Variation of Polystyrene Concentration and its Effects on Heterogeneous Membrane Behaviour

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THE variation in binder concentration and its effects on the membrane properties like swelling, porosity membrane conductance and membrane potential of aluminium hydroxide and zirconium hydroxide gels have been studied. The values of swelling, porosity and membrane conductance decrease with the increase of binder concentration in the membranes. Swelling and porosity in these membranes almost vanish when polystyrene (binder) is more than 50%. The membrane conductance is a function of particular ionic form and shows the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Ba^{++} < Sr^{++} < Ca^{++} < Mg^{++}$. For these membranes the order of porosity and membrane conductance is the same as that of swelling i. e. aluminium hydroxide > zirconium hydroxide. It is also investigated that there is no appreciable effect of ths π electrons of the binder as electro-chemical performance of the exchangers in moderate concentration.

A necessary requirement for an heterogeneous membrane is that the ion-exchanger particles should remain in contact with one another rather than be separated by the binder and it should have a good mechanical stability. The concentration of the binder has a great deal to do with the electrochemical behaviour of the membrane. Our present communication represents the effect of polystyrene as a binder on the properties of aluminium hydroxide and zirconium hydroxide membranes.

EXPERIMENTAL

Preparation of Membranes : Polystyrene supported membranes (0.1 cm to 1.5 cm thickness) of aluminium hydroxide and zirconium hydroxide gels with different amount of polystyrene as binder (20 to 50%) were prepared by usual methods[1-3] employed by Malik et al.

Swelling and Porosity : The membranes of known thickness with different gel to binder ratio were abraded with fine glass paper and were immersed in 1-2 M NaCl for about 24 hours. The difference between the thickness of the dry membrane and that of the swollen one, measured after wiping out the adhering electrolyte with a blotting paper was taken as the value of swelling. The wiped membrane was weighed in a stoppered bottle, dried at 110°C, in a vacuum desicator and was again weighed. The difference between the two weighings divided by the weight of the wet membrane was taken as the water content and the porosity E (the volume of water incorporated in cavities of a unit membrane volume) was calculated by formula[4]

$$\epsilon = \frac{\text{Water content}}{A \times L \times d_w}$$

where A and L are the area and thickness of the membrane respectively while d_w is density of water.

Membrane conductance : Membrane conductance was measured by the method recommended by Lakshminarayanaiah[5]. The membrane in the required cationic form was cemented between the two half cells with an adhesive (araldite). It was then equilibrated by filling the half cell with 0.05 M metal chloride solution. The solution was then replaced with mercury which had already been equilibrated with the same metal chloride solution. The conductance was measured by connecting the platinum electrodes in the two limbs of the cell to the conductivity bridge working at 3 kc/s.

Membrane Potential : Michealis[6] method was employed to determine the membrane potential using the cell

SCE / Solution (C_1)// Membrane//Solution(C_2)/SCE

The same electrolyte solution was taken on both sides and the dilute side always remained positive.

RESULTS AND DISCUSSION

An heterogeneous membrane swells when it is immersed in water or an electrolyte solution. The solution penetrates into the membrane structure occupying the interstices which are already present or which develop as a result of the difference

between the volume of the membrane material and that of the binder. The interstices act as a film and diffusion of the different electrolytes become possible also by film diffusion beside the normal diffusion through the membrane material. In some cases, swelling results in the permeation of otherwise impermeable species. The increase in the thickness (extent of swelling) is found to depend upon the amount of the binder present in the membrane (Fig. 1). When the concentration of binder is increased the amount of water incorporated in the membrane structure decreases. This suggests that in membranes, containing a higher proportion of polystyrene, complete swelling of the respective gel is not possible either as a results of mechanical restraint imposed by the binder or because some of the gel is inaccessible to water. Higher proportion of the binder causes a decrease in the amount of water incorporated in the cavities of the membrane ; the porosity also decreases with the increase of binder concentration (Fig. 2). The porosity almost vanishes when the binder concentration is more than 50 per cent. The membranes with amount of binder less than 20 per cent, were found unsuitable because they started dispersing due to large swelling.

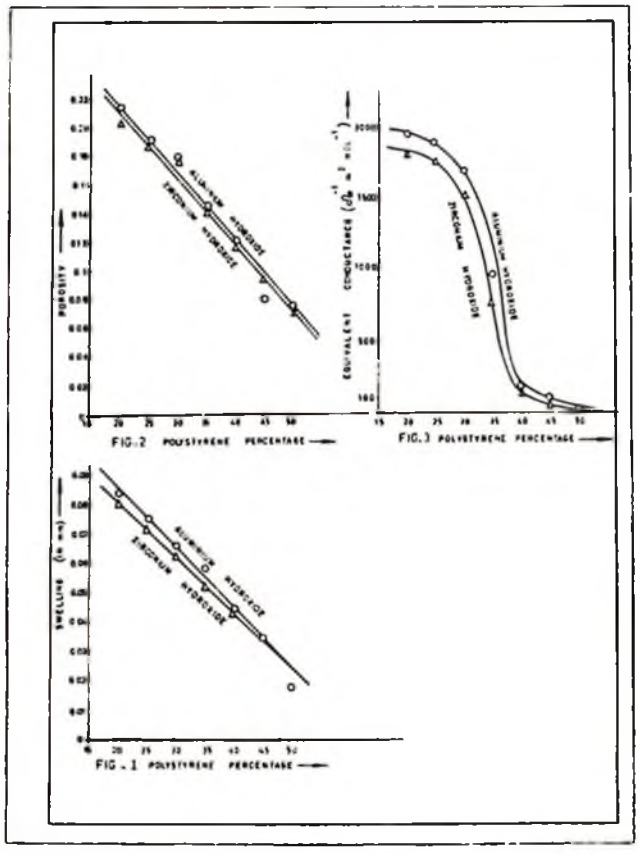


Fig. 1. Variation in swelling with polystyrene concentration (Sodium form)

Fig. 2. Variation in porosity with polystyrene concentration (Sodium form)

Fig. 3. Variation in equivalent conductance of the membranes with polystyrene concentration (Sodium) form

Membranes of different exchangers swell to different extent. The swelling in case of aluminium hydroxide is greater than zirconium hydroxide and the order is the same as that of porosity. The low values of swelling and porosity in zirconium hydroxide gel suggests that in this case the diffusion through the membrane would almost wholly take place through exchange sites.

The equivalent conductance of the membranes in different cationic forms as well as the effect of various factors like percentage of binder, time taken to attain the maximum value of conductance etc show that the value of membrane conductance charges initially very slowly with time but becomes constant after 10 to 15 mts. and after that it remains constant for sufficiently long time. It is only after 4 to 5 hrs. when it shows a slight change. The results show a negligible polarisation on the membrane faces.

The results of conductivity data are given in Tables 1-2. The order of membrane conductance for alkali metal cations is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (the normal sequence observed in their aqueous solutions) and $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$ for alkaline earth metal cations. Lakshminarayanaiah[5], George[7], Gregor[8] etc have also observed a similar behaviour. The lower conductance for bi-valent cations as compared to monovalent cations show that as the charge on the counter ion is increased, the membrane conductance is increased. It is due to the ion association of the diffusing ions with the membrane exchange sites. The conductance values in case of aluminium hydroxide are greater than zirconium hydroxide membrane. It is suggested that when the membrane is equilibrated with 0.05 N metal chloride solutions, the interstices which are already present or which are formed by the swelling of the gel particles, retain the electrolyte solution. The absorbed solution alongwith the counter ions carries the charge. The present of these interstices may facilitate the passage of ions through the membrane from one particle to the other. This has been also suggested by Gregor[9] that a thin film of water between the gel particle and binder may also provide

TABLE I

Effect of polystyrene content on equivalent conductance of aluminium hydroxide membrane in different cationic from (in $\Omega^{-1}m^{2}mol^{-1}$)

%age of binder	Li^+	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Sr^{2+}	Ca^{2+}	Mg^{2+}
20	1890	1950	2000	2300	2900	280	350	410	590
25	1750	1890	1940	2100	2700	240	310	380	570
30	1500	1590	1680	1840	2520	220	280	360	550
35	820	940	1480	1760	2400	210	260	350	520
40	125	150	1310	1700	2300	200	250	330	510
45	108	123	1290	1680	2250	195	230	320	495

TABLE II

Effect of polystyrene content on equivalent conductance of zirconium hydroxide membrane in different cationic form (in $\Omega^{-1}m^{2}$ mol^{-1})

%age of binder	Li^+	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Sr^{2+}	Ca^{2+}	Mg^{2+}
20	1690	1770	1880	2200	2680	250	300	380	560
25	1500	1750	1780	2000	2400	230	280	360	540
30	1300	1500	1650	1780	2350	210	250	340	520
35	1220	750	1450	1700	2220	200	240	330	510
40	1150	300	1300	1650	2150	195	235	325	505
45	1100	200	1250	1600	2100	190	220	310	495

a pathway through the membrane for ions and water. Also the extent of swelling (interstices formed) in case of aluminium hydroxide is very large as compared to zirconium hydroxide membrane. This would result in large electrolyte absorption and and gives rise to higher conductance values. Similarly, the conductance in case of alkaline earth cations (Ba^{2+} ∠Sr^{2+} ∠Ca^{2+} ∠Mg^{2+}) may be explained.

The variation in binder concentration shows that the membrane conductance decreases with the increase of binder content (Fig. 3). With increase of the amount of binder, a decrease in interstial volume takes place which gives rise to low value of conductance. Therefore, it may be concluded that the conductance developed in the membrane phase is due to the combined effect of the counter ions and absorbed electrolytes.

Membrane potentials (with different amount of binder) in varying concentration of electrolyte solutions were measured to study the role of additional charge developed by the π electrons. Membranes with less than 20% binder are mechanically unstable, therefore, the effect of low concentration of polystyrene on membrane behaviour could not be observed. A similar situation is encountred with the membranes having more than 30% polystyrene due to the separation of exchanger particles by the polystyrene. However, no appreciable effect of the binder concentration on membrane potential is observed in the range of 20% to 30%

of the binder (Tables 3-4). It is, therefore, concluded that the π electrons of the binder do not effect the electrochemical performance of the exchanger, atleast in this concentration range. The possibility of this factor influencing the membrane behaviour in very dilute solutions, cannot, however be completely ruled out.

TABLE III

Potentials of Aluminium hydroxide membrane having varying concentration of polystyrene

Inside Solution conc. of KCl	Observed potential in mV with polystyrene		
Outside solution conc. of KCl	20%	25%	30%
1.0M/0.1M	21.2	21.3	21.5
0.5/0.05	25.3	25.2	25.3
0.2/0.02	35.9	35.8	40.0
0.1/0.01	36.6	36.4	36.6
0.05/0.005	41.4	41.4	41.4
0.02/0.002	44.0	44.1	44.1
0.01/0.001	45.3	45.2	45.3
0.005/0.0005	47.6	47.6	47.8

TABLE IV

Potentials of Zicronium hydroxide membrane having varying concentration of polystyrene

Inside solution conc. of KCl	Observed membrane potential in mV with polystyrene		
Outside solution conc. of KCl	20%	25%	30%
0.02M/0.002M	58.3	58.5	58.3
0.016/0.002	52.5	52.5	52.4
0.014/0.002	49.3	49.2	49.1
0.012/0.002	45.6	45.8	45.8
0.010/0.002	41.0	41.0	41.1
0.008/0.002	34.2	34.2	34.0
0.006/0.002	27.9	27.8	27.8
0.004/0.002	17.6	17.8	17.8

Acknowledgement

Authors are thankful to Principal B. K. Chanana for providing facilities and to Shri T. R. Chadha for constant encouragement.

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