STUDIES WITH ZIRCONIUM HYDROXIDE MEMBRANES

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A correlation has been observed between the ion-exchange property and membrane behaviour. The results on the dynamic response time, fixed charge density and selectivity of zirconium hydroxide membrane are reported.

With the development of synthetic membranes, extensive studies on membrane behaviour have been made by several workers[1—4]. A majority of these investigations have been carried out with polymeric membranes, both natural and artificial. Malik and co-workers[5-8] in a series of communications have emphasised the bearing of membrane potential and adsorption on the permeability of ions through inorganic membranes. No attempt, however, was made by them to determine the co-relation between ion-exchange property and membrane behaviour. The present communication deals with this aspect of the membrane phenomenon and the results of the investigations on the dynamic response time, fixed charge density and selectivity of zirconium hydroxide membrane are reported

Experimental Methods

Preparation of zirconium hydroxide membrane :

Zirconium hydroxide gel was prepared by mixing 0.1 M zirconyl oxychloride (A R.) solution with 20% ammonia solution. It was thoroughly washed with double distilled water, filtered, dried in an oven at 80°C for 8 hours and finally sieved into 200 mesh size powder.

Polystyrene supported membranes of zirconium hydroxide were prepared[9] by heating polystyrene granules in a pyrex tube in a sulphuric acid bath at 200°C. After cooling the molten mass, the rod-like material was ground and sieved to 200 mesh powder size. Zirconium hydroxide gel and polystyrene were mixed in the ratio 4 : 1 by weight. The mixture was homogenised in a mortar for about half an hour 1.5 grams of the homogenised mass was put in a die of 2.5 cms diameter. The die was then kept in a specimen mount press and heated gradually up to a temperature of 110° under pressure ranging between 6500 to 7000 psi (kg/mm^2). In order to assess the effect of binder concentration on membrane potential, three membranes of varying percentage of polystyrene, (20, 25 and 30%) were also prepared.

Determination of Membrane Potential :—

Membranes in their various cationic forms were obtained by dipping them in 2 N solution of a particular electrolyte for 48 hours to ensure complete exchange. After drying for 4 hours the membrane was connected with one end of a pyrex glass tube. The tube was inserted in a corked beaker provided with two holes. Solutions of different concentration of electrolytes were filled in the tube and in the beaker. The membrane potentials were determined with the help of a reference electrode (SCE) kept dipped in the two solutions. All the measurements were made in a thermostatic water bath at 35±1°C.

Results and Discussions

Ion-exchange membrane electrodes have been used for many years in the study of ion activity. The measurement of ion activity by means of membrane electrode is most successful in the concentration range over which the membrane behaves as an ideally selective one and hence the Nernst equation is obeyed. Zirconium hydroxide membrane has been truly selective and specific to K^+ (Table 1). The effect of other anions were also

Table 1 : Potentials of zirconium hydroxide membrane having 20% binder (Polystyrene).

Inside solution concentration / Outside solution concentration	Observed potentials in millivolts in various electrolytes					Theoretical values (Nernst)
	KCC	KBr	KI	KNO_3	K_2SO_4	
0.02 (M) / 0.002	58.3	58.2	58.3	58.3	58.3	58.3
0.016 / 0.002	52.5	52.5	52.7	52.7	52.6	52.7
0.014 / 0.002	49.3	49.4	49.4	49.2	49.3	49.4
0.012 / 0.002	45.6	45.5	45.4	45.7	45.4	45.6
0.010 / 0.002	41.0	40.9	40.9	40.8	40.6	41.0
0.008 / 0.002	34.2	34.3	34.3	34.1	34.2	34.3
0.006 / 0.002	27.9	27.9	27.8	27.9	28.0	28.0
0.004 / 0.002	17.6	17.7	17.6	17.8	17.6	17.7

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studied by measuring the membrane potential in contact with solutions of KBr, KI, KNO_3, and K_2SO_4 as shown in Table-1, and it is seen that the nature and the charge of the anion present do not influence the membrane potential. It is observed that in the higher concentration range, that is, when the ratio of the inside and outside solutions concentration is 1 : 2 to 1 : 8, the Nernst equation is valid very closely and the deviations from the Nernstian behaviour is quite high when the potentials are measured in low concentration range. Probably the semi-crystalline nature of zirconium hydroxide and the degree of hydration of cations in dilute range are responsible for such a behaviour. Apart from this the predominant potential-determining process is an exchange of ions between the sample and the membrane phase and at low concentration range, the hydration shell surrounding the lower alkali metals like Na, K etc. inhibits the exchange process. Thus, at lower concentration the membrane potential values are not in accordance with the theories discussed earlier. However, at higher concentration of the electrolytes, a shrinking of hydrated shell takes place simultaneously resulting in an increased uptake of the exchanging cations on the membrane surface. Thus the idea of the total exchange capacity, independent of the nature and concentration of exchanging ions, is not valid for this inorganic gel.

The effect of additional charge developed by the π - electrons of the binder (polystyrene) was also studied by performance of the membranes having varying degree of the binder. The effect of concentration of binder on membrane behaviour was not investigated in membranes having less than 20% polystyrene due to their instability. A similar situation was met in the case of membranes containing more than 30% polystyrene due to the separation of the exchange particles by the binder. The effect of the binder concentration on membrane potential can be observed at least in the range 20 to 30% (Table-2). It was therefore, concluded that the π-electrons of the binder do not affect the electrochemical behaviour of the exchanger, at least in these concentration ranges. However, possibility of this factor influencing the membrane behaviour in dilute solutions cannot be completely ignored.

The selectivity of the membranes for various cations was determined by observing the membrane potentials in solutions of salts with the same anion and in the same concentration range as mentioned earlier. A large divergence is noted in the values of membrane potential in solutions of salts other than potassium.

Table 2: Potentials of zirconium hydroxide membrane having varying amount of binder.

Inside solution concentration / Outside solution concentration	Observed potentials (mv) in the membranes having 20% Binder	25% Binder	30% Binder
0.02/0.002 (M)	58.3	58.5	58.3
0.016/0.002	52.5	52.8	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	41.3
0.008/0.002	34.2	34.2	34.4
0.006/0.002	27.9	27.8	27.8
0.004/0.002	17.6	18.0	17.8

Thus, it is observed that the selectivity depends on the nature of cations. The apparent selectivity ratio, which has been taken to be the ratio of other cations concentration to potassium concentration required to yield the same potential values under similar conditions, has been calculated and is listed below :

Cation pair	Selectivity Ratio
Na^+/K^+	1.05
Li^+/K^+	1.15
Ba^{++}/K^+	1.20
Ca^{++}/K^+	1.30

The selectivity order of the membrane electrode is $K^+ > Na^+ > Li^+ > Ba^{++} > Ca^{++}$. The variation among different alkali ions may be regarded in terms of ion-exchange process and the hydrated ionic volumes of these ions. The greater is the hydrated size of the ion, the smaller is the number which may go to membrane surface. A similar reason may be given for Ca^{++} and Ba^{++} ions. A much smaller number of these ions would be incorporated on the membrane surface as compared with alkali ions, with the result that a considerably higher concentration of these ions in solution phase would be required for appreciable exchange and for their association with the fixed charges of the membrane (Table-3).

The method developed by Altug and Hair[10] based on TMS theory was employed to determine the fixed charge density ($w\bar{X}$) of the membrane material. The theoretical values of the membrane potential, E_{TOT} were calculated[8] by affixing arbitrary values of $\bar{X}$, w being $\pm$ 1, depending on the nature of dissociation sites. These E_{TOT} values were plotted against the log of external

Table 3: Potentials of zirconium hydroxide membrane having 20% Binder.

Inside solution concentration	Observed potentials (mv) in various electrolytes				
Outside solution concentration	LiCl	NaCl	KCl	$BaCl_2$	$CaCl_2$
0.02/0.002 (M)	54.3	56 3	58.3	21.7	20 0
0.018/0 002	51.9	54.3	—	20.5	19.6
0.016/0.002	49.0	51.2	52.5	20.1	19.2
0.014/0 002	46.2	48 1	49 3	19.7	18.7
0.012 0 002	42.2	44.6	45 6	19.2	18 1
0.010/0.002	36.7	39.1	41.0	18.8	17.6
0.008/0 002	30.6	32.2	34.2	17.9	16.8
0.006 0.002	23.4	25.4	27.9	17.4	16.4
0.004/0.002	—	—	17.6	17 0	16.1

solution concentration (Fig. 1). The experimental values of membrane potential were also plotted against log concentration of external solution in the same diagram. The theoretical curve which coincides with experimental one, gives the value of fixed charge density of the membrane. The fixed charge density of zirconium hydroxide membrane is −0.08 N at concentration ratio 0.1/0.01 M. These studies show that fixed charge density of the membrane is not a constant quantity but depends upon the concentration of the solutions separating the membrane.

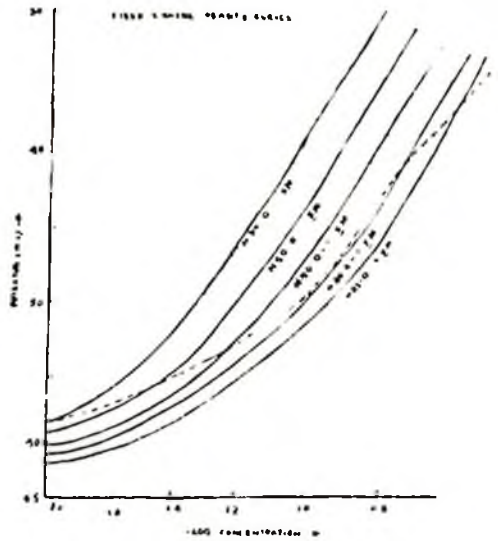


Fig. 1. Membrane potentials for different values of fixed charge density.

The dynamic response time of the membrane electrode was determined by rapidly changing the concentration of solutions and recording the resulting potentials vs time (Fig. 2). The slow equilibration of

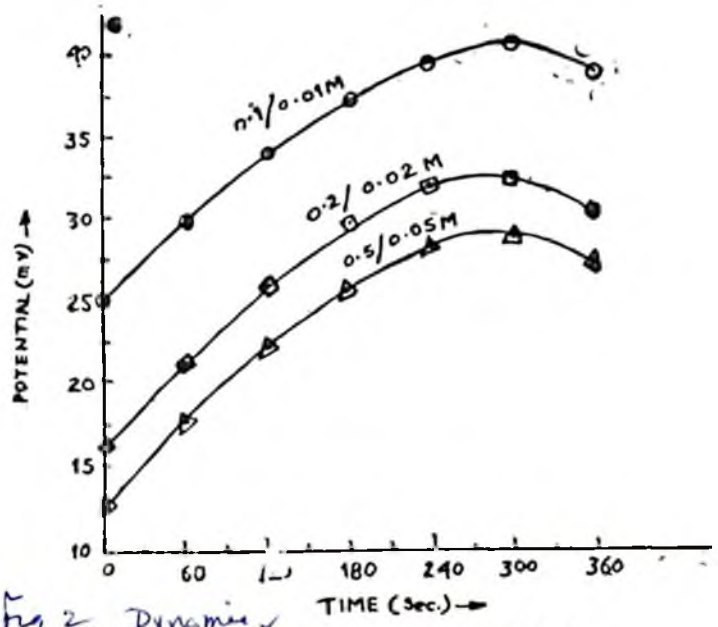


Fig. 2. Dynamic response time of membrane electrode.

this membrane electrode (about 300 sec.) in comparison to almost neglible equilibration time of other ion selective electrodes is probably due to its semicrystalline nature.

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