

Studies on Electroactivity of Anion Exchange Alumina Membrane Supported on a Polyvinylidene Fluoride Matrix

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An anion exchange alumina membrane supported on a polyvinylidene fluoride matrix has been prepared. Membrane potential measurements have been carried out using sodium chloride, barium chloride and aluminium chloride solutions of different concentrations. The data have been used for the estimation of transport numbers of ions and membrane fixed charge densities.

Inorganic ion exchange membranes are of considerable interest because of their attractive electrochemical characteristics and ability to withstand impairment in functional activity at elevated temperatures and hostile environments^{1,2}. There is need to prepare and characterize inorganic ion exchange membranes to explore the possibilities of their use in accomplishing separations of practical importance and as ion selective electrodes. We have presently prepared an anion exchange alumina membrane supported on polyvinylidene fluoride matrix, and measured its membrane potential to derive transport numbers, permselectivities and fixed charge densities using sodium chloride, barium chloride and aluminium chloride solutions. It has been observed that polyvinylidene fluoride itself is not ion selective. Incorporation of alumina on a polyvinylidene fluoride matrix is essential for ion selectivity.

Materials and Methods

Aluminium oxide (basic, BDH) was sieved to obtain particles not exceeding 200 mesh in size. Polyvinylidene fluoride or Kynar was a gift sample (Pennwalt Corp, Philadelphia, USA) and N,N-dimethylacetamide was procured from Riedel De Haen A.G., Germany. All other reagents used were of analytical grade. Deionized water was used for the preparation of solution.

Alumina membrane was prepared³ as follows: A desired quantity of alumina was added to a 20% solution of Kynar in N,N-dimethylacetamide and stirred for 3-4 hr till a thick slurry was obtained. It was uniformly spread on a clean, dried glass plate, kept in an electric oven at 80-90°C for 30 min to remove the solvent and the plate was immersed in distilled water to detach the membrane. Thereafter, the membrane was kept pressed between the folds of a filter paper to avoid wrinkles. The water content of the 1:3 Kynar-alumina

membrane was determined in the usual manner⁴ and found to be 8%. Ion exchange capacity of the ion exchanger estimated by pH titration method⁵ was found to be 1.5 milli equiv g⁻¹ of the dry material.

A piece of the Kynar-alumina membrane was fixed in an all glass cell shown schematically in Fig. 1. The membrane was equilibrated with 1 *m* solution of sodium chloride to convert it into the chloride form, washed with distilled water and kept overnight in the experimental solutions. The solutions on either side were changed repeatedly till a constant difference of potential was observed. The solutions were renewed and potential difference across the membrane was recorded with a digital multimeter (HIL-2142). The membrane used in the present study was 2.5 × 10⁻² cm. thick and had cross sectional area equal to 1.33 cm². The membrane was equilibrated with 1 *m* BaCl₂ and 1 *m* AlCl₃ solutions overnight before making measurements with these solutions. All the measurements were carried out at 35 ± 0.5°C.

Results and Discussion

Membrane potentials measured using a Kynar-alumina membrane are given in Table 1. In order to clearly bring out the dependence of membrane potential on mean concentration, C₁/C₂ was kept fixed in all the cases. There was progressive decline in the magnitude of membrane potential with increase in mean concentration of experimental solutions.

For the description of membrane potential across ion exchange membrane, Teorell-Meyers-Siever theory is invariably used⁶. In the case of an anion exchange membrane, the membrane potential, (Δφ)₁₌₀ is given by Eq. (1), where

$$(\Delta\phi)_{1=0} = \frac{RT}{F} (\bar{t}_- - \bar{t}_+) \ln \frac{a_1}{a_2} \quad \dots (1)$$

$\bar{t}_+$ and $\bar{t}_-$ denote transport numbers of ions in the

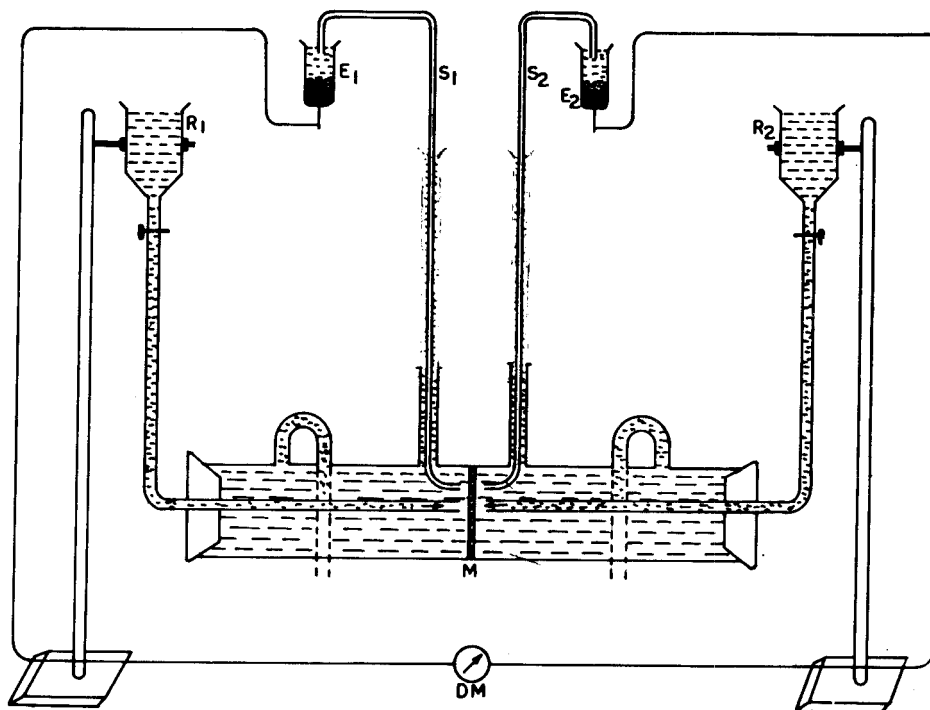


Fig. 1—Experimental setup for the measurement of membrane potential of Kynar-alumina (1:3) membrane [E₁, E₂, calomel electrodes; S₁, S₂, agar-agar salt bridges; R₁, R₂, reservoirs; M, membrane; and DM, digital multimeter]

Table 1—Membrane Potential Data of 1:3 Kynar-Alumina Membrane in Presence of Solutions of Sodium, Barium and Aluminium Chlorides

Mean conc. (<i>m</i>)	C ₁ (<i>m</i>)	C ₂ (<i>m</i>)	(Δφ) _{I=0} (mV)		
			NaCl	BaCl ₂	AlCl ₃
0.01	0.005	0.015	27.3	31.3	20.2
0.05	0.025	0.075	24.4	28.4	18.2
0.10	0.05	0.15	22.4	26.4	16.1
0.20	0.10	0.30	20.6	24.1	13.1
0.40	0.20	0.60	19.3	19.2	10.3
0.60	0.30	0.90	17.3	15.3	8.2

membrane phase. Variation of membrane potential with mean concentration even when concentration ratio was kept constant indicated a change in the membrane characteristics⁷ as a result of which counterion transport was affected. In an ideal ion exchange membrane co-ion transfer does not take place at all and a maximum value of the membrane potential given by Eq. (2)

$$[(\Delta\phi)_{I=0}]_{\max} = \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (2)$$

is expected. $[(\Delta\phi)_{I=0}]_{\max}$ values calculated using Eq. (2) are included in Table 2.

From Eqs (1) and (2) it follows that

$$\bar{t}_- = \frac{(\Delta\phi)_{I=0}}{[(\Delta\phi)_{I=0}]_{\max}} + 0.5 \quad \dots (3)$$

Transport numbers of counterion, Cl⁻, estimated using Eq. (3) are given in Table 3. Values in the case of sodium chloride are in satisfactory agreement with the reported values using other ion selective membranes⁸. Due to non-availability of literature values for barium and aluminium chlorides, comparison could not be made. Activity coefficient values used for the computation of activities are also included in Table 3.

At lower concentration of sodium chloride Kynar-alumina (1:3) membrane is nearly ideal. However, with increase in concentration there is marked reduction in the transport number of the counterion. When barium chloride and aluminium chloride solutions are used, the transport numbers are lower at comparable concentrations. This indicates that transmission characteristics of the counterion change with change in the nature of co-ions. Enhanced charge on the co-ion results in lower transport of the counterions at comparable concentrations, in spite of possibility of increased exclusion of co-ions on account of stronger electrostatic repulsion by the membrane matrix charge. Intrusion of co-ions within the membrane to varying degrees seems responsible for the observed alteration in transmission characteristics.

The electrical character of a membrane is usually expressed in terms of fixed charge density. Effective

Table 2—Maximum Membrane Potential of Kynar-Alumina Membrane and Transport Numbers of Counterions in Presence of Solutions of Sodium, Barium and Aluminium Chlorides

Mean conc (m)	NaCl				BaCl ₂				AlCl ₃			
	<i>f</i> ₁	<i>f</i> ₂	[(Δφ) _{<i>f</i>=0}] _{max} (mV)	<i>t</i> ₋	<i>f</i> ₁	<i>f</i> ₂	[(Δφ) _{<i>f</i>=0}] _{max} (mV)	<i>t</i> ₋	<i>f</i> ₁	<i>f</i> ₂	[(Δφ) _{<i>f</i>=0}] _{max} (mV)	<i>t</i> ₋
0.01	0.8753	0.9260	27.68	0.9931	0.670	0.715	39.786	0.8934	—	—	37.64	0.7683
0.05	0.790	0.850	27.23	0.9480	0.550	0.590	37.64	0.8773	0.398	0.440	34.20	0.7660
0.10	0.755	0.820	26.99	0.9149	0.470	0.560	35.58	0.8709	0.340	0.420	31.39	0.7564
0.20	0.710	0.778	26.74	0.8852	0.435	0.470	35.46	0.8398	0.302	0.337	33.88	0.6933
0.40	0.673	0.735	26.83	0.8596	0.413	0.415	37.51	0.7559	0.356	0.305	42.94	0.6204
0.60	0.659	0.710	22.23	0.8180	0.397	0.425	39.71	0.6926	0.479	0.302	53.45	0.5767

Table 3—Permselectivities and Fixed Charge Densities of Kynar-Alumina Membrane in Presence of Solutions of Sodium, Barium and Aluminium Chlorides

Mean conc (m)	NaCl				BaCl ₂				AlCl ₃			
	<i>t</i> ₋	<i>t</i> ₋	<i>P</i> _s	φX	<i>t</i> ₋	<i>t</i> ₋	<i>P</i> _s	φX	<i>t</i> ₋	<i>t</i> ₋	<i>P</i> _s	φX
0.01	0.6082	0.9931	0.979	0.096	0.56	0.8934	0.937	0.022	0.4599	0.768	0.591	0.015
0.05	0.6124	0.9480	0.841	0.155	0.5683	0.8773	0.695	0.097	0.4603	0.7660	0.587	0.121
0.10	0.6146	0.9149	0.708	0.200	0.5747	0.8709	0.674	0.182	0.4603	0.7564	0.569	0.139
0.20	0.6179	0.8862	0.655	0.347	0.5838	0.8398	0.590	0.292	0.4590	0.6933	0.454	0.204
0.40	0.6350	0.8596	0.601	0.606	0.605	0.7559	0.377	0.325	0.4602	0.6204	0.314	0.266
0.60	0.6500	0.8180	0.491	0.642	0.630	0.6926	0.194	0.237	0.4602	0.5767	0.230	0.284

fixed charge density of a membrane can be expressed in terms of permselectivity defined as⁹

$$P_s = \frac{\bar{t}_- - t_-}{t_- - 2(t_- - 1)\bar{t}_-} \quad \dots (4)$$

where *t*₋ denotes the transport number of the anion in solution of mean concentration, C.

Permselectivity is related to effective fixed charge density, φX, by Eq. (5)¹⁰

$$\phi X = \frac{2 C P_s}{\sqrt{1 - P_s^2}} \quad \dots (5)$$

Permselectivity and fixed charge density values derived using Eqs (4) and (5) respectively are included in Table 3. *t*₋ values^{11,12} used for calculations are also included in Table 3.

It is clear from the data in Table 3 that effective fixed charge densities change with the nature of co-ion and follow the sequence: Na⁺ > Ba²⁺ > Al³⁺

Equimolar solutions of sodium chloride, barium chloride and aluminium chloride contain unequal concentrations of co-ions with respect to chloride ion. The enhanced counterion i.e., chloride ion concentration seems to result in progressive lowering of fixed charge density due to association with the membrane matrix. Association is believed to be

responsible for reduction in membrane fixed charge density⁸.

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References

- 1 Clearfield A, *Preparation and characterization of materials*, edited by J H Honig and C N R Rao (Academic Press, New York) 1981.
- 2 Alberti G, Casciola M & Constantino U, *J membrane Sci*, **16** (1983) 137.
- 3 Rajan K S, Boies D B, Casolo A J & Bregman J I, *Desalination*, **1** (1966) 231.
- 4 Tasaka M, Aoki N, Kondo Y & Nagasawa M, *J phys Chem*, **79** (1975) 1357.
- 5 Helfferich F, *Ion exchange* (McGraw Hill, New York) 1962.
- 6 Lakshminarayanaiah N, *Membrane electrodes* (Academic Press, New York) 1976, 64.
- 7 Essig A & Caplan S R, *Am J Phys Chem*, **236** (1979), 211.
- 8 Singh K, Shabd R & Srivastava V N, *Indian J Chem*, **20A** (1981) 391.
- 9 Kobatke Y & Kamo N, *Prog Polym Sci, Japan*, **5** (1973) 257.
- 10 Lakshminarayanaiah N, *J membrane Sci*, **21** (1975) 175.
- 11 Conuway E E, *Electrochemical data* (Elsevier, London) 1952.
- 12 Robinson R A & Stokes R H, *Electrolyte solutions* (Butterworths, London) 1959.