

CHAPTER II

Physico-Chemical Parameters Studied in Solution Chemistry

Solution chemistry is developed side by side with the growing of the fundamental chemistry. The alchemist's always try to find out universal solvent socalled "Alkahest". Chemists of the past era found the fundamental truth about the solvation, *i.e.* "like dissolves like".¹ Raoult in his study found systematically that freezing points and boiling point of any liquids are very much influenced by the presence of dissolved nonionic solute particle and he found that the vapour pressure depend on the mole fraction of solvent above the solution and is directly proportional to the mole fraction of pure solvent in solution which is familiar as Raoult's law.² In addition to this for electrolyte system Arrhenius's theory throw a light on the dissociation of ionic solutes into cations and anions in solution. Arrhenius established his theory on the basis of complete and incomplete dissociation takes place different type of electrolyte and by a comparing of the acquired results data from the calculation of osmotic pressure and specific conductivity of dilute electrolyte solutions.³ Except this many scientist of the solution chemistry feild share their valuable knowledge some of them are like Nernst ,Debye Huckel Ostwald, Lewis.¹

Solution chemistry is a significant branch of chemistry that deal with the alter in particular solution parameters. This will happen while different type solute is dissolved in a solvent or in a mixture of different solvent. This branch will provide the valuable information about physio-chemical behaviour of both the solvent and the solute depends on the solubility of the solute in the solvent or in solution. Most of the solution mixtures formed from solute and the sovent do not obey the Raoults law *i.e.* behave as non-ideal solution. This type deviation from ideality can be explain by using different types thermodynamic parameters. In case of liquid-liquid systems various excess or deviated properties helpful for giving explanation of the deviation from Raoults law. But for solid-liquid systems apparent or partial molar properties can be helpful for the explanation of the same. Molecular arrangements and interactions present in any solution can be better understood with the help of these thermodynamic parameters. Significantly it shows the interaction taking place between the solute-solute, solute-cosolute and solvent-solvent molecules in the solution. The exact molecular structure however for a solvent in solution certainly

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understood. The solvent structure gets reformed by the involving solute particle or an ion often to an certain extent that can also upset the solute molecules. The extent to which a solute or ion can get dissolute is depends on the degree of interactions amongst the solvent-solvent, solute-solute, solute-co solutes molecules or between the molecules if any present in the solution except solute and solvent molecule. Thermodynamic parameter enthalpy change and entropy changes, free energy change, *etc.*, accompanied with a specific physiochemical reaction are evaluated by using different physico-chemical techniques like viscometry, densitometry, ultrasonic interferometry, conductometry, refractometry, *etc.*,. Then the data of different analysis performed in physico-chemical process utilisable to explore the factors that attached with the solute-solvent or ion-solvent interactions. Some Spectroscopic technique like IR spectroscopy, NMR spectroscopy, UV-Visible spectroscopy are also showing their presence in this regard. Therefore, the present dissertation dedicated to research works on some biologically active compounds in various aqueous media to know their solution behaviour.

2.1. Density measurement

Density data of solute-solvent and solvent-solvent systems very much informative in order to predict the interaction present in the solution mixture. In addition to this some valuable information about the nature and degree of the molecular interactions in such mixture of solution can be examined from different volumetric properties. The volumetric information derived from density data as a mass function, excess volumes of mixing and volume and mole fraction. Some fundamental properties such as entropy, enthalpy, and Gibbs free energy, *etc.*, shows the macroscopic state as an average of various microscopic states of the system at a specific pressure and temperature. Proper explanation of these macroscopic properties through the molecular phenomena is found to be difficult. Sometimes higher derivatives of these properties found to explain more appropriately in terms of molecular interactions. Various type of molecular phenomena found in the solutions like micellization⁶, hydrophobic hydration,⁵ electrostriction,⁴ and co-sphere overlap during the solute-solvent interactions⁷ can be interpreted from their partial molar volumes of the various dissolved compound.

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2.1.1. Partial Molar Volumes calculation

It is well-known from the phase rule: $F = C - P + 2$. For a one component and single phase system, $F = 2$. This suggests that at least two properties of a 'single phase one component' required to define its state. These parameters are generally atmospheric pressure and temperature. These variables can be easily guided or manipulated. The solution thermodynamic concern about the influence by the knowledge of partial properties that suggest in order to calculate each components effect and their concentration on thermodynamic state properties like entropy, volume, enthalpy, Gibb's free energy, *etc.* These all are extensive properties which depend upon the mass or the no of mole of solute present in the solution. These parameters being a state dependent function in a closed system, depending upon any two of the state variables, *viz.*, atmospheric pressure, temperature and volume of a system of definite composition. But in case of open system of variable composition (*e.g.*, liquid system) that contains two or even more components and the exchange of matter occurs with its surroundings gone through a change in composition (number of moles). So, the total extensive property is not considered only as a function of pressure and temperature but also as the actual number of mole of each component present in the system. Hence for a multi-component system a thermodynamic state function (Y) can be shown as follows:^{8,9}

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

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

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

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

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

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

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

In the molecular level, the solute-solvent interaction or solvation has little bit affect on partial molar volume, like the partial molar volume of Li^+ ion is found to be negative and such unexpected negative value of volume is a proof of presence of electrostriction in the solution,¹⁰ *i.e.*, strong electrostatic interaction takes place between Li^+ ion and the water molecules. Therefore, the partial molar volume give valuable informative data about the solute-solvent interactions takes place in the solution. The partial molar quantities are additive and integration of Eq. (4) yields:

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

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

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

where $V_{m,1}^*$ and $V_{m,2}^*$ are the molar volumes of components 1 and 2, respectively. In case of ideal solutions, the partial molar volume of each substance is same as their respective molar volumes. However, in case of non-ideal solutions the existence of the second component (*i.e.* solute) affect value of the molar volume of the first component and *vice versa*, *i.e.*, $\bar{V}_{m,1} \neq V_{m,1}^*$ and $\bar{V}_{m,2} \neq V_{m,2}^*$. So for non-ideal mixtures total volumes are either decreases *i.e.* volumetric contraction takes place or increases *i.e.* volumetric inflation takes place than that for the ideal solution. This implies that partial molar volumes of the components do not equal to their molar volumes but can change with the composition of the mixture due to change in the molecular surrounding environment by packing or salvation of each molecule. This is shown below in Figure 2.1 for water-ethanol system¹¹ at 20 °C at the overall composition range.

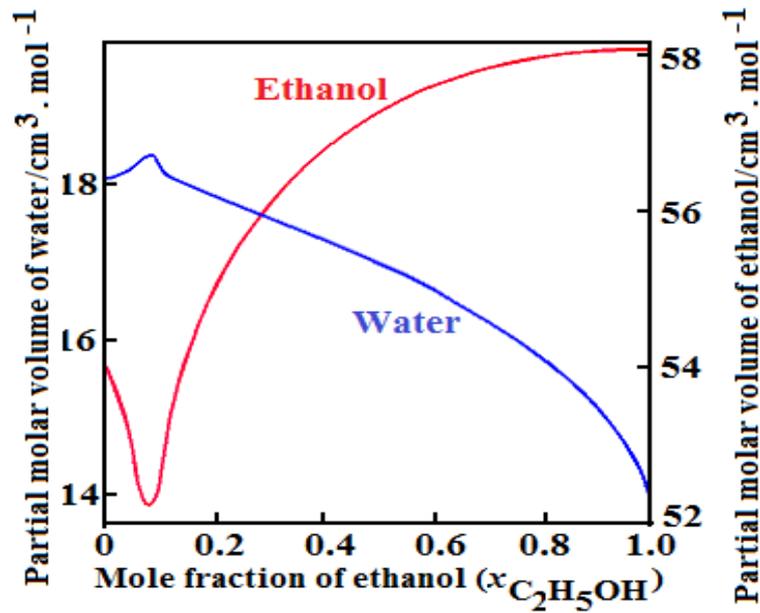


Fig 2.1. Partial molar volumes of ethanol and water in aqueous ethanol at 20 °C.

2.1.2. Apparent Molar Volume calculation

Partial molar volume evaluated carefully by calculating the solution densities of known concentrations. Apparent molar volume (ϕ_V) can be determine from the density data. It is the changes volume of the solution due to addition of the solute per mole.

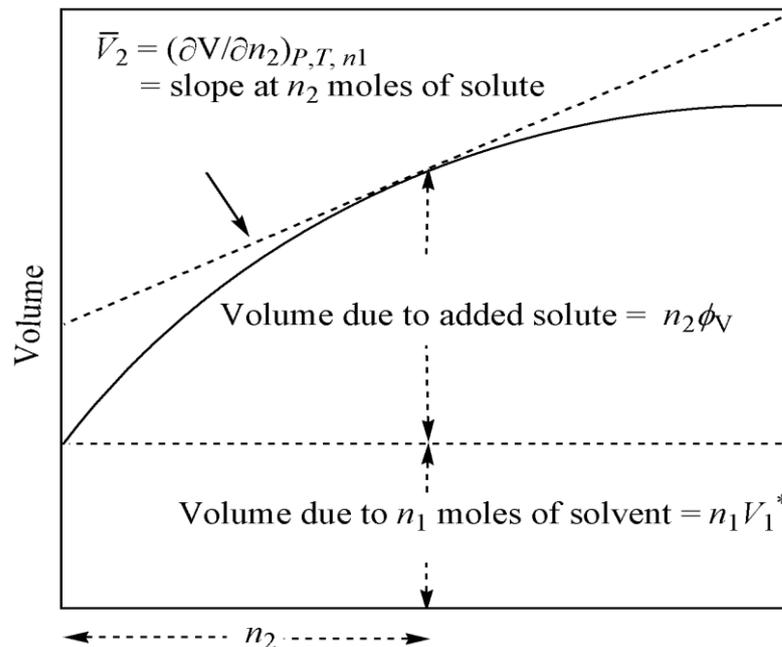


Fig 2.2. Relationship among the total solution volume, pure solvent volume and the apparent molar volume (ϕ_V) of the solute.

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From **Figure 2.2** it can be realized that with the addition of n_2 moles of a solute to a solution containing a fixed n_1 moles of a solvent, the volume of the solution changes and the apparent molar volume (ϕ_V) is shown below,

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

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

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

Since the number of moles of both the solute and solvent can't remain fixed simultaneously throughout the process, it does not have any importance to define the apparent molar volume of the solvent. The apparent molar volume of the solute and solvent can give the idea of the partial molar volumes of both the solute and solvent. Partial differentiation of Eq. (8) with respect to n_2 at constant n_1 provides the partial molar volume of the solute,

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

When determining the apparent molar volume (ϕ_V) from experimental data it is better to use the molarity scale (c) for the solute concentration⁴ and densities (ρ). The apparent molar volumes (ϕ_V) of solutes can be had from the following relation:⁴

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

where ρ_1 and ρ denote the densities of solvent and solution, respectively and M denotes the molecular weight of the solute. If concentrations are expressed in molalities (m) of the solute, Eq. (10) converts into the following expression:⁴

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

In order to extrapolate the apparent molar volume of an electrolyte or a solute at infinite dilution four major equations, *viz.*, the Masson equation,¹² Owen-Brinkley equation¹⁴ the Redlich-Meyer equation,¹³ and the Pitzer equation¹⁵ are taken into consideration. In the Masson equation the apparent molar volume of electrolytes or ionic solutes (ϕ_V) follows a linear relation with the square root of the solute molalities (c) as given below:

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

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where ϕ_V^0 represents the apparent molar volume at infinite dilution or standard partial molar volume (equal to the partial molar volume at infinite dilution, \bar{V}_2^0) and S_V^* is the slope of the linear fit. Eq. (12) has been used for a majority of ϕ_V data in aqueous medium¹⁶ and nearly all ϕ_V data in non-aqueous¹⁷⁻²¹ solvents. But according to Redlich and Meyer,¹³ Eq. (12) is a limiting law and for a specific solvent and temperature, the slope S_V^* should depend on the valence type. They suggested the following expression for deducing ϕ_V :

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

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

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

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

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

where β indicate the compressibility factor of the solvent. However, the variation of dielectric constant (ϵ_r) with pressure is remain unclear, even in water, to determine the theoretical limiting slope (A_V) accurately. Redlich-Meyer¹³ equation adequately shows that the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However it represents disagreement when applied for some 2:1, 3:1 and 4:1 electrolytes.²²⁻²⁴ Actually, the volume provide to a solvent by the addition of 1 mole of an solute(ion) is very tough to determine. The reason for it is that when ion enter into the solvent the ion may disintegrate the solvent structure and thereby alter the volume of the solution and the compression of the solvent under the influence of the ion's electric field is called electrostriction.²⁵ It is very common event that may found whenever the electric fields is present in the order of 10^9 - 10^{10} V m⁻¹. But for polyvalent electrolytes, the Owen-Brinkley¹⁴ equation is more precise for such extrapolation and to satisfactorily shown the concentration dependency of ϕ_V . The Owen-Brinkley equation includes the ion-size parameter (a) and is represented by:

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

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where the symbols have their usual significance.¹⁴ Pogue and Atkinson²⁶ used the Pitzer formalism to fit the apparent molar volumes. The Pitzer equation for the apparent molal volume of a single salt $M_{\nu_M} X_{\nu_X}$ is given by:

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

where

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

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

$$\nu = \nu_M + \nu_X \quad (21)$$

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

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

and other symbols have their usual significance.²⁶

2.1.3. Ionic Partial Molar Volume

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

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

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

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

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where $\phi_{V,\text{int}}^0$ = intrinsic volume of the ion and ΔV = volume change of the system due to ion-solvent interactions. Some other pioneer²⁹ supposed the anion solvation to be nullified for the electrolyte solutions and suggested the solvation number at infinite dilution to be associated with the extent of the cation solvation. Therefore, Eq. (25) represented as:

$$\phi_{V,\text{ion}}^0 = \phi_{V,\text{int}}^0(\text{R}_4\text{N}^+) + \Delta V \quad (26)$$

and the term $\phi_{V,\text{int}}^0(\text{R}_4\text{N}^+)$ can be had from the following relation:³⁰

$$\phi_{V,\text{int}}^0(\text{R}_4\text{N}^+) = 2.52r_{\text{R}_4\text{N}^+}^3 \quad (27)$$

where $r_{\text{R}_4\text{N}^+}$ is the crystallographic radii of the R_4N^+ ion. Uosaki *et al.*³¹ used this approach for separating $\phi_{V,\text{R}_4\text{NX}}^0$ values into ionic contributions in organic electrolyte solutions. Krungalz³⁰ also applied the same method for a large set of partial molar volume data for non-aqueous electrolyte solutions. Based on Frank and Wen model,³² Millero³³ has given the relation for the standard partial molar volume ($\phi_{V,\text{ion}}^0$) of an ion:

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

where $\phi_{V,\text{elect}}^0$ is the partial molar volume due to electrostriction, $\phi_{V,\text{disord}}^0$ is the partial molar volume due to void space and $\phi_{V,\text{caged}}^0$ is the caged partial molar volume for the caged water structure around ions. Although it is difficult to determine the various contributions to $\phi_{V,\text{ion}}^0$, Millero³³ has examined $\phi_{V,\text{ion}}^0$ values in water and methanol using the relations relations:³⁴

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

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

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

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

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where ε_r = dielectric constant of the solvent and B''' = solvent dependent constant. Other symbols have their usual significance.³⁵ There is strong competition between ion and the solvent molecules for highly ordered solvents in order to increase the order. There will be a torque like situation arise where ions attempts to orient solvent molecules around themselves, whereas the solvent molecules try to keep the highly ordered bulk structure. Thus, a relatively large agitating region surround the solvated ions is produce that resulting into large values for $\phi_{V,\text{disord}}^0$ and S_{ion}^0 called partial molar entropy of the ion. In case of less structured solvents, the solvent molecules are get affected by ion-solvent interactions that results in to a smaller voids space around the ion with smaller $\phi_{V,\text{disord}}^0$, negative $\phi_{V,\text{elect}}^0$ and S_{ion}^0 values. Hence the degree of the solvent structure and the dielectric constant of the solvent have playing a crucial role for ion-solvent interactions.

2.1.4. Standard Partial Molar Volume of Transfer

Partial molar volume of solutes at infinite dilution can be employed to discover the solute (or ion)-solvent and solvent–solvent interactions in various solvent systems.^{16,30,36,37} Transfer volume ($\Delta_t \phi_V^0$) is defined as the difference between the partial molar volumes of the solute in a particular solvent from that in a reference solvent present at infinite dilution. So $\Delta_t \phi_V^0$ is given by:

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

The above equation shows the degrees and nature of solute-solvent or ion-solvent and solute-cosolute interactions, since at infinite dilution the solute-solute or ion-ion interactions are assumed to be negligible. Franks *et al.*³⁸ suggested that the partial molar volume of a non-electrolyte can be represented by a combination of it's intrinsic volume ($\phi_{V,\text{int}}^0$) and the volume ($\phi_{V,\text{solv}}^0$) for its interactions with the solvent. The intrinsic volume ($\phi_{V,\text{int}}^0$) is a sum of two types of contributions, *i.e.*, $\phi_{V,\text{int}}^0 = \phi_{V,\text{vw}} + \phi_{V,\text{void}}$; where $\phi_{V,\text{vw}}$ and $\phi_{V,\text{void}}$ denote the van der Waals volume and voids in the solution, respectively. According to Shahidi *et al.*³⁹ the intrinsic volume ($\phi_{V,\text{int}}^0$) of a non-electrolyte solute in solution is given by:

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

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

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

Generally $\phi_{V,\text{vw}}$ and $\phi_{V,\text{void}}$ are assumed⁴⁰ to have same magnitude in water and in mixed solvent for the same type of solutes. Thus, $\phi_{V,\text{int}}^0$ depends on $\phi_{V,\text{shrinkage}}^0$, that is actually caused by the electrostriction in the solution. In this regard the cosphere overlap model^{41,42} helps to analyze $\Delta_t\phi_V^0$ values in terms of solute-cosolute interactions. According to this model behaviour of water molecules in the hydration cosphere depend on the nature of the solute molecules present in the aqueous media. During the time of cosphere overlapping, when two solute particles come close enough so that their cospheres overlap, some of the molecules in the cosphere are override and thus the thermodynamic parameter of the solution may change. There are various types of interactions are taking place: (i) polar-ionic and polar-polar group interactions (*e.g.*, ion-dipole, ion-quadrupole, ion-induced dipole interactions), (ii) polar-non-polar and non-polar-non-polar group interactions (*e.g.*, hydrophobic-hydrophilic interactions, hydrophobic-hydrophobic interactions), *etc.*, depending on the nature of the solvent and solute. Interactions of type (i) contribute positive values to transfer volumes ($\Delta_t\phi_V^0$), while the interactions of types (ii) and (iii) contribute negative values to transfer volumes ($\Delta_t\phi_V^0$). The overlap of hydration cospheres of charged species results into decrease in the electrostriction of the solute that leading to a lowering in $\phi_{V,\text{shrinkage}}^0$ and thus positive $\Delta_t\phi_V^0$ values obtained.⁴¹ Kozak *et al.*⁴³ suggest a theory based on the McMillan-Mayer theory of solutions that allow the formal separation of the various type of effects due to pair-wise interactions of solute molecules as well as those due to interactions amongst three or more solvent molecules. Friedman and Krishnan⁴⁴ as well as Franks and Evans³⁸ interpret this consideration to incorporate the solute-cosolute interactions in the solvation sphere. Thus the transfer volume ($\Delta_t\phi_V^0$) is given by:

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

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

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

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

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

Once $\Delta_t \phi_V^0(\text{Ph}_4\text{As}^+)$ or $\Delta_t \phi_V^0(\text{BPh}_4^-)$ has been determined, other single ion transfer volumes can be obtained from the transfer volume of the electrolyte. Conway⁴⁶ expressed the partial molar volume of an ion at infinite dilution as follows:

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

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

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

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

2.1.5. Apparent Molar Expansibility

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

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

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where α and α_1 are the thermal expansion coefficients of the solution and the solvent, respectively; *i.e.*, $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$. The apparent molar expansibility (ϕ_E) can be determined using the densities and their temperature coefficients as follows:

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

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

2.1.6. Standard Partial Molar Expansibility

The standard partial molar expansibilities (ϕ_E^0) is represented by the following equation:⁴

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

where solute concentrations are given in molalities (m), Eq. (43) becomes:

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

and the value $(\partial\phi_E^0/\partial T)_P$ is obtained from the slope while ϕ_E^0 values are plotted linearly regressed against the experimental temperatures (T). Further, the temperature dependence of ϕ_V^0 for numerous solutes can be represent by :

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (45)$$

where a_0 , a_1 and a_2 denotes the regression coefficients for the solute and T is the absolute temperature for a given solution. Eq. (45) when differentiated with respect to T at constant pressure P results into the partial molar expansibilities (ϕ_E^0) of the solute present in the mixture:

$$\phi_E^0 = (\partial\phi_V^0/\partial T)_P = a_1 + 2a_2T \quad (46)$$

The partial molar heat capacities of electrolytes found to be are negative and the fact that $(\partial C_P^0/\partial P)_T$ should be positive for the structure breaking solutes/electrolytes according to structural model⁴⁷ yields the following thermodynamic equation:

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

Therefore the structure breaking solutes have negative $(\partial^2\phi_V^0/\partial T^2)_P$ values. Similarly the structure-making solutes should have positive $(\partial^2\phi_V^0/\partial T^2)_P$ values. According to

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Hepler⁴⁷ the sign of $(\partial\phi_E^0/\partial T)_P$ represents the long-range structure-making and breaking capacity of the electrolytes or solutes in various solvent systems. The general thermodynamic expression for $(\partial\phi_E^0/\partial T)_P$ is as follows:

$$(\partial\phi_E^0/\partial T)_P = (\partial^2\phi_V^0/\partial T^2)_P = 2\alpha_2 \quad (48)$$

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

2.1.7. Ionic Partial Molar Expansibility

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

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

where $\phi_{E,+}^0$ and $\phi_{E,-}^0$ are the partial molar expansibility of the cation and anion, respectively. Similar to $\phi_{V,\text{ion}}^0$, $\phi_{E,\text{ion}}^0$ can be turned into various contributions as per Frank and Wen model³³ for the hydration of ions:

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

Here the intrinsic expansibility ($\phi_{E,\text{int}}^0$) is represents volume change due to expansion of the ion and it negligible for monovalent ions. This term in Eq. (50) incorporates the expansibility of covalent bonds in the ions with hydrocarbon part. The electrostriction expansibility ($\phi_{E,\text{elect}}^0$) is accompanied with the alter in volume due to electrostriction. This value is negative and proportional to z^2/r ; where z = charge of the ion and r = crystal radius of the ion. The untidy expansibility ($\phi_{E,\text{disord}}^0$) is due to alter in a disarranged region and it is found to dissimilar for cations and anions of same size but dissimilar in orientation of water molecules around them in the vicinity of first electrostricted zone. This factor depends on the T and magnitude of z^2/r . Hence for the ions with a high electrostricted zone (*i.e.*, large z^2/r), the disordered zone is very small or even not exist. Even so but for ions with a little electrostricted region (*i.e.*, small z^2/r), the disordered zone has an impactful contribution. The caged expansion

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($\phi_{E,caged}^0$) is due to the alter in highly structured water surround the hydrocarbon part of an ion. The value of it is positive and it's magnitude rises with the size of the hydrocarbon part of the ion.

2.1.8. Apparent specific volumes and taste quality

Taste sensor bud present in our tongue have a relationship with solute in presence of a cosolute in a solution and can be expressed from the apparent specific volumes (ϕ_{ASV}). It can be used to understand the difference between the four basic tastes: salty, sour, sweet and bitter. It shows the extent of bonding compatibility of a solute present in the water structure and can be obtained from apparent molar volumes (ϕ_V) at the experimental temperatures using the relation:

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

Apparent specific volume provide an knowledge about its relation with taste quality which in the order of salty < sour < sweet < bitter.⁴⁸⁻⁵⁰ The human taste bud have range lies with apparent specific volumes (ϕ_{Vsp}) between 0.1 and 0.95 cm³. g⁻¹; for salty the range is $\phi_{Vsp} < 0.33$ cm³. g⁻¹, for sour the range is $\phi_{Vsp} = 0.33-0.52$ cm³. g⁻¹, for sweet the range is $\phi_{Vsp} = 0.52-0.71$ cm³. g⁻¹ and for bitter the range is $\phi_{Vsp} = 0.71-0.93$ cm³.g⁻¹).⁵¹ When the degree of solute-solvent interaction is found to be large, the solute molecules reach easily the taste receptors present much deeper in the lingual epithelium. Thus solvation or hydration of solutes can be useful to understand the particular solute tastes phenomena characteristically bitter or salty, sour, *etc.*

2.2. Viscosity

Viscosity is another important non-thermodynamic transport property of liquid that shows the force needed to produce unit shear rate between two layers of the molecules separated by unit distance. It important tool for the measuring the solute-solvent or ion-solvent interactions. Viscosities of an electrolytic solution will give us noticeable information about the solute-solvent or ion-solvent interactions and also the structural behaviour of the electrolytic solutions.

2.2.1. Viscosity of Electrolyte Solution

The viscosity equations for electrolytic solutions are much complicated, since numerous type of interactions like ion-ion and ion-solvent interactions are found in

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the solution and differentiate between these two forces is really a hard task. Since viscosity is attached with the friction between adjacent, relatively moving parallel planes of the liquid, anything which influence the interaction between these planes will shows collateral effect on the viscosity. In general large spheres when placed in the liquid, the planes will be pile up together and viscosity will rises. In the same way if the hydrogen bonding takes place in between the planes, it will rises the friction between two planes and this will impact overall rise in viscosity. An ion having large rigid co-sphere will also behave like a rigid sphere and it can rises the inter-planar friction. In the same way, ion can rises the extent of hydrogen bonding between the nearest solvent molecules and that will rises the viscosity. On the other hand, ions that try to destroy above-mentioned effect will lower down the viscosity value. Jones and Dole propound an empirical equation to relate between the relative viscosities of the electrolytes present in the solution with molar concentrations⁵² (c):

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

By rearranging the equation can be written as:

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

Here the coefficients A and B denotes the ion-ion and ion-solvent interactions. Eq. (53) is universally applicable for aqueous and non-aqueous solutions mixture with minimum ionic association. The term $A\sqrt{c}$ in Eq. (52) denote Grüneisen effect (*i.e.*, the long-range coulombic forces between the ions) can be expressed as Debye-Hückel theory⁵³ of inter-ionic attractions. The ion-ion interaction coefficient A can be measured from interionic attraction theory^{54,55} by the Falkenhagen Vernon⁵⁵ equation:

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

where Λ_0 , λ_+^0 and λ_-^0 are the limiting molar conductances of the electrolyte as a whole and its cation and anion, respectively; other symbols have their usual significance. When the A -coefficients obtained by fitting η_r values to Eq. (53) for aqueous solutions⁵⁶ were compared with the values derived from Eq. (54), are found to good agreement with each other. But the accuracy was fond to be very poor with partially aqueous solutions.⁵⁷ Crudden *et al.*⁵⁸ Suggested that if association of the ions happened to produce an ion pair, the viscosity must be measured by the equation:

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

where A , B_i and B_p are the constants and α_{IP} is the extent of dissociation of ion pair of the electrolyte. Thus an extrapolation of the $(\eta_r - 1 - A\sqrt{\alpha_{IP}c})/\alpha_{IP}c$ versus $(1 - \alpha_{IP})/\alpha_{IP}$ plot to $(1 - \alpha_{IP})/\alpha_{IP} = 0$ results the intercept B_i . However for the most of the electrolytic solutions both in aqueous and non-aqueous media, the Eq. (53) is valid up to 0.1 (M)^{4, 59, 60} within experimental errors. However, for higher concentrations the modified Jones-Dole equation, with an additional coefficient D was originally used by Kaminsky, is used⁶¹:

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

The significance of the coefficient D is not always meaningful and therefore, Eq. (53) is the most popular. The A -coefficients, obtained from the $(\eta/\eta_1 - 1)/\sqrt{c}$ versus \sqrt{c} plots for the electrolytes, are found to be somewhat negative, scattered and distracted from linearity.^{4, 62, 63} In these cases the coefficients A determined by Eq. (54). In accordance with the inter-ionic attraction theory of the electrolytes the ions try to construct and regulate a space lattice structure in solution and that hindered any influence or force that tend to disturb this space lattice structure; hence the inter-ionic forces try to congeal or rises the viscosity of the solution mixture. Thus the A -coefficient expected to might have a negative value for all type of strong electrolytes and a value of zero for non-electrolytes.⁵² The value of B -coefficient may have any of positive or negative value. The influence of solute size on the B -coefficient is realized from hydrodynamic theories applied to particles in a fluid persistence. While probing between the solute and solvent happened, the steric effect may lead to the B -coefficient and thus B -coefficient is very much sensitive towards the “rigidity” or “flexibility” of the solute. So the B -coefficient is measured from the solute or ion size and the behavior of the solvent. The viscosity coefficient B are calculated from the slopes of the straight lines by using the least square method and intercepts represents the magnitude of A . The factors that govern the viscosity coefficient B - are as follows: ^{64, 65}(i) solvation of ions and the exertion of the field of the ion create long-range order in solvent molecules and thereby increases η or B -values, (ii) By destroying the three dimensional bulk structure of the solvent molecules that lowers η

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values,(iii) high molar volume and low dielectric constant results into high B -values for the same type of solvents and (iv) high molar volume solvents or weak solvation of any of the ion of the binary electrolyte system results into steric hindrance of the primary solvation of ions causing lowers the B -values.

Water is a structured solvent and like it others solvent having a solute with or without a primary solvation shell can impart recognizable influence on the extent of ‘structure’ of the solvent molecules at relatively longer distances. A ‘structure-making’ solute can minimize the mean effective temperature of the solvent molecules. So it increases the viscosity of the solution mixture and which results into a high B -coefficient values. Due to the exponential relationship between temperature and viscosity, a increase in temperature of the solution may results into fall of B -coefficients. This fall is found to be more at lower temperature than at high temperatures.⁵⁹ This behavior can be utilise to detect the ‘structure-making’ solutes.⁶⁶ However, ‘structure-breaking’ solutes possesses low B -coefficients that may rises with increase in temperatures.⁵⁴ If it is obtained that solvation minimizes with rising in temperature, the B -coefficient of a solvated species also minimize and hence both structure making and primary salvation should have more B -coefficient at low temperature and the derivative with respect to temperature i.e $\partial B/\partial T$ give negative values.

2.2.2. Ionic Viscosity B -Coefficients

The viscosity B -coefficients of ionic compound is somewhat different from the nonionic compound, so it can measured based on some additional thermodynamic theory. The methods that can use for differentiating the viscosity B -coefficients in the ionic contributions:

(1) Cox and Wolfenden consider that B_{ion} values of Li^+ and IO_3^- in LiIO_3 are proportional to their respective ionic volumes⁶⁷, that are again proportional to the third power of the individual ionic motilities. Gurney⁴¹ and Kaminsky⁶¹ are propped that:

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

This can explained on the regards that the B -coefficients for KCl is lower and that the mobilities of K^+ and Cl^- are same type though out the temperature range 15-45 °C. This theory is supported by other thermodynamic parameters.

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(2) The Desnoyers and Perron method⁶⁸ another type of method that consider the Et_4N^+ ion in water is nearest to be neither structure breaker nor a structure maker. They proposed that the application of the Einstein's equation⁶⁹ with a higher extent of accuracy:

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

and with an precise value of the partial molar volume ($\phi_{V, \text{ion}}^0$) of the ion, it is very much easier to measure a value of 0.359 for $B_{\text{Et}_4\text{N}^+}$ in water at 25 °C. Sacco *et al.*⁷⁰ put forward that the “reference electrolytic” method for the differentiation of the B -values, *e.g.*, for tetraphenyl phosphonium tetraphenyl borate (Ph_4PBPh_4) in water:

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

Since As Ph_4PBPh_4 is sparingly soluble in water, $B_{\text{Ph}_4\text{PBPh}_4}$ represents as:

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

The benchmark to adopt for the differentiating of the viscosity B -coefficients in non-aqueous solvents separated from those used for aqueous solutions, Although these methods^{63, 64, 71, 72} are based on the similarity of the equivalent conductance of the counter ions at zero dilution.

According to Krumgalz^{73, 74} the method useful for the separation of the B -coefficients into ionic components is based on the fact that the large. Hence the ionic viscosity B -values for large tetraalkylammonium ions, R_4N^+ (where $\text{R} > \text{Bu}$) in organic solvents, are proportional to their ionic dimensions, *i. e.*,

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

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

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

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

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using the radii of the tetraalkylammonium ions ($r_{R_4N^+}^3$ and $r_{R_4N^+}^3$) obtained from the conductance measurement.⁷⁷

Gill and Sharma⁷⁸ used Bu_4NBPh_4 as a reference electrolyte. The method of resolution is based on the consideration that Bu_4N^+ and Ph_4B^- ions with big size R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are remain fixed. The ionic radii of Bu_4N^+ (5.00Å) and Ph_4B^- (5.35 Å) were remain fixed in different non-aqueous and mixed non-aqueous solvents used by Gill and co-workers. They given the following equations:

$$B_{Ph_4B^-} / B_{Bu_4N^+} = r_{Ph_4B^-}^3 / r_{Bu_4N^+}^3 = (5.35/5.00)^3 \quad (64)$$

$$\text{and, } B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (65)$$

The method need only the B -values of Bu_4NBPh_4 and is applicable in the same way to non-aqueous solvents. The B -ion values measured from this method quite agree with those shown by Lawrence *et al.*⁷⁰ in various organic solvents using the consideration as given below:

$$B_{[(i-Am)_3 BuN^+]} = B_{Ph_4B^-} = 1/2 B_{[(i-Am)_3 BuNPh_4B]} \quad (66)$$

Lawrence *et al.*⁷⁰ utilise tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) as ‘reference electrolyte’ since the cation and anion are similar in shape and have nearly same van der Waals volumes. Thus,

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

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

A same type differentiation can be created for Ph_4PBPh_4 system and Lawrence *et al.*⁷⁰ done the viscosity measurements of tetraalkylammonium bromides (from Pr to Hept.) in DMSO and HMPT. The B -coefficients, $B_{R_4NBr} = B_{Br^-} + a[f(r_{R_4N^+})]$, were plotted against van der Waals volumes. The B_{Br^-} values thus calculated and were compared with the precisely measured B_{Br^-} value by using Bu_4NBBu_4 and Ph_4PBPh_4 as ‘reference electrolyte’. They stated that the ‘reference electrolyte’ method is one of the best obtainable method for division into ionic contributions. However, all these methods are based on certain approximations and anomalous results may arise except the proper mathematical theory is developed to calculate B -values.

2.2.3. Viscosity B – Coefficients and it relations with temperature

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A fixed nature of B_{\pm} and $\partial B_{\pm}/\partial T$ has been found in both aqueous and non-aqueous solvents. This is depicted by Kaminsky.⁷⁹ He found that (i) In periodic table within a group the B -ion values decrease with the increase in the radius of the ion, and (ii) the temperature co-efficient of B_{ion} values while rises with the increase the ionic radius along down the group. In summary of result, it shows:

For structure breaking ions-

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

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

For structure making ions-

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

When water molecules around an ion forming a solvent shell, the behavior of the solvent in the solvation layer may be deviate from those found in the bulk structure. Gurney,⁴¹ in his 'Co-sphere' model of A, B, C zones of Frank and Wen³² and hydrated radius of Nightingale clearly explain this property.⁸⁰ The viscosity of a dilute electrolyte solution measured from the summative value of viscosity of the solvent (η_1) with the the viscosity alteration obtaining from the contesting between numerous effects happening in the ionic background. So the Jones-Dole equation becomes redefined as,

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

Where η^* , the positive rise in viscosity is results from a columbic interaction. The viscosity B -coefficient then can be elucidate in terms of the competitive viscosity effects. According to the following Stokes, Mills and Krumgalz⁷³ the B_{ion} is represented by:

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

whereas Lawrence and Sacco suggested the following:⁷⁰

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

$B_{\text{ion}}^{\text{Einst}}$ is the positive enhancement arising due to the hindrance in the viscous flow of the solvent which caused by the shape and size of the ions (the term corresponds to η^E or B_{shape}). $B_{\text{ion}}^{\text{Orient}}$ is the positive enhancement evolving from the alignment or the structure making action of the electrostatic region of the ion on the dipoles of the solvent molecules (the term corresponds to η^A or B_{ord}). $B_{\text{ion}}^{\text{Str}}$ is the negative

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enhancement which shows the disrupter of the solvent structure in the vicinity of the ionic co-sphere evolving from the opposing inclination of the ion to orientate the molecules around itself centro symmetrically and solvent to retain its self structure (this are correlate with η^D or B_{disord}). B_{disord} is showing positive enhancement govern by the effect of ‘reinforcement of the water structure’ by large tetraalkylammonium ions (R_4N^+) which due to hydrophobic hydration. The event is built-in the intrinsic water structure but it is not found in organic solvents. B_w and B_{solv} represents for viscosity rising and contributing towards the van der Waals volume and the solvated ion’s volume. Hence, a tiny and highly charged cations such as Li^+ and Mg^{2+} produce a strongly adjoin primary solvation shell surrounding these ions ($B_{\text{ion}}^{\text{Einst}}$ or η^E positive). At the normal temperature, the arrangement of the solvent molecules surrounding the inner layer also results into increase in $B_{\text{ion}}^{\text{Orient}}(\eta^A)$, $B_{\text{ion}}^{\text{Str}}(\eta^D)$ is found to be lower for these ions. Hence, B_{ion} will found to be higher and positive as $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} > B_{\text{ion}}^{\text{Str}}$. But for the, $B_{\text{ion}}^{\text{Einst}}$ and $B_{\text{ion}}^{\text{Orient}}$ will be lower for the ions of highest ionic radii (present in a group) such as Cs^+ or I^- cause of lower surface charge densities yielding in poor orienting and structure forming effect. It is expected that $B_{\text{ion}}^{\text{Str}}$ will have a higher value due to structural disarray in the next neighbor zone of the ion due to competition between the ionic field and the bulk structure. So $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} < B_{\text{ion}}^{\text{Str}}$ and B_{ion} is found to be negative. The Ions with the moderate size (*like* K^+ and Cl^-) have maintain a close balance of viscous forces in their vicinity, *i.e.*, $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} = B_{\text{ion}}^{\text{Str}}$, hence value of B_{ion} is approaches to zero. Large molecular ions like tetra alkyl ammonium ions (R_4N^+) have a large $B_{\text{ion}}^{\text{Einst}}$ because of big size but $B_{\text{ion}}^{\text{Orient}}$ and $B_{\text{ion}}^{\text{Str}}$ found to be lower, *i.e.*, $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} \gg B_{\text{ion}}^{\text{Str}}$ and B_{ion} must be positive and higher in values. The value will be further strenghtened in water evolving from $B_{\text{ion}}^{\text{Reinf}}$ because of hydrophobic hydrations. Rising in temperature do not impact on $B_{\text{ion}}^{\text{Einst}}$. But the solvent molecules that present in the second layer have somewhat restricted its orientation due to rise in the thermal motion that results into lower the $B_{\text{ion}}^{\text{Str}}$. $B_{\text{ion}}^{\text{Orient}}$ will lowered slowly with the rise in the temperature. Since there will be a fewer confliction between reduced solvent structure and the ionic field. The relative

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magnitudes of $B_{\text{ion}}^{\text{Orient}}$ and $B_{\text{ion}}^{\text{Str}}$ will impart a net effect on positive or negative temperature co-efficient. In addition to this the change in viscosity of ions due to temperature (or entropy of solvation or mobility of ions) would be more effective in case of smaller ions than the larger ions of electrolyte. So there exist a relation among the viscosity, entropy of solvation and mobility of ions (a factor of temperature). Hence the ionic B -coefficient and the entropy of solvation of ions can be utilize as exploring of ion-solvent interactions and can provide valuable information about the structure making and structure breaking character of ions.

2.2.4. Viscosity of Non-Electrolyte Solutions

Falkenhagen suggested that,^{54, 55} for a neutral solutes are havin the A -coefficients is zero and solution viscosities (η) of non-electrolytes examined with the rectified Jones-Dole equation:^{41, 59}

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

where $\eta_r = \eta/\eta_1$; η_1 , η and c represent solvent viscosity, solution viscosity and molar concentration of the solute in the solution, respectively. The experimental results of viscosities can be fitted to the following linear relation with equal weights to all the viscosities:⁸¹

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

where B' and C' are fixed; C' values are fairly agree with the perceived η_1 values within the experimental error and B' is related to the B - coefficients as follows:⁸¹

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

2.2.5. Viscosity B -Coefficient of Transfer

As like $\Delta_t \phi_v^0$, viscosity B -coefficient of transfer ($\Delta_t B$) is independent from solute-solute or ion-ion interactions and gives us valuable information about solute-cosolute interactions taking place in soltion. $\Delta_t B$ values measured from the following equation:

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

Gurney's 'Co-sphere' model.⁴¹ explore different types of interaction by the obtained value from the above equation. Normally negative $\Delta_t B$ values supposed that the

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solute must be in less structured environment in the solution than that in the solvent whereas positive $\Delta_{\pm}B$ values suggest that the solute must be present in the more structured environment in the solution than in the solvent. Such results disclosed the governance of 'solvent structure modification' with the help of solute and cosolute molecules.

2.2.6. Viscous flow causing the change in the shape and size

The ions in solution are supposed to be rigid spheres that are suspended in continuum. The hydrodynamic treatment represented by Einstein leads to the equation:⁶⁹

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

where ϕ is the fraction of volume that captured by the particles. New alternate of the above relation have been proposed by: (i) Simha⁸² based on the departures from spherical shape and (ii) on the basis of dependence of the flow patterns surrounding the closest particles at a larger concentrations.⁸³ But considering the various aspects of the problem, spherical shapes have been considered for electrolytes to be hydrated ions of higher effective size. Thus from Eq. (79):

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

Since $A\sqrt{c}$ term can be nullified compared with Bc and $\phi = c\phi_{v,ion}^0$, where $\phi_{v,ion}^0$ is known as partial molar volume of the ion, so the above equation turn into:

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

The ionic B_{\pm} -coefficient varied linearly of partial molar volume of the ion, $\phi_{v,ion}^0$ with slope to 2.5 in an ideal cases.

Thus, B_{\pm} represented by :

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

In such cases, the ions are supposed to as rigid spheres with an effective radii (R_{\pm}) which proceed in a continuum and 2.5 is the shape factor for a sphere. R_{\pm} , calculated by using Eq. (82), should be nearest to crystallographic radii or corrected Stoke's radii⁸⁴ if the ions are barely solvated and act as spherical entities. However, normally, R_{\pm} values are found to be higher than those of the crystallographic radii of the ions

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supporting the appreciable solvation of the ions. The number n_s of the solvent molecules held to the ion in the primary solvation shell can be had from the relation:⁶⁹

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

Where V_i is the molar volume of the stripped ion and V_s , the molar volume of the solvent.

2.2.7. Viscosity and its thermodynamic character:

Viscosity supposed to be by means of the theory of absolute reaction rates.⁸⁵ As a gas is supposed to be made up of molecules mobile about in vacant space, aslike that liquid may also be considered as made up of “holes” moving about the matter. So the “holes” act similar role in a liquid as molecules do in the gas phase. The energy needed to produce a hole of molecular dimension in a liquid system is same as that of the energy of vaporization per molecule of the liquid.⁸⁵ If the two layers of molecules present in a liquid are detached by a distance λ_1 and one layer slips over the other under the influence of a force f per square centimeter and Δu denotes the difference in the velocity of the two layers, then the coefficient of viscosity (η) is represent by the relation: $\eta = f\lambda_1 / \Delta u$. A molecule from one equilibrium position to another position through a passage, in the same layer needs a appropriate hole to be available and energy is utilize to produce that type of a hole in the liquid. The overall process is represent in following Figure 2.3 below.

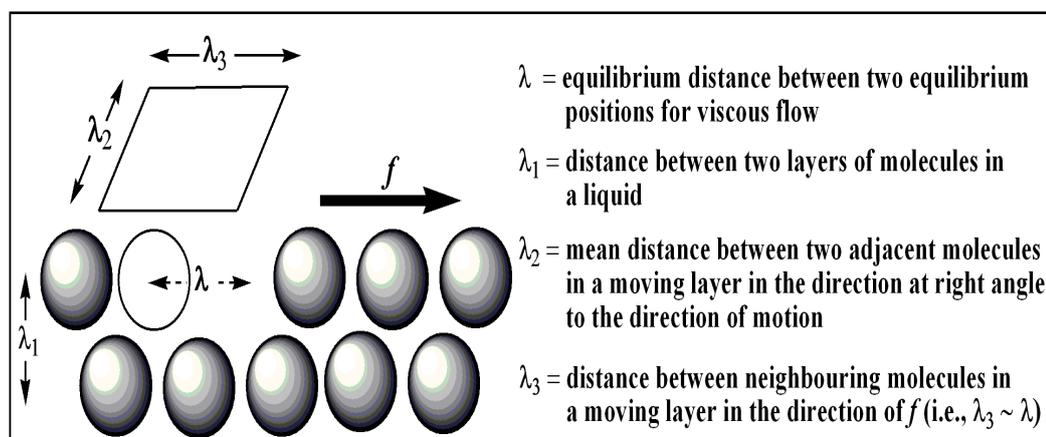


Fig 2.3. A molecule travel from one equilibrium position to another in the similar layer of a liquid with the availability of a appropriate hole.

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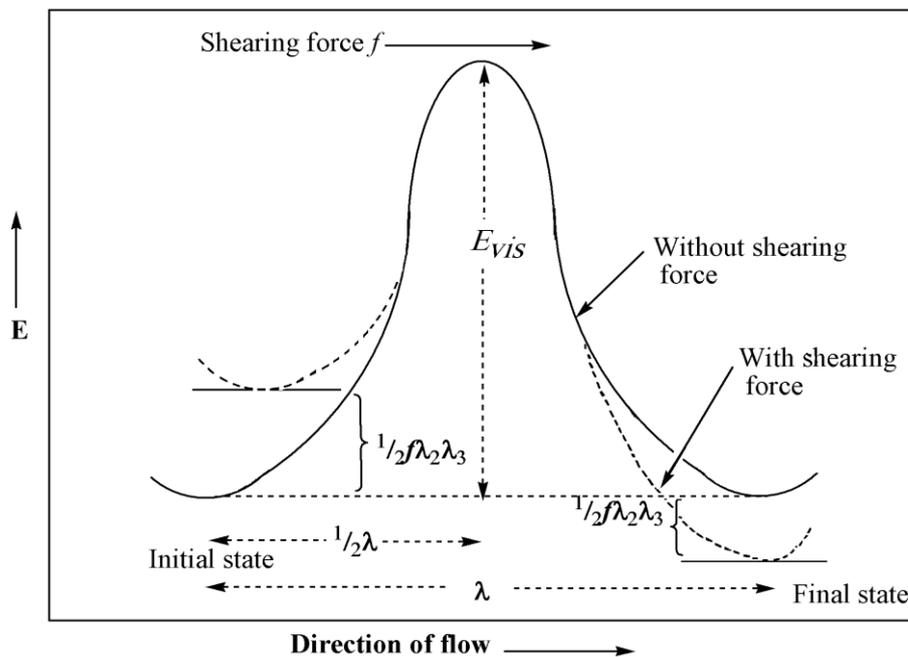


Fig 2.4. Potential energy barrier of viscous flow.

This phenomena can be expressed with the help of the symmetrical potential energy barrier represented in the Figure 2.4. consider that the potential energy barrier is found to be symmetrical, and the distance between the initial equilibrium position and the activated state is given by $\lambda/2$. The applied force on a molecule in the way of motion is thus given as $f\lambda_2\lambda_3$, Since $\lambda_2\lambda_3$ is representing effective area per molecule. So the energy possessed by the molecule in motion that has reached to the top of the potential energy barrier is $f\lambda_2\lambda_3\lambda/2$. Such energy is minimize the height of the energy barrier in the forward direction by the amount of $f\lambda_2\lambda_3\lambda/2$ and rises the height of the energy barrier in the backward direction by the same amount. With some consideration and statistical thermodynamic operation, described in the literature,⁸⁵ the viscosity (η) of a solution can be shown by the Eyring's relation:⁸⁵

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

Here, E_{vis} = experimental energy of activation calculated from a plot of $\ln\eta$ against $1/T$; ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger are the free energy, enthalpy and entropy for the activation of viscous flow, respectively. The net activation energy for viscous flow may be considered as consisting of two parts: (i) the energy needed to create the hole, (ii) that needed to the molecule to go towards the hole and maximum of the energy is needed

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for the creation of the holes rather than that needed to move the molecules into the holes. According to Eq. (84), the free energy of activation for viscous flow per mole of the solvent/solvent mixture ($\Delta\mu_1^{0\neq}$) as:

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

Where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volume of the solvent, respectively. The other symbols have their usual significances. For a binary system utilize as solvents, $\phi_{V,1}^0$ is considered as the mole fraction average of molecular weights of components normalized by densities at the study temperature. Another form of the above equation is like that^{57, 86}

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

Therefore linear regression of the ($\ln(\eta_1 \phi_{V,1}^0 / h N_A)$) data Vs $1/T$ provides the $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ values. A relation between the viscosity B - coefficients and the separation between the contribution per mole of a solute towards 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 given by Feakins *et al.*⁸⁶:

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

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

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

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of i^{th} component in the solution. Therefore a linear regression of Eq. (88) provides the values of ($\Delta S_2^{0\neq} - \Delta S_1^{0\neq}$) and ($\Delta H_2^{0\neq} - \Delta H_1^{0\neq}$) from the slopes and intercepts. According to Eq. (87), $\Delta\mu_2^{0\neq}$ is depends on the viscosity B -coefficients and ($\phi_{V,2}^0 - \phi_{V,1}^0$) terms. In various cases $\Delta\mu_1^{0\neq}$

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are almost unchanging of the solvent compositions and temperatures, shows that $\Delta\mu_2^{0\neq}$ is dependent on the viscosity B -coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The $\Delta\mu_2^{0\neq}$ values show the free energy of activation of solute molecules and the contribution from the motion of the solute molecules. If $\Delta\mu_2^{0\neq}$ values are found to be positive and higher than $\Delta\mu_1^{0\neq}$ values at the study temperatures, the solute (ion)-solvent interactions is found to be higher in the ground state than in the transition state. In the transition state the solvation of the solute (ions) becomes poorly favored energetically. However, a popular method uses the following relations,

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

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

in order to calculate of the entropy and enthalpy of activation of viscous flow for the respective solute.

2.2.8. Solvation Number

The term ‘primary solvate ion’⁸⁷ for a electrolyte denotes the compacted fitting of solvent molecules towards the ion so that the ions and the solvent molecules move as a single entity in the vicinity of electrolyte transport process, mean the solvent molecules loose their individual translation degree of freedom. While the term ‘secondary solvation’ designate all of the other solvent molecules. It’s solvation number of a considered ion, depends on this union of solvent molecules. The first solvation shell composed of the set of next nearest solvent molecules surround the ion. Primary solvation layer created by the interaction of solvent strongly or coordinately with the ion. The second solvation shell is represents the set of next nearest solvent molecules of the ion. Solvent molecules present in the primary and secondary solvation sheath of the ion are arranged in such a way by its field that it is separate from the normal orientation of the solvent molecules present in the bulk solvent. There will be a zone present around the ion by the solvent molecules with neither the central orientation nor the bulk orientation. This untidy region is familiar as the “thawed zone”.⁸⁸ The volume of the solvation layer(V_s) can be calculated from the relation:

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

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where r_c = crystal radius of the ion; (S_n) = the solvation number then be hydration no. calculated as:

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

Considering Stokes' relation to hold, the ionic solvated volume should be calculated, due to packing effects⁸⁷ from:

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

where V_s^0 is expressed in mol.L⁻¹ and r_s in angstroms. In another way, solvation numbers (S_n) can easily derived from the following relation:⁸⁹

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

S_n is signifies that the formation of a primary solvation sphere surrounding a solute molecule and the range 0-2.5 for S_n which shows that the unsolvated solutes present in the solution.⁸⁹ If the magnitudes of ionic viscosity B -coefficients (B_{\pm}) are known, then the ionic solvation numbers ($S_{n,\pm}$) can be derived from Eq. (94) by utilizing ionic partial molar volumes ($\phi_{V,\pm}^0$) of the ions.

2.3. Ultrasonic Speed measurement for acoustic property

The acoustic property- 'ultrasonic speed' is a very much important factor to reveal the molecular interactions and can give valuable information about these event, Mostly when partial molar volumes alone fail to gives an unambiguous explanation of the interactions. Ultrasonic speed is measured of the interactions between the components of liquid mixtures and alter with the structures and binding forces in the solutions.

2.3.1. Apparent Molal Adiabatic Compressibility

The apparent molal adiabatic compressibility calculated for the electrolytes are more familiar techniques used for a long time to investigate the interaction between the solute, solvent other compounds in aqueous solutions⁹⁰. But the experiment done in non-aqueous⁷ solvents are still limited. It is propose by many pioneers that the apparent molal adiabatic compressibility is a valuable parameter to reveal the interactions taking place between solute-solvent and solute-solute. The easiest procedure to measure the compressibility of a solvent or solution is from the

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ultrasonic speed of sound in it. The isentropic compressibility (β_s) of a solvent or solution measured from the following relation:⁹¹

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

Where ρ = solution density and u = ultrasonic speed in the solvent or solution. The isentropic compressibility (β_s) calculated by Eq. (95) is adiabatic in nature,²⁵ not an isothermal one, since when the ultrasound passes through the solvent or solution neighborhood compressions occurred were too much rapid to allow an get away of the heat formed. The apparent molal isentropic compressibility (ϕ_K) of the solutions was measure from the following relation:

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

$\beta_{s,1}$ = isentropic compressibility of the solvent mixture, M = molar mass of the solute, m = molality of the solution. The limiting apparent molal isentropic compressibility (ϕ_K^0) can be obtained by extrapolating the plots of ϕ_K Vs the square root of molal concentration of the solute (\sqrt{m}) to zero concentration with the help of least-squares method.^{92, 93}

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

Where, S_K^* = experimental slope showing solute-solute or solute-cosolute interaction. The apparent molal isentropic compressibility (ϕ_K^0) at infinite depicted about the solute-solvent and solute-solute interactions, respectively. It is already proven that due to the electrostriction of the solute, the compressibility will tends to decrease in the solution.⁹⁴ Negative values of ϕ_K^0 of electrolytic solutions is reflected by the hydrophobic solutes due to the ordering bring about by them in the water structure.⁹⁴ The compressibility of structure having hydrogen-bonding within it, however, variation depending on the behavior of the hydrogen bonding get engaged.⁹⁴ However, the weak fit of the solute molecules^{95, 96} and the probabilities of flexible hydrogen bond creation found to be answerable for a more compressible neighborhood and so positive ϕ_K^0 values are often for aqueous non-electrolyte⁹⁷ and non-aqueous non-electrolyte⁹⁸ solutions.

2.4. Refractive Index

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Refractive index (n_D) is another important parameter which obtained from optical property of the solution and it varies with the change of molecular arrangement of solutions, pure liquids and mixtures. Refractive index (n_D) of the substance supposed to the ratio between the speed of light in vacuum to another substance, *i.e.*,

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

Lorentz and Lorenz⁹⁹ suggested a theoretical relation between refractive index (n_D) and density (ρ) of a respective solution as follows:

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

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

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

M denote the molar mass of the solute. Molar refractivity (R_M) for a solution mixture can be calculated from the following equation:

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

where M_i = molecular weight and x_i = mole fraction for the i^{th} component of the solution mixture. Molar refraction is found to be independent on the phase and behave as a fundamental property of a compound.¹⁰⁰ The atomic refractions as well as refraction of the bonds results in the molar refraction for most organic compounds. However, some exception is found in case of many inorganic or organometallic solid materials or substances such as metal complexes. Marcus *et al.*¹⁰¹ give following equation for the apparent molar refractivity (R_D) for a solute:

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

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Where n_D and $n_{D,1}$ representing the refractive indices of the solution and solvent or solvent mixture, and other symbols have their own usual meanings. The molecular polarizability (α_M)¹⁰² denotes the ability of deformation of the molecular orbital's under the influence of electrical field. In addition to this, it is observed that if the structure of a molecule is more complex, then its electron cloud is supposed to be decentralized at a greater extent. So the molecular polarizability rises cause molecular polarizability (α_M) is directly proportional to the R_D , So the trend of rising in R_D magnitude indicate net increase in molecular polarizabilities.¹⁰³ This is shown by the following relation:¹⁰¹

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

2.5. Study of UV-Visible Spectra for solvent effect in solution:

The absorptions spectra of organic solutes are often shifted due to the solvation, mainly in solvents of variable polarity. As a result of these the solvents can alter the intensities, positions and shapes of the absorption bands.¹⁰²⁻¹⁰⁵ The reason behind of shifts of the absorption band are due to specific solute-solvent and solute-solute interactions through ion-dipole, hydrogen bonding, dipole-dipole, dipole-induced dipole interactions, *etc.* Many other things like acid-base chemistry and charge-transfer interactions do also play a role in spectral shifts in solutions. All these forces causing the change in the energy between the excited and the ground state of the absorbing species through as a physical agitation of appropriate molecular states of the chromophores.¹⁰⁶⁻¹⁰⁸ Therefore, the effect of solvent on the absorption spectra can give important information about any respective solute-solvent interactions¹⁰²⁻¹⁰⁵ and it helpful to reveal the primary solvation structure of the solvated ion.¹⁰⁹ The net effects of solvents on the absorption band depend mainly on the chromospheres and the type of the transitions: where $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ are charge-transfer transitions. The extent and behavior of shifting in the band in different solvents of varying polarity depend on the strength of intermolecular hydrogen bonding between the certain groups (contain N, For O atom) of the solute and those of the solvent molecules. If intermolecular hydrogen bonding does not takes place between the solute and the solvent then the spectral shifts depend only on the solvent polarity. In such cases, if

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the solvent polarity rises due to hydrogen bonding takes place between the solute and solvent molecules, the $\pi \rightarrow \pi^*$ bathochromic or hypsochromic shift in the band are found. On the other hand, for solutes having intramolecular hydrogen bonding, the spectral shifts are very negligible. The spectral shifts can be well expressed by solvent polarities when the solute-solvent systems are lacking of intermolecular hydrogen bonds. It is familiar that π -electrons containing molecules shows effective solvatochromism. These electrons are mainly accountable for the change in charge distribution, accordingly in the dipole moment between the electronic excited and ground state of the solute. The Negative solvatochromism is obtained during blue or hypsochromic shift with rising in polarity of solvent and the positive solvatochromism is depicted as the bathochromic (or red) shift. The higher negative solvatochromism is obtained for various solvation of the zwitterionic electronic ground state, highly dipolar, and the relatively lower dipolar first excited state.¹¹⁰ If it found that the excited state more polar than ground state, mainly a bathochromic shift with increased polarity of solvents for a long-wave length absorption band is found and if the ground state is more polar than the excited state, rising solvent polarity results into the hypsochromic shift. Inverted solvatochromism shown by Polyene dye,¹¹¹ Since there is a shifts obtained from positive to negative solvatochromism when solvent polarity become rises. Solvatochromism is also helpful to know the solute-solvent interactions in respect of the polarizability or dipolarity parameter (π^*), hydrogen bond acceptor (β) and hydrogen bond donor (α) abilities of the solvents.

2.6. Theoretical Approach

2.6.1. Molecular Theory for Partial Molar Volume

In Statistical mechanics of liquids proposed two theoretical model for the measurement of the partial molar volumes of the solute. First one model is the scaled particle theory (SPT) and second one is the Kirkwood-Buff (KB) solution theory.¹¹²⁻¹¹³ In the first approach solute-solvent interactions in solution can be expressed as interms of interaction volume ($\bar{\phi}_{\text{int}}$) as follows:

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

$\bar{\phi}_{\text{cav}}$ = contributed volume to the partial molar volume of the solute that associated with a cavity produce in the water, κ_1^0 is the isothermal compressibility of water and

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other symbols retain their usual significances. $\bar{\phi}_{\text{cav}}$ derived from the following relation:¹¹⁴

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

Here $z = \sigma_2 / \sigma_1$, σ_1 and σ_2 are hard sphere diameters of water and the solute. The parameter y is equal to the ratio of volume occupied by one mole of hard sphere solvent molecules to its molar volume $\phi_{V,1}^0$. So an imprecise free energy for cavity creation in a fluid can be measured with the help of SPT theory. In spite of broad application of the SPT theory, there is found two major limitations when applied to chemical and biochemical field. First one is it is only applicable for the spherical solute that can be understood by the original SPT and second one is the theory does not incorporate the electrostatic effects on partial molar volumes. Nagayama, Irisa and Hirata¹¹⁵ expanded this theory for solutes of random shape. They successfully achieved to measure the partial molar volumes of molecular solutes with the help of extended SPT¹¹⁶ and resolved the previous problem. However, the second limitation was not solved even with the merger of the dielectric continuum models.^{117, 118} The other perspective is based on the Kirkwood-Buff (KB) solution theory.¹¹⁹ This theory, suggest that the partial molar volumes of solutes can be measured from the relation below:

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

κ_T = isothermal compressibility of the solution, k_B = Boltzman constant and $g(r)$ = radial distribution function (RDF) between the solvent and solute. The radial distribution function (RDF) obtained from molecular simulation. Various attempts were done to adjoin molecular simulation with the KB theory but it still restricted to the small molecules.¹²⁰⁻¹²² There are many other molecular liquid theories like Reference Hypernetted Chain (RHNC)¹²³ and Reference Interaction Site Model (RISM)¹²⁴ were proposed. The KB theory adjoint with RHNC theory was used to measure the partial molar volume of the ions or solute in aqueous media.^{125, 126} Where as the RISM theory combined with the KB theory has successfully measured and interpret the partial molar volumes for wide range of molecular systems such as hydrocarbons,^{139, 130} ions,^{127, 128} and biomolecules^{131, 132} in non-aqueous and aqueous and solutions.^{133, 134} The RISM theory has been transformed to include the three-

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dimensional spatial correlation functions of solvent molecules surrounding a solute molecule.^{135, 136} The 3D-RISM theory adjoin with the KB theory was able to interpret the partial molar volumes of the bimolecular systems.¹³⁷⁻¹⁴⁴ Hence the RISM theory is considered as most beneficial method to interpret the partial molar volumes and other thermodynamic parameters of solutions mixture.

2.6.2. Solvation Models

Two methods are applied here to short out the interaction¹⁴⁴: the semi-empirical CNDO-type theory and the *ab initio* calculation theory. The *ab initio* calculation depicts the energy gap between a solvate and the different constituents is analyzed as a function of the geometry, *i.e.*, in respect of bond angles and bond length. According to these parameters Solvation energy is turned to maximum. Same as in the Free State, the solvent molecules may be regarded as rigid spheres having similar geometry. By omitting the electron correlation, the self-consistent field version of molecular orbital theory has been employed to solve Schrödinger equation for the all component and the solvate ion individually. The main problem arising is due to the genuine selection of basis set of orbitals. Although the separation in energy between the different component and a solvate is measured with less error while given basis of set (Slater or Gaussian type) of full molecular Hamiltonian is introduce for the measurement . Pople *et al.*¹⁴⁵ proposed an theory for semi-empirical calculations. Differential overlap (CNDO) of basis set of orbitals was entirely omitted in this theory. The total number of integrals have to measured is reduced with a set of orbitals. So this version introduce some empirical parameters which based on electron affinities, ionization potential in the Hamiltonian is known as CNDO/2. The energy of the system represented as a addition of total of two-atom and one-atom terms.

In terms of molecular dynamic (MD) , a fewer number of molecules, ions and Newtonian mechanics of movement for all type of solution particles are measured. This theory is dependent on the intermolecular energy of interactions between a pair of particles. A Computer programming simulation model found to be more helpful in this regards and in previous year some pioneer showing their interest to develop a computer soft wares and solvation models and in this event pronounced role played by. A. Galindo *et al.*^{146, 147} They are create a Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to explore the phase equilibrium and thermodynamic parameter of an electrolyte in aqueous solutions. The water molecules with the hard

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sphered are again related to the four short-range interactive sites to examine the hydrogen-bond interactions. The electrolyte is considered as two hard spheres of dissimilar diameter were employed in expressing the cation and anion. The interactions are again expressed in terms of Debye-Hückel and the mean spherical approximations model. There are many aqueous electrolyte solutions found which shows good agreement with the experimental data.

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