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Electroosmosis of Methanol-Water Mixtures Across Pyrex G_4 Membrane : Excess Phenomenological Coefficients

KEHAR SINGH*†, RAM SHABD, RAJ KUMAR‡ & M. M. PANDE**
Department of Chemistry, University of Gorakhpur, Gorakhpur 273 001

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Hydrodynamic and electroosmotic permeation of methanol-water mixtures across a pyrex G_4 membrane has been studied with a view to ascertaining excess phenomenological coefficients. The dependence of these coefficients on composition has been examined. It appears that the excess functions arise predominantly on account of interactions amongst the components of the mixtures. Membrane conductance measurements have also been carried out and used to ascertain the electrical character of the membrane.

PERMEATION through membranes, when the differences in hydrostatic pressure and electrical potential act separately or in combination, is now commonly studied using non-equilibrium thermodynamic theory which yields transport equations between fluxes and forces in terms of the phenomenological coefficients. Estimation of these coefficients has been carried out by a number of workers[1-4]. Srivastava *et al.*[5,6] investigated electroosmosis of binary liquid mixtures through pyrex membranes with a view to studying the dependence of these coefficients on composition. We report in this paper the results on hydrodynamic and electroosmotic permeation of methanol-water mixtures through a pyrex G_4 membrane within the linear range. Excess transport coefficients have been estimated and their dependence on composition of the permeating mixtures has been studied. Membrane conductance measurements have also been carried out and used to estimate zeta potentials.

Materials and Methods

Conductivity water (sp. cond. 0.72×10^{-6} mho cm^{-1}) and analar methanol (BDH; density = 0.790 at 20°C) were used. Pyrex G_4 membrane having average pore radius equal to 3.62×10^{-4} cm as estimated from hydrodynamic and electroosmotic permeabilities was used. Experimental techniques described in our earlier publication[7] was used for measurements of hydrodynamic and electroosmotic permeabilities. Conductance measurements were carried out with a conductivity bridge at 50 Hz. All the measurements were carried out in an air thermostat at 30° ± 0.1°C.

Results and Discussion

When a binary liquid mixture of a uniform composition at constant temperature is partitioned by a membrane, the volumetric flux, arising on account of the existence of differences of hydrodynamic pressure, $\triangle P$, and electrical potential, $\triangle \phi$, across the membrane is given by Eq. (1)[1].

$$J_v = L_{11}\frac{(\triangle P)}{T} + L_{12}\frac{(\triangle \phi)}{T} \qquad \ldots (1)$$

L_{ij} $(i, j = 1,2)$ are the phenomenological coefficients. It is evident that

$$(J_v)_{\triangle\phi=0} = \frac{L_{11}(\triangle P)}{T}$$

$$(J_v)_{\triangle P=0} = \frac{L_{12}(\triangle \phi)}{T}$$

L_{11}/T obtained from $(J_v)_{\triangle\phi=0}$ versus $\triangle P$ plots and L_{12}/T obtained from $(J_v)_{\triangle P=0}$ versus $\triangle\phi$ plots are given in Table 1 for various mixtures. The dependence of these coefficients on composition is depicted in Fig. 1.

The phenomenological coefficients L_{11}/T, L_{12}/T for the mixtures may be expressed in terms of these coefficients for the components in the following manner[5,6,8].

$$\frac{L_{11}}{T} = \left(\frac{L_{11}}{T}\right)_m X_m + \left(\frac{L_{11}}{T}\right)_w X_w \qquad \ldots (2)$$

$$\frac{L_{12}}{T} = \left(\frac{L_{12}}{T}\right)_m X_m + \left(\frac{L_{12}}{T}\right)_w X_w \qquad \ldots (3)$$

The subscript m and w respectively represent methanol and water and X is the mass fraction. These equations strictly speaking hold good when the interaction amongst the components of the mixtures and alteration in the membrane-permeant interaction with change in composition are negligible. Water and methanol interact strongly. This is borne out clearly by the excess volumes estimated from the density data[9]. The validity of the Eqs (2) and (3) is examined in Table 1. It is seen that calculated and experimental values of the phenomenological coefficients L_{11}/T and L_{12}/T are no tin agreement. We

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†Visiting Scientist, Department of Membrane Research, The Weizmann Institute of Science, Rehovot, Israel.

‡Chemistry Division, ATIRA, Ahmedabad, Gujarat.

**Department of Chemistry, Post-graduate College, Pratapgarh, UP

TABLE 1 — PHENOMENOLOGICAL COEFFICIENTS

Mole fraction of water	$[L_{11}/T]_{exp} \times 10^7$ ($cm^5\ sec^{-1}\ dyne^{-1}$)	$[L_{12}/T]_{exp} \times 10^5$ ($cm^3\ sec^{-1}\ V^{-1}$)	$[L_{11}/T]_{calc} \times 10^7$ ($cm^5\ sec^{-1} dyne^{-1}$) (using Eq. 2)	$[L_{12}/T]_{calc} \times 10^5$ ($cm^3 sec^{-1} V^{-1}$) (using Eq. 3)	$[L_{11}/T]^E \times 10^7$ ($cm^5\ sec^{-1}\ dyne^{-1}$)	$[L_{12}/T]^E \times 10^5$ ($cm^3\ sec^{-1} V^{-1}$)
0.00	1.830	2.40	1.830	2.40	0	0
0.31	0.972	1.65	1.522	2.23	—0.550	—0.58
0.54	0.337	1.00	1.214	2.08	—0.877	—1.08
0.87	0.163	1.10	0.598	1.72	—0.435	—0.62
1.00	0.290	1.55	0.290	1.55	0	0

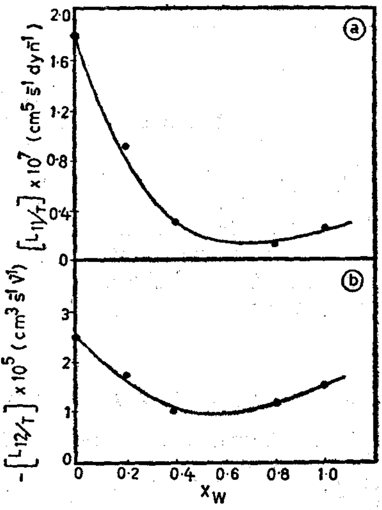

Fig. 1—Dependence of $[L_{11}/T]$ (curve a) and $[L_{12}/T]$ (curve b) on composition [XW=mass fraction of water in the alcoholic mixtures].

define excess phenomenological coefficients as

$$\left[\frac{L_{11}}{T}\right]^E = \left[\frac{L_{11}}{T}\right] - \left[\left(\frac{L_{11}}{T}\right)_m X_m + \left(\frac{L_{11}}{T}\right)_w X_w\right] \quad \text{... (4)}$$

and

$$\left[\frac{L_{12}}{T}\right]^E = \left[\frac{L_{12}}{T}\right] - \left[\left(\frac{L_{12}}{T}\right)_m X_m + \left(\frac{L_{12}}{T}\right)_w X_w\right] \quad \text{... (5)}$$

$[L_{11}/T]$ and $[L_{12}/T]$ are the experimental values of the phenomenological coefficients. The excess phenomenological coefficients are also included in Table 1. The $(L_{11}/T)^E$ are negative which indicate that hydrodynamic permeation of the mixtures has lowered values because of interactions between the mixture components. The dependence of $[L_{11}/T]^E$ on composition depicted in Fig. 2, can be understood readily. The addition of water leads to net structural loss and densification owing to strong intermolecular interactions arising on account of the greater proton accepting ability of the alcoholic OH groups[10]. However, beyond a certain composition of the water rich mixtures the interactions decline because the alcohol molecules progressively fit into the open structures within the water clusters without affecting any alteration in its openness.

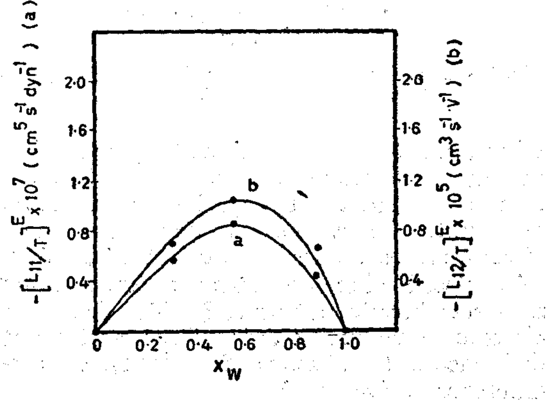

Fig. 2—Dependence of $[L_{11}/T]^E$ (curve a) and $[L_{12}/T]^E$ (curve b) on mole fraction of water (x_w).

The dependence of the excess cross phenomenological coefficient $[L_{12}/T]^E$ on composition is also depicted in Fig. 2. With polar solvents like water and methanol, the solvent flux due to electrical potential difference occurs due to the formation of an electrified region in the neighbourhood of the membrane matrix chiefly on account of autoprotolysis; $2H_2O \rightleftharpoons H_3O^+ + OH^-$ and $2\,CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$. In the alcoholic mixtures, however, an additional source of ions is also available because of the greater proton accepting tendency of alcoholic OH groups in comparison to water OH groups ($CH_3OH + OH_2O \rightleftharpoons CH_3OH_2^+ + OH^-$).

The excess phenomenological coefficients versus excess volume curves given in Fig. 3 exhibit a linear relationship. It can, therefore, be inferred that excess phenomenological coefficients predominantly arise on account of interactions amongst the mixture components during transmission. The membrane permeant interactions are not significantly affected when permeation of methanol-water mixtures of different compositions occurs through the membrane. Spectral studies show that surface-permeant interactions are significant only when narrow pores of molecular dimensions are involved[11].

Conductance of a porous membrane equilibrated with the permeant may be expressed as:

$$K = \frac{n \pi r^2 k}{l} \quad \text{... (6)}$$

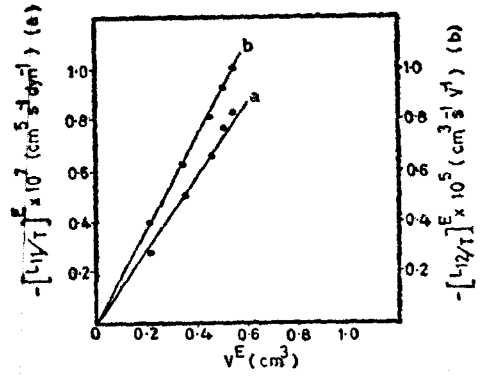

Fig. 3—Plots of (a) $[L_{11}/T]^E$ versus V^E and (b) $[L_{12}/T]^E$ versus V^E.

where, n, is the number of capillary channels having average pore radius, r; l is the thickness of the membrane; and k is the specific conductance of the permeant. In a porous uncharged membrane electroosmosis occurs on account of the formation of an electrified region at the interface endowed with an electrokinetic potential, ξ. The dependence of electroosmotic flux on the applied electrical potential difference in the absence of hydrodynamic pressure difference is given by[12]

$$(J_v)_{\Delta P=0} = \frac{n r^2 \xi D}{4 \eta l} (\Delta \phi) \qquad \dots (7)$$

where ξ is electrokinetic potential, η and D are the coefficient of viscosity and dielectric constant of the permeant respectively. Equations (1) and (7) can be combined to yield Eq. (8).

$$\frac{L_{12}}{T} = \frac{n r^2 \xi D}{4 \eta l} \qquad \dots (8)$$

Using Eqs. (8) and (6) we get.

$$\xi = \frac{4 \pi \eta k}{K D} \frac{L_{12}}{T}\, 9 \times 10^4 \text{ volts} \qquad \dots (9)$$

The values of zeta potential obtained using equation (9) along with the values of η, D, k and K, given in Table 2, show that addition of water lowers the zeta potential. The effect is more pronounced in methanol rich mixtures presumably because of a significant change in ionic content due to reaction $CH_3OH + H_2O \rightleftharpoons CH_3OH_2^+ + OH^-$. This increased ionic content leads to a progressive compaction of the electrical double layer as evidenced by the profound lowering of the zeta potential. In water rich mixtures ionic content does not significantly change because of lowered contribution of the above reaction and the zeta potentials exhibit only a mild variation.

TABLE 2 — VISCOSITY, DIELECTRIC CONSTANT, MEMBRANE CONDUCTANCE, SPECIFIC CONDUCTANCE OF PERMEANT AND CALCULATED ZETA POTENTIALS

Mole fraction of water	$\eta \times 10^3$ poise	D	$K \times 10^6$ mhos	$k \times 10^6$ mhos cm^{-1}	ξ mV
0.00	4.66	34.0	0.52	1.02	72.93
0.31	6.66	38.0	0.80	0.45	33.01
0.54	8.73	43.5	0.84	0.72	19.86
0.87	13.03	61.0	1.50	1.13	20.00
1.00	15.14	80.0	1.30	0.72	18.33

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