CHAPTER-I

INTRODUCTION
The study of transport phenomena through membranes has been a field of active research for the last two decades. It has attracted the attention of chemists, chemical engineers and biologists. Numerous books and research papers on various aspects of membrane phenomena have appeared in the recent past. The growing interest of researchers in the study of transport properties through different type of membranes lies in the fact that they are useful in industrial, agriculture, engineering and biological fields. Their uses in dialysis as a mean of industrial, chemical and biomedical separations\(^1,2\), in fuel cells\(^2\) are some of their most important technological applications. Many physiological processes in plants and animals involve transport through membranes. From the view point of agriculture, water transport through roots and soil is of particular interest. Exchange of matter and energy, which is the principal function of organisms takes place through membranes\(^3\).

Despite many attempts, no definition of membrane has been emerged as yet which is complete and precise because membranes varies in composition structure and function from system to system. Any phase, usually heterogeneous which separates two other phases preventing mass movement between them but permitting passage with various degrees of restrictions may be called membrane.\(^2\) Membrane has also been defined\(^4\) as a phase that acts as a barrier to the flow of
heat or matter except pure liquids and solids and it is heterogeneous in structure. Due to this hetero, a variety of transport phenomena arise which distinguish membrane systems and make them important in life processes and in science and technology.

Very recently, it has been recognised\textsuperscript{5} that a membrane is thin, usually polymeric film that exhibit permselectivity. The term permselectivity may be defined as a property of a membrane characterised by exhibiting a much bigger permeability to one species than to another or other species. However the final definition, complete in every respect is yet to be emerged.

Classification of Membranes:

Due to their wide applications in life processes and science and technological importance, membranes have been classified in a number of ways. Broadly, membranes may be classified into two groups:

I. Natural membranes.
II. Artificial membranes.

I. Natural Membranes: - All biological membranes come under this heading. Lipids and proteins are the principal constituents of biological membranes. At present, it is becoming known that biological membranes are the loci for carrying out such vital processes as energy transduction,
active transport and ATP synthysis. In order to have better understanding of these basic life processes in physiochemical terms, it has been recognised by many investigators that approaches using model membrane systems are highly desirable, owing to complex structural and environmental factors associated with the biological membranes.

Biological membranes have a common basic lipid bilayer structure, containing external internal and transmembrane proteins with chemical asymmetry as a fundamental feature. The asymmetry involves both lipid and proteins. Proteins represent the main component of the most biological membranes (Table 1). They play an important role not only in the mechanical structure of the membrane but also as carriers or channels serving for transport. They may also be involved in regulatory or ligand recognition properties. Membrane proteins have been classified as integral (intrinsic) or peripheral (extrinsic) according to degree of their association with membrane and method by which they can be solublized. Criteria for distinguishing peripheral and integral protein has been given in table-1.2.

The molecular organisation of the proteins is highly asymmetrical. Present knowledge about the molecular organisation of biological membranes comes mainly from an integration of data on chemical analysis and from the application of several biophysical techniques.
Table 1.1: Lipid and Protein Ratios in Some Cell Membranes:

<table>
<thead>
<tr>
<th>Species and Tissue</th>
<th>Protein (%)</th>
<th>Lipid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human CNS myelin</td>
<td>20</td>
<td>79</td>
</tr>
<tr>
<td>Bovine PNS myelin</td>
<td>23</td>
<td>76</td>
</tr>
<tr>
<td>Rat Muscle (Skeletal)</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>Rat Liver</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Human Erythrocyte</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Rat Liver mitochondrion</td>
<td>70</td>
<td>27-29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Molar Ratio</th>
<th>Area Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amino Acid</td>
<td>Phospholipid</td>
</tr>
<tr>
<td>Myelin</td>
<td>264</td>
<td>111</td>
</tr>
<tr>
<td>Erythrocyte</td>
<td>500</td>
<td>31</td>
</tr>
</tbody>
</table>
Table 1.2: Criteria for Distinguishing Peripheral and Integral Membrane Protein:

<table>
<thead>
<tr>
<th>Property</th>
<th>Peripheral Proteins</th>
<th>Integral Protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Requirement for dissociation</td>
<td>Mild treatment sufficient hydrophobic bond</td>
<td>Hydrophobic bond breaking agents</td>
</tr>
<tr>
<td>from membrane</td>
<td>high ionic strength metal ion chelating agents.</td>
<td>required; detergents, organic solvents.</td>
</tr>
<tr>
<td>Association with lipid when solublized</td>
<td>Usually soluble free of lipids.</td>
<td>Usually associated with lipids when solublized.</td>
</tr>
<tr>
<td>Solubility after dissociation from membrane</td>
<td>Soluble and molecularity dispersed in neutral aqueous buffers.</td>
<td>Usually insoluble or aggregated in neutral aqueous buffers.</td>
</tr>
<tr>
<td>Examples</td>
<td>Cytochrome C of mitochondria, spectrin of erythrocytes.</td>
<td>Most membrane bound enzymes; drug and hormone receptors.</td>
</tr>
</tbody>
</table>
To better understand the molecular organisation of the biological membrane, it is necessary to remember that not only the lipids, but also many of the intrinsic proteins and glycoproteins of the membrane are amphipathic molecules i.e. molecules with a hydrophilic and hydrophobic molecules. These amphipathic molecules constitute liquid crystalline aggregates in which the polar groups are directed toward the water phase and the non-polar groups are situated inside the bilayer.  

All biological membranes are heterogeneous and are anisotropic i.e. surface characteristics of both the sides of the membrane differ considerably. Permeability is fundamental to the functioning of the biological membranes and to the maintenance of satisfactory intercellular physiologic conditions. The passage of molecules and ions across membranes may be the result of two principal mechanisms. Permeability may be passive, if it occurs only because of physical laws such as diffusion. If it requires energy for transport then it is called active permeability. Active membrane transport is one of the most important features of life processes. When in a cell membrane, species move against a concentration electrical or pressure gradient, the process is called active transport. Among different substances that are actively transported through cell membranes are sodium ions, potassium ions, calcium ions, iron ions, hydrogen ions,
chloride ions, iodide ions, urate ions and several different sugars and amino acids.\textsuperscript{17,18}

Soil may also be treated as a natural membrane and transport of water through soil takes place through a bundle of capillaries which are connected with each other in various ways.

In plant membranes, interesting phenomena have been observed\textsuperscript{19} in the study of transport processes. Recent research has shown that transport through green plant cells is intimately linked to photo synthetic reactions.

II. \textbf{Artificial Membranes} :- Artificial membranes have been classified by Eisenman et al.\textsuperscript{20} on the basis of their structure. This classification has been given in fig. 1.1. Membranes can also be classified either on the basis of their nature or on the nature of the chemical reaction in their formation. Because of the extensive applications of membrane processes in industry and elsewhere, artificial membranes may further be classified in to three groups, (A) made of biological substances which will build suitable models to understand the properties of natural membranes. These membranes can be successfully used to understand the permeability pattern of biological systems, (B) composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physiological phenomena
Fig. 1.1: Classification of Artificial Membranes on the Basis of their Structure.
associated with the rectification of alternating current and other special membranes with specific purposes, and (C) membranes with good chemical and mechanical stability and favourable electrical performance suitable for fundamental transport studies and for application in some industrial operations. Though categories (A) and (B) overlap somewhat, but for clear presentation they have been given under separate headings.

(A) Membranes as Model to Understand the Properties of Natural Membranes:

As already discussed, natural membranes have lipid bilayer structure, having thickness 75-100 Å, the aqueous surfaces of which are bound by proteins. Extensive literature exists which describes the preparation and physico and electrochemical behaviour of natural membranes. Membranes having thickness 77-100 Å have been prepared from various materials, but due to very small thickness, these membrane possessed very fragile structure. Some techniques have been described by Lakshminarayanaiah and Shanes for handling such membranes.

Gershfeld casted thin films of thickness 300 Å or less on an aqueous surface using parlodion solution in isoamyl acetate. This technique has further been improved to prepare more thin membranes. Lakshminarayanaiah used different
techniques to incorporate stearic acid or phopholipids in to the membrane phase. Carnell\textsuperscript{43} prepared thin membranes from a number of polymers dissolved in different solvents. The different variables such as temperature, pressure and solvent properties have been studied by Carnell and MC. Gunge\textsuperscript{44} in order to understand their ability to generate membrane potential.

A cellophane membrane has been used\textsuperscript{45} as a model for a biological system to demonstrate the movement of water from a high salt concentration to a low salt concentration side.

Oparin and Deborin\textsuperscript{46} have prepared a membrane as a model to understand the transport of proteins across lipid membranes by impregnating a filter paper with olive oil.

Due to very complex characteristics of biological membrane, a number of attempts have been made by different workers to explain the phenomena of living systems by making experimental observations across an analogous membranes which have similar characteristics as encountered in biological membranes. Diamond\textsuperscript{47} studied the transport of water and salt in rabbit and guinea pig gall bladder. Permeability pattern of several non-electrolytes has been studied across gall bladder membrane\textsuperscript{48} Shukla and Tripathi\textsuperscript{49} have studied electro-osmotic pattern of water and aqueous solutions of urea, acetamide, glucose and sucrose in case of goat urinary membrane. Very recently, Shukla and Misra\textsuperscript{50,51} have studied
the electro-kinetic phenomena across goat urinary bladder membrane. Since surface activities and biological effects are closely related, these studies may also be useful in understanding different biological transport processes.

Alongwith this, a number of research articles have appeared in recent past emphasising the usefulness of model membranes in order to understand the properties of natural membranes.

(C) Composite Membranes :- This type of membranes are obtained by joining simple anion and cation-exchange membranes in different configurations. These composite structures in the form of membranes in different configurations exhibit a number of interesting phenomena, some of which are predicted on theoretical grounds. Different configurations, which may be formed by composite membranes are :-

(a) The cationic and anionic regions are intermingled so intimately that they become physically indistinguishable and form the amphoteric membranes.

(b) Both cationic and anionic regions are clearly defined and distinguishable and form the mosaic membrane.

(c) Bipolar membranes, formed by a laminar combination of indivisible cationic and anionic membranes either physically touching or separated by a porous spacer.

All these membranes have been formed by different
workers and have found to exhibit diverse electrical properties.

A membrane, capable of being changed in charge density and in charge sign has been formed by Jacobson. Mixtures of finally powdered cation and anion exchange resins were pressed together to form a self-supporting flexible membrane. An amphoteric ion selective membrane containing both strong base and strong acid groups has been prepared by Yamene et al. Mosaic membranes composed of small regions with cationic and anionic properties have also been prepared. Korosy obtained a bipolar membrane by hydrolyzing one side and aminating the other side of a chloro sulphonated polyethylene sheet. A bipolar membrane has also been prepared to study the electric potentials arising across it when it separated salt solutions. Rogers and co-workers have prepared membranes possessing a fixed gradient of composition from one face to the other. Artificial lipid systems have also been built from a number of drying oils.

(C) **Operationally Useful Membranes**:- A large amount of interesting work has been published in recent years regarding the preparation of membranes, which are useful in different industrial operations and possess good chemical and mechanical strength, favourable for the study of fundamental transport. These membranes are useful for chemists and chemical engineers to understand the mechanism of transport so that they may be
able to prepare membranes of desired properties from different viewpoints. Though it is difficult to rationalise different procedures in preparation of these membranes, they may be classified in two categories (A) homogeneous membranes and (B) heterogeneous membranes.

(A) **Homogeneous Membranes**: These membranes are essential for fundamental transport studies. Homogeneous membranes have been obtained in the form of disc, foil, film and ribbon etc. Their structure is that of ion-exchange resins. Much work has been devoted toward finding suitable material for the preparation of membranes for effective desalting of sea water by application of pressure. Polymethacrylic acid (PMA), phenosulphonic acid (PSA) polystyrene sulphonic acid (PSSA) and cellulose esters have proved very useful. PMA and PSA membranes have been prepared by different workers in the manner described by Lakshminarayanaiah and Jakubouic. Details of preparation of these membranes have been given elsewhere.

Semipermeable membranes for use in osmotic pressure determinations have been prepared. A 3% solution of cellulose nitrate in a mixture of acetone, methyl ethyl ketone and cyclohexanone in the ratio of 60:39:1 was deposited on a mercury surface. The solvents were allowed to evaporate in a CO₂ atmosphere and the membrane was left overnight in
the same environment.

Variety of membranes have been prepared for use as filters in their studies on ultra filtration of salt solution by Reid and Spenser. They prepared the membranes by casting the solution of the polymer material on a level glass plate under suitable conditions.

In recent past cellulose acetate has received the widest attention of different workers to prepare membranes, suitable to desalinate salt waters. Loeb and Co-worker have successfully shown that these membranes reject salt more effectively from sea or saline water if prepared under suitable conditions.

Cellulose acetate was dissolved in acetone and made up with water to which magnesium perchlorate had been added. The materials taken in the proportion of 22:2:66.7:1.1 respectively. The solution was casted on cold glass plates at 0 to 10°C. Uniformity of thickness was obtained by passing an inclined knife across the top of the plate. The solvent was allowed to evaporate in the cold box for about 3-4 minutes after which the plate with film was immersed in ice water for at least an hour. The membrane was removed from the glass plate and heated in hot water at 75 to 80°C. These membranes withstood pressure upto 1500 psi.

A number of membranes employing a variety of cellulose
acetate have been prepared using the above procedure. A number of operational characteristics are investigated, depending upon the different membrane forming parameters. The transport of water through cellulose acetate reverse membranes has also been studied from various grades of cellulose acetate membranes\(^7\). Cellulose acetate membranes are also prepared by taking different materials in different compositions\(^7\). Dioxane was used in place of acetone and enabled the evaporation to be performed at room temperature rather than at much lower temperature. Mg(Clo\(_4\))\(_2\) was also used and after the membrane was prepared, it was extracted with remaining solvent. Manjikinan\(^7\) prepared the membrane by using ternary system of cellulose acetate, formamide and acetone. Formamide proved to be very useful due to its high dielectric constant and miscibility with acetone.

In recent years, Blokhra and Co-workers\(^7\) have studied the transport phenomena of different electrolytes and non-electrolytes through a cellulose acetate membrane impregnated in a sintered disc. Electro-kinetic energy conversion from one form to another form has also been discussed.

(B) **Heterogeneous Membranes** :- To simplify the classification, these membranes are further divided into (a) nonreinforced membranes (b) Fabric backet or reinforced membranes (c)
membranes formed by chemical treatment (d) membranes formed by photochemical treatment and (e) membranes formed by mechanical treatment. Mechanical stability of heterogeneous membranes is superior but their electro-chemical properties are not as good as found in homogeneous membranes. These membranes consists of colloidal ion-exchanger particles embodied in to an inert binder. Regarding their mechanical structure, these membranes may be treated as a bundle of capillaries having characteristic pore size and length. Heterogeneous membranes, both organic and inorganic sorb solvents in which they are placed. They expand or swell while taking up solvent till an equilibrium is attained beyond which swelling does not proceed. The swelling equilibrium is a balance of opposing forces.\textsuperscript{78}

Nonreinforced membranes can be prepared with the help of suitable casting techniques for the solution of membrane forming substances. For spin casting of small polymer films within a cylindrical open faced mold has been described by Kaelble.\textsuperscript{79} High centripital acceleration at which the mold was spun gave good uniformity in thickness and absence of interior defects. Anion exchange membranes have also been prepared by different workers\textsuperscript{80,81}. Parker and Wentworth\textsuperscript{82} made an ion permeable membrane with polyvinyl chloride, polyimidazoline, a phthalate plasticizer and approximately 1 wt 90 ZnO. Bucur and Stoïncovici\textsuperscript{83} made membranes for
laboratory use with finally powdered Amberlite IR-120, a binder polyvinyl chloride dibutyl phthalate-plasticizer and chlorobenzene. All constituents were mixed together and a fluid paste was formed. It was casted on a glass plate and left for 15-20 minutes. It was then warmed to 40-50°C for five minutes and heated for five minutes at 175°C. The membrane was cooled and washed with alcohol.

Reinforced membranes are formed by solublization of monomers in suitable solvents and impregnation with the solution of monomer. After this introduction of ionogenic groups are carried out by conventional procedures. These membranes are suitable for dialysis and electrodialysis. These types of membranes have been prepared by Nishihard. A number of membranes have also been prepared by different workers and the procedure involved in the preparation of these membranes has been given elsewhere.

Membranes are also prepared by chemical treatment by applying paste or polymeric materials to existing sheets of films by different workers. Amicon corporation has developed a new class of synthetic hydrated polymer membranes for use in the separation and purification of macromolecules by ultrafiltration. On ultra filters, membranes of calcium oxalate, silver oxalate, calcium carbonate, barium carbonate, strontium carbonate, silver carbonate, calcium silicate,
silver silicate, calcium phosphate, calcium fluoride, calcium palmitate and barium sulphate have been prepared by Liberman et. al. Thorium tungstate membranes by depositing thorium tungstate in the pores of a parchment thimble have also been prepared.

Electrolytic transport across a parchment supported cobalt and nickle phosphate membranes have been studied by Beg et al. from the measurement of membrane potential (E_m) and membrane resistance etc. It has been found that the diffusion rates are primarily dependent upon the difference in the hydration energy of the counter ions. Different thermodynamic parameter viz. enthalpy of activation (ΔH*) entropy of activation (ΔS*) and free energy of activation (ΔF*) have also been evaluated.

Bey and coworkers have prepared a parchment supported Pb₃(VO₄)₂ membrane and used as a barrier in diffusion rate measurement. The experiments have been performed at different temperatures and different thermodynamic parameters viz. enthalpy of activation (ΔH*) entropy of activation (ΔS*) and free energy of activation (ΔF*) have been derived. The partial immobility, which took place within the membrane has been attributed to the interaction of ionic species with membrane fixed charges.

The conductance of a parchment supported cupric
orthophosphate membrane in contact with various alkali metal chlorides at different temperatures and concentrations has been studied. The mechanism of transport through membrane has been studied from the viewpoint of absolute reaction rate theory. The thermodynamic parameters viz. enthalpy of activation (\( \Delta H^* \)), entropy of activation (\( \Delta S^* \)) and free energy of activation (\( \Delta G^* \)) have been evaluated along with their inter-ionc distances. The negative value of \( \Delta S^* \) has been attributed to the partial immobilization of the ions within the membrane.

A comparative study of permeability for various electrolytes on parchment polystyrene and araldite based membranes of \( T \) tungstoarsenate has been made by Srivastava et al. The order of permeability at a given temperature has been found as \( K^+ > Na^+ > Li^+ \) for 1:1 electrolytes permeability values have been found to be higher for parchment based membrane. The diffusion of electrolytic solution across araldite based membrane is almost negligible. The thermodynamic parameters of diffusion process have been evaluated. The entropy values are found to be negative for all the cations except \( Li^+ \). It has also been found that the free energy vallies are higher for polystyrene based membranes than for the parchment based membranes.

Very recently, Srivastava et al. have carried out permeability studies of \( LiCl, NaCl, KCl, BaCl_2, CaCl_2 \) and
$\text{MgCl}_2$ through a parchment supported titanium arsenate membrane. Permeability study reveals the order, $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ and $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$. The thermodynamic parameters for the diffusion process have also been evaluated and have been related to hydration number and heat of hydration etc.

Membranes have also been prepared by photochemical treatment. Powerful ionising radiations have been used to bring about the polymerization of monomers incorporated in to various materials.

Membranes have also been formed by mechanical treatment. A polyelectrolyte or a conventional ion-exchanger at ordinary or elevated temperature is bound to a thermo plastic polymers together by mechanical pressure.

Hodgdon and Boyack have prepared ion-exchange membranes. The procedure of the preparation of these membranes has been given in detail elsewhere. Membranes of precipitates of $\text{BaSO}_4$ and $\text{BaCr}_2\text{O}_4$ are formed by bounding in paraffin. These membranes are used as indicator electrodes in potentiometric titrations. A series of membrane electrodes have been prepared by Pungor et al. by incorporation of electrode material in to a thin layer polymerised silicone rubber. These membranes are exploited in the form of membrane electrodes to specific ions.

Srivastava et. al. prepared a solid membrane electrode with titanium arsenate as membrane material using araldite as
binder to measure the activity of lead in the concentration range from 0.1 to \(5 \times 10^{-6}\) m.

Kumar\(^{100}\) has prepared a porous membrane of Zeokarb 225 (H\(^+\) form) resin particles. The membrane has been prepared by compressing the resin under high pressure using araldite as a binder.

The electro-osmosis of methanol and its aqueous mixtures across this membrane has been studied in the non-linear region. The concentration dependence has been examined and discussed in the light of kinetic molecular theory of electro-osmotic phenomena based on the electrical double layer. The efficiency of the electro-osmotic energy conversion has been calculated from transport data utilizing the formalism of non-equilibrium thermodynamic membrane transport theory of electro-osmotic flux. The dependence of the energy conversion efficiency on the magnitude of input and output forces has been examined, the degree of coupling in the non-linear region has been defined.

Caballero et. al.\(^{101}\) have prepared a porous diaphragms of pyrex glass particles by mechanical treatment and studied the electro-osmosis of methyl-, ethyl- and isopropyl alcohols in the non-linear region. Hidalgo-Alverz et. al.\(^{102-104}\) have prepared a porous membrane by compressing quartz particles under high pressure and studied the transport of different ternary mixtures of acetone, methanol 2-propanol and water in
linear as well as non-linear regions. It has been found that the geometric parameters of membrane are independent of the composition of the mixture. The results confirmed the decisive influence of the physical properties of the liquid on the actual values of the electro-kinetic transport coefficients.

Blokhra et al.\textsuperscript{105} have reported the transport of urea and thiourea across a cation exchange membrane prepared by the mechanical treatment using araldite as a binder. The membrane so formed has been characterised in terms of its number of pores, pore radius and zeta potential developed during the transport.

Geyer and Syring\textsuperscript{106} have described a number of salts of hydrous oxides such as antimonates, arsenates, chromates, molybdates, oxalates, phosphates tungstates, vandates and carbonates of thorium, titanium and zirconium as ion-exchangers. A number of quadrivalent metal oxides such as SnO\textsubscript{2}, SiO\textsubscript{2}, ThO\textsubscript{2}, TiO\textsubscript{2}, SbO\textsubscript{2}, ZrO\textsubscript{2} behave as ion exchangers. These inorganic ion exchangers in the form of membranes have been prepared recently.\textsuperscript{107} Zirconium Phosphate was obtained in the form of membrane first by Alberti\textsuperscript{108}.

These inorganic ion-exchangers are more stable than the organic resins under certain conditions e.g. high temperature and the presence of ionising radiations. These were developed primarily for use in fuel cells. Much work has been done and
a lot more is in progress for their possible use in the conversion of sea or brackish water to fresh water.

Srivastava and Lal\textsuperscript{109-111} have prepared a thorium oxide plug membrane and carried out a detailed study of electro-osmotic phenomena through this membrane. Experimental studies of hydrodynamic permeability, electro-osmotic permeability and electro-osmotic pressure across the membrane using D.M.F., methanol, acetone and their binary mixtures with water as permeant have been carried out. Streaming potential developed during the transport of these aqueous binary mixtures through the membrane has also been measured. The non-linear results are explained on the basis of electrical double layer theory. Plug membrane has been characterised in terms of number of pores, pore radius and zeta potential and the degree of coupling and efficiency of maximum energy have also been evaluated. Electro-phoretic velocities of ThO\textsubscript{2} particles dispersed in the solvents have also been measured.

Kehar Singh and Vijay Kumar\textsuperscript{112} have measured the electro-osmotic fluxes and volumetric fluxes of transport of NaCl, BaCl\textsubscript{2} and AlCl\textsubscript{3} solutions across a sintered disc impregnated with zirconium phosphate. The data have been used to ascertain the electrical character of membrane permeant interface.

Srivasta et al.\textsuperscript{113} have also reported the results of hydrodynamic and electro-osmotic permeabilities of methanol,
ethanol, n-propanol and n-butanol. It has been found that solvodynamic fluxes vary with applied pressure in a linear manner while electro-osmotic fluxes vary with potential difference in non-linear manner. The results are analysed in the light of thermodynamics of irreversible processes. Variation in phenomenological coefficients has been explained on the basis of electrical double layer theory. Membrane characterization has been done by estimating average pore radii, average number of pores and zeta potentials.

Very recently, Blokhra and Kumar have investigated the transport of sodium chloride-potassium chloride and lithium chloride in aqueous dextrose across a silicon dioxide plug prepared by mechanical treatment using PVA as a binder. The phenomenological coefficients, membrane characteristics and zeta potential have been estimated for various systems. Maximum conversion efficiencies for electro-osmotic flow have also been estimated. The maximum values of efficiency of energy conversion have been found to be independent of input force, the optimum values predicted by figure of merit agree with those obtained experimentally.

Survey of literature reveals that inorganic ion-exchange membranes are stable in character and important from technological view point. Keeping all important properties and uses of these membranes in mind, the present work has been planned with objectives given below.
Objectives of Investigations

Due to the stable character and applications of inorganic membranes, the transport studies through some inorganic membranes namely titanium oxide, zirconium oxide and antimony oxide involving EG, DEG and their aqueous mixtures have been planned. The binary mixtures have been chosen so that viscosity and dielectric constant could be varied considerably because the behaviour of transport has also been shown to depend on the viscosity and dielectric constant of the liquid interface. Following are the objectives of present investigations.

(I) The behaviour of hydrodynamic transport will be studied and various activation parameters viz. enthalpy of activation (ΔH*), entropy of activation (ΔS*) and free energy of activation (ΔG*) will be estimated. The effect of viscosity and the dielectric constant of the medium on the activation parameters will be investigated.

(II) To characterise the membranes in terms of their equivalent pore radii, number of pores and zeta potential. The efficiency of electro-osmotic energy conversion will be estimated and the validity of Speigler's model will also be checked in present investigations.

(III) To estimate the higher order coefficients $L_{212}, L_{222}$
and $L_{211}$ owing to the non-validity of linear phenomena relations at higher values of potential difference from the data of electro-osmosis and electro-osmotic pressure difference. An attempt shall be made to compare the results of higher order coefficients with the higher order coefficients derived on the bases of kinetic consideration.

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