

CHAPTER II

2.1. Investigation on viscous Synergy and Antagonism

Grouping of solvents into classes is often based on the nature of the intermolecular forces because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. Rheology is the branch of science¹ that studies material deformation and flow, and is increasingly applied to analyses the viscous behaviors of many pharmaceutical products,²⁻⁷ and to establish their stability and even bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.^{8,9}

The study of the viscous behaviour of pharmaceutical, foodstuffs, cosmetics or industrial products ,etc..., is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

Viscous synergy is defined as the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component in the system.^{10,11}

In contraposition to viscous synergy, Viscous antagonism is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be less than the sum of the viscosities of each component in the system.

If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system would lack interaction.

The method most widely used to analyze the synergic and antagonic behavior of various solvent mixtures studied is that developed by Kalentune-Gencer and Peleg,¹² allowing the quantification of the antagonic and synergic interactions taking place in mixtures involving variable proportions of the constituent components.

The method compares the viscosity of the system, determined experimentally, η_{exp} with the viscosity expected in the absence of interaction, η_{calcd} , defined as,¹³

$$\eta_{\text{calcd}} = \sum_{i=1}^{n=3} W_i \eta_i \quad (1)$$

Where, where W_A , W_B and W_C are the weight fractions and η_A , η_B and η_C are the measured viscosities, of the components A, B and C respectively.

Accordingly, viscous synergy is exists when, $\eta_{exp} > \eta_{calcd}$ and while when, $\eta_{exp} < \eta_{calcd}$ viscous antagonism is exists. This procedure is used when Newtonian fluids are involved.
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In order to secure more comparable viscous synergy results, the so called synergy index (I_s), introduced by Howell¹³ is taken into account:

$$I_s = (\eta_{exp} - \eta_{calcd}) / \eta_{calcd} \quad (2)$$

The negative value of gives I_s antagonic interaction index I_A .

The method used to analyze volume contraction and expansion is carrying out the following equation analogous to that used for viscosity of mixture.

$$\rho_{mix} = \sum_{i=1}^{n=3} W_i \rho_i \quad (3)$$

Where, W_i and ρ_i are the fractions by weight and densities measured experimentally of the pure components respectably. Accordingly, when $\rho_{exp} > \rho_{mix}$, volume contraction occurs while, when $\rho_{exp} < \rho_{mix}$, volume expansion occurs in the system.

Besides this, power factor, F_η has also be studied which is the enhancement index of the viscosity given as

$$F_\eta = \frac{\eta_{max}}{\eta_0} \quad (4)$$

where η_{max} is the maximum viscosity attained in the mixtures, and η_0 is the experimental viscosity of the pure components. The investigations have been carried out with various binary as well as ternary mixtures

2.1. Investigation on Ion-Solvent Interaction

The formation of mobile ions in solution is a basic aspect to electrochemistry. There are two distinct ways that mobile ions form in solution to create ionically conducting phases. The first one is illustrated for aqueous acetic acid in figure 1:¹⁴

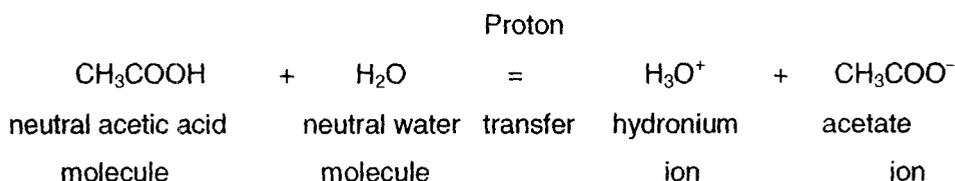


Figure 1. The chemical method of producing ionic solutions.

The second one involves dissociation of a solid lattice of ions such as the lattice of sodium chloride. The ion formation, as shown in figure 2,¹⁴ is as if the solvent colliding with the walls of the crystal gives the ions in the crystal lattice a better deal energetically than they have within the lattice. It entices them out and into the solution. Thus there is a considerable energy of interaction between the ions and the solvent molecules. These interactions are collectively termed as ion-solvent interactions.

The spherically symmetrical electric field of the ion may tear solvent dipoles out of the solvent lattice and orient them with appropriate charged end toward the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents.¹⁵⁻²⁴

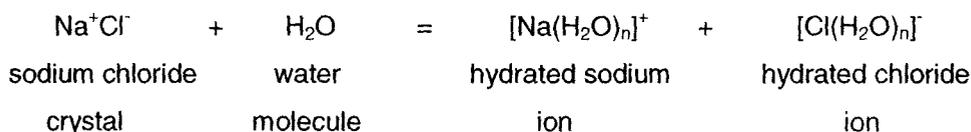


Figure 2. Dissolution of an ionic crystal by the action of a solvent.



Though water is the most abundant and versatile solvent in nature but its uniqueness as a solvent has been questioned^{25,26} and it has been realized that the studies of other solvent media like non-aqueous and mixed solvents would be of great help in understanding different molecular interactions and a host of complicated phenomena. Non-aqueous and mixed solvents increase the range of applicability of electrochemical techniques to many organic and inorganic compounds either due to its instability or insolubility in water and many novel battery systems require their use²⁷ for important new developments.

The organic solvents have been classified based on the dielectric constants, functional group types, acid-base properties or association through hydrogen bonding,²⁴ donor-acceptor properties,²⁸⁻²⁹ hard and soft acid-base principles,³⁰ etc. As a result, the different solvents show a wide divergence of properties ultimately influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non-electrolytes in these solvents. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a key role to understand the physico-chemical properties of solutions.

One of the causes for the intricacies in solution chemistry is the uncertainty about the structure of the solvent molecules in solution. The introduction of a solute modifies the solvent structure to an uncertain extent and solute structure also gets modified by the solvent molecule. Thus the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemist.

Ion-solvent interactions can be studied by spectrometry.³¹⁻³² But even qualitative or quantitative apportioning of ion-solvent interactions into the various possible factors is still an uphill task.

The aspect embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc. and such thermodynamic properties as apparent and partial molar volumes and apparent molal adiabatic compressibility.

2.2. Ion-ion interaction

Ion-solvent interactions are only a part of the story of an ion related to its environment. The surrounding of an ion sees solvent molecules as well as also other ions. The mutual interactions between these ions constitute the essential part of 'ion-ion interactions'. The degree of these interactions affects the properties of solution.

While proton transfer reactions are particularly sensitive to the nature of the solvent, it is now clear that the majority of the solutes are significantly modified by the solvents. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. 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 dissertation is intimately related to the studies of solute-solute, solute-solvent and solvent-solvent interactions in some solvent media.

2.3. Theory of Mixed Solvents

As the non-aqueous and mixed solvents are widely used in various field of modern science, a number of molecular theory have been developed. L. Jones and Devonshire³³ were first to evaluate the thermodynamic functions for a single fluid in terms of interchange energy parameters. They used "Free volume" or "Cell model". Prigogine and Garikian³⁴ extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans³⁵ developed a two fluid version of the cell model. Treszczanowicz et al.³⁶ suggested that V^E is the result of several contributions from several opposing effects. These may be divided arbitrarily into three types, viz. physical, chemical and structural. Physical contributions contribute a positive term to V^E . The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E . The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change would therefore depend on the relative strength of these effects. However, it is generally assumed that when V^E is negative, viscosity deviation ($\Delta\eta$) may be positive and vice-versa. This assumption is not a concrete one, as evident from some

studies.³⁷⁻³⁹ It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Based on the principle of corresponding states as suggested by Pitzer,⁴⁰ L. Huggins⁴¹ introduced a new approach in his theory of conformal solutions. Using a simple perturbation approach, he showed that the properties of mixtures could be obtained from the knowledge of intermolecular forces and thermodynamic properties of the pure components. Recently, Rowlinson et al.⁴²⁻⁴⁴ reformulated the average rules for van der Waals mixtures and their calculated values were in much better agreement with the experimental values even when one fluid theory was applied. The more recent independent effort is the perturbation theory of Baker and Henderson.⁴⁵ Flory et al.⁴⁶⁻⁴⁹ developed a statistical theory for predicting the excess properties of binary mixtures by using the equation of state and the properties of pure components along with some adjustable parameters. This theory is applicable to mixtures containing components with molecules of different shapes and sizes. Recently, Heintz⁵⁰⁻⁵² and coworkers suggested a theoretical model based on a statistical mechanical derivation and accounts for self-association and cross-association in hydrogen bonded solvent mixtures termed as extended real associated solution model (ERAS). It combines the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory et al.⁴⁶⁻⁴⁸ But Pineiro et al.⁵³ noticed that some of the mixing rules of the ERAS model have an asymmetrical form signifying that the components should be distinguishable from one another. Subsequently they introduced a new symmetrical reformulation⁵⁶ of ERAS model called 'Symmetrical-ERAS' model, which can be used to describe the excess molar enthalpies and excess molar volumes of binary mixtures containing very similar compounds like alcohol-alcohol mixtures.⁵⁷

2.4. Volumetric measurement

The volumetric information includes 'Density' as a function of composition on the bases of weight, volume and mole fraction and excess volumes of mixing. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Interpretation of fundamental macroscopic state of the system such as enthalpy, entropy and Gibbs free energy in terms of molecular

phenomena is generally difficult. The volumetric information may be of immense importance in this regard.

Various concepts regarding molecular processes in solutions like electrostriction,⁵⁸ hydrophobic hydration,⁵⁹ micellization⁶⁰ and co-sphere overlap during solute-solvent interactions⁶¹ to a large extent have been derived and interpreted from the partial molar volume data of many compounds.

2.4.1. Apparent and Partial Molar Volumes

The molar volume of a pure substance can be determined from density measurements. However, the volume contributed to a solvent by the addition of one 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. The effective volume of an ion in solution, the partial molar volume, can be determined from a directly obtainable quantity, apparent molar volume (V_ϕ). The apparent molar volumes, V_ϕ of the solutes can be calculated by using the following relation:⁶²

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/(c\rho_0) \quad (5)$$

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of solvent and solution respectively and c is the molarity of the solution.

The partial molar volumes, \bar{V}_2 can be obtained from the equation:⁶³

$$\bar{V}_2 = V_\phi + (1000 - cV_\phi)/(2000 + c^{3/2} \cdot \partial V_\phi / \partial \sqrt{c}) \sqrt{c} \cdot \partial V_\phi / \partial \sqrt{c} \quad (6)$$

The extrapolation of the apparent molar volume of electrolyte 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,⁶⁴ the Redlich-Meyer equation,⁶⁵ the Owen-Brinkley equation⁶⁶ and the Pitzer equation.⁴⁰ Masson found that the apparent molar volume of electrolyte, V_ϕ , vary with the square root of the molar concentration by the linear equation:

$$V_{\phi} = V_{\phi}^{\circ} + S_v^* \sqrt{c} \quad (7)$$

where, V_{ϕ}° is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution, \bar{V}_2°) and S_v^* is the experimental slope. The majority of V_{ϕ} data in water⁶⁷ and nearly all V_{ϕ} data in non-aqueous⁶⁸⁻⁷² solvents have been extrapolated to infinite dilution through the use of equation (7).

The temperature dependence of V_{ϕ}° for various investigated electrolytes in various solvents can be expressed by the general equation as follows:

$$V_{\phi}^{\circ} = a_0 + a_1 T + a_2 T^2 \quad (8)$$

Where, a_0 , a_1 and a_2 are the coefficients of a particular electrolyte and T is the temperature in Kelvin.

The limiting apparent molar expansibilities (ϕ_E°) can be calculated from the general equation (9). Thus,
$$\phi_E^{\circ} = (\partial V_{\phi}^{\circ} / \partial T)_P = a_1 + 2a_2 T^2 \quad (9)$$

The limiting apparent molar expansibilities (ϕ_E°) change in magnitude with the change of temperature. During the past few years, different workers emphasized that S_v^* is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler⁷³ developed a technique of examining the sign of $(\delta^2 V_{\phi}^{\circ} / \delta T^2)_P$ for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$(\partial C_P / \partial P)_T = -(\partial^2 V_{\phi}^{\circ} / \partial T^2)_P \quad (10)$$

On the basis of this expression, it has been deduced that structure-making solutes should have positive value, whereas structure-breaking solutes should have negative value.

However, Redlich and Meyer⁶⁵ have shown that equation (11) 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 V_{ϕ} as follows:

$$V_{\phi} = V_{\phi}^{\circ} + S_v \sqrt{c} + b_v c \quad (11)$$

where,
$$S_v = K w^{3/2} \quad (12)$$

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

$$w = 0.5 \sum_i^j \gamma_i z_i^2 \quad (13)$$

and,
$$K = N^2 e^2 (8\pi / 1000 \epsilon^3 RT)^{1/2} [(\partial \ln \epsilon / \partial P)_T - \beta / 3] \quad (14)$$

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

Thus for polyvalent electrolytes, the more complete Owen-Brinkley equation⁶⁶ can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of V_ϕ . The Owen-Brinkley equation derived by including the ion-size parameter is given by:

$$V_\phi = V_\phi^0 + S_V \tau(Ka) \sqrt{c} + 0.5 w_v \theta(Ka) + 0.5 K_V c \quad (15)$$

where the symbols have their usual significance. However, equation (15) has not been widely employed for the treatment of results for non-aqueous solutions.

2.4.2. Ionic Limiting Partial Molar Volumes

The individual partial ionic 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 one. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions⁷⁴⁻⁷⁸ to non-aqueous electrolyte solutions.

In the last few years, the method suggested by Conway et al.⁷⁸ has been used more 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,

$\bar{V}_{R_4NX}^0$ for a series of these salts with a halide ion in common as a function of the

formula weight of the cation, $M_{R_4N^+}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + bM_{R_4N^+} \quad (16)$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, $\bar{V}_{X^-}^0$

2.4.3. Excess Molar Volumes

The study has been carried out with the binary and ternary aqueous and non-aqueous solvent mixtures. The excess molar volumes (V^E) are calculated from density of these solvent mixtures according to the following equation:⁷⁹⁻⁸²

$$V^E = \sum_{i=1}^j x_i M_i (1/\rho - 1/\rho_i) \quad (17)$$

where, ρ is the density of the mixture and M_i , x_i and ρ_i are the molecular weight, mole fraction and density of i^{th} component in the mixture, respectively.

5. Viscometric measurement

The viscometric information includes 'Viscosity' as a function of composition on the bases of weight, volume and mole fraction, comparison of experimental viscosities with those calculated with several equations and excess Gibbs free energy of viscous flow. Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively.⁸²⁻⁸⁴ Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, \bar{V}_2^0 , i.e., the partial molar volume, gives a lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

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 viscosity. In 1905, Grüneisen⁸⁵ 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, Jones and Dole⁸⁶ suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations, c :

$$\eta/\eta_0 = \eta_r = 1 + A\sqrt{c} + Bc \quad (18)$$

The above equation can be rearranged as:

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc + Dc^2 \quad (19)$$

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 where there is no ionic association and has been used extensively. The term $A\sqrt{c}$, originally ascribed to Grüneisen effect, arose from the long-range coulombic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory⁸⁷ of inter ionic attractions in 1923.

At higher concentrations the extended Jones-Dole equation (18), involving an additional coefficient D , originally used by Kaminsky,⁸⁸ has been used by several workers^{89, 90} and is given below:

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc + Dc^2 \quad (20)$$

The coefficient D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (20) is used by the most of the workers.

The plots of $(\eta / \eta_0 - 1) / \sqrt{c}$ against \sqrt{c} for the electrolytes should give the value of A -coefficient. But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur.⁸⁸⁻⁹²

A -coefficient should be zero for non-electrolytes. According to Jones and Dole, the A -coefficient probably represents the stiffening effect on the solution of the electric forces between the ions, which tend to maintain a space-lattice structure.⁸⁶

The B -coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ion-size and the solvent and cannot be calculated a priori. 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:^{93,94}

- (i) The effect of ionic solvation and the action of the field of the ion in producing long-range order in solvent molecules, increase η or B -value.
- (ii) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking or depolymeriation effect) decrease η values.
- (iii) High molal volume and low dielectric constant, which yield high B -values for similar solvents.
- (iv) Reduced B -values are obtained when the primary solution of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

2.5.1. Viscosities at Higher Concentration

It had been found that the viscosity at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade:⁹⁵

$$\eta = A \exp^{b/T} \quad (21)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range⁹⁶⁻¹⁰⁰ and the equation suggested

by Angell^{101, 102} based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly noteworthy.

The equation is:
$$1/\eta = A \exp[-K_1/(N_0 - N)] \quad (22)$$

Where, N represents the concentration of the salt in eqv.Litre⁻¹, A and K_1 are constants supposed to be independent of the salt composition and N_0 is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumder et al.¹⁰³⁻¹⁰⁵ introducing the limiting condition, that is; which is the viscosity of the pure solvent. Thus, we have:

$$\ln \eta/\eta_0 = \ln \eta_{\text{Rel}} = K_1 N/N_0(N_0 - N) \quad (23)$$

The equation (23) predicts a straight line passing through the origin for the plot of $\ln \eta_{\text{Rel}}$ vs. $N / (N_0 - N)$ if a suitable choice for N_0 is made. Majumder et al. tested the equation (23) by using literature data as well as their own experimental data. The best choice for N_0 and K_1 was selected by trial and error methods. The set of K_1 and N_0 producing minimum deviations between $\eta_{\text{Rel}}^{\text{Exp}}$ and $\eta_{\text{Rel}}^{\text{theo}}$ was accepted. In dilute solutions, $N \ll N_0$ and we have:

$$\eta_{\text{Rel}} = \exp(K_1 N/N_0^2) \cong 1 + K_1 N/N_0^2 \quad (24)$$

Equation (23) is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K_1/N_0^2$. The arrangement between B-values determined in this way and using Jones-Dole equation has been found to be good for several electrolytes.

Further, the equation (23) written in the form:

$$N/\ln \eta_{\text{Rel}} = N_0^2/K_1 - (N_0/K_1)N \quad (25)$$

It closely resembles the Vand's equation¹⁰⁶ for fluidity (reciprocal for viscosity):

$$2.5c/2.3 \log \eta_{\text{Rel}} = 1/V - Qc \quad (26)$$

where, c is the molar concentration of the solute and V is the effective rigid molar volume of the salt and Q is the interaction constant.

2.5.2. Division of B -coefficient

The viscosity B -coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents.^{92,107-137} However, the B -coefficients as determined experimentally using the Jones-Dole equation, does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total solute-solvent interaction. The division of B -values into ionic components is quite arbitrary and based on some assumptions, the validity of which may be questioned.

The following methods have been used for the division of B -values in the ionic components –

(i) Cox and Wolfenden¹³⁸ carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in $LiIO_3$ are proportional to the ionic volumes which are proportional to the third power of the ionic mobilities. The method of Gurney¹³⁹ and also of Kaminsky⁹³ is based on:

$$B_{K^+} = B_{Cl^-} \text{ (in water)} \quad (27)$$

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 (15–45) °C. The assignment is supported from other thermodynamic properties. Nightingale,¹⁴⁰ however preferred $RbCl$ or $CsCl$ to KCl from mobility considerations.

(ii) The method suggested by Desnoyers and Perron⁹⁴ 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,¹⁴¹

$$B = 0.0025\bar{V}_0 \quad (28)$$

and by having an accurate value of the partial molar volume of the ion, V_0 , it is possible

to calculate the value of 0.359 for $B_{\text{Et}_4\text{N}^+}$ in water at 25°C.

Recently Sacco et al. proposed the “reference electrolytic” method for the division of B -values.

Thus, for tetraphenyl phosphonium tetraphenyl borate in water, we have:

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{BPh}_4\text{PPh}_4} / 2 \quad (29)$$

$B_{\text{BPh}_4\text{PPh}_4}$ (Scarcely soluble in water) has been obtained by the following method:

$$B_{\text{BPh}_4\text{PPh}_4} = B_{\text{NaBPh}_4} + B_{\text{PPh}_4\text{Br}} - B_{\text{NaBr}} \quad (30)$$

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 are based on the equality of equivalent conductances of counter ions at infinite dilutions.

(a) Criss and Mastroianni assumed $B_{\text{K}^+} = B_{\text{Cl}^-}$ in ethanol based on equal mobility of ions.¹⁴² They also adopted $B_{\text{Me}_4\text{N}^+}^{25} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss¹⁴³ proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer et al.¹⁴⁴

$\lambda_{25}^0(\text{Bu}_4\text{N}^+) = 61.4$ and $\lambda_{25}^0(\text{Ph}_4\text{B}^-) = 58.3$ in acetonitrile.

$$B_{\text{Bu}_4\text{N}^+} = B_{\text{Ph}_4\text{B}^-} \quad (31)$$

(c) Gopal and Rastogi⁸⁴ resolved the B -coefficient in N-methyl propionamide solutions assumin that $B_{\text{Et}_4\text{N}^+} = B_{\text{I}^-}$ at all temperatures.

(d) In dimethyl sulphoxide, the division of B -coefficients were carried out by Yao and Beunion⁹² assuming:

$$B_{[(i-\text{pc})_2\text{BuN}^+]} = B_{\text{Ph}_4\text{B}^-} = 1/2 B_{[(i-\text{pc})_2\text{BuNPh}_4\text{B}]} \quad (32)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate¹⁴⁵ solutions.

The methods, however, have been strongly criticized by Krumgalz.¹⁴⁶ According to him, any method of resolution based on the equality of equivalent conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which

$\lambda_{+}^{\circ} = \lambda_{-}^{\circ}$ in all solvents at all temperatures. Thus, though $\lambda_{K^{+}}^{\circ} = \lambda_{Cl^{-}}^{\circ}$ at 25°C in methanol, but is not so in ethanol or in any other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the *B*-coefficient values are calculated. Further, according to him, equality of dimensions of (i-pe)₃BuN⁺ or (i-Am)₃BuN⁺ and Ph₄B⁻ does not necessarily imply the equality of *B*-coefficients of these ions and they are likely to be solvent and ion-structure dependent.

Krumgalz¹⁴⁶⁻¹⁴⁸ has recently proposed a method for the resolution of *B*-coefficients. The method is based on the fact that the large tetraalkylammonium cations are not solvated^{149, 150} in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic *B*-values for large tetraalkylammonium ions, R₄B⁺ (where R > Bu) in organic solvents are proportional to their ionic dimensions. So, we have:

$$B_{R_4NX} = a + br^3R_4N^+ \quad (33)$$

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 $r^3R_4N^+$ to zero cation dimension gives directly $B_{X^{-}}$ in the proper solvent and thus *B*-ion values can be calculated.

The *B*-ion values can also be calculated from the equations:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (34)$$

$$B_{R_4N^+} / B_{R'_4N^+} = r_{R_4N^+}^3 / r_{R'_4N^+}^3 \quad (35)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data.¹⁵¹

The method of resolution is based on the assumption, like Krumgalz, 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^+ (5.35 Å) and Ph_4B^-

(5.45 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers.¹²⁸ They proposed the equations:

$$B_{\text{Ph}_4\text{B}^-} / B_{\text{Bu}_4\text{N}^+} = r_{\text{Ph}_4\text{B}^-}^3 / r_{\text{Bu}_4\text{N}^+}^3 = (5.35/5.00)^3 \quad (36)$$

$$B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{Ph}_4\text{B}^-} \quad (37)$$

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 Sacco et al. in different organic solvents using the assumption as given below:

$$B_{[(i-\text{Am})_3\text{BuN}^+]} = B_{\text{Ph}_4\text{B}^-} = 1/2 B_{[(i-\text{Am})_3\text{BuNPh}_4\text{B}]} \quad (38)$$

Recently, Lawrence and Sacco¹³¹ used tetrabutylammonium tetra-butylborate (Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal van der Waals volume. Thus, we have:

$$B_{\text{Bu}_4\text{N}^+} / B_{\text{Bu}_4\text{B}^-} = V_{\text{W}(\text{Bu}_4\text{N}^+)} / V_{\text{W}(\text{Bu}_4\text{B}^-)} \quad (39)$$

$$\text{or. } B_{\text{Bu}_4\text{N}^+} = B_{\text{Bu}_4\text{NBBu}_4} / [1 + V_{\text{W}(\text{Bu}_4\text{B}^-)} / V_{\text{W}(\text{Bu}_4\text{N}^+)}] \quad (40)$$

Recently, Lawrence et al. made the viscosity measurements of tetraalkyl (from Pr to Hept.) ammonium bromides in DMSO and HMPT. The B -coefficients values were $B_{\text{R}_4\text{NBr}} = B_{\text{Br}^-} + a[f_x R_4\text{N}^+]$ plotted as functions of the van der Waals volumes. The B_{Br^-} values thus obtained were compared with the accurately determined B_{Br^-} value using Bu_4NBBu_4 and Ph_4NBPh_4 as reference salts. They concluded that the 'reference electrolyte' method is the best available method for division into ionic contributions.

The principle was extended to derive absolute single ion B -coefficients for alkali metals and halides in water.¹⁵²⁻¹⁵³ They also observed that $B_{\text{Cs}^+} = B_{\text{I}^-}$ suggested by Krumgalz¹⁴⁹

to be more reliable than $B_{K^+} = B_{Cl^-}$ in aqueous solutions. However, we require more data to test the validity of this method.

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.

2.5.3. Temperature dependence of B -ion Values

Regularity in the behaviors of B_{\pm} and dB_{\pm}/dT has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminsky. 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 system, the temperature co-efficient of B_{ion} values increase as the ionic radius increases. The results can be summarized as follows:

$$(i) A \text{ and } dA/dT > 0 \quad (41)$$

$$(ii) B_{ion} < 0 \text{ and } dB_{ion}/dT > 0 \quad (42)$$

Characteristic of the structure breaking ions.

$$(iii) B_{ion} > 0 \text{ and } dB_{ion}/dT < 0 \quad (43)$$

Characteristic of the structure making ions.

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,¹⁵⁴ A, B, C Zones of Frank and Wen¹⁵⁵ and hydrated radius of Nightingale.¹⁴⁰

Stokes and Mills gave an analysis of the viscosity data incorporating the basic ideas presented before. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent (η_0) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation:

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta(A\sqrt{c} + Bc) \quad (44)$$

where η^* , the positive increment in viscosity is caused by coulombic interaction. Thus :

$$\eta^E + \eta^A + \eta^D = \eta_0 BC \quad (45)$$

B -coefficient can thus be interpreted in terms of the competitive viscosity effects. Following Stokes, Mills and Krumgalz¹⁴⁷ we can write for B_{ion} as:

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{Sr} + B_{ion}^{Reinf} \quad (46)$$

where as according to Lawrence and Sacco:

$$B_{ion} = B_w + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \quad (47)$$

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 η^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 η^A or B_{Ord}). B_{ion}^{Sr} is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymmetrically and solvent to keep its own structure (this corresponds to η^D or B_{Disord}). B_{ion}^{Reinf} is the positive increment conditioned by the effect of ‘reinforcement of the water structure’ by large tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents. B_w and B_{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 ion (B_{ion}^{Einst} or B_{Solv} positive). At ordinary temperature,

alignment of the solvent molecules around the inner layer also cause increase in

$B_{ion}^{Orient} (\eta^A)$, $B_{ion}^{Sr} (\eta^D)$ is small for these ions. Thus, B_{ion} will be large and positive as

$B_{ion}^{Einst} + B_{ion}^{Orient} > B_{ion}^{Sr}$. However, B_{ion}^{Orient} and B_{ion}^{Einst} 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_{ion}^{Sr} 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 $B_{ion}^{Einst} + B_{ion}^{Orient} < B_{ion}^{Sr}$ and B_{ion} is negative.

Ions of intermediate size (e.g. K^+ and Cl^-) have a close balance of viscous forces in their vicinity, i.e., $B_{lon}^{Einst} + B_{lon}^{Orient} = B_{lon}^{Str}$, so that B is close to zero.

Large molecular ions like tetraalkylammonium ions have large B_{lon}^{Einst} because of large size but B_{lon}^{Orient} and B_{lon}^{Str} would be small, i.e. $B_{lon}^{Einst} + B_{lon}^{Orient} \gg B_{lon}^{Str}$ and B would be positive and large. The value would be further reinforced in water arising from B_{lon}^{Str} due to hydrophobic hydrations.

The increase in temperature will have no effect on B_{lon}^{Orient} . But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in B_{lon}^{Str} . B_{lon}^{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_{lon}^{Orient} , and B_{lon}^{Str} .

In case of structure-making ions, the ions are firmly surrounded by a primary solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in B -ion and concomitant decrease in entropy of solvation and the mobility of ions. Structure breaking ions, on the other hand, are not solvated to a great extent and the secondary solvation zone will be disordered leading to a decrease in B -ion values and increases in entropy of solvation and the mobility of ions. Moreover, the temperature induced change in viscosity of ions would be more pronounced in case of smaller ions than in case of the larger ions. So there is a correlation between the viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic B -coefficient and the entropy of solvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication of structure making and structure breaking character of ions.

The linear plot of ionic B -coefficients against the ratios of mobility viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney¹⁵⁴ clearly demonstrates a close relation between ionic B -coefficients and ionic mobilities.

Gurney also demonstrated a clear correlation between the molar entropy of solution values with B -coefficient of salts. The ionic B -values show a linear relationship with the partial molar ionic entropies or partial molar entropies of hydration (\bar{S}_h^0) as:

$$\bar{S}_h^0 = \bar{S}_{aq}^0 - \bar{S}_g^0 \quad (48)$$

Gurney obtained a single linear plot between ionic entropies and ionic B -coefficients for all monoatomic ions by equating the entropy of the hydrogen ion ($\bar{S}_{H^+}^0$) to $-5.5 \text{ cal Mol}^{-1}\text{.deg}^{-1}$. Asmus¹⁵⁶ used the entropy of hydration to correlate ionic B -values and Nightingale¹⁴⁰ showed that a single linear relationship can be obtained with it for both monoatomic and polyatomic ions.

The correlation was utilized by Abraham et al.¹⁵⁷ to assign single ion B -coefficients so that a plot of ΔS_e^0 ,^{158, 159} the electrostatic entropy of solvation or $\Delta S_{I,II}^0$,^{158, 159} the entropic contributions of the first and second solvation layers of ions against B -points (taken from the works of Nightingale) for both cations and anions lie on the same curve.

There are excellent linear correlations between ΔS_e^0 and ΔS_f^0 and the single ion B -coefficients.

2.5.4. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's¹⁶⁰ approach as:

$$\eta = Ae^{E_{vis}/RT} = (hN/V)e^{\Delta G^*/RT} = (hN/V)e^{(\Delta H^*/RT - \Delta S^*/R)} \quad (49)$$

where E_{vis} = the experimental entropy of activation determined from a plot of $\ln \eta$ against $1/T$. ΔG^* , ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation respectively.

Nightingale and Benck¹⁶¹ dealt in the problem in a different way and calculated the thermodynamics of viscous flow of salts in aqueous solution with the help of the Jones-Dole equation (neglecting the $A\sqrt{c}$ term). Thus, we have:

$$R[d \ln \eta / d(1/T)] = r[d \ln \eta_0 / d(1/T)] + R/(1 + Bc) \cdot d(1 + Bc) / d(1/T)$$

$$\Delta E_{\eta(Soln)}^\ddagger = \Delta E_{\eta_0(Solv)}^\ddagger + \Delta E_V^\ddagger \quad (51)$$

ΔE_v^\ddagger can be interpreted as the increase or decrease of the activation energies for viscous flow of the pure solvents due to the presence of ions, i.e., the effective influence of the ions upon the viscous flow of the solvent molecules.

Feakins et al.¹⁶² have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = (\bar{V}_1^0 - \bar{V}_2^0)/1000 + \bar{V}_1^0 (\Delta\mu_2^{0\ddagger} - \Delta\mu_1^{0\ddagger})/1000RT \quad (52)$$

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

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln \eta_1 \bar{V}_1^0 / hN \quad (53)$$

2.5.5. Effects of Shape and Size

Stokes and Mills 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 Einstein¹⁴¹ leads to the equation:

$$\eta/\eta_0 = 1 + 2.5\phi \quad (54)$$

where, ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by

- (i) Sinha¹⁶³ on the basis of departures from spherical shape and
- (ii) Vand 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 monatomic cations). Thus we have from equation (54):

$$2.5\phi = A\sqrt{c} + Bc \quad (55)$$

Since $A\sqrt{c}$ term can be neglected in comparison with Bc and $\phi = c\bar{V}_1$, where \bar{V}_1 is

the partial molar volume of the ion, we get:

$$2.5\bar{V}_1 = B \quad (56)$$

In the ideal case, the B -coefficient is a linear function of partial molar volume of the solute, \bar{V}_1 with slope to 2.5. Thus, B_{\pm} can be equated to:

$$B_{\pm} = 2.5\bar{V}_{\pm} = 2.5 \times 4/3(\pi R_{\pm}^3 N/1000) \quad (57)$$

assuming that the ions behave like rigid spheres with a effective radii, R_{\pm} , moving in a continuum. R_{\pm} , calculated using the equation (57) should be close to crystallographic radii or corrected Stoke's radii 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_b 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:

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$$B_{\pm} = 2.5/1000(V_i + n_b V_s) \quad (58)$$

where V_i is the molar volume of the base ion and V_s , the molar volume of the solvent. The equation (58) has been used by a number of workers to study the nature of solvation and solvation number.

2.5.6. Viscosity Deviation

Viscosity of liquid mixtures can also provide information for the elucidation of the fundamental behaviors of liquid mixtures, aid in the correlation of mixture viscosities with those of pure components, and may provide a basis for the selection of physicochemical methods of analysis.^{164, 165} Quantitatively, as per the absolute reaction rates theory,¹⁶⁶ the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^j (x_i \eta_i) \quad (59)$$

where η is the dynamic viscosities of the mixture and X_i , η_i are the mole fraction and viscosity of i th component in the mixture, respectively.

2.5.7. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow, G^{*E} can be calculated as:¹⁶⁶

$$G^{*E} = RT[\ln \eta V - \sum_{i=1}^j x_i \ln \eta_i V_i] \quad (60)$$

2.6. Ultrasonic Speed

The acoustic property ‘ultrasonic speed’ is a sensitive indicator of molecular interactions and can provide useful information about these phenomena, particularly in cases where partial molar volume data alone fail to provide an unequivocal interpretation of the interactions.

2.6.1. Apparent Molal Isentropic Compressibility

Although for a long time attention has been paid to the apparent molal isentropic compressibility for electrolytes and other compounds in aqueous solutions,¹⁶⁷⁻¹⁷¹ measurements in non-aqueous⁶¹⁻⁶⁴ solvents are still scarce. It has been emphasized by many authors that the apparent molal isentropic compressibility data can be used as a useful parameter in elucidating the solutesolvent and solute-solute interactions. The isentropic compressibility (K_S) of a solvent/solution can be calculated from the Laplace’s equation:¹⁷²

$$K_S = 1/(u^2 \rho) \quad (61)$$

where ρ is the solution density and u is the ultrasonic speed in the solvent/solution.

The apparent molal isentropic compressibility (ϕ_K) of the solutions was determined from the relation:

$$\phi_K = MK_S / \rho_0 + 1000(K_S \rho_0 - K_S^0 \rho) / m \rho \rho_0 \quad (62)$$

K_s^0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute, \sqrt{m} is the molality of the solution.

The limiting apparent molal isentropic compressibility (ϕ_K^0) was obtained by extrapolating the plots of ϕ_K versus the square root of molal concentration of the solute, m to zero concentration by a least-squares method:¹⁶⁸⁻¹⁷¹

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m} \quad (63)$$

where S_K^* is the experimental slope.

The limiting apparent molal isentropic compressibility (ϕ_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 the decrease in the compressibility of the solution.^{173, 174} This is reflected by the negative values of ϕ_K^0 , of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure.^{62, 173}

The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved.¹⁷³ However, the poor fit of the solute molecules^{175, 176} as well as the possibility of flexible hydrogen bond formation appear to be responsible for causing a more compressible environment and hence positive ϕ_K^0 values have been reported in aqueous non-electrolyte¹⁷⁶ and non-aqueous non-electrolyte¹⁷⁴ solutions.

2.6.2. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility, ΔK_s can be calculated using the following equation:¹⁷⁹⁻¹⁸¹

$$\Delta K_s = K_s - \sum_{i=1}^j X_i K_{s,i} \quad (64)$$

where X_i , $K_{s,i}$ are the mole fraction and isentropic compressibility of i th component in the mixture, respectively.

2.6.3. Acoustical parameters

In an attempt to explore the nature of the interactions occurring between the component liquids in a mixture, various acoustic parameters such as intermolecular free length,¹⁸² L_f ; specific acoustic impedance,¹⁸³ Z ; Van der Waal's constant,¹⁸⁴ b ; molecular radius,¹⁸² r ; geometrical volume,¹⁸² B ; molar surface area,¹⁸⁴ Y ; available volume,¹⁸² V_a ; molar speed of sound,¹⁸⁵ R_s ; relative association,^{185, 186} R_A and molecular association,^{185, 186} M_A of the binary mixtures have been calculated using the following equations:

$$L_f = K \sqrt{K_S} \quad (65)$$

$$Z = u \rho \quad (66)$$

$$b = (M / \rho) - (RT / \rho^2 u^2) \{ [1 + (Mu^2 / 3RT)]^{\frac{1}{2}} - 1 \} \quad (67)$$

$$r = (3b / 16 \pi N_A)^{\frac{1}{3}} \quad (68)$$

$$Y = [36 \pi N_A B^2]^{\frac{1}{3}} \quad (69)$$

$$V_a = V (1 - u / u_\infty) \quad (70)$$

$$V_0 = V - V_a \quad (71)$$

$$R_s = \overline{M} u^{\frac{1}{3}} / \rho \quad (72)$$

$$R_A = (\rho_{\text{mix}} / \rho) (u / u_{\text{mix}})^{\frac{1}{3}} \quad (73)$$

$$M_A = [(76)^2 - 1] \quad (74)$$

where K is a temperature dependent constant,¹⁸² T is the absolute temperature, R is the universal gas constant, N_A is the Avogadro's number, \overline{M} is the average molecular weight, V_0 is the volume at absolute zero, ρ_{mix} and u_{mix} are the density and speed of sound of the mixture, respectively.

2.7. Correlating Equations

Several semi-empirical models have been proposed to estimate the dynamic viscosity (η) of the binary liquid mixtures in terms of pure-component data.^{187, 188} Some of them we examined are as follows:

a) The viscosity values can be further used to determine the Grunberg-Nissan parameter, d_{12} as:¹⁸⁹

$$\eta = \exp\left[\sum_{i=1}^j (x_i \ln \eta_i) + d_{12} \prod_{i=1}^j x_i\right] \quad (75)$$

and d_{12} is proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The negative values of d_{12} indicate the presence of dispersion forces¹⁹⁰ between the mixing components in the mixtures while its positive values indicate the presence of specific interactions¹⁹⁰ between them.

b) Tamura-Kurata¹⁹¹ put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^j x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^j [x_i \phi_i]^{1/2} \quad (76)$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of i^{th} pure component in the mixture.

c) Molecular interactions may also be interpreted by the following viscosity model of Hind et al:¹⁹²

$$\eta = \sum_{i=1}^j x_i^2 \eta_i + 2H_{12} \prod_{i=1}^j x_i \quad (77)$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction.¹⁹³ It has been observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other, this is in agreement with the view put forward by Fort and Moore¹⁹⁰ in regard to the nature of parameter T_{12} and H_{12} .

d) McAllister's three-body model:¹⁹⁵

$$\begin{aligned} \ln v = & x_1^3 \ln v_1 + x_2^3 \ln v_2 + 3x_1^2 x_2 \ln v_{12} + 3x_2^3 x_1 \ln v_{21} - \ln \left[x_1 + \frac{x_2 M_2}{M_1} \right] \\ & + 3x_1^2 x_2 \ln \left[\frac{2}{3} + \frac{M_2}{3M_1} \right] + 3x_2^3 x_1 \ln \left[\frac{1}{3} + \frac{2M_2}{3M_1} \right] + x_2^3 \ln \left[\frac{M_2}{M_1} \right] \end{aligned} \quad (78)$$

e) McAllister's four-body model: ¹¹⁵

$$\begin{aligned} \ln v = & x_1^4 \ln v_1 + 4x_1^3 x_2 \ln v_{1112} + 6x_1^2 x_2^2 \ln v_{1122} + 4x_1 x_2^3 \ln v_{2221} + x_2^4 \ln v_2 \\ & - \ln \left[x_1 + x_2 \left(\frac{M_2}{M_1} \right) \right] + 4x_1^3 x_2 \ln \left[\frac{3}{4} + \frac{M_2}{4M_1} \right] + 6x_1^2 x_2^2 \ln \left[\frac{1}{2} + \frac{M_2}{2M_1} \right] \\ & + 4x_1 x_2^3 \ln \left[\frac{1}{3} + \frac{3M_2}{4M_1} \right] + x_2^4 \ln \left[\frac{M_2}{M_1} \right] \end{aligned} \quad (79)$$

f) Heric-Brewer model: ¹⁹⁶

$$v = x_1 v_1 + x_2 v_2 + x_1 x_2 \left\{ a + b(x_1 - x_2) + c(x_1 - x_2)^2 \right\} \quad (80)$$

where v_1 and v_2 are kinematic viscosities of the mixture, the pure component 1 and 2, respectively. v_{12} , v_{21} , v_{1112} , v_{1122} , v_{2221} , a , b and c are model parameters and X_i and M_i are the mole fraction and molecular weight of the i^{th} pure component in the mixture, respectively.

Moreover, The excess or deviation properties (V^E , $\Delta\eta$, G^E and ΔK_s) have been fitted to Redlich-Kister¹⁹⁴ polynomial equation using the method of least squares involving the Marquardt algorithm¹⁹⁷ and the binary coefficients, a_i were determined as follows:

$$Y^E = x_1 x_2 \sum_{i=1}^J a_i (x_1 - x_2)^i \quad (81)$$

where Y^E refers to an excess or deviation property X_1 and X_2 are the mole fraction of the solvent 1 and solvent 2, respectively. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The standard deviation (σ) was calculated using,

$$\sigma = [(Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2 / (n - m)]^{1/2} \quad (82)$$

where n is the number of data points and m is the number of coefficients.

2.8. Conductance

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte of solutions.^{198, 199} The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic theories are not applicable. Recently developed experimental techniques provide an accuracy of $\pm 0.01\%$ or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitation, however, is the colligative like nature of the information obtained.

Since the conductometric method primarily depends on the mobility of ions, it can be suitably utilized to determine the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents. The conductometric method in conjunction with viscosity measurements gives us much information regarding the ion-ion and ion-solvent interactions. However, the choice and application of theoretical equations as well as equipment and experimental techniques are of great importance for precise measurements. These aspects have been described in details in a number of authoritative books and reviews.¹⁹⁸⁻²¹¹

The study of conductance measurements were pursued vigorously both theoretically and experimentally during the last five decades and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents.

The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager²¹² to derive the Kohlrausch's equation representing the molar conductance of an electrolyte. For solutions of a single symmetrical electrolyte the equation is given by:

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (83)$$

$$\text{where, } S = \alpha\Lambda_0 + \beta \quad (84)$$

$$\alpha = (ze)^2 \kappa / 3(2 + \sqrt{2})\epsilon_r kT\sqrt{c} = 82.406 \times 10^4 z^3 / (\epsilon_r T)^{3/2} \quad (85a)$$

$$\beta = z^2 e F \kappa / 3\pi\eta\sqrt{c} = 82.487 z^3 / \eta\sqrt{\epsilon_r T} \quad (85b)$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution.

However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss Onsager theory differed considerably²¹³ from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned.^{199, 214-216} The original Fuoss-Onsager equation was further modified by Fuoss and Hsia²¹⁷ who recalculated the relaxation field, retaining the terms which had previously been neglected.

The results of conductance theories can be expressed in a general form by:

$$\Lambda = \Lambda_0 - \alpha\Lambda_0\sqrt{c} / (1 + \kappa a)(1 + \kappa a / \sqrt{2}) - \beta\sqrt{c} / (1 + \kappa a) + G(\kappa a) \quad (86)$$

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt[3]{c} \quad (87)$$

is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini.^{199, 218, 219} Further correction of the equation (87) was made by Fuoss and Accascina.²⁰³

They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt[3]{c} - F\Lambda c \quad (88)$$

In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions.²²⁰

2.8.1. Ionic Association

The equation (83) successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against \sqrt{c} (limiting Onsager equation) is used to assign the dissociation or association of electrolytes. Thus, if Λ_{exp}^0 is greater than Λ_{theo}^0 i.e., if positive deviation occurs (ascribed to short range hard core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviation ($\Lambda_{\text{exp}}^0 < \Lambda_{\text{theo}}^0$) or positive deviation from the Onsager limiting tangent ($\alpha \Lambda_0 + \beta$) occurs, the electrolyte may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in Λ_{theo}^0 and Λ_{exp}^0 would be considerable with increasing association.²²¹

Conductance measurements help us to determine the values of the ion-pair association constant, K_A for the process:



$$K_A = (1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 \quad (90)$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (91)$$

where γ_{\pm} is the mean activity coefficient of the free ions at concentration αc .

For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation²²³ or Shedlovsky's equation:²²⁴

$$T(z)/\Lambda = 1/\Lambda_0 + K_A/\Lambda_0^2 c \gamma_{\pm}^2 \Lambda/T(z) \quad (92)$$

where $T(z) = F(z)$ (Fuoss-Kraus method) and $1/T(z) = S(z)$ (Shedlovsky's method):

$$F(z) = 1 - z(1 - z(1 - \dots)^{-1/2})^{-1/2} \quad (93a)$$

$$\text{and } 1/T(z) \equiv S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (93b)$$

A plot of $T(z) / \Lambda$ against $c \gamma_{\pm}^2 A / T(z)$ should be a straight line having $1 / \Lambda_0$ for its intercept and K_A / Λ_0^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (92).

The Fuoss-Hsia²¹⁸ conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (94)$$

The equation was modified by Justice.²²⁵ The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c}) + E(\alpha c)\ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \quad (95)$$

$$(1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 = K_A \quad (96)$$

$$\ln \gamma_{\pm} = -k\sqrt{q} / (1 + kR\sqrt{\alpha c}) \quad (97)$$

According to Justice the method of fixing the J -coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. Since the equation (95) is a series expansion truncated at the $C^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much as possible by J_2 rather than by K_A , whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction.

From the experimental values of the association constant K_A , one can use two methods in order to determine the distance of closest approach, a , of two free ions to form an ion-pair. The following equation has been proposed by Fuoss:²²⁶

$$K_A = (4\pi N_A a^3 / 3000) \exp(e^2 / a \epsilon kT) \quad (98)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a . The distance parameter was finally determined from the more general equation due to Bjerrum:²²⁷

$$K_A = 4\pi N_A a / 1000 \int_{r=a}^{r=q} r^2 \exp(z^2 e^2 / r \epsilon kT) dr \quad (99)$$

The equations neglect specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilized by Douheret.²²⁸

2.8.2. Ion size Parameter and Ionic Association

For plotting, equation (80) can be rearranged to the 'A' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec \ln c = \Lambda_0 + J_1c + J_2\sqrt[3]{c} = \Lambda_0 + J_1c \quad (100)$$

with J_2 term omitted.

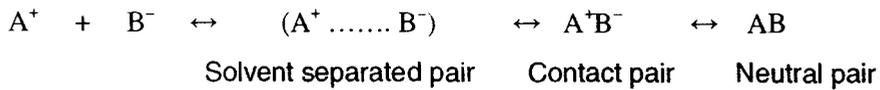
Thus, a plot of Λ_0 vs c gives a straight line with Λ_0 as intercept and J_1 as slope and 'a' values can be calculated from J_1 values. One of the reasons attributed to it is that ion-solvent interactions are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in 'a' values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction leads to a larger value of 'a'²²⁹ but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J_1 .²³⁰

Fuoss²³¹ in 1978 proposed a new conductance equation. Later he subsequently put forward another conductance equation in 1978 replacing the old one as suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

(i) Ions finding an ion of opposite charge in the first shell of nearest neighbours (contact pairs) with $r_{ij} = a$. The nearest neighbors to a contact pair are the solvent molecules forming a cage around the pairs.

(ii) Ions with overlapping Gurney's co-spheres (solvent separated pairs). For them $r_{ij} = (a + ns)$, where n is generally 1 but may be 2, 3 etc.; 's' is the diameter of sphere corresponding to the average volume (actual plus free) per solvent molecule.

(iii) Ions finding no other unpaired ion in a surrounding sphere of radius R , the diameter of the co-sphere (unpaired ions). Thermal motions and interionic forces establish a steady state, represented by the following equilibria:



Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- = AB$

e.g., H_3O^+ and CH_3COO^- . Let γ be the fraction of solute present as unpaired ($r > R$) ions.

If $c\gamma$ is the concentration of unpaired ion and α is the fraction of paired ions ($r \leq R$), then the concentration of the solvent separated pair is $c(1-\alpha)(1-\gamma)$ and that of contact pair is $\alpha c(1-\gamma)$.

The equation constants for (93) are:

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 f^2 \tag{101}$$

$$K_S = \alpha/(1-\alpha) = \exp(-E_s/kT) = e^{-\epsilon} \tag{102}$$

where K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter R around cations and can be calculated by continuum theory; K_S is the constant describing the specific shortrange ion-solvent and ion-ion interactions by which contact pairs form and dissociate. E_s is the difference in energy between a pair in the states ($r = R$) and ($r = a$); ϵ is E_s measured in units of kT .

Now, $(1-\alpha) = 1/(1+K_S)$ (103)

And the conductometric pairing constant is given by:

$$K_A = (1-\alpha)/c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \tag{104}$$

The equation determines the concentration, $c\gamma$, of active ions that produce longrange interionic effects by unpaired ions, their interaction with unpaired ions is, therefore, neglected in calculating long-range effects (activity coefficients, relaxation field ΔX and electrophoresis ΔA_e). The various patterns can be reproduced by theoretical fractions in the form:

$$\Lambda = p[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e] = p[\Lambda_0(1+R_x) + E_L] \tag{105}$$

which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_0, R, E_s)$ and $\Delta\Lambda/X$ (the relaxation field) and $\Delta\Lambda_e$ (the electrophoretic counter current) are long-range effects due to electrostatic interionic forces and p is the fraction of solute which contributes to conductance current. R is the diameter of the Gurney co-sphere.

The parameter K_R (or E_s) is a catch-all for all short-range effects:

$$p = 1 - \alpha(1 - \gamma) \quad (106)$$

In case of ionogens or for ionophores in solvents of low dielectric constant, α is very near to unity ($-E_s/kT \gg 1$) and the equation becomes:

$$\Lambda = \gamma[\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e] \quad (107)$$

The equilibrium constant for the effective reaction, $A^+ + B^- = AB$, is then:

$$K_A = (1 - \gamma)/c\gamma^2 f^2 \approx K_R K_S \quad (108)$$

as $K_S \gg 1$. The parameters and the variables are related by the set of equations:

$$\gamma = 1 - K_R c \gamma^2 f^2 / (1 - \alpha) \quad (109)$$

$$K_R = (4\pi N_A R^3 / 3000) \exp(\beta/R) \quad (110)$$

$$-\ln f = \beta_\kappa / 2(1 + \kappa R), \quad \beta = e^2 / \epsilon kT \quad (111)$$

$$\kappa^2 = 8\pi\beta\gamma n = \pi\beta N_A \gamma c / 125 \quad (112)$$

$$-\epsilon = \ln[\alpha/(1 - \alpha)] \quad (113)$$

The details of the calculations are presented in the 1978 paper.²³¹ The shortcomings of the previous equations have been rectified in the present equation that is also more general than the previous equations and can be used for higher concentrations (0.1 N in aqueous solutions).

2.8.3. Limiting Equivalent Conductance

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surrounding solvent molecules, as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \quad (114)$$

At present, limiting equivalent conductance is the only function that can be divided into ionic components using experimentally determined transport number of ions, i.e., and

$$\lambda_+^0 = t_+ \Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_- \Lambda_0 \quad (115)$$

Thus, from accurate value of λ^0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions.²³² However, accurate transference number determinations are limited to few solvents only. Spiro²³³ and Krumgalz²³⁴ have made extensive reviews on the subject.

In absence of experimentally measured transference numbers, it would be useful to develop indirect methods to obtain the limiting equivalent conductance in organic solvents for which experimental transference numbers are not yet available.

The method has been summarized by Krumgalz²³⁴ and some important points are mentioned below:

(i) Walden equation,²³⁵ $(\lambda_{\pm}^0)_{\text{water}}^{25} \cdot \eta_{0, \text{water}} = (\lambda_{\pm}^0)_{\text{acetone}}^{25} \cdot \eta_{0, \text{acetone}}$ (116)

(ii)

$$\left. \begin{array}{l} \lambda_{\text{pic}^-}^0 \eta_0 = 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^0 \eta_0 = 0.296 \end{array} \right|_{\text{based on } \Lambda_{\text{Et}_4\text{N}^+\text{pic}^-}^0 = 0.563}^{231, 232} \quad (117)$$

Walden considered the products to be independent of temperature and solvent. However the $\lambda_{\text{Et}_4\text{N}_{\text{pic}}}^0$ values used by Walden was found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

$$(iii) \quad \lambda_{25}^0(\text{Bu}_4\text{N}^+) = \lambda_{25}^0(\text{Ph}_4\text{B}^-)^{232} \quad (118)$$

The equality holds good in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

$$(iv) \quad \lambda_{25}^0(\text{Bu}_4\text{N}^+) = \lambda_{25}^0(\text{Bu}_4\text{B}^-)^{233} \quad (119)$$

The method appears to be sound as the negative charge on boron in the Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^- .

(v) The equation suggested by Gill²³⁸ is:

$$\lambda_{25}^0(\text{R}_4\text{N}^+) = zF^2 / 6\pi N_A \eta_0 [r_i - (0.0103 \epsilon_0 + r_y)] \quad (120)$$

where Z and r_i are charge and crystallographic radius of proper ion, respectively; η_0 and ϵ_0 are solvent viscosity and dielectric constant of the medium, respectively; r_y = adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents respectively.

In a paper,^{234(b)} Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents e.g. butan-1-ol, acetonitrile and nitromethane.

$$(vi) \quad \lambda_{25}^0[(i - \text{Am})_3\text{BuN}^+] = \lambda_{25}^0(\text{Ph}_4\text{B}^-)^{235} \quad (121)$$

It has been found from transference number measurements that the $\lambda_{25}^0[(i - \text{Am})_3\text{BuN}^+]$

and $\lambda_{25}^0(\text{Ph}_4\text{B}^-)$ values differ from one another by 1%.

$$(vii) \quad \lambda_{25}^0(\text{Ph}_4\text{B}^-) = 1.01\lambda_{25}^0(i - \text{Am}_4\text{B}^-)^{2.36} \quad (122)$$

The value is found to be true for various organic solvents. Krumgalz²³⁴ suggested a method for determining the limiting ion conductance in organic solvents. The method is based on the fact that large tetraalkyl(aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_0 values into ionic components for non-aqueous electrolytic solutions.

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

$$r_s = \left| z \right| F^2 / A \pi \eta_0 \lambda_{\pm}^0 \quad (123)$$

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

$$\lambda_{\pm}^0 \eta_0 = \text{constant} \quad (124)$$

This relation has been verified using λ_{\pm}^0 values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^-$, Ph_4As^+ and Ph_4B^- ions and for tetraalkylammonium cations starting with Et_4N^+ . The relationship can be well utilized to determine λ_{\pm}^0 of ions in other organic solvents from the determined Λ_0 values.

2.8.4. Solvation Number

If the limiting conductance of the ion i of charge z is known, the effective radius of the solvated ion can easily be determined from the Stokes' law. The volume of the solvation shell V_s , can be written as:

$$V_s = (4\pi/3)(r_s^3 - r_c^3) \quad (125)$$

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

$$n_s = V_s / V_0 \quad (126)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects²⁴¹ from

$$V_s^0 = 4.35r_s^3 \quad (127)$$

where V_s^0 is expressed in mol/litre 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 equations²⁰⁴ and theoretical corrections²⁴²⁻²⁴⁵ have been suggested to make the general method.

2.8.5. Stokes' Law and Walden's Rule

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

$$\lambda_i^0 = |z_i e| \hat{e} F / 6\pi\eta_0 R_i = 0.819|z_i| / \eta_0 R_i \quad (128)$$

where η_0 = macroscopic viscosity by the solvent in poise, R_i is in angstroms. If the radius R_i is assumed to be the same in every organic solvent, as would be the case in case of bulky organic ions, we get:

$$\lambda_i^0 \eta_0 = 0.819|z_i| / R_i = \text{constant} \quad (129)$$

This is known as Walden's rule.²⁴⁶ The effective radii obtained using the equation can be used to obtain solvation number. The failure of Stokes' radii to give the effective size of the solvated ion for small ions is generally ascribed to the inapplicability of Stokes' law to molecular motions.

Robinson and Stokes,²⁰⁴ Nightingale¹⁴⁰ and others²⁴⁷⁻²⁴⁹ have suggested a method of correcting the radii. However, the experimental results indicate that the method is incorrect as the method is based on the wrong assumption of the invariance of Walden's

product with temperature. The idea of microscopic viscosity²⁵⁰ was invoked without much success^{251, 252} but it has been found that:

$$\lambda_i^0 \eta^p = \text{constant} \quad (130)$$

where p is usually 0.7 for alkali metal or halide ions and p = 1 for the large ions.^{253, 254}

Attempts to explain the change in the Stokes' radius R_i have been made. The apparent increase in the real radius, r has been attributed to ion-dipole polarization and the effect of dielectric saturation on R.

The dependence of Walden product on the dielectric constant led Fuoss²⁵⁵ to consider the effect of the electrostatic forces on the hydrodynamics of the system. Considering the excess frictional resistance caused by the dielectric relaxation in the solvent caused by ionic motion, Fuoss proposed the relation:

$$\lambda_{i,0}^0 = F e |z_i| / 6\pi R_\infty (1 + A/\epsilon R_\infty^2) \quad (131)$$

$$\text{or, } R_i = R_\infty + A/\epsilon \quad (132)$$

where R_∞ is the hydrodynamic radius of the ion in a hypothetical medium of dielectric constant where all electrostatic forces vanish and A is an empirical constant.

Boyd²⁴³ gave the expression:

$$\lambda_i^0 = F e |z_i| / 6\pi \eta_0 r_i [1 + (2/27 \pi \eta_0 \cdot Z_i^2 e^2 \tau / r_i^4 \epsilon_0)] \quad (133)$$

by considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles.

Zwanzig²⁴⁴ treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda_i^0 = z_i^2 e F / \{A_V \pi \eta_0 r_i + A_D [z_i^2 e^2 (\epsilon_r^0 - \epsilon_r^\infty) \tau / \epsilon_r^0 (2\epsilon_r^0 + 1) r_i^3]\} \quad (134)$$

$\epsilon_r^0, \epsilon_r^\infty$ are the static and limiting high frequency (optical) dielectric constants. $A_V = 6$ and $A_D = 3/8$ for perfect sticking and $A_V = 4$ and $A_D = 3/4$ for perfect slipping. It has been found that Born's²⁴² and Zwanzig's²⁴⁴ equations are very similar and both may be written in the form:

$$\lambda_i^0 = A r_i^3 / (r_i^4 + B) \quad (135)$$

The theory predicts²⁵⁶ that λ_i^0 pass through a maximum of $27^{1/4} A / 4 B^{1/4}$ at $r_i = (3B)^{1/4}$. The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius.

For comparison with results in different solvents, the equation (129) can be rearranged as:²⁵⁷

$$z_i^2 e F / \lambda_i^0 \eta_0 = A_V \pi r_i + A_D z_i^2 / r_i^3 \cdot e^2 (\epsilon_r^0 - \epsilon_r^\infty) / \epsilon_r^0 (2\epsilon_r^0 + 1) \cdot \tau / \eta_0 \quad (136)$$

$$\text{or, } L^* = A_V \pi r_i + A_D z_i^2 / r_i^3 P^* \quad (137)$$

In order to test Zwanzig's theory, the equation (130) was applied for Me_4N^+ and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol.²⁵⁶⁻²⁷¹ Plots of L^* against the solvent function P^* were found to be straight line. But the radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that relaxation effect is not the predominant factor affecting ionic mobility and these mobility differences could be explained quantitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from the Stokes' law.²³²

It is found that the Zwanzig's theory is successful for large organic cations in aprotic media where solvation is likely to be minimum and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large, i.e., for solvents of high P^* and for ions of small r_i . Like any continuum theory Zwanzig has the inherent weakness of its inability to account for the structural features,²⁵⁷ e.g.,

(i) It does not allow for any correlation in the orientation of the solvent molecules as the ion passes by and this may be the reason why the equation is not applicable to the hydrogen-bonded solvents.²⁵⁸

(ii) The theory does not distinguish between positively and negatively charged ions and therefore, cannot explain why certain anions in dipolar aprotic media possess considerably higher molar concentrations than the fastest cations.²⁵⁷

The Walden product in case of mixed solvents does not show any constancy but it shows a maximum in case of DMF + water and DMA + water²⁵⁶⁻²⁶⁶ mixtures and other aqueous binary mixtures.²⁷⁰⁻²⁷³ To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts^{243, 244, 274} have been made with different models for ion-solvent interactions but no satisfactory expression has been derived taking into account all types of ion solvent interactions because (i) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression and (ii) it is not possible to account for some specific properties of different kinds of ions and solvent molecules.

Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Though Zwanzig's expression accounts for a change in Walden product with solvent composition but does not account for the maxima. According to Hemmes,²⁷² the major deviations in the Walden products are due to the variation in the electrochemical equilibrium between ions and solvent molecules of mixed polar solvent composition.

In cases where more than one types of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Hubbard and Onsager²⁷³ have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the concept of kinetic polarization deficiency has been introduced.

However, quantitative expression is still awaited. Further, improvements²⁷⁴⁻²⁷⁶ naturally must be in terms of (i) sophisticated treatment of dielectric saturation, (ii) specific structural effects involving ion-solvent interactions.

From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to explore this problem using different experimental

techniques. We have, therefore, utilized four important methods, viz., volumetric, viscometric, interferometric and conductometric for the physico-chemical studies in different solvent media.

2.9. Solvation Models- Some Recent Trends

The advantage of models like SM 1- SM 5 series is that they can be used to predict the free energy of self-solvation to better than 1 KCl /mole. These are especially useful when other methods are not available. One can also analyze factors like electrostatics, dispersion, hydrogen bonding, etc. using these tools. They are also relatively inexpensive and available in easy to use computer codes.

A.Galindo et al.^{282, 283} 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 is found for a number of aqueous electrolyte solutions. The relative permittivity becomes very close to unity, especially when the mean spherical approximation is used, indicating a good description of the solvent. E. Bosch et al.²⁸³ of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

2.10. Conductance- Some Recent Trends

Recently Blum, Turq and coworkers^{284, 285} have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from the same continuity and hydrodynamic equations used in the more classical treatment; however, an important difference exists in the use of MSA expressions for the equilibrium and structural properties of the electrolytic solutions. They compared the results obtained using the old and new equations in order to evaluate their capacity to

describe the conductivity of different electrolytic solutions. In 2000, Chandra and Bagchi^{286,287} developed a new microscopic approach to ionic conductance and viscosity based on the mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structural factors of charge and number density of the electrolytic solutions. They claim that their new equation is applicable at low as well as at high concentrations and it describes the cross over from low to high concentration smoothly. Debye-Huckel, Onsager and Falkenhagen expressions can be derived from this self-consistent theory at very low concentrations. For conductance, the agreement seems to be satisfactory up to 1 M.

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