1.1 Thermodynamics of Solutions

Thermodynamics is mainly concerned with the dependence of equilibrium states and their relation between the various properties which depend on temperature. A thermodynamic property is a measurement which serves to describe a system. Fundamental variables of thermodynamic properties are pressure, volume, temperature, energy (enthalpy, entropy, free energy etc.) and the amount of substance.

Properties which do not depend on the amount of substance are called as intensive properties e.g. pressure, temperature, density etc. whereas the properties which change with the amount of the substance are called as extensive properties e.g. energy, mass, volume. All these properties ultimately depend on the nature of the compound.

Thermodynamic properties of pure substances and solutions are relatively easy to be determined, while those of mixtures of pure substances are complex, in the sense that they cannot be derived from properties of individual components of the mixture applying simple mixture laws. Thus in technical terms, 'liquid mixture' can be differentiated from a 'solution'. In a solution, at least one component is a solvent and remaining are regarded as solutes. Further, solvent is
treated differently from solutes, as solute is assumed to be non volatile, while in the case of liquid mixture, all the components are treated alike from technical point of view. Moreover the science of solution involves principles of mechanics, electrostatics and hydrodynamics.

It was van't Hoff\textsuperscript{1} who first applied the powerful methods of thermodynamics to solutions, in a systematic manner. Later, Gibbs\textsuperscript{2} offered treatise which provided all essential basic principles required for thermodynamics of solutions. From 1887 to the present, the knowledge of ionic solutions has been advanced immensely. Improvements have been made in the experimental methods of measuring properties associated with thermodynamic equilibrium. Properties such as conductance, viscosity, diffusion involve ions under the influence of externally imposed fields. These properties received much attention in the past and a substantial development was made. This development led to a great volume of information concerning a large number of nonionic as well as ionic systems. For ionic systems, exact theory of dilute solutions was evolved by Debye and Hückel\textsuperscript{3} jointly in 1923.

1.2 Viscosity

Some liquids flow more easily than others. The property of liquids which determines their flow is called viscosity. It is defined as the frictional resistance offered by a liquid (pure liquid or solution) against the displacement of its own molecules. Viscosity of a liquid depends on intermolecular attractive forces, molecular weight of the liquid, structure and
shape of the molecules, temperature and pressure. Viscosity of solution depends on the above mentioned as well as on concentration of solute.

1.2.1 Viscosity of suspensions

In the case of suspensions, Einstein developed an equation (1.1) giving the relative viscosity of dilute suspensions of rigid spheres.

\[ \frac{\eta}{\eta_0} = 1 + 2.5 \phi \]  \hspace{1cm} [1.1]

Where \( \eta \) and \( \eta_0 \) are the viscosity of suspension and suspending medium respectively and \( \phi \) is the particle volume fraction. Equation (1.1) is based on hydrodynamic considerations alone and strictly valid only when applied to microscopic rigid spheres in the limiting case of infinite dilution. Experimentally however it has been found effective up to volume fraction \( \phi \approx 0.01 \).

1.2.2 Viscosity of electrolytes

Electrolytic solutions behave differently (compared to solutions of nonelectrolytes) due to the inherent charges on cations and anions. Debye and Hückel studied the unusual properties of electrolytes and proposed a theory which explained many observations regarding electrolytic solutions.

According to the Debye-Hückel theory, each ion in solution is surrounded by an atmosphere of other ions whose net charge is on the average opposite to that of the central ion. When potential is applied across two electrodes immersed in the solution, the ions are set in motion, and as a consequence certain effects and changes in the ionic atmosphere arise which result in a decrease in the speed of the ions. Debye and
Hückel pointed out that these effects were due to relaxation of ionic atmosphere and electrophoretic phenomena.

In an electrolytic solution part of the stress is caused by the deformation of the ionic atmosphere. In the unperturbed solution, each ion is surrounded by an atmosphere of ions of opposite charge at an average distance of $I/K$ and this distribution possesses a spherical symmetry as per assumption made by Debye-Hückel. A velocity gradient in the solution deforms ionic atmospheres from a spherical to ellipsoidal form. The electrostatic forces and the thermal motion tends to restore the atmospheres to the original form. Since these two opposite tendencies and time of relaxation is definite, a stationary deformation persists. This deformation of the ionic atmosphere is of the order of magnitude.

$$\frac{\rho_1}{\omega^2 k} - \frac{\partial v_x}{\partial y}$$  

[1.2]

Where $\rho_1$, $\omega$, $k$, $T$ and $\partial v_x / \partial y$ the frictional coefficient of the ion, reciprocal of thickness of ionic atmosphere, Boltzmann constant, the absolute temperature and velocity gradient of moving solutions in Y direction respectively.

The forces between two ions of charge $\epsilon$ at a distance of $1/\omega$ is $e^2 \omega^2 / D$ and the total transfer of force between the ion and its atmosphere is $e^2 \omega / D$ where $D$ is the dielectric constant of the medium.
The magnitude of the stress transfer between the ion and its atmosphere obtained is

$$\frac{e^2 e_1}{n D k T} \frac{\partial v_x}{\partial y}$$

and

$$\sigma^2 = \frac{4 \pi e^2}{D k T} \sum_{i=1}^{n_i} n_i Z_i^2$$

where $e$ is the electronic charge $Z_i$ the valence to the $i^{th}$ kind of ion and $n_i$ is the number of $i^{th}$ kind of ion per unit volume of the solution. Thus electrostatic contribution to the stress $S_{yx}^*$, is given by

$$S_{yx}^* = \frac{n \rho_i \partial v_x}{\partial y}$$

This equation is correct for a proportionality factor $1/480$ which can only be obtained by the more general consideration of the exact deformation of the ionic atmosphere. Thus for the case where

$$\frac{1}{\rho} = \omega_1 = \omega_2 = \ldots = \omega_n$$

$$S_{yx}^* = \frac{1}{480 \pi} \rho_i$$

where $\omega$ represents the mobility of ion. The stress between the solvent molecules is given by the equation

$$S_{yx}^* = \eta \frac{\partial v_x}{\partial y}$$
where $\eta_0$ is the viscosity of the solvent. Hence the contribution of ionic atmosphere to the viscosity of solution can be expressed as

$$\eta^* = \frac{\rho_i}{480 \pi}$$  \[1.9\]

1.2.3 Other theories of viscosity

From the Debye Hückel theory of interionic attraction it was established that equivalent conductance is a function of square root of concentration of electrolyte. Jones and Dole correctly guessed that similar relationship would be true for viscosity i.e. viscosity should also depend on square root of concentration. The basis of this guess was that both conductance and viscosity are due to long range coulombic forces. They proposed the following equation.

$$\eta / \eta_0 = 1 + A \sqrt{C} + B C$$  \[1.10\]

where $A$ and $B$ are constants

Gruneisen measured the viscosity of many electrolyte solutions and found that in the dilute solutions, the viscosities were not approximately linear with the concentration as in higher range but instead showed a characteristic curvature. This curvature was always negative and therefore the viscosity initially increases at higher concentrations. The third term on the right hand side of the equation (1.10) was ascribed to the Gruneisen effect.

Stokes and Mills equated the viscosity of dilute electrolyte solutions to that of solvent and the contribution of five other parameters, in the following manner
\[ \eta = \eta_o + \eta^* + \eta^E + \eta^A + \eta^D \]  

where \( \eta, \eta_o \) and \( \eta^* \) have their usual meanings, \( \eta^E \) is the viscosity increment arising from the size and shape of an ion, which is closely related to the Einstein effect. \( \eta^A \) is the increment in viscosity due to the alignment or orientation of polar molecules by the ionic field. \( \eta^D \) is the viscosity change associated with distortion of the solvent structure leading to greater fluidity. If equation (1.11) is substituted in Jones-Dole equation (1.10), one gets a new equation (1.12).

\[ \eta^* + \eta^E + \eta^A + \eta^D = \eta_o \left( \frac{A}{BC} + BC \right) \]  

Eliminating the ionic interaction contribution from both sides,

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

In general the ratio \( A/B \) is very much small, hence may be neglected and Jones-Dole equation may be written as

\[ \frac{\eta}{\eta_o} = 1 + BC \]  

The equation (1.14) has been found to be valid only for the concentration range 0.002 < \( C < 0.1 \) M. For application to higher concentration a quadratic term \( DC^2 \) has been included in Jones-Dole equation.  

\[ \frac{\eta}{\eta_o} = \eta_r = 1 + A C^{1/2} + BC + DC^2 \]
The DC term in the above equation is generally positive and includes all solute-solvent and solute-solute interactions that were not accounted for by terms AC^{1/2} and BC. The main contributions by D are higher terms of the long range coulombic force, higher terms of the hydrodynamic effect, and interactions arising from changes in solute-solvent interactions with concentration. Alternatively an estimate of the influence of long range coulombic force on D can be obtained from ionic conductances at infinite dilution.

Fuoss and coworkers\textsuperscript{14,15} Kurucsev et al\textsuperscript{16} and Moulik\textsuperscript{17} made attempt to relate Einstein's equation (1.1) and the Jones-Dole equation (1.14) by substituting

\[ \phi = C \overline{V} \]

where \( \overline{V} \) is the molar volume of the solute in solution. The 'B' coefficient can then be related to \( \overline{V} \) by

\[ B = 2.5 \overline{V} \]  

Fuoss and his colleagues studied molar volumes and demonstrated that the parameter B and \( \phi_v \) are additive properties of ion contributions. They could not confirm equation (1.17) completely and recorded that the equation was valid only for larger ions. For smaller ions, the ratio \( B/\phi_v \) was greater than 0.25 and it was pointed out that the ratio increased with a decrease in size of ions. In particular, Kurucsev et al reported that equation (1.17) is valid only for ions of radius greater than 5 Å. This equation has been used to estimate degree of hydration\textsuperscript{18}. 
Considerable efforts have been made by Kirich and Ford to determine viscosity of concentrated suspensions in the form of a polynomial.

\[
\frac{\eta}{\eta_0} = 1 + 2.5 \phi + K_1 \phi^2 + K_2 \phi^3
\]  \[1.18\]

Vand demonstrated that the addition of second and higher order terms were due to particle interactions of various types. He proposed following equation.

\[
\ln \frac{\eta_r}{\eta_0} = \frac{2.5 \phi}{1 - Q \phi}
\]  \[1.19\]

where \( Q \) is a particle interaction factor,

Thomas made a critical analysis of extensive experimental data and determined the coefficients of the power series expressed in equation (1.18) to the seventh degree. He further demonstrated that a simple second degree equation (1.20) correlated the experimental data of \( \eta/\eta_0 \) values for \( \phi \leq 0.25 \).

\[
\frac{\eta}{\eta_0} = 1 + 2.5 \phi + 10.05 \phi^2
\]  \[1.20\]

Since at \( \phi = 0.25 \), the average particle separation is only 0.35 particle diameter, this equation seems to be valid for quite highly concentrated suspensions.

Bresslau and Miller performed transformation presented in equation (1.1) on equation (1.20) resulting in
\[ \frac{\eta}{\eta_o} = 1 + 2.5C \cdot V_e + 10.05C^2 \cdot V_e^2 \] \[ \text{[1.21]} \]

The subscript 'e' has been added to 'V' to designate it as an effective rigid molar volume. It follows that

\[ V_e = \frac{-2.5C \pm \sqrt{(2.5C)^2 - 4(10.05C^2)(1 - \eta/\eta_o)}}{2 \times 10.05C} \] \[ \text{[1.22]} \]

If magnitudes of viscosity, concentration are known for any given salt, its effective rigid molar volume, \( V_e \), may be obtained from equation (1.22).

Moulik has shown that at higher concentrations (beyond the region where the Einstein's relation holds) the relative viscosities of many solute-solvent systems including electrolyte-water systems are given by the

\[ \eta_r^2 = 1 + KC^2 \] \[ \text{[1.23]} \]

Where \( I \) and \( K \) are constants.

Desnoyers and Perron suggested that structural solute-solute interactions play an important role in the concentration dependence of most physico-chemical properties. If equation (1.13) is written in the form.

\[ \frac{\eta_r - 1 - AC^{1/2}}{C} = B + DC \] \[ \text{[1.24]} \]
It becomes a pseudo reduced quantity and as such resembles an apparent molar quantity. Then it would be reasonable to relate 'B' and 'D' to solute-solvent interactions and to solute-solute interactions respectively. If the coulombic forces were mostly accounted for by the \( A 1/2 \), 'D' would be essentially a solute-solute structural interaction term. Consequently 'D' parameter should depend on the nature of the ion in a way similar to the deviations of the Debye-Hückel theory for the activity coefficients.

Falkenhagen et al\(^25-28\) initiated the theoretical calculation of the constant 'A' using the equilibrium theory as a starting point. He gave an expression for water as a solvent at 25°C.

\[
A = 0.7536 \left[ \frac{\lambda_1^o \lambda_2^o}{4 \lambda_1^o \lambda_2^o} - \frac{(\lambda_1 - \lambda_2)^2}{4.41 \lambda_1^o \lambda_2^o (\lambda_1^o + \lambda_2^o)} \right] \quad [1.25]
\]

In the first instance, the development was applied only to simple electrolytes whose constituent ions were of similar mobilities but later, it was extended to the cases where they differed. Then in 1932 Onsagar and Fuoss\(^29\) developed a theory to describe viscosity, conductance and diffusion in dilute solutions.

To summarise the theory of long range interionic contribution to the viscosity of electrolyte is well justified by Jones - Dole equation. Experimental evidence indicates that this effect can explain the behaviour of concentration on viscosity curve up to about 0.002 M. It was
pointed out also that elaboration of dilute solution theory to include a parameter for the finite size of the ions fails to extend the range of equations significantly. At concentrations above 0.002 M a marked linear variation of viscosity with concentration is shown by strong electrolytes, extending to 0.1 M and higher in aqueous solution and to somewhat lower concentration in some non-aqueous systems. The coefficient \( B \) of the Jones - Dole equation is probably related to the disturbance of the structure which is present in liquids. Its magnitudes also vary widely for different solvents and show progressive changes in mixed solvents. The viewpoint is generally accepted that \( B \) coefficient are manifestation of ion-solvent interactions and this is of course supported by the linearity of BC terms in the equation (1.6).

The second important deduction concerns the evidence for the additivity of ionic contributions. \( B \) values for pairs of salts with same anion but different cations have constant differences proved this. The division of \( B \) coefficients into individual ionic values is rather arbitrary process.

Generally in mixed solvent systems, no division into ionic \( B \) values has been attempted. It is observed that as the temperature increases \( B \) values suffer changes. The dependenc of \( B \) on temperature is explained on the basis of modified solvent, differing from the bulk in structure and properties. Gurney's cosphere\(^\text{30}\), Frank and Wen's\(^\text{31}\) A, B and C zones and Nightingale's\(^\text{32}\) hydrated radius are reflections of this idea.
1.3 Molar volumes of Electrolytes

Consider a solution composed of \( j \) constituents and let \( n_1, n_2, \ldots, n_j \) be the numbers of moles of the various constituents present. Further, let \( G \) be any extensive property of the system, \( G \) must be a function of \( P, T \) and the numbers of moles of the various constituents present i.e.

\[
G = \phi (P, T, n_1, n_2, \ldots, n_j) \tag{1.26}
\]

Partial differentiation of equation (1.26) yields for \( dG \)

\[
dG = \left[ \frac{\partial G}{\partial T} \right]_{P,n_j} dT + \left[ \frac{\partial G}{\partial P} \right]_{T,n_j} dP + \left[ \frac{\partial G}{\partial n_1} \right]_{P,T,n_1} dn_1 \\
+ \left[ \frac{\partial G}{\partial n_2} \right]_{P,T,n_2} dn_2 + \ldots + \left[ \frac{\partial G}{\partial n_j} \right]_{P,T,n_j} dn_j \tag{1.27}
\]

Further, at constant temperature and pressure the first two terms in equation (1.27) are zero, and we get thus

\[
dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \ldots + \bar{G}_j dn_j \tag{1.28}
\]

By use of Euler's theorem for homogeneous functions, equation (1.29) can be integrated to yield

\[
G = \bar{G}_1 n_1 + \bar{G}_2 n_2 + \ldots + \bar{G}_j n_j \tag{1.30}
\]
Equation (1.30) shows that any extensive property of a solution can, at constant $T$ and $P$, be expressed as a sum of $G$ products for the individual solution components. Further, since in each product the $n$ represents a capacity factor, the $G$, called a partial molar quantity, must represent an intensive factor. Consequently the partial molar quantities must be intensive properties of a solution.

Equation (1.30) if differentiated completely,

$$dG = \overline{G}_1 \, dn_1 + n_1 \, \overline{dG}_1 + \overline{G}_2 \, dn_2 + n_2 \, \overline{dG}_2 + \cdots + \overline{G}_j \, dn_j + n_j \, \overline{dG}_j$$

$$= (\overline{G}_1 \, dn_1 + \overline{G}_2 \, dn_2 + \cdots + \overline{G}_j \, dn_j)$$

$$+ (n_1 \, \overline{dG}_1 + n_2 \, \overline{dG}_2 + \cdots + n_j \, \overline{dG}_j)$$

Comparing equations (1.29) and (1.30)

$$n_1 \overline{dG}_1 + n_2 \overline{dG}_2 + n_j \overline{dG}_j = 0$$

and for only two constituents, i.e. a binary solution,

$$n_1 \overline{dG}_1 + n_2 \overline{dG}_2 = 0$$

or

$$\overline{dG}_1 = -\frac{n_2}{n_1} \overline{dG}_2$$

The above equations are two forms of the Gibbs-Duhem equation. They show that the partial molar quantities are not independent of each other, and that variation of one partial molar quantity affects the others in the manner given by the equations. For instance, equation (1.33) indicates that if $dG$ is positive, i.e. $G$ increases, then $dG$ must be negative and $G$ must decreases at the same time, and vice versa.
1.3.1 Determination of partial molar volumes

Partial molar quantities can be determined by a variety of methods, both graphical and analytical. It is desired to ascertain the partial molar volumes of a binary solution, and suppose that for this purpose the total volume $V$ of the solution as a function of the molarity $M$ of solute is measured. The number of moles of solvent present in each instance is fixed and given by $n_1 = \frac{1000}{M_1}$ where $M_1$ is the molecular weight of the solvent. Again $M$ must be $n_2$. Therefore if plot $V_2$ verses $M$ is drawn, the slopes of the curve at various concentrations, will be the values of $V_1$ at the selected concentrations. Having thus obtained $V_2$, the corresponding values of $V$ can be calculated by substitution of $V$, $n_1$ and $n_2$ for each concentration in to equation (1.30), which in this instance takes the form.

$$V = \overline{V}_1 n_1 + \overline{V}_2 n_2$$

[1.34]

An alternate method of handling the same data is as follows. A function $v$ is calculated from $V$, $n_1$ and $n_2$

$$v = \frac{V}{n_1 + n_2}$$

[1.35]

and plot $v$ against the mole fraction of solute $N_2$ is a curve. If tangent is drawn to the curve at any point, the intercept of the tangent on the $N_2 = 0$ axis gives $\overline{V}_1$ and the intercept on the $N_2 = 1.0$ axis gives $\overline{V}_2$. By repeating this procedure at various points along the curve, $\overline{V}_1$ and $\overline{V}_2$ can be evaluated for various solution concentrations.
The another method of analytic expression of $V$ as a function of $m$. Suppose that $V$ as a function of $m$ can be expressed by the relation

$$V = a + bm + cm^2$$  \[1.36\]

where $a$, $b$ and $c$ are constants at a given temperature and pressure. Differentiating equation (1.36) with respect to $m$ yields then $V_2$, namely,

$$\bar{v}_2 = \frac{\partial V}{\partial m} = b + 2cm$$  \[1.37\]

and substitution of equation (1.36) and (1.37) in to (1.34) gives for $\bar{v}_1$

$$a + bm + cm^2 = \bar{v}_1 \, n_1 + \bar{v}_2m$$

$$= \bar{v}_1 \, n_1 + (b + 2cm)m$$

$$\bar{v}_1 = \frac{a - cm^2}{n_1}$$  \[1.38\]

All these methods are equally applicable, and in the same manner for the determination of partial molar quantities.

1.3.2 Partial molar volumes review

The apparent and partial molar volumes of electrolyte solutions have proved to be a very useful tool in elucidating the structural interactions occurring in solution. The partial molar volumes at infinite dilutions can be used to study ion-solvent and solvent-solvent interactions, and concentration dependence of the apparent and partial molar volumes of electrolytes at infinite dilutions can be used to
study ion-solvent and solvent-solvent interactions.

Thus the study of the partial molar volumes of electrolytes at understanding of ion-solvent and solvent-solvent interactions.

The partial molar volume of electrolytes can also be used to calculate the effect of pressure on ionic equilibria for processes of engineering and oceanographic importance.

Watson\textsuperscript{33} made the first accurate measurements on the volume change of adding electrolytes to water, in 1887, Arrehenius\textsuperscript{34} presented his theory on the dissociation of electrolytes into ions. In 1957, various workers like Ackermann\textsuperscript{35} Buckingham\textsuperscript{36}, Eigen\textsuperscript{37}, Kaminsky\textsuperscript{38}, Somolov\textsuperscript{39}, Young Wu and Krawetz\textsuperscript{40} etc. put forth their idea on structural hydration interaction in the discussions of Faraday society. In 1840 when Datton\textsuperscript{41} made some volume measurements which, he thought, supported the porosity theory of water. Holker\textsuperscript{42} found that the volume change on addition salt to water could be positive or negative depending on the salt, the temperature and the concentration. Playfair and Joule\textsuperscript{43} repeated Holker's work and found a relationship between the volume of a salt in solution and in crystal. Marignac\textsuperscript{44} showed that Playfair and Joule's work was incorrect and that Holker's work was correct.

By 1850, the decrease in volume upon the addition of a salt to water was generally accepted and in 1854, Michel and Krafft\textsuperscript{45} solutions. Kremers\textsuperscript{46} showed that the density was not a linear function of concentration and that the relative volumes of electrolyte solutions go through a maximum with
increasing temperature. Schiff\textsuperscript{47} studied the density of concentrated salt solutions and calculated the volume of water bound in the crystal.

The apparent molar volume, $\phi_v$, of an electrolyte in solution was first introduced in 1871 by Marignac\textsuperscript{48}.

$$\phi_v = \frac{(V - n_1 \overline{V}_1^0)}{n_2}$$  \[1.39\]

Where $V$ is the volume of the solution, $n_1 \overline{V}_1^0$, is the volume of water in solution, $n_1$, is the moles of water, $\overline{V}_1^0$, is the molar electrolyte in solution. He found that magnitude of $\phi_v$ increase with concentration and temperature for the salts he studied.

Favre and Valson\textsuperscript{49} were the first to observe regularity between the additivity of the densities or magnitudes of $\phi_v$ of different salt solutions. They further assumed that the volume change on adding salt to water was the result of two opposing effects (1) contraction in volume due to the adsorption of water dissociation.

Nicol\textsuperscript{50,51} was the first to attempt to explain why do the magnitudes of of $\phi_v$ electrolytes increase with increasing concentration by using the so called attraction theory. A salt was thought to get dissolved when the attraction of water for salt exceeded that of salt for salt.

The theory of Arrhenius in 1887 was of great important in the development of the theory of solution volumes. Using this theory. Schmidt\textsuperscript{52} in 1890 showed the additivity of the
magnitudes of $\phi_v$ for various salt pairs. In 1692, Tranbe\textsuperscript{53} believed that the $\phi_v$ represented the actual volume of the salt in solution, he explained negative magnitudes of $\phi_v$ on the basis of the crystal water that the salt contained. He noted the change of the $\phi_v$ with valance type.

Two very important theories about magnitudes of $\phi_v$ viz. Drude & Nernst's\textsuperscript{54} electrostriction theory and Tammann's\textsuperscript{55}, internal pressure theory, were developed directly from Arrhenius work and are still the basis for many theories of ion solvent interactions today.

Tammann gave a reasonable theoretical explanation of solution volumes. The fundamental idea of his theory of internal pressure ($\Pi$) was developed by noting that an increase in pressure and the addition of a salt to water, lowered the temperature of maximum density. Thus a dissolved salt appears to cause the water to behave as if it were under a high external pressure. He explained this theory of solution volumes\textsuperscript{56} by attributing the $\phi_v$ to (i) the change in volume of the salt due to the pressure from 1 atm. to $\Pi$ (ii) the change in volume of the solvent due to change in the pressure from 1 atm. to $\Pi$ and (iii) the change in volume to give a solution at $\Pi$ atm. internal pressure and 1 atm. external pressure.

Drude and Nernst developed their electrostriction theory by assuming that ions can be treated as charge spheres in a continuous dielectric medium. They calculated the electrostrictive decrease in volume from the equation
Where \( Z \) is the charge on the ion, 'e' is the electrostatic charge, 'D' is the dielectric constant of the solvent, 'r' is the radius of the ion and 'P' is the pressure.

Kohlrausch developed a sinker method (based on hydrostatic balance) to study the densities of electrolyte solutions. Kohlrausch and Hallwachs work laid to the general use of the symbol \( \phi_v \) for the apparent or equivalent molar volume. They also showed experimentally that the \( \phi_v \) is proportional to \((S-1)/C\) where 'S' is the specific gravity, which follows from the definition of the apparent molar volume.

\[
\phi_v = - \frac{1000 (S - 1)}{C} + \frac{M}{d_0} \tag{1.41}
\]

Where 'C' is the molar concentration, 'M' is the molecular weight of the solute, 'd_0' is the density of pure solvent.

Baxter and Coworkers applied the theory of Richards on the compressible ion to solution volumes, their theory differed from that of Tammann and that of Drude and Nernst in that, they thought the salt and solvent contracted. Baxter thought that the \( \phi_v \) was due to (i) an expansion due to
freezing of the ions from the crystalline restraints, (ii) a smaller expansion due to repulsion of like charges and (iii) a contraction due to ion-water interactions mostly due to the contraction of water. The decrease in $\phi_v$ with decreasing concentration was attributed to ionization and the increase in the $\phi_v$ with temperature was attributed to decrease in hydration.

In 1913, Lamb and Lee developed a magnetic float method of measuring the densities of solutions. Although this method can be considered as development or modification of the hydrostatic weighing method, the magnetic float method requires no suspension measuring densities to a precision of a 0.1 ppm, and they were able to determine magnitudes of $\phi_v$ for innumerable inorganic salts in very dilute aqueous solution (0.0001 to 0.01 M).

After 1925, due to the new advances made in the knowledge of solutions, it became evident that there was a need for a revision and reinterpretation of solution volumes. Campbell attempted to calculate the true volume of certain salt solutions and Redlich and coworkers applied the Debye Hückel theory to the concentration dependence of $\phi_v$.

In 1926, Webb developed a theory for the volume change produced by electrostriction in the vicinity of an ion. The electrostriction of a solvent was given by the equation as

$$\bar{V}^{\infty}_{\text{elect.}} = \int_{r_o}^{\infty} \frac{-\Delta V_r}{V} \cdot \frac{4 \pi r^2}{r} \, dr$$

[1.42]
Where \( \Delta V_{r/y} \) is the fractional change of volume at a distance from the centre of the ion where the pressure is \( P_r \) and \( r \) is the radius of the ion (i.e. the region into which no solvent molecules could enter). The fractional change in volume can be obtained directly from the observed relative volume of the solvent at pressure \( P_r \) or from the compressibility equation.

\[
- \frac{\Delta V}{V} = \int_{0}^{P_r} \rho \, dP
\]

[1.43]

Where \( \rho \) the compressibility is a function of pressure.

In 1929, Masson found a valuable empirical generalization equation (1.44) on the change of the with the square root of concentration.

\[
\phi_v = \phi_v^0 + S_v^* \sqrt{C}
\]

[1.44]

Where \( \phi_v^0 \) the apparent molar volume at infinite dilution (equal to the partial molar volume of the solute) and is the characteristic constant that varies with each electrolyte. This equation adequately represented the concentration dependence of the magnitudes of of \( \phi_v \) electrolyte over a wide range of temperature and concentration.

1.4 Electrolytic Conduction

Flow of electricity through a conductor involves a transfer of electrons from a point of higher negative potential to lower. Conduction takes place by direct migration of electrons through the conductor under the influence of an applied potential. Here the atoms or ions composing the conductor are not involved in the process, except for a vibration about their main positions of equilibrium, they
remains stationary. On the other hand, in electrolytic conductors, which include solutions of strong and weak electrolytes, fused salts, and also some solid salts such as sodium chloride and silver nitrate, electron transfer takes place by a migration of ions, both positive and negative, towards the electrodes. This migration involves not only a transfer of electricity from one electrode to the other, but also a transport of matter from one part of the conductor to the another. Further, current flow in electrolytic conductors is always accompanied by chemical changes at the electrodes which are quite characteristic and specific for the substances composing the conductor and the electrodes.

1.4.1 Electrolytic conductance

The resistance of an electrolytic conductor to current passage can be determined by the application of Ohm's law to such conductors. However, instead of resistance, its reciprocal i.e. conductance is customarily studied. As is well known, the resistance of any conductor is directly proportional to its length and inversely to its cross sectional area, namely,

$$\text{R} = \dfrac{\rho}{A}$$  \[1.45\]

Where R is the resistance in ohms, l is the length in centimeters, A the area in square centimeters and \(\rho\) the specific resistivity. The value of \(\rho\) depends on and is characteristic of the nature of the conductor. From equation (1.45) the expression for the corresponding conductance L follows as
\[ L = \frac{1}{R} = \frac{1}{\rho} \left( \frac{A}{1} \right) \]

\[ = L_s \left( \frac{A}{1} \right) \quad [1.46] \]

Where \( L_s = 1/\rho \) is the specific conductance of the conductor. This quantity may be considered to be the conductance of 1 cm cube of material, and is expressed in reciprocal ohms or mhos per centimeter.

Although the specific conductance is a property of the conducting medium, in dealing with solutions of electrolytes a quantity of greater significance is the equivalent conductance, \( A \). The equivalent conductance of an electrolyte is defined as the conductance of a volume of a solution containing one equivalent weight of dissolved substance when placed between two parallel electrodes one cm. apart, and large enough to contain between them all the solution. \( A \) is never determined directly, but is calculated from the specific conductance by equation (1.47).

\[ A = \frac{1000 L_s}{C} \quad [1.47] \]

1.4.2 Equivalent conductance at infinite dilution

Kohlrausch was the first to point out that when \( A \) for strong electrolytes is plotted against \( C \), the curve approaches linearity in dilute solutions,

\[ A = A_o - b \sqrt{C} \quad [1.48] \]

where \( b \) is a constant.
The Kohlrausch extrapolation method for evaluation of $A_0$ cannot be used for weak electrolytes instead; those at infinite dilution are obtained by application of Kohlrausch's law of independent migration of ions, which states that at infinite dilution, where dissociation for all electrolytes is complete and where all interionic effects disappear, each ion migrates independently of its co-ion, and contributes to the total equivalent conductance of an electrolyte a definite share which only on its own nature and not at all on that of the ion with which it is associated.

1.4.3 Conductivity of electrolyte solutions

The study of electrolyte solutions has occupied a central position in physical chemistry. This study constituted the early basis of electrochemistry. The understanding of the nature of electrolytic dissociation, ionic migration, conductance served to clarify early views on electrical nature of matter and the significance of chemical combination\(^6\)\(^8\)-\(^7\)\(^0\). Later, study of behaviour of electrolytic solution led to some of the first satisfactory ideas about ionic interaction effects and nonideal solutions\(^3\)\(^4\),\(^7\)\(^1\). Debye and Hückel\(^3\) provided more useful study in 1929.

In the early work on conductance only little attention was paid to specificity of ionic behaviour in solution, although significance of specificity was stressed by Bronsted\(^7\)\(^2\), Guggenhein and Turgeon\(^7\)\(^3\) and others\(^7\)\(^4\),\(^7\)\(^5\). The early work was done on aqueous solutions and the special role of solvent in relation to the behaviour of electrolytes was
generally overlooked viz. the unique properties of water were not fully appreciated. It was latter understood as to why electrolytes in aqueous solution exhibited surprisingly high degree of specific behaviour at moderate concentrations (0.01 to 0.2 M). The further study indicated that at higher concentrations ion-solvent interactions become quite prominent.\textsuperscript{71-77} Effects of addition of electrolytes were studied eventually and it was found that in certain cases, the effects were similar to those caused by increase in temperature.\textsuperscript{80,81}

1.5 Scope of the Present Work

Solute-Solvent studies in electrolyte solutions have been a subject of interest to solution chemists for quite some time. Such studies on the transport and thermodynamic properties of electrolytes in aqueous, nonaqueous and mixed solvents are of interest in various technologies like high energy, density barriers, photoelectrochemical cells, electro deposition and wet electrolytic capacitors and in electro organic synthesis.

Measurements of viscosities, apparent molar volumes in solution provide an excellent method of obtaining data on solute-solute and solute-solvent interactions. Apparent and partial molar volumes of electrolytes obtained from density measurements of electrolyte solutions have been used to examine the ion-ion, ion-solvent and solvent-solvent interactions, as well as structural changes in the solvent induced by the solute. Since viscosity is a property of liquid which depends on the inter-molecular forces, the structural aspects of
liquids can be inferred from the viscosity of solutions at different concentrations and temperatures. Accurate thermodynamic data on electrolyte solutions are frequently needed.

Solute-solvent, solute-solute and solvent-solvent interactions have been studied in aqueous and non-aqueous solutions by many workers, but such investigations in mixed solvents are scanty. Wherever studies in mixed solvents are reported, attention has never been given to the mutual interactions of the solvent molecules in the interpretation of transport and thermodynamic properties of electrolytes in mixed solvents.

The present investigation is undertaken to examine the structural changes in alcohol-water, 1,4-dioxane-water and dimethyl sulfoxide-water on addition of benzyl trimethyl-, ethyl and butyl ammonium chloride and the results are presented in this thesis. The present work involves the measurements of viscosity, density and conductivity of benzyl trimethyl-, ethyl and butyl ammonium chloride in aqueous alcohol, dioxane and dimethyl sulfoxide at different temperatures. The viscosity A and B coefficients, apparent and partial molar volume of these salts in aqueous alcohols, dioxane and dimethyl sulfoxide have been calculated to detect solute-solvent, solute-solute interactions. These interactions are further investigated from conductivity studies and parameters like limiting molar conductance, association constant and cosphere diameter R, which have been calculated from Fuoss conductance concentration equation (1978).
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