Electro-osmotic Permeability of Cation Exchange Membranes

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In a recent paper Mackay and Meares¹⁾ have reported the measurements of rates of electro-osmotic flow of liquid through Permutit Zeo-Karb 315. By measuring its specific conductivity $k_{\rm sp}$ (ohm⁻¹ cm⁻¹), electro-osmotic permeability, w, (cm² V⁻¹ sec⁻¹), defined as the volume of solvent flowing per second through unit area of membrane for a potential gradient of one volt per cm., has been computed. w is found to decrease with increasing external electrolyte concentration, and for any given concentration it is found to be independent of current in the range of 0.02 to 1.0 mA·cm⁻².

Similar work is in progress in our laboratories. Rates of electro-osmotic flow of liquid through differently cross-linked polymethacrylate (PMA) membranes and cross-linked phenol

sulphonate (PSA) membranes have been measured at 30°C employing a cell of the type described by Despic' and Hills²).

The results of measurements of rates of electro-osmotic transport of liquid through 5, 10 and 15% cross-linked PMA membranes at one external electrolyte concentration (0.01 g. ions of Na⁺ per litre) and at different currents in the range of 3 mA·cm⁻² to 60 mA·cm⁻² are collected in Table I. Measurements using PSA membranes in 0.01, 0.1, 0.5 and 1.0 N sodium chloride external electrolyte solutions at current densities ranging from 0.5 to 10.1 mA·cm⁻² are presented in Table II.

The electro-osmotic permeability w, can be written as $w = \frac{V}{I} \times k_{\rm sp}$, where V is the rate of electro-osmotic flow of liquid in ml. per sec., I is the constant current flowing through the system in amp. and $k_{\rm sp}$ is the specific conductance of the membrane in reciprocal ohms per cm. At any given external electrolyte concentration in which the membrane is in equilibrium, $k_{\rm sp}$ of the membrane is constant and is independent of current strength³). Therefore for the value of w to remain constant over a range of current densities the ratio V/I should be a constant. Mackay and Meares find this

TABLE I. CROSS-LINKED PMA MEMBRANES

,	5%		10%		15%	
I mA	$(\text{ml. sec}^{-1} \times 10^{-5})$	V/I (ml. sec ⁻¹ · amp ⁻¹ ×10 ⁻²)	v	V/I	V	$\widetilde{V/I}$
2	0.57	0.285			0.54	0.270
3					0.67	0.223
5	1.31	0.262	1.73	0.346	0.96	0.192
10			3.07	0.307	1.88	0.188
15	3.52	0.235	4.30	0.287		
20	4.39	0.220	5.63	0.282	3.83	0.192
25	5.19	0.208	6.90	0.276		
30	6.00	0.200	8.25	0.275		
35	7.01	0.200				
40	8.20	0.205				

TABLE II. PSA MEMBRANES

I mA	0.01 N NaCl		0.1 N		0.5 N		1.0 N	
	\overline{v}	V/I	\overline{v}	V/I	\overline{v}	V/I	\overline{v}	V/I
1	1.61	1.610	0.77	0.770	0.34	0.340	0.21	0.210
2	2.73	1.365	1.49	0.745	0.68	0.340	0.41	0.205
5	5.34	1.068	3.68	0.736	1.72	0.344	1.04	0.208
10	9.68	0.968	7.00	0.700	3.34	0.334	2.05	0.205
15	14.70	0.980	10.34	0.689	5.01	0.334	3.09	0.206
20	18.30	0.915	14.00	0.700	6.82	0.341	4.13	0.207

¹⁾ D. Mackay and P. Meares, Trans. Faraday Soc., 55, 1221 (1959).

A. Despic' and G. J. Hills, Discussions Faraday Soc., No. 21, 150 (1956).

³⁾ N. Lakshminarayanaiah, Current Sci., 28, 321 (1959).

to be so for their membranes. But the V/I values given in columns 3, 5 and 7 of Table I and columns 3 and 5 of Table II contradict their findings. The values actually decrease with increasing currents and attain a limiting value. But V/I values of PSA membranes in equilibrium with concentrated solutions (concentration \geq 0.1 N) are constant over the current range studied and agree with their findings.

As the PSA membranes are chemically similar to Permutit Zeo-Karb 315, V/I values for our membranes in equilibrium with 1.0, 0.5 and 0.1 N sodium chloride solution and those of Mackay and Meares for their membranes computed from the values of w and $k_{\rm sp}$ taken from their graphs are given in Table III.

TABLE III

External electrolyte solution, NaCl	V/I	V/I Mackay & Meares
$1.0\mathrm{N}$	0.207×10^{-2}	0.159×10^{-2}
0.5 N	0.339 //	0.298 //
0.1 N	0.714 "	0.639 //

It is obvious from those values that our PSA membranes are more permeable electro-osmotically to liquid than Zeo-Karb 315.

Details including other aspects will be published elsewhere.

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