

## **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 a universal solvent "Alkahest" provided ancient chemists experiences that arose the earliest chemical rule: "like dissolves like" [1]. Raoult systematically studied the effects of dissolved nonionic substances on the freezing and boiling point of liquids and his observation that the vapour pressure of a solvent above a solution is proportional to the mole fraction of the solvent in solution is known as Raoult's law [2]. The difficulty in explaining the effects of inorganic solutes on the physical properties of solutions led in 1884 to Arrhenius's theory of incomplete and complete dissociation of ionic solutes into cations and anions in solution. Arrhenius derived his dissociation theory from a comparison of the results obtained from measurements of conductivity and osmotic pressure of dilute electrolyte solutions [3]. The further development of solution chemistry reminds us the pioneering work of Ostwald (1853-1932), Nernst (1864-1941), Lewis (1875-1946), Debye (1884-1966), Bjerrum (1879-1958) and E. Huckel (1896-1980) and the likes [1].

Anyway solution chemistry stands as an important branch of chemistry wherein studies on the change in properties that arise when one substance dissolves in another substance is made. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally, i.e., deviate from Raoult's law. This deviation from ideality is expressed in terms of many thermodynamic parameters, by excess properties in case of liquid-liquid mixtures and apparent molar properties in case of solid-liquid mixtures. These thermodynamic properties of solvent mixtures corresponds to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species. However, the exact structure of the solvent molecules in solution is unknown with certainty many times. The addition of an ion or solute modifies the solvent structure to an extent that can also

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modify or perturb the solute molecules. The extent of solute (ion)-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes in free energy, enthalpy and entropy, etc. associated with a particular reaction can be qualitatively and quantitatively evaluated by using various physico-chemical techniques and analysis of the data on physico-chemical properties can help to reach conclusions regarding the factors associated with the ion-solvent interactions can be worked out.

Such phenomena thus pave the path for research in solution chemistry to elucidate the nature of interaction through experimental studies involving densitometry, viscometry, Ultrasonic Interferometry, conductometry, refractometry and other suitable methods like UV-Visible, infrared and NMR spectroscopy. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus the present research work is intimately related to the solution properties of some food additives and drugs in different aqueous media: a physico-chemical study.

### 2.1. Density

The physico-chemical properties of solvent mixtures have attracted much attention from both theoretical and engineering applications points of view. Many engineering applications require quantitative data on the density of solvent mixtures. Such properties also provide information about the nature and molecular interactions between liquid mixture components. The volumetric information includes 'Density' as a function of mass, volume and mole fraction and excess volumes of mixing. One of the well-recognized approaches to the study of molecular interactions in fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. 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 macroscopic properties in terms of molecular phenomena is difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of

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molecular interactions. Various concepts regarding molecular processes in solutions like electrostriction [4], hydrophobic hydration [5], micellization [6] and co-sphere overlap during solute-solvent interactions [7] to a large extent have been derived and interpreted from the partial molar volume data of many compounds.

### 2.1.1. Partial Molar Volumes

According to phase rule:  $F = C - P + 2$ , for a single phase and a one component system,  $F = 2$ . This means minimum two properties of a 'one component one phase' system must be known to specify its state. These properties are usually pressure and temperature since these variables can be controlled easily. Similarly for a two component system,  $F = 3$ . Hence for a two-component system, any extensive thermodynamic property  $Y$  (such as  $V$ ,  $G$ ,  $H$ ,  $S$ , etc.) can be expressed as:

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

where  $n_1$  and  $n_2$  are mole numbers of the solvent and the solute, respectively and the total differential becomes,

$$dY = (\partial Y / \partial P)_{T, n_1, n_2} dP + (\partial Y / \partial T)_{P, n_1, n_2} dT \\ + (\partial Y / \partial n_2)_{P, T, n_1} dn_2 + (\partial Y / \partial n_1)_{P, T, n_2} dn_1 \quad (2)$$

The partial molar property  $\bar{Y}_i$  is defined as:

$$\bar{Y}_i = (\partial Y / \partial n_i)_{P, T, n_j} \quad (3)$$

At constant temperature and pressure equation (1) becomes,

$$Y = f(n_1, n_2) \quad (4)$$

and consequently the total differential becomes,

$$dY = (\partial Y / \partial n_2)_{P, T, n_1} dn_2 + (\partial Y / \partial n_1)_{P, T, n_2} dn_1 \quad (5)$$

Equation (5) can be written more compactly as:

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$$dY = \bar{Y}_1 dn_1 + \bar{Y}_2 dn_2 \quad (6)$$

Of all the extensive thermodynamic properties, the volume is the easiest to visualize and the molar volume of a pure substance can be determined simply from density measurements. This visualization also holds true for partial molar volume defined as:

$$\bar{V}_i = (\partial V / \partial n_i)_{P,T,n_j} \quad (7)$$

thus equation (6) becomes,

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \quad (8)$$

and its integral form is:

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (9)$$

For an ideal solution, its volume is just the sum of the molar volumes of the solute and the solvent, e.g., benzene and toluene solution.

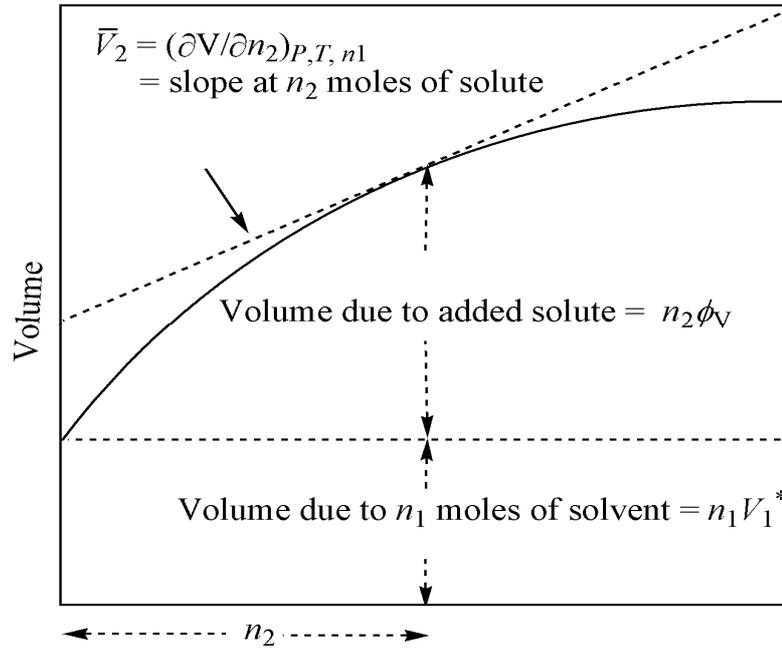
$$V = n_1 V_1^* + n_2 V_2^* \quad (10)$$

where  $V_1^*$  and  $V_2^*$  are molar volumes of the solvent and the solute, respectively. But for a non-ideal solution, e.g., water and ethanol solution, according to equation (9) it is the partial molar volumes that are additive or extensive. Thus partial molar volume of a component is not equal to its molar volume and partial molar volumes of components vary with composition of the mixture.

### 2.1.2. Apparent Molar Volume

The experimental determination of partial molar volume is quite simple and involves the careful measurement of the densities of solutions of known concentrations. The calculation is simplified by the use of a related quantity called apparent molar volume ( $\phi_V$ ); it is the volume due to added solute per mole in the solution.

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**Fig. 2.1.** Dependence of the total volume of a solution on the volume of the pure solvent and the apparent molar volume ( $\phi_V$ ) of the solute.

Figure 2.1 depicts the volume changes of a solution as  $n_2$  moles of a solute are added to a fixed  $n_1$  moles of a solvent and shows that apparent molar volume ( $\phi_V$ ) is,

$$\phi_V = \frac{V_{\text{solution}} - V_{\text{solvent}}}{\text{moles of solute}} = \frac{V - n_1 V_1^*}{n_2} \quad (11)$$

and the volume of the solution at any particular added  $n_2$  moles of the solute is given by:

$$V = n_1 V_1^* + n_2 \phi_V \quad (12)$$

However, it does not make any sense to define apparent molar volume for the solvent because number of moles of both the solute and solvent can't be held constant simultaneously. The apparent molar volume can be measured easily and it gives estimates of the partial molar volumes of both the solute and solvent. Partial differentiation of equation (12) with respect to  $n_2$  at constant  $n_1$  gives the partial molar volume of the solute,

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$$\bar{V}_2 = (\partial V / \partial n_2)_{n_1} = \phi_V + n_2 (\partial \phi_V / \partial n_2)_{n_1} \quad (13)$$

For the determination of apparent molar volume ( $\phi_V$ ) from experimental data it is more convenient [4] to use the molarity scale ( $c$ ) for solute concentration and densities ( $\rho$ ). The apparent molar volumes ( $\phi_V$ ) of solutes can be calculated by using the following relation [4]:

$$\phi_V = M/\rho_1 - 1000(\rho - \rho_1)/(c\rho\rho_1) \quad (14)$$

where  $M$  is the molecular weight of the solute,  $\rho_1$  and  $\rho$  are the densities of solvent and solution, respectively. However, if concentrations are expressed in terms of molality ( $m$ ) of the solute, equation (14) can also be expressed as [4]:

$$\phi_V = M/\rho - 1000(\rho - \rho_1)/(m\rho\rho_1) \quad (15)$$

The extrapolation of the apparent molar volume of an electrolyte/a solute to infinite dilution and the expression of the concentration dependence of the apparent molar volume have been made by four major equations over a period of years – the Masson equation [8], the Redlich-Meyer equation [9], the Owen-Brinkley equation [10] and the Pitzer equation [11]. Masson found that the apparent molar volume ( $\phi_V$ ) of electrolytes follows a linear relation with the square root of the solute molarities ( $c$ ):

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \quad (16)$$

where  $\phi_V^0$  is 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 corresponding slope. The majority of  $\phi_V$  data in water [12] and nearly all  $\phi_V$  data in non-aqueous [13-17] solvents have been extrapolated to infinite dilution through the use of equation (16). However, Redlich and Meyer [9] have shown that equation (16) cannot be more than a limiting law and for a given solvent and temperature, the slope  $S_V^*$  should depend only upon the valence type. They suggested an equation for representing  $\phi_V$  as follows:

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$$\phi_V = \phi_V^0 + A_V \sqrt{c} + b_V c \quad (17)$$

$$\text{where } A_V = kW^{3/2} \quad (18)$$

$A_V$  is the theoretical slope, based on molar concentration, including the valence factor:

$$w = 0.5 \sum_i^j \nu_i z_i^2 \quad (19)$$

$$\text{and, } k = N_A^2 e^2 (8\pi/1000 \epsilon_r^3 RT)^{1/2} [(\partial \ln \epsilon_r / \partial P)_T - \beta/3] \quad (20)$$

where  $\beta$  is the compressibility of the solvent. But the variation of dielectric constant ( $\epsilon_r$ ) with pressure was not known accurately enough, even in water, to calculate accurate values of the theoretical limiting slope.

The Redlich-Meyer [9] extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However, studies [18-20] on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Actually, the volume contributed to a solvent by the addition of 1 mole of an ion is difficult to determine. This is so because, upon entry into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the influence of the ion's electric field, i.e., Electrostriction [21] which is a general phenomenon and whenever there are electric fields of the order of  $10^9$ - $10^{10}$  V m<sup>-1</sup>, the compression of ions and molecules is likely to be significant. However, for polyvalent electrolytes, the more complete Owen-Brinkley [10] equation can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of  $\phi_V$ . The Owen-Brinkley equation derived by including the ion-size parameter ( $a$ ) is given by:

$$\phi_V = \phi_V^0 + A_V \tau(\kappa a) \sqrt{c} + 0.5 w_V \theta(\kappa a) + 0.5 K_V c \quad (21)$$

where the symbols have their usual significance [10]. However, equation (21) has not been widely employed for the treatment of results for non-aqueous solutions. Pogue

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and Atkinson [22] used the Pitzer formalism to fit the apparent molar volume data. The Pitzer equation for the apparent molal volume of a single salt  $M_{\nu_M} X_{\nu_X}$  is:

$$\phi_V = \phi_V^0 + V |z_M z_X| A_V [2b \ln(I + bI^{1/2}) + 2\nu_M \nu_X RT [m B_{MX}^V + m^2 (\gamma_M \gamma_X)^{1/2} C_{MX}^V]] \quad (22)$$

where

$$B_{MX}^V = (\partial \beta^0 / \partial P)_T + (\partial \beta^1 / \partial P)_T (2 / \alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (23)$$

$$C_{MX}^V = (\partial C^\phi / \partial P)_T / 2 \quad (24)$$

$$\nu = \nu_M + \nu_X \quad (25)$$

$$\alpha = 2.0(\text{kg/mol})^{1/2} \quad (26)$$

$$b = 1.2(\text{kg/mol})^{1/2} \quad (27)$$

and other symbols have their usual significance [22].

### 2.1.3. Ionic Partial Molar Volume

The individual ionic partial molar volumes provide information relevant to the general question of the structure near the ion, i.e., its solvation. The calculation of the ionic limiting partial molar volumes in organic solvents is, however, a difficult. At present most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions [23] to non-aqueous electrolyte solutions. In the last few years, the method suggested by Conway *et al.* [23] has been used most frequently. These authors used the method to determine the limiting partial molar volumes of the anion for a series of homologous tetraalkylammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume,  $\phi_{V, R_4NX}^0$  for a series of these salts with a common halide ion as a function of the formula weight of the cation,  $M_{R_4N^+}$  and obtained straight lines for each series and suggested the following equation:

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$$\phi_{V,R_4NX}^0 = \phi_{V,X^-}^0 + bM_{R_4N^+} \quad (28)$$

The extrapolation to zero cationic formula weight thus provided the limiting partial molar volumes of the halide ions,  $\phi_{V,X^-}^0$ . When an ion is introduced into a solvent,  $\phi_V^0$  can be expressed as [24]:

$$\phi_{V,ion}^0 = \phi_{V,int}^0 + \Delta V \quad (29)$$

where  $\phi_{V,int}^0$  is the intrinsic volume of the ion and  $\Delta V$  is the change in volume of the system due to ion-solvent interactions. Some authors [25] have suggested that the anion solvation can be considered as negligible in electrolyte solutions. These authors argued that the solvation number at infinite dilution is a measure of the extent to which the cation is solvated. Therefore equation (29) can also be expressed as:

$$\phi_{V,ion}^0 = \phi_{V,int}^0(R_4N^+) + \Delta V \quad (30)$$

and the term  $\phi_{V,int}^0(R_4N^+)$  can be calculated with the help of the following relation [26]:

$$\phi_{V,int}^0(R_4N^+) = 2.52 r_{R_4N^+}^3 \quad (31)$$

where  $r_{R_4N^+}$  is the crystallographic radii of the  $R_4N^+$  ion. Uosaki *et al.* [27] used this method for the separation of some literature values and of their own  $\phi_{V,R_4NX}^0$  values into ionic contributions in organic electrolyte solutions. Krungalz [26] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

However, Millero [28] on the basis of Frank and Wen model [29] has expressed the standard partial molar volume of an ion ( $\phi_{V,ion}^0$ ) by the relation:

$$\phi_{V,ion}^0 = \phi_{V,int}^0 + \phi_{V,elect}^0 + \phi_{V,disord}^0 + \phi_{V,caged}^0 \quad (32)$$

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where  $\phi_{V,\text{elect}}^0$  is the electrostriction partial molar volume due to ion-solvent interactions,  $\phi_{V,\text{disord}}^0$  is the disordered partial molar volume due void space and  $\phi_{V,\text{caged}}^0$  is the caged partial molar volume due to a caged water structure around ions containing hydrophobic groups such as the tetraalkylammonium ions. It is difficult to determine the importance of the various contributions to  $\phi_{V,\text{ion}}^0$ . Millero [28] has examined  $\phi_{V,\text{ion}}^0$  values in water and methanol with the help of following relations: [30]

$$\phi_{V,\text{ion}}^0 = 2.52r^3 + A' r^2 - B' z^2 / r \quad (33)$$

$$\phi_{V,\text{ion}}^0 = 2.52(r+a)^3 - B'' z^2 / r \quad (34)$$

where  $r$  is the crystallographic radii of the ion,  $z$  is ionic charge,  $a$ ,  $A'$ ,  $B'$  and  $B''$  are constants. These constants like ionic entropies show no simple correlation to any of the common physical properties. The electrostriction of an ion can be estimated, when dielectric saturation is negligible, by the Drude-Nernst equation: [31]

$$\phi_{V,\text{elect}}^0 = -\frac{N_A z^2 e^2}{2 \epsilon_r r} (\partial \ln \epsilon_r / \partial P) = -\frac{B''' z^2}{r} \quad (35)$$

where  $\epsilon_r$  is the dielectric constant of the solvent,  $B'''$  is a solvent dependent constant and other symbols have their usual significance [31]. For highly ordered solvents there is strong competition between ion and other solvent molecules to increase the order. While ions attempts to orient solvent molecules around themselves, the solvent molecules attempt to stay in the highly structured bulk liquid. This leads to a relatively large disturbed region surrounding the solvated ions thus leading to large values for  $\phi_{V,\text{disord}}^0$  and  $S_{\text{ion}}^0$  (partial molar entropy of the ion). For solvents with less ordered structure, ion-solvent interactions are in favor of the ion and the solvent molecules will be influenced by the ions. This leads to a smaller voids space surrounding the ion and consequently a smaller  $\phi_{V,\text{disord}}^0$ , negative  $\phi_{V,\text{elect}}^0$  and  $S_{\text{ion}}^0$

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values. Thus the actual number of solvent molecules ordered by an ion depends on both the degree of the solvent structure and the dielectric constant of the solvent.

### 2.1.4. Standard Partial Molar Volume of Transfer

Studies on partial molar volume of solutes at infinite dilution have proved to be useful practice for exploring solute (or ion)-solvent and solvent-solvent interactions in aqueous [12], non-aqueous [26, 32], and mixed solvents [33]. Since the solute-solute or ion-ion interactions are absent at infinite dilution, the difference or changes in the partial molar volume of the solute in a particular solvent system from that in a reference solvent, i.e., transfer volume reflects the extent and nature of solute-solvent or ion-solvent and solute-cosolute interactions. These changes are expressed by means of a transfer function,  $\Delta_t \phi_V^0$ , defined as:

$$\Delta_t \phi_V^0 = \phi_V^0 (\text{solute} + \text{cosolute} + \text{solvent}) - \phi_V^0 (\text{solute} + \text{solvent}) \quad (36)$$

This transfer function gives a measure of the differences in solute-solvent interactions between the reference solvent and solvent system or mixed solvent. Franks *et al.* [34] showed that the partial molar volume of a non-electrolyte is a combination of its intrinsic volume  $\phi_{V,\text{int}}^0$  and volume  $\phi_{V,\text{solv}}^0$  due to its interactions with the solvent. The intrinsic volume is considered to have two types of contributions, i.e.,  $\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}}$ ; where  $\phi_{V,\text{vw}}$  is the van der Waals volume and  $\phi_{V,\text{void}}$  is voids or empty spaces therein the solution. Shahidi *et al.* [35] modified this equation to include the contribution of interactions of a non-electrolyte solute with the solvent as follows:

$$\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}} - n\sigma_s \quad (37)$$

where  $\sigma_s$  is the shrinkage in volume produced by the interactions of hydrogen bonding groups present in the solute with solvent molecules (water) and  $n$  is the potential number of hydrogen bonding sites in the solute. For electrolytes and zwitterionic solutes, the shrinkage is caused by the electrostriction and hence the equation (37) can be expressed as:

$$\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}} - \phi_{V,\text{shrinkage}} \quad (38)$$

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and generally  $\phi_{V, \text{vw}}$  and  $\phi_{V, \text{void}}$  are taken [36] to have same magnitude in water and in mixed solvent for the same type of solutes. Thus,  $\phi_{V, \text{int}}^0$  depends on  $\phi_{V, \text{shrinkage}}^0$ , which is controlled by the extent of electrostriction in the solution. The cosphere overlap model developed by Gurney [37] and Frank and Evans [38] can also be utilized to analyze  $\Delta_t \phi_V^0$  values in terms of solute-cosolute interactions. According to these model properties of water molecules in the hydration cosphere depend on the nature of the solute molecules. When two solute particles come close enough so that their cospheres overlap, some of the cosphere material is displaced leading to changes in the thermodynamic properties. The following types of 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 molecules. The first type of interaction contributes positive volumes of transfer, while the second and third type of interactions contributes negative volumes of transfer. The overlap of hydration cospheres of charged species reduces electrostriction and leads to a decrease in  $\phi_{V, \text{shrinkage}}^0$  resulting into positive  $\Delta_t \phi_V^0$  values [37]. Kozak *et al.* [39] proposed a theory based on the McMillan-Mayer theory of solutions that permit the formal separation of effects due to interactions between pairs of solute molecules and those due to interactions involving three or more solvent molecules. Friedman and Krishnan [40] as well as Franks and Evans [38] further developed this approach to include the solute-cosolute interactions in the solvation sphere. According to this treatment, the thermodynamic function  $\Delta_t \phi_V^0$  can be expressed as:

$$\Delta_t \phi_V^0 = 2Z_{12}m_2 + 3Z_{122}m_2^2 + 4Z_{1222}m_2^3 \quad (39)$$

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 interpret the changes in  $\Delta_t \phi_V^0$  with solvent composition in terms of ionic effects because of treating the electrolytes as a whole. Obtaining individual ionic thermodynamic quantities involves adoption of some

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extra-thermodynamic assumptions (as discussed for partial molar volume in section 2.1.3 above) in order to split the transfer function  $\Delta_t \phi_V^0$  into ionic components. Maestre *et al.* [41] used the hypothesis of reference electrolyte ( $\text{Ph}_4\text{AsBPh}_4$ ) method to split  $\Delta_t \phi_V^0$  into ionic contributions by means of the following relations:

$$\Delta_t \phi_V^0(\text{Ph}_4\text{AsBPh}_4) = 2\Delta_t \phi_V^0(\text{Ph}_4\text{As}^+) = 2\Delta_t \phi_V^0(\text{BPh}_4^-) \quad (40)$$

$$\Delta_t \phi_V^0(\text{Ph}_4\text{AsBPh}_4) = \Delta_t \phi_V^0(\text{Ph}_4\text{AsCl}) + \Delta_t \phi_V^0(\text{NaBPh}_4) - \Delta_t \phi_V^0(\text{NaCl}) \quad (41)$$

Thus once  $\Delta_t \phi_V^0(\text{Ph}_4\text{As}^+)$  or  $\Delta_t \phi_V^0(\text{BPh}_4^-)$  has been obtained, other single ion volumes of transfer can be had from the whole electrolyte data. According to Conway, [42] the partial molar volume of an ion at infinite dilution can be split into three terms:

$$\phi_{V,\text{ion}}^0 = \phi_{V,\text{int}}^0 + \phi_{V,\text{elect}}^0 + \phi_{V,\text{struc}}^0 \quad (42)$$

where  $\phi_{V,\text{int}}^0$  is a positive term consisting of the molar volume of the ion itself,  $\phi_{V,\text{elect}}^0$  is a negative term owing to the electrostriction of the solvent and  $\phi_{V,\text{struc}}^0$  is the structural contribution to the volume. The last term can be further split into two parts: one negative corresponding to the accommodation of the ion in a cavity in the solvent and the other positive resulting from a local reinforcement of the solvent structure. So equation (42) in terms of transfer volume becomes:

$$\Delta_t \phi_{V,\text{ion}}^0 = \Delta_t \phi_{V,\text{elect}}^0 + \Delta_t \phi_{V,\text{struc}}^0 \quad (43)$$

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 thus depend on the balance between electrostriction and structural contributions.

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### 2.1.5. Apparent Molar Expansibility

The apparent molar expansibility ( $\phi_E$ ) of a solution is defined by  $\phi_E = (\partial\phi_V / \partial T)_P$  and combining this equation with the equation (11), we have:

$$\phi_E = \frac{\alpha V - \alpha_1 n_1 V_1^*}{n_2} \quad (44)$$

where  $\alpha$  and  $\alpha_1$  are the coefficients of thermal expansion of the solution and the solvent, respectively and are defined as:  $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$  and  $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$ . The apparent molar expansibility ( $\phi_E$ ) can be calculated from densities and their temperature coefficients by the equations:

$$\phi_E = \alpha_1 \phi_V + \frac{1000(\alpha - \alpha_1)}{c} \quad (45)$$

and

$$\phi_E = \alpha \phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \quad (46)$$

### 2.1.6. Standard Partial Molar Expansibility

The standard partial molar expansibilities ( $\phi_E^0$ ) can be determined from the relation [4]:

$$\phi_E = \phi_E^0 + S_E \sqrt{c} \quad (47)$$

When solute concentrations are in molalities ( $m$ ), equation (47) can be written as:

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \quad (48)$$

and  $(\partial\phi_E^0/\partial T)_P$  values can then be obtained from the slope of a least squares linear regression of  $\phi_E^0$  values against experimental temperatures ( $T$ ).

Alternatively, the temperature dependence of  $\phi_V^0$  for various investigated electrolytes in various solvents can be expressed as:

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$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (49)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are the coefficients for a solute and  $T$  is the absolute temperature. The partial molar expansibilities ( $\phi_E^0$ ) can be obtained by differentiating equation (49) with respect to  $T$  at constant pressure  $P$ ,

$$\phi_E^0 = (\partial\phi_V^0/\partial T)_P = a_1 + 2a_2T \quad (50)$$

Thus the standard molar expansibilities ( $\phi_E^0$ ) change in magnitude with the change of temperature. Since partial molar heat capacities of electrolytes are commonly negative and on the basis of the structural model [43], the explanation in terms of structure breaking leads to the prediction that  $(\partial C_p^0/\partial P)_T$  should be positive; hence on the basis of the thermodynamic equation,

$$(\partial C_p^0/\partial P)_T = -T(\partial^2\phi_V^0/\partial T^2)_P \quad (51)$$

It is evident structure breaking solutes should have negative  $(\partial^2\phi_V^0/\partial T^2)_P$  values. Similar reasoning indicates that positive  $(\partial^2\phi_V^0/\partial T^2)_P$  should be associated with the structure-making solutes. Hence, according to Hepler [43] the sign of  $(\partial\phi_E^0/\partial T)_P$  can be used to reveal the long-range structure-making and breaking capacity of the electrolytes/solutes in the solvent systems. The general thermodynamic expression used is as follows:

$$(\partial\phi_E^0/\partial T)_P = (\partial^2\phi_V^0/\partial T^2)_P = 2a_2 \quad (52)$$

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

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### 2.1.7. Ionic Partial Molar Expansibility

If  $\phi_{V,\text{ion}}^0$  values are available at several temperatures ( $T$ ),  $\phi_{E,\text{ion}}^0$  values can be obtained from the slopes of a plot of  $\phi_{V,\text{ion}}^0$  values against  $T$ . Partial molar expansibilities ( $\phi_E^0$ ) of the electrolytes can be split into ionic contributions by following the relation:

$$\phi_E^0 = \phi_{E,+}^0 + \phi_{E,-}^0 \quad (53)$$

where  $\phi_{E,+}^0$  and  $\phi_{E,-}^0$  are the partial molar expansibility of the cation and anion, respectively. Millero and coworkers [44] examined  $\phi_{E,\text{ion}}^0$  values of a large number of ions in water at 298.15 K. For simple monovalent cations and anions they found that  $\phi_{E,\text{ion}}^0$  varies in size or radius in the inverse order as observed by Fajans and Johnson [45] and that ion-water interactions are different for cations and anions of similar size. Similar to  $\phi_{V,\text{ion}}^0$ ,  $\phi_{E,\text{ion}}^0$  can also be resolved into different contributions according to Frank and Wen model [29] for the hydration of ions as expressed by the relation:

$$\phi_{E,\text{ion}}^0 = \phi_{E,\text{int}}^0 + \phi_{E,\text{elect}}^0 + \phi_{E,\text{disord}}^0 + \phi_{E,\text{caged}}^0 \quad (54)$$

According to this model the intrinsic expansibility,  $\phi_{E,\text{int}}^0$ , is the volume change due to expansion of the ion and can be neglected for monovalent ions. However, this term in equation (54) is dictated mostly by the expansibility of covalent bonds in the ions with hydrocarbon portion. The electrostriction expansibility,  $\phi_{E,\text{elect}}^0$ , is the volume change due to changes in electrostriction region and is negative as well as proportional to  $z^2/r$ ; where  $z$  is the charge on the ion and  $r$  is its crystal radius. 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 same size owing to different orientation of water molecules 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 is also an important

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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 and is important for ions with hydrocarbon portion, it is positive and increases in magnitude with the size of the hydrocarbon portion of the ion.

### 2.2. Viscosity

Viscosity, the force required to produce unit rate of shear between two layers separated by unit distance, is an important transport property of liquids and is used for the determination of ion-solvent interactions and studied extensively. Viscosity is not a thermodynamic quantity but viscosity of an electrolytic solution along with the thermodynamic property,  $\phi_V^0$ , i.e., the standard partial molar volume gives a lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

#### 2.2.1. Viscosity of Electrolyte Solution

The viscosity relationships of electrolytic solutions are highly complicated. Because ion-ion and ion-solvent interactions are occurring in the solution and separation of the related forces is a difficult task. But from careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system. As viscosity is a measure of the friction between adjacent, relatively moving parallel planes of the liquid, anything that increases or decreases the interaction between the planes will raise or lower the friction and thus, increase or decrease the viscosity. If large spheres are placed in the liquid, the planes will be keyed together in increasing the viscosity. Similarly, increase in the average degree of hydrogen bonding between the planes will increase the friction between the planes, thereby increasing viscosity.

An ion with a large rigid co-sphere for a structure-promoting ion will behave as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity. In 1905 Grüneisen [46] performed the first systematic measurement of viscosities of a number of electrolytic solutions over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929,

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Jones and Dole [47] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations ( $c$ ):

$$\eta/\eta_1 = \eta_r = 1 + A\sqrt{c} + Bc \quad (55)$$

The above equation can be rearranged as:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (56)$$

where  $A$  and  $B$  are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non-aqueous solvent systems with negligible ionic association and has been used extensively. The term  $A\sqrt{c}$ , originally ascribed to Grüneisen effect (due to the long-range coulombic forces between the ions) can, in principle, be discussed in the light of Debye-Hückel theory [48] of inter-ionic attractions. The  $A$ -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [49, 50] and is given by the Falkenhagen Vernon [50] equation:

$$A_{\text{Theo}} = \frac{0.2577\Lambda_0}{\eta_1(\epsilon_r T)^{0.5} \lambda_+^0 \lambda_-^0} \left[ 1 - 0.6863 \left( \frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0} \right)^2 \right] \quad (57)$$

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  $A$ -coefficients obtained by fitting  $\eta_r$  values to equation (56) for aqueous solutions [51] were compared with the values calculated from equation (55), good agreement was observed. But the accuracy was poor with partially aqueous solutions [52]. Crudden *et al.* [53] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analyzed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha_{\text{IP}} c}}{\alpha_{\text{IP}} c} = B_i + B_p \left( \frac{1 - \alpha_{\text{IP}}}{\alpha_{\text{IP}}} \right) \quad (58)$$

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where  $A$ ,  $B_i$  and  $B_p$  are characteristic constants and  $\alpha_{ip}$  is the degree of dissociation of ion pair. Thus extrapolation of a plot of  $(\eta_r - 1 - A\sqrt{\alpha_{ip}c})/\alpha_{ip}c$  versus to  $(1 - \alpha_{ip})/\alpha_{ip} = 0$  gave the intercept  $B_i$ . However for the most of the electrolytic solutions both in aqueous and non-aqueous media, the equation (56) is valid up to 0.1 (M) [4, 54, 55] within experimental errors. At higher concentrations the extended Jones-Dole equation (59), involving an additional coefficient  $D$ , originally used by Kaminsky [56], is given below:

$$\eta/\eta_1 = 1 + A\sqrt{c} + Bc + Dc^2 \quad (59)$$

The significance of the coefficient  $D$  is also not always meaningful and therefore, equation (56) is the most popular. The plots of  $(\eta/\eta_1 - 1)/\sqrt{c}$  against  $\sqrt{c}$  for the electrolytes should give the value of  $A$ -coefficient. But sometimes, the values are negative or considerably scattered and also deviate from linearity [4, 57, 58]. Thus, instead of determining  $A$ -coefficient from the plots or by the least square method, the  $A$ -coefficients should be calculated by using Falkenhagen-Vernon equation (57). 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 [47]. The  $B$ -coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. 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  $B$ -coefficients are [59, 60]: (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

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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 [54], a rise in temperature of the solution causes  $B$ -coefficients to fall, this fall being greater at low than at high temperatures. Such behaviour can be used to identify ‘structure-making’ solutes [61]. Conversely, ‘structure-breaking’ solutes should have rather low  $B$ -coefficient that increases with temperature [54]. If solvation decreases with increasing temperature,  $B$ -coefficient of a solvated species should also fall and consequently both primary solvation and structure making should have high  $B$ -coefficient at low temperature and negative values of  $\partial B/\partial T$ .

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

Viscosity  $B$ -coefficients, as determined experimentally by using the Jones-Dole equation, do not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contributions from cations and anions to the total ion-solvent interaction. The division of viscosity  $B$ -values into ionic components is quite arbitrary and based on some extra-thermodynamic assumptions. The following methods have been used for the division of  $B$ -values in the ionic components:

(1) Cox and Wolfenden [62] carried out the division on the assumption that  $B_{\text{ion}}$  values of  $\text{Li}^+$  and  $\text{IO}_3^-$  in  $\text{LiIO}_3$  are proportional to the respective ionic volumes that are proportional to the third power of the respective ionic mobilities. The method of Gurney [37] and also of Kaminsky [56] is based on:

$$B_{\text{K}^+} = B_{\text{Cl}^-} \text{ (in water)} \quad (60)$$

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The argument in favour of this assignment is based on the fact that the  $B$ -coefficients for KCl is very small and that the mobilities of  $K^+$  and  $Cl^-$  are very similar over the temperature range 288-318 K. The assignment is supported by other thermodynamic properties. Nightingale [63], however, preferred RbCl or CsCl to KCl on mobility considerations.

(2) The method suggested by Desnoyers and Perron [64] is based on the assumption that the  $Et_4N^+$  ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation, [65]

$$B = 0.0025 \phi_{V, ion}^0 \quad (61)$$

and with an accurate value of the partial molar volume of the ion,  $\phi_{V, ion}^0$ , it is possible to calculate a value of 0.359 for  $B_{Et_4N^+}$  in water at 25 °C. Sacco *et al.* [66] proposed the “reference electrolytic” method for the division of  $B$ -values. Thus, for tetraphenyl phosphonium tetraphenyl borate ( $Ph_4PBPh_4$ ) in water, we have:

$$B_{Ph_4B^-} = B_{Ph_4P^+} = B_{Ph_4PBPh_4} / 2 \quad (62)$$

As  $Ph_4PBPh_4$  is sparingly soluble in water,  $B_{Ph_4PBPh_4}$  can be obtained from:

$$B_{Ph_4PBPh_4} = B_{NaBPh_4} + B_{Ph_4PBr} - B_{NaBr} \quad (63)$$

The values obtained are in good agreement with those obtained by other methods. The criteria adopted for the separation of  $B$ -coefficients in non-aqueous solvents differ from those generally used in water. However, the methods [58, 59, 67, 68] are based on the equality of equivalent conductance of the counter ions at infinite dilution.

According to Krumgalz [69, 70] the method for the resolution of  $B$ -coefficients into ionic parts is based on the fact that the large tetraalkylammonium cations ( $R_4N^+$ ) are not solvated [71, 72] in organic solvents. Thus, the ionic  $B$ -values for large tetraalkylammonium ions,  $R_4N^+$  (where  $R > Bu$ ) in organic solvents, are proportional to their ionic dimensions. So, we have:

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$$B_{R_4NX} = a + br_{R_4N^+}^3 \quad (64)$$

where  $a = B_{X^-}$  and  $b$  is a constant dependent on temperature and solvent nature. The extrapolation of the plot of  $B_{R_4NX}$  ( $R > Pr$  or  $Bu$ ) against  $r_{R_4N^+}^3$  to zero cation dimension gives directly  $B_{X^-}$  in the proper solvent and thus  $B$ -ion values can be had. The  $B$ -ion values can also be calculated from the equations:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (65)$$

$$B_{R_4N^+} / B_{R'_4N^+} = r_{R_4N^+}^3 / r_{R'_4N^+}^3 \quad (66)$$

by using the radii of the tetraalkylammonium ions ( $r_{R_4N^+}^3$  and  $r_{R'_4N^+}^3$ ) calculated from the conductometric data [73].

Gill and Sharma [74] used  $Bu_4NBPh_4$  as a reference electrolyte. The method of resolution is based on the assumption, like Krungalz, that  $Bu_4N^+$  and  $Ph_4B^-$  ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of  $Bu_4N^+$  (5.00 Å) and  $Ph_4B^-$  (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents used by Gill and co-workers. They proposed the equations:

$$B_{Ph_4B^-} / B_{Bu_4N^+} = r_{Ph_4B^-}^3 / r_{Bu_4N^+}^3 = (5.35/5.00)^3 \quad (67)$$

$$\text{and, } B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (68)$$

The method requires only the  $B$ -values of  $Bu_4NBPh_4$  and is equally applicable to mixed non-aqueous solvents. The  $B$ -ion values obtained by this method agree well with those reported by Lawrence *et al.* [66] in different organic solvents using the assumption as given below:

$$B_{[(i-Am)_3BuN^+]} = B_{Ph_4B^-} = 1/2 B_{[(i-Am)_3BuNPh_4B]} \quad (69)$$

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Lawrence *et al.* [66] used tetrabutylammonium tetrabutylborate ( $\text{Bu}_4\text{NBBu}_4$ ) as ‘reference electrolyte’ because the cation and anion are symmetrical in shape and have almost equal van der Waals volumes. Thus, we have:

$$B_{\text{Bu}_4\text{N}^+} / B_{\text{Bu}_4\text{B}^-} = V_{W(\text{Bu}_4\text{N}^+)} / V_{W(\text{Bu}_4\text{B}^-)} \quad (70)$$

$$\text{or, } B_{\text{Bu}_4\text{N}^+} = B_{\text{Bu}_4\text{NBBu}_4} / [1 + V_{W(\text{Bu}_4\text{B}^-)} / V_{W(\text{Bu}_4\text{N}^+)}] \quad (71)$$

A similar division can be made for  $\text{Ph}_4\text{PBPh}_4$  system. Lawrence *et al.* [66] made the viscosity measurements of tetraalkylammonium bromides (from Pr to Hept.) in DMSO and HMPT. The  $B$ -coefficients,  $B_{\text{R}_4\text{NBr}} = B_{\text{Br}^-} + a[f(r_{\text{R}_4\text{N}^+})]$ , were plotted as functions of the van der Waals volumes. The  $B_{\text{Br}^-}$  values thus obtained were compared with the accurately determined  $B_{\text{Br}^-}$  value using  $\text{Bu}_4\text{NBBu}_4$  and  $\text{Ph}_4\text{PBPh}_4$  as ‘reference electrolyte’. They concluded that the ‘reference electrolyte’ method is the best available method for division into ionic contributions.

Jenkins and Pritchett [75] observed that  $B_{\text{Cs}^+} = B_{\text{I}^-}$ , as suggested by Krumgalz [71], to be more reliable than  $B_{\text{K}^+} = B_{\text{Cl}^-}$  in aqueous solutions. Anyway, it is apparent that almost 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 [76]. 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  $B_{\text{ion}}$  values increase as the ionic radius increases. The results can be summarized as follows:

For structure breaking ions-

$$(i) A \text{ and } \partial A / \partial T > 0 \quad (72)$$

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$$(ii) B_{ion} < 0 \text{ and } \partial B_{ion} / \partial T > 0 \quad (73)$$

For structure making ions-

$$(iii) B_{ion} > 0 \text{ and } \partial B_{ion} / \partial T < 0 \quad (74)$$

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvational layer may be different from those present in the bulk structure. This is well reflected in the ‘Co-sphere’ model of Gurney [37], A, B, C zones of Frank and Wen [29] and hydrated radius of Nightingale [63]. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent ( $\eta_0$ ) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation becomes,

$$\eta = \eta_1 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_1 + \eta(A\sqrt{c} + Bc) \quad (75)$$

where  $\eta^*$ , the positive increment in viscosity, is caused by coulombic interaction.  $B$ -coefficient can thus be interpreted in terms of the competitive viscosity effects. Following Stokes, Mills and Krumgalz [69] we can write for  $B_{ion}$  as:

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{Str} + B_{ion}^{Reinf} \quad (76)$$

whereas according to Lawrence and Sacco [66]:

$$B_{ion} = B_w + B_{solv} + B_{shape} + B_{ord} + B_{disord} \quad (77)$$

$B_{ion}^{Einst}$  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  $B_{shape}$ ).

$B_{ion}^{Orient}$  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  $B_{ord}$ ).

$B_{ion}^{Str}$  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

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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 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  $Cs^+$  or  $I^-$  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.,  $K^+$  and  $Cl^-$ ) 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 ( $R_4N^+$ ) 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

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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

Thermodynamics of non-electrolytes cover an area of knowledge at least equal in magnitude to that of electrolyte solutions. Hildebrand and Scott have thoroughly discussed this subject, mostly in non-polar solvents [77]. According to Falkenhagen [49, 50],  $A$ -coefficient values for uncharged solutes are zero. Solution viscosities ( $\eta$ ) of non-electrolytes can be analyzed with the modified Jones-Dole equation [37, 54]:

$$\eta_r = 1 + Bc \quad (78)$$

where  $\eta_r = \eta/\eta_1$ ;  $\eta_1$ ,  $\eta$  and  $c$  are viscosities of the solvents, viscosities of the solutions and molar concentration of the solute in the studied solutions, respectively.  $A$ -coefficients may be found to be zero or very close to zero within the experimental error limit with Jones-Dole equation (56) fitted to the experimental viscosity data. In such cases the experimental viscosities can be fitted to the following linear regression relation giving equal weights to all the viscosities [78]:

$$\eta = C' + B'c \quad (79)$$

where  $B'$  and  $C'$  are constants;  $C'$  values are found to agree with the observed  $\eta_1$  values within the experimental error limit and  $B'$  is related to  $B$ -coefficients by the following relation [78]:

$$B = B'/C' \quad (80)$$

### 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:

$$\Delta_t B = B(\text{solute} + \text{cosolute} + \text{solvent}) - B(\text{solute} + \text{solvent}) \quad (81)$$

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and can be discussed with the aid of Gurney's 'Co-sphere' model [37]. Generally negative  $\Delta_{\pm}B$  values indicate that the solute is in less structured environment in the solution compared to that in the solvent and positive  $\Delta_{\pm}B$  values indicate that the solute is in more structured environment in the solution compared to that in that solvent. These results reflect the influence of 'solvent structure modification' by the solute and cosolute molecules.

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

Stokes and Mills [54] have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein [65] leads to the equation:

$$\eta/\eta_1 = 1 + 2.5\phi \quad (82)$$

where  $\phi$  is the volume fraction occupied by the particles. Modifications of the equation have been proposed by: (i) Simha [79] on the basis of departures from spherical shape and (ii) Vand [80] 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 hydrated ions of large effective size (particularly polyvalent monoatomic cations). Thus we have from equation (82):

$$2.5\phi = A\sqrt{c} + Bc \quad (83)$$

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

$$2.5\phi_{v,ion}^0 = B \quad (84)$$

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

$$B_{\pm} = 2.5\phi_{v,ion}^0 = 2.5 \times 4/3 (\pi R_{\pm}^3 N_A / 1000) \quad (85)$$

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assuming that the ions behave like rigid spheres with an effective radii,  $R_{\pm}$  moving in a continuum and 2.5 is the shape factor for a sphere.  $R_{\pm}$ , calculated by using the equation (85), should be close to crystallographic radii or corrected Stoke's radii [81] if the ions are scarcely solvated and behave as spherical entities. But, in general,  $R_{\pm}$  values of the ions are higher than the crystallographic radii indicating appreciable solvation. The number  $n_s$  of solvent molecules bound to the ion in the primary solvation shell can be easily calculated by comparing the Jones-Dole equation with the Einstein's equation [65]:

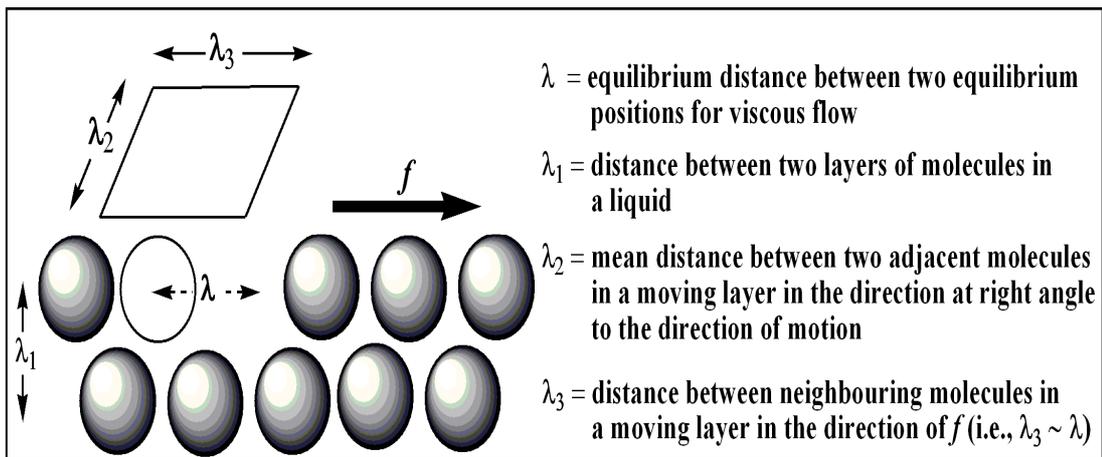
$$B_{\pm} = 2.5/1000(V_i + n_s V_s) \quad (86)$$

where  $V_i$  is the molar volume of the bare ion and  $V_s$ , the molar volume of the solvent. The equation (86) has been used by a number of workers to study the nature of solvation and solvation number.

### 2.2.7. Thermodynamics of Viscous Flow

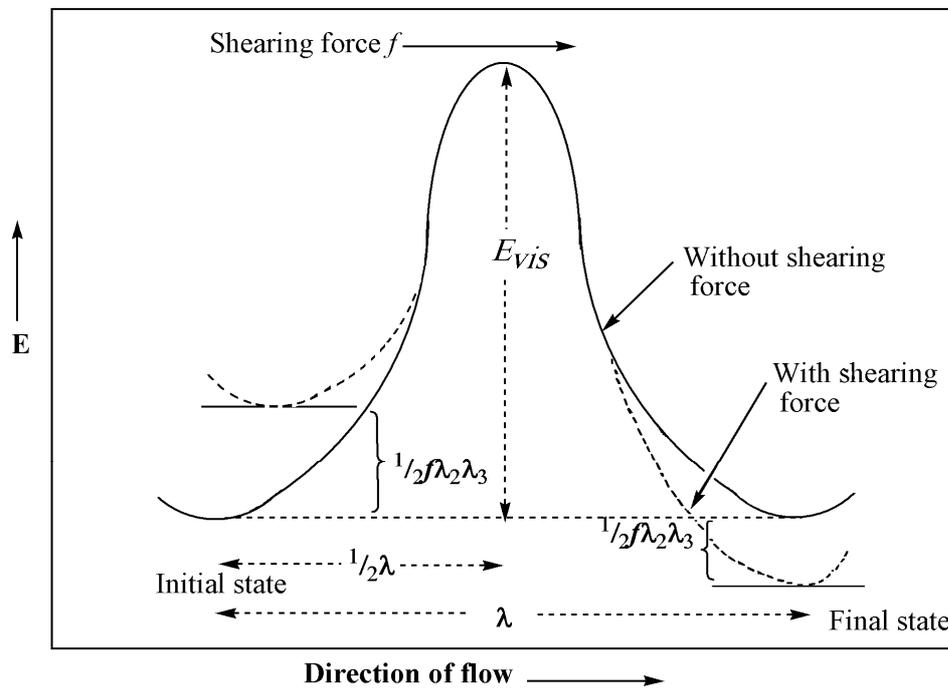
Like diffusion, viscosity can be treated by means of the theory of absolute reaction rates [82]. As a gas is considered to consist of molecules moving about in empty space, a liquid may be regarded as made up of "holes" moving about in matter. Thus "holes" are to be taken as playing the same part in a liquid as moles do in 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 [82]. If two layers of molecules in a liquid are apart 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 is given by the relation:  $\eta = f\lambda_1 / \Delta u$ . The passage of a molecule from one equilibrium position to another such position in the same layer requires that a suitable hole is available and energy must be utilized to create such a hole in the liquid. The process is shown in figure 2.2 below.

## Theoretical Background



**Fig. 2.2.** Passage of a molecule from one equilibrium position to another position in the same layer of a liquid with the creation of a suitable hole.

This process can be discussed with the aid of a symmetrical potential energy barrier depicted in figure 2.3.



**Fig. 2.3.** Potential energy barrier for viscous flow with and without shearing force.

As the potential energy barrier has been taken as 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

## Theoretical Background

effective area per molecule. So the energy acquired by the moving molecule that 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 [82], the viscosity ( $\eta$ ) of a solution can be represented by the Eyring's relation [82]:

$$\eta = Ae^{E_{\text{vis}}/RT} = (hN/V)e^{\Delta G^\ddagger/RT} = (hN/V)e^{(\Delta H^\ddagger/RT - \Delta S^\ddagger/R)} \quad (87)$$

where  $E_{\text{vis}}$  = 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 required to move the molecules into the holes. According to equation (87), the free energy of activation for viscous flow per mole of the solvent/solvent mixture ( $\Delta\mu_1^{0\ddagger}$ ) as:

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln(\eta_1 \phi_{V,1}^0 / hN_A) \quad (88)$$

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 relation can also be expressed as [52, 83]:

$$\ln(\eta_1 \phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\ddagger}}{R} + \left( \frac{\Delta H_1^{0\ddagger}}{R} \right) \frac{1}{T} \quad (89)$$

## Theoretical Background

So a linear regression of the  $(\ln(\eta_1 \phi_{V,1}^0 / hN_A))$  data against  $1/T$  provides the  $\Delta H_1^{0\neq}$  and  $\Delta S_1^{0\neq}$  values. A correlation between 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 ( $\Delta\mu_2^{0\neq}$ ) and the free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ( $\Delta\mu_1^{0\neq}$ ) was suggested by Feakins *et al.* [83] in the form of the following relation:

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0 \left( \frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT} \right) \quad (90)$$

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 equation (90) by using the  $B$ -coefficient values.  $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$  values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{ \frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R} \right\} \frac{1}{T} \quad (91)$$

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 treatment of equation (91) 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 corresponding slopes and intercepts. According to equation (90),  $\Delta\mu_2^{0\neq}$  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, implying that  $\Delta\mu_2^{0\neq}$  is dependent mainly 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 as well as 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

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solute (ions) becomes less favored energetically. However, a popular method uses the following relations,

$$d(\Delta\mu_2^{0\neq})/dT = -\Delta S_2^{0\neq} \quad (92)$$

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \quad (93)$$

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

### 2.2.8. Solvation Number

Bockris [84] suggested that the term ‘primary solvation’ should refer to the comparatively firm attachment of solvent molecules to the ions in such a way that an ion and its solvent molecules move as an entity in an electrolyte transport process, the solvent molecules having lost their own translation degree of freedom and ‘secondary solvation’ would designate all other solvent molecules. There are few cases where the inner sheath of water molecules is permanent in a long-term sense and the water molecules are firmly attached by coordinate links. Chromium and cobalt are transition elements with such a marked tendency to form coordinate links [85]. For a given ion, the solvation number depends on the manner of this association of solvent molecules and the method by which it is determined. The first solvation shell constitutes the set of immediate neighbouring solvent molecules around ion. If the solvent molecules interact strongly or coordinate with the ion and thus they constitute the primary solvation of the ion. The second solvation shell is the set of solvent molecules that are next nearest neighbours of the ion. Solvent molecules belonging to the primary and secondary solvation of the ion are oriented by its field in a manner that is incompatible with the normal mutual orientation of the solvent molecules in the bulk solvent. There will exist a region around the ion with solvent molecules having neither the central orientation nor the bulk orientation. This disordered region is called the thawed zone [86].

Anyway, if the limiting conductance of the ion is known, the effective radius of the solvated ion can easily be determined from the Stokes’ law [81]. The volume of the solvation shell  $V_s$ , can be written as:

## Theoretical Background

$$V_s = (4\pi/3)(r_s^3 - r_c^3) \quad (94)$$

where  $r_c$  is the crystal radius of the ion; the solvation number,  $S_n$  would then be obtained from:

$$S_n = V_s/V_0 \quad (95)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects [81] from:

$$V_s^0 = 4.35r_s^3 \quad (96)$$

where  $V_s^0$  is expressed in mol.L<sup>-1</sup> and  $r_s$  in angstroms. However, the method of determination of solvation number is not applicable to ions of medium size though a number of empirical equation [87] and theoretical corrections [88-91] have been suggested. Alternatively, solvation numbers  $S_n$  can easily be had from the relation [92]:

$$S_n = B/\phi_V^0 \quad (97)$$

$S_n$  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 [92]. If values of ionic viscosity  $B$ -coefficients ( $B_{\pm}$ ) are available, ionic solvation numbers ( $S_{n,\pm}$ ) can also be calculated from the equation (97) by using ionic partial molar volumes ( $\phi_{V,\pm}^0$ ) of the ions.

### 2.3. Ultrasonic sound velocity

The study of propagation of ultrasonic waves in liquid systems is a powerful tool for examining certain properties of the materials. It is particularly well adapted to examining changes in such physical properties at the macro level. The data obtained from ultrasonic propagation parameters in liquid mixtures and solutions and their variation with concentration and temperature helps to understand the nature of molecular interactions in mixtures. Sound velocity itself is highly sensitive to the

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structures and interactions present in the liquid mixtures as it is fundamentally related to binding forces between the constituents of the medium. For the quantitative estimation of the molecular interactions ultrasonic sound velocity method may be applied.

### 2.3.1. Apparent Molal Adiabatic Compressibility

It has been emphasized by many authors that the apparent molal adiabatic compressibility data can be used as a useful parameter in elucidating the solute-solvent and solute-solute interactions.

Adiabatic compressibility coefficients ( $\beta_s$ ), were derived from the following relation:

$$\beta_s = \frac{1}{u^2 \rho} \quad (98)$$

where  $u$  is the speed of sound in the solution and  $\rho$  is the density of solution. The apparent molar adiabatic compressibility ( $\phi_k$ ) of the solutions was found out from the relation,

$$\phi_k = \frac{M\beta_s / \rho + 1000(\beta_s \rho_1 - \beta_1 \rho)}{m\rho\rho_1} \quad (99)$$

where  $\beta_s$  and  $\beta_1$  are the adiabatic compressibilities of the solution and solvent respectively and  $m$  is the molality of the solution. The plotting of apparent molal adiabatic compressibility ( $\phi_k$ ) against the square root of the molal concentration of the solutes and extrapolation to zero molal concentration gives the limiting apparent molal adiabatic compressibility ( $\phi_k^0$ ) according to equation [93, 94]

$$\phi_k = \phi_k^0 + S_k^* \sqrt{m} \quad (100)$$

where  $S_k^*$  is the experimental slope.

The limiting apparent molal adiabatic compressibility ( $\phi_k^0$ ) 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 leads to decrease the compressibility of the solution [95, 96]. This is

## Theoretical Background

reflected by the negative values of  $\phi_k^0$  of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering that is induced by them in the water structure [95, 97].

The compressibility of hydrogen bonded structure, however, varies depending on the nature of the hydrogen bonding involved [95]. On the other hand, the poor fit of the solute molecules [98, 99] as well as the possibility of flexible H-bond formation appear to be responsible for causing a more compressible environment (and hence a positive  $\phi_k^0$  values have been reported in aqueous non electrolyte [99] and non-electrolyte-non electrolyte [101] solutions.

### 2.4. Refractive Index

The dimensionless optical property refractive index ( $n_D$ ) is very sensitive to changes in molecular organization of pure liquids, solutions and mixtures. The ratio of the speed of light in vacuum to that in another substance is defined as the refractive index ( $n_D$ ) of the substance, i.e.,

$$n_D = \frac{\text{Speed of light in vacuum}}{\text{Sped of light in the substance}} \quad (124)$$

The most significant works on refractive index were results of independent studies by Lorentz and Lorenz [102]. They deduced a theoretical relationship between refractive index ( $n_D$ ) and density ( $\rho$ ) of a substance as given by the relation:

$$R_s = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{1}{\rho} \quad (125)$$

where  $R_s$  stands for specific refraction. Accordingly, the molar refraction ( $R_M$ ) can be defined by multiplying both sides of equation (125) by molar mass ( $M$ ) of the substance and thus molar refractivity ( $R_M$ ) is given by:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\rho} \quad (126)$$

## Theoretical Background

However, for mixture molar refractivity ( $R_M$ ) can be obtained from the relation:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \sum_{i=1}^n \frac{x_i M_i}{\rho} \quad (127)$$

where  $x_i$  and  $M_i$  are the mole fraction and molecular weight of the  $i^{\text{th}}$  component in the mixture, respectively. Molar refraction is a fundamental property of a compound and it is apparently independent on the phase. Physically, it can be regarded as the actual or hard-core volume of a mole of substance, since the surrounding environment created by the solvent or the presences for other solutes does not significantly affect this quantity [103]. For most organic compounds, molar refraction can be estimated based on atomic refractions and refraction of bonds.<sup>120</sup> However, such information is very rare or even non-existent for many class of inorganic or organometallic solid substances or materials e.g., metal complexes. Hence equation (127) is undoubtedly very useful to determine molar refraction of a substance from a mixture or solution experiment. The applications of refractive index individually or combined with other properties, such as density and dielectric permittivity are abundant. The most frequent uses of refractive index and molar refraction data are to assess purity of a compound, to calculate the molecular electronic polarizability, to estimate liquid viscosity, to determine molecular structure and size [103], and to calculate the dipole moment of a molecule when combined with a relative permittivity measurement.

According to Marcus *et al.* [104] the apparent molar refractivity ( $R_D$ ) of a solute can be expressed as:

$$R_D = \frac{1000}{c} \left[ \frac{n_D^2 - 1}{n_D^2 + 2} - \frac{1}{\rho_1} \left( \rho - \frac{cM}{1000} \right) \frac{n_{D,1}^2 - 1}{n_{D,1}^2 + 2} \right] \quad (128)$$

where  $n_D$  and  $n_{D,1}$  are the refractive indices of the solution and solvent or solvent mixture, respectively and other symbols have their usual meanings. Again the molecular polarizability ( $\alpha_M$ ) [105], measures the ability of the molecular orbitals to be deformed under an electrical field and when the structure of a molecule becomes

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more complex, its electron cloud becomes more decentralized and thus the polarizability of the molecule increases. As  $R_D$  is directly proportional to the molecular polarizability [106], the increasing trend in  $R_D$  values indicates an overall increase in the molecular polarizabilities as expressed by the relation [104]:

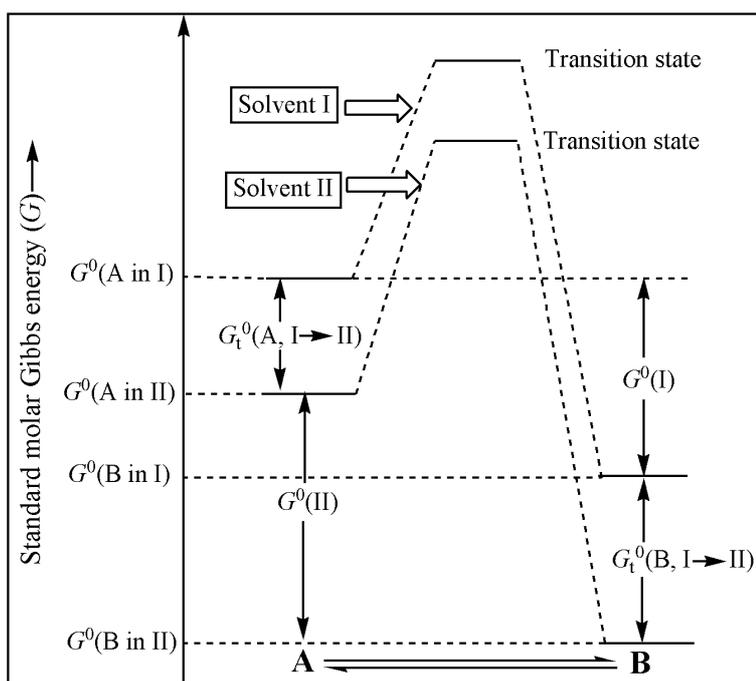
$$\alpha_M = \frac{3R_M}{4\pi N_A} \quad (129)$$

### 2.5. Solvent Effects on Reaction Rates

When reactants are dissolved, the standard molar Gibbs energy of solvation,  $\Delta G_{\text{solv}}^0$  is liberated due to the intermolecular interactions between solvent and solute. For the simple isomerization reaction  $A \leftrightarrow B$  in the solvents I and II with different solvation capacities to solvate A and B, the difference in the molar transfer Gibbs energies of reactant A and product B,  $\Delta\Delta G^0(I \rightarrow II)$  is given by [107],

$$\begin{aligned} \Delta G^0(\text{II}) - \Delta G^0(\text{I}) &= \Delta\Delta G^0(I \rightarrow II) \\ &= \Delta G_t^0(B, I \rightarrow II) - \Delta G_t^0(A, I \rightarrow II) \end{aligned} \quad (130)$$

This corresponds to the Gibbs energy diagram shown in figure 2.4. The difference in the molar transfer Gibbs energies of reactant A and product B,  $\Delta\Delta G^0(I \rightarrow II)$  determines the solvent effect on the position of this equilibrium.



**Fig. 2.4.** One-dimensional Gibbs energy diagram for an equilibrium reaction,  $A \leftrightarrow B$  in the solvents I and II.  $\Delta G^0(\text{I})$  and  $\Delta G^0(\text{II})$ : standard molar Gibbs energies of reaction in solvents I and II, respectively;  $\Delta G_t^0(A, I \rightarrow II)$  and  $\Delta G_t^0(B, I \rightarrow II)$ : standard molar Gibbs energies of transfer of the solutes A and B from solvent I to solvent II, respectively.

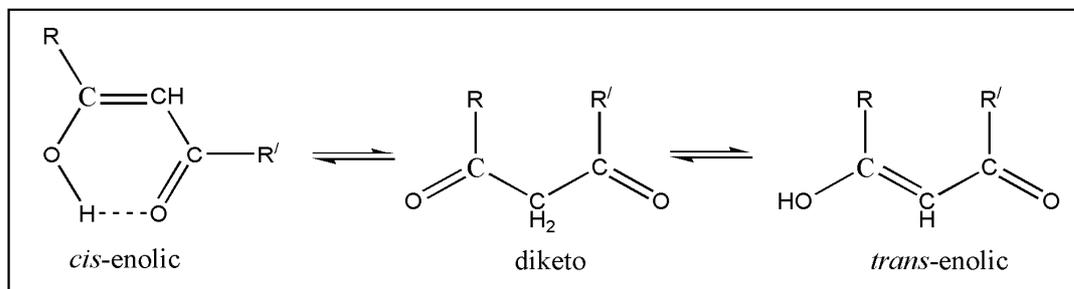
## Theoretical Background

As shown in figure 2.4 when  $\Delta G_t^0(\text{B}, \text{I} \rightarrow \text{II}) > \Delta G_t^0(\text{A}, \text{I} \rightarrow \text{II})$ , the equilibrium is displaced towards B on changing the solvent from I to II. The required standard molar Gibbs energies of transfer can be obtained from activity coefficients by using the equation (131):

$$\Delta G_t^0(\text{X}, \text{I} \rightarrow \text{II}) = -RT \ln(\gamma_{\text{I}}/\gamma_{\text{II}}) \quad (131)$$

where  $\gamma_{\text{I}}$  and  $\gamma_{\text{II}}$  refers to activity coefficients of solute X in solvents I and II. A quantitative description of the influence of the solvent on the position of chemical equilibria by means of physical or empirical parameters of solvent polarity is only possible in favorable and simple cases due to the complexity of intermolecular solute/solvent interactions. However, much progress has recently been made in theoretical calculations of solvation enthalpies of solutes that can participate as reaction partners in chemical equilibria. If the solvation enthalpies of all participants in a chemical equilibrium reaction carried out in solvents of different polarity are known, then the solvent influence on this equilibrium can be quantified [108].

In addition, the solvation capability or polarity of a solvent is not described by its relative permittivity alone. Besides the purely electrostatic Coulomb interactions, there exist other specific and unspecific interaction forces such as ion-dipole, dipole-dipole, hydrogen bonding, ion-pair formation, etc. For example, 1,3-dicarbonyl compounds can exist in three tautomeric forms as shown in figure 2.5 below:



**Fig. 2.5.** Three tautomeric forms of 1,3-dicarbonyl compounds.

Since open chain 1,3-dicarbonyl compounds rarely remain in the *trans*-enolic form and if this form is neglected, the above equilibrium is simply the keto-enol

## Theoretical Background

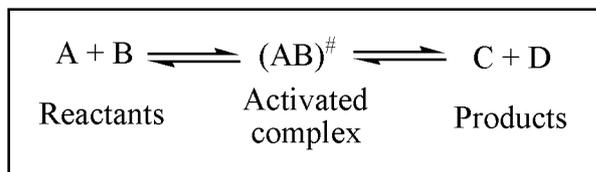
equilibrium. It has been found that increasing solvent polarity diminishes the enol content. The enol form is the least polar of the two tautomers because intramolecular hydrogen bonding reduces the dipole-dipole repulsion of the carbonyl groups and this is unreduced in the diketo form. Furthermore, the enol stabilization due to the intramolecular hydrogen bonding will be more pronounced when intermolecular hydrogen bonding with the solvent does not compete. Thus, a change to a more polar solvent with a tendency towards intermolecular hydrogen bonding (EPD solvents) is generally associated with a decline in enol content. In a nonpolar solvent, stronger solvation leads to a higher degree of order of the solvent molecules and hence to a decrease in the entropy. In contrast, polar solvent molecules show a high degree of order even in the absence of a dipolar solute. Such solvent effects can also be found for other tautomerisms, e.g. lactim/lactam, azo/hydrazone, ring/chain equilibria, etc [107].

The dependence of the reaction rate on the medium can be studied through two approaches: (i) comparison of the reaction rates in gas phase and in solution and (ii) comparison of the reaction rates in different solvents. Until recently only few reactions that occur in solution have been studied in gas phase [109] and hence approach (ii) is normally adopted. There are two ways in which solvents can affect the reaction rates of homogeneous chemical reactions: (i) through static or equilibrium solvent effects and (ii) through dynamic or frictional solvent effects [110-116]. The static effects of solvents on rate constants can be understood in terms of transition state theory. According to this theory, solvents can modify the Gibbs energy of activation by differential solvation of the reactants and the activated complex and consequently activation enthalpies, activation entropies and activation volumes are influenced. Reaction rates are very sensitive to barrier heights, e.g., a change of only 8.4 kJ/mol in an activation barrier can alter the reaction rate at room temperature by a factor of 31.

The Hughes-Ingold rules of solvent effects on reaction rates are based of equilibrium solvation of the activated complex. Solvents can also influence reaction rates through dynamic or frictional effects. For broad barrier reactions in strongly dipolar solvents, non-equilibrium solvation of the activated complex can occur and solvent reorientation may influence the reaction rate. In the extreme case, solvent

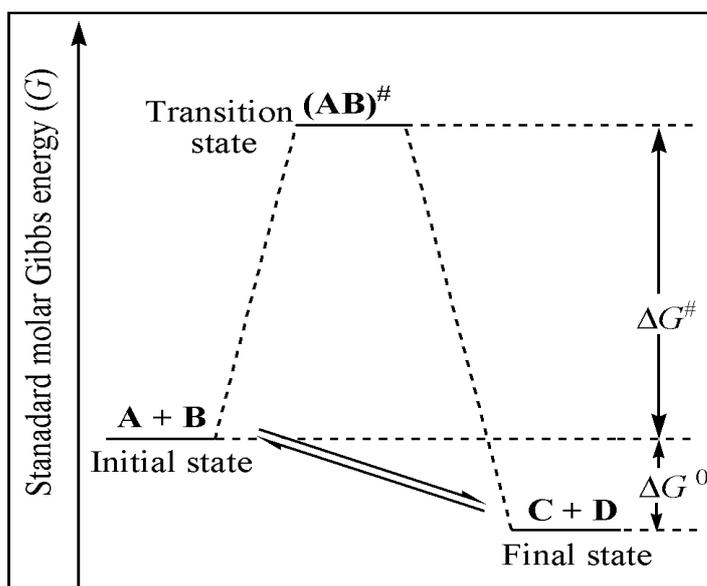
## Theoretical Background

reorientation becomes rate limiting and the transition state theory breaks down. In this situation, rate constants depend on the solvent dynamics and will vary with friction coupled with solvent's properties like density, internal pressure or viscosity. For a chemical reaction as shown in figure 2.6:



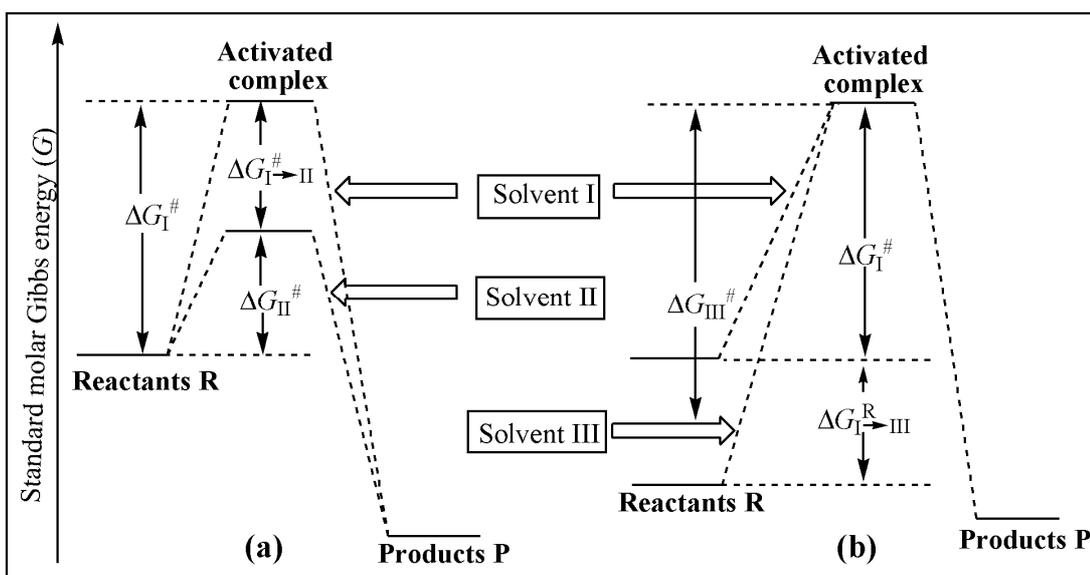
**Fig. 2.6.** Reactants A and B react through the activated complex  $(AB)^\ddagger$  to products C and D.

**Fig. 2.7.** One-dimensional Gibbs energy diagram for the above reaction in solution.  $\Delta G^0$ : standard molar Gibbs energies of reaction,  $\Delta G^\ddagger$ : standard molar Gibbs energies of activation for the reaction from the left to the right.



The influence of solvent on reaction rates is best treated with the transition state theory and its Gibbs energy diagram is shown in figure 2.7. The change in the Gibbs energy of activation in going from one solvent to another is evaluated as the relative modification in Gibbs energy by differential solvation of the reactants and the activated complex (shown in figure 2.8) and it is assumed that the reactants and the activated complex are in thermal equilibrium with the solvent.

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**Fig. 2.8.** One-dimensional Gibbs energy diagram for a chemical reaction in three different solvents I, II and III. (a) Reaction with non-solvated (solvent I) and solvated (solvent II) activated complex (preferential solvation of the activated complex); (b) Reaction with non-solvated (solvent I) and solvated (solvent II) reactants (preferential solvation of the reactants).  $\Delta G_I^\ddagger$ ,  $\Delta G_{II}^\ddagger$  and  $\Delta G_{III}^\ddagger$ : standard molar Gibbs energies of activation in solvents I, II and III, respectively.  $\Delta G_{I \rightarrow II}^\ddagger$  and  $\Delta G_{I \rightarrow III}^R$ : standard molar Gibbs energies of transfer of the activated complex and the reactants from solvent I to solvents II and III, respectively [117].

The smaller the  $\Delta G^\ddagger$  value, the greater is the reaction rate. The fastest reaction (with  $\Delta G^\ddagger = 0$ ) is given by  $RT/N_A h$  corresponding to the frequency for the passage of the activated complex through the transition state. At 298 K, this value is  $6 \times 10^{12} \text{ s}^{-1}$ , a typical value for the molecular vibrations. In principle, it is not sufficient to study only the change in  $\Delta G^\ddagger$ , because this term is related to an enthalpy and entropy terms ( $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ ); thus there are four types of reaction rate control: (i) cooperative effects when both  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  have same sign, (ii) enthalpy controlled reactions when  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  have opposite effects and  $\Delta H^\ddagger > T\Delta S^\ddagger$ , (iii) entropy controlled reactions when  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  have opposite effects and  $\Delta H^\ddagger < T\Delta S^\ddagger$ , and (iv) compensating effects when  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  have opposite effects but nearly equal. The solvation of the products, however, does not have any influence on the reaction rate. This is because the initial reactants and the activated complex are solvated usually to different extents and the difference between both Gibbs transfer energies determines the reaction rate in solution.

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### 2.6. Solvent Effects of UV-Visible Spectra of Solutions

When absorption spectra are measured in solvents of different polarity, the positions, intensities and shapes of the absorption bands usually gets modified by these solvents [118-121]. These changes are a result of intermolecular solute-solvent interactions forces such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc; all these forces alter the energy difference between the ground and excited state of the absorbing species. Theories of solvent effects on absorption spectra assume principally that the chemical states of the isolated and solvated chromophore-containing molecules are the same and treat these effects only as a physical perturbation of the relevant molecular states of the chromophores [122-124]. Thus, solvent effects on absorption spectra can provide information about solute solvent interactions [118-121] and can also provide information on primary solvation of solvated ion [125]. The solvent effect on spectra resulting from electronic transitions is primarily dependent on the chromospheres and the nature of the transitions. The electronic transitions of particular interest are  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  as well as charge-transfer absorptions. It has been established experimentally that only those molecules with  $\pi$ -electrons for which the charge distribution and consequently the dipole moment in the electronic ground state is different from that in the excited state exhibit pronounced solvatochromism. This term is used to describe the pronounced change in position of a UV-Visible absorption band that accompanies a change in the polarity of the solvent. A hypsochromic (or blue) shift with increasing solvent polarity is called negative solvatochromism and the corresponding bathochromic (or red) shift is termed as positive solvatochromism. Interestingly, solutions of pyridinium N-phenolate betaine dye are red coloured in methanol, violet in ethanol, blue in isoamyl alcohol, green in acetone and yellow in anisol; thus covering the whole visible range. This extraordinary large solvent induced shift of the visible  $\pi \rightarrow \pi^*$  absorption band of intra-molecular charge transfer character (from the phenolate to the pyridinium moiety) has been used to introduce an empirical solvent scale called  $E_T(30)$  [126-128]. Differential solvation of the highly dipolar, zwitterionic electronic ground state and the less dipolar first excited state leads to the large negative solvatochromism [129]. Usually long-wave length absorption band undergoes a bathochromic shift as the solvent polarity increases, if the excited state is

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more polar than the ground state and if the ground state is more polar than the excited state, hypsochromic shift occurs with increasing solvent polarity. For metal complexes of ligands with  $\pi$ -electron system two kinds of solvent-dependent charge transfer absorptions depending on the relative electron-donor/electron acceptor properties of the metal and ligand: (i) metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT). Strong solvatochromism for both types of charge transfer transitions were observed.

### 2.7. Theoretical Approach

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

There are mainly two theoretical approaches based on statistical mechanics of liquids to the calculation of the partial molar volume. One of them is the scaled particle theory (SPT) [130-132]. The SPT yields an approximate expression for free energy of cavity formation into a fluid. Hirata and Arakawa [133] obtained an analytical expression for the partial molar volume of cavity formation by taking the pressure derivative of the cavity formation free energy and succeeded in extracting the intrinsic volume of ions in aqueous solution. However, the SPT has two essential difficulties in its application to the systems of chemical and biochemical interest. First, the application of the original SPT is limited to spherical solute only. The other difficulty is with the SPT is its inefficiency in calculating the electrostatic effects on the partial molar volume. Irida, Nagayama, and Hirata [134] resolved the former problem by extending the theory to arbitrary shaped solutes. They succeeded in calculating the partial molar volume of molecular solutes by using the extended SPT [135]. However, the latter problem remains unresolved even though the combination with dielectric continuum models was proposed [136, 137]. The other approach is based on the Kirkwood-Buff (KB) solution theory [138]. In the KB theory, the partial molar volume of a solute is given by:

$$\phi_V^0 = k_B T \kappa_T - \int_0^\infty [g(r) - 1] 4\pi r^2 \partial r \quad (132)$$

where  $\kappa_T$  is the isothermal compressibility of solution,  $k_B$  is the Boltzman constant and  $g(r)$  is the radial distribution function between the solute and solvent. If the radial distribution function is obtained, the partial molar volume can be readily

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calculated through this equation. Molecular simulation may possibly give the radial distribution function. But attempts to combine the KB theory with molecular simulation are still limited to small molecules [139-141]. Another approach is to employ molecular liquid theories such as the reference hypernetted chain (RHNC) [142] and the reference interaction site model (RISM) [143]. The RHNC theory coupled with the KB theory was applied to the partial molar volume of ions in aqueous solution [144, 145]. With the KB theory, the RISM theory has succeeded in calculating and analyzing the partial molar volume for various molecular systems: ions [146, 147], hydrocarbons [148, 149] and biomolecules [150, 151] in aqueous solution as well as other non-aqueous solutions [152, 153]. Recently, the RISM theory was further developed to describe the three-dimensional spatial correlation functions of solvent around a solute molecule [154, 155]. The theory, called 3D-RISM theory, was also combined with the KB theory and was applied for the analysis of the partial molar volumes of bimolecular [156-163]. Thus, the RISM theory is the most successful method for investigating the partial molar volume and other thermodynamic properties in solution chemistry.

### 2.7.2. Solvation Models

There are essentially two methods [163]: the *ab initio* calculation and the semi-empirical CNDO-type approach. In the *ab initio* calculation, the difference in energy between a solvate and the separate constituents is determined as a function of the geometry, i.e., bond angles and bond length. Solvation energy is then maximized with respect to these parameters. The solvent molecules may be regarded as rigid spheres having the same geometry as in the free state. The calculation employs the self-consistent field version of molecular orbital theory to solve the Schrödinger equation for the solvate and for the constituents separately neglecting electron correlation. The main problem is the proper choice of the basis set of orbitals (Gaussian or Slater type). After all the difference in energy between a solvate and the separate constituents is obtained with minimum error and with a given basis set the full molecular Hamiltonian is used for the calculation. The semi-empirical calculations employ an approach suggested by Pople *et al.* [164] The approach involves complete neglect of differential overlap (CNDO) of the basis set of orbitals. With a given basis set of orbitals this decreases the number of integrals to be

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calculated. This version is called CNDO/2 and involves empirical parameters based on ionization potential and electron affinities in the Hamiltonian and the energy of the system is expressed as a sum of one-atom and two-atom terms.

In molecular dynamic (MD) approach, a limited number of ions and molecules and Newtonian mechanics of movement of all particles in solution is studied. This requires the knowledge of the intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last few decades witnessed some interesting trends in the development of solvation models and computer softwares. A. Galindo *et al.* [165, 166] have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibrium of electrolytic aqueous solutions. The water molecules are modeled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions. Good agreement with experimental data was found for a number of aqueous electrolyte solutions.

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