}}^{\text{Orient}}$  and  $B_{\text{ion}}^{\text{Str}}$ . Moreover, the temperature-induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So there is a correlation between viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic  $B$ -coefficient and the entropy of solvation of ions have been used as probes of ion-solvent interactions and can provide information about the structure making and structure breaking character of ions.

### 2.2.4. Viscosity of Non-Electrolyte Solutions

According to Falkenhagen,<sup>54, 55</sup> the  $A$ - coefficients for uncharged solutes are zero and solution viscosities ( $\eta$ ) of non-electrolytes is analyzed with the modified Jones-Dole equation:<sup>41, 59</sup>

$$\eta_r = 1 + Bc \quad (75)$$

## Theoretical background

where  $\eta_r = \eta/\eta_1$ ;  $\eta_1$ ,  $\eta$  and  $c$  represent solvent viscosity, solution viscosity and molar concentration of the solute in the solution, respectively. The experimental viscosities can also be fitted to the following linear relation with equal weights to all the viscosities:<sup>81</sup>

$$\eta = C' + B'c \quad (76)$$

where  $B'$  and  $C'$  are constants;  $C'$  values are found to agree with the observed  $\eta_1$  values within the experimental error and  $B'$  is related to the  $B$ - coefficients as follows:<sup>81</sup>

$$B = B'/C' \quad (77)$$

### 2.2.5. Viscosity $B$ -Coefficient of Transfer

Similar to  $\Delta_t\phi_v^0$ , viscosity  $B$ -coefficient of transfer ( $\Delta_t B$ ) is free from solute-solute or ion-ion interactions and provides information about solute-cosolute interactions.  $\Delta_t B$  values can be calculated from the following relation:

$$\Delta_t B = B(\text{solute} + \text{cosolute} + \text{solvent}) - B(\text{solute} + \text{solvent}) \quad (78)$$

and these values can be interpreted in the light of Gurney's 'Co-sphere' model.<sup>41</sup> Generally negative  $\Delta_t B$  values suggest the solute to be less structured environment in the solution than that in the solvent and positive  $\Delta_t B$  values suggest the solute to be in more structured environment in the solution than in the solvent. Thus these results reveal the influence of 'solvent structure modification' by the solute and cosolute molecules.

### 2.2.6. Effects of Shape and Size on Viscous Flow

The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein<sup>69</sup> leads to the equation:

$$\eta/\eta_1 = 1 + 2.5\phi \quad (79)$$

where  $\phi$  is the volume fraction occupied by the particles. Modifications of the above relation have been proposed by: (i) Simha<sup>82</sup> on the basis of departures from spherical shape and (ii) Vand<sup>83</sup> on the basis of dependence of the flow patterns around the neighboring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having

## Theoretical background

hydrated ions of large effective size (particularly polyvalent monoatomic cations). Thus from Eq. (79):

$$2.5\phi = A\sqrt{c} + Bc \quad (80)$$

Since  $A\sqrt{c}$  term can be neglected in comparison with  $Bc$  and  $\phi = c\phi_{v,\text{ion}}^0$ , where  $\phi_{v,\text{ion}}^0$  is the partial molar volume of the ion, the above equation becomes:

$$2.5\phi_{v,\text{ion}}^0 = B \quad (81)$$

In the ideal case, the ionic  $B_{\pm}$ -coefficient is a linear function of partial molar volume of the ion,  $\phi_{v,\text{ion}}^0$  with slope to 2.5. Thus,  $B_{\pm}$  can be equated to:

$$B_{\pm} = 2.5\phi_{v,\text{ion}}^0 = 2.5 \times 4/3 (\pi R_{\pm}^3 N_A / 1000) \quad (82)$$

where the ions are treated like rigid spheres with an effective radii ( $R_{\pm}$ ) that move in a continuum and 2.5 is the shape factor for a sphere.  $R_{\pm}$ , calculated using Eq. (82), should be close to crystallographic radii or corrected Stoke's radii<sup>84</sup> if the ions are scarcely solvated and behave as spherical entities. But, in general,  $R_{\pm}$  values are higher than the crystallographic radii of the ions suggesting appreciable solvation of the ions. The number  $n_s$  of solvent molecules bound to the ion in the primary solvation shell can be had from the relation:<sup>69</sup>

$$B_{\pm} = 2.5/1000(V_i + n_s V_s) \quad (83)$$

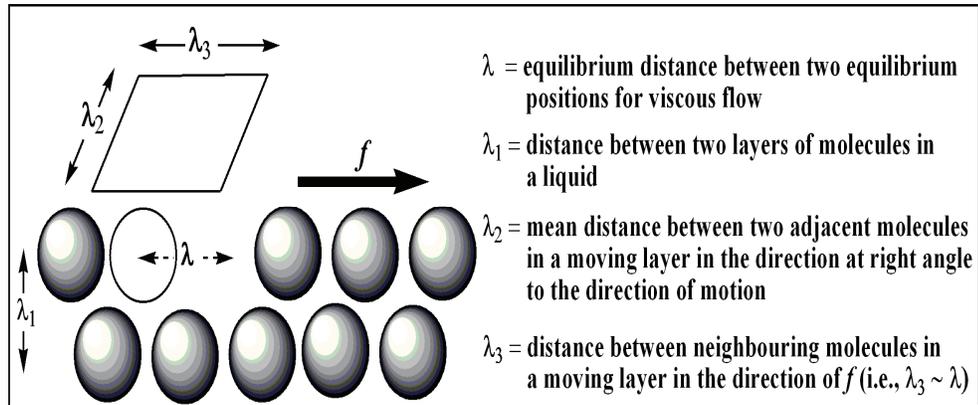
where  $V_i$  is the molar volume of the bare ion and  $V_s$ , the molar volume of the solvent.

### 2.2.7. Thermodynamics of Viscous Flow

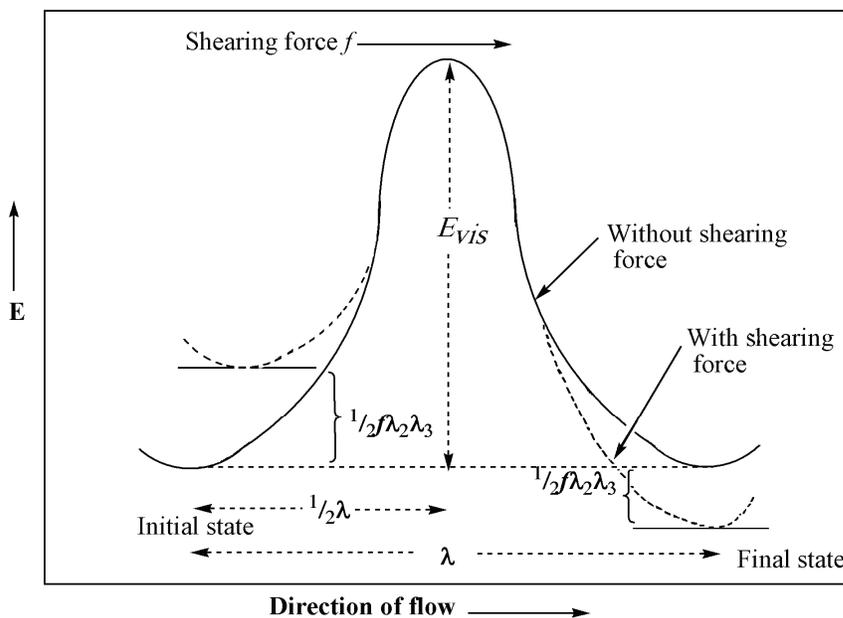
Viscosity can be treated by means of the theory of absolute reaction rates.<sup>85</sup> As a gas is considered to consist of molecules moving about in empty space, a liquid may be regarded as made up of "holes" moving about the matter. Thus "holes" play the same part in a liquid as molecules do in the gas phase. The energy required to create a hole of molecular dimension in a liquid is equal to the energy of vaporization per molecule of the liquid.<sup>85</sup> If two layers of molecules in a liquid are separated by a distance  $\lambda_1$  and one layer slides over the other under the influence of a force  $f$  per square centimeter and  $\Delta u$  is the difference in the velocity of the two layers, then the coefficient of viscosity ( $\eta$ ) is given by the relation:  $\eta = f\lambda_1 / \Delta u$ . The passage of a molecule from one equilibrium position to another position in the same layer requires

## Theoretical background

a suitable hole to be available and energy must be utilized to create such a hole in the liquid. The process is shown in Figure 2.3 below.



**Fig 2.3.** A molecule moves from one equilibrium position to another in the same layer of a liquid with the availability of a suitable hole.



**Fig 2.4.** Potential energy barrier for viscous flow with and without shearing force.

This process can be discussed with the aid of a symmetrical potential energy barrier as depicted in Figure 2.4. Assuming the potential energy barrier to be symmetrical, the distance between the initial equilibrium position and the activated state is  $\lambda/2$ . The applied force acting on a molecule in the direction of motion is thus  $f\lambda_2\lambda_3$ , since  $\lambda_2\lambda_3$  is the effective area per molecule. So the energy acquired by the moving

## Theoretical background

molecule that has reached the top of the potential energy barrier is  $f\lambda_2\lambda_3\lambda/2$ . This energy reduces the height of the energy barrier in the forward direction by the amount of  $f\lambda_2\lambda_3\lambda/2$  and increases the height of the energy barrier in the backward direction by the same amount. With some assumptions and statistical thermodynamic treatments, described in the literature,<sup>85</sup> the viscosity ( $\eta$ ) of a solution can be represented by the Eyring's relation:<sup>85</sup>

$$\eta = Ae^{E_{vis}/RT} = (hN/V)e^{\Delta G^*/RT} = (hN/V)e^{(\Delta H^*/RT - \Delta S^*/R)} \quad (84)$$

where  $E_{vis}$  = the experimental energy of activation determined from a plot of  $\ln\eta$  against  $1/T$ ;  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the free energy, enthalpy and entropy for the activation of viscous flow, respectively. The total activation energy for viscous flow may be regarded as consisting of two parts: (i) the energy required forming the hole, (ii) that required for the molecule to move into the hole and most of the energy is required for the preparation of the holes rather than that required to move the molecules into the holes. According to Eq. (84), the free energy of activation for viscous flow per mole of the solvent/solvent mixture ( $\Delta\mu_1^{0\ddagger}$ ) as:

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln(\eta_1 \phi_{V,1}^0 / hN_A) \quad (85)$$

where  $N_A$ ,  $\phi_{V,1}^0$  are the Avogadro's number and the molar volume of the solvent, respectively. The other symbols have their usual significances. For a binary mixture used as solvents,  $\phi_{V,1}^0$  is taken as the mole fraction average of molecular weights of components normalized by densities at the experimental temperatures. The above equation can also be expressed as:<sup>57, 86</sup>

$$\ln(\eta_1 \phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\ddagger}}{R} + \left(\frac{\Delta H_1^{0\ddagger}}{R}\right) \frac{1}{T} \quad (86)$$

So a linear regression of the  $(\ln(\eta_1 \phi_{V,1}^0 / hN_A))$  data against  $1/T$  provides the  $\Delta H_1^{0\ddagger}$  and  $\Delta S_1^{0\ddagger}$  values. A correlation between the viscosity  $B$ - coefficients and the deviation between the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ( $\Delta\mu_2^{0\ddagger}$ ) and the free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ( $\Delta\mu_1^{0\ddagger}$ ) was suggested by Feakins *et al.*<sup>86</sup> in the form:

## Theoretical background

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0 \left( \frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT} \right) \quad (87)$$

where the coefficient  $\nu$  is 1 for non-electrolytes, 2 for 1:1 electrolytes and so on. Thus  $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$  values can be obtained from Eq. (87) using the  $B$ - coefficients.  $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$  values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{ \frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R} \right\} \frac{1}{T} \quad (88)$$

where  $\Delta S_i^{0\neq}$  and  $\Delta H_i^{0\neq}$  are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of  $i^{\text{th}}$  component in the solution. So a linear regression of Eq. (88) provides the values of  $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$  and  $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$  from the slopes and intercepts. According to Eq. (87),  $\Delta\mu_2^{0\neq}$  is dependent mainly on the viscosity  $B$ -coefficients and  $(\phi_{V,2}^0 - \phi_{V,1}^0)$  terms. In many cases  $\Delta\mu_1^{0\neq}$  are almost invariant of the solvent compositions and temperatures, suggesting that  $\Delta\mu_2^{0\neq}$  is dependent on the viscosity  $B$ -coefficients and  $(\phi_{V,2}^0 - \phi_{V,1}^0)$  terms. The  $\Delta\mu_2^{0\neq}$  values contain the change in the free energy of activation of solute molecules and the contribution from the movement of solute molecules. If  $\Delta\mu_2^{0\neq}$  values are positive and greater than  $\Delta\mu_1^{0\neq}$  values at the experimental temperatures, the solute (ion)-solvent interactions is stronger in the ground state than in the transition state and in the transition state the solvation of the solute (ions) becomes less favored energetically. However, a popular method uses the following relations,

$$d(\Delta\mu_2^{0\neq})/dT = -\Delta S_2^{0\neq} \quad (89)$$

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \quad (90)$$

for the calculation of the entropy and enthalpy of activation of viscous flow for the solute, respectively.

### 2.2.8. Solvation Number

The term ‘primary solvation’<sup>87</sup> for an electrolyte signifies the firm attachment of solvent molecules to the ions so that the ions and the solvent molecules move as a single entity in an electrolyte transport process, *i.e.*, the solvent molecules lost their own translation degree of freedom and the term ‘secondary solvation’ designate all

## Theoretical background

other solvent molecules. For a given ion, its solvation number depends on this association of solvent molecules. The first solvation shell constitutes the set of immediate neighboring solvent molecules around ion. If the solvent molecules interact strongly or coordinate with the ion, they constitute its primary solvation. The second solvation shell is the set of next nearest solvent molecules of the ion. Solvent molecules of the primary and secondary solvation shell of the ion are oriented in such a fashion by its field that is different from the normal orientation of the solvent molecules in the bulk solvent. There will exist a region around the ion with solvent molecules with neither the central orientation nor the bulk orientation. This disordered region is known as the thawed zone.<sup>88</sup> The volume of the solvation shell ( $V_s$ ) can be had from the relation:

$$V_s = (4\pi/3)(r_s^3 - r_c^3) \quad (91)$$

where  $r_c$  is the crystal radius of the ion; the solvation number ( $S_n$ ) would then be had from:

$$S_n = V_s/V_0 \quad (92)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects<sup>87</sup> from:

$$V_s^0 = 4.35r_s^3 \quad (93)$$

where  $V_s^0$  is expressed in mol.L<sup>-1</sup> and  $r_s$  in angstroms. Alternatively, solvation numbers ( $S_n$ ) can easily be had from the relation:<sup>89</sup>

$$S_n = B/\phi_V^0 \quad (94)$$

$S_n$  is indicative of the formation of a primary solvation sphere around a solute and the range 0-2.5 for  $S_n$  indicates unsolvated solutes in the solution.<sup>89</sup> If values of ionic viscosity  $B$ -coefficients ( $B_{\pm}$ ) are available, ionic solvation numbers ( $S_{n,\pm}$ ) can be had from Eq. (94) by using ionic partial molar volumes ( $\phi_{V,\pm}^0$ ) of the ions.

### 2.3. Ultrasonic Speed

The acoustic property- 'ultrasonic speed' is a sensitive indicator of molecular interactions and can provide useful information about these phenomena, particularly when partial molar volumes alone fail to provide an unequivocal interpretation of the interactions. Ultrasonic speed is associated with the interactions between the

## Theoretical background

components of liquid mixtures and varies with the structures and binding forces in the solutions.

### 2.3.1. Apparent Molal Adiabatic Compressibility

Although for a long time attention has been paid to the apparent molal isentropic compressibility for electrolytes and other compounds in aqueous solutions,<sup>90</sup> measurements in non-aqueous<sup>7</sup> solvents are still limited. It has been emphasized by many authors that the apparent molal isentropic compressibilities can be used as a useful parameter to unveil the solute-solvent and solute-solute interactions. The most convenient way to measure the compressibility of a solvent/solution is from the ultrasonic speed of sound in it. The isentropic adiabatic compressibility ( $\beta_s$ ) of a solvent/solution can be had from the relation:<sup>91</sup>

$$\beta_s = 1/(u^2 \rho) \quad (95)$$

where  $\rho$  is the solution density and  $u$  is the ultrasonic speed in the solvent/solution. The isentropic compressibility ( $\beta_s$ ) determined by Eq. (95) is adiabatic,<sup>25</sup> not an isothermal one, because the local compressions occurring when the ultrasound passes through the solvent/solution are too rapid to allow an escape of the heat produced. The apparent molal isentropic compressibility ( $\phi_K$ ) of the solutions was determined from the relation:

$$\phi_K = M\beta_s/\rho_1 + 1000(\beta_s\rho_1 - \beta_{s,1}\rho)/m\rho\rho_1 \quad (96)$$

$\beta_{s,1}$  is the isentropic compressibility of the solvent mixture,  $M$  is the molar mass of the solute,  $m$  is the molality of the solution. The limiting apparent molal isentropic compressibility ( $\phi_K^0$ ) can be obtained by extrapolating the plots of  $\phi_K$  versus the square root of molal concentration of the solute ( $\sqrt{m}$ ) to zero concentration by a least-squares method:<sup>92, 93</sup>

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m} \quad (97)$$

where  $S_K^*$  is the experimental slope. The limiting apparent molal isentropic compressibility ( $\phi_K^0$ ) and the 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 leads to the decrease in the compressibility of the solution.<sup>94</sup> This is reflected by the negative values of  $\phi_K^0$  of electrolytic solutions. Hydrophobic

## Theoretical background

solutes often show negative compressibilities due to the ordering induced by them in the water structure.<sup>94</sup> The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved.<sup>94</sup> However, the poor fit of the solute molecules<sup>95, 96</sup> and the possibility of flexible hydrogen bond formation appear to be responsible for a more compressible environment and hence positive  $\phi_k^0$  values have been reported in aqueous non-electrolyte<sup>97</sup> and non-aqueous non-electrolyte<sup>98</sup> solutions.

### 2.4. Refractive Index

Refractive index ( $n_D$ ) is a dimensionless optical property and it changes with the variation of molecular organization of solutions, pure liquids and mixtures. Refractive index ( $n_D$ ) of the substance is defined as the ratio of the speed of light in vacuum to another substance, *i.e.*,

$$n_D = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in the substance}} \quad (98)$$

Lorentz and Lorenz<sup>99</sup> derived a theoretical correlation between refractive index ( $n_D$ ) and density ( $\rho$ ) of a substance as follows:

$$R_s = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{1}{\rho} \quad (99)$$

where  $R_s$  is the specific refraction. The molar refraction or refractivity ( $R_M$ ) can be obtained from the relation:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\rho} \quad (100)$$

where  $M$  is the molar mass of the solute. Molar refractivity ( $R_M$ ) for a mixture can be had from the relation:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \sum_{i=1}^n \frac{x_i M_i}{\rho} \quad (101)$$

where  $M_i$  and  $x_i$  stand for the molecular weight and mole fraction for the  $i^{\text{th}}$  component of the mixture, respectively. Molar refraction is independent on the phase and act as a fundamental property of a compound.<sup>100</sup> Atomic refractions and refraction of bonds estimate the molar refraction for most organic compounds with the

## Theoretical background

exception of many inorganic or organometallic solid materials or substances like metal complexes. As per Marcus *et al.*<sup>101</sup> the apparent molar refractivity ( $R_D$ ) for a solute is be had from the equation:

$$R_D = \frac{1000}{c} \left[ \frac{n_D^2 - 1}{n_D^2 + 2} - \frac{1}{\rho_1} \left( \rho - \frac{cM}{1000} \right) \frac{n_{D,1}^2 - 1}{n_{D,1}^2 + 2} \right] \quad (102)$$

where  $n_D$  and  $n_{D,1}$  stand for the refractive indices of the solution and solvent or solvent mixture, respectively and all other symbols have their own usual meanings. However, the molecular polarizability ( $\alpha_M$ )<sup>102</sup> calculates the ability of deformation of the molecular orbitals under an electrical field. Moreover, it is found that for more complex structure of a molecule, its electron cloud is more decentralized and thus the molecular polarizability increases. As molecular polarizability ( $\alpha_M$ ) is directly proportional to the  $R_D$ , the trend of increasing  $R_D$  values suggests overall increased molecular polarizabilities.<sup>103</sup> This is expressed by the relation:<sup>101</sup>

$$\alpha_M = \frac{3R_M}{4\pi N_A} \quad (103)$$

### 2.5. Solvent Effects on UV-Visible Spectra of Solutions

The electronic absorptions of organic solutes are often modified due to solvation, particularly in solvents of different polarity. Because these solvents can alter the intensities, positions and shapes of the absorption bands.<sup>102-105</sup> The spectral shifts are due to specific solute-solvent and solute-solute interactions through dipole-dipole, ion-dipole, hydrogen bonding, dipole-induced dipole interactions, *etc.* Several other factors like acid-base chemistry and charge-transfer interactions can also cause spectral shifts in solutions. All these forces influent the energy difference between the excited and the ground state of the absorbing species through as a physical perturbation of relevant molecular states of the chromophores.<sup>106-108</sup> Hence, solvent effects on absorption spectra can give valuable information about specific solute-solvent interactions<sup>102-105</sup> and can be useful to unveil the primary solvation of the solvated ion.<sup>109</sup> The effects of solvents on absorption spectra depend primarily on the chromospheres and the type of the transitions:  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and charge-transfer transitions. The degree and nature of spectral shifts in different solvents of varying polarity depend on the strength of intermolecular hydrogen bonding between the

## Theoretical background

certain groups of the solute and those of the solvent molecules. For solutes without intramolecular hydrogen bonding, the spectral shifts depend on the solvent polarity. In such cases the  $\pi \rightarrow \pi^*$  bands shift bathochromically as the solvent polarity increases due to hydrogen bonding interactions between the solute and solvent molecules. On the contrary, for solutes with intramolecular hydrogen bonding, the spectral shifts are very small. However, the spectral shifts can be well interpreted by solvent polarities when the solute-solvent systems are devoid of intermolecular hydrogen bonds. It has been well known that  $\pi$ -electrons containing molecules exhibit pronounced solvatochromism. These electrons are responsible for the difference in charge distribution, consequently the dipole moment between the electronic excited and ground state of the solute. Negative solvatochromism is observed during blue or hypsochromic shift with increasing polarity of solvent and the positive solvatochromism is defined as the corresponding bathochromic (or red) shift. Large negative solvatochromism is found for differential solvation of the zwitterionic electronic ground state, highly dipolar, and the relatively less dipolar first excited state.<sup>110</sup> When the excited state is found to be more polar than ground state, usually a bathochromic shift with increased polarity of solvents for long-wave length absorption band is observed and if the ground state is more polar than the excited state, increasing solvent polarity leads to hypsochromic shift. Polyene dye shows inverted solvatochromism,<sup>111</sup> because there are shifts from positive to negative solvatochromism when solvent polarity increases. Solvatochromism can be used to understand the solute-solvent interactions in terms of the polarizability or dipolarity parameter ( $\pi^*$ ), hydrogen bond donor ( $\alpha$ ) and hydrogen bond acceptor ( $\beta$ ) abilities of the solvents.

### 2.6. Theoretical Approach

#### 2.6.1. Molecular Theory for Partial Molar Volume

Statistical mechanics of liquids suggests two theoretical approaches for the calculation of the partial molar volumes. One of these two approaches is the scaled particle theory (SPT).<sup>112-113</sup> In this approach solute-solvent interactions in solution can be described with the interaction volume ( $\bar{\phi}_{\text{int}}$ ) as follows:

$$\phi_V^0 = \bar{\phi}_{\text{cav}} + \bar{\phi}_{\text{int}} + \kappa_1^0 RT \quad (104)$$

## Theoretical background

where  $\bar{\phi}_{\text{cav}}$  is the volume contribution to the partial molar volume of the solute associated with cavity formation in water,  $\kappa_1^0$  is the isothermal compressibility of water and other symbols have their usual significances.  $\bar{\phi}_{\text{cav}}$  can be calculated from the relation:<sup>114</sup>

$$\bar{\phi}_{\text{cav}} = \kappa_1^0 RT \{ y/(1-y) + 3yz(1+z)/(1-y)^2 + 9y^2z^2/(1-y)^3 \} + \pi\sigma_2^3 N_A / 6 \quad (105)$$

where  $z = \sigma_2 / \sigma_1$ ,  $\sigma_1$  and  $\sigma_2$  are hard sphere diameters of water and the solute. The parameter  $y$  is the ratio of volume occupied by one mole of hard sphere solvent molecules to its molar volume  $\phi_{V,1}^0$ . Thus an approximate free energy for cavity formation in a fluid can be determined by the SPT theory. However, the SPT theory has two major limitations when applied to chemical and biochemical field. First of all, only the spherical solute can be studied by the original SPT. The other limitation is that this theory does not include the electrostatic effects on partial molar volumes. Nagayama, Irida and Hirata<sup>115</sup> extended this theory for solutes of arbitrary shape. They successfully calculated the partial molar volumes of molecular solutes in terms of extended SPT<sup>116</sup> and solved the former problem. The latter problem was, however, not solved even with the combination of the dielectric continuum models.<sup>117, 118</sup> The other approach is based on the Kirkwood-Buff (KB) solution theory.<sup>119</sup> According to this theory, the partial molar volumes of solutes can be had from the relation:

$$\phi_V^0 = k_B T \kappa_T - \int_0^{\infty} [g(r) - 1] 4\pi r^2 \partial r \quad (106)$$

where  $\kappa_T$  stands for the isothermal compressibility of the solution,  $k_B$  is the Boltzman constant and  $g(r)$  is the radial distribution function (RDF) between the solvent and solute. The radial distribution function (RDF) can be had from molecular simulation. Many attempts were made to combine molecular simulation with the KB theory but they are still limited to small molecules.<sup>120-122</sup> Other molecular liquid theories like Reference Hypernetted Chain (RHNC)<sup>123</sup> and Reference Interaction Site Model (RISM)<sup>124</sup> were approached. The KB theory when coupled with RHNC theory was used to determine the partial molar volume of the ions in aqueous media.<sup>125, 126</sup> The RISM theory combined with the KB theory has successfully calculated and analyzed the partial molar volumes for vast molecular systems like ions,<sup>127,128</sup> hydrocarbons,<sup>139, 130</sup> and biomolecules<sup>131, 132</sup> in non-aqueous and aqueous and

## Theoretical background

solutions.<sup>133,134</sup> The RISM theory has been modified to include the three-dimensional spatial correlation functions of solvent molecules around a solute molecule.<sup>135, 136</sup> The 3D-RISM theory combined with the KB theory was approached to analyze the partial molar volumes of bimolecular systems.<sup>137-144</sup> Thus, the RISM theory is the most useful method to investigate the partial molar volumes and other thermodynamic parameters of solutions.

### 2.6.2. Solvation Models

There are normally two methods<sup>144</sup>: the semi-empirical CNDO-type approach and the *ab initio* calculation. In the *ab initio* calculation, the energy difference between a solvate and the separate constituents is measured as a function of the geometry, *i.e.*, bond angles and bond length. Solvation energy is then made maximum according to these parameters. Like in the free state, the solvent molecules may be considered as rigid spheres with the same geometry. Neglecting the electron correlation, the self-consistent field version of molecular orbital theory has been used to solve Schrödinger equation for the constituents and the solvate separately. The main difficulty is the proper selection of basis set of orbitals. However the difference in energy between the separate constituents and a solvate is calculated with minimum error when given basis set (Slater or Gaussian type) of full molecular Hamiltonian is applied for the calculation. Pople *et al.*<sup>145</sup> suggested an approach for semi-empirical calculations. Differential overlap (CNDO) of basis set of orbitals was completely neglected by this approach. The number of integrals to be calculated decreases with a given basis set of orbitals. This version involving empirical parameters based on electron affinities, ionization potential in the Hamiltonian is called CNDO/2. The energy of the system is expressed as sum total of two-atom and one-atom terms.

By the molecular dynamic (MD) approach, a certain number of molecules, ions and Newtonian mechanics of movement of all solution particles are observed. This field is dependent on the understanding of the intermolecular energy of interactions between a pair of particles. Computer simulation theories may be found useful in this situation and the last few decades appointed some interesting trends to develop computer soft wares and solvation models and. A. Galindo *et al.*<sup>146, 147</sup> have developed a Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to elucidate the phase equilibrium and thermodynamics of electrolytic aqueous solutions.

## Theoretical background

The hard sphered water molecules are further connected with four short-range attractive sites to study the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter were modeled in describing the cation and anion. The interactions are further described in light of Debye-Hückel and mean spherical approximations. Many aqueous electrolyte solutions show good agreement with respect to experimental data.

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