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PARENTS
CHAPTER-I

INTRODUCTION
Experimental studies of physical and inorganic chemistry of solutions have been restricted mainly to aqueous systems in the early days of research in solution chemistry and the solution theories have been largely based on results so obtained. Solutions of electrolytes in water have attracted more attention than the corresponding solutions in non-aqueous and aquo-organic solvent systems, even though it has been realised for a long time that water can not be regarded as the prototype of electrolytic solvents. Hildebrand and Scatchard, together with their many colleagues, have drawn the attention of scientists and technologists to the fact that solutions need not necessarily be aqueous, and the study of other solvent media is more likely to help in elucidation of solute-solvent interactions in condensed phases.

During recent years a great attention is being paid to interpret solute-solvent interactions in mixed solvents because water does not conform to some or all the solution theories based on experiments performed with simple solvents. The incapability of solution theories used to describe the various phenomena in aqueous solutions, suggests the application of the results of various theoretical investigations to mixed solvent systems. The mixed solvent
systems in multicomponent solutions have the advantage of varying dielectric constant and viscosity and the behaviour of the ions tend to reveal their peculiar individualities more clearly. Moreover, mixed binary aqueous solvent systems behave in an unexpected manner as compared with behaviour of aqueous and mixed nonaqueous systems. In recent years an increasing interest has been shown in study of electrolytes and mixed solvents, with a view to investigate solute-solute and solute-solvent interactions under varied conditions.

The study in mixed solvent systems is important from the following view points:

1. It has been observed that various aquo-organic mixtures like water-sulfolane, water-dioxane, water-tetrahydrofurane, and water-acetone tend to disorder the water structure and this results in depolymerisation of water by organic component. The studies in such solvent mixtures may effect interaction between ions and water. Moreover, it has been observed earlier, that interaction between ions and water decreases in water-sulfolane mixtures.

2. Solvent systems like 'water + sucrose' offer frictional resistance to the mobility of ions, and it
tends to form cage like structure\textsuperscript{14b}.

The study of transport processes in mixed solvents provide an opportunity of extending the phenomenology of various theories of electrolytic solutions and structural aspects of solvent systems. Electrolytic behaviour in solutions\textsuperscript{15-28} can be revealed through studies of transport processes such as viscous flow, electrical conduction and diffusion etc. Apart from the importance of transport processes in understanding the solute-solute, solute-solvent interactions and structural aspects of solvent in solutions, the atomic transport processes also play a major role in properties of solids such as sintering, tarnishing reactions, precipitation of separate phases, electrolysis, fuel cells, dielectric loss and photographic process\textsuperscript{29}. In following paragraphs a brief introduction of transport phenomena and of transport processes viz. viscous flow, electrical conduction, transport number thermal diffusion and electrokinetic effects, is given:

**TRANSPORT PROCESSES** :

Various transport processes may be described under the following headings:

A. Uncoupled transport processes.
B. Coupled transport processes.

If an equilibrium system is changed to non-equilibrium state by some external or internal disturbance, one of the state functions becomes a function of position. When disturbance is removed, an irreversible decay process occurs spontaneously and system advances through a series of non-equilibrium states until equilibrium is reached and the decay process is a transport process. A system in equilibrium has all the intensive state variables (for example, temperature and density) constant at all times and these variables have same magnitude at all positions in the system. At equilibrium, the gradients of parameters are absent, spontaneous processes do not occur and there is no net exchange of matter or energy with the system or the surroundings or between one part of the system and another. If a system is in a state in which these conditions are not satisfied, the system is said to be in a non-equilibrium state. During this process of change, gradients of one or more intensive properties are set up in the system and transfer of mass or energy takes place under the influence of gradients of the properties. The transport processes are concerned with transference of mass and/or energy and the dependence of parameters is associated with flux of some kind.
A. **UNCOUPLED TRANSPORT PROCESSES**

For a steady state transport there exists a linear relationship between gradients of the extensive properties, $X$, called force, and its conjugate flux, $J$, thus:

$$ J = LX $$

Equation (I.1) is valid for those non-equilibrium states which are not far removed from equilibrium.

For a transport process guided by $n$ independent forces, relation (I.1) assumes the general form:

$$ J_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i = 1, 2, \ldots, n) $$

where $X$ is the generalised force, $J$ is generalised flux and $L_{ik}$ the transport coefficient. When $L_{ik} = 0 (i \neq k)$, equation (I.2) is reduced to $J_i = L_{ii} X_i$. It is a phenomenological representation of several empirical laws involving systems which are in non-equilibrium state on account of the presence of gradients of temperature, density or local macroscopic
velocity. They are associated with transport processes such as that conduction, electrical conductance, diffusion and viscous flow etc. In the following paragraphs a brief introduction of viscous flow and electrical conductance studies along with some of the latest work and the state of art in the field is described.

1. VISCOS FLOW:

   The viscosity of the liquid is a measure of its resistance to flow or its rate of strain. Since flow takes place by the displacement of the equilibrium position of molecules, studies of viscosity can lead to information about these displacements.

   The viscosity studies are important from the viewpoint to establish the nature of solute-solvent, solute-solute interactions and structural effects on solvent in solution. Solute-solvent interactions have been a subject of interest for the past few decades.\(^8,16,23,24,25,30-44\).

   In a very dilute solution, the interstitial solvent between the co-spheres of ions is unmodified and has the same properties as in pure solvent. Each species of ions would be expected to contribute towards a change in the viscosity, but the electrostatic forces between oppositely
charged ions must be taken to account. The concentration dependence of electrolytic solution has been interpreted in terms of semi-empirical Jones-Dole equation \(^{45}\):

\[
\eta_{\text{rel.}} = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC
\]  

(I.3)

where \(\eta\) and \(\eta_0\) are the viscosities of the solution and solvent respectively, \(C\) is molar concentration of electrolyte, \(A\) is a parameter obtained from inter ionic theory \(^{46, 47}\) and \(B\) is a adjustable parameter, either positive or negative and it accounts for solute-solvent interaction \(^{18}\).

A co-efficient can be calculated from inter ionic attraction theory \(^{9}\) for a uni-univalent electrolyte with the help of the equation:

\[
A = \frac{0.2577 \Lambda^0}{\eta_1 (\varepsilon_1 T)^{1/2} \lambda^0 \lambda^-} \left[ 1 - 0.6863 \left( \frac{\lambda^0_+ - \lambda^0_-}{\Lambda^0} \right) \right]
\]  

(I.4)

where \(\Lambda^0\) is limiting equivalent conductance, \(\eta_1\) is the viscosity of solvent, \(\varepsilon_1\), dielectric constant of solvent and \(\lambda^0_+, \lambda^0_-\) are limiting equivalent conductances for respective ions. It has been claimed by Feakins et. al. \(^9\) that in
partially aqueous systems $A$-value is more accurate from equation (I.4) as compared to $A$-value from equation (I.3). B-values can be calculated from equation (I.3) by fitting the value of $A$ obtained from equation (I.4).

Bhattacharyya and Sengupta have calculated $B$-coefficient for mixture of 1:1 electrolytes from $B$-coefficient values of individual electrolytes with the use of the following equation:

$$B_{\text{mix}} = \frac{m_1 B_1 + m_2 B_2}{m_1 + m_2} = x_1 B_1 + x_2 B_2$$  \hspace{1cm} (I.5)

where $x_1$, $x_2$ are the mole fractions and $B_1$, $B_2$ the individual $B$-coefficients of the respective electrolytes. To calculate $B_{\text{mix}}$ from equation (I.5) care is to be taken that total concentration range to which experimentally determined $B$-values of the mixture refer, should be restricted to lie closely within those to which the $B$-coefficients of the individual electrolytes refer.

$B$-coefficient is important in deciding order or disorder introduced by solute into solvent structure. Since it is usually difficult to separate the ionic size effect from the structure effect of $B$-coefficients, better criterion for
solvent structural influences would be temperature dependence values of the B-coefficients i.e. $\frac{dB}{dT}$. According to this criterion, structure makers will have negative values of $\frac{dB}{dT}$, while structure breakers will have positive values of $dB/dT$.

A useful method for study of B-coefficient is to make use of transition state theory. Application of this theory gives rise of the following equation:

$$B = \left( \frac{\bar{V}_1^o - \bar{V}_2^o}{V_{1000}} \right) + \left( \frac{\bar{V}_1^o}{V_{1000}} \right) \times \left( \Delta \mu_2^0 - \Delta \mu_1^0 \right) / RT$$  (I.6)

where $\bar{V}_1^o$ and $\bar{V}_2^o$ are the limiting partial molar volumes of solvent and solute. $\Delta \mu_1^0$ is the free energy of activation per mole of the solvent and $\Delta \mu_2^0$ is the contribution per mole of the solute to free energy of activation for viscous flow of the solution. The quantity $(\Delta \mu_2^0 - \Delta \mu_1^0)$ represents the change in the activation free energy per mole of the solute replacing one mole of the solvent by one mole of the solute. For a ternary system the subscript 3 is used instead of 2 for solution. The free energy of activation for pure solvent is given by:

$$\Delta \mu_1^0 = RT \ln \left( \frac{\eta_1 \bar{V}_1^o}{kN} \right) $$  (I.7)
where \( h \) is Planck's constant and \( N \) is the Avogadro's number. From the B-coefficient determined from viscosity studies, \( \Delta \mu_{b}^{\phi} \) (\( \Delta \mu_{b}^{\phi} \) for ternary system), can be estimated. If a series of determinations of B-coefficient at different temperatures are made, the enthalpy and entropy of activation for viscous flow can also be calculated. Domenech and Costa\textsuperscript{54} calculated the B-value of tetraethyl-ammoniumbromide in DMF-water mixtures at 25\(^{\circ}\), 30\(^{\circ}\) and 35\(^{\circ}\)C and results were analysed in terms of the transition theory from view point of ion-solvent interaction.

The intermediate range of concentration between anhydrous molten electrolytes and dilute electrolyte solutions is of interest to researchers from theoretical and industrial viewpoints. A number of papers dealing with viscosity studies have appeared recently\textsuperscript{55-62}.

Goldsack and Franchetto\textsuperscript{57} developed the following relationship deduced from absolute rate theory:

\[
\ln \left[ \eta_{\text{rel.}} (1 + XV) \right] = XE
\]

where \( X \) is the mole fraction of solute, \( E \) and \( V \) are parameters characteristic of electrolytes. The values of \( E \) and \( V \) are obtained by solving the equation by non-linear least square
method. The values of \( E \) and \( V \) can also be calculated by fitting an appropriate value of \( V \) in left hand side of equation (I.8) and plotting a graph between natural log of \( \left[ \eta_{\text{rel.}}(1 + XV) \right] \) and \( X \). The value of \( V \) is that which gives the straight line fit for the data with intercept zero and accordingly the slope of plot is \( E \). The values of \( V \) tried by Franchetto et. al., were from 0 to 50 in increments of 0.01. \( B \)-coefficient is calculated using the relation:

\[
B = \frac{(E - V)}{55.51}
\]  

(I.9)

Choudhary and Majumdar\(^{60,61}\) have put forward a modified form of Angell's equation\(^{60,61,63}\) based on free volume theory of transport phenomena in liquids and fused salts to ionic solutions\(^{61,63,64}\). The equation relates relative viscosity, \( \eta_{\text{rel.}} \), at concentration, \( N \), to hypothetical concentration, \( N_0 \), at which glass formation occurs.

According to Angell, the equation of fluidity (reciprocal of viscosity, \( \frac{1}{\eta} \))\(^{60,63}\) is expressed as:

\[
\frac{1}{\eta} = A \exp \left[ - \frac{k}{(N_0 - N)} \right]
\]

(I.10)
where \( N \) represents the concentration of the salt in equiv. litre\(^{-1}\), \( A \) and \( k \) are constants supposed to be independent of salt composition and, \( N_0 \), is the hypothetical concentration at which the system becomes glass. It has been demonstrated by Angell that the function \( 1/(N_0 - N) \) is able to produce straight line for plot of \( \ln \frac{1}{\eta} \) versus \( \frac{1}{N_0 - N} \) provided an appropriate value of, \( N_0 \), is inserted into equation (I.10) and further the linearity extends to zero salt concentration. When \( N \to 0 \) and \( \eta \to \eta_0 \) (viscosity of pure solvent) the equation (I.10) can be written as:

\[
\ln \eta_{\text{rel.}} = \frac{k' \, N}{N_0 (N_0 - N)} \quad \text{(I.11)}
\]

where \( \eta_{\text{rel.}} = \frac{\eta}{\eta_0} \) is relative viscosity. Equation (I.11) predicts straight line passing through origin for plot of \( \ln \eta_{\text{rel.}} \) vs \( N/(N_0 - N) \), if a suitable choice of, \( N_0 \), is made.

2. **Electrical Conductance**:

Electrical conductance of a material means the ease with which the electric current flows through the solution of material. Electrical conductance of a material depends on concentration and mobility of the charge carriers i.e. ions in the solution. There are two aspects to these ionic motions.
First aspect concerns with the dynamical behaviour of ions as individuals, the trajectories they trace out in electrolyte, and the speeds with which they dart around. These ionic movements are basically random in direction and speed. Secondly, ionic motions have a group aspect which is of particular significance when more ions move in certain directions than in others and thus produce a drift or flux of ions. This drift has important consequences because an ion has a mass and bears a charge. Consequently, the flux of ions in a preferred direction results in transport of matter and flow of electric current.

A flux of ions can come about in three ways. If there is a difference in concentration of ions in different regions of the electrolyte, the resulting concentration gradient produce a flow of ions. If there are differences in electrostatic potential at various points in the electrolyte, then the resulting electric field produces a flow of charge in the direction of field. This is termed migration or conduction. Finally, if a difference of pressure or density or temperature exists in various parts of the electrolyte, then the liquid begins to move as a whole or parts of it move relative to other parts. This is called the hydrodynamic flow. The drift of ions occurs precisely because the system
is not at equilibrium and the system is seeking to attain equilibrium. During electrical conductance, condition of electroneutrality is maintained.

The investigation of conductance as a function of concentration gives the conductance at infinite dilution, the dissociation constant of ionophores, the association constant of ionogens, ionic radii and information about structure of solution in the vicinity of ion. The analysis of data has usually been carried out in terms of Fuoss-Onsager conductance theory which is basically an application of interionic attraction theory to the specified model of rigid charged spheres representing the ions in an electrostatic and hydrodynamic continuum, that is, the solvent. By the use of best available conductance theories of Onsager-Fuoss-Hasia, Pitts and Guggenheim for dilute regions, ion association, distance of closest approach between the ions can be estimated.

Recently, Lee and Wheaton published a conductance equation applicable to unsymmetrical electrolytes in which ions approaching more closely than a distance R are considered to be associated. This conductance equation would allow one to account for multiple ion association in a mixed electrolyte solution. The free ion concentration range over
which the Lee-Wheaton conductance equation is useful has been given \(^{74c}\) for water at 25\(^{\circ}\)C as 0–0.1 M for a 1:1 electrolyte and 0–0.002 M for a 2:2 electrolyte. Lee and Wheaton have been taken an approach first used by Onsager and Kim \(^{75}\) in treatment of a solution containing more than two kinds of ions. Pethybridge has demonstrated the application of Lee-Wheaton equation to the conductance of 2:2 electrolytes, as well as unsymmetrical electrolytes such as calcium chloride in water and in other solvents \(^{76,77}\). Gilkerson \(^{78}\) has applied the equation to the problem of ionisation of moderately strong acid HSO\(_4^-\) in both aqueous sulphuric acid (at 25\(^{\circ}\) and 50\(^{\circ}\)C) and in sodium bisulfate (at 25\(^{\circ}\)C) and to the problem including formation of HF\(_2^-\) in the ionisation of moderately weak acid HF in aqueous solution (at 25\(^{\circ}\)C). In addition Gilkerson has applied Lee-Wheaton equation to the problem of conductances of naphthalene trisulfonic acid, trisodium naphthalene trisulfonate and lanthanum naphthalene trisulfonate, all in aqueous solution \(^{79}\).

In state of infinite dilution, the motion of an ion is limited solely by its interactions with surrounding solvent molecules for there are no other ions within a finite distance. Therefore, evaluation of equivalent conductance at infinite dilution should give equally reliable information.
regarding ion-solvent interaction. Further, structural
effects on ions in aqueous solutions are derived by a
comparison of their Walden product, \( \Lambda_o \eta_0 \). It is
expected\(^{81}\) that the large Walden product and their large
negative temperature coefficients will shows that the
electrolyte is a structure breaker\(^{82}\) in that solvent.

Recently, Crudden et. al.\(^9\) have established a
relationship for solutions in which ion association takes
place:

\[
\eta_{rel.} = 1 + A (\alpha C)^{\frac{1}{2}} + B_1 (\alpha C) + B_p (1-\alpha) C.
\]  \hspace{1cm} (I.12)

where \( \alpha \) is degree of association of ion pair, \( B_p \) is \( B \)-
coefficient of ion pairs and \( B_1 \) is \( B \)-coefficient of free ions.

\( \Lambda_o \), \( K_d \) and \( \gamma^\pm \) are calculated by the relations:

\[
K_d = \frac{\alpha^2 C \gamma_+^2}{1-\alpha} \hspace{1cm} (I.13)
\]

\[
\log \gamma_+ = \frac{-A y (\alpha C)^{\frac{1}{2}}}{1 + q B^y (\alpha C)^{\frac{1}{2}}} \hspace{1cm} (I.14)
\]

\[
\Lambda = \Lambda_o - \left( \frac{A \Lambda + B \Lambda}{1 + q B^y (\alpha C)^{\frac{1}{2}}} \right) (\alpha C)^{\frac{1}{2}} \hspace{1cm} (I.15)
\]
The Bjerrum distance, \( q \), is written for distance of closest approach of free ions in the equation (I.14). In these equations, \( \Lambda \), is the conductivity of the ionised fraction of electrolyte, and \( A_y, B_y, A_\Lambda, \) and \( B_\Lambda \) are the appropriate Debye-Hückel coefficients. Equation (I.12) can be rearranged to give:

\[
\eta_{\Lambda\text{el}} \frac{1 - A (\alpha C)^{1/2}}{(\alpha C)} = B_i + B_\beta \left( \frac{1 - \alpha}{\alpha} \right)
\]  

(I.16)

Conductance studies are useful to understand solute-solvent effect, and structural effects on solvent in solution. Studies are being made\(^{14,83-105}\) in light of different theories on conductance to highlight different aspects in solution chemistry.

3. **Transport Number (Transference Number)**;

When an electric current is passed in an electrolyte solution the electricity is carried out by ions towards respective direction viz., cation carry it towards cathode and anions towards anode. The quantity of positive electricity carried by the cations in one direction is proportional to their speed \( v^+ \) and their equivalent concentration \( C^+ \).
Similarly the quantity of negative electricity is proportional to $C_\text{-} V_\text{-}$. The transference number is defined as the fraction of the total current carried by ion.

Accordingly the cation transference number, $t_+$, is given by:

$$
t_+ = \frac{C_+ v_+}{C_+ v_+ + C_- v_-} \quad (I.17)
$$

and anionic transference number

$$
t_- = \frac{C_- v_-}{C_- v_- + C_+ v_+} \quad (I.18)
$$

In terms of electrolytic conductance, the definition of transference number, therefore, can be written as:

$$
t_i = \frac{\lambda_i}{\Lambda} \quad t_i^* = \frac{\lambda_i^0}{\Lambda^0} \quad (I.19)
$$

where $\lambda_i$ is the mobility and is the equivalent conductance at a concentration at which $t_i$ is determined. The subscript '0' refers to a state of infinite dilution. Conductance studies of different electrolytes show that each ion is
hydrated and that too, to different extent. More hydrated the ion, lesser will be its mobility, provided the ions have approximately the same ionic radii.

For 1:1 electrolyte in solution in which only two ions are formed, the concentration of anion will be equal to that of cation i.e. $C_+ = C_-$ and accordingly, the transference number becomes:

\[ t_+ = \frac{v_+}{v_+ + v_-} \quad t_- = \frac{v_-}{v_- + v_+} \]  

Since both the ions have different ionic radii and it is natural to expect that the fraction of current carried by two ions will be different. If one volt per cm. is passed through the solution, the velocities of ions can be considered as mobility of ions, and it is obtained from:

\[ t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \quad t_- = \frac{\lambda_-}{\lambda_- + \lambda_+} \]  

and further

\[ t_+ + t_- = 1 \]
or

\[ \sum_{i=1}^{n} t_i = 1 \]

\[ i = 1, 2 \]

If there is a mixture of electrolytes and a number of ions are present in the solution, the sum of transference numbers will again be unity.

\[ \sum_{i=1}^{n} t_i = 1 \quad i = \text{number of ions, } 1, 2 \ldots \ldots \ldots n \quad (I.23) \]

The study of transference numbers is an indirect method for study of solute-solute and solute-solvent interactions. The transport number can also be used to verify the interionic attraction theory\(^{106}\). In a transference cell, solvent molecules also migrate alongwith the ions due to solvation of ions and as a result of which an overall solvent transfer takes place. On account of solvent transfer a concentration gradient is established and it disturbs the equilibrium. To avoid solvent migration a suitable membrane may be placed between cathode and anode.

The transport numbers have been determined by moving boundary method\(^{107}\), e.m.f. method\(^{108}\) and Hitroff's method\(^{109}\), for study in mixed solvents and the results obtained have
been explained on the basis of selective solvation effects and preferential solvation.

B. COUPLED TRANSPORT PROCESSES:

If a transport process involves two or more forces, the flow \( J_i \) will be influenced by other forces \( X_k (k \neq i) \) as well as its conjugate force, \( X_i \). Such transport processes are called coupled transport processes. For instance, thermal diffusion, electrokinetic effects and many of the biological processes are coupled transport processes.

1. Thermal Diffusion:

In case of systems where there is a temperature gradient along with concentration gradient, two phenomena viz. ordinary diffusion and heat conduction exist simultaneously. These two phenomena interfere and coupling of diffusion and heat conduction give rise to thermal diffusion. This expresses that a flow of matter can be caused by a concentration gradient and also by a temperature gradient. The thermal diffusion coefficient has been interpreted in terms of heat of transfer which is defined as the amount of heat transfer per unit transfer of mass at a constant temperature gradient.
Thermal diffusion is observed, for instance, when a bulb filled with a gaseous component at a certain temperature is connected to another bulb with another component at a different temperature. It is found that the diffusion of the components depends not only on the concentration gradient but on the temperature gradient as well. A reciprocal effect is also observed; if originally the two bulbs are at same temperature, the diffusion process is found to cause a temperature difference between the two bulbs. This later phenomenon is known as the 'Dufour effect' or the diffusion thermo effect. If thermal energy flux is represented as $J_q$ and its conjugate gradient as $X_q$, the diffusion flux of species $i$ as $J_i$ and its conjugate gradient as $X_i$, then the forces and fluxes are related as:

$$J_q = L_i q_i X_q + \sum_{k=1}^{\eta} L_k q_k X_k$$

(I.24)

$$J_i = L_i q_i X_i + \sum_{k=1}^{\eta} L_k q_k X_k \quad (i = 1, 2, \ldots, \eta)$$

(I.25)

If there is no concentration gradient of any component,
i.e. when $X_k$ is zero, equation (1.24) reduces to $J_q = L_{qq}X_q$, a form of Fourier's law of heat conduction. If, however, there is no temperature gradient i.e. $X_q$ is zero, equation (1.25) reduces to:

$$J_i = \sum_{\ell=1}^{\eta} L_{q\ell} X_{\ell q}$$

(I.26)

which is a form of Fick's law for a multicomponent mixture. Thus, the remaining terms, $\sum L_{qk}X_k$ and $L_{1q}X_q$, are responsible for thermal diffusion and Dufour effect, respectively.

2. **Electrokinetics Effect**:

Electrokinetic phenomenon is a transport process across a membrane or capillary and is due to potential gradient and/or pressure gradient. It arises due to the presence of an electrical double layer at the interface. Electrokinetic phenomenon are technically important from view point of desalination, reverse osmosis, ultrafiltration and electrodialysis. There are a number of applications of electrokinetic phenomenon which include the use of these effects to pump fluids and to generate electricity. In
biological transport the electrokinetic phenomenon are of considerable interest as they have been used to understand the permeability phenomena and secretion processes since dynamic structure of a biological membrane can be understood by study of dynamic properties through the membranes\textsuperscript{113}.

The value of electrokinetic phenomena lies in the fact that they afford convenient methods for studying several steady state phenomena for the explanation of underlying principles of irreversible thermodynamics. The thermodynamics of irreversible processes\textsuperscript{112,114-116} can be conveniently applied to describe mathematically the electrokinetic effects\textsuperscript{117-130} by the relations (I.28) and (I.29) similar to relations (I.24) and (I.25)

\[
I = L_{11} \Delta \phi + L_{12} \Delta P \tag{I.28}
\]

\[
J = L_{21} \Delta \phi + L_{22} \Delta P \tag{I.29}
\]

where \(L_{11}, L_{12} = L_{21}, L_{22}\) represent the phenomenological coefficients, \(I\), the current flow, \(J\) the mass flow, \(\Delta \phi\), the potential gradient across the membrane and \(\Delta P\) the pressure difference. According to relations (I.28) and (I.29) it should be understood that two forces and two
corresponding fluxes, namely current flux and volume flux, are involved in electrokinetic phenomena. The terms $L_{12} \Delta P$ and $L_{21} \Delta \phi$ in these relations, represent the coupling of electric current flow and volume flow. Blokhra et al. have shown that these phenomenological coefficients can be interpreted in terms of the structure of the solvent.

Alvarez et al. investigated the concentration dependence of electrokinetic transport coefficients of methanol + ethanol mixtures through a quartz plug. Electro-osmotic flow and streaming potential measurements have also been carried out. The Onsager's reciprocity relation has also been checked. The hydrodynamic permeability of systems and fluidity of mixtures vary with composition in a similar way. The concentration dependence of second order coefficients has been partially explained on the basis of Jha's equation.

Kehar Singh and Vijay Kumar measured the electro-osmotic fluxes and volumetric fluxes of the transport of sodium chloride, barium chloride and aluminium chloride solutions of different concentrations across a sintered disc impregnated with zirconium phosphate at electric current of different densities. The data have been used to ascertain the electrical character of membrane permeant interface and to investigate its dependence on the nature and concentration
of electrolyte solutions. Membrane potentials have also been measured for the determination of the fixed charge density. The electrical character of the interface with membrane fixed charge density has also been correlated.

**OBJECT OF INVESTIGATION:**

The study from the view point to investigate different ionic interactions and structural changes of solvent in solution is important not only for itself but also because of insight it provides to nature and extent of interactions taking place in biological systems, and especially for the clear indication it provides as to important role that water and solvation must play in such systems. Since carbohydrates are one of the important constituents of biological systems, an understanding of the solution behaviour of aqueous systems involving carbohydrate can be seen as an essential pre-requisite to a full understanding of the solution behaviour of the complex processes occurring in biological systems. In the present study 1:1 salts viz. sodium chloride, potassium chloride and lithium chloride in aqueous dextrose have been selected.

The object of investigations described in the present
dissertation is two fold as mentioned in the following:

1. To investigate the nature of solute-solvent interaction and structural changes of solvent in solution with the help of conductance and viscosity studies at different concentrations and temperatures. 1:1 electrolytes viz. lithium chloride, sodium chloride and potassium chloride have been selected for study in different compositions of aqueous dextrose.

2. To investigate coupled transport phenomenon viz. electrokinetic effects involving 1:1 electrolytes such as lithium chloride, sodium chloride and potassium chloride in aqueous dextrose across an organic as well as inorganic membrane from the view point of non-equilibrium thermodynamics. A pyrex sintered disc (G2) impregnated with cellulose acetate and a silicon dioxide plug with polyvinyl alcohol as adhesive, have been chosen for the present work.
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