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Membranes, Membranes Phenomena and Applications -A Review

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ABSTRACT

This Paper deals some generalized concepts on membrane behavior. Membrane classification and classification based on pore size are mentioned. Transport through the membrane is arranged in terms of active transport, passive transport, facilitated diffusion etc. Transport process driven by concentration gradient is cited with ion transport and concentration. A short accounts of Ultrafiltration, /Reverse-Osmosis, Nanofiltration processes are given. Factor affecting transport across membranes, membrane-solution interaction, time dependent flux, the concentration polarization, and mass transfer coefficient are discussed. Diffusion potential and applications of the membrane are included in this chapter. Various membrane processes, e.g. electrodialysis, piezodialysis, hemodialysis etc. are cited in this chapter. Polymers/ resins used for the membrane preparation are also mentioned.

Kewords: Membranes, Transport

Introduction:

Membranes continue to be the object of intensive research in the field of physical and polymer chemistry, biology, medicine and physiology. Moreover, synthetic membranes are being applied to the solution of process engineering separation problem in the pharmaceutical industry and in medicine for therapeutic (artificial kidney) and diagnostic purpose (multilayer, thin-film colorimetric assay for clinical analysis). Further impetus for application of membrane comes from biotechnology where the substrates and/or products are concentrated and purified by means of synthetic membranes [1]. Additional fields for the application of synthetic membranes include the preparation of ultrapure water for the electronics industry, deacdification of natural gas, enrichment of oxygen for combustion processes, and last but not least brackish and sea water desalination.

1.1. Definition of Membranes:

A Membrane is simple terms, may be defined as a phase that act as a barrier to prevent mass movement but allows restricted and / or regulated passage of one or several species through it. It can be solid or liquid containing ionized or ionizable groups, or it can be completely un-ionized. Functionally allmembranes are active when used as barrier to separate two other phases unless they are too porous or too fragile [2,3]. If the membrane functioned as an absolute barrier between bulk phases, it would not be very interesting.

1.2. Classification of Membranes:

Membranes may be broadly classified on the basis of nature structure, applications and mechanism of action.

1.2.1. Natural or Biological Membrane:

Natural or biological Membrane is thin (less than 10 nm) and contains a variety of structurally well organized lipids and proteins. Although it has not been possible so far to form a membrane artificially from known compounds (lipid and proteins) of biological membranes. In the living membrane such as cell membrane, active transport takes place [4]. According to Stein, in the active transport movement of molecules and ions are in a direction opposite to that of a prevailing electrochemical gradient. In these cases the energy for permeation is supplied by the cell. The movement is ‘uphill’ from low concentration to high concentration against the forces of passive transport. In this active mode of transport, the membrane is no more passive barrier but functions as a dynamic organ [5-11].

1.2.2. Man Made or Artificial Membrane:

Man made or artificial membranes that are used in several technologies are generally thick (more than 10 nm) although thin membranes from parlodion(nitrocellulose) have been prepared. In the artificial membrane passive transport takes place. If the solute crosses the membrane matrix without interacting with any molecular species the transport is said to be passive. It is 'downhill' movement i.e., from high concentration to low concentration. The diffusing solute particle requires no energy for the diffusion process throughthe membrane. The energy for permeation is supplied by the environment [12]. Broadly artificial membranes are of two types:

.3.2.1. Uncharged or Slightly Charged:

The uncharged membranes can be either solid e.g., paraffin, quartz, or liquid e.g., benzene or silicon oil.

.3.2.2. Highly Charged (Ion Exchange Membrane):

The characteristic which distinguishes ion exchange membrane from other type is the presence of charged or ionic group in its component polymer molecule. Mobile ion bearing a charge opposite to that borne by the fixed ion are known as 'counter ions', those bearing the same charge are 'co ions'. Ion exchange membranes repel similarly charged ionic solute (co ions) and admit oppositely charged ionic solute (counter ions). The ion exchange membranes are again classified in two types [13-14]. These are:

(i) Heterogeneous Membrane:

Heterogeneous membranes refer to structure composed of colloidal particles ofion exchange materials embedded in an inert polymeric substrate. **(ii)Homogeneous Membrane:**

Term homogeneous as applied to ion exchange membrane refers to the absenceof the structure on the colloidal level.

Classification of membranes is shown in Figure1.1 and Table1.1

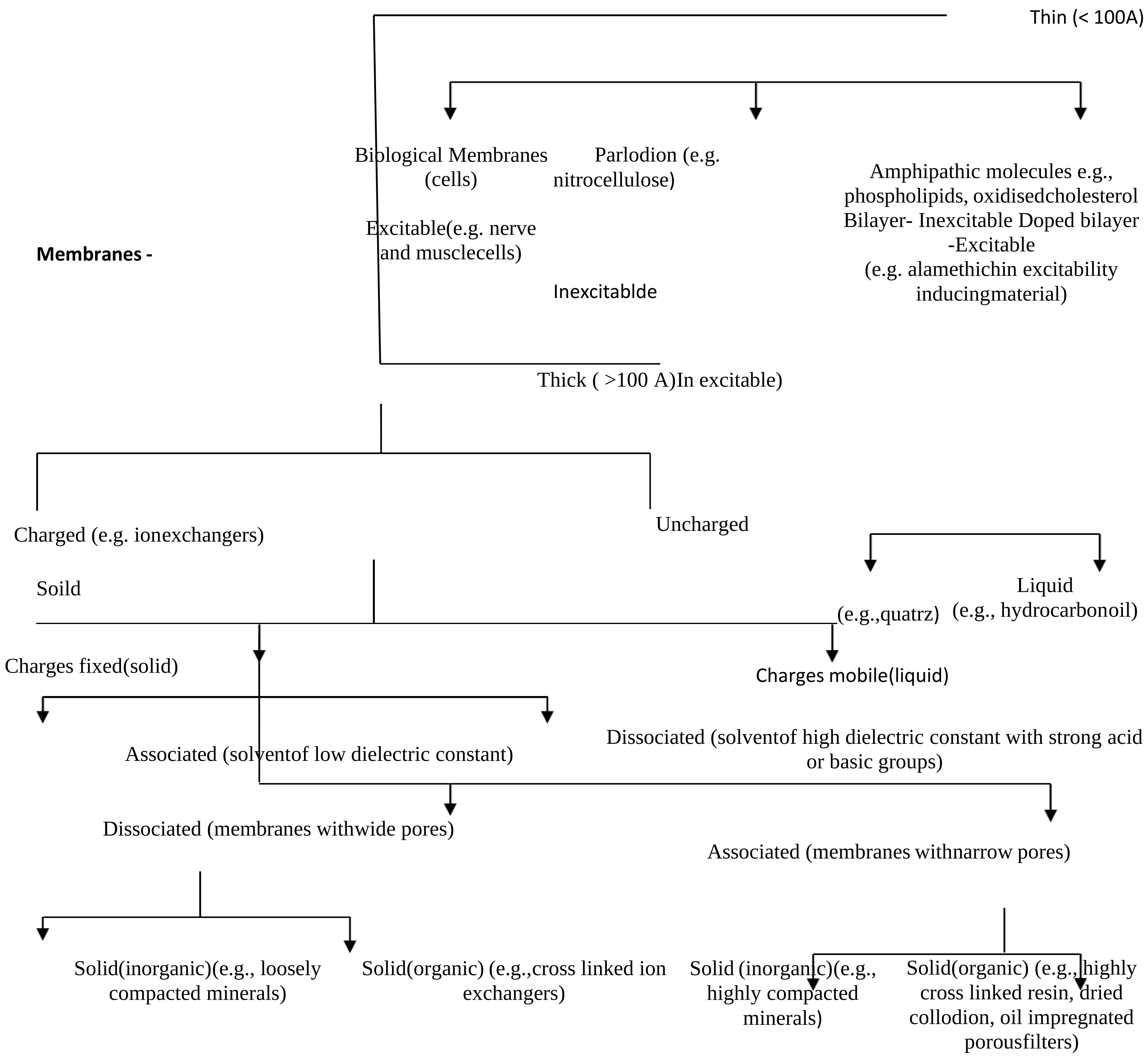


Figure 1.1Classification of Membranes [3]

Table 1.1 Classifications of Membranes [15]

eparation Materials	Structure	Morphology	Geometry	Methods of Fabrication	Typical Application
Polymers	Homogeneous	Nonporous	Flat sheet, hollow fibre	Extrusion,casting	Dialysis, electrodialysis, electrodialysis reversal
		Micro porous	Flat sheet, tubular	Phase inversion, casting, sintering, tracketching, biaxialstretching	Microfiltration Membrane distillation
	Asymmetric	Microporous	Flat sheet, tubular, hollow fibre	Phase inversion, casting	Microfiltration Ultrafiltration membrane distillation
		Nonporous, skinned	Flat sheet, tubular, hollow fibre	Phase inversion, casting	Reverse osmosis gas separation, pervaporation
	Composite	Nonporous, barrier on microporous substrate	Flat sheet, hollow fibre	Interfacial/ Plasma polymerization direct coating	Reverse osmosis, gas separation, pervaporation

Liquid	Continuous	Liquid immobilizedin - microporous substrate	Flat sheet, hollow fibre	Impregnation	Membrane liquid extraction, coupled transport, gasseparation.
	Emulsion	---	--	Single or multistage emulsification	Membrane liquid extraction
Gas	Continuous	Gas trapped in microporous substrate byliquid	Flat sheet, hollow fibre	--	Recovery of volatile substances fromliquid

1.3. Pore size of Membrane:

Existing membranes are generally regarded as belonging to one of the three classes: Coarsely porous, finely porous, or non-porous. When employed for the separation of substances differing markedly in molecular size (salt from polymer for instance), such membrane should not interact strongly with either solvent or solute. Such interactions may interfere with the sieve effect separation which depends upon geometric consideration alone. Membrane possesses pore diameter than about large than about $50A^0$ are usually considered as coarsely porous membranes. Therefore, a porous plug or glass frit might serve as prototype of a coarsely porous membrane.

Substances differing in their valences and / or other physicochemical features can be separated by either a finely porous or solution diffusion (SD) membrane. Finely porous membranes possess pore diameter from about $10A^0$ up to $50A^0$. SD membranes either have no pores(liquid membrane) or behave as a homogeneous phase, for polymer films this means that the interstices between polymer chain of the membrane matrix are smaller than 10A^0. Hydrogels of lower water content (<30wt %) are a good example of finely porous membranes. Most of the finely porous membranes (e.g., ion exchange, cellulose, and cellulose acetate membranes) show a moderate to strong interaction between solvent (typically water) and the membrane matrix whichis observable e.g. by swelling of the membrane [1].

1.4.1. Classification of Pore size:

The pore systems of solid are of different kinds. The pores may vary greatly both in size and in shape within a given solid, and as between one solid and another. A feature of special interest for many purpose is the width of the pore e.g., the diameter of a cylindrical pore or the distance between the sides of the slit – shaped pore and a convenient classification of pores accordingto their average width has been proposed by Dubinin[16].

.4.1.1. Macropores:

Macro pores membrane possesses widths in excess of 0.05µm (50nm). Capillary condensation does not take place in these pores which are essentially avenues of transport of smaller pores.

.4.1.2. Mesopores:

Mesopores are known as intermediate or transition pore having widths between 2 and 50nm.

.4.1.3. Micropores:

Micropores having width not exceeding 2nm. Since the concept of surface of a solid body is a macroscopic motion surface area loses its significance when micro pores are present. However, pore volume remains an applicable concept [17]. Mikhail and Robens extended this classification to include:

.4.1.4. Ultramicropores:

Membrane with ultramicropores possesses diameters smaller than the adsorptive molecular diameters (about 0.6nm) [18].

1.4. Transports through the Membranes:

Transport across artificial membranes has been the subject of numerous investigations [19-21]. A complete listing of these studies is given by Helfferich. Several theoretical description of transport of ions and water across artificial membranes have also been presented. Transport phenomena through the membranes depend on:

- The nature of the membrane viz. size, shape of the channels of capillaries.
- Size and Shape of the permeate molecules and ions
- Nature of the interface, charged and uncharged.

The interface can facilitate surface migration and influence the structure of the solvent, particularly water. The passage of ions and molecules through a membrane can take place in four ways [22].

1.4.1. Active Transport:

Solute is accumulated against an electrochemical or osmotic gradient at the expense of metabolic energy. The mechanism like facilitated diffusion requires a specific membrane carrier molecule. The movement is ‘Uphill’ from low concentration to high concentration.

1.4.2. Passive Transport:

The solute crosses the membrane as a result of random motion and does not interact specifically with any molecular species in the membrane. The movement is ‘downhill’ from high concentration to low concentration. The rateof passive diffusion can be altered by membrane charge and solvent drag.

1.4.3. Facilitated Diffusion:

Solute combines reversibly with a specific molecule in the membrane and the carrier solute complex oscillates between the inner and outer surfaces of membrane releasing and binding solute on either side. Thermal energy is adequate for small amount of movement involved [23-28].

1.4.4. Group Translation:

The solute is modified chemically. A covalent charge is exerted upon the transported molecule so that the reaction itself results in the passage of molecule through the diffusion barrier. Group translation and active transport are specific to biological systems.

Diffusion of solvent (osmosis) across charged membranes can occur in a different manner than with uncharged membranes, in which the net flow (in the absence of applied pressure) is always from the more dilute to the more concentrated side of the membrane. In such cases the osmotic transfer of solvent is a strictly colligative function of the solute concentration on either side of the membrane. For ion exchange membranes such normal osmosis may be replaced by anomalous osmosis, in which solvent transfer may occur in normal direction but be quantitatively greater than that expected on the basis of concentration difference (anomalous positive osmosis) or in the opposite direction (anomalous negative osmosis).Although earlier investigators [29-30] ascribed anomalous osmosis to structural inhomogeneties in the membrane. Schlogl [31] contends that anomalous is the rule rather than exception for ionic solutes and charged membranes irrespective of structure. Wyman and Kostin [32] studied theoretically anomalous osmosis by using coupled Nernst- Planck and Navier – Stokes equation to investigate diffusion of electrolyte through an ion exchange membrane.

1.5. Transport Phenomena in Membrane:

The four developed industrial membrane separation processes are microfiltration, ultrafiltration, reverse osmosis and electrodialysis. Although reverse osmosis, ultrafiltration and microfiltration are conceptually similar processes, the difference in pore diameter produces dramatic differences in the way the membrane are used. In the electrodialysis a charged membranes are used to separate ions from aqueous solution under the driving force of an electrical potential difference. Various types of transport phenomena and their driving forces are shown in Table 1.2.

Table 1.2 Transport Phenomena in Membranes [3]

Driving force	**Phenomena**	**Primary flow**	**Comments**
Chemical or electro chemical Potential μ or $\Delta\bar{\mu}$	Mixing or diffusion	Chemical constituents	Establishment of chemical equilibrium
Δ	Osmosis	Solvent	Solvent enters Concentrated Solution (osmometry)
	Membrane Potential	Ionic solutes	Source of emf; negligible solvent flow
	Dialysis	Solute	Solute leaves concentrated solution (hemodialysis)
	Diasolysis	More mobile component	Selective flow of more mobile species

	Osmoionosis	Ionic solutes	Three streams of different Concentrationproduce driving forces.Similar to electrodialysis without application of external electric field.
	Dufour effect	Thermal	Give rise to ΔT
Electric field ΔE	Electric conduction	Current	Evaluation of membrane Resistance
	Transport number of species	Fraction of current carried by the species	Evaluation ofmembrane permselectivity
	Piezoelectricity	Residual polarization onof storage and electricity	Production of electrets
	Electroosmosis	Solvent	Solvent transfer
	Electrodialysis	Ionic solute and / or solventtransfer	Solute removal
	Electrophoresis	Ionic solute	Separation of large molecules
	Transport depletion	Ionic solute	Simplified high current density electrodialysis

Pressure ΔP	Hydraulic or mechanical permeability	Solvent	Relates to space available for laminar and / or diffusional flow
	Filtration	Solvent	Particulate matter retained by sieving
	Pressure permeation	Selective transport of mostmobile component	Separation of liquid and / or gases
	Ultrafiltration or reverse osmosis	Solvent	Solvent leaves and solution concentrated
	Piezodialysis	Ionic solute	Product of reduced salinity
	Streaming potential	Solvent	Generation of emf
	Streaming current	Ionic solute	Current very small; studies rare.
Vacuum	Pervaporation	Selective transport of mostmobile component	Separation of liquid and / or gases
Temperature ΔT	Heat conduction	Heat	Thermal conductance
	Thermoosmosis	Solvent	Solvent may move from hot to cold site or vice versa.
	Thermo-emf.	Ionic solute	Source of emf.

	Soreteffect	Ionic solute	Give rise to $\Delta\mu$; difficult to measure
Electric field plus pressure($\Delta E + \Delta P$)	Forced flow Electrophoresis	Ionic solute and solvent	Purification of blood sewage; in experiential stage.
Electric fieldplus temperature ($\Delta E + \Delta T$)	Electrodecantation	Ionic solute and solvent	Electrical heating &/ or cooling supplies ΔT; Ionic matter concentrates downward and solvent concentrates upward

1.6. Transport Process Driven by Gradient of Concentration:

In the study of biological membranes whose thickness is not known with any degree of precision, diffusion of molecules across them has been described by a permeability coefficient P instead of a diffusion coefficient D. Consider a membrane of thickness d cm interposed between two phase i(inside) and o(outside), where the concentration of substance is measured at C_i and C_o as shown in Figure 1.2. In principle the concentration profile through the membrane is determined by solving the diffusion equation,

$$\frac{6C}{6t} = D\frac{6^2C}{6x^2} \qquad (1.1)$$

Where D is diffusion coefficient and $\frac{6C}{6x}$ is concentration gradient. But as diffusion through the membrane reaches a steady state, $\frac{6C}{6t} = 0$, consequently $\frac{6^2C}{6x^2} = 0$, the solution of this equation is:

$$C_{(X)} = A.x+B \qquad (1.2)$$

where A and B are constants. It follows that the concentration profile is linear in a one dimensional steady state diffusion process. The constant A and B are found by satisfying the boundary condition $C_{(x)} = C_i$ for $x = 0$, and $C_{(x)} = C_0$ for $x = d$, This gives,

$$C_{(x)} = \frac{C0-Ci}{d} x + C_i \qquad (1.3)$$

which describes the concentration profile in the membrane during steady state diffusion

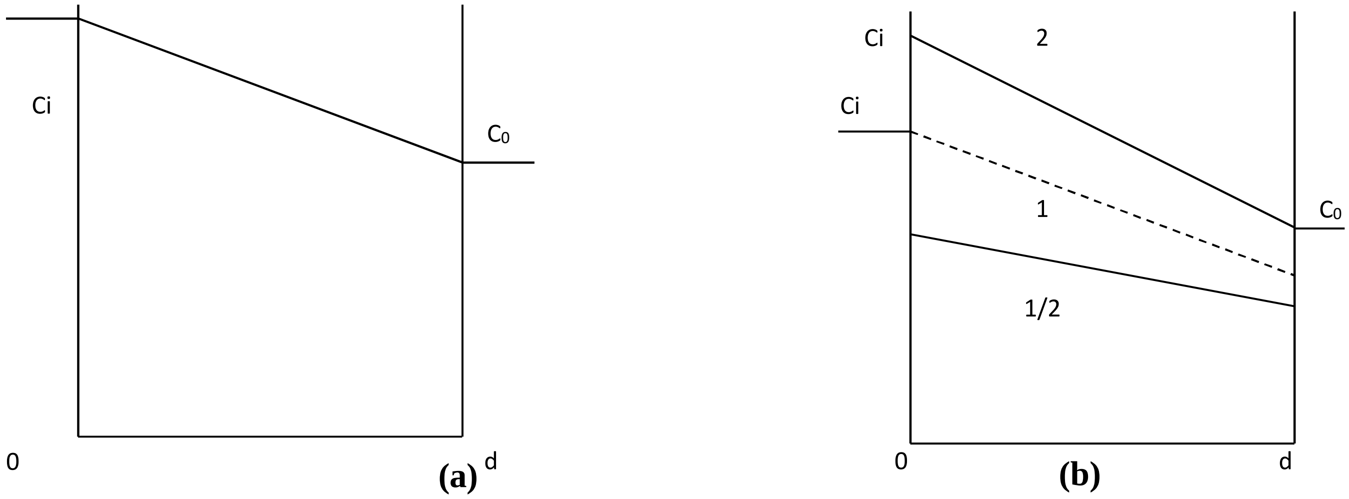


Figure1.2. Schematic Representation of Concentration Profile in the Membrane of Thickness of d cm (a) Linear Profile (b) Linear Profile when the Solubility of the Permeating Species in the Membrane is Greater, Equal to, and Less than Unity.

The flux is given by Fick’s law,

$$J = -D\frac{\partial C}{\partial x} \tag{1.4}$$

Where J is the flux of matter, so that,

$$J = -D\frac{C_0 - C_i}{d} = \frac{D}{d}(C_i - C_0) \tag{1.5}$$

This solution is based on the assumption that the substance has the same solubility in both the inside and outside phases and the membrane.

If the solubility of the substances in the membrane differs from the solubility in the phase on either side of the membrane, the concentration profile is still determined by equation (1.2), but the boundary condition for $C_{(x)}$ are,

$$C_0 = \begin{cases} \beta C_i & \text{f or } x = 0 \\ \beta C_0 & \text{f or } x = d \end{cases}$$

Where β is the distribution or partition coefficient for the substance. Solvingequation (1.2) for these boundary conditions give,

$$C_{(x)} = \frac{\beta}{d}(C_0 - C_i)x + \beta C_i \qquad (1.6)$$

Figure1.2 (b) shows the concentration profiles corresponding to $\beta > 1$ and $\beta < 1$.The flux now becomes,

$$J = \frac{\beta D}{d}(C_i - C_0) \qquad (1.7)$$

For a given C_i and C_o the flux is thus determined by the term,

$$P = \frac{\beta D}{d} = \frac{\beta BRT}{d} \qquad (1.8)$$

The last term in the equation (1.8) is obtained by using Nernst relation (D = BRT), P is called the permeability coefficient or permeability for the substance under consideration. Its units may be cm.sec^{-1} or sec^{-1}. When the thickness of the membrane is known approximately equation (1.7) can be written in the form, [3]

$$J = P\,(c_i - c_o)$$

1.7. Ion Transport and Concentration Polarization:

By Faraday's law, the total amount of transferred substance (in gram ions) is,

$$m = \frac{q}{2F}$$

where q is amount of the electricity. For each species of ions, the flow is proportional to the fraction of their participation in the transfer of electricity t_i

This fraction is called the transport number of ion:

$$m_i = \frac{q\,t_i}{2F} \qquad (1.9)$$

By definition,

$$\sum m_i = m \quad ; \quad \sum_i t_i = 1 \qquad (1.10)$$

The transport number is determined as the fraction of electricity carried by a given ion species,

$$t_i = \frac{I_i}{I} = \frac{Z_iC_iU_i}{\sum_i Z_iC_iU_i} \qquad (1.11)$$

where U_i is speed of an ion in the electric field. For a binary symmetric electrolyte in a free solution ($C^0_+ = C^0_-$), we have,

$$t^0_+ = \frac{U^0_+}{U^0_+ + U^0_-} \qquad (1.12)$$

and,

$$t^0_- = \frac{U^0_-}{U^0_+ + U^0_-} \qquad (1.13)$$

where the subscript “o” signifies a free solution. In the pores of a capillary system,

$$t_+ = \frac{C_+U_+}{C_+U_+ + C_-U_-} \qquad (1.14)$$

$$t_- = \frac{C_-U_-}{C_+U_+ + C_-U_-} \qquad (1.15)$$

where C_i are the mean values of the ion concentrations over the cross section. For negatively charged system, $C_+ > C_-$ and consequently, if the ion mobilities or their ratio do not change appreciably when passing from a free solution to a

pore one, we have $t_+ > t_-$. If the ions of the surface layer (electric double layer) from a substantial fraction of all the ions in a capillary system, it is necessaryto establish the change in the transport number $\Delta t = t_i - t^0$ in the system (in comparison with a_i free solution) due to the unequal participation of the electric double layer ions in the transfer of electricity. The transport number of a counter ion (and also Δt together with it) increases with a growth in the part played by the surface excess in transference, i.e., with diminishing of C.It is evident that t_+ may vary from to t^0_+ to 1 (at $C_+ >> C_-$), and Δt from 0 to$(1 - t^0_-) = t^0_+$.

The ability to change the transport number is characteristic not only of heterogeneous capillary system, but also of homogeneous membranes made from ion exchange resins. Electricity is carried virtually completely by mobile counter ions ($t_+ \approx 1$), whereas the ions fixed in the matrix (anion in our case) do not participate in the transfer. In these system there is also observed an excess conductance (due to high ion concentration) similar to surface conductance. Since the ability to change conductance and transport lead to results that are the same for both classes of system, we shall combine them in the following treatment by the common term ‘membrane’.

Membrane varying t_i is known as electrochemically active or ion selective ones. When only counter ions participate in transfer ($t_i = 1$, mobile ions of the opposite sign are absent) we speak of ideal electrochemical activity (or selectivity) of the membranes. The change in electrolyte concentration because of the flow of a current through finely porous system, which is concentration polarization, induces secondary emf's that slowlydiminish after switching off of the primary field [33].

Case(A), When $C_+ > C_-$

$$t_+ = \frac{C_+U_+}{\sum C_iU_i} \qquad (1.16)$$

$$t^0_+ = \frac{U^0_+}{\sum U_i} \qquad (1.17)$$

$$C_+ = \frac{t_+\sum C_iU_i}{U_+} \qquad (1.18)$$

$$C_- = \frac{t_-\sum C_iU_i}{U_-} \qquad (1.19)$$

but, $$\frac{t_+\sum C_iU_i}{U_+} > \frac{t_-\sum C_iU_i}{U_-}$$

or $$\frac{t_+}{U_+} > \frac{t_-}{U_-}$$

or $$\frac{t_+}{t_-} > \frac{U_+}{U_-} = \text{constant} \qquad (1.20)$$

or $$\frac{t_+}{t_-} > \text{constant}$$

or $$t_+ > t_-$$

Case(B) $t_+ > t^0_+$

$$t_+ = \frac{C_+U_+}{C_+U_+ + C_-U_-} \qquad (1.21)$$

$$t^0_+ = \frac{U^0_+}{U^0_+ + U^0_-} \qquad (1.22)$$

$$\overset{0}{\underset{+}{=}} \frac{+ \quad \frac{1}{t^0} \quad U\ + U^0_-}{U^0_+} = 1 + \frac{U^0_-}{U^0_+} \qquad (1.23)$$

$$\frac{1}{t^0}(\quad - 1) = \frac{U}{U^0}(\ =) = \alpha \qquad (1.24)$$

$$0 \quad + \quad +$$

$$\frac{1}{t_+} = \frac{C_+U_+ + C_-U_-}{C_+U_+} = 1 + \frac{C_-U_-}{C_+U_+} \qquad (1.25)$$

$$\frac{}{t_+}(\frac{1}{} - 1) = \frac{C_-U_-}{C_+U_+} = \frac{(C_-)}{C_+}\frac{(U_-)}{U_+} \qquad (1.26)$$

$$\text{Let} \quad \frac{U^0_-}{U^0_+} = \frac{U_-}{U_+} = \alpha$$

$$\frac{}{t_+} \quad (\frac{1}{} - 1) = \frac{(C_-)}{C_+}\alpha = \frac{(C_-)}{C_+}(\frac{1}{t^0_+} - 1) \qquad (1.27)$$

$$\frac{}{+} \quad \{(\frac{1}{t} - 1)/(\frac{1}{t^0_+} - 1)\} = \frac{(C_-)}{C_+} < 1 \qquad (1.28)$$

$$(\frac{1}{} - 1) < (\frac{1}{t} - 1) \quad \frac{}{t} \quad + \quad {}^0_+$$

$$(\frac{1}{}) < (\frac{1}{}) \quad t \quad t \quad + \quad {}^0_+$$

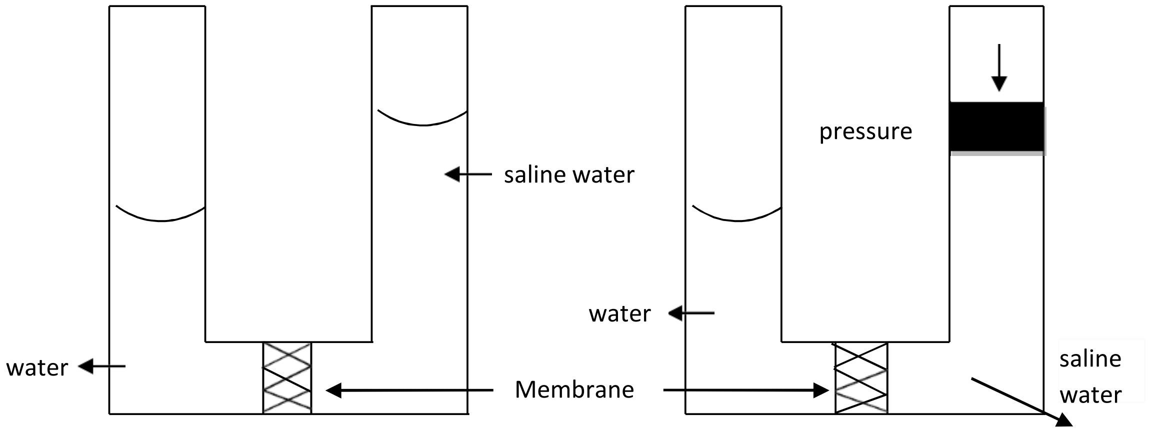
$$\text{or} \qquad t_+ > t^0_+$$

1.8. Ultrafiltration / Reverse - Osmosis:

Osmosis is the phenomenon whereby solvent permeates a semi permeable membrane separating two solutions of different concentrations. A net flow of solvent occurs from the less concentration to the more concentrated solution. Osmosis differs from diffusion in following respect as shown in Table1.3. When pressure in excess of the osmotic pressure is applied to the more concentrated solution, the net flow of solvent is into the more diluted solution, and the process is known as reverse osmosis [13].

Table 1.3

Osmosis		**Diffusion**
1.	Presence of semipermeable membrane is essential.	No semipermeable membrane is required.
2.	Solvent flows from the solution of lower concentration to solution of higher concentration.	Both solute as well as solvent molecules flow in opposite direction or solution flows from higher concentration to lower concentration until an equilibrium in concentration is achieved.



(a) Osmosis

(b)Rerverse osmosis

Figure 1.3 Schematic of Osmosis and Reverse Osmosis Process

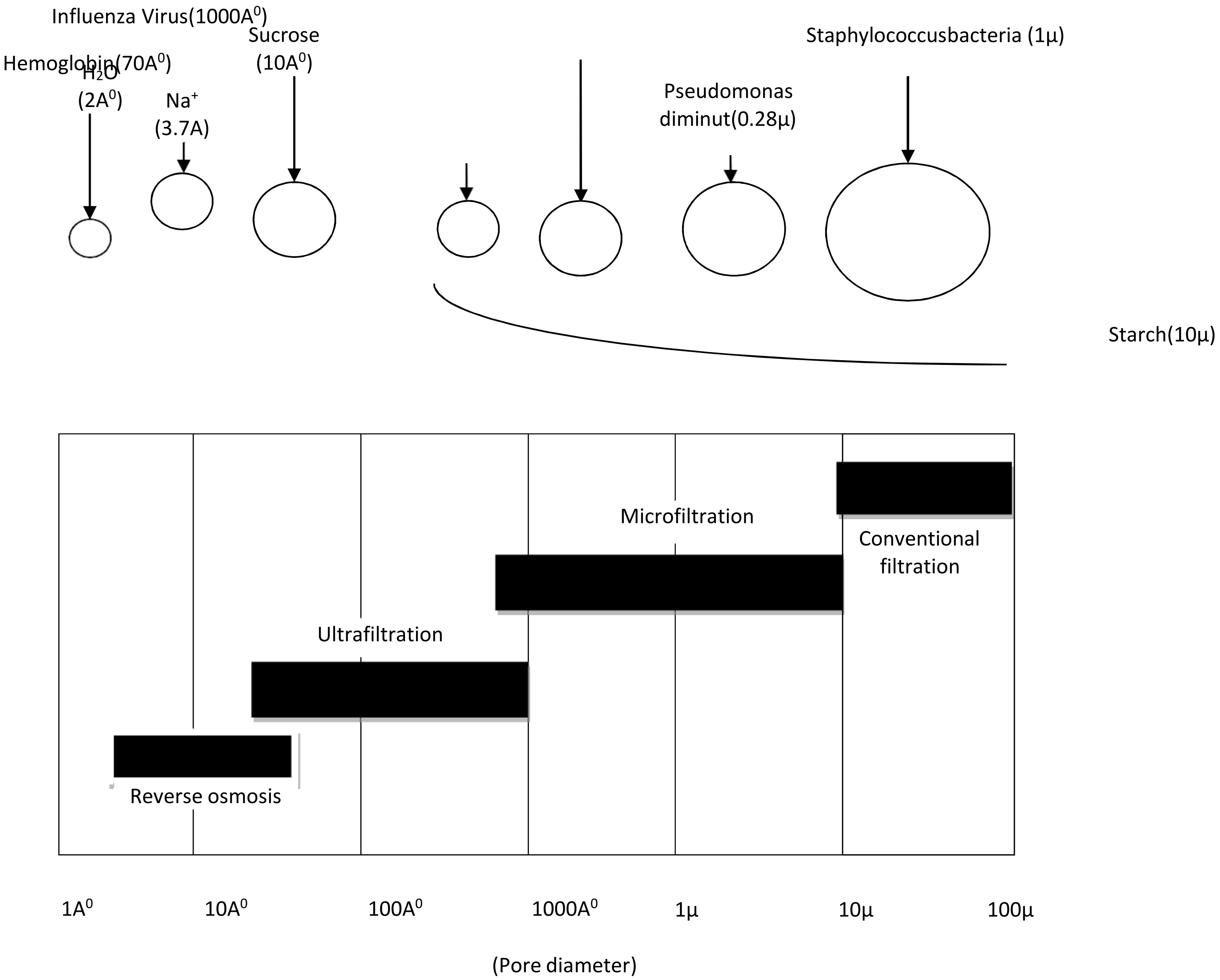


Figure1.4 Reverse Osmosis, Ultrafiltration, Microfiltration and Conventional Filtration are All Related Processes Differing Principally in the Average Pore Diameter of the Membrane. Reverse Osmosis Membraneare so Dense that Discrete Pores may not Exists [34].

Ultrafiltration is closely related to reverse osmosis. Both processes utilize pressure to force solvent to permeate a membrane while the solute is retained toa greater or lesser extent. The difference between the two processes is ill defined, and in fact they overlap to some extent. Reverse osmosis is the preferred term when osmotic pressure is not negligible, viz. separation of smaller solute particle from the solution. Ultrafiltration, on other hand, implies the separation of large solutes particles from the solvent. The particles may be so large that a suspension rather than a true solution is present [35-46].

In ultrafiltration the dispersed phase (solute) passes through the membrane less readily than the solvent for one of the reasons.

- It is adsorbed in the surface of the filter and its pores (primary adsorption).
- It is either retained within the pores or excluded therefrom (blocking).
- It is mechanically retained on top of the filter (sieving).

1.9. Nanofiltration:

The goal of most of the early work on reverse osmosis was to produce desalination membranes with sodium chloride rejection greater than 98%.More recently membranes with lower sodium chloride rejection but much higher water permeabilities have been produced. These membranes, which fall into a transition region between pure reverse osmosis membranes and pure ultrafiltration membranes, are called loose reverse osmosis, low-pressure reverse osmosis, or more commonly, nanofiltration membranes. Typically nanofiltration membranes have sodium chloride rejection between 20 and 80% and molecular weight cut-offs for dissolved organic solutes of 200-1000 dalton. These properties are intermediate between reverse osmosis membranes with a salt rejection of more than 90% and molecular weights cut-off of less than 50 and ultrafiltration membranes with a salt rejection of less than5% [47]. Nanofiltration membrane usually have high rejection to most dissolved organic solutes with molecular weights above 100-200 and goal salt rejection at salt concentrations below 1000-2000 ppm salt. The membranes are also two- to five-fold more permeable than brackish and sea water reverse osmosis membranes, so they can be operated at pressures as low as 50- 150 psig and still produce useful fluxes. For these reasons, their principal application has been in the removal of low levels of contaminants from already relatively clean water [48-51]. For example, nanofiltration membranes are widely used as point-of-use drinking water treatment units in southern California and the southwestern United States.

1.10. Factors Affecting Transport across Membranes:

1.10.1. Membrane - Solution Interactions:

Interactions between a membrane and a solution are of two general types.

1. Chemical
2. Physical

Chemical interactions are not, however of the type which involves rupture and formation of chemical bonds, although formation does sometimes inadvertently occur as a result of hydrolytic or oxidative degradation of the membrane polymer. They consist rather of what may be termed physicochemical interactions involving the process of eliminating or ‘neutralizing’ differences in electric and magnetic fields caused by the unequal distribution of electrons in the various atoms and molecules constituting the membrane solution system. Chemical interactions vary from ion–ion, through ion–dipole, to dipole-dipole types.

Physical interaction includes purely mechanical obstruction, or sieving effects, as well as blocking phenomena, which are a combination of physicochemical sorption and mechanical obstruction. In attempting to analyse the results of a membrane separation, every possible interaction should be considered. Chemical and physical interactions within the membrane itself (membrane structure) influence interactions between both membrane and solvent, and membrane and solute. Likewise solute-solute and solvent-solvent interactions can indirectly influence membrane–solvent and membrane–solute relationships. The complexity of the membrane separation system increases rapidly with the number of components in a geometrical manner [13]. When solutes are added to water, water structure will be enhanced or destructed depending upon the nature of the interactions. In structure enhancement (or structure making), the presence of solute shifts the water structure to layer or more ordered clusters at the expense of the dense monomeric species. In structure breaking, on other hand, the presence of solute shifts the structure equilibrium towards smaller and / or less ordered clusters and increasing concentrations of dense monomeric water.

The net structure-making ions include relatively small or multivalent ions such as Li^+, Na^+, H_3O^+, Ca^{2+},Mg^{2+},Al^{3+},OH^-, and F^-. Water molecules about the ion are less mobile than those in the bulk, a phenomenon which has been called positive hydration by Samoilov [52-53]. Such ions increase the viscosity of water and in the case of neutral (uncharged) membranes permeates less readily than structure breaking ions [54].

Large monovalent ions such as K^+, NH_4^+, Cs^+, Cl^-, Br^-, I^-, NO_3^-, BrO_3^-, and ClO_4^- generally exert a net structure breaking effect. Their weak field is capable at most of orienting water molecules in the layer immediately adjoining the ion, while beyond this layer a structure- breaking effect is noted. Water molecules other than those in the layer adjacent to the ion have a higher mobility in the presence of such ions than in the bulk, i.e., negative hydration [52-53], so that solution viscosity decreases and membrane permeability increases.

The behavior of water within membranes and at their surface has beenthe subject of broad speculation. There is a dichotomy of opinion, with the phenomenologists appearing reluctant to accept the idea of any form of long – range ordering near aqueous interfaces and the molecularty oriented scientists tending to credit the existence of considerable amount of bound water. The existence of bound water is indicated whenever the physical properties of a macromolecular suspension cannot be readily accounted for by the properties of the suspending medium and those of the macromolecules [55]. This concept can also be extended to membrane gels, i.e., three-dimensional arrays of macromolecules which have been insolubilized by one means or another.

Bound water relaxes at frequencies between those characteristic for ice and those characteristic for normal water. Therefore, from a structural point of views, bound water stands between normal water and ice. A broader spectrum of time constants is involved in the relaxation of bound water than in that normal water, which is indicative of variation in the characteristics of the former associated with different activation energies. In other words not only can water be bound, but it can also be bound to various extents. Very probably a continuum exists, with the more highly (primarily) bound water molecules in the inner hydration shell and less highly (secondarily) bound water moleculesin successive hydration shells. The lower dielectric constant of bound as compared to normal water indicates lower mobility and hence lower capacity for hydration of ionic solutes.

By analogy to the known effect of solutes on the structure of water, Berendsen and Migchelsen [56] predicted the following polymer–water influences.

- Polar side chains should hydrate individually but have a structure breaking influence beyond the first layer, (Actually not all polar groups are capable of hydration, so that polarity does not always indicate hydrophilicity).
- Non polar side chains should induce order of the cage type similar to theeffect of nonpolar solutes.
- Backbone structures with no available hydrogen-bond donors or acceptors will act as nonpolar solutes.
- Backbone structures are able to form hydrogen bonds to water will have structure- breaking or structure- promoting effects, depending on the geometry of hydrogen – bonding sites.

Bound water is believed to be of importance in many separations of aqueous solutions. It is one of the reason for the selectivity of ion-exchange membranes, and its presence in the active layer of reverse osmosis desalination membranes is believed to constitute the basis for their salt retention capability.

Lack of membrane-water interactions, as in the case of hydrophobic materials such as polyethylene, leads to higher interfacial tension. In such an environment the water molecules tend to form cluster with others of their own kind rather than to wet the membrane surface. Since the passage of large clusters of water molecules quite obviously meets with greater resistance than the passage of smaller cluster of individual molecules, permeability decrease with decreasing membrane solvent interaction.

Strong interactions between membrane and solute can have pronounced effects upon permeability as well as permselectivity. If the average residence time of a solutes molecule at a given permeation site too greatly exceeds that of a solvent or solute molecules in the solution environment, permeability can decrease rather than increase.

1.10.2. Concentration Polarization:

During an actual separation, the membrane performance may change with time, and often a typical flux-time behavior may be observed, the flux

through the membrane decrease over time as shown schematically in Figure1.5.

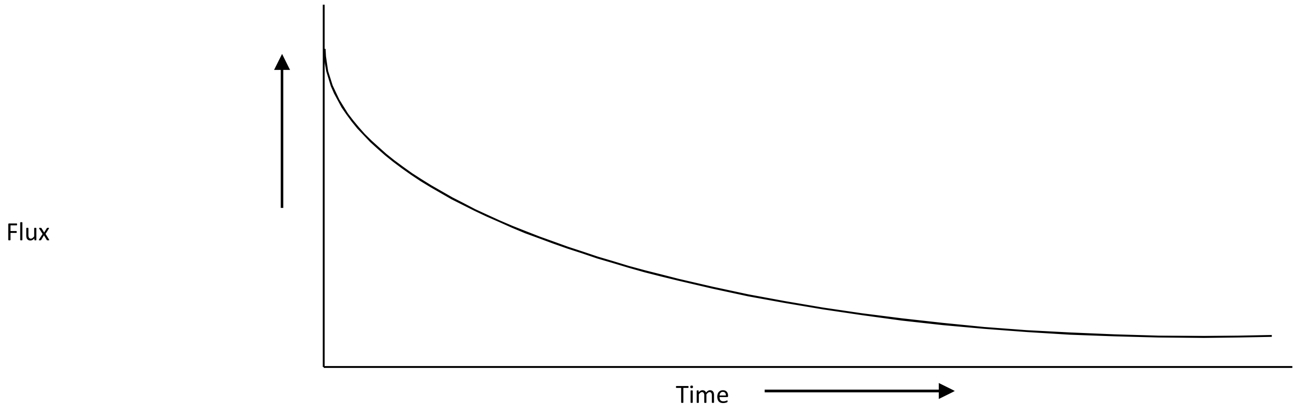


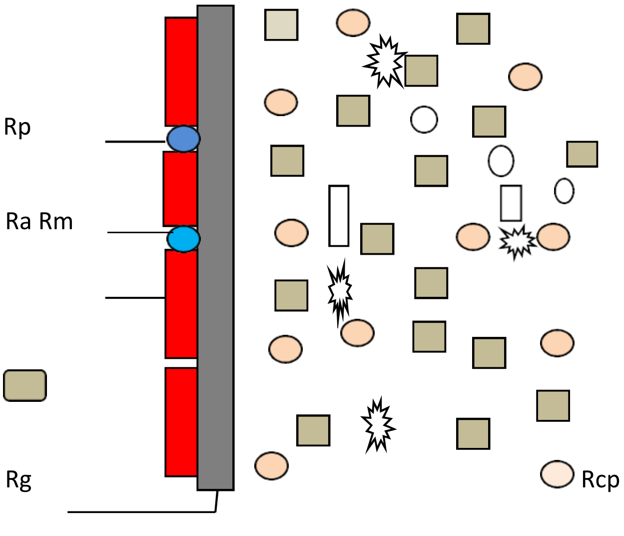
Figure 1.5 Flux Behaviors as a Function of Time

Flux decline has a negative influence on the economics of a given membrane operation and it can be caused by several factors, such as concentration polarization, adsorption, gel – layer formation and plugging of the pores. All these factor induce additional resistances on the feed side to the transport across the membrane. The extent of this phenomenon is strongly dependent upon the types of membrane process and feed solution employed. Figure1.6 provides a schematic representation of the various resistances that can arise. The flux through the membrane can be written as:

$$\text{Flux} = \frac{\text{driving force viscosity x total resistance}}{}$$

The various resistance depicted in figure contribute to a different extent to the total resistance, $R_{tot.}$ because the membrane has the ability to transport one component more readily than other components or in some cases completely retain the solutes, and there will be an accumulation of retained

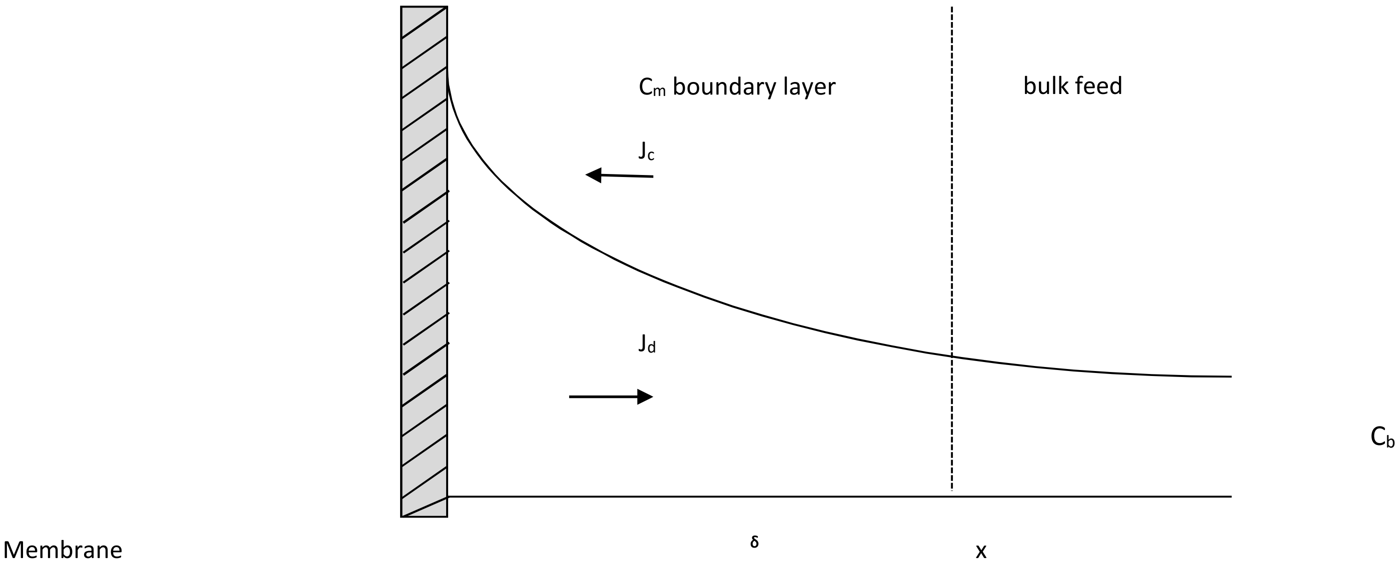
molecules near the membrane surface. This results in a highly concentration layer near the membrane and this layer exerts a resistance towards mass transfer i.e., the concentration polarization resistance, R_{cp}.



Rp : : pore blocking
Ra : adsorption
Rm : membrane
Rg : gel layer formation
Rcp : concentration polarization

Figure 1.6 Overview of Various Types of Resistance towards Mass Transfer across a Membrane [34]

The retained solutes can accumulate at the membrane surface where their concentration will gradually increase. Such a concentration build–up will generate a diffusive flow back to the bulk of the feed, but after a given period of time steady state condition will be established. The solute flow to themembrane surface due to convection flow will be balanced by the solute flux through the membrane plus the diffusive flow from the membrane surface tothe bulk. A concentration profile has now been established in the boundary layer as shown in Figure1.7



centration Polarization: Concentration Profile underSteady-State Condition

Steady- state condition are reached when the convective transport of solute to the membrane is equal to the sum of the permeate flow plus the diffusive back- transport of the solute i.e.,

$$J + D\,\frac{dc}{dx} = J.C \quad {}_{c} \quad - \quad {}_{P} \qquad (1.29)$$

The boundary conditions are,

$x = 0 \rightarrow C = C_m x = \delta \rightarrow C = C_b$

So that integration of equation 1.29 results in the well known ‘film model’relationship.

$$\mathrm{In}\,\frac{C_m - C_p}{C_b - C_p} = \frac{J\delta}{D} \qquad (1.30)$$

$$\text{or}\quad \frac{C_m - C_p}{C_b - C_p} = \exp\left[\frac{J\delta}{D}\right] \qquad (1.31)$$

The ratio of diffusion coefficient D and the thickness of the boundary layer ð iscalled the mass-transfer coefficient k, i.e.,

$$k = \frac{D}{\delta} \qquad -$$

If we introduce the equation for the intrinsic retention,

$$R_{int} = 1 - \frac{C_p}{C_m}$$

Then equation becomes,

$$\frac{C_m}{C_b} = \frac{\exp[\frac{J}{k}]}{R_{int}+(1-R_{int})\exp[\frac{J}{k}]} \qquad (1.32)$$

The ratio $\frac{C_m}{C_b}$ is called the concentration polarization modulus. This ratio increase(i.e., the concentration C_m at the membrane surface increases) with increasing flux J, with increasing retention and with decreasing mass- transfer coefficient k, when the solute is completely retained by the membrane ($R_{int} = 1.0$ and $C_p = 0$), equation 1.32 becomes.

$$\frac{C_m}{C_b} = \exp\left[\frac{J}{K}\right] \qquad (1.33)$$

This is the basic equation for concentration polarization, which illustrates in a simple form the two factors (the flux J and the mass- transfer coefficient k) and their origins (membrane part → J, hydrodynamics → k) responsible for concentration polarization [57-59].

Concentration polarization (boundary layer) can effect influence material transport in several ways:

(i) The osmotic pressure π at the membrane/ solution interface is increased because of the increase in solute concentration near the membrane surface over that in the bulk solution. Water permeability thereforedecrease since the effective pressure (the applied pressure $\Delta P - \pi$) is decreased.

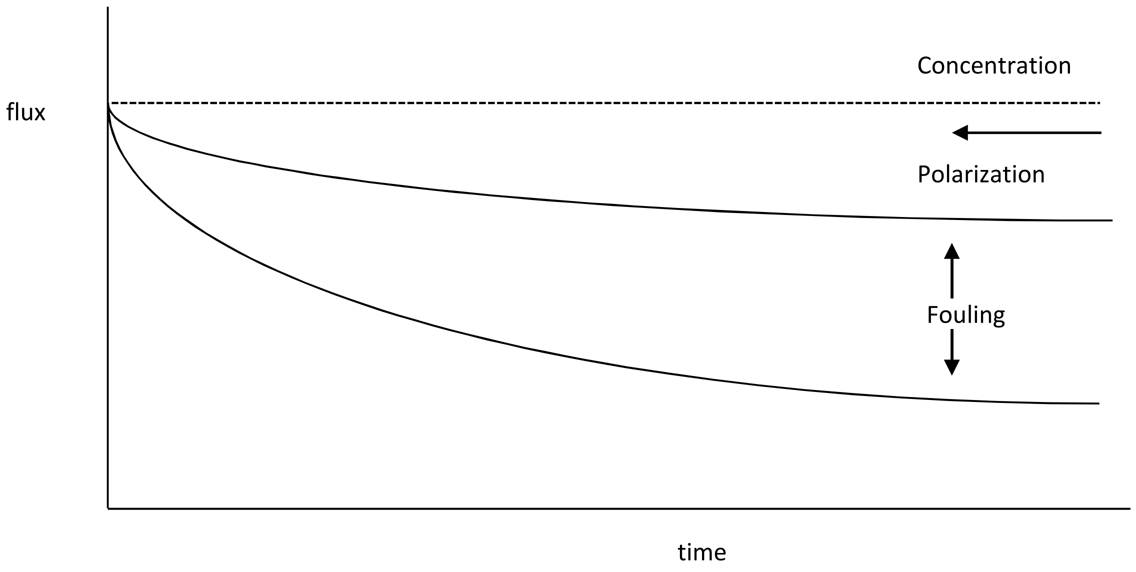
(ii) Since the fraction of solute retained by the membrane is, to a first approximation, independent of concentration, more solute will permeate because the interfacial concentration is higher than it would be in the absence of a boundary layer.

(iii) If the interfacial concentration of such solutes as are capable of forming insoluble precipitates exceeds a certain value, surface scaling will occur such a development may lead to physical blocking.

Concentration polarization becomes increasingly significant with increasing solution concentration, increasing permeability, increasing permselectivity. Although it cannot be completely eliminated, it can be minimized by agitation of the fluid layer by passage of the bulk solution past the membrane surface at velocities where turbulence develops, by utilizing entrance effects in thin channels in the laminar flow region, and by the insertion of baffles in narrow channels to promote turbulence [13].

1.10.3. Membrane Fouling:

Fouling may be defined as the irreversible deposition of retainedparticles, colloids, macromolecules, salts, etc., at the membrane surface or inside the membrane at the pore wall, which cause a continuous flux decline asshown in Figure1.8.



ux as a Function of Time Concentration Polarization andFouling can be Distinguished.

Fouling occurs mainly in microfiltration/ultrafiltrations where porous membranes are used, which are inherently susceptible to fouling. The fouling behavior in microfiltration is much more complex compared with ultra filtration [60-64]. Fouling is a major problem in all membrane operations. It causes significant problems in measuring and interpreting pore size in both MF and UF membranes.

MF and UF membranes contain ‘pores’ and for most membranes, they are not all of the same size. Fouling affects pore differently. Belfort [65]illustrates three cases affecting MF membranes to which needs to be added a fourth primarily affecting UF as shown in Figure 1.9.

Case A: Adsorption causes all pores to become smaller, and may result in the smallest pores plugging.

Case B: Pore plugging. In the absence of any adsorption, particles may plug pores.

Case C: Represents the deposition of a material that supersedes the porous structure of the membrane. The membrane now becomes analogous to a precoat filter.

Case D: It is peculiar to membranes with small pores filtering particles much larger than the pores. An example is UF membranes processing electrodedeposition point, all of whose particles are much larger than most membrane pores. The types of separation problem and the type of membrane are used to determine the extent of fouling. For this reason fouling phenomena will be described in relation to hyperfiltration, ultrafiltration and microfiltration. Roughly three types of foulant can be distinguished:

(i) Organic precipitates (macromolecules, biological substances, etc)

(ii) Inorganic precipitates (metal hydroxides, calcium salts, etc.)

(iii) Particulates

Fouling Schematics

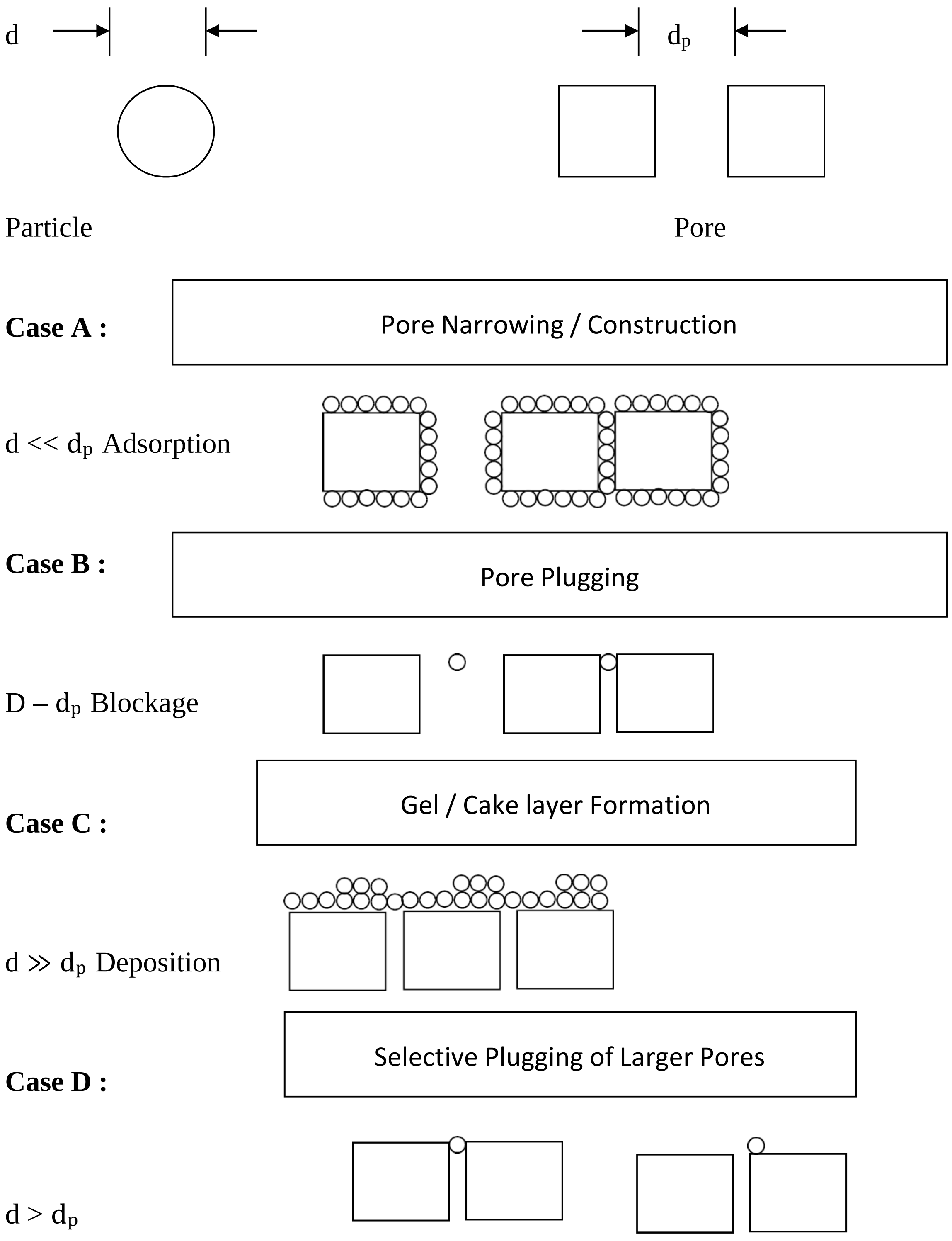


Figure 1.9 Schematics of Fouling in the Membranes [34].

The phenomenon of fouling is very specific for a given application and is difficult to describe theoretically. Even for a certain solution, fouling will depend on the physical and chemical parameter such as concentration, temperature, pH, ionic strength or choice of membrane material [66-69].

Fouling is very specific to a certain application and because of its complex nature it is hardly possible to describe a general theory. A very simple relationship, which has been widely used, is,

$$J = J_0 t^n, \qquad n < 0$$

Where J is the actual flux while J_0 is the initial flux and the exponent n is a function of the cross-flow velocity.

Fouling is different from concentration polarization. Both reduce output, and their resistance are additive. Both are not completely independent of each other since fouling can result from polarization phenomenon. However concentration polarization is a reversible phenomenon that occurs immediately when a process has been started and will reach an equilibrium value, whereas fouling is often an irreversible process that occurs in the long- term [34].

1.10.4. Temperature:

Variations in temperature have a great many largely interrelated effects upon membrane separation processes. In addition to the increased motion of solvent and solutes molecules and decreasing interactions between the two, membrane structure can undergo temperature dependent changes on the molecular, microcrystalline, and colloidal levels. Membrane – solvent and membrane- solute interactions are also affected. It should be noted, however, that the solubility factor involved in membrane separations can either increase or decrease with increasing temperature. It will decrease for substances (such as non-condensible gases) whose solubility decrease with increasing temperature, and it will increase where the reverse is true. For dense membranes like those employed in gas separations and skin layer of asymmetric reverse–osmosis types, the temperature dependence of the permeability constant P can be expressed as an Arrhenius relationship in which,

$$P = P_0 e^{-Ep/RT} \tag{1.34}$$

Here E_p is the activation energy, and P_0 is the factor associated with the overall permeation process [70]. Since,

$$P_0 = S_0 D_0 \tag{1.35}$$

Where S is the solubility of permeant species in the membrane and D is the diffusion coefficient, S and D can also expressed as Arrhenius function with,

$$S = S_0 e^{-Hs/RT} \tag{1.36}$$

and $$D = D_0 e^{-ED/RT} \tag{1.37}$$

Where H_s is the heat in solution and E_d is the activation energy for the different process. In most cases permeability increases and activation energy decreases with increasing temperature. Exceptions do, however, occur as when permeant solubility in the membrane and temperature are inversely related.

In the transport of water and salt across asymmetric cellulose acetate membrane in reverse osmosis, activation energies decrease with increasingmembrane water content [13].

1.10.5. Pressure:

Increasing pressure generally acts to increase the permeation rate of a given species through a membrane. The effects of pressure are mitigated by themechanism of permeability e.g., diffusive vs viscous flow, by membrane structure, by the various interactions between membrane and permeant species (and between the permeant species themselves) by solute concentration, and bythe charge characteristics of membrane and solute. In addition, pressure in excess of the membrane's compressive yield point results in compaction and resultant loss of void volume (porosity) and permeability. Not only the average porosity of the membrane vary with pressure, but also porosity decreases with distance from the high pressure side. Pressurization causes a change in void dimension in the plane perpendicular to the surface, where heating causes shrinkage in all three dimensions.

1.11. Control of Concentration Polarization and Fouling:

The consequence of concentration polarization and fouling is always reduction in separation performance. The methods to improve the performance can be classified in following categories:

- Pretreatment of feed solution
- Adjustment of membrane properties
- Membrane Cleaning

1.11.1. Pretreatment of Feed Solution:

A reduction of concentration polarization and fouling starts in developing a proper pretreatment. Many methods have been used and tested, which depend mainly on the type(sea water, brackish water) and quality of feed with respect to the type of foulants (suspended solids, bacteria, organics). Typical methods of pretreatment are the addition of Cl_2 (to remove bacteria, algae), flocculants (polyelectrolytes or $FeCl_3$ to remove suspended solids), pH adjustment (H_2SO_4 to prevent scaling) $NaHSO_3$ (Cl_2 removal), heat treatment, UV treatment, activated carbon, and all types of filters such as multilayer filters, and 1-5µm cartridge filters.

1.11.2. Adjustment of Membrane Properties:

Membrane properties mainly affect the solute- membrane interactions and, consequently the extent of adsorption and fouling. In the cases of proteins, which adsorb more strongly to hydrophobic surfaces rather than to hydrophilic ones the development of hydrophilic membranes (cellulose esters, aliphatic polyamides) can help to reduce fouling. Also chemical modification (e.g. sulfonation of polysulfone) can be used to achieve this. Conventional ultrafiltration membranes such as polysulfone, polyethersulfone or polyvinylidene fluoride can be made more hydrophilic by surface modification of the membrane [34].

1.11.3. Membrane Cleaning:

Although all the above methods reduce fouling to some extent, cleaning methods will always be employed in practice as shown in Table 1.4 & 1.5. The cleaning techniques may be classified in three broad categories:

- Techniques to weaken or prevent adherence between the membrane and the fouling layers.
- Techniques to solubilize the fouling layers.
- Techniques to remove the foulant by physical scouring.

Table 1.4 Cleaning Solutions

Cleaning Solutions	**Fouling Removal**
Acid (pH = 3-5), typically HCl.	Dissolution of iron or aluminiumoxides / hydroxides, calcium carbonate.
Citric acid, ammonia, EDTA	Complexation of Fe, or Al oxides, $CaCO_3$ and $CaSO_4$ (limited)

Detergent	To provide wetting characteristic and dissolve oil / fats and organic colloids
Soil dispersant (sodium hexametaphosphate)	Dispersal of inorganic particles and colloids

Table 1.5 Cleaning Methods [71]

Category	**Examples**
Physical : Mechanical Back flushing Air / Water flushing	Foam ball swabs Depressurizing and development of osmotic flow High velocity scouring of system often with countercurrent flow
Chemical : Feed additives Flushing Coagulation	Soil dispersant, coagulants etc. Detergent / complexing solutions and oxidizing agents. Acid or alkali treatment of fouling layer to neutralize its zeta potential
Others : Charged membranes Precoating membranes witha diatomaceous earth	

1.12. Liquid Junction Potential or Diffusion Potential:

A liquid junction potential represents a boundary between two dissimilar solutions across which ions move by diffusion. A liquid junction potential (V_L) arises from the differences in the mobility of positive and negative ions. If the cation has a higher mobility than the anion, the former will move ahead of the latter into dilute solution that will become positively charged with respect tothe concentrated solution. If the anion moves faster, the dilute solution will be negatively charged. In either case, a 'double layer' on a microscopic scale is produced at the junction between the two solutions. In other words, a gradient of electrical potential will be set up. This will oppose the diffusional flow of ions by increasing the speed of the slower ion and slowing that of the faster ion. In the steady state, the diffusional flux will be exactly balanced by the electric flux. The concentrations and the electrostatic potential through the boundary region become invariant with time. On this basis of the sum of the electricaland diffusional work of transporting ions cross a thin boundary dx becomes zero.

Consider solution 1 and solution 2 each containing several ions 1,2,…. i…., at concentrations indicated and forming a liquid junction as shown in Figure 1.10, z's are valencies and t's are transference numbers which are assumed constant. A potential dV_L will arise from the processes occurring inthe thin boundary indicated by the dashed line.

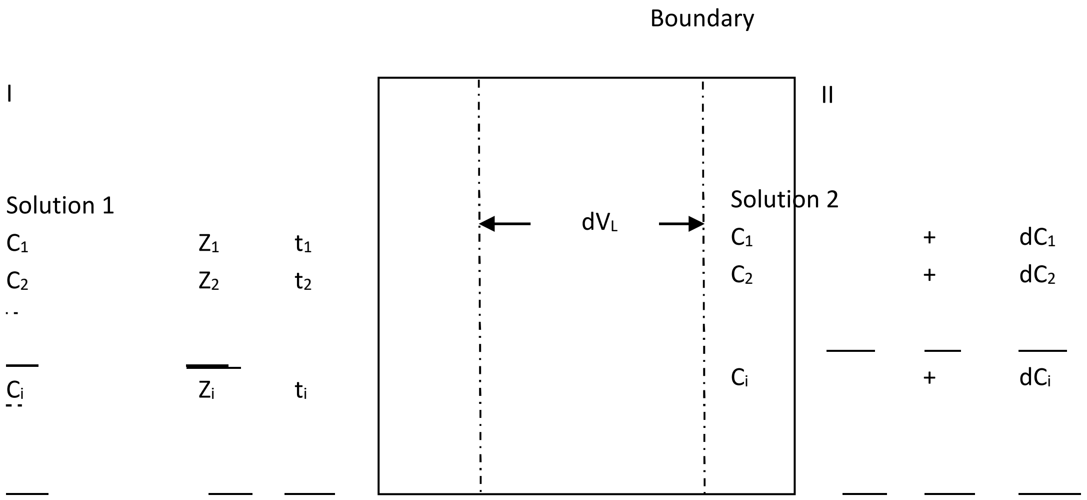


Figure 1.10 Diffusion Boundary

If a faraday of current is passed reversibly from solution 1 to 2, (t_i / z_i) g ofeach species will be transferred across the thin boundary, the electrical work is FdV_L. The diffusional work, therefore, is given by $\sum_i (t_i/z_i) d\mu_i$. Hence,

$$F dV_L + \sum_i \frac{t_i}{z_i} d\mu_i = 0 \qquad (1.38)$$

$$dV_L = -\frac{RT}{F} \sum_i \frac{t_i}{z_i} d \ln a_i \qquad (1.39)$$

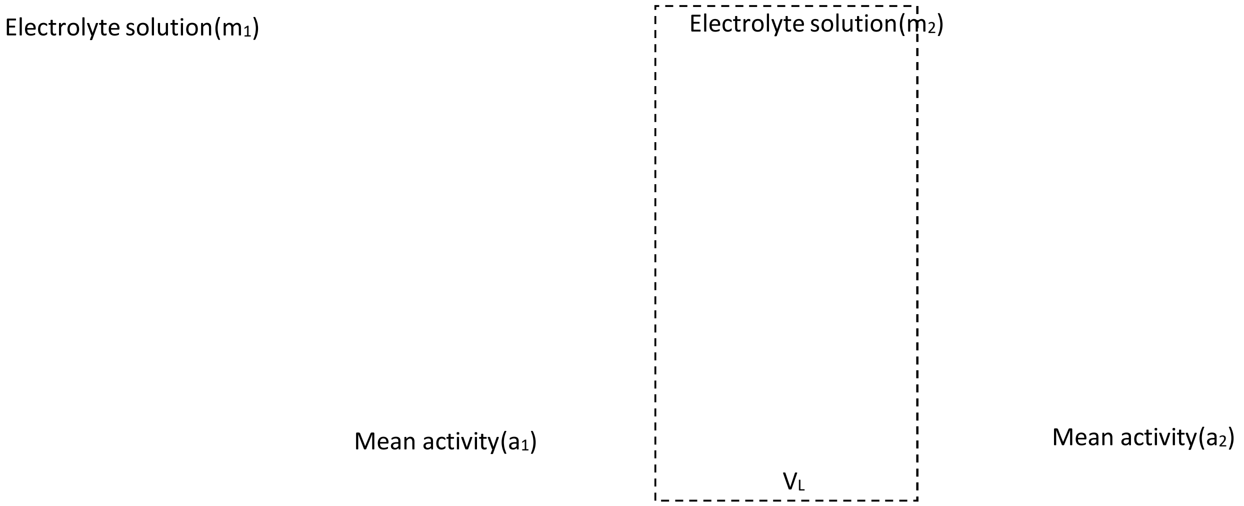
Any liquid junction between solution 1 and solution 2 will contain an innumerable number of thin boundaries bounded by I and II. The diffusion potential V_L across the diffusion zone between two solution phase 1 and 2 of activity a_1 and a_2 is given by:

$$V_L = -\frac{RT}{F} \int_{a_1}^{a_2} \sum_i \frac{t_i}{z_i} d \ln a_i \qquad (1.40)$$

Integration of equation (1.40) is difficult. Approximations have to be made about a_i, a single ion property which is not directly measurable, about concentration dependence of t_i and about concentration profile of the species in the diffusion zone [2-3].

1.13. Diffusion Potential between Two Solutions of Same Electrolyte:

Application of equation (1.40) to the case of diffusion of a simple($z_+ : z_-$) electrolyte in a concentration cell of the type:



The total potential is given according to equation (1.40) by,

$$V_L = -\frac{RT}{F}\int_{(a_+)_1}^{(a_+)_2} \frac{t_+}{z_+} d\ln a_+ + \frac{RT}{F}\int_{(a_-)_1}^{(a_-)_2} \frac{t_-}{z_-} d\ln a_- \quad (1.41)$$

where t_+ and t_- are assumed to be concentration independent. Then,

$$V_L = -\frac{RT\,t_+}{F\,z_+}\ln\frac{(a_+)_2}{(a_+)_1} + \frac{RT\,t_-}{F\,z_-}\ln\frac{(a_-)_2}{(a_-)_1} \quad (1.42)$$

Since $t_+ + t_- = 1$, and $z_+ = z_- = z$,

$$V_L = \frac{RT}{zF}\left[-2t_+ \ln\frac{a_2}{a_1} + \ln\frac{(a_-)_2}{(a_-)_1}\right] \quad (1.43)$$

where a_2 and a_1 are the mean activities of the two solutions. Furthersimplification of equation (1.43) is not possible without an extra nonthermodynamic assumption. Generally, it is assumed that the ratio of the singleion activities in the two solutions is equal to the ratio of their mean activities

i.e. $[(a_-)_2 / (a_-)_1 = a_2 / a_1]$. With this assumption equation (1.43) becomes,

$$V_L = (1 - 2t_+)\frac{RT}{ZF}\ln\frac{a_2}{a_1} \qquad (1.44)$$

In the terms of anion and cation mobilities u_- and u_+, equation (1.44) becomes,

$$V_L = \frac{u_- - u_+}{u_- + u_+}\frac{RT}{ZF}\ln\frac{a_2}{a_1} \qquad (1.45)$$

The sign of V_L depends on the relative values of u_+ and u_- . In the case of two solutions of the same electrolyte forming a liquid junction, the structure of the boundary is not important. The potential does not depend on the manner in which the boundary is constituted. At any point in the boundary layer the electrolyte solution is the same and has a definite activity and transference number. But if different electrolyte is present in the liquid junction, the ionic concentration at any point in it is determined by its structure and so t_i and a_i will depend on the nature of boundary [72].

1.14. Application of Membranes:

1.14.1. Desalination and Water Purification:

Any reverse osmosis system can separate physical contaminants from water extremely efficiently, but the presence of contaminants produces many complications. Membrane treating liquids that contain particulate and dissolved impurities tend to become fouled. Fouling invariably reduces water flux and produces deterioration in the quality of water penetrating the membrane. These dirty waters are obviously undesirable because they impair the efficiency of the system. Because of these difficulties reverse osmosis system have only been successfully used for treating clean waters. Such waters are either naturally clean or alternatively are subjected to extensive pretreatment before they reach the reverse osmosis plants [73]. The pretreatment required for given water is often difficult to anticipate without operational experience and may be complex or costly to undertake. These factors obviate against reverse osmosis as a treatment for ‘dirty water’.

In reality, of course, the major opportunities for reverse osmosis involve dirty waters, such as effluents streams or polluted waters, where water reuse or recovery of dissolved contaminates is a very attractive preposition.

The efficiency of reverse osmosis desalination varies with the nature of the dissolved solute. Ions which have a high charge density (small radius and / or high charge) tend to be more strongly hydrated than those with a low charge density. Since an ion must exchange its water of hydration in solution for the less efficiently hydrating molecules of ordered water, the less strongly hydrated solutions permeate more readily. Thus for a given ionic charge, permeability and crystal radii are inversely related. It should be realized however, that if an ion exceeds a certain crystal radius its size will result in sieving effects which will contribute to its rejection by the membrane.

The purification of water containing low total dissolved solutes but such widely differing elements as viral and bacterial microorganisms and organic and inorganic solutes is ideally suited to the reverse osmosis process. Although low molecular weight solutes which are capable of hydrogen bonding will dissolve in the ordered water, high molecular weight species are almost completely rejected by the membrane [74-79].

1.14.2. Waste Water Treatment:

In recent years it has become more apparent that conventional waste water treatment processes such as biological conversion, sedimentation, flocculation etc. are often unsatisfactory when large quantities of industrial effluents, which contain large amounts of highly toxic, biological non- degradable, or high oxygen demanding constituents, have to be treated. Especially in heavy industrialized areas which are in general also densely populated and where surface area is used for domestic water supply, the conventional waste water treatment methods have to be supplemented by more efficient physical or chemical procedure.

Although modern technology has made a large number of sophisticated processes available which are capable of solving many waste water problems. Most have some disadvantages. Rectification or sorption techniques are prohibitively expensive, incineration often causes air pollution problem, and many chemical precipitation processes produce large amounts of sludge which can pollute potable water sources.

For many industrial effluents, however, there are procedures available which are not only highly efficient but also economical. These are membrane separation processes, especially reverse osmosis, ultrafiltration and to a lesser extent electrodialysis. For the treatment of industrial effluents, membrane separation processes offer significant advantages over most other procedures. Waste water constituents, for example are not destroyed or chemically altered, and valuable products, such as certain metal ions, proteins, or other organic materials can be recovered and commercially utilized. The product water is relatively clean and can often be directly reused with a minimum or no further treatment. By selecting the proper membrane the process can be made highly specific and its costs can be kept relatively low, even for comparatively small size treatment plants [80-83]. Membrane separation processes, which can be successfully used to treat industrial effluents, are summarized in Table 1.6.

Table 1.6 Membrane Separation Process in Waste Water Treatment

	Membrane Separation Process		
	Ultra filtration	**Reverse Osmosis**	**Electrodialysis**
Effluents which can completely by recycled	Waste water containing oil, emulsion, electrophoretic paints, wash solutionfrom metal washing industries, pigment dyes and latex solution from textiles industry	Wastewaters from electroplating and textile industries	Wastewaters from electroplating industries.
Effluents from which valuable products can be recovered	Wastewaters containing proteins as obtained from dairy, meat and fishindustry or breweries	Waste waters from the electroplating and certain food industries	Waste waters from electroplating industries
Effluents with toxics or non biodegradable constituents of no commercial	Waste waters of the paper, textile and chemical industry	Waste waters ofthe chemical, electrochemicaland pharmaceutical industries	Waste waters of the chemical and electrochemical industries.

value.			

1.14.3. Electrodialysis:

Electrodialysis is the process wherein a flow of current across ion exchange membrane is utilized to hasten the transport of counter-ions across the membrane, or it is a mass separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components [47].

A multiple cell arrangement is often employed, in which an indefinite number of chambers is alternately separated by positive (cationic) and negative (anionic) membranes in series, such that the passage of current depletes the solution in alternate chambers while concentrating that in others. A cell consists of a volume with two adjacent membranes. The driving force for the ion transport in the electrodialysis process is the applied electrical potential between the anode and cathode. The principal factors involved in the efficiency of electrodialysis are the cell resistance and the magnitude of the emf opposing the applied potential.

Electrodialysis is used widely today for desalination of brackish water and in some areas of the world; it is the main process for the production of potable water. But other applications, such as the treatment of industrial effluents, the production of boiler feed water; demineralization of whey and deacidification of fruit juices, production of table salt from sea water, production of ultrapure water are gaining increasing importance. Electro dialysis perhaps is best utilized for treatment of weakly saline (brackish) watercontaining < 5000 ppm of total dissolved solids [84-88].

1.14.4. Piezodialysis:

The process of piezodialysis is almost conserved of reverse osmosis and ultrafiltration. When solutes permeate preferentially under the effects of applied pressure difference across a membrane, this phenomenon is described by the term 'Piezodialysis' (pressure dialysis). In this case, the pressure is equivalent to the electrical potential difference in electro dialysis.

In piezodialysis solute is made to pass through membrane unlike the other processes in which solvent flow through the membrane is sought. Thus,in this process feed solution is diluted and more concentrated solution is passedout under the action of pressure gradient. When solution of an electrolyte is forced through an ion exchange membrane under pressure, a streaming potential is generated which prevents the flow of counter ions. If membrane is thin and has low resistance, the overall effect of pressure will be to force out a mixture of ions and water similar to swelling of the membrane. This solution will be more concentrated than the feed solution so the feed solution will get diluted [89].

1.14.5. Hemodialysis:

The membrane kidney has a number of important functions, one of which is to remove certain waste products such as urea, creatinine, and uric acid from the blood, which circulates in small capillaries part of nephrons.

When as a result of illness (renal failure), renal function decreases below a certain fraction (~20 percent) of normal efficiency, the effects upon a patient’s well-being manifest themselves in such symptoms as edema, hypertension, weakness, fatigue vomiting and eventually death. To alleviate these symptoms and to speed recovery of normal renal function or permit the patient to recover sufficiently for a renal transplant, devices known as artificial kidneys are employed [13].

Artificial kidney basically consists of hemodialyzers and their supporting equipments. A hemodialyzer in turn is a membrane containing device which separates blood from dialysate solution. The blood is introduced into the dialyser (preferable under the patient’s own perfusion pressure) and flows pasts the cellulose membrane (cellophane and cuprophane are the only commercially available hemodialysis membrane types). Blood solutes permeate the membrane into the dialysate, in the process known as hemodialysis. Solute permeability varies with the composition of the dialysate, which must, therefore, be separately established for each individual patient. Because osmosis may result in a net transfer of water from the dialysate into the blood with resultant edema, hemodialysis is often utilized in conjunction with ultrafiltration to remove excess water [90-93].

1.14.6. Electrocoat Paint:

Recovery of electrocoat paint is economically the most important application of ultrafiltration. An efficient way of applying a corrosion resistant coating on industrial metal is electrophoretic deposition of colloidal paint from an aqueous bath. In the 1960s automobile companies were begun to use electrodeposition of paint on a large scale. The paint solution is an emulsion of charged paint particles. The metal piece to be coated is made into an electrode of opposite charge to the paint particles and is immersed in a large tank of the paint. When a voltage is applied between the metal part and the paint tank, the charged paint particles migrate under the influence of the voltage and aredeposited on the metal surface, forming a coating over the entire wetted surface of the metal part. After electrodeposition, the piece is removed from the tank and rinsed to remove excess paint, after which the paint is cured in an oven.

The rinse water from the washing step rapidly becomes contaminated with excess paint, while the stability of the paint emulsion is gradually degraded by ionic impurities carried over from the cleaning operation before the paint tank. Both of these problems are solved by the ultrafiltration system. The ultrafiltration plant takes paint solution containing 15-20% solids and produces a clean permeate containing the ionic impurities but no paint particles, which is sent to the counter-current rinsing operation, and a slightly concentrated paint to be returned to the paint tank. A portion of the ultrafiltration permeate is bled from the tank and replaced with water to maintain the ionic balance of the process [47].

Electrocoat paint is a challenging feed solution for an ultrafiltration process. The solid content of the solution is high, typically 15-20 wt% so a gel layer easily forms on the membrane. The gel formation results in relatively low fluxes. However, the value of the paint recovered from the rinse water and elimination of other rinse-water cleanup steps made the ultrafiltration process an immediate success. The first electrocoat paint was anionic because the latex emulsion particles carried a negative charge. These emulsions were best treated with membranes having a slight negative charge to minimize fouling. Cationic latex paints carrying a positive charge were introduced in the late 1970s. Ultrafiltration of these paints required development of membranes carrying a slight positive charge [94-95].

1.14.7. Citrus Juice Sweetening:

A significant portion of the important citrus crop (lemon family) isconverted into juice for human consumption. Since all natural products are extremely complex system which vary according to climate, local soil condition, etc. It is to be expected that a certain percentage of any given fruit will produce juice which is sour than the norm. Although such products can be sweetened by blending or by the addition of sugar, the end result is not equivalent to the desired premium product, nor can it be marketed as such. Therefore, to upgrade this costly item means for eliminating the excess citric acid responsible for the sour taste have been sought. A particularly promising approach is the electrodialytic removal of the citrate ion by the utilization of an all -anion exchange membrane electrodialysis stock [96].

1.14.8. Food Industry (Cheese Production):

Ultrafiltration has found a major application in the production of cheese; the technology is now widely used throughout the dairy industry. During cheese production the milk is coagulated (or curdled) by precipitation of the milk proteins. The solid that forms (curd) is sent to the cheese fermentation plant. The supernatant liquor (whey) represents a disposal problem. Whey contains most of the dissolved salts and sugars present in the original milk and about 25% of the original protein. In the past, whey was often discharged to the sewer because its high salt and lactose content makes direct use as a food supplement difficult. Now about half of the whey produced in the United States is processed to obtain additional value and avoid troublesome waste disposal problems. The composition of milk and cheese whey is shown in Table 1.7. The objective of ultrafiltration membrane is to increase the fraction of milk proteins used as cheese or some other useful product and to reduce the waste disposal problem represented by the whey. Although whey protein products have several food uses, the lactose contained in the permeate is less valuable, and many plants discharge the permeate to a biological waste water treatment plant [97-98].

Table 1.7 Composition of Milk and Cheese Whey [47]

Component (wt %)	**Milk**	**Whey**
Total solids	12.3	7.0
Protein	3.3	0.9
Fat	3.7	0.7
Lactose/other carbohydrate	4.6	4.8
Ash	0.7	0.6

Various types of typical membrane applications are shown in Table 1.8 andrelative states of membranes technologies are shown in **Figure 1.11**

Table 1.8 Typical of Membrane Application [1]

	General Application	Specific Application	Solution Type	Process
1.	Desalination	Production of potable water from brackish water and sea water	Aqueous inorganic	Reverse osmosis. Electrodialysis
2.	Water Purification	Removal of pollutantsfrom pulping spent liquors.	Aqueous inorganic – organic	Reverse osmosis , Electrodialysis, Forced flow electrophoresis
3.	Biomedical	Hemodialysis	Complex aqueous	Dialysis, assisted by ultra filtration
4.	Food Upgrading	Reduction of acidity of citrus juice.	Complex aqueous	Electrodialysis
5.	Food Concentration	Concentration of tomato juice.	Complex aqueous	Reverseosmosis
6.	Dairy	Concentration of milk whey prior to evaporation, Fabricationof milk for cheese manufacture	Complex aqueous	Reverse osmosis, Ultrafiltration

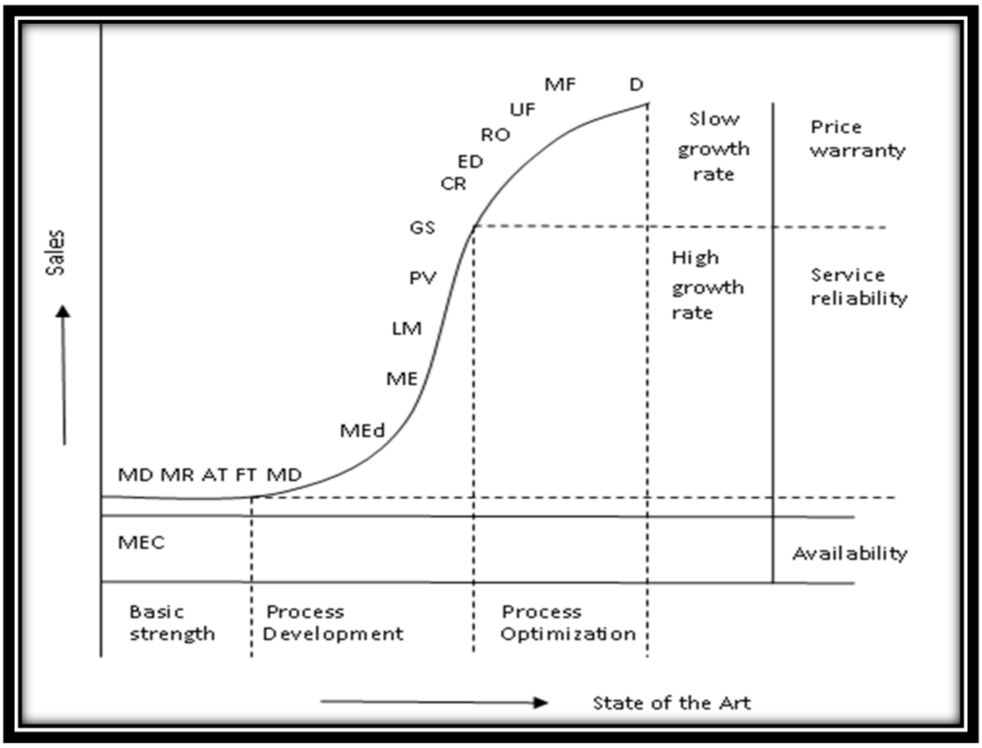


Figure 1.11 Relative Status of Various Membrane Technologies, D, Dialysis (including Hemodialysis); MF, Microfiltration : UF, Ultrafiltration; RO, Reverse Osmosis;ED, Electrodialysis (including electrodialysis reversal); CR, Controlled Release; GS, Gas Separation; PV, Pervaporation; LM, Liquid Membrane;; ME, Membrane Electrodes; MEd, Membrane Electro Synthesis; MD, Membrane Medical Devices (including artificial organs); FT, Fascilitated or Carrier-Mediated Transport; MR, Membrane Reactor, and MEC, Membrane Energy Conversion Systems [15].

1.15. Polymer used for Membrane Preparation:

Cellulose Acetate Butyrate

Cellulose acetate butyrate is a group of cellulose esters. These polymers are produced from renewable material sources. Acting as thermoplastic polymer properties when CAB, which is highly-purified cellulose, has been plasticized.CAB was introduced as tougher versions of CA. It exhibits an elasticity property. The higher butyryl content of CAB, flexibility, solubility, hydrocarbon tolerance, and compatibility will increase. Moreover, the higher molecular weight, compatibility and solubility decrease, toughness and melting point increase, and hardness and density are unaffected, [99]. cellulose acetate butyrate is biodegradable thermoplastic polymer [100-102]. cellulose acetate butyrate membrane is semipermeable [103]. ATIR-FTIR study reveals that cellulose acetate butyrate membrane has been associated to the presence of weakly H- bonded water clusters. It is also mentioned that there should be a relation between the permeation properties of the membrane and the structure of the water in the active layer. Rejection values also affected by the size of water clusters present [104-106], and it is also asymmetric [107]. CAB is considered as one of the good membrane materials because of its good resistance to fouling, chlorine tolerance, chemical stability and the ability to control the molecular weight cut-off (MWCO) [108-110].

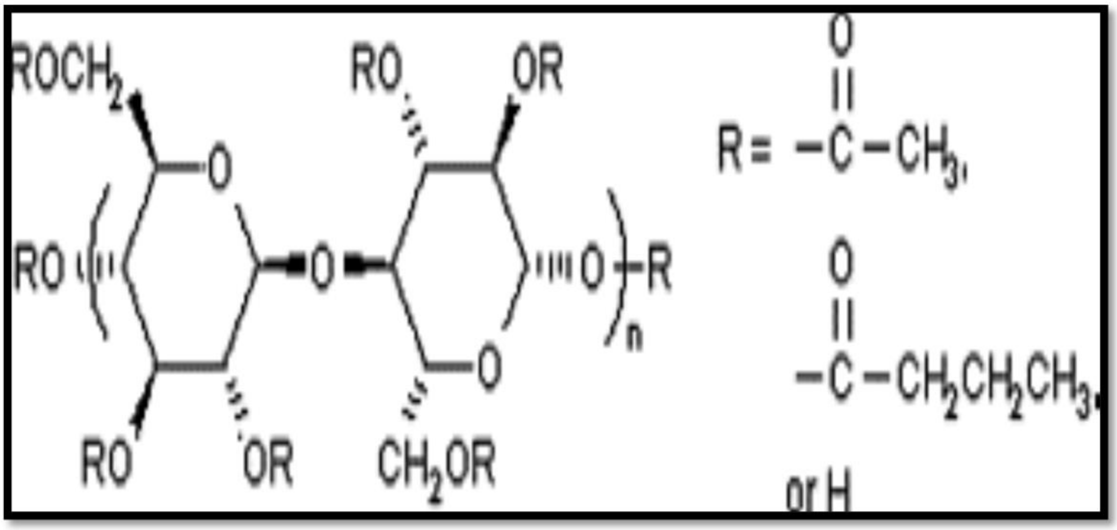


Figure: 1.12 Structure of Cellulose Acetate Butyrate [111]

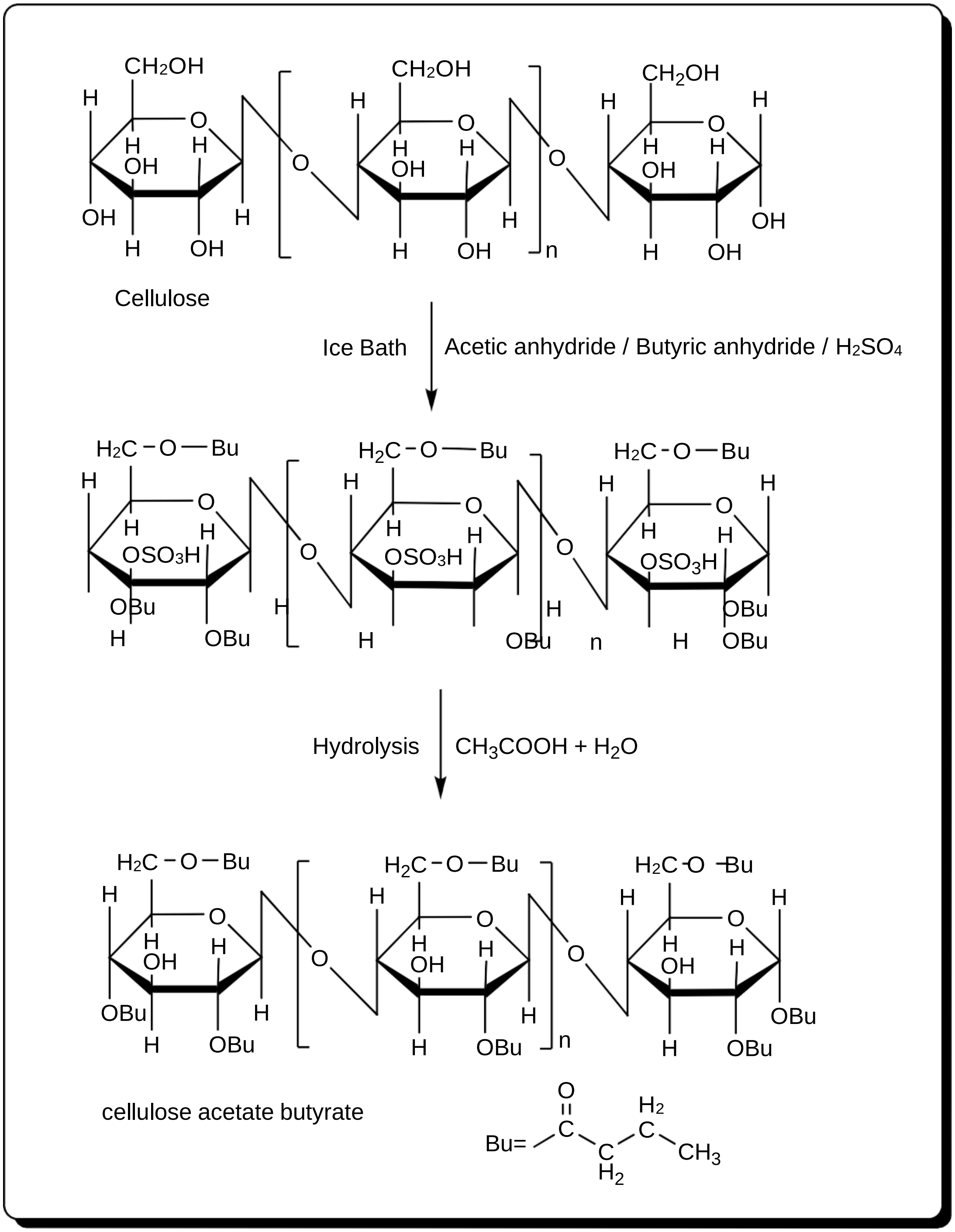


Figure:1.12.1 Representation of Cellulose Acetate Butyrate Preparationfrom Cellulose.

Zeolite

Zeolite are crystalline, microporous, hydrated aluminosilicates that are built from an infinitely extending three dimensional network of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$tetrahedra linked to each other by the sharing of oxygen atom. Generally, their structure can be considered as inorganic polymer built from tetrahedral TO_4 units where T is Si^{+4} or Al^{3+}ion. Each O atom is shared between two T atoms. The structure formula of zeolite is based on the crystallographic unit cell. $M_{x/n}[(AlO_2)_x(SiO_2)_y].wH_2O$, Where M is an alkali, or alkaline earth cation, n is the valence of the cation ,w is the number of water molecules per unit, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has valence of 1 to 5, for the silica zeolite y/x can be ranging from10 to100. Zeolite open-structure frame work consists of many channels and /or interconnected voids of discrete size(in the range 0.3 - $20A^0$) which are occupied by cation and water. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation. The cations can reversibly be exchanged for other ions possessing the same sign charge when water passed through channels and voids.This replacement results in the narrowing of the pore diameter of the zeolite channels[112-116]. The most important property of zeolites for these application is their well-defined pore diameter lying in the same range as that of common chemical molecules. This gives rise to shape selectivity effects in adsorption and heterogeneous catalysis with zeolites. Molecules of adsorptives as well as reactants, products or transition states of chemical reactions can be selectivity excluded from access to and / or egress from the zeolite pore due to the local constraints within the zeolite pore systems. These shape selectivity effects are the basis of the molecular sieve properties of zeolities [117-120].

Dowex-50

An ion exchange resin or ion–exchange polymer is an insoluble matrix (or support structure) normally in the form of small (0.5-1mm diameter) beads, usually white or yellowish, fabricated from an organic polymer substrate. The beads are typically porous, providing a high surface area.

The trapping of ions occurs with concomitant releasing of other ions, thus the process is called ion-exchange. Ion–exchange resins are widely used in different separations, purifications, and decontamination processes. The most common examples are water softening and water purification. In many cases ion-exchange resins were introduced in such processes as a more flexible resins alternative to the use of natural or artificial zeolites. Also, Ion exchange resins are highly effective in the biodiesel filtration process. Most of the present ion-exchange resins are addition copolymers prepared from vinyl monomers. These polymers have a higher chemical and thermal stability than the condensation polymers. Also, addition polymerization has the advantage that the degree of cross linking and the particle size of the resins are more readily adjusted. Dowex-50 is identified as a cross linked polystyrines with sulphonic acidgroups. Divinylbenzene is used as the cross linking agent. The Sulphonic acid group is responsible for its cation selectivity [121].

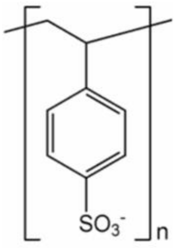


Figure 1.13 The structure of Dowex-50 Resin.

Dowex-50 is a type of ion-exchange resins, called a strongly acidic cation exchanger, used for ion-exchange chromatography. It is useful for swapping a metal cation for a proton (e.g. Na^+ for H^+) or one metal cation for another (eg. K^+ for Na^+). This can be an important way for purifying aminoacids, Carboxylate salts or removing unwanted metal ions from water solution.

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