ELECTROCHEMICAL CHARACTERIZATION OF CELLULOSE ACETATE BUTYRATE-PRMUTIT COMPOSITE MEMBRANE IN AQUEOUS UNI-UNI VALENT ELECTROLYTE SOLUTIONS

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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.

Introduction

Membrane processes are currently being studied for numerous applications of practical interest (Singh K and Tiwari A K 1999; Tiwari AK and Ahmad S 2006). Co-mixing is effective methods for modification in membrane activity (Tiwari AK and Ahmad S 2006). To examine it, cellulose acetate butyrate (CAB) and permutit were mixed and their characteristic properties were determined on the basis of membrane potential and conductance-time studies. Membrane potential is determined by the combination of the properties of ions and of the membrane. There is, therefore, a possibility that the properties of ions can be reflected in the membrane potential more effectively by modifying the membrane properties. The transport number, reflecting the membrane selectivity, is determined by the product of the total ionic uptake and the average mobility, which contains the dissociation equilibria (Asaka K 1990; Buchanan, C.M., Edgar, K.J., Wilson, A.K.1991; Kimura Y Lim H J Iijima T I 1984). It, follows that a membrane may be selectively permeable to ions either by preferential uptake or as a consequence of high mobility. The mobility ratio and the effective fixed charge density can be estimated from the membrane potential. These parameters are associated with the interactions between ions and membrane texture which are the key to understanding the salt separation mechanism (Bontha J. R. and Pintauro P.N.1994; Lobo V M M et al 1998; Mills, R.1965).

Conductance-time study furnishes information regarding the ion dynamics through the membrane along with ionic adsorption on to the membrane/solution interface (Lobo, V M M et al 1994; Magnar O et al 1992; Mills, R.1965). These data have been used to estimate permeability, flow and flux parameters for the membrane/solution system. Permeability and flow parameters concavely depend on external electrolyte concentration but flux depends differently.

Experimental

Chemicals and Membrane Materials

Cellulose acetate butyrate, CAB (John Baker Inc., Colrado, USA) and permutit (CDH, India) were used for membrane formation. Sodium chloride (AR Grade, S.D.Fine Chemicals, India) and acetone (Qualigens Fine Chemicals, India) were used as received.

Membrane preparation

Cellulose acetate butyrate, CAB, and permutit were mixed with 40mL acetone in proportion given below for the membrane formation. MRS-2 membrane contains 4g CAB and 1g Permutit. To ensure uniformity of composition, the mixture was stirred for over 4h over a magnetic stirrer. The
slurry thus obtained was spread on a clean dried glass plate using a knife to form a desired thick layer. The film was allowed to dry for 15-20 min at laboratory temperature. It was then removed from the glass plate by submerging it in a distilled water bath. Membrane pieces of the required dimensions are cut from the film and fixed in the experimental setup.

**Membrane Potential Measurement**

The membrane potential was measured as a function of the salt concentration for the system mentioned elsewhere (Singh K, Tiwari A K 1999; Magnar O et al 1992). The potential / conductance-time measuring cell is illustrated in Figure 1 and was made of glass. Each compartment of the system was filled with aqueous electrolyte solution of different concentrations. The membrane area was cm². Characteristic properties of the membrane are summarised in Table 1.

![Figure 1: Schematic presentation of membrane system from which conductance-time and membrane potential data was acquired](image)

**Table 1: Characteristic properties of the membrane used during study**

| Characteristic properties of the membrane used | R (%) | Qw (wt%) | L (cm) |
|-----------------------------------------------|-------|----------|--------|
|                                               | 56.25 | 45.40    | 0.00212|

Abbreviations used: R=Rejection of a salt; Qw = Water content; l = Thickness of swollen membrane.

**Water Content**

The membrane was conditioned by immersing it for 24h in water at 25°C, after which it was removed from the water, blotted with a filter paper to remove any excess water, weighed; its weight was recorded as ‘wet weight’. The membrane was then dried for 24h in desiccators and weighed; its weight was recorded as ‘dry weight’. The water content was calculated as:

\[ Q_w = \frac{(\text{wet weight} - \text{dry weight})}{\text{dry weight}} \]

**Results and Discussion**

Fig.2 shows the concentration dependence of the membrane potential across the CAB-Permutit (zeolite) membrane. Membrane potential decreases with the increase in external sodium chloride mean concentration.

![Figure 2: Dependence of membrane potential on the mean concentration of external electrolyte.](image)

The concentration dependence of the membrane potentials shows the characteristics of positively charged membrane. According to the TMS theory (Okita, M (1995); Piedade, A.P.et al.1995), the membrane potential, \( E_m \) consists of the difference of the two Donnan potentials at the interfaces between membrane and solutions, \( E_{Don} \) and diffusion potential inside the membrane, \( E_d \) being obtained by the following equation:

\[ E_m = E_{Don} + E_d \]

Membrane potential in a more general and convenient form can be expressed as

\[ E_m = \frac{RT}{F} \left( \frac{c_m^{m}}{Z_m} - \frac{c_m^{t}}{Z_t} \right) \ln \left( \frac{c_1}{c_2} \right) \]

Where \( \frac{c_m^{m}}{Z_m} \) and \( \frac{c_m^{t}}{Z_t} \) denote ratio of membrane phase anion transport number to anion valency and membrane phase cation transport number to cation valency respectively. \( C_1 \) and \( C_2 \) denote concentration of external electrolyte bathing the membrane on either sides.

Transport number in the membrane phase is defined in different way in comparison to the transport number in the solution phase. Both can be expressed as

\[ t_m^{m} = \frac{c_m^{m}U_m^{m}}{\sum c_i^{m}U_i^{m}} \quad \text{and} \quad t_t^{m} = \frac{U_t^{m}}{\sum U_i^{m}} \]

Both phases obey electroneutrality condition. Membrane phase consists of counter-ion, co-ion and effective fixed charge density but in the solution phase there is no existence of effective fixed charge density and only cation and anion play their respective role. Membrane phase nomenclature is not applicable to the solution phase.
In present system \( t_m^m > t_m^n \) and \( t_m^n \) value decreases with the increase in mean concentration of NaCl. \( t_m^n \) follows the opposite trend of variation. When both transporting ions possess approximately equal transport number value leads to zero membrane potential value. But membrane selectivity retains its character at this value also (Tiwari AK Ahmad S 2006; Theresa M. et al 2013). Variation of membrane potential with mean concentration even when concentration ratio was kept constant indicated a change in the membrane characteristics as a result of which counter-ion was affected. Membrane potential \( E_m \) can be expressed in terms of mean concentration \( C_e \) as \( E_{m}=A+B.Ce(M) \) where A and B are adjusting parameters, and A>0 and B<0. This variation may be attributed to (i) increased adsorbability of ion (ii) reduction in swelling of the membrane matrix with increase in concentration, or (iii) increase in membrane conductance at higher mean concentration. In present case ionic adsorbability onto the membrane-solution interface increases with the electrolyte concentration. Membrane system adsorbability is found of concave nature. Reduction in swelling of the membrane matrix in the electrolyte solution is found of concave nature.

With the increase of electrolyte concentration, membrane conductance increases and giving rise convex type curve. Increased membrane conductance will also contribute towards lowering of membrane potential. It appears that factors (i) and (ii) together predominates, since a substantial decrease in membrane potential with increase in mean concentration has been observed.

The conductance of the membrane denotes the ability of a membrane to conduct charges through the selectivity is the ability of a membrane to separations. There is no strict relationship between the synthesis parameters and properties. Some of them are even counteracting. Generally speaking, a high value of conductivity does not favour a high selectivity (Tiwari AK 2013; Xuan T L 2008). In our case membrane selectivity concavely depends on the membrane conductance as shown in Fig. 3.

The explanation of the variation in membrane conductance has been explained elsewhere (Tiwari AK Ahmad S 2006) in terms of two equilibrium constants, (i) \( K_d^S=f(C_m^m, C_m^n \text{ and } C_s^m) \) (ii) \( K_d^s=f(C_m^s, φ_{XT} \text{ and } X_T) \) terms used herein have usual significance. The dependence of the ratio \( K_d^S/K_d^s \) on NaCl concentration is shown in Fig. 4:

![Fig 4: Dependence of the ratio, \([ K_d^S / K_d^s \)]\ on the mean concentration of external electrolyte.](image)

The fixed groups, counter-ions and co-ions, are related by the following Donnan membrane equilibrium, which holds between solutions inside and out-side of the membrane (Tiwari A.K. and Ahmad S 2006; Tiwari A.K 2013)

\[
(y^m_± - C) = y^m_± C_m^m y^m_± C_m^n + y^m_± X_T)
\]  

where \( y^m_± \) is the mean activity coefficient of the electrolyte in solution, \( y^m_± \) is that in the membrane and \( y^m_± \) is the activity coefficient of counter-ions in the membrane phase.

Here \( φ = \frac{y^m_±}{y^m_±} \), \( φ \) increases with the increase of the external electrolyte concentration. After introducing \( φ \), in the above equation, it becomes

\[
(y^m_± - C)^2 = (y^m_±)^2 = C_m^m y^m_± C_m^n + φX_T)
\]  

Dividing both sides of the above by \( C_m^m + φX_T \), one can obtain

\[
\frac{C_m^m + φ^2X_T}{C_m^m + X_T} = \frac{[(y^m_±)^2/(C_m^m + X_T)]}{(y^m_±)^2/(C_m^m + X_T)} \]

The above expression is dependent of an external electrolyte, NaCl. There is possibility that \( C_m^m + φ^2X_T \approx (C_m^m + X_T) \) when NaCl concentration becomes equal to 5.124 mM. Under such condition following equality can be obtained

\[
\frac{C_m^m + φ^2X_T}{C_m^m + X_T} = \frac{C_m^m}{C_m^m + X_T}\]

In the above relation, \( y^m_± \) and \( y^m_± \), both are the function of external electrolyte and their values decreases with the increase of external electrolyte. It indicates solute uptake by the membrane increases with the increase external salt concentration. Donnan membrane equilibrium (i) affects

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salt concentration and (ii) vary the ratio of co-ion and counter-ions within the membrane. It has been estimated that \( C_T < X_T \) and \( K_d^a > K_d^i \) where \( C_T \) and \( X_T \) denote the total concentrations of salt and fixed groups in the membrane phase. It is obvious that the variation in the \( \phi_{XT} \) value must affect the counter –ion and co-ion concentrations in the membrane phase, along with \( K_{ds} \) and \( K_{df} \). The necessary condition to observe Donnan exclusion is also examined for the system which is shown in Fig. 5 below wherein \( r_1 \) denotes ratio of co-ion to counter-ion concentrations and \( r_2 \) denotes ratio of \([K_d^a \cdot C_T]/[K_d^i \cdot X_T]\):

\[
\text{Fig 5: Dependence of the ratio,} \frac{r_1}{r_2}, \text{ on the mean concentration of external electrolyte.}
\]

The system under consideration follows the criteria of efficient salt rejection (Valente A J M. et al 2000; Tiwari AK 2013; Tiwari AK and Ahmad S 2006)

\[
\frac{C_w^m}{C_w} \gg \frac{C_a^m}{C_a} \text{ or } \left( \frac{C_w^m}{C_w} - \frac{C_a^m}{C_a} \right) = H
\]

where \( H \) is extent of hydrophilicity of the membrane which depends on solute-solvent coupling, sieve action with hindrance factor of the membrane. The collective effect of these parameters is shown in Fig. 6. Membrane hydrophobicity shows concave dependence on the external electrolyte concentration. It means that membrane hydrophobicity increases with the increase of external electrolyte concentration.

\[
\text{Fig 6: Dependence of membrane hydrophobicity, } H, \text{ on the mean concentration of external electrolyte.}
\]

For the conductance-time study (Okita, M 1995), membrane is arranged in such a way that it separates source and receiving compartments. Source compartment contains known electrolyte concentration and receiving compartment has distilled water of known volume is connected with conductivity bridge. As time passes, conductance of the receiving phase increases which imparts information regarding the membrane permeability, \( P(\text{cm/s}); \text{flow, } F(\text{cm}^3/\text{s}) \) and flux, \( J_s(\text{mole.cm}^2.\text{s}^{-1}). \) The representative plot of conductance vs time is mentioned in Fig. 7 and dependence of \( P, F \) and \( J_s \) on the concentration of external electrolyte is shown in Fig. 7, 8 & 9. The conductance-time data imparts the information regarding the variation of concentration difference between the source and receiving compartments with time. Percentage of reduction in concentration difference between the two compartments estimated is 34.41%.

\[
\text{Fig 7: A representative plot of membrane-solution conductance (receiving compartment) versus time.}
\]

\[
\text{Fig 8: Dependence of membrane permeability, } P \text{ and flow, } F \text{ on the mean concentration of external electrolyte.}
\]

\[
\text{Fig 9: Dependence of membrane flux, } J_s, \text{ on the mean concentration of external electrolyte.}
\]
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.
2. Effective fixed charge density, $\varphi_X$, of the membrane increases with external electrolyte concentration.
3. $K_d^s$ and $K_d^f$ both increase with increased NaCl concentration.
4. Membrane hydrophobicity increases with increase of electrolyte concentration.
5. Since moderate hydrophobicity is the dominating characteristic of the current membrane, and expected that there will be no water flooding during the membrane operation.

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