

CHAPTER II

General Introduction

2.1. Investigation on Viscous Synergy and Antagonism

Rheology is the branch of science¹ that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products²⁻¹¹, and to establish their stability and even bioavailability, since it has been firmly established that viscosity influences the drug absorption rate in the body^{12, 13}.

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

If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction^{14, 15}.

Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of each component considered separately.

In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately.

The method most widely used to analyze the synergic and antagonistic behavior of the ternary liquid mixtures used here is that developed by Kaletunc-Gencer and Peleg¹⁶ allowing quantification of the synergic and antagonistic interactions taking place in the 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_{calc} defined by the simple mixing rule as:

$$\eta_{calc} = \sum_i w_i \eta_i \quad(1)$$

where w is the fraction by weight of the system and η is the viscosity of the system, measured experimentally and i is an integer having values 1,2,3...

Accordingly, when $\eta_{\text{exp}} > \eta_{\text{calc}}$, viscous synergy exists, while, when $\eta_{\text{calc}} > \eta_{\text{exp}}$, the system is said to exhibit viscous antagonism.

This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other synergy indices are defined in consequence¹⁷.

In order to secure more comparable viscous synergy results, the so called synergic interaction index (I_S) introduced by Howell¹⁸ is taken into account:

$$I_S = (\eta_{\text{exp}} - \eta_{\text{calc}}) / \eta_{\text{calc}} = \Delta\eta / \eta_{\text{calc}} \quad \dots\dots\dots(2)$$

The negative value of I_S gives antagonistic interaction index (I_A).

The method used to analyze volume contraction and expansion is similar to that applied to viscosity, i.e., the density of the mixture is determined experimentally, ρ_{exp} , and a calculation is made for ρ_{calc} based on the expression:

$$\rho_{\text{calc}} = \sum_i w_i \rho_i \quad \dots\dots\dots(3)$$

where ρ is the experimentally measured density of the system. Other symbols have their usual significance.

Accordingly, when $\rho_{\text{exp}} > \rho_{\text{calc}}$, volume contraction occurs, while, when $\rho_{\text{calc}} > \rho_{\text{exp}}$, there is volume expansion in the system.

Besides this, a power factor, F_η has also been studied¹ which is the enhancement index of the viscosity given as:

$$F_\eta = \eta_{\text{max}} / \eta_0 \quad \dots\dots\dots(4)$$

where, η_{max} is the maximum viscosity attained in the mixture and η_0 is the experimental viscosity of the pure components.

The investigations have been carried out with the binary mixture of ethylene glycol, tetrahydrofuran and 1,4-dioxane; ternary mixture of

ethylene glycol, water, tetrahydrofuran, 1,4-dioxane, N,N-dimethylformamide and dimethyl sulphoxide; ternary mixture of tetrahydrofuran, methanol, benzene, i-propanol and n-hexane; ternary mixture of 1,3-dioxolane, water and monoalkanols. The monoalkanols include methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), t-butanol (t-BuOH) and i-amyl alcohol (i-AmOH). These have been chosen for better comparison. Beyond this, higher alcohols are found to be practically insoluble in the aqueous medium of cyclic diether i.e., 1,3-dioxolane.

2.2. Investigation on Ion-Solvent Interaction

The majority of reactions occurring in solutions are of chemical or biological in nature. 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 solvents¹⁹⁻²⁸.

In nature water is the most abundant solvent. In view of the major importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic and equilibrium studies. In spite of this, our knowledge of molecular interactions in water is extremely limited. Moreover, the uniqueness of water as a solvent has been questioned^{29,30} and it has been realized that the studies in other solvent media like non-aqueous and mixed solvents would be of great help in understanding different molecular interactions and a host of complicated phenomena¹⁹⁻²⁸.

The organic solvents have been classified based on the dielectric constants, organic group types, acid base properties or association through hydrogen bonding²⁸, donor-acceptor properties^{31,32}, hard and soft acid-base principles³³, etc. As a result, the different solvent systems show a wide divergence of properties which would naturally be reflected on the thermodynamic, transport and acoustic properties of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions which are the controlling forces

in infinitely dilute solutions where ion-ion interactions are absent. It is possible by separating these functions into ionic contributions to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a very important role to understand the physico-chemical properties of solutions.

One of the causes for the intricacies in solution chemistry is that the structure of the solvent molecule is not known with certainty. The introduction of a solute also modifies the solvent structure to an uncertain magnitude whereas the solute molecule is also modified and 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.

The problems of ion-solvent interactions which are closely akin to ionic solvations can be studied from different angles using almost all the available physico-chemical techniques.

Ion-solvent interactions can be studied spectroscopically: the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes of free energy, enthalpy and entropy, etc. associated with a particular reaction can be qualitatively and quantitatively evaluated using various physico-chemical techniques from which conclusions regarding the factors associated with the ion-solvent interactions can be worked out.

Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of different properties such as, **density, viscosity, ultrasonic speed and conductance** of electrolytes and derive the various factors associated with ionic solvation.

We shall particularly dwell upon the different aspects of these thermodynamic, transport and acoustic properties as the present dissertation is intimately related to the studies of ion-ion, ion-solvent and solvent-solvent interactions.

2.3. Density

One of the well recognized approaches to the study of molecular interactions in fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions.

Various concepts regarding molecular processes in solutions, electrostriction³⁴, hydrophobic hydration³⁵, micellization³⁶ and cosphere overlap during solute-solvent interactions³⁷ to a large extent have been derived and interpreted from the partial molar volume data of many compounds.

2.3.1. Apparent and Partial Molar Volumes

The apparent molar volumes, V_φ of the solutes can be calculated by using the following relation³⁸:

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

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 equation³⁹:

$$\bar{V}_2 = V_\varphi + (1000 - c V_\varphi) / (2000 + c^{3/2} \cdot \partial V_\varphi / \partial \sqrt{c}) c^{1/2} \cdot \partial V_\varphi / \partial \sqrt{c} \quad \dots(6)$$

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 the period of years – the Masson equation⁴⁰, the Redlich-Meyer equation⁴¹, the Owen-Brinkley equation⁴² and the Pitzer equation⁴³. Masson⁴⁰ found that

the apparent molar volume of electrolyte, V_ϕ , vary with the square root of the molar concentration by the linear equation:

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \quad \dots\dots\dots(7)$$

where V_ϕ^0 is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution, \bar{V}_2^0) and S_V^* is the experimental slope. The majority of V_ϕ data in water⁴⁴ and nearly all V_ϕ data in non-aqueous⁴⁵⁻⁴⁹ solvents have been extrapolated to infinite dilution through the use of equation (7).

The temperature dependence of V_ϕ^0 for various investigated electrolytes in various solvents can be expressed by the general equation as follows:

$$V_\phi^0 = a_0 + a_1 \cdot T + a_2 \cdot T^2 \quad \dots\dots\dots(8)$$

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

The limiting apparent molar expansibilities (Φ_E^0) can be calculated from the general equation (8). Thus,

$$\Phi_E^0 = (\delta V_\phi^0 / \delta T)_P = a_0 + 2 a_2 T \quad \dots\dots\dots(9)$$

The limiting apparent molar expansibilities (Φ_E^0) change in magnitude with the change of temperature.

During the past few years it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler⁵⁰ developed a technique of examining the sign of $(\delta^2 V_\phi^0 / \delta T^2)_P$ for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$(\delta c_P / \delta P)_T = - (\delta^2 V_\phi^0 / \delta T^2)_P \quad \dots\dots\dots(10)$$

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 Meyer⁴¹ have shown that an equation of the form of (7) cannot be more than a limiting law, where for a given solvent and temperature the slope, S_V^* should depend only upon the valence type. They suggest representing V_ϕ by:

$$V_\phi = V_\phi^0 + S_V \sqrt{c} + b_V c \quad \dots\dots\dots(11)$$

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

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

$$w = 0.5 \sum_i \gamma_i Z_i^2 \quad \dots\dots\dots(13)$$

$$\text{and, } K = N^2 e^3 (8 \pi / 1000 \epsilon^3 R T)^{1/2} [(\partial \ln \epsilon / \partial p)_T \cdot \beta / 3] \quad \dots(14)$$

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.

The Redlich-Meyer⁴¹ extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However, studies⁵¹⁻⁵³ on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation.

Thus for polyvalent electrolytes, the more complete Owen-Brinkley equation⁴² 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:

$$V_\phi = V_\phi^0 + S_V \tau(k a) c^{1/2} + 0.5 W_V \theta(k a) c + 0.5 K_V c \quad \dots\dots\dots(15)$$

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

Recently, the Pitzer formalism has been used by Pogue⁵⁴ and Atkinson to fit the apparent molar volume data. The Pitzer equation for the apparent molar volume of a single salt $M\gamma_M M\gamma_X$ is:

$$V_\phi = V_\phi^0 + V | Z_M Z_X | A_V | 2 b I n (I + b I^{1/2}) + 2 \gamma_M \gamma_X R T [m B_{MX}^2 + m^2 (\gamma_M \gamma_X)^{1/2} C v_{MX}] \dots\dots\dots(16)$$

where the symbols have their usual significance.

2.3.2. Apparent and Partial Molar Expansibility

The partial molar expansibility (E_2) has been calculated from the equation¹⁹:

$$E_2 = E_\phi + [(1000 - c E_\phi) (2000 + S_E c^{3/2})^{-1}] S_E c^{1/2} \dots\dots\dots(17)$$

Here, E_ϕ is the apparent molar expansibility and is determined from equation:

$$E_\phi = a_0 V_\phi + (a - a_0) 1000 c^{-1} \dots\dots\dots(18)$$

where, a_0 and a are the coefficient of thermal expansion of the solvent and solution respectively and are obtained by the usual relation as follows:

$$a_0 = -1 / \rho_0 (\delta \rho_0 / \delta T) \text{ and } a = -1 / \rho (\delta \rho / \delta T) \dots\dots\dots(19)$$

The apparent molar expansibility of electrolyte, E_ϕ , vary with the square root of the molar concentration by the linear equation:

$$E_\phi = E_\phi^0 + S_E \sqrt{c} \dots\dots\dots(20)$$

where E_ϕ^0 is the limiting apparent molar expansibility or the partial molar expansibility at infinite dilution (E_2^0) and S_E is the experimental slope.

2.3.3. Ionic Limiting Partial Molar Volumes

The calculation of the ionic limiting partial molar volumes in organic solvents is a very difficult task. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions⁵⁵ to non-aqueous electrolyte solutions.

In the last few years, the method suggested by Conway et al.⁵⁵ 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}_{RNX}^θ for a series of these salts with a halide ion in common as a function of the formula weight of the cation, M_{RN^+} and obtained straight-line graphs for each series. They suggested, therefore, their results fitted the equation:

$$\bar{V}_{RNX}^\theta = \bar{V}_x^\theta + b M_{RN^+} \quad \dots\dots\dots(21)$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, \bar{V}_x^θ .

Josaki et al.⁵⁶ have used this method for the separation of some literature values and of their own \bar{V}_{RNX}^θ values into ionic contributions in organic electrolyte solutions. Krumgalz⁵⁷ applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.3.4. 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^{58, 59}:

$$V^E = \sum_{i=1}^n x_i M_i (1/\rho - 1/\rho_i) \quad \dots\dots\dots(22)$$

where M_i , ρ_i and ρ are the molar mass of the i^{th} component, density of the i^{th} component and density of the solution mixture respectively.

2.4. Viscosity

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively^{60,61}. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, \bar{V}_2 , i.e., the partial molar volume, gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solutions.

The viscosity relationships of electrolytic solutions are highly complicated. There are strong electrical forces between the ions and between the ions and solvent and separation of the forces are not really possible. But from careful analysis, valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system.

The 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 therefore, 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. An ion with a large rigid co-sphere for a structure promoting ion will behave as a rigid sphere placed in the liquid and increase the inter planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules, will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity.

The first systematic measurements of viscosities of a number of electrolyte solutions over a wide concentration range were performed by Grüneisen⁶² in 1905. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole⁶³ suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations, c :

$$\eta / \eta_0 = 1 + A c^{1/2} + B c \quad \dots \dots \dots (23)$$

The above equation can be rearranged as:

$$(\eta / \eta_0 - 1) / c^{1/2} = A + B c^{1/2} \quad \dots \dots \dots (24)$$

Here, 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 $A.c^{1/2}$, 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 theory⁶⁴ of inter-ionic attractions in 1923.

Falkenhagen's⁶⁵⁻⁶⁷ did the theoretical calculations of the constant, A using the equilibrium theory and the theory of irreversible processes in electrolytes developed by Onsager and Fuoss⁶⁸. The A -coefficient depends on the ion-ion interactions and can be calculated from the physical properties of solvent and solution using the Falkenhagen Vernon⁶⁷ equation:

$$A_{\text{theo}} = \frac{0.2577 \Lambda_0}{\eta_0 (\epsilon T)^{1/2} \lambda_+^\theta \lambda_-^\theta} [1 - 0.6863 (\lambda_+^\theta \lambda_-^\theta / \Lambda_0)^2] \dots \dots \dots (25)$$

where Λ_0 , λ_+^θ , λ_-^θ are the limiting conductances of the electrolyte and the ions respectively at temperature T , ϵ and η_0 are the dielectric constant and viscosity of the solvent. For the most of the solutions, both aqueous and non-aqueous, the equation is valid upto 0.1 (M)^{60, 69}.

At higher concentrations, the extended Jones-Dole equation (26) involving an additional constant, D , originally used by Kaminsky⁷⁰ has been used by several workers^{71, 72}. The constant D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (23) is used by the most of the workers.

$$\eta / \eta_0 = 1 + A c^{1/2} + B c + D c^2 \quad \dots \dots \dots (26)$$

The plots of $(\eta/\eta_0 - 1)/c^{1/2}$ against $c^{1/2}$ for the electrolytes should give the value of A . But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur^{69,73,74}. Thus, instead of determining A -values from the plots or by the least square method, the A -values are generally calculated using Falkenhagen-Vernon equation (25).

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 structure⁶³.

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 which influence B -values are^{75, 76}:

- (1) 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.
- (2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or de-polymerisation effect) decrease η values.
- (3) High molal volume and low dielectric constant, which yield high B -values for similar solvents.
- (4) 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.

2.4.1. Viscosities at Higher Concentration

It had been found that the viscosity values at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade⁷⁷:

$$\eta = A \exp^{-b/T} \quad \dots\dots\dots(27)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration

range⁷⁸⁻⁸³ and the equation suggested by Angell^{84,85} 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:

$$1/\eta = A \exp [-K_I / (N_0 - N)] \quad \dots\dots\dots(28)$$

where N represents the concentration of the salt in eqv. litre⁻¹, A and K_I 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.⁸⁶⁻⁸⁸ introducing the limiting condition, that as $N \rightarrow 0$, $\eta \rightarrow \eta_0$ which is the viscosity of the pure solvent. Thus, we have:

$$\ln \eta / \eta_0 = \ln \eta_{rel} = K_I N / N_0 (N_0 - N) \quad \dots\dots\dots(29)$$

The equation (29) predicts a straight line passing through the origin for the plot of $\ln \eta_{rel}$ vs. $N / (N_0 - N)$ if a suitable choice for N_0 is made. The equation (29) has been tested by Majumder et al. using the data from the literature and from their own experimental results. The best choice for N_0 and K_I was selected by a trial and error methods. The set of K_I and N_0 which produce minimum deviation between $\eta^{(expt)}_{rel}$ and $\eta^{(theo)}_{rel}$ was accepted.

In dilute solutions, $N \ll N_0$ and we have:

$$\eta_{rel} = \exp (K_I N / N_0^2) \approx 1 + K_I N / N_0^2 \quad \dots\dots\dots(30)$$

which is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K_I / N_0^2$. 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 (29) written in the form:

$$N / \ln \eta_{rel} = N_0^2 / K_I - (N_0 / K_I) N \quad \dots\dots\dots(31)$$

It closely resembles the Vand's equation⁸¹ for fluidity (reciprocal for viscosity):

$$2.5 c / 2.3 \log \eta_{rel} = 1 / V - Q c \quad \dots\dots\dots(32)$$

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.

2.4.2. Division of B -coefficient into Ionic Values

The viscosity B -coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents^{74,89-119}. 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 in the total solute-solvent interactions. 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 –

(1) Cox and Wolfenden¹²⁰ 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 Gurney¹²¹ and also of Kaminsky⁷⁰ is based on:

$$B_{\text{K}}^+ = B_{\text{Cl}^-} \text{ (in water)} \quad \dots\dots\dots(33)$$

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. Nightingale¹²², however preferred RbCl or CsCl rather than KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron⁷¹ is based on the assumption that the Et_4N^+ ion in water is probably closest to being 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 equation¹²³:

$$B = 0.0025 \bar{V}_o \quad \dots\dots\dots(34)$$

and by having an accurate value of the partial molar volume of the ion, \bar{V}_o , 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:

$$B_{BPPh_4} = B_{PPPh_4^+} = B_{BPPh_4PPh_4}/2 \quad \dots\dots\dots(35)$$

$B_{BPPh_4PPh_4}$ (scarcely soluble in water) has been obtained by the following method:

$$B_{NaBPPh_4} + B_{PPPh_4Br} - B_{NaBr} = B_{BPPh_4PPh_4} \quad \dots\dots\dots(36)$$

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 $B_K^+ = B_{Cl^-}$ in ethanol based on equal mobilities of ions¹²⁴. They also adopted $B_{^{25}Me_4N^+}^\theta = 0.25$ as the initial value for acetonitrile solutions.
- (b) For acetonitrile solutions, Tuan and Fuoss¹²⁵ proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.*¹²⁶, $\lambda_{^{25}Bu_4N^+}^\theta = 61.4$ and $\lambda_{^{25}Ph_4B^-}^\theta = 58.3$ in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \quad \dots\dots\dots(37)$$

- (c) Gopal and Rastogi⁷⁵ resolved the *B*-coefficient in N-methyl propionamide solutions assuming that $B_{Et_4N^+} = B_I^-$ at all temperatures.
- (d) In dimethyl sulphoxide, the division of *B*-coefficients were carried out by Yao and Beunion⁷⁴ assuming:

$$B_{[(i-pe)_3BuN]^+} = B_{Ph_4B^-} = 1/2 \ B_{[(i-pe)_3BuNPh_4B]} \quad \dots\dots\dots(38)$$

at all temperatures.

Wide use of this method have been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate¹²⁷ solutions.

The methods, however, have been strongly criticized by Krumgalz¹²⁸. 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 $\lambda_+^\theta = \lambda_-^\theta$ in all solvents at all temperatures. Thus, though, $\lambda_{K^+}^\theta = \lambda_{Cl^-}^\theta$ at 25°C in methanol, but 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.

Krumgalz^{128, 129} 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^{130,131} in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic *B*-values for large tetraalkylammonium ions, R₄N⁺ (where R > Bu) in organic solvents are proportional to their ionic dimensions. So, we have:

$$B_{R_4N^+} = a + b r^3_{R_4N^+} \quad \dots\dots\dots(39)$$

where *a* = *B_X* and *b* is a constant dependent on temperature and solvent nature.

The extrapolation of the plot of *B_{R₄N⁺}* (R > Pr or Bu) against *r³_{R₄N⁺}* to zero cation dimension gives directly *B_X* in the proper solvent from which *B*-ion values can be calculated.

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

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4N^+} - B_{R'_4N^+} \quad \dots\dots\dots(40)$$

$$B_{R_4N^+} / B_{R'_4N^+} = r^3_{R_4N^+} / r^3_{R'_4N^+} \quad \dots\dots\dots(41)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data¹³².

Gill and Sharma¹¹⁰ used Bu_4NBPh_4 as a reference electrolyte. 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^+ (5.00 Å) and Ph_4B^- (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

$$B_{Ph_4B^-} / B_{Bu_4N^+} = r^3_{Ph_4B^-} / r^3_{Bu_4N^+} = (5.35 / 5.00)^3 \quad \dots\dots\dots(42)$$

and,

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad \dots\dots\dots(43)$$

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:

$$B_{[(i-Am)_3BuN]^+} = B_{Ph_4B^-} = 1/2 \ B_{[(i-Am)_3BuN]Ph_4B^-} \quad \dots\dots\dots(44)$$

Recently, Lawrence and Sacco¹¹³ used tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrically shaped and have almost equal van der Waals volume. Thus, we have:

$$B_{Bu_4N^+} / B_{Bu_4B^-} = V_{WBu_4N^+} / V_{WBu_4B^-} \quad \dots\dots\dots(45)$$

$$\text{or, } B_{Bu_4N^+} = B_{Bu_4NBBu_4} / 1 + V_{WBu_4B^-} / V_{WBu_4N^+} \quad \dots\dots\dots(46)$$

A similar division can be made for Ph_4PBPh_4 system.

Recently, Lawrence et al. made the viscosity measurements of tetraalkyl (from Pr to Hept.) ammonium bromides in DMSO and HMPT. The B -coefficients $B_{R_4NBr} = B_{Br^-} + a [f_{xR_4N^+}]$ were plotted as functions of the van der Waals volumes. The B_{Br^-} values thus obtained were compared with the accurately determined B_{Br^-} value using Bu_4NBBu_4 and Ph_4PBPh_4 as reference

salts. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritchett¹³³ suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali metal halide salts by employing Fajans' competition principle¹³⁴ and 'volcano plots' of Morris¹³⁵. The principle was extended to derive absolute single ion B -coefficients for alkali metals and halides in water. They also observed that $B_{Cs^+} = B_I^-$ suggested by Krumgalz¹³⁰ 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.

2.4.3. Temperature dependence of B - ion Values

A regularity in the behaviour of B_t and dB_t/dt has been observed both in aqueous and non-aqueous solvents and useful generalisations 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:

$$(i) \quad A \text{ and } dB_t/dt > 0 \quad \dots\dots\dots(47)$$

$$(ii) \quad B_{ion} < 0 \text{ and } dB_{ion}/dT > 0 \quad \dots\dots\dots(48)$$

characteristic of the structure breaking ions.

$$(iii) \quad B_{ion} > 0 \text{ and } dB_{ion}/dT < 0 \quad \dots\dots\dots(49)$$

characteristic of the structure making ions.

When an ion is surrounded by a solvent sheath, the properties of the solvent in the solvation layer may be different from those present in the bulk structure. This is well reflected in the 'Co-sphere' model of Gurney¹³⁶, A, B, C Zones of Frank and Wen¹³⁷ and hydrated radius of Nightingale¹²².

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 neighbourhood. Thus, the Jones-Dole equation:

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta (A \sqrt[4]{C} + B C) \quad \dots\dots\dots(50)$$

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

$$\eta^E + \eta^A + \eta^D = \eta_0 B C \quad \dots\dots\dots(51)$$

B -coefficient can thus be interpreted in terms of the competitive viscosity effects.

Following Stokes and Mills and Krumgalz ¹²⁸ we can write for B_{ion} as:

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{Str} + B_{ion}^{reinf} \quad \dots\dots\dots(52)$$

whereas according to Lawrence and Sacco:

$$B_{ion} = B_W + B_{solv} + B_{shape} + B_{ord} + B_{disord} \quad \dots\dots\dots(53)$$

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}^{Str} is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymmetrically and solvent to keep its own structure (this corresponds to 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 ions (B_{ion}^{Einst} or η^E positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in B_{ion}^{Orient} (η^A), B_{ion}^{Str} (η^D) is small for these ions. Thus, B_{ion} will be large and positive as $(B_{ion}^{Einst} + B_{ion}^{Orient}) > B_{ion}^{Str}$. However, B_{ion}^{Einst} and B_{ion}^{Orient} would be small for ions of greatest crystal radii (within a group) like Cs^+ or I^- due to small surface charge densities resulting in weak orienting and structure forming effect. B_{ion}^{Str} would be large due to structural disorder in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure. Thus $(B_{ion}^{Einst} + B_{ion}^{Orient}) < B_{ion}^{Str}$ 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., $B_{ion}^{Einst} + B_{ion}^{Orient} = B_{ion}^{Str}$, so that B is close to zero.

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

The increase in temperature will have no effect on B_{ion}^{Einst} . But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion-leading to decrease in B_{ion}^{Str} . B_{ion}^{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_{ion}^{Orient} and B_{ion}^{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 (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So there is a correlation between 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 Gurney¹³⁶ 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^θ) as:

$$\bar{S}_h^\theta = \bar{S}_{aq}^\theta - \bar{S}_g^\theta \quad \dots\dots\dots(54)$$

where, $\bar{S}_{aq}^\theta = \bar{S}_{ref}^\theta + \Delta S^\theta$, \bar{S}_g^θ is the calculated sum of the translational and rotational entropies of the gaseous ions. 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 (\dot{S}_{H^+}) to $-5.5 \text{ cal. mol}^{-1}. \text{ deg}^{-1}$. Asmus¹³⁸ used the entropy of hydration to correlate ionic *B*-values and Nightingale¹²² 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.¹³⁹ to assign single ion *B*-coefficients so that a plot of ΔS_e^θ ^{140,141}, the electrostatic entropy of solvation or $\Delta S_{I, II}^\theta$ ^{140,141}, 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^θ and ΔS_I^θ and the single ion *B*-coefficients. Both entropy criteria (ΔS_e^θ and $\Delta S_{I, II}^\theta$) and *B*-ion values indicate that in water the ions Li^+ , Na^+ , Ag^+ and F^- are not structure makers, and the ions Rb^+ , Cs^+ , Cl^- , Br^- , I^- and ClO_4^- are structure breakers and K^+ is a border line case.

2.4.4. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's¹⁴² approach as:

$$\eta = A e^{E_{vis}/RT} = (h N / V) \exp \Delta G^*/RT = (h N / V) \exp(\Delta H^* / RT - \Delta S^* / R) \dots\dots\dots(55)$$

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.

The problem was dealt in a different way by Nightingale and Benck¹⁴³ who calculated the thermodynamics of viscous flow of salts in aqueous solution with the help of the Jones-Dole equation (neglecting the $A.c^{1/2}$ term). Thus, we have:

$$R [d \ln \eta / d(1/T)] = R [d \ln \eta_0 / d(1/T)] + R / (1 + B.c) . d(1 + B.c) / d(1/T) \dots\dots\dots(56)$$

$$\Delta E\eta^*_{(solution)} = \Delta E\eta^*_{(solvent)} + \Delta E_v^* \dots\dots\dots(57)$$

ΔE_v^* 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.¹⁴⁴ have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = (\bar{V}_1^\theta + \bar{V}_2^\theta) / 1000 + \bar{V}_1^\theta (\Delta \mu^{0*}_2 - \Delta \mu^{0*}_1) / 1000 R T \dots\dots\dots(58)$$

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

$$\Delta \mu^{0*}_1 = \Delta G^{0*}_1 = R T \ln \eta_0 V_1^\theta / h N \dots\dots\dots(59)$$

Further, if B is known at various temperatures, we can calculate the entropy and enthalpy of activation of viscous flow respectively from the following equations as given below:

$$\frac{d(\Delta\mu^0)_2}{dT} = -\Delta S^0{}_2 \quad \dots\dots\dots(60)$$

$$\Delta H^0{}_2 = \Delta\mu^0{}_2 + T\Delta S^0{}_2 \quad \dots\dots\dots(61)$$

2.4.5. Effects of Shape and Size

This aspect of the problem has been dealt extensively by Stokes and Mills. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein ¹²³ leads to the equation:

$$\eta/\eta_0 = 1 + 2.5\phi \quad \dots\dots\dots(62)$$

where ϕ is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by (i) Sinha ¹⁴⁵ on the basis of departures from spherical shape and (ii) Vaud on the basis of dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monoatomic cations).

Thus we have from equation (62):

$$2.5\phi = A\sqrt{c} + Bc \quad \dots\dots\dots(63)$$

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

$$2.5\bar{V}_i = B \quad \dots\dots\dots(64)$$

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

$$B_{\pm} = 2.5 \quad \bar{V}_{\pm} = 2.5 \times 4/3 (\pi R^3 \pm N/1000) \quad \dots\dots\dots(65)$$

assuring that the ions behave like rigid spheres with a effective radii, R_{\pm} moving in a continuum. R_{\pm} calculated using the equation (65) 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 ¹⁴⁶:

$$B_{\pm} = 2.5 / 1000 (V_i + n_b V_s) \quad \dots\dots\dots(66)$$

where V_i is the molar volume of the base ion and V_s , the molar volume of the solvent. The equation (66) has been used by a number of workers to study the nature of solvation and solvation number.

2.4.6. Viscosity Deviations

Quantitatively, as per the absolute reaction rates theory¹⁴⁷, the deviations of viscosities from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad \dots\dots\dots(67)$$

where η is the viscosity of the mixture and x_i , η_i are the mole fraction and viscosity of pure component, i respectively.

2.4.7. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow, G^{*E} can be calculated as ¹⁴⁸:

$$G^{\star E} = R T \left[\ln \eta V - \left(\sum_{i=1}^n x_i \ln \eta_i V_i \right) \right] \quad \dots \dots \dots (68)$$

where, η and V are the viscosity and molar volume of the mixture, η_i and V_i are the viscosities and molar volumes of pure component, i respectively.

2.5. 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.

2.5.1. 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 solutions¹⁴⁹⁻¹⁵³, measurements in non-aqueous^{37,40} 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 solute-solvent and solute-solute interactions.

The isentropic compressibility (K_S) of the solution was calculated from the Laplace's equation¹⁵⁴:

$$K_S = 1 / (u^2 \rho) \quad \dots \dots \dots (69)$$

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

The apparent molal isentropic compressibility ($K_{S,\phi}$) of the solutions was determined from the relation:

$$K_{S,\phi} = M K_S / \rho_0 + 1000 (K_S \rho_0 - K_S^0 \rho) / (m \rho \rho_0) \quad \dots \dots \dots (70)$$

K_S^0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute, m is the molality of the solution.

The limiting apparent molal isentropic compressibility ($K_{S,\phi}^0$) was obtained by extrapolating the plots of $K_{S,\phi}$ versus the square root of molal

concentration of the solute, $m^{1/2}$ to zero concentration by a least-squares method^{150, 153}:

$$K_{S,\phi} = K^0_{S,\phi} + S^*_K m^{1/2} \quad \dots\dots\dots(71)$$

where, S^*_K is the experimental slope.

The limiting apparent molal isentropic compressibility ($K^0_{S,\phi}$) 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^{155, 156}. This is reflected by the negative values of $K^0_{S,\phi}$ of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering that is induced by them in the water structure^{36, 155}.

The compressibility of hydrogen bonded structure, however, varies depending on the nature of the hydrogen bonding involved¹⁵⁵. On the other hand, the poor fit of the solute molecules^{157, 158} as well as the possibility of flexible H-bond formation appear to be responsible for causing a more compressible environment (and hence positive $K^0_{S,\phi}$ values have been reported in aqueous non-electrolyte¹⁵⁹ and non-aqueous non-electrolyte¹⁶⁰ solutions.

2.5.2. Excess Isentropic Compressibility

The excess isentropic compressibility, K_S^E can be calculated using the following equation¹⁶¹⁻¹⁶³:

$$K_S^E = K_S - \sum_{i=1}^n x_i K_{S,i} \quad \dots\dots\dots(72)$$

where, x_i , $K_{S,i}$ are the mole fraction and isentropic compressibility of component i , respectively.

2.5.3. Acoustical Parameters

Various acoustical parameters such as specific acoustic impedance Z , intermolecular free length L_f , van der Waals constant b , molecular radius r , geometrical volume B , molar surface area Y , available volume V_a , molar

speed of sound R' , collision factor S , relaxation strength r' and space filling factor r_f can be calculated from the speeds of sound and density data of the solvent mixtures using the following relations¹⁶⁴:

$$b = \left(M / \rho \right) - \left(R T / \rho u^2 \right) \{ [1 + (M u^2 / 3 R T)]^{1/2} - 1 \} \quad \dots\dots\dots(74)$$

$$r = (3 b / 16 \pi N)^{1/3} \quad \dots \dots \dots (75)$$

$$L_f = K / (u \rho^{1/2}) \quad \dots\dots\dots (76)$$

$$B' = (4/3)\pi r^3 N \quad \dots\dots\dots (77)$$

$$Y = (36 \pi N B'^2)^{1/3} \quad \dots \dots \dots (78)$$

$$V_a = V - V_0 = V(1 - u/u_\infty) \quad \dots \dots \dots (79)$$

$$r' = 1 - (u/u_\infty)^2 \quad \dots\dots\dots(82)$$

where K is a temperature dependent Jacobson's constant ($= (93.875 + 0.375 T) \times 10^{-8}$), V_0 is volume at absolute zero, V is the molecular volume, u_∞ is taken as 1600 m. s⁻¹. The relative association R_A , for the salt solutions can be calculated by the following equation:

$$R_A = \rho_S / \rho_0 (u_0 / u_S)^{1/3} \quad \dots \dots \dots (84)$$

ρ_0 , ρ_s and u_0 , u_s are the densities and ultrasonic or sound speeds of solvent mixtures and solution, respectively.

2.6. Correlating Equations

The viscosity values can be further used to determine the Grunberg-Nissan parameter, d^1 as¹⁶⁵:

$$\ln \eta = \sum_{i=1}^n x_i \ln \eta_i + d^1 \prod_{i=1}^n x_i \quad \dots\dots\dots(85)$$

where d^1 is proportional to the interchange energy.

Again, the V^E , $\Delta\eta$, G^{*E} and K_S^E values can be fitted to Redlich-Kister¹⁶⁶ equation using the method of least squares involving the Marquardt algorithm¹⁶⁷ to derive the binary coefficient, A_J :

$$Y^E = x_1 x_2 \sum_{J=1}^k A_{J-1} (x_1 - x_2)^{J-1} \quad \dots\dots\dots(86)$$

Here, Y^E denotes V^E , $\Delta\eta$, G^{*E} and K_S^E . In each case, the optimum number of coefficients, A_J is ascertained from an examination of the variation of the standard deviation, σ , with:

$$\sigma = [(Y_{exp}^E - Y_{cal}^E)^2 / (n - m)]^{1/2} \quad \dots\dots\dots(87)$$

where n represents the number of measurements and m the number of coefficients.

2.7. Conductance

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte of solutions^{168, 169}. 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. Fortunately for us, accurate theories of electrolytic conductances are available to explain the results even upto a concentration limit of $K d$ (K = Debye-Huckel-length, d = distance of closest approach of free ions). Recent development of experimental technique provides an

accuracy to the extent of 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 utilised 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 reviews¹⁶⁸⁻¹⁸¹.

The study of conductance measurements were pursued vigorously both theoretically and experimentally during the last fifty years and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects and our discussion will be related 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 Onsager¹⁸² in deriving the Kohlrausch's equation:

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad \dots\dots\dots(88)$$

$$\text{where,} \quad S = \alpha \Lambda_0 + \beta \quad \dots\dots\dots(89)$$

$$\alpha = (Z e)^2 K / 3 (2 + \sqrt{2}) \epsilon_r R T c^{1/2} = 82.406 \times 10^{-4} Z^3 / (\epsilon_r T)^{3/2} \quad \dots\dots\dots(90a)$$

$$\beta = Z^2 e F K / 3 \pi \eta c^{1/2} = 82.487 Z^3 / \eta (\epsilon_r T)^{1/2} \quad \dots\dots\dots(90b)$$

The equation took no account for the short range interactions and also of shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent¹⁸³. In the subsequent years, Pitts (1953)¹⁸⁴ and Fuoss and Onsager (1957)^{173,185} independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably¹⁸³ from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned^{169,186,187}. The original F.O. equation was modified by Fuoss and Hsia¹⁸⁸ who recalculated the relaxation field, retaining the terms which had previously been neglected.

The equation usually employed is of the form:

$$\Lambda = \Lambda_0 - \alpha \Lambda_0 c^{1/2} / (1 + \kappa a) (1 + \kappa a / \sqrt{2}) - B c^{1/2} / (1 + \kappa a) + G(\kappa a) \quad \dots(91)$$

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

$$\Lambda = \Lambda_0 - S \sqrt{c} + E c \ln c + J_1 c - J_2 c^{1/2} \quad \dots\dots\dots(92)$$

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^{169,189,190}. Further, correction of the equation (92) was made by Fuoss¹⁷³ and Accascina.

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

$$\Lambda = \Lambda_0 - S \sqrt{c} + E c \ln c + J_1 c - J_2 c^{3/2} - B \Lambda_0 c \quad \dots\dots\dots(93)$$

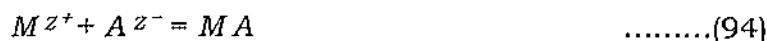
In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions¹⁹¹.

2.7.1. Ionic Association

The equation (90) successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against \sqrt{c} (limiting Onsager equation) are used to assign the dissociation or association of electrolytes. Thus, if Λ^0_{expt} is greater than Λ^0_{theo} , 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 ($\Lambda^0_{expt} < \Lambda^0_{theo}$) or positive deviation from the Onsager limiting tangent ($\alpha \Lambda_0 + B$) 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^0_{expt} and Λ^0_{theo} would be considerable with increasing association.¹⁹²

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



$$K_A = (1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 \quad \dots \dots \dots (95)$$

$$\text{and, } \alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad \dots \dots \dots (96)$$

For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation¹⁹³ or Shedlovsky's equation¹⁹⁴:

$$T(Z) / \Lambda = 1 / \Lambda_0 + K_A / (\Lambda_0)^2 c \gamma_{\pm}^2 \Lambda / T(Z) \quad \dots \dots \dots (97)$$

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

$$F(Z) = 1 - Z(1 - Z(1 - Z(\dots)^{1/2})^{1/2})^{1/2} \quad \dots \dots \dots (98)$$

$$\text{and } 1/T(Z) = S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \dots \quad \dots \dots \dots (99)$$

The plot of $T(Z) / \Lambda$ against $c \gamma_{\pm}^2 \Lambda / T(Z)$ should be a straight line having $1/\Lambda_0$ for its intercept and $K_A / (\Lambda_0)^2$ 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 (97).

The Fuoss-Hsia¹⁸⁸ conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S \sqrt{\alpha c} + \overline{E(\alpha c)} \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^2 (\alpha c) \dots (100)$$

The equation was modified by Justice¹⁹⁵. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$A = \alpha (A_0 - S\sqrt{\alpha c}) + \overline{E}(\alpha c) \ln(\alpha c) + J_1(R) \alpha c - J_2(R) (\alpha c)^{3/2} \quad \dots(101)$$

$$(1 - \alpha)/\alpha^2 c \gamma_{\pm}^2 = K_A, \quad \dots\dots\dots(102)$$

$$\ln \gamma_{\pm} = -K q^{1/2}/(1 + KR\sqrt{\alpha c}) \quad \dots\dots\dots(103)$$

The conductance parameters are obtained from a least square treatment after setting:

$$R = q = e^2/2 \varepsilon K T \quad \text{(Bjerrum's critical distance)} \quad \dots\dots\dots(104)$$

According to Justice, the method of fixing the J -coefficient by setting $R = q$ clearly permits a better defined value of K_A to be obtained. Since the equation (101) 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^o , of two free ions to form an ion-pair. The following equation has been proposed by Fuoss¹⁹⁶:

$$K_A = (4 \pi N a^3 / 3000) \exp(e^2 / a \varepsilon K T) \quad \dots\dots\dots(105)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a^o . The distance parameter was finally determined from the more general equation due to Bjerrum¹⁹⁷:

$$K_A = 4\pi Na / 1000 \int_{r=a}^{r=q} r^2 \exp(-Z^2 e^2 / r \varepsilon K T) dr \quad \dots\dots\dots(106)$$

The equations neglects 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 Douheret¹⁹⁸.

2.7.2. Ion size Parameter and Ionic Association

For plotting, equation (91) can be rearranged to the ' Λ ' function as:

$$\Lambda_J = \Lambda + S\sqrt{c} - E c \ln c = \Lambda_0 + (J - B \Lambda_0) c = \Lambda_0 + J_1 c \quad \dots\dots\dots(107)$$

with J_2 term omitted.

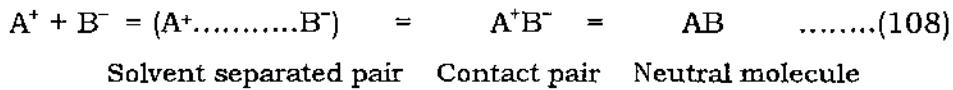
Thus, a plot of Λ_0 vs c gives a straight line with Λ_0 as intercept and J or $(J - B \Lambda_0)$ as slope. Assuming $(B \Lambda_0)$ to be negligible, a° values can be calculated from J . The a° value obtained by this method for DMSO were much smaller¹⁹² than would be expected from sums of crystallographic radii. One of the reasons attributed to it is ion-solvent interactions which 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 (which should be $B \Lambda c$ rather than $B \Lambda_0 c$) leads to a larger value of a° ¹⁹⁹ but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J ²⁰⁰.

Fuoss²⁰¹ in 1975 proposed a new conductance equation. He subsequently put forward another conductance equation in 1978 which replaces the old equations suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

- (i) Those which find an ion of opposite charge in the first shell of nearest neighbours (contact pairs) with $r_{ij} = a$. The nearest neighbours to a contact pair are the solvent molecules which form a cage around the pairs.
- (ii) Those 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) Those which find no other unpaired ion in a surrounding sphere of radius R , where R is the diameter of the co-sphere (unpaired ions).

Thermal motions and interionic forces establish a steady state, represented by the equilibria:



Contact pairs of ionogens may rearrange to neutral molecules $\text{A}^+\text{B}^- = \text{AB}$ e.g., H_3O^+ and CH_3COO^- . Let γ be the fraction of solute present as unpaired ($r > R$) ions. The concentration of unpaired ion becomes $c \gamma$, if α is the fraction of paired ions ($r \leq R$), then the concentration of the solvent separated pair is $c(1-\gamma)(1-\alpha)$ and that of contact pair is $\alpha c(1-\alpha)$.

The equation constants for (108) are:

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

$$K_S = \alpha / (1 - \alpha) = \exp(-E_S / K T) = e^{-\epsilon} \quad \dots \quad (110)$$

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 short-range 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 $K T$. Now:

$$(1 - \alpha) = 1 / (1 + K_S) \quad \dots \quad (111)$$

And the conductometric pairing constant is given by:

$$K_A = (1 - \alpha) / c \gamma^2 f^2 = K_R / (1 - \alpha) = K_R (1 + K_S) \quad \dots \quad (112)$$

The equation determines the concentration of active ions which produce long-range interionic effects. The contact pairs react as dipoles to an external field, X and contribute only to changing current. Both contact pairs

and solvent separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is, therefore, neglected in calculated long-range effects (activity coefficients, relaxation field ΔX and electrophoresis ΔA_e). The various patterns can all be reproduced by theoretical fractions of the form:

$$\Lambda = p[\Lambda_0(1 + \Delta X/X) + \Delta A_e] = p[\Lambda_0(1 + RX) + EL] \quad \dots\dots\dots (113)$$

which is a three parameter equation $\Lambda = \Lambda_0(c, \Lambda_0, R, E_S)$. $\Delta X/X$ (the relaxation field, RX) and ΔA_e (the electrophoretic counter current, EL) 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_S (or E_S) is a catch-all for all short-range effects:

$$p = 1 - \alpha(1 - \alpha) \quad \dots\dots\dots (114)$$

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:

$$\Lambda = \gamma [\Lambda_0(1 + \Delta X/X) + \Delta A_e] \quad \dots\dots\dots (115)$$

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

$$K_A = (1 - \alpha)/c \gamma^2 f^2 \approx K_R K_S \quad \dots\dots\dots (116)$$

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

$$\gamma = 1 - K_R c \gamma^2 f^2 / (1 - \alpha) \quad \dots\dots\dots (117)$$

$$K_R = (4\pi N R^3/3000) \exp(\beta/R) \quad \dots\dots\dots (118)$$

$$-\ln f = \beta^{1/2} (1 + \kappa R), \beta = e^2/\epsilon \kappa T \quad \dots\dots\dots (119)$$

$$K^2 = \pi \beta N \gamma c / 125 \quad \dots\dots\dots (120)$$

$$-\varepsilon = \ln [\alpha / (1 - \alpha)] \quad \dots\dots\dots(121)$$

The details of the calculations are presented in the 1978 paper ²⁰¹. The shortcomings of the previous equations have been rectified in the present equation which is more general than the previous equations and can be used in the higher concentration region (0.1 N in aqueous solutions).

2.7.3. Limiting Equivalent Conductances

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:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \quad \dots\dots\dots(122)$$

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

$$\lambda_+^0 = t_+ \Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_- \Lambda_0 \quad \dots\dots\dots(123)$$

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 interactions²⁰². However, accurate transference number determinations are limited to few solvents only. Spiro ²⁰³ and Krumgalz ²⁰⁴ 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 conductances in organic solvents for which experimental transference numbers are not yet available.

The methods have been summarized by Krumgalz ²⁰⁴ and some important points are mentioned below:

(i) Walden equation ²⁰⁵, $(\lambda_{\pm}^0)^{25}_{\text{water}} \cdot \eta_0^{\text{water}} = (\lambda_{\pm}^0)^{25}_{\text{acetone}} \cdot \eta_0^{\text{acetone}}$ (124)

$$(ii) \lambda_{\text{pic}}^0 \eta_0 = 0.267$$

^{205, 206}

$$\text{based on } \Lambda_{Et_4N^+}^0 = 0.563 \dots\dots\dots(125)$$

$$\lambda_{Et_4N^+}^0 \cdot \eta_0 = 0.296$$

Walden considered the products to be independent of temperature and solvent. However the $\Lambda_{Et_4N^+}^0$ 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.

$$(iii) \lambda_{25 Bu_4N^+}^0 = \lambda_{25 Ph_4B^-}^0 \quad \dots\dots\dots(126)$$

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

$$(iv) \lambda_{25 Bu_4N^+}^0 = \lambda_{25 Bu_4B^-}^0 \quad \dots\dots\dots(127)$$

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 Gill ²⁰⁸ is:

$$\lambda_{25 R_4N^+}^0 = Z F^2 / 6 \pi N \eta_0 [r_i - (0.0103 \epsilon_0 + r_y)] \quad \dots\dots\dots(128)$$

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.

However, large discrepancies were observed between the experimental and calculated values ^{204(a)}. In a paper ^{204(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.

$$(vi) \lambda_{25 [(i-Am)_3BuN^+]}^0 = \lambda_{25 Ph_4B^-}^0 \quad \dots\dots\dots(129)$$

It has been found from transference number measurements that the $\lambda_{25}^{\theta} [i\text{-Am}_3\text{BuN}^+]$ and $\lambda_{25}^{\theta} \text{Ph}_4\text{B}^-$ values differ from one another by 1%.

$$(vii) \lambda_{25}^{\theta} \text{Ph}_4\text{B}^- = 1.01 \lambda_{25}^{\theta} i\text{-Am}_3\text{B}^- \quad \dots\dots\dots(130)$$

The value is found to be true for various organic solvents.

Krumgalz ²⁰⁴ suggested a method for determining the limiting ion conductances 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 A_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:

$$r_s = |Z| F^2 / A \pi \eta_0 \lambda_{\pm}^{\theta} \quad \dots\dots\dots(131)$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (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:

$$\lambda_{\pm}^{\theta} \eta_0 = \text{constant} \quad \dots\dots\dots(132)$$

This relation has been verified using λ_{\pm}^{θ} values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_3\text{B}^-$, Ph_4As^+ and Ph_4B^- ions and for tetraalkylammonium cations starting with $n\text{-Et}_4\text{N}^+$. The relationship can be well utilized to determine λ_{\pm}^{θ} of ions in other organic solvents from the determined A_0 values.

2.7.4. Solvation Number

If the limiting conductance of the ion i of charge Z_i 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:

$$V_S = (4\pi/3) (r_S^3 - r_C^3) \quad \dots\dots\dots(133)$$

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

$$n_S = V_S / V_0 \quad \dots\dots\dots(134)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects²¹¹ from:

$$V_S^\theta = 4.35 r_S^3 \quad \dots\dots\dots(135)$$

where V_S^θ 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 equations¹⁷⁴ and theoretical corrections²¹²⁻²¹⁵ have been suggested to make the general method.

2.7.5. Stokes' Law and Walden's Rule

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

$$\lambda_i^\theta = |Z_i e| \epsilon F / 6 \pi \eta_0 R_i = 0.819 |Z_i| / \eta_0 R_i \quad \dots\dots\dots(136)$$

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:

$$\lambda_i^\theta \eta_0 = 0.819 |Z_i| / R_i = \text{constant} \quad \dots\dots\dots(137)$$

This is known as Walden's rule²¹⁶. 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 Stokes¹⁷⁴, Nightingale¹²² and others²¹⁷⁻²¹⁹ have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of those large ions, a calibration curve was obtained for each solvent. 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 viscosity²²⁰ was invoked without much success^{221, 222} but it has been found that:

$$\lambda_i^\theta \eta^p = \text{constant} \quad \dots\dots\dots(138)$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions^{223, 224}.

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 Fuoss²²⁵ 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:

$$\lambda_{i,0}^\theta = F e |Z_i| / 6 \pi R_\alpha (1 + A/\epsilon R_\alpha^2) \quad \dots\dots\dots(139)$$

$$\text{or,} \quad R_i = R_\alpha + A/\epsilon \quad \dots\dots\dots(140)$$

where R_α 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.

Boyd¹⁹⁴ gave the expression:

$$\lambda_i^\theta = F e |Z_i| / 6 \pi \eta_0 r_i [1 + (2/27 \pi \eta_0 \cdot Z_i^2 e^2 \tau / r_i^4 \epsilon_0)] \quad \dots\dots\dots(141)$$

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

Zwanzig²¹⁴ 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:

$$\lambda_i^0 = Z_i^2 e F / A_v \pi \eta_0 r_i + A_D [Z_i^2 e^2 (\varepsilon_r^0 - \varepsilon_r^\alpha) \tau / \varepsilon_r^0 (2 \varepsilon_r^0 + 1) r_i^3] \dots \dots \dots (142)$$

where ε_r^0 , ε_r^α 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's²¹² and Zwanzig's²¹⁴ equations are very similar and both may be written in the form:

$$\lambda_i^0 = A r_i^3 / (r_i^4 + B) \dots \dots \dots (143)$$

The theory predicts²²⁶ that λ_i^0 passes through a maximum of $3^{3/4} A / 4 B^{1/4}$ at $r_i = (3B)^{1/4} \text{ \AA}$. 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 (142) can be rearranged as²²⁷:

$$Z_i^2 e F / \lambda_i^0 \eta_0 = A_v \pi r_i + A_D Z_i^2 / r_i^3 e^2 (\varepsilon_r^0 - \varepsilon_r^\alpha) / \varepsilon_r^0 (2 \varepsilon_r^0 + 1) \tau / \eta_0 \dots \dots \dots (144)$$

$$\text{or, } L^* = A_v \pi r_i + A_D Z_i^2 / r_i^3 P^* \dots \dots \dots (145)$$

In order to test Zwanzig's theory, the equation (145) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available²²⁶⁻²³¹. All the plots 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 mobilities 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' law²⁰².

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 n . Like any continuum theory Zwanzig has the inherent weakness of its inability to account for the structural features²²⁷, 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 does not apply to the hydrogen bonded solvents²²⁸.
- (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 cations²²⁷.

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 + water²²⁶⁻²³⁶ mixtures and other aqueous binary mixtures²³⁷⁻²⁴⁰. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts^{213,214,241} 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. Zwanzig's expression though account for a change in Walden product with solvent composition but does not account for the maxima. Hemmes²⁴² suggested that the major deviation in the Walden product is due to the variation of the electrochemical equilibrium between ions and solvent molecules with the composition of mixed polar solvents.

In cases where more than one type 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 Onsager²⁴³ 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, improvements^{244, 245} 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 attack 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 systems.

2.8. Some recent Trends in Solvation Models

The last decade (1990-2000) witnessed some interesting trends in development of some solvation models and computer software. Based on a vast collection of experimental free energy of solvation data, C.J. Cramer, D.G. Truhlar and co-workers from the University of Minnesota, U.S.A. constructed a series of solvation models (SM1-SM5 series) to predict and calculate the free energy of solvation of a chemical compound²⁴⁶⁻²⁵⁰. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are, molecular formula, geometry, refractive index, surface tension, Abraham's α (acidity parameter) and β (basicity parameter) values, and, in the latest models, the dielectric constants. Many of these parameters for a number of compounds are available in the internet at <http://comp.chem.nwu.edu/solvation>²⁵¹.

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 KJ/mole. They can also be used to predict the vapour pressure of 298.15 K with useful accuracy. They are specially 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.^{252,253} have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibrium of electrolyte aqueous solutions. The water molecules are modelled as hard spheres with four short range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modelled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions.

Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity takes values very close to unity, especially, in the case in which the mean spherical approximation is used indicating a good description of the solvent. E. Bosch et al.²⁵⁴ of the University of Barcelona, Spain, have compared several Preferential Solvation Models specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

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