

Studies on Electrodriven Transport Phenomenon: Electroosmosis of Electrolyte Solutions Across a Zirconium Phosphate Membrane

KEHAR SINGH* & VIJAI KUMAR

Department of Chemistry, University of Gorakhpur, Gorakhpur

Received 21 November 1983; revised and accepted 2 April 1984

Electroosmotic fluxes and volumetric fluxes of the transport of sodium chloride, barium chloride and aluminium chloride solutions of different concentrations across a zirconium phosphate membrane accompanying electric currents of different densities have been measured. The data have been used to ascertain the electrical character of the membrane-permeant interface and to investigate its dependence on the nature and concentration of the electrolyte solutions. Membrane potentials have also been measured for the determination of the fixed charge density. Attempt has also been made to correlate the electrical character of the interface with the membrane fixed charge density.

Electrically driven transference across a membrane occurs on account of the formation of an electrified region at the membrane permeant interface. Theories based on atomistic considerations¹ and non-equilibrium thermodynamics^{2,3} predict a linear dependence between volumetric transference and applied potential difference. In some experimental studies, this dependence has been found to be nonlinear⁴⁻⁹. Exact determination of electrical field which brings about electroosmosis across a membrane is difficult to determine on account of possibility of polarization of the membrane and the electrodes and the difficulty associated with keeping the electrodes in actual contact with the membrane faces. The current passing through the system can, however, be determined without any ambiguity. It was, therefore, thought proper to investigate the dependence of electroosmotic flux on current density with a view to obtaining information about the electrified region at the membrane-permeant interface.

Volumetric fluxes driven by hydrostatic pressure and membrane conductance have also been measured to characterise the ion exchange membrane. Sodium chloride, barium chloride and aluminium chloride solutions of different concentrations have been used as permeants.

Membrane potentials have also been measured to ascertain the electrical character of the membrane surface with a view to correlating it with that of the membrane-permeant interface.

Materials and Methods

Preparation of zirconium phosphate and determination of its ion exchange capacity

Solutions (0.1 M) of zirconium sulphate and diammonium hydrogen phosphate (both B D H) in 4 N H₂SO₄ were heated and mixed slowly with constant

stirring. The precipitate thus obtained was filtered, washed repeatedly with deionized water till free from sulphate ions and dried at 150°C.

The ion exchange capacity of the material thus prepared was determined by pH titration technique as follows: Zirconium phosphate (0.5 g) was equilibrated with deionized water (25 ml) for over 24 hr and titrated with 0.1 N sodium hydroxide. To obviate difficulties associated with hydrolysis¹⁰ of zirconium phosphate at pH above and below 4.5, all the data were gathered at pH = 4.5. At this pH, capacity of the ion exchanger was 0.60 meq/g dry ion exchange resin.

Membrane formation: (a) Dynamically formed membrane

A suspension of zirconium phosphate was prepared as described above. A few millilitres of this suspension were put on a glass support, G₃ pyrex sinter fitted in the middle of a glass column. The suspension was filtered through the support under suction till a disc of zirconium phosphate about 2 mm in thickness was formed. The disc or membrane was repeatedly washed with distilled water to remove sulphate ions completely. The membrane thereafter was kept submerged in deionized water before being compounded with the experimental solution.

(b) Membrane formed by impregnation

In this method, solutions (0.1 M) of diammonium hydrogen phosphate and zirconium sulphate were allowed to react within the pores of a pyrex G₃ sinter for 24 hr. Effective impregnation occurred only when the glass column fitted with the pyrex sinter was fixed vertically and the zirconium sulphate solution was touching the phosphate solution filled on the lower side of the sinter. In order to adjust the permeability of the system to desired level impregnation was allowed

for another 24 hr but this time the column was inverted with lower part having the phosphate solution. The solutions were removed and membrane was thoroughly washed with distilled water till free of sulphate ions. The membrane was then kept in deionized water.

Estimation of hydrodynamic and electroosmotic permeabilities

Hydrodynamic and electroosmotic permeabilities were measured as already reported¹¹. Volumetric fluxes induced by known different magnitudes of pressure difference were measured by observing movement of the liquid in a horizontally fixed capillary tube having radius of 0.10 cm. For the estimation of electroosmotic permeability, a known electric current was passed through the membrane with the help of an electronically operated power-supply using Ag/AgCl electrodes and the ensuing volumetric flux estimated as above.

The potential difference across the electrodes was also measured. Volumetric fluxes at different current densities up to 80 mA were similarly measured. Current versus potential values were used to ascertain the absence/occurrence of polarization during electroosmotic flux measurements. In the absence of polarization, current versus potential curves were linear. No deviation from linearity was observed within the current density domain used in the present investigation except where specifically indicated.

Measurement of membrane potentials

Membrane potentials were measured using an all glass apparatus as already reported¹². Electrolyte solutions of desired concentrations were filled in the half-cells and the membrane was allowed to equilibrate overnight. The equilibrating solutions were renewed before starting the experiment so that solution compositions remained the same as before equilibration. The salt bridges positioned near the membrane faces were connected to saturated calomel electrodes to measure membrane potentials. A digital multimeter, HIL 2142 was used for this purpose. The observations were repeated for each concentration difference till a constant difference of potential could be measured. Concentration differences were varied at a fixed mean concentration to keep the membrane characteristics unaltered¹³.

All the measurements were carried out in an air thermostat maintained at $30 \pm 0.5^\circ\text{C}$.

Results and Discussion

The experimental results on hydrodynamic permeation and electroosmotic permeation are given in Table 1. The volumetric flux, $(J_v)_{\Delta P=0}$ depends linearly

Table 1—Hydrodynamic and Electroosmotic Permeation Data

Conc. $\times 10^3 M$	$\left(\frac{J_v}{P}\right)_{\Delta P=0} \times 10^{10}$ $\text{m}^5 \text{N}^{-1} \text{S}^3$	$\left(\frac{J_v}{I}\right)_{\Delta P=0} \times 10^7$ $\text{m}^3 \text{Amp}^{-1} \text{S}^{-1}$	$\left(\frac{I}{\Delta\Phi}\right)_{\Delta P=0} \times 10^3$ Amp V^{-1}
NaCl			
1	3.55	12.14	0.33
5	3.35	7.69	0.54
10	3.28	4.20	0.98
20	2.82	2.22	1.05
30	2.50	1.35	1.35
BaCl ₂			
1	2.89	6.47	Nonlinear*
5	2.81	2.33	0.24
10	2.70	0.73	0.60
15	2.62	0.38	1.42
20	2.27	0.51	1.18
AlCl ₃			
1	3.21	1.41	0.66
5	3.21	2.24	0.80
10	2.96	1.03	1.23
20	2.89	0.58	1.66
30	2.95	0.66	3.12

*I versus $\Delta\Phi$ curve exhibits deviation from linearity due to polarization.

on pressure difference up to $\Delta P = 50$ cm of the experimental liquid used in these studies. The electroosmotic flux, $(J_v)_{\Delta P=0}$ also varies linearly within the current density domain (up to 80 mA) investigated in the present case. Some typical results are plotted in Fig. 1.

The experimental results show that while the hydrodynamic permeability $(J_v/\Delta P)_{I=0}$ decreases to a small extent with increase in electrolyte concentration, the electroosmotic permeability substantially decreases with increase in electrolyte concentration. Electroosmotic effect decreases when the valency of the counterions increases. This is consistent with the finding of Rosenberg *et al.*¹⁴. The lower values of electroosmotic permeability in the case of AlCl₃ solutions in comparison to sodium or barium chloride solutions arise on account of reduction in the membrane matrix charge on adsorption of the Al³⁺ ions¹⁵ (Table 2).

For an examination of the mode of dependence of the electroosmotic permeability on concentration and nature of the electrolyte solutions, characterization of the membrane interface in terms of zeta potentials is essential. This atomistic concept is, however, valid only if the ion exchange membrane is macroporous^{16,17}. The equivalent pore radius¹⁸ of a membrane estimated using hydrodynamic flux and conductivity data has been found to be of the order of 10^{-5} cm.

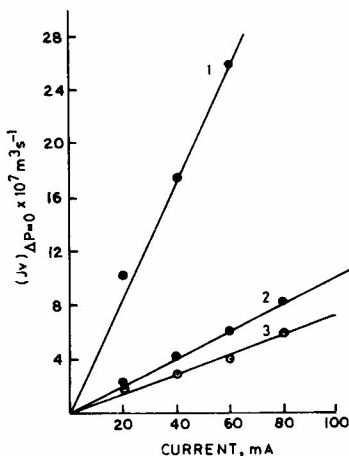


Fig. 1—Variation of electroosmotic flux (J_v) _{$\Delta P=0$} with current density (I) in the presence of electrolyte solutions [(1), 10.0 mM NaCl; (2) 10.0 mM BaCl₂; and (3) 10.0 mM AlCl₃]

Table 2—Zeta-potential Values in Microvolts

Conc. $\times 10^3 M$	NaCl	BaCl ₂	AlCl ₃
1.0	20.58	12.25	17.51
5.0	64.10	21.07	44.31
10.0	70.02	12.68	36.82
15.0	—	9.82	—
20.0	73.08	17.15	38.50
30.0	65.42	—	82.99

For the purpose of estimation of zeta-potential from electroosmotic permeability data, following equation¹⁹ may be used.

$$\xi = \frac{4\pi\eta k}{D} \left(\frac{J_v}{I} \right)_{\Delta P=0} \times 9 \times 10^4 \text{ V} \quad \dots (1)$$

The calculated zeta-values are presented in Table 2.

In the calculation of zeta-potential, contribution of surface conductivity has been ignored. This is justified²⁰ since the equivalent pore radius is large enough in comparison to the thickness of the double layer²¹ ($< 10^{-6}$ cm) near the wall, where the surface conductivity is exhibited. The average surface electrical conductivity remains the same as that in the bulk.

The zeta-potential arises on account of formation of an electrical double layer at the membrane-permeant interface. The surface of an ion exchanger in a state of equilibration with an electrolyte solution is endowed with a fixed charge density. It is therefore worthwhile to investigate its influence on the character of the double layer. The zirconium phosphate membrane used in this study is fairly porous and does not exhibit any selectivity. For the determination of fixed charge density, a dense membrane formed by impregnation under conditions identical to those employed for dynamically formed membrane has been used. It is

Table 3—Membrane Characteristics Derived from Membrane Potentials $C_1 = 20 \times 10^{-3} M$; $C_2 = 30 \times 10^{-3} M$; pH=4.5; temp.=30°C

Electrolyte	Membrane potential (mV)	t_+	$\bar{t}_+$	P_s	$\overline{\Phi X}$ mol per litre of water
NaCl	4.6	0.3902	0.7149	0.0596	0.0371
BaCl ₂	6.6	0.4375	0.7149	0.5308	0.0288
AlCl ₃	3.0	0.5397	0.6401	0.2053	0.0104

therefore, legitimate to presume that electrical character of the interface is similar to the dynamically formed membrane.

The effective charge density, $\overline{\Phi X}$ that an ion exchanger surface carries is expressed in terms of perm-selectivity, P_s , as²²

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

Kobatake *et al.*²³ defined P_s in terms of transport numbers by Eq. (3)

$$P_s = \frac{\bar{t}_+ - t_+}{t_+ - (2t_+ - 1) \bar{t}_+} \quad \dots (3)$$

The transference number of the counterion, t_+ in the membrane phase is related to membrane potential E_m , when the two faces of the membrane are maintained in a state of equilibration with solutions of concentrations C_1 and C_2 .

$$E_m = 2t_+ \frac{RT}{F} \ln \frac{C_2}{C_1} \quad \dots (4)$$

The symbol C used in Eq. (2) denotes mean concentration $C_1 + C_2/2$, and t_+ denotes the transport number of the cation at the mean concentration. Equation (3) applies when a cation-exchange membrane is being considered.

Membrane potential data alongwith the computed values of t_+ , P_s and $\overline{\Phi X}$ are summarised in Table 3, in the presence of sodium chloride solutions of different concentration. It appears from Tables 2 and 3 that a higher fixed charge density leads to an increase in zeta-potential.

Acknowledgement

The authors thank Prof. R P Rastogi for facilities. Financial assistance from SCST (UP) to one of them (V K) is gratefully acknowledged.

References

- 1 Kruyt H R, *Colloid science* (Elsevier, New York) 1952, p. 201.
- 2 De Groot S R, *Thermodynamics of irreversible processes* (North Holland, Amsterdam) 1963, p. 198.
- 3 Carter J W, Jagannadhaswamy B, *Proceedings of the symposium on the less common means of separation*, 1964, p. 35.

- 4 Rastogi R P, Singh K, Srivastava M L, *J phys Chem*, **73**(1969) 46.
- 5 Tombalkain A S, *J phys Chem*, **72** (1968) 1566.
- 6 Hadermann A F, Waters P F & Woo J W, *J phys Chem*, **78**(1975) 2574.
- 7 Rastogi R P, Singh K & Singh J, *J phys Chem*, **79** (1975) 2575.
- 8 Rastogi R P & Khan K M, *J phys Chem*, **70** (1966) 1017.
- 9 Singh K & Srivastava V N, *J nonequib Thermodyn*, **6**(1981) 195.
- 10 Ampelett C B, *Inorganic ion-exchange* (Elsevier Publishing Company, Amsterdam) 1964, p. 106.
- 11 Singh K, Srivastava V N & Chandra M, *J nonequib Thermodyn*, **6** (1981) 181.
- 12 Singh K, Shabd R & Srivastava V N, *Indian J Chem*, **20A** (1981) 391.
- 13 Essig A & Caplan S R, *Am J Phys*, **236** (1939) 211.
- 14 Rosenberg N W, George J H W & Potter, *J electrochem Soc*, **104** (1957) 111.
- 15 Kruyt H R & Torrestsha S A, *Kolloid Bertrifle*, **54** (1943) 262.
- 16 Helfrich F, *Ion-exchange* (McGraw Hill, New York) 1962, p. 233.
- 17 Rastogi R P, Singh K, Raj Kumar & Shabd R, *J Membrane Sci*, **2** (1977) 317.
- 18 Singh K, Raj Kumar, *Indian J Chem*, **17A** (1979) 607.
- 19 Davis J T & Rideal E K, *Interfacial phenomenon* (Academic Press, New York) 1961, p. 117.
- 20 Voyntsky S, *Colloid chemistry* (Mir Publishers, Moscow) 1978, p. 234.
- 21 Glasstone S, *An introduction to electro chemistry* (Affiliated East-West Press, New Delhi) 1977, p. 85.
- 22 Lakshminariniah N, *J Membrane Sci*, **21** (1975) 175.
- 23 Kobatake Y & Kamo N, *Prog Polymer Sci Japan*, **5** (1973) 257.