Electroosmotic Transport Across Amphoteric & Layered Membranes
Obtained from Anionic Dowex 1 & Cationic Zeokarb 225

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Electroosmotic transport of methanol across composite membranes prepared by mixing Dowex 1 (Cl- form) with Zeokarb 225 (Na+ form) in different proportions have been measured. Electroosmotic permeability and hydrodynamic permeability of methanol across composite membrane prepared by arranging Zeokarb 225 (Na+ form) and Dowex 1 (Cl- form) in series have also been measured. Methanol flows towards the negative electrode when Zeokarb 225 (Na+ form) alone is used. It flows in opposite direction through Dowex 1 (Cl- form) membrane. The composite membrane exhibits an unusual behaviour. The electroosmotic flux always occurs towards the Dowex 1 side irrespective of the direction in which the electrical field is applied.

ELECTROKINETIC phenomena using ion-exchange membranes have been studied extensively. In some cases some unusual effects have been observed. Very few such studies with composite membranes have, however, been reported.

In the present paper we report electroosmotic and hydrodynamic permeability measurements of methanol across composite ion-exchange membranes prepared by mixing Dowex 1 (Cl- form) and Zeokarb 225 (Na+ form) in different proportions. Electroosmotic behaviour of membranes composed of layers of cation and anion-exchange materials has also been studied.

Materials and Methods

Zeokarb 225 (Na+ form) (Permutit Company, London) and Dowex 1 (Cl- form) (Dow Chemical Company, USA) were used for the preparation of the membranes. Important characteristics of Zeokarb 225 and Dowex 1 ion-exchange materials respectively, are: functional groups, -SO;Na+ and I-N+Cl-; exchange capacity -4.8 and 3.5 meq/g of dry resin; and moisture content, 45-50% and 44.7%.

Methyl alcohol (BDH) was used as such.

Preparation of the membranes — The cation and the anion-exchangers (both 200 mesh size) were mixed completely so that they were physically indistinguishable. The membrane was prepared from this homogeneous mixture by mechanical compression as described elsewhere.

For the preparation of the composite membrane arranged in series, the cation exchanger particles were cast in the form of a membrane. A desired amount of the anion-exchanger was then placed besides one of the porous supports and compressed mechanically. The component membranes in the composite structure were bound between porous supports.

Results and Discussion

The results on electroosmotic permeability of methanol across the amphoteric membranes are graphically shown in Fig. 1 as plots of electro-
osmotic flux, \( J_o \), of methanol versus potential difference, \( \Delta \phi \), across amphoteric membranes. Electroosmotic migration of methanol across membranes having Zeokarb 225 and Dowex 1 in proportions 2:1 and 1:5:1 occurs towards the negative electrode, whereas when membrane composition is 1:2:1 and 1:1, the migration occurs towards the positive electrode. Thus direction of electroosmotic flux is reversed when membrane composition is varied from 1:5:1 to 1:2:1.

The data on electroosmotic migration of methanol when Zeokarb 225 (Na\(^+\) form), Dowex 1 (Cl\(^-\) form) membranes used separately and in combination in a series arrangement are included in Fig. 2. The hydrodynamic permeability data are included in Fig. 3. Methanol flows towards the negative electrode during electroosmosis when Zeokarb 225 (Na\(^+\) form) alone is used. It flows in opposite direction through Dowex 1 (Cl\(^-\) form) membrane. The layered membrane exhibits an unusual behaviour. The electroosmotic flux always occurs towards the Dowex 1 side of the membrane irrespective of the direction in which the electrical field is applied.

Exchange capacities\(^{18} \) of Zeokarb 225 (Na\(^+\) form) and Dowex 1 (Cl\(^-\) form) are 4.8 and 3.5 meq/g dry resin respectively. It is therefore, expected that electroosmotic migration of methanol across amphoteric membranes having 1:1 composition should occur towards the negative electrode. This is in contrast to the experimental results. The results can, however, be explained if we postulate that,

\[
\zeta_c = \zeta_z M_z + \zeta_d M_d
\]

(1)

where \( \zeta_c \), \( \zeta_z \), and \( \zeta_d \) are zeta potentials for composite, Zeokarb 225 and Dowex 1 membranes respectively. \( M_z \) and \( M_d \) are the mass fractions of Zeokarb 225 and Dowex 1 respectively. Zeta potentials have been estimated from electroosmotic flux data using Smoluchowski's relationship\(^{19,20} \):

\[
\zeta = \frac{4\pi \eta k \Delta \phi}{\varepsilon \varepsilon_0} \times 9 \times 10^4 \text{ volts} \quad \ldots (2)
\]
where \( \eta \) = coefficient of viscosity of the permeant; 
\( \varepsilon \) = dielectric constant of the permeant; 
\( k \) = specific conductivity of the permeant; 
\( J/V_{\Delta \phi=0} \) = electroosmotic flux per unit time; and 
\( i \) = current flowing through the system.

On substituting the values of \( \eta \), \( \varepsilon \) and \( k \) from literature\textsuperscript{21,22}, it has been found that,
\[
\zeta_{\text{Zeokarb/methanol}} = -3.98 \text{ mV}
\]
and
\[
\zeta_{\text{Dowex/methanol}} = 4.95 \text{ mV}.
\]

Using above values of \( \zeta \), we find that zeta potential, \( \zeta \), of amphoteric membrane becomes zero for the composition of the membrane equal to 1:25:1. This indicates that direction of electroosmotic migration of methanol across membranes having compositions up to 1:25:1 will occur towards the negative electrode, whereas when mass ratio less than 1:25:1 is used it will occur towards the positive electrode. This is in conformity with our actual observations since sign reversals in electroosmosis occurs when the mass ratio of Zeokarb 225: Dowex 1 is reduced from 1:5:1 to 1:2:1. The explanation of the observed electroosmotic behaviour on the basis of Eq. (1) will be suspect if the mixed ion exchanger undergoes leaching on equilibration. In the present case no leaching was, however, detected when the mixed ion exchanger was kept submerged in methanol for over 24 hr.

Hydrodynamic permeability data in the case of amphoteric membranes, layered membranes and its constituent membranes can be adequately described with the help of Eq. (3).

\[
(J_P) = \frac{L_{\text{f}}}{T_{\Delta \phi=0}} \Delta P \quad \ldots (3)
\]

since \((J_P)_{\Delta \phi=0}\) versus \(\Delta P\) plots have been found to be linear in all cases. \(L_{\text{f}}\) values were estimated from slopes of these linear curves.

It is clear from the Figs. 1 and 2 that electroosmotic flux depends non-linearly on potential.
difference. Analysis of the data indicates that a second order phenomenological equation (4).

\[
(J_v)_{\Delta P=0} = L_{13} \left( \frac{\Delta \phi}{T} \right) + \frac{1}{2} L_{122} \left( \frac{\Delta \phi}{T} \right)^2
\] ...

(4)

holds good for layered and amphoteric membranes as well. Validity of Eq. (4) has been tested in Figs. 4 and 5 where \((J_v)_{\Delta P=0}/\Delta \phi\) has been plotted against \(\Delta \phi\). All the plots are linear as required by Eq. (4). Phenomenological coefficients \(L_{12}\) and \(L_{122}\) were estimated from intercepts and slopes respectively of these linear plots.

Phenomenological analysis of the data of the layered and component membranes indicates that overall resistances (reciprocal permeability coefficients) are not additive. This is shown in Table 1.

Similar conclusion has been drawn by Kedem and Katchalsky on the basis of theoretical considerations.

Flux measurements carried out with a view to examining the directional dependence of hydrodynamic permeability and electroosmotic permeability are included in Figs. 6, 7 and 8, 9 for amphoteric and layered membranes respectively. The conclusions are summarized in Table 2. It is seen that membranes composed of the cation and anion

![Fig. 8](image_url)

**Fig. 8** — (a) Directional dependence of hydrodynamic permeability for Zeokarb 225 (Na⁺ form)/methanol system. (△) Flow in one direction; and (●) flow in opposite direction. (b) Directional dependence of hydrodynamic permeability for Dowex 1 (Cl⁻ form)/methanol system. (△) Flow in one direction; and (●) flow in opposite direction. (c) Directional dependence of hydrodynamic permeability for series array/methanol system. (△) Flow in one direction; and (●) flow in opposite direction.
Table 2 — Directional Dependence of Phenomenological Coefficients for the Permeation of Methanol

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$L_{11} \times 10^8$ cm$^2$ sec$^{-1}$</th>
<th>$L_{11} \times 10^8$</th>
<th>$L_{12} \times 10^8$ cm$^2$ sec$^{-1}$</th>
<th>$L_{12} \times 10^8$</th>
<th>$L_{12} \times 10^8$</th>
<th>$L_{12} \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeokarb 225 (Na$^+$ form)</td>
<td>1·64 10·66 1·64 10·66</td>
<td>0·80 0·56 0·12 0·11</td>
<td>2·12 0·25 0·10 0·24</td>
<td>0·81 1·10 0·90 0·50</td>
<td>0·36 0·08 0·02 0·10</td>
<td></td>
</tr>
<tr>
<td>Dowex 1 (Cl$^-$ form)</td>
<td>4·33 10·64 4·33 10·64</td>
<td></td>
<td>4·33 0·80 0·12 0·11</td>
<td></td>
<td>0·81 1·10 0·90 0·50</td>
<td></td>
</tr>
<tr>
<td>Amphoteric</td>
<td>1·09 0·71 1·09 0·71</td>
<td></td>
<td>1·09 0·71 0·36 0·36</td>
<td></td>
<td>0·81 1·10 0·90 0·50</td>
<td></td>
</tr>
<tr>
<td>Series array</td>
<td></td>
<td></td>
<td>4·33 0·80 0·12 0·11</td>
<td></td>
<td>0·81 1·10 0·90 0·50</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9 — Directional dependence of electroosmotic permeability for permeation of methanol. (Zeokarb; 1) flow in one direction; and (2) flow in opposite direction; Dowex; (3) flow in one direction; and (4) flow in opposite direction. Series array; (5) flow in one direction; and (6) flow in opposite direction.

exchange materials used separately and their amphoteric mixture are hydrodynamically isotropic and electroosmotically anisotropic. The layered membrane is however, anisotropic in both the respects. The observed electroosmotic migration in the case of layered membrane towards the Dowex 1 side of the membrane irrespective of the direction in which electrical field acts is presumably because of pronounced anisotropic character of the layered membrane.

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References