CHAPTER-II

General Introduction (Review of the Earlier Works)

Some Important Three Dimensional Pictures Associated with the Thesis:

1. **Intermolecular forces:**

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<table>
<thead>
<tr>
<th>Intermolecular forces</th>
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<tbody>
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<td>Ion-dipole</td>
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<td>Methanol</td>
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<td>H bond</td>
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<td>Ion-induced dipole</td>
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<td>Dipole-induced dipole</td>
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<td>Dispersion</td>
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2. **Three types of interactions in the solution process:**

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<td>Separation of solute molecules</td>
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<tr>
<td>Formation of solute-solvent interactions</td>
<td>Formation of solute-solvent interactions</td>
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3. **possible processes after solvation of a molecule**
4. **Solubility of methanol in water:**

It is seen that if such associates exist, the electric field produced by each individual dipole would oppose the field produced by the other. It is clear that this would result in a reduction in the net electric field as measured externally.

5. **Ion-Solvent Interaction**

The force may be understood by decomposing each of the dipole into two equal but opposite charges and adding up the resulting charge-charge forces. Notice that the Charge-Dipole Forces depend on relative molecular orientation.

6. **Solvation Number**
2.1. Solution Chemistry

Thermo-physical and bulk properties of solutions are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover, knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research.

The branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance is termed as solution chemistry. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent.

The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed in terms of many thermodynamic parameters, by excess properties in case of liquid-liquid mixtures and apparent molar properties in case of solid-liquid mixtures. These thermodynamic properties of solvent mixtures corresponds to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arraangements. In particular, they reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species. However, the exact structure of the solvent molecule is not known with certainty. The addition of an
ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The assessment of ion-pairing in these systems is important because of its effect on the ionic mobility and hence on the ionic conductivity of the ions in solution. These phenomenon thus paves the path for research in solution chemistry to elucidate the nature of interaction through experimental studies involving densitometry, viscometry, interferrometry, refractometry and other suitable methods and to interpret the experimental data collected.

2.2. Various types of Interactions

The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions constitute the essential part- ‘ion-ion interactions’. The degree of ion-ion interactions affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions, in general, are stronger than ion-solvent interactions. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but ion-solvent interactions or ion-solvation still remains a complex process. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the solvents significantly modify the majority of the solutes. 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, and solvent-solvent interactions in some solvent media.

2.2.1. Forces binding atoms in a molecule

In a molecule the forces binding atoms are due to chemical bonding. The energy required to break a bond is called the bond-energy. For example the average bond-energy for O-H bonds in water is 463 kJ/mol. The forces holding molecules
together are generally called intermolecular forces. The energy required to break molecules apart is much smaller than a typical bond-energy, but intermolecular forces play important roles in determining the properties of a substance. Intermolecular forces are particularly important in terms how molecules interact and form biological organisms or even life. This link gives an excellent introduction to the interactions between molecules. In general, intermolecular forces can be divided into several categories. The four prominent types are:

a. **Hydrogen bond:** Certain substances such as H₂O, HF, NH₃ form hydrogen bonds, and the formation of which affects properties (MP, BP, solubility) of substance. Other compounds containing OH and NH₂ groups also form hydrogen bonds. Molecules of many organic compounds such as alcohols, acids, amines, and aminoacids contain these groups, and thus hydrogen bonding plays a important role in biological science.

b. **Covalent bonding:** Covalent is really intramolecular force rather than intermolecular force. It is mentioned here, because some solids are formed due to covalent bonding. For example, in diamond, silicon, quartz etc., the all atoms in the entire crystal are linked together by covalent bonding. These solids are hard, brittle, and have high melting points. Covalent bonding holds atoms tighter than ionic attraction.

c. **Strong ionic attraction:** It has relations to properties of solids. The more ionic compound has the higher lattice energy. The following result can be explained by way of ionic attraction: LiF, 1036; LiI, 737; KF, 821; MgF₂, 2957 kJ/mol.

d. **Weak London dispersion forces or van der Waal's force:** These forces alway operate in any substance. The force arisen from induced dipole and the interaction is weaker than the dipole-dipole interaction. In general, the heavier the molecule, the stronger the van der Waal's force of interaction. For example, the boiling points of inert gases increase as their atomic masses increases due to stronger Landon dispersion interactions.
e. **Intermediate dipole-dipole forces:** Substances, whose molecules have dipole moment have higher melting point or boiling point than those of similar molecular mass, having no dipole moment.

f. **Metallic bonding:** Forces between atom in metallic solids belong to another category. Valence electrons in metals are rampant. They are not restricted to certain atoms or bonds. Rather they run freely in the entire solid, providing good conductivity for heat and electric energy. These behaviors of electrons give special properties such as ductility and mechanical strength to metals.

The division into types is for convenience in their discussion. Of course all types can be present simultaneously for many substances. Usually, intermolecular forces are discussed together with “The States of Matter”. Intermolecular forces also play important roles in solutions. A summary of the interactions is illustrated in the following diagram:
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 solvents. \(^{1-9}\) Intermolecular forces are also important in determining the solubility of a substance. “Like” intermolecular forces for solute and solvent will make the solute soluble in the solvent. In this regard \(\Delta H_{\text{soln}}\) is sometimes negative and sometimes positive.

**There are three types of interactions in the solution process:**

**Solvent – solvent interactions:** energy required to break weak bonds between solvent molecules.

**Solute – solute interactions:** energy required to break intermolecular bonds between the solute molecules.

**Solute – solvent interactions:** \(\Delta H\) is negative since bonds are formed between them.
Furthermore, solubility is affected by:

(a) Energy of attraction (due to ion-dipole force) affects the solubility. Also called hydration energy,
(b) Lattice energy (energy holding the ions together in the lattice),
(c) Charge on ions; larger charge means higher lattice energy,
(d) Size of the ion—large ions mean smaller lattice energy.

For liquid systems, the macroscopic properties are usually quite well known, whereas the microscopic structure is often much less studied. The liquid phase is characterized by local order and long-range disorder, and to study processes in liquids, it is therefore valuable to use methods that probe the local surrounding of the constituent particles. The same is also true for solvation processes: a local probe is important to obtain insight into the physical and chemical processes going on.

Schematic figure of possible processes after solvation of a molecule.

A molecule ABC may after solvation by solvent molecule S for instance remain essentially unchanged (left), it may change its geometric conformation (center left), it may dissociate, for instance into ionic fragments (center right), or it may migrate to the surface, with a hydrophobic end sticking out (right).
2.2.2. Liquids dissolving in liquids

In liquid molecular solutions, when both the solute and solvent are covalent compounds, the intermolecular attractive forces are London dispersion, dipole-dipole and hydrogen bonding. For example, when we mix carbon tetrachloride with hexane a solution is formed whereas when carbon tetrachloride is added to water the two do not mix. CCl$_4$ and C$_6$H$_{14}$ have identical intermolecular attractive forces--London dispersion type. However, water has hydrogen bonding type of intermolecular attractive forces. The CCl$_4$ molecules are unable to displace the hydrogen-bonded water molecules from one another because the interaction between two water molecules is stronger than the interaction between a water molecule and a carbon tetrachloride molecule. Look at the solution process at the microscopic level for mixing CCl$_4$ and C$_6$H$_{14}$ and for mixing C$_6$H$_{14}$ and H$_2$O. When we mix ethanol with water the two liquids form a homogeneous solution because the intermolecular attractive forces are identical. In fact, water and ethanol are miscible, that is, they will form a solution in any proportion. The solubility of molecular solutions depends on the similarity of intermolecular attractive forces--like dissolves like. When ethanol dissolves in water we can write a chemical equation which expresses the solution process. It is:

$$\text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH(aq)}$$

Because ethanol is a covalent compound and it does not dissociate in water we write the product as an aqueous species. The solution consists of molecules of ethanol and water in a mixture. It is the intermolecular attractive forces which are important in understanding the solution process. We must be able to separate the solution process into its component parts and evaluate what is happening.

Water associates very strongly with itself by so called 'hydrogen bonding'. This self-association could reduce the net dipole character of the associated molecules calculated from bulk dielectric constant measurements of the pure substance. In a similar manner, methanol also associates strongly with itself. Examples of possible associates of water and methanol are shown in the following figure.
Solubility of methanol in water:

It is seen that if such associates exist, the electric field produced by each individual dipole would oppose the field produced by the other. It is clear that this would result in a reduction in the net electric field as measured externally. Consequently, bulk property measurements can provide false values for the moments of the individual dipoles. Another molecule, however, approaching a dipole of the water or methanol molecule would experience the uncompensated field of the single dipole and interact accordingly.

Thus despite the presence of intermolecular H-bonding both in water and alcohol, after mixing new H-bonding prevails in the mixture due to solvent-solvent interaction. 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 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 phenomena.

The organic solvents have been classified based on the dielectric constants, organic group types, acid base properties or association through hydrogen bonding, donor-acceptor properties, hard and soft acid-base principles, 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.

2.2.3. Ion-Solvent Interaction

When salt is dissolved in water, the ions of the salt dissociate from each other and associate with the dipole of the water molecules. This results in a solution called an electrolyte.

The force may be understood by decomposing each of the dipole into two equal but opposite charges and adding up the resulting charge-charge forces. Notice that the Charge-Dipole Forces depend on relative molecular orientation.

This means that the forces can be attractive or repulsive depending on whether like or unlike charges are closer together. On average, dipoles in a liquid orient themselves to form attractive interactions with their neighbors, but thermal motion makes some instantaneous configurations unfavorable.

Moreover if a salt crystal is put in water, the polar water molecules are attracted to ions on the crystal surfaces. The water molecules gradually surround and isolate the surface ions. The ions become hydrated

They gradually move away from the crystal into solution. This separation of ions from each other is called dissociation. The surrounding of solute particles by solvent particles is called solvation. The dissociation of ions in solution leads to a factor which is important to keep in mind any time you are working with a solution of an ionic material. When the ions are dissociated, each ion species in the solution acts as though it were present alone. Thus, a solution of sodium chloride acts as a solution of sodium ions and chloride ions.

The determination of thermodynamic, transport, acoustic and optical 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.

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, conductance, density, viscosity, ultrasonic speed, and refractive index of electrolytes and derive the various factors associated with ionic solvation.

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

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte solutions. 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 up to a concentration limit of $Kd$ ($K$ = 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 reviews.

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 Onsager in deriving the Kohlrausch’s equation:

$$\Lambda = \Lambda_0 - S\sqrt{c}$$ ..........................(01)
where, \[ S = \alpha \Lambda_0 + \beta \] \hspace{1cm} \text{............(02)}

\[
\alpha = \frac{\left(ze^2\right)\kappa}{3\left(2 + \sqrt{2}\right)c, KT\sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(e, T)^{3/2}} \] \hspace{1cm} \text{.........(3a)}

\[
\beta = \frac{ze^2F\kappa}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{e, T}} \] \hspace{1cm} \text{.............(3b)}

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 solvent. In the subsequent years, Pitts (1953) and Fuoss and Onsager (1957) independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the \( \Lambda_0 \) values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably from that obtained using Pitt’s theory and the derivation of the Fuoss-Onsager equation was questioned. The original F.O. equation was modified by Fuoss and Hsia who recalculated the relaxation field, retaining the terms which had previously been neglected.

The equation usually employed is of the form:

\[
\Lambda = \Lambda_0 - \frac{\alpha \Lambda_0 \sqrt{c}}{(1 + \kappa a)(1 + \frac{\kappa a}{\sqrt{2}})} - \frac{\beta \sqrt{c}}{(1 + \kappa a)} + G(\kappa a) \] \hspace{1cm} \text{..............(04)}

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

\[
\Lambda = \Lambda_0 - S \sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt{c} \] \hspace{1cm} \text{......................(05)}
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 $^{36,37}$. Further, correction of the equation (05) was made by Fuoss $^{20}$ 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:

$$A = A_0 - S \sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt{c} - BA_0 c$$  \hspace{1cm} ..........(06)

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 $^{37}$.

2.3.1. Ionic Association

The equation (03) successfully represents the behaviour of completely dissociated electrolytes. The plots of $A$ against $\sqrt{c}$ (limiting Onsager equation) are used to assign the dissociation or association of electrolytes. Thus, if $A^0_{\text{expt}}$ is greater than $A_{\text{theo}}^0$, 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 ($A^0_{\text{expt}} < A_{\text{theo}}^0$) or positive deviation from the Onsager limiting tangent ($\alpha A_0 + B$) 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 $A^0_{\text{expt}}$ and $A^0_{\text{theo}}$ would be considerable with increasing association $^{38}$. Conductance measurements help us to determine the values of the ion-pair association constant, $K_A$ for the process:

$$M^{Z+} + A^{Z+} = MA$$  \hspace{1cm} ..................(07)
For strongly associated electrolytes, the constant, \( K_A \) and \( \Lambda_0 \) has been determined using Fuoss-Kraus equation \(^{40}\) or Shedlovsky’s equation: \(^{41}\)

\[
\frac{T(Z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_A \gamma_z^2 \Lambda}{\Lambda_0} T(Z) \tag{10}
\]

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

\[
F(z) = 1 - z \left(1 - z \left(1 - ... \right)^{1/2} \right)^{1/2} \tag{11}
\]

and

\[
\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \tag{12}
\]

The plot of \( T(Z)/\Lambda \) against \( c \gamma_z^2 \Lambda/T(Z) \) 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 \( \Lambda_0 \) and \( K_A \) from equation (10). The Fuoss-Hsia \(^{35}\) conductance equation for associated electrolytes is given by:

\[
\Lambda = \Lambda_0 - S\sqrt{ac} + E(ac) \ln(ac) + j_1(ac) - j_2(ac)^{3/2} - K_A \gamma_z^2(ac) \tag{13}
\]

The equation was modified by Justic \(^{42}\). The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

\[
\Lambda = \alpha \left( \Lambda_0 - S\sqrt{ac} \right) + E(ac) \ln(ac) + j_1(R)ac - j_2(R)(ac)^{3/2} \tag{14}
\]
$\frac{(1 - \alpha)}{\alpha^2 c \gamma_z^2} = K_A$ ..........................(15)

$\ln \gamma_z = \frac{-k\sqrt{q}}{1+kR\sqrt{ac}}$ ..........................(16)

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

$R = q = \frac{e^2}{2ekT}$ (Bjerrum's critical distance) ..........................(17)

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 (14) 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, $a^0$, of two free ions to form an ion-pair. The following equation has been proposed by Fuoss: 43

$$K_A = \left(\frac{4\pi N_A a^3}{3000}\right) \exp \left(\frac{e^2}{a e KT}\right)$$ ..........................(18)

In some cases, the magnitude of $K_A$ was too small to permit a calculation of $a^0$. The distance parameter was finally determined from the more general equation due to Bjerrum: 44

$$K_A = \left(\frac{4\pi N_A a^3}{1000}\right) \int_{r=a}^{r=q} r^2 \exp \left(\frac{z^2 e^2}{r e KT}\right) dr$$ ..........................(19)
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.  

### 2.3.2. Ion size Parameter and Ionic Association

For plotting, equation (100) can be rearranged to the \( \Lambda \) function as:

\[
\Lambda_i = \Lambda + S \sqrt{c - Ec \ln c} = \Lambda_0 + (J - B \Lambda_0)c = \Lambda_0 + Jc
\]

with \( J_2 \) term omitted.

Thus, a plot of \( \Lambda_0 \) vs \( c \) gives a straight line with \( \Lambda_0 \) as intercept and \( J \) or \( (J - B \Lambda_0) \) as slope. Assuming \( (B \Lambda_0) \) to be negligible, \( a^0 \) values can be calculated from \( J \). The \( a^0 \) values obtained by this method for DMSO were much smaller 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 \( a^0 \) 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 \( a^0 \) but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from \( J \).

Fuoss 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 these 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:

\[
\begin{align*}
A^+ + B^- & \leftrightarrow (A^+ \ldots \ldots \ldots B^-) & \leftrightarrow A^+B^- & \leftrightarrow AB & \ldots \ldots (21)
\end{align*}
\]

Solvent separated pair \hspace{1cm} Contact pair \hspace{1cm} Neutral molecule

Contact pairs of ionogens may rearrange to neutral molecules \( A^+B^- = AB \) e.g. \( H_2O^+ \) and \( CH_3COO^- \). Let \( \gamma \) be the fraction of solute present as unpaired \((r > R)\) ions. The concentration of unpaired ion becomes \( c \gamma \) if \( \alpha \) is the fraction of paired ions \((r \leq R)\), then the concentration of the solvent separated pair is \( c(1 - \gamma)(1 - \gamma) \) and that of contact pair is \( \alpha c (1 - \alpha) \).

The equation constants for (21) are:

\[
K_R = \frac{(1 - \alpha)(1 - \gamma)}{c\gamma^2 f^2} \quad \ldots \ldots (22)
\]

\[
K_S = \frac{\alpha}{(1 - \alpha)} = \exp\left(-\frac{E_S}{KT}\right) = e^{-\varepsilon} \quad \ldots \ldots (23)
\]

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 \((r = a)\); \(E\) is \(E_S\) measured in units of \(KT\). Now:

\[
1 - \alpha = \frac{1}{1 + K_S}
\]

\[\text{..................(24)}\]

And the conductometric pairing constant is given by:

\[
K_A = \frac{1 - \alpha}{c r^2 f^2} = \frac{K_R}{(1 - \alpha)} = K_R(1 + K_S)
\]

\[\text{.............(25)}\]

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 \(\Delta X\) and electrophoresis \(\Delta \Lambda_e\)). The various patterns can all be reproduced by theoretical fractions of the form:

\[
A = P \left[ A_0 \left(1 + \frac{\Delta X}{X}\right) + \Delta \Lambda_e \right] = P \left[ A_0 (1 + R) + EL \right]
\]

\[\text{..................(26)}\]

which is a three parameter equation \(A = A_0 (c, A_0, R, E_S) \Delta X/X\) (the relaxation field, \(R\) and \(\Delta \Lambda_e\) (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:

\[
P = 1 - \alpha (1 - \gamma)
\]

\[\text{..................(27)}\]
In case of ionogens or for ionophores in solvents of low dielectric constant, \( \alpha \) is very near to unity \((-E_S/K T) >> 1\) and the equation becomes:

\[
A = \gamma \left[ \Lambda_0 \left( 1 + \frac{AX}{X} \right) + \Delta \lambda \right]
\]

........................................(28)

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

\[
K_A = \frac{1 - \gamma}{c \gamma^2 f^2} \approx K_r K_S
\]

........................................(29)

as \( K_S >> 1 \). The parameters and the variables are related by the set of equations:

\[
\gamma = \frac{1 - K_r c \gamma^2 f^2}{(1 - \alpha)}
\]

........................................(30)

\[
K_r = \frac{4\pi N_A R^3}{3000} \exp \left( \frac{\beta}{R} \right)
\]

........................................(31)

\[
-\ln f = \frac{\beta_k}{2(1 + \kappa R)}, \beta = \frac{e^2}{\varepsilon kT}
\]

........................................(32)

\[
\kappa^2 = 8\pi \beta \gamma n = \frac{\pi \beta N \gamma c}{125}
\]

........................................(33)

\[
-\varepsilon = \ln \left[ \frac{\alpha}{1 - \alpha} \right]
\]

........................................(34)

The details of the calculations are presented in the 1978 paper \(^{49}\). 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).
2.3.3. Lee-Wheaton Conductance Equation

As Fuoss 1978 conductance equation contained a boundary condition error\(^{50,51}\). Fuoss introduced a slight modification to his model\(^{52,53}\). According to him, the ion pairs (ion approaching with their Gurney co-sphere) are divided into two categories—contact pairs (with no contribution to conductance) and solvent separated ion pairs (which can only contribute to the net transfer of charge). To rectify the boundary errors contained in Fuoss 1978 conductance equation, Lee-Wheaton\(^{54}\) in the same year described in the derivation of a new conductance equation, based on the Gurney co-sphere model and henceforth the new equation is referred to as the Lee-Wheaton equation\(^{55}\). The conductance data were analyzed by means of the Lee-Wheaton conductance equation\(^{56}\) in the form:

\[
A = \alpha_i\{A_i[1 + C_1\beta\kappa + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3] - \frac{\rho\kappa}{1 + \kappa R}[1 + C_4\beta\kappa + C_5(\beta\kappa)^2 + \frac{\kappa R}{12}]\} \quad \text{.........(35)}
\]

The mass action law association\(^{57,58}\) is

\[
K_{A,\pm} = \frac{(1 - \alpha_i)\gamma_A}{\alpha_i^2 c_i\gamma_{\pm}^2} \quad \text{..........(36)}
\]

and the equation for the mean ionic activity coefficient:

\[
\gamma_{\pm} = \exp\left[-\frac{q\kappa}{1 + \kappa R}\right] \quad \text{..........(37)}
\]

where \(C_1\) to \(C_5\) are least square fitting coefficients as described by Pethybridge and Taba\(^{59}\), \(\Lambda_x\) is the limiting molar conductivity, \(K_{A,\pm}\), is the association constant, \(\alpha_i\) is the dissociation degree, \(q\) is the Bjerrum parameter and \(\gamma\) the activity coefficient and \(\beta = 2q\). The distance parameter \(R\) is the least distance that two free ions can approach before they merge into ion pair. The Debye parameter \(\kappa\), the Bjerrum parameter \(q\) and \(\rho\) are defined by the expressions\(^{59}\)

\[
\kappa = 16000\pi N_A e_c^2 \alpha_i \quad \text{..........(38)}
\]

\[
q = \frac{e^2}{8\varepsilon_0 e_c KT} \quad \text{..........(39)}
\]
\[ \rho = \frac{Fe}{299.79 \times 3 \pi \eta} \]  
\[ \text{..........................(40)} \]

where the symbols have their usual significance. The equation (32) was resolved by an iterative procedure. For a definite \( R \) value the initial value of \( \Lambda_0 \) and \( K_{A,c} \), were obtained by the Kraus-Bray method. The parameter \( \Lambda_0 \) and \( K_{A,c} \), were made to approach gradually their best values by a sequence of alternating linearization and least squares optimizations by the Gauss-Siedel method until satisfying the criterion for convergence. The best value of a parameter is the one when equation (32) is best fitted to the experimental data corresponding to minimum standard deviation \( \sigma_\Lambda \) for a sequence of predetermined \( R \) value and standard deviation \( \sigma_\Lambda \) was calculated by the following equation:

\[
\sigma_\Lambda^2 = \sum_{i=1}^{n} \frac{[A_i(\text{calc}) - A_i(\text{obs})]^2}{n - m} \]  
\[ \text{..........................(41)} \]

where \( n \) is the number of experimental points and \( m \) is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach \( R \) with two parameter fit \((m=2)\). For the electrolytes with no significant minima observed in the \( \sigma_\Lambda \) versus \( R \) curves, the \( R \) values were arbitrarily preset at the centre to centre distance of solvent-separated pair.

\[
R = a + d \]  
\[ \text{..........................(42)} \]

where \( a = r_c^+ + r_c^- \), i.e., the sum of the crystallographic radii of the cation and anion and \( d \) is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of \( d \) and related terms are described in the literature. \( R \) was generally varied by a step 0.1 Å and the iterative process was continued with equation (32).

**2.3.4. 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 surroundings 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:

\[ \Lambda_0 = \lambda_+^0 + \lambda_-^0 \]  \hspace{1cm} (43)

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.,

\[ \lambda_+^0 = t_+ \Lambda_0 \] \hspace{1cm} \text{and} \hspace{1cm} \lambda_-^0 = t_- \Lambda_0 \]  \hspace{1cm} (44)

Thus, from accurate value of \( \lambda^0 \) of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions. However, accurate transference number determinations are limited to few solvents only. Spiro and Krumgalz 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 and some important points are mentioned below:

(i) Walden equation \(^{66,67}\),

\[ \left( \lambda_+^0 \right)_{\text{water}} \eta_{0,\text{water}} = \left( \lambda_+^0 \right)_{\text{acetone}} \eta_{0,\text{acetone}} \]  \hspace{1cm} (45)

\( \lambda_0 \text{pic} \cdot \eta_0 = 0.267 \hspace{1cm} \lambda_0 \text{Et}_4N \cdot \eta_0 = 0.296 \)  \hspace{1cm} (46)

Walden considered the products to be independent of temperature and solvent. However the \( \lambda^0 \text{Et}_4\text{Npic} \) 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.

\[ \lambda_{25}^0 \left( Bu_4 N^+ \right) = \lambda_{25}^0 \left( Ph_4 B^- \right) \]

(iii)

The equality holds good in nitrobenzene and in mixture with CCl$_4$ but not realized in methanol, acetonitrile and nitromethane.

(iv) \[ \lambda_{25}^0 \left( Bu_4 N^+ \right) = \lambda_{25}^0 \left( Bu_4 B^- \right) \]

The method appears to be sound as the negative charge on boron in the Bu$_4$B$^-$ ion is completely shielded by four inert butyl groups as in the Bu$_4$N$^+$ ion while this phenomenon was not observed in case of Ph$_4$B$^-$. 

(v) The equation suggested by Gill is:

\[ \lambda_{25}^0 \left( R_4 N^+ \right) = \frac{zF^2}{6\pi \varepsilon_0 \eta_0 \left[ r_i - (0.0103\varepsilon_0 + r_y) \right]} \]

where \( Z \) and \( r_i \) are charge and crystallographic radius of proper ion, respectively; \( \eta_0 \) and \( \varepsilon_0 \) 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. In a paper, 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) \[ \lambda_{25}^0 \left[ \left( i - Am \right)_3 BuN^+ \right] = \lambda_{25}^0 \left( Ph_4 B^- \right)^{70} \]
It has been found from transference number measurements that the $\lambda^0_{25}(i-Am)_3BuN^+$ and $\lambda^0_{25}Ph_4B^-$ values differ from one another by 1%.

$$\text{(vii)} \lambda^0_{25}(Ph_4B^-) = 1.01\lambda^0_{25}(i-Am_4B^-)^{71} \hspace{1cm} \text{..........................(51)}$$

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

Krumgalz 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 $\Lambda_o$ 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:

$$r_S = \frac{|z|F^2}{A\pi\eta_0\lambda^0_\pm} \hspace{1cm} \text{..........................(52)}$$

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:

$$\lambda^0_\pm\eta_0 = \text{constant} \hspace{1cm} \text{..........................(53)}$$

This relation has been verified using $\lambda^0_\pm$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i-Am_4B^-$, $Ph_4As^+$ and $Ph_4B^-$ ions and for tetraalkylammonium cations starting with n-Et$_4N^+$. The relationship can be well
utilized to determine $\lambda^0_\pm$ of ions in other organic solvents from the determined $A_0$ values.

2.3.5. Solvation Number

Various types of interactions exist between the ions in solutions. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number. Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

\[
V_S = \left(\frac{4\pi}{3}\right)(r_S^3 - r_C^3)
\]

**Schematic diagram for solvation**

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:

\[
V_S = \left(\frac{4\pi}{3}\right)(r_S^3 - r_C^3) \quad \text{..................(54)}
\]
where $r_c$ is the crystal radius of the ion; the solvation number, $n_S$ would then be obtained from:

$$n_S = \frac{V_S}{V_0} \quad \text{..........................(55)}$$

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

$$V_S^0 = 4.35r_S^3 \quad \text{..........................(56)}$$

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 equations and theoretical corrections have been suggested to make the general method.

2.3.6. Stokes’ Law and Walden’s Rule

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

$$\lambda_i^0 = \frac{|z_i e| eF}{6\pi \eta_0 R_i} = \frac{0.819 |z_i|}{\eta_0 R_i} \quad \text{..........................(57)}$$

where $\eta_0 =$ 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:

$$\lambda_i^0 \eta_0 = 0.819 \frac{z_i}{R_i} = \text{constant} \quad \text{..........................(58)}$$
This is known as Walden’s rule. 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, Nightingale and others 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 viscosity was invoked without much success but it has been found that:

$$\lambda^0_0 \eta^p = \text{constant} \hspace{1cm} (59)$$

where $p$ is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions.

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 Fuoss 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:

$$\lambda^0_0 = Fe^{|z_i|} \sqrt{\frac{6\pi R_a}{\varepsilon R_s^2}} \left(1 + \frac{A}{\varepsilon R_s^2}\right) \hspace{1cm} (60)$$

or,

$$R_i = R_s + \frac{A}{\varepsilon} \hspace{1cm} (61)$$
where $R_\alpha$ 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.

Boyd gave the expression:

$$\lambda_i^0 = Fe|z_i| \sqrt{6\pi \eta_0 r_i} \left[ 1 + \left( \frac{2}{27\pi \eta_0} \frac{z_i^2 e^2 \tau}{r_i^4 \varepsilon_0} \right) \right] \text{.......................}(62)$$

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

Zwanzig 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:

$$\lambda_i^0 = z_i^2 eF \left\{ A_v \pi \eta_0 r_i + A_D \left[ z_i^2 e^2 \left( \varepsilon_r^0 - \varepsilon_r^\alpha \right) \tau / \varepsilon_r^0 \left( 2\varepsilon_r^0 + 1 \right) r_i^3 \right] \right\} \text{..............}(63)$$

where $\varepsilon_r^0$, $\varepsilon_r^\alpha$ 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’s and Zwanzig’s equations are very similar and both may be written in the form:

$$\lambda_i^0 = \frac{A_r^3}{(r_i^4 + B)} \text{..........................}(64)$$

The theory predicts that $\lambda_i^0$ passes through a maximum of $27^{\frac{1}{4}} A / 4 B^{\frac{1}{4}}$ at $r_i = 3B^{\frac{1}{4}}$ Å. 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 (64) can be rearranged as:

\[ Z_i^2 eF / \lambda_i \eta_0 = A_v \pi r_i + A_p Z_i^z / r_i^3 \varepsilon^2 \left( \varepsilon_r^0 - \varepsilon_r^\infty \right) / \varepsilon_r^0 (2\varepsilon_r^0 + 1)\tau / \eta_0 \]

or,

\[ \bar{L} = A_v \pi r_i + A_p Z_i^z / \bar{P}_0 r_i^3 \]

In order to test Zwanzig’s theory, the equation (66) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available. 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’ law.

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,\(^{86}\) 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 solvents.\(^{88}\)

(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 $^{88}$.

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 + water $^{87-97}$ mixtures and other aqueous binary mixtures $^{98-102}$. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts $^{103}$ 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 accounts for a change in Walden product with solvent composition but does not account for the maxima. Hemmes $^{104}$ 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 Onsager $^{105}$ 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.

### 2.3.7. Conductance- Some Recent Trends

Recently Blum, Turq and co-workers $^{106-107}$ 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. Although the differences in the derivation of the classical and MSA conductivity theories seem
to be relatively small, it has been claimed that the performance of MSA equation is better with a much wider concentration range than that covered by the classical equations. However, no through study of the performance of the new equation at the experimental uncertainty level of conductivity measurement is yet available in the literature, except the study by Bianchi et al. 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 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.

2.3.8. Solvation Models- Some Recent Trends

The interactions between particles in chemistry have been based upon empirical laws- principally on Coulomb's law. This is also the basis of the attractive part of the potential energy used in the Schödinger equation. Quantum mechanical approach for ion-water interactions was begun by Clementi in 1970s. A quantum mechanical approach to salvation can provide information on the energy of the individual ion-water interactions provided it is relevant to solution chemistry, because it concerns potential energy rather than the entropic aspect of salvation. Another problem in quantum approach is the mobility of ions in solution affecting salvation number and coordination number. However, the Clementi calculations concerned stationary models and can not have much to do with the dynamic salvation numbers. Covalent bond formation enters little into the aqueous calculations, however, with organic solvents the quantum mechanical approaches to bonding may be essential. The trend pointing to the future is thus the molecular dynamics technique. In molecular dynamic approach, a limited number of ions and
molecules and Newtonian mechanics of movement of all particles in solution is concerned. The foundation of such a approach is the knowledge of the intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last decade (1990-2000) witnessed some interesting trends in the development of solvation models and computer softwares. Based on a 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 compound\textsuperscript{110-114}. 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 a (acidity parameter) and b (basicity parameter) values, and, in the latest models, the dielectric constants. 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 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 \textit{et al.}\textsuperscript{115,116} 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 \textit{et al.}\textsuperscript{117} of the University of Barcelona, Spain, have compared several “Preferential Solvation Models” specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.
2.4. 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, electrostriction,\textsuperscript{118} hydrophobic hydration,\textsuperscript{119} micellization\textsuperscript{120} and cosphere overlap during solute-solvent interactions\textsuperscript{121} 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 apparent molar volumes, $\phi_\text{a}$, of the solutes can be calculated by using the following relation:\textsuperscript{122}

$$\phi_\text{a} = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad \text{............................(67)}$$

where $M$ is the molecular weight of the solute, $\rho_0$ and $\rho$ are the densities of solvent and solution respectively and $c$ is the molarity of the solution.

The partial molar volumes, $\phi_2$, can be obtained from the equation:\textsuperscript{123}

$$\bar{\phi}_2 = \phi_\text{a} + \frac{(1000 - c\phi_\text{a})}{2000 + c^{\gamma/2} \left( \frac{\partial \phi_\text{a}}{\partial \sqrt{c}} \right)^{\gamma/2}} c^{\gamma/2} \left( \frac{\partial \phi_\text{a}}{\partial \sqrt{c}} \right) \quad \text{............................(68)}$$
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 equation,\textsuperscript{124} the Redlich-Meyer equation,\textsuperscript{125} the Owen-Brinkley equation\textsuperscript{126} and the Pitzer equation.\textsuperscript{127} Masson\textsuperscript{124} found that the apparent molar volumes of electrolyte, $\phi_{v}$, vary with the square root of the molar concentration by the linear equation:

$$\phi_{v} = \phi_{v}^{0} + S_{v}^{*} \sqrt{c} \quad \text{...........................................(69)}$$

where $\phi_{v}^{0}$ is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution, $\phi_{v}^{0}$) and $S_{v}^{*}$ is the experimental slope. The majority of $\phi_{v}$ data in water\textsuperscript{128} and nearly all $\phi_{v}$ data in non-aqueous\textsuperscript{129-133} solvents have been extrapolated to infinite dilution through the use of equation (69).

The temperature dependence of $\phi_{v}^{0}$ for various investigated electrolytes in various solvents can be expressed by the general equation as follows:

$$\phi_{v}^{0} = a_{0} + a_{1} T + a_{2} T^{2} \quad \text{...........................................(70)}$$

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 ($\phi_{E}^{0}$) can be calculated from the general equation (70). Thus,

$$\phi_{E}^{0} = \left( \frac{\partial \phi_{v}^{0}}{\partial T^{2}} \right)_{p} = a_{1} + 2a_{2} T \quad \text{...........................................(71)}$$
The limiting apparent molar expansibilities ($\phi^0_L$) change in magnitude with the change of temperature.

During the past few years it has been emphasized by different workers that $S_{\nu}^*$ is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler $^{134}$ developed a technique of examining the sign of $\left(\frac{\partial \phi^0}{\partial T^2}\right)_p$ for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -\left(\frac{\partial^2 \phi^0}{\partial T^2}\right)_p$$

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 Meyer $^{125}$ have shown that an equation of the form of (69) cannot be more than a limiting law, where for a given solvent and temperature the slope, $S_{\nu}^*$ should depend only upon the valence type. They suggest representing $\phi_{\nu}$ by:

$$\phi_{\nu} = \phi^0_{\nu} + S_{\nu} \sqrt{c} + h_c c$$

$$S_{\nu} = Kw^{\frac{1}{2}}$$

$S_{\nu}$ is the theoretical slope, based on molar concentration, including the valence factor:
where $\beta$ 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-Meyer extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However, studies on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation.

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

$$\phi_v = \phi_v^0 + S_i \tau (\kappa a) \sqrt{c} + 0.5 w_i \theta (\kappa a) c + 0.5 K_i c$$ ........................................(77)

where the symbols have their usual significance. However, equation (77) has not been widely employed for the treatment of results for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue 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:

$$\phi_v = \phi_v^0 + V M Z_X A_i \left( 2 \ln \left( 1 + b l^{1/2} \right) + 2 \gamma_M \gamma_X RT \left[ m B_X^{2.2} + m^2 \left( \gamma_M \gamma_X \right)^{1/2} C_X^{V} \right] \right)$$ ........................................(78)

where the symbols have their usual significance.
2.4.2. Apparent and Partial Molar Expansibility

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

\[
E_2 = E\phi + [(1000 - cE\phi)(2000 + S_c c^2)^{-1}] S_c c^2 \\
\leq 79 \leq (80) \\
\]

Here, \( E\phi \) is the apparent molar expansibility and is determined from equation:

\[
E\phi = a_0 \phi + (a - a_0)1000c^{-1} \\
\leq (81) \leq (82) \\
\]

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:

\[
a_0 = -1 / \rho_0 (\delta \rho_0 / \delta T) \quad \text{and} \quad a = -1 / \rho (\delta \rho / \delta T) \\
\leq (83) \leq (84) \\
\]

The apparent molar expansibility of electrolyte, \( E\phi \), vary with the square root of the molar concentration by the linear equation:

\[
E\phi = E\phi^0 + S_E \sqrt{c} \\
\leq (85) \leq (86) \\
\]

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

2.4.3. 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 solutions \(^{139}\) to non-aqueous electrolyte solutions.
In the last few years, the method suggested by Conway et al.\textsuperscript{139} 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, $V_{R_4NX}^0$ for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{R4N^+}$ and obtained straight-line graphs for each series. They suggested, therefore, their results fitted the equation:

$$V_{R_4NX}^0 = bM_{R4N^+} + V_{X^-}^0$$ .......................... (83)

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

Uosaki et al.\textsuperscript{140} have used this method for the separation of some literature values and of their own $V_{R_4NX}^0$ values into ionic contributions in organic electrolyte solutions. Krumgalz\textsuperscript{141} applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

### 2.4.4. 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\textsuperscript{142, 143}:

$$V^E = \sum_{i=1}^{j} x_i M_i \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right)$$ .......................... (84)

where $M_i$, $\rho_i$ and $\rho$ are the molar mass of the $i^{th}$ component, density of the $i^{th}$ component and density of the solution mixture respectively.

### 2.5. Viscosity

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively\textsuperscript{144, 145}. Viscosity is
not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, \( V_2 \), 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 Grüneisen \(^{146}\) in 1905. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole \(^{147}\) suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations, \( c \):

\[
\frac{\eta}{\eta_0} = \eta_r = 1 + A\sqrt{c} + Bc
\]

The above equation can be rearranged as:
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 $Ac^{1/2}$, 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 of the Debye-Hückel theory of inter-ionic attractions in 1923.

Falkenhagen’s did the theoretical calculations of the constant, $A$ using the equilibrium theory and the theory of irreversible processes in electrolytes developed by Onsager and Fuoss. The $A$-coefficient depends on the ion-ion interactions and can be calculated from the physical properties of solvent and solution using the Falkenhagen Vernon equation:

$$\eta = \eta_0 \left(1 + \frac{A}{c^{1/2}} \right)$$

where $\eta_0$, $\eta$ and $\lambda_0$, $\lambda$ are the limiting conductances of the electrolyte and the ions respectively at temperature $T$, $\varepsilon$ and $\eta_0$ 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).

At higher concentrations, the extended Jones-Dole equation involving an additional constant, $D$, originally used by Kaminsky has been used by several workers. The constant $D$ cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (86) is used by the most of the workers.

$$\eta = \eta_0 \left(1 + \frac{A}{c^{1/2}} \right)$$

where $\eta_0$, $\eta$ and $\lambda_0$, $\lambda$ are the limiting conductances of the electrolyte and the ions respectively at temperature $T$, $\varepsilon$ and $\eta_0$ 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).
The plots of \((\eta / \eta_0 - 1) / \sqrt{c}\) against \(\sqrt{c}\) 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 \(^{153,157,158}\). 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 (87).

The coefficients \(A\) and \(B\) can be evaluated by rearranging equation (85) to

\[
\frac{\eta}{\eta_0} - 1 = A + B \sqrt{c} \quad \text{.................................}(89)
\]

and plotting the left hand side against \(c^{1/2}\).

\(A\)-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 \(^{147}\).

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: \(^{159,160}\)

1. The effect of ionic solvation and the action of the field of the ion in producing long range order in solvent molecules, increase or \(B\)-value.
2. The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or de-polymerisation effect) decrease \(\eta\) 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.
2.5.1. 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 Andrade:\textsuperscript{161}

\[ \eta = A \exp^{b/T} \] \hspace{1cm} (90)

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range \textsuperscript{162-167} and the equation suggested by Angell \textsuperscript{168, 169} 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:

\[ \frac{1}{\eta} = A \exp^{\left[\frac{-K_1}{N_0-N}\right]} \] \hspace{1cm} (91)

Where \( N \) represents the concentration of the salt in eqv. litre\textsuperscript{-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. \textsuperscript{170-172} introducing the limiting condition, that as \( N \to 0 \), \( \eta \to \eta_0 \) which is the viscosity of the pure solvent. Thus, we have:

\[ \ln \frac{\eta}{\eta_0} = \ln \eta_{rel} = \frac{K_1 N}{N_0 \left( N_0 - N \right)} \] \hspace{1cm} (92)

The equation (92) 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 (92) 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 \( K_1 \) was selected by a trial and error
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method. The set of $K_1$ and $N_0$ which produce minimum deviation between $\eta_{rel}^{(exp)}$ and $\eta_{rel}^{(theo)}$ were accepted.

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

$$\eta_{rel} = \exp\left(\frac{K_1N}{N_0^2}\right) \approx 1 + \frac{K_1N}{N_0^2} \quad \cdots \quad (93)$$

Which 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 (92) written in the form:

$$\frac{N}{\ln \eta_{rel}} = \frac{N_0^2}{K_1} - \left(\frac{N_0}{K_1}\right)N \quad \cdots \quad (94)$$

It closely resembles the Vand’s equation for fluidity (reciprocal for viscosity):

$$\frac{2.5c}{2.303\log \eta_{rel}} = \frac{1}{V} - Qc \quad \cdots \quad (95)$$

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 into Ionic Values

The viscosity $B$-coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents. 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 Wolfenden \textsuperscript{204} carried out the division on the assumption that $B_{\text{ion}}$ values of Li\textsuperscript{+} and IO\textsuperscript{3−} in LiIO\textsubscript{3} are proportional to the ionic volumes which are proportional to the third power of the ionic mobilities. The method of Gurney \textsuperscript{205} and also of Kaminsky \textsuperscript{154} is based on:

$$B_{k^+} = B_{cl^−} \ (\text{in water}) \quad \text{..................................}(96)$$

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\textsuperscript{+} and Cl\textsuperscript{−} are very similar over the temperature range 15-45°C. The assignment is supported from other thermodynamic properties. Nightingle \textsuperscript{206}, however preferred RbCl or CsCl rather than KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron \textsuperscript{155} is based on the assumption that the Et\textsubscript{4}N\textsuperscript{+} 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 equation: \textsuperscript{207}

$$B = 0.0025V_0' \quad \text{..................................}(97)$$

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 $B_{Et4N^+}$ in water at 25°C.

Recently Sacco \textit{et al.} proposed the “reference electrolytic” method for the division of $B$-values.

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

$$B_{\text{EtPh}_4^+} = B_{\text{PPh}_4^−} = \frac{B_{\text{EtPh}_4^+\text{PPh}_4^−}}{2} \quad \text{..................................}(98)$$
BBPh₄PPh₄ (scarcely soluble in water) has been obtained by the following method:

\[
B_{\text{BBPh₄PPh₄}} = B_{\text{NaBBPh₄}} + B_{\text{PPh₄Br}} - B_{\text{NaBr}} \quad \text{..................................(99)}
\]

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 mobilities of ions. \(^{208}\)

(b) For acetonitrile solutions, Tuan and Fuoss \(^{209}\) proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer et al., \(^{210}\) \(\lambda_{25,\text{BuN}}^0 = 61.4\) and \(\lambda_{25,\text{PhB}}^0 = 58.3\) in acetonitrile.

\[
B_{\text{BuN}^+} = B_{\text{PhB}^-} \quad \text{...........................................(100)}
\]

(c) Gopal and Rastogi \(^{159}\) resolved the \(B\)-coefficient in N-methyl propionamide solutions assuming that \(B_{\text{EtN}} = B_{\text{I}}\) at all temperatures.

(d) In dimethyl sulphoxide, the division of \(B\)-coefficients was carried out by Yao and Beunion \(^{158}\) assuming:

\[
B_{\left[\text{(i-pee)BuN}^+\right]} = B_{\text{PhB}^-} = \frac{1}{2B\left[\left(i-pee\right),\text{BuNPh₄B}\right]} \quad \text{...................................(101)}
\]

at all temperatures.

Wide use of this method have been made by other authors for dimethyl sulphoxide, sulfolane, hexamethyl phosphotriamide and ethylene carbonate \(^{211}\) solutions.

The methods, however, have been strongly criticized by Krumgalz \(^{212}\). 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 \( \lambda_{f}^0 = \lambda_{cl}^0 \) in all solvents at all temperatures. Thus, though, \( \lambda_{f}^0 = \lambda_{cl}^0 \) at 25ºC 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 \((i-\text{pe})_3\text{BuN}^+\) or \((i-\text{Am})_3\text{BuN}^+\) and \(\text{Ph}_4\text{B}^-\) does not necessarily imply the equality of \( B \)-coefficients of these ions and they are likely to be solvent and ion-structure dependent.

Krumgalz \(212,213\) 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 \(214,215\) in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic \( B \)-values for large tetraalkylammonium ions, \( R_4\text{N}^+ \) (where \( R > \text{Bu} \)) in organic solvents are proportional to their ionic dimensions. So, we have:

\[
B_{R,NX} = a + br^3R_4\text{N}^+ \quad \text{..........................(102)}
\]

where \( a = B_X \) and \( b \) is a constant dependent on temperature and solvent nature.

The extrapolation of the plot of \( B_{R,NX} (R > \text{Pr or Bu}) \) against \( r^3R_4\text{N}^+ \) 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:

\[
B_{R,N'} - B_{R,N'} = B_{R,NX} - B_{R,NX} \quad \text{..........................(103)}
\]

\[
\frac{B_{R,N'}}{B_{R,N'}} = \frac{r^3_{N'}}{r^3_{N^+}} \quad \text{..........................(104)}
\]

The radii of the tetraalkylammonium ions have been calculated from the conductometric data \(216\).
Gill and Sharma \textsuperscript{194} used Bu\textsubscript{4}NBPh\textsubscript{4} as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that Bu\textsubscript{4}N\textsuperscript{+} and Ph\textsubscript{4}B\textsuperscript{−} 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\textsubscript{4}N\textsuperscript{+} (5.00 Å) and Ph\textsubscript{4}B (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:

\[
\frac{B_{\text{Ph}_4B^-}}{B_{\text{Bu}_4N^+}} = \frac{r_{\text{Ph}_4B^-}^3}{r_{\text{Bu}_4N^+}^3} = \left( \frac{5.35}{5.00} \right)^3
\]

\[
B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{Ph}_4\text{B}^-}
\]

The method requires only the \(B\)-values of Bu\textsubscript{4}NBPh\textsubscript{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:

\[
B_{[(i-Am)_3\text{Bu}N^+]} = B_{\text{Ph}_4\text{B}^-} = \frac{1}{2B[(i-Am)_3\text{BuNPh}_4\text{B}^-]}
\]

Recently, Lawrence and Sacco \textsuperscript{197} used tetrabutylammonium tetrabutylborate (Bu\textsubscript{4}NBBu\textsubscript{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:

\[
\frac{B_{\text{Bu}_4\text{N}^+}}{B_{\text{Bu}_4\text{B}^-}} = \frac{V_{\text{Bu}_4\text{N}^+}}{V_{\text{Bu}_4\text{B}^-}}
\]
or, \[ B_{Bu_4N^{+}} = \frac{B_{Bu_4NBBu_4}}{1 + \frac{V_{w(Bu_4B^-)}}{V_{w(Bu_4N^{+})}}} \] ..................................................(109)

A similar division can be made for Ph₄PBPh₄ system.

Recently, Lawrence et al. made the viscosity measurements of tetraalkyl (from Pr to Hept.) ammonium bromides in DMSO and HMPT. The \( B \)-coefficients \( BR_4NBr = BB_r + a \left[ f_x R_4N^+ \right] \) were plotted as functions of the van der Waals volumes. The \( BB_r \) values thus obtained were compared with the accurately determined \( BB_r \) 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 Pritcheit \(^{217}\) 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 principle \(^{218}\) and ‘volcano plots’ of Morris. \(^{219}\) The principle was extended to derive absolute single ion \( B \)-coefficients for alkali metals and halides in water. They also observed that \( BCs^+ = Br^- \) suggested by Krumgalz \(^{214}\) to be more reliable than \( BK^+ = BCl^- \) 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

A regularity in the behaviour of \( B_z \) and \( dB_z/dt \) 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) \( A \) and \( dA/dT > 0 \) \hspace{1cm} (110)

(ii) \( B_{\text{ion}} < 0 \) and \( dB_{\text{ion}}/dT > 0 \) \hspace{1cm} (111)

characteristic of the structure breaking ions.

(iii) \( B_{\text{ion}} > 0 \) and \( dB_{\text{ion}}/dT < 0 \) \hspace{1cm} (112)

Characteristic of the structure making ions.

When an ion is 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, A, B, C Zones of Frank and Wen and hydrated radius of Nightingle.

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 (\( \eta_0 \)) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighbourhood. Thus, the Jones-Dole equation:

\[
\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta(AC + BC) \]

\( \eta^* \) is the positive increment in viscosity caused by coulombic interaction. Thus:

\[
\eta^E + \eta^A + \eta^D = \eta_0 BC \]

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

Following Stokes and Mills and Krumgalz we can write for \( B_{\text{ion}} \) as:

\[
B_{\text{ion}} = B_{\text{ion}}^{\text{Inst}} + B_{\text{ion}}^{\text{Orient}} + B_{\text{ion}}^{\text{Str}} + B_{\text{ion}}^{\text{Reinf}} \]

whereas according to Lawrence and Sacco:
\[ B_{\text{ion}} = B_w + B_{\text{solv}} + B_{\text{shape}} + B_{\text{Ord}} + B_{\text{Disord}} \] ........................(116)

\( B_{\text{ion}}^{\text{Einst}} \) is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to \( \eta^E \) or \( B_{\text{shape}} \)). \( B_{\text{ion}}^{\text{Orient}} \) is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to \( \eta^A \) or \( B_{\text{ord}} \)). \( B_{\text{ion}}^{\text{Str}} \) is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymetrically and solvent to keep its own structure (this corresponds to \( \eta^D \) or \( B_{\text{disord}} \)). \( B_{\text{ion}}^{\text{reinf}} \) 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 \( B_{\text{solv}} \) account for viscosity increases and attributed to the van der Waals volume and the volume of the solvation of ions.

Thus, small and highly charged cations like Li\(^+\) and Mg\(^{2+}\) form a firmly attached primary solvation sheath around these ions (\( B_{\text{ion}}^{\text{Einst}} \) or \( \eta^E \) positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in \( B_{\text{ion}}^{\text{Orient}} \) (\( \eta^A \)), \( B_{\text{ion}}^{\text{Str}} \) (\( \eta^D \)) is small for these ions. Thus, \( B_{\text{ion}} \) will be large and positive as \( (B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}}) > B_{\text{ion}}^{\text{Str}} \). However, \( B_{\text{ion}}^{\text{Einst}} \) and \( B_{\text{ion}}^{\text{Orient}} \) would be small for ions of greatest crystal radii (within a group) like Cs\(^+\) or I\(^-\) due to small surface charge densities resulting in weak orienting and structure forming effect. \( B_{\text{ion}}^{\text{Str}} \) would be large due to structural disorder in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure. Thus \( (B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}}) < B_{\text{ion}}^{\text{Str}} \) and \( B_{\text{ion}} \) is negative.

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

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

The increase in temperature will have no effect on $B_{\text{ion Einst}}$. But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion-leading to decrease in $B_{\text{ion Str}}$, $B_{\text{ion Orient}}$ 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 $B_{\text{ion Orient}}$ and $B_{\text{ion Str}}$.

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 $B_{\text{ion}}$ 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 $B_{\text{ion}}$ 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 Gurney \cite{221} 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 ($S_{h}^{0}$) as:
\[ \dot{S}_h = \dot{S}_{aq} + \dot{S}_g \]  

(117)

where, \( \dot{S}_{aq} = \dot{S}_{ref} + \Delta S^0 \), \( \dot{S}_g \) 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 \(-5.5 \text{ cal. Mol}^{-1} \text{deg}^{-1}\). Asmus \(^{222}\) used the entropy of hydration to correlate ionic \( B \)-values and Nightingale \(^{206}\) 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. \(^{223}\) to assign single ion \( B \)-coefficients so that a plot of \( \Delta S^0_e \), \(^{224,225}\) the electrostatic entropy of solvation or \( \Delta S^0_l \), \(^{224,225}\) 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 \( \Delta S^0_e \) and \( \Delta S^0_l \) and the single ion \( B \)-coefficients. Both entropy criteria (\( \Delta S^0_e \) and \( \Delta S^0_l, ii \)) 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.

### 2.5.4. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity \((\eta)\) can be represented from Eyring’s \(^{226}\) approach as:

\[
\eta = A e^{E_{vis}/RT} = \left(\frac{hN}{V}\right)^{\Delta G^*/RT} = \left(\frac{hN}{V}\right)^{\left(\frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}\right)} \]

(118)

where \( E_{vis} \) = the experimental entropy of activation determined from a plot of ln \( \eta \) against \( 1/T \). \( \Delta G^* \), \( \Delta H^* \) and \( \Delta S^* \) are the free energy, enthalpy and entropy of activation respectively.
The problem was dealt in a different way by Nightingale and Benck 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:

$$R \left[ \frac{d \ln \eta}{d \left( \frac{1}{T} \right)} \right] = R \left[ \frac{d \ln \eta_0}{d \left( \frac{1}{T} \right)} \right] + \frac{R}{(1 + Bc)} \frac{d \left( 1 + Bc \right)}{d \left( \frac{1}{T} \right)}$$

$$\Delta E^x_{\eta (soln)} = \Delta E^x_{\eta_0 (solv)} + \Delta E^x_{\nu}$$

$\Delta E^x_{\nu}$ 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. have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = \left( \frac{V_1^0 - V_2^0}{1000} \right) + \frac{V_1^0 \left( \Delta \mu^0_2 - \Delta \mu^0_1 \right)}{1000RT}$$

where $V_1^0$ and $V_2^0$ 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:

$$\Delta \mu_1^0 = \Delta G_1^0 = \frac{RT \ln \eta_1 V_1^0}{hN}$$
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:

\[
\frac{d(\Delta \mu_2^{0x})}{dT} = -\Delta S_2^{0x}
\]

..............................................(123)

\[
\Delta H_2^{0x} = \Delta \mu_2^{0x} + T \Delta S_2^{0x}
\]

..............................(124)

### 2.5.5. 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\(^{207}\) leads to the equation:

\[
\frac{\eta}{\eta_0} = 1 + 2.5\phi
\]

..............................(125)

where \( \phi \) is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by (i) Sinha\(^{229}\) 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 (126):

\[
2.5\phi = A\sqrt{c} + Bc
\]

..............................(126)
Since $A \sqrt{c}$ term can be neglected in comparison with $Bc$ and $\phi = c\tilde{V}_i$, where, $\tilde{V}_i$ is the partial molar volume of the ion, we get:

$$2.5\tilde{V}_i = B \quad \text{..........................(127)}$$

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

$$B_\pm = 2.5\tilde{V}_\pm = \frac{2.5 \times 4 (\pi R^3 N)}{3 \times 1000} \quad \text{..........................(128)}$$

assuring that the ions behave like rigid spheres with a effective radii, $R_\pm$ moving in a continuum. $R_\pm$ calculated using the equation (128) 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:

$$B_\pm = \frac{2.5}{1000(V_i + n_b V_b)} \quad \text{..........................(129)}$$

where $V_i$ is the molar volume of the base ion and $V_b$ the molar volume of the solvent. The equation (129) has been used by a number of workers to study the nature of solvation and solvation number.

### 2.5.6. Viscosity Deviations

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

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i\eta_i) \quad \text{..........................(130)}$$
where \( \eta \) is the viscosity of the mixture and \( x_i, \eta_i \) are the mole fraction and viscosity of pure component, \( i \) 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

\[
G^E = RT \left[ \ln \eta V - \sum_{i=1}^{I} x_i \ln \eta_i V_i \right] \tag{131}
\]

where, \( \eta \) and \( V \) are the viscosity and molar volume of the mixture, \( \eta_i \) and \( V_i \) are the viscosities and molar volumes of pure component, \( i \) respectively.

### 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,\(^{233-237}\) measurements in non-aqueous \(^{121,124}\) 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 equation:\(^{238}\)

\[
K_s = \frac{1}{u^2 \rho} \tag{132}
\]

where \( \rho \) 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:

$$
K_s = \frac{MK_s}{\rho_0} + \frac{1000(K_s\rho - K_s^0\rho)}{m\rho_0}
$$

.......................... (133)

$K_s^0$ 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: 234, 237

$$
K_{s,\phi} = K_{s,\phi}^0 + S^* \sqrt{m}
$$

.......................... (134)

where, $S^*_{K}$ is the experimental slope.

The limiting apparent molal isentropic compressibility ($K_{s,\phi}^0$) 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 239, 240. This is reflected by the negative values of $K_{s,\phi}^0$ of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering that is induced by them in the water structure 120, 239.

The compressibility of hydrogen bonded structure, however, varies depending on the nature of the hydrogen bonding involved 239. On the other hand, the poor fit of the solute molecules 241, 242 as well as the possibility of flexible H-bond formation appear to be responsible for causing a more compressible environment (and hence positive $K_{s,\phi}^0$ values have been reported in aqueous non-electrolyte 243 and non-aqueous non-electrolyte 244 solutions.
2.6.2. Excess Isentropic Compressibility

The excess isentropic compressibility, $K_{sE}$ can be calculated using the following equation: \(^{245-247}\)

$$K_{sE} = K_s - \sum_{i=1}^{j} x_i K_{s,i} \tag{135}$$

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

2.6.3. 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 relations: \(^{248}\)

$$Z = u \rho \tag{136}$$

$$b = \frac{M \left( \frac{RT}{\rho u^2} \right)^2 \left[ 1 + \left( \frac{Mr^2}{3RT} \right) \right]^{1/2}}{\rho} - 1 \tag{137}$$

$$r = \left( \frac{3b}{16\pi N} \right)^{1/2} \tag{138}$$

$$L_f = K / (u \rho^{1/2}) \tag{139}$$

$$B' = \frac{4}{3} \pi r^3 N \tag{140}$$

$$Y = \left[ 36\pi NB^3 \right]^{1/3} \tag{141}$$
General Introduction (Review of the Earlier Works)

\[ V_a = V \left(1 - \frac{u}{u_\infty}\right) \] ..........................(142)

\[ R' = \frac{\frac{1}{3} \mu u}{\rho} \] ..............................(143)

\[ S = \frac{u V}{u_\infty B'} \] ..............................(144)

\[ r' = 1 - \left(\frac{u}{u_\infty}\right)^2 \] ..............................(145)

\[ r_f = \frac{B'}{V} \] ..............................(146)

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, \( u_\infty \) is taken as \( 1600 \text{ m. s}^{-1} \). The relative association \( R_{A,a} \) for the salt solutions can be calculated by the following equation:

\[ R_{A,a} = \frac{\rho_s}{\rho_0} \left(\frac{u_0}{u_s}\right)^{\frac{1}{3}} \] ..............................(147)

\( \rho_0, \rho_s \) and \( u_0, u_s \) are the densities and ultrasonic or sound speeds of solvent mixtures and solution, respectively.

2.7. Correlating Equations

The viscosity values can be further used to determine the Grunberg-Nissan parameter, \( d^I \) as:

\[ \ln \eta = \exp \left[ \sum_{i=1}^{n} x_i \ln \eta_i + d^I \prod_{i=1}^{n} x_i \prod_{i=1}^{n} \right] \] ..............................(148)

where \( d^I \) is proportional to the interchange energy.
Again, the $V^E$, $\Delta \eta$, $G^*E$ and $K^SE$ values can be fitted to Redlich-Kister equation using the method of least squares involving the Marquardt algorithm to derive the binary coefficient, $A_j$:

$$Y^E = \sum_{J=1}^{i} A_j x_i (x_j - x_k)^{J-1}$$

Here, $Y^E$ denotes $V^E$, $\Delta \eta$, $G^*E$ and $K^SE$. In each case, the optimum number of coefficients, $A_j$ is ascertained from an examination of the variation of the standard deviation, $\sigma$, with:

$$\sigma = \left[ \frac{(y_{exp} - y_{cal})^2}{(n-m)} \right]^{1/2}$$

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

### 2.8. Viscous Synergy and Antagonism

Rheology, the field of science which studies material deformation and flow, is implicated in the mixing and flow of medicinal formulations and cosmetics, and is increasingly applied to the analysis of the viscous behaviour of numerous pharmaceutical products.

In addition, the rheological and molecular behaviour of a formulation can influence aspects such as patient acceptability – since it has been well demonstrated that viscosity and density both influence the absorption rate of such products in the body.

The study of the viscous behaviour of pharmaceuticals, 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 mutual enhancement of the physico-chemical, biological, or pharmaceutical activity between different components of a given mixture, as a result of which the combined activity is greater than the simple sum of the activities of the individual constituent components.
Viscous synergy is the term used in application to the interaction between the components of a system characterized by a net viscosity greater than the sum of the viscosities of the individual constituent components.

In contraposition to viscous synergy, the term viscous antagonism refers to interaction between the components of a system whereby the net viscosity is less than the simple sum of the viscosities of the individual constituent components. Finally, if the net viscosity of the mixture coincides with the sum of the viscosities of its individual components, then the system is said to lack interaction among its components.265, 266

The method most widely used to analyze the synergic and antagonic behaviour of the ternary liquid mixtures used here is that developed by Kalentunc-Gencer and Peleg267 allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, $\eta_{\text{exp}}$, with the viscosity expected in the absence of interaction, $\eta_{\text{calc}}$ defined by the simple mixing rule as:

$$\eta_{\text{calc}} = \sum_{i=1}^{n} w_i \eta_i$$

where $w$ is the fraction by weight of the system and $\eta$ 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 consequence.268

In order to secure more comparable viscous synergy results, the so called synergic interaction index ($I_s$) introduced by Howell269 is taken into account:

$$I_s = (\eta_{\text{exp}} - \eta_{\text{calc}}) / \eta_{\text{calc}} = \Delta\eta / \eta_{\text{calc}}$$

The negative value of $I_s$ gives antagonic 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, \( \rho_{\text{exp}} \), and a calculation is made for \( \rho_{\text{calc}} \) based on the expression:

\[
\rho_{\text{calc}} = \sum_{i=1}^{n} w_i \rho_i
\]

.......................... (153)

where \( \rho \) 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, \( F_\eta \) has also been studied which is the enhancement index of the viscosity given as:

\[
F_\eta = \eta_{\text{max}} / \eta_0
\]

.......................... (154)

where, \( \eta_{\text{max}} \) is the maximum viscosity attained in the mixture and \( \eta_0 \) is the experimental viscosity of the pure components.

### 2.9. Refractive Index and Refractivity

Optical data (refractive index) of electrolyte mixtures provide interesting information related to molecular interactions and structure of the solutions, as well as complementary data on practical procedures, such as concentration measurement or estimation of other properties. The refractive index of mixing can be correlated by the application of a composition-dependent polynomial equation. Molar refractivity, was obtained from the Lorentz- Lorenz relation by using, \( n_0 \) experimental data according to the following expression

\[
R = \left( n_D^2 - 1 \right) / n_D^2 + 2 \left( M / \rho \right)
\]

.......................... (155)

where \( M \) is the mean molecular weight of the mixture and \( \rho \) is the mixture density. \( n_0 \) can be expressed as the following:

\[
n_D = [ (2A + 1) / (1 - A) ]^{0.5}
\]

.......................... (156)

where \( A \) is given by:

\[
A = \left[ \left( \frac{n_D^2 - 1}{n_D^2 + 2} \right) (1 / \rho_1) \right] - \left( \frac{n_D^2 - 1}{n_D^2 + 2} \right) (w_2 / \rho_2) + \left( \frac{n_D^2 - 1}{n_D^2 + 2} \right) (w_3 / \rho_3) \rho
\]

.......................... (157)
where \( n_1 \) and \( n_2 \) are the pure component refractive indices, \( w_j \) the weight fraction, \( \rho \) the mixture density, and \( \rho_1 \) and \( \rho_2 \) the pure component densities.

The molar refractivity deviation is calculated by the following expression:

\[
\Delta R = R - \phi_1 R_1 - \phi_2 R_2
\]

where \( \phi_1 \) and \( \phi_2 \) are volume fractions and \( R, R_1, \) and \( R_2 \) the molar refractivity of the mixture and of the pure components, respectively.

The deviations of refractive index were used for the correlation of the binary solvent mixtures:

\[
\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2}
\]

where \( \Delta n_D \) is the deviation of the refractive index for this binary system and \( n_D, n_{D1}, \) and \( n_{D2} \) are the refractive index of the binary mixture, refractive index of component-1, and refractive index of component-2, respectively. \( x \) is the mole fraction.

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich-Kister expression\(^{272}\).

\[
\Delta n_{Dew} = w_c w_w \sum_{p=0}^{S} B_p (w_c w_w)^p
\]

where \( B_p \) are the adjustable parameters obtained by a least squares fitting method, \( w \) is the mass fraction, and \( S \) is the number of terms in the polynomial.

In case of salt-solvent solution the binary systems were fitted to polynomials of the form:

\[
n_{D,sol} = n_{Dsol} + \sum_{i=1}^{N} A_i m^i
\]

where \( n_{D,sol} \) is the refractive index of the salt + solvent system and \( n_{Dsol} \) is the refractive index of the solvent respectively, \( m \) is the molality of the salt in the solution, \( A_i \) are the fitting parameters, and \( N \) is the number of terms in the polynomial.

For the ternary systems of the salt + solvent-1 + solvent-2 solutions a polynomial expansion \(^{273}\). Similar to that obtained for the salt + solvent solutions was used to represent ternary refractive indices:
\[ n_D = n_{D_0} + \sum_{i=1}^{P} C_i m^i \] 

\( n_D \) is the refractive index of the ternary solution, \( C_i \) are the parameters, and \( P \) is the number of terms in the polynomial.

There is no general rule that states how to calculate a refractivity deviation function. However, the molar refractivity is isomorphic to a volume for which the ideal behavior may be expressed in terms of mole fraction: in this case smaller deviations occur but data are more scattered because of the higher sensitivity of the expression to rounding errors in the mole fraction. For the sake of completeness, both calculations of refractivity deviation function, molar refractivity deviation was fitted to a Redlich and Kister-type expression and the adjustable parameters and the relevant standard deviation \( \sigma \) are calculated for the expression in terms of volume fractions and in terms of mole fractions, respectively.

However, quantitative expression is still awaited. Further, improvements 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 five important methods, viz., volumetric, viscometric, interferometric, conductometric and refractometric for the physico-chemical studies in different solvent systems.
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