Electrochemical Characterization of Cellulose Acetate Butyrate-PRMUTIT Composite Membrane in Aqueous UNI-UNI VALENT Electrolyte Solutions- A Review

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Abstract
Co-mixed cellulose acetate butyrate and permutit in a definite composition was prepared and coded as MRS-2.The membrane potential was measured with uni-uni valent electrolyte, NaCl solutions using saturated calomel electrodes (SCEs).The effective fixed charge density of the membrane was determined by TMS method and it showed dependence on the porosity, charge on the membrane matrix, charge and size of permeating ions. Other important electrochemical parameters were calculated. Conductance-time data were generated for the kinetic study of the permeating ions in terms of membrane permeability, flow and flux parameters. Donnan membrane equilibrium condition was examined. Membrane adsorbability showed concave dependence with external electrolyte solution and convex type dependence was showed by swelling and conductance parameters. This membrane had no characteristic of anomalous osmosis, indicates that there is no water flooding will take place during membrane operation.
Keywords: *Membrane potential; Effective fixed charge density; Donnan membrane equilibrium;co-mixed membrane; Dissociation equilibrium; Solvent uptake.*

I.   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.

1.2. 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 all membranes 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.

1.3. Classification of Membranes:

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

1.3.1. 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

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of passive transport. In this active mode of transport, the membrane is no more passive barrier but functions as a dynamic organ [5-11].

1.3.2. 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 through the membrane. The energy for permeation is supplied by the environment [12]. Broadly artificial membranes are of two types:

1.3.2.1. Uncharged or Slightly Charged:
The uncharged membranes can be either solid e.g., paraffin, quartz, or liquid e.g., benzene or silicon oil.

1.3.2.2. 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 of
ion exchange materials embedded in an inert polymeric substrate.
(ii)   Homogeneous Membrane:
Term homogeneous as applied to ion exchange membrane refers to the absence
of the structure on the colloidal level.

1.4. 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 50A0 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 10A0 up to 50A0. 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 10A0. 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 which is 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 according
to their average width has been proposed by Dubinin[16].

1.4.1.1. 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.
1.4.1.2. Mesopores:
Mesopores are known as intermediate or transition pore having widths between 2 and 50nm.

1.4.1.3. 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:

1.4.1.4. Ultramicropores:

Membrane with ultramicropores possesses diameters smaller than the adsorptive molecular diameters (about0.6nm) [18].

1.5. 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].

1.5.1. 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.

1.5.2. 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 rate of passive diffusion can be altered by membrane charge and solvent drag.

1.5.3. 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].

1.5.4. 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.

1.6. 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.

II.   Conclusions

In a separation process, it is a basic requirement for the membrane to have uniform distribution of water through it. When such membrane comes in to contact with electrolyte solution, sorption takes place in the membrane texture. This sorption depends on fixed charge groups. These charge

groups are responsible for the performance of the membrane.

1. Undissociated salt concentration in the membrane phase increases with external electrolyte.

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