

Effect of hydrotrope on the electrochemical behavior of Dowex-50 membrane in aqueous solution of uni–univalent electrolyte

Rajat Kumar¹ and Rajesh Kumar²

1. Associate Professor, DAV –PG College Kanpur
2. Associate Professor, PEC Kanpur

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, Membrane conductance, Solute rejection, Transport number, Peclet number

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). Comixing 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., Colorado, 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

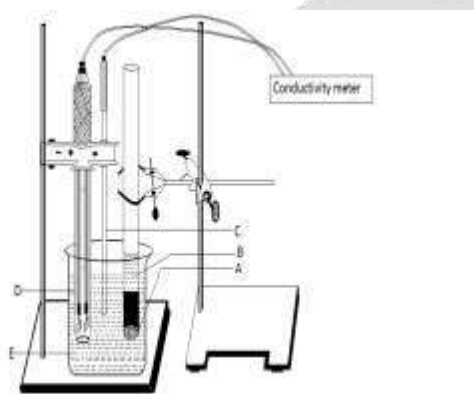


Fig 1: Schematic presentation of membrane system from which conductance-time and membrane potential data was acquired

[A= Cellulose acetate Butyrate membrane fixed with glass joint; B= Electrolyte Solution (Source); C= Automatic Temperature Compensation; D= Conductivity cell; E= Distilled Water (Sink)]

Table 1: Characteristic properties of the membrane used during study

Characteristic properties of the membrane used		
R (%)	Q _w (wt%)	L (cm)
56.15	45.10	0.00210

Abbreviations used: R=Rejection of a salt; Q_w = 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 $Q_w = (\text{wet weight} - \text{dry weight}) / \text{dry weight}$

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.

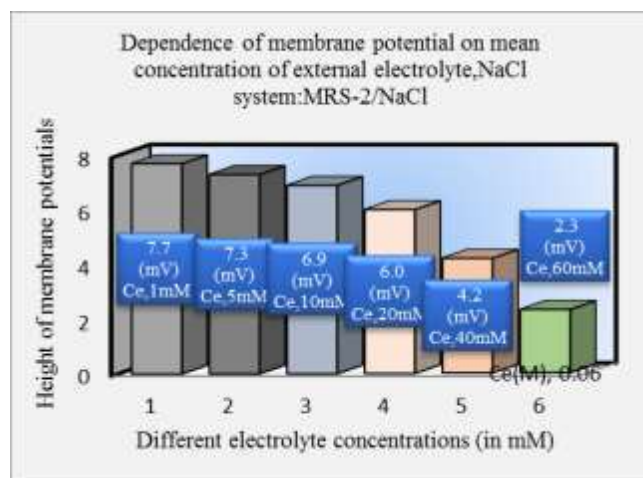


Fig 2: Dependence of membrane potential on the mean concentration of external electrolyte.

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

$$E_m = E_{Don} + E_d \quad [1]$$

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

$$E_m = R.T/F (t_-^m/z_- - t_+^m/z_+) \ln (c_1/c_2) \quad [2]$$

Where $(t_-^m/z_- - t_+^m/z_+) \ln (c_1/c_2)$ denote ratio of membrane phase anion transport number to anion valence 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 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 $t_-^m > t_+^m$ and t_-^m value decreases with the increase in mean concentration of NaCl. t_+^m 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 counterion was affected. Membrane potential E_m can be expressed in terms of mean concentration C_e as $E_m = A + B.C_e(M)$ 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 convex 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.

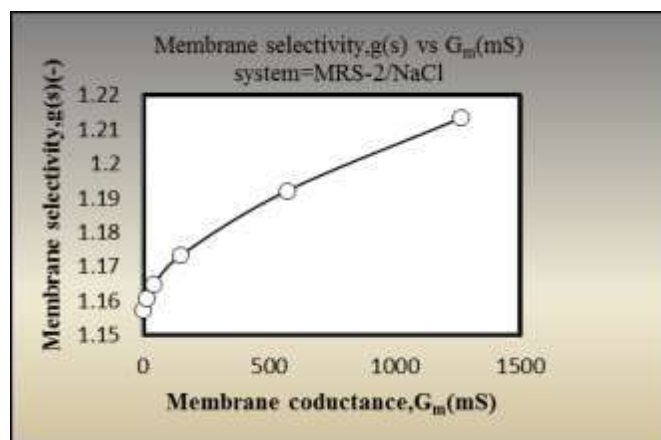


Fig 3: Dependence of membrane selectivity, g(s) on membrane conductance, G_m .

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.

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