FUNCTIONAL PROPERTIES OF ZIRCONIUM HYDROXIDE MEMBRANE

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Functional properties like swelling, porosity, electrolytic uptake and membrane conductance of polystyrene-supported zirconium hydroxide membrane have been studied. The results show that the extent of swelling, porosity and electrolytic absorption depend upon the amount of the binder present in the membrane. The conductance of the membrane is a function of the particular ionic form and shows the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Ba^{++} < Ca^{++}$.

Membranes are well known for their importance as models for physicochemical studies and the membrane phenomenon has been extensively studied by several workers[1-4]. In recent years Malik and co-workers[5-10] have done a lot of work on permeability and potential of the membranes prepared from inorganic gels. However, no attempt has been made to study the functional properties of the membranes. As a prelude to a systematic study of the electrochemical performance of the inorganic membranes, the electrolytic uptake, porosity, swelling and conductance of zirconium hydroxide membrane in the presence of different amounts of the binder were undertaken. In order to discuss the role of various cations on the exchange behaviour of the membrane, studies on conductance of several cationic forms of the membrane were also taken up.

EXPERIMENTAL METHOD

Preparation of Membranes

Zirconium hydroxide gel was prepared by mixing 0.1 M zirconyl oxychloride (A.R.) solution with 20% ammonia solution. A large number of membranes with varying percentage of polystyrene (20 to 45%) were prepared by heating zirconium hydroxide gel and polystyrene powder in a specimen mount press at 110–125°C under pressure[10].

Swelling, Water content and porosity

Membranes with different gel-to-binder ratio were abraded with fine glass-paper, weighed and then immersed in 1 M NaCl for about 36 hours. The membranes were washed several times with deionised water, adhering liquid was wiped out with blotting paper and then weighed. Later on, membranes were dried at 60°C and weight of the membranes dried to a constant value was recorded. The difference between the two weighings divided by the weight of wet membrane was taken as water content, and the difference between the thickness of the dry membrane and that of the swollen one was taken as the measure of swelling. The porosity was calculated by the formula[11] :

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

where A is area and L is the thickness of membrane, and d_w is the density of water.

Measurement of Membrane conductance

The method recommended by Lakshminarayanaiah[12] was used to measure the conductance of the membranes in different cationic forms. The membrane in requisite cationic form was cemented between the two half cells (pyrex) with the help of an adhesive (Araldite). It was then equilibrated by filling the half cells with 0.05 M metal chloride solution. The solution was then replaced with mercury which had been previously equilibrated with the same metal chloride solution (0.05M). The conductance was measured by connecting the platinum electrode in the two limbs of the cell to the conductivity bridge at 3 KC/S. The effect of various factors such as amount of binder, time taken to attain the maximum value of conductance etc. was also investigated.

Electrolytic absorption

Membranes with different amount of binder were placed in different conical flasks and varying amounts of the various electrolytes were added in each set of experiments. The total volume of the liquid was made up to 100 ml. After keeping the flasks to stand for about 36 hours in a thermostat maintained at 35±1°C, the samples of the supernatant liquids were pipetted out and estimated for electrolytes under study. The absorption of electrolyte was taken as the difference between the initial concentration and equilibrium concentration.

Results and Discussions

When a dry homogeneous membrane is immersed in water or electrolyte solution, swelling takes place. The solution penetrates into the membrane structure and occupies the interstices which are already present or which develop as a result of difference between the volume of membrane material and that of binder. The

interstices act as a film and diffusion of different electrolytes become possible also by film diffusion besides the normal diffusion through the membrane material. In some cases swelling results in the permeation of the otherwise impermeable species. The increase in thickness (extent of swelling) is found to depend upon the amount of binder present in the membrane (Table-1).

Table No. 1 Effect of Binder on swelling, water content, porosity, specific conductance and electrolytic absorption values of zirconium hydroxide membrane (Sodium form)

% age binder	Swelling Cms.	Water content per g.wet membrane	Porosity per g wet membrane	Specific conductance, mhos cms.	Conc of Na^+ absorbed per g.wet membrane
20	0.0080	0.1560	0.2044	0.0885	0.0340
25	0.0073	0.1544	0.1890	0.0875	0.0216
30	0.0063	0.1298	0.1750	0.0870	0.0160
35	0.0057	0.1108	0.1430	0.0875	0.0090
40	0.0050	0.0757	0.1175	0.0015	0.0075
45	0.0040	0.0740	0.0840	0.0275×10^{-2}	0.0067

Water content data shows that the amount of water incorporated differs from membrane to membrane. It was found to vary with the percentage of binder used (Table-1). When the percentage of the binder is increased, the amount of water incorporated in the membrane structure goes on decreasing. This suggests that in the membrane containing a higher proportion of polystyrene, complete swelling of respective gel is not attained either as a result of mechanical restraint imposed by the binder or because some of the gel is inaccessible to water. Hence, when the amount of binder is increased, the role of binder is enhanced, which causes a decrease in porosity.

It was observed that the value of membrane conductance changes initially very slowly with time, but becomes constant after 10 to 15 minutes, and remains constant for sufficiently long time. It is only after 4 to 5 hours that it shows a slight polarisation on the membrane phase. The sequence of membrane conductance for various cations are : (alkali metals) $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (for monovalent ions), and $Ba^{++} < Ca^{++}$ (alkaline earth cations). The lower values of conductance for bivalent cations as compared to monovalent cations show that as the charge on the counter ion is increased the membrane conductance gets decreased. This may probably be due to increased ion association of the diffusing ions at membrane exchange sites.

As these membranes are equilibrated with 0.05 M metal chlorlde solution, the interstices which were already present or formed by the swelling of the gel particles retain the electrolyte solution which consequently facilitates the passage of the ions through the membranes from one particle to another. It has been suggested[13] that a thin film of water between the gel particles and binder may also provide a pathway through the membrane for ions and water.

Among the bivalent ions the conductance of Ba^{++} is lower than that of Ca^{++}. According to Mullin[14] the hydration of the pores of the material themselves may provide a favourable water environment for particular ion so that it slips into the pore away from their water molecules with which it was already associated before entering the membrane phase. This could result in the selection of a particular size with discrimination against both smaller and larger hydrated ions. It appears that the fraction of the ions losing water of hydration on coming in contact with the pore material is higher in case of Ca^{++} than Ba^{++}, with the result that the former gets easily diffused than the later. It is worth pointing out that the size of the hydrated Ca^{++} (0.99°A) is smaller than Ba^{++} (1.35°A), and therefore its diffusion through the pores will also be favoured. Once it has left its rigid hydration shell, the membrane conductance of Ca^{++} will be increased as compared to Ba^{++} (Table-2).

Table No. 2 Specific conductance of zirconium hydroxide membrane in different cationic forms in mhos cm^{-1}.

Electrolytic form	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{++}	Ba^{++}
Specific conductance	0.0835	0.0885	0.0940	0.1100	0.1340	0.190×10^{-2}	0.125×10^{-2}

The role of different amounts of binder-gel ratio on the conductance of the membrane in question was also studied. The membrane prepared with binder-to-gel ratio 20 to 45% were used and their studies show that the conductance decreases with the increase in binder concentration. With increasing amount of binder a decrease in interstitial volume takes place, thus resulting in lower electrolytic absorption. This factor accounts for the lower value of the conductance with the increasing binder.

Electrolytic absorption studies of various electrolytes (NaCl, KCl, LiCl, $BaCl_2$) reveal that the amount of electrolyte absorbed in case of LiCl is maximum. Moreover, when the binder-to-gel ratio is increased the amount of electrolytic absorption decreases. This behaviour finds support from the studies of water content, porosity, swelling and specific conductance of the membranes investigated.

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