883. *Effect of Pressure on the Transport of Non-electrolytes through Ion-selective Membranes.*

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The transport number of glycerol in a Permaplex C-10 ion-selective membrane is shown to be markedly reduced by the application of a pressure differential across the membrane. The mechanism of the phenomenon is discussed.

THE removal of electrolytes from non-electrolytes or from substances of zero net charge can be conveniently carried out by electrodialysis through ion-selective membranes. Although the method has been widely practised [1] it has only recently been appreciated that substantial amounts of non-electrolyte may be lost by passage through the membranes.[2] Previous work [2] demonstrated that transport of glycerol and D-glucose through Permaplex C-10 and A-10 membranes (The Permutit Co., Ltd.) occurred largely by electro-osmosis. A simple theoretical treatment showed that the percentage loss of non-electrolyte by electro-osmosis was directly proportional to the reduction in electrolyte concentration. It follows that the percentage loss of electrolyte can be reduced simply by diluting the solution before electrodialysis, as in this way the reduction in electrolyte concentration is made smaller for the same total amount of electrolyte removed. This procedure naturally leads to the non-electrolyte's being obtained as a solution more dilute than the original.

It was noted previously [2] that an osmotic flow of water through the membranes in the reverse direction reduced the transport of non-electrolyte. Hence it seemed possible that reversed water flow caused by a pressure differential across the membrane might also reduce non-electrolyte transport. The purpose of this paper is to report the effect of pressure on the transport number of glycerol in a Permaplex C-10 membrane.

Experimental.—The materials, analysis, and general procedure were as described previously.[2] The cell also was similar except that provision was made for a pressure differential to be applied across the central cation-selective membrane. To prevent bowing, this membrane

[1] *Inter al.*, Lightfoot and Friedman, *Ind. Eng. Chem.*, 1954, **46**, 1599; Wingerd and Block, *J. Dairy Sci.*, 1954, **27**, 932; Burianek and Slechtova, *Listy Cukr.*, 1959, **75**, 62, 82.
[2] Jarvis and Tye, *J.*, 1960, 620.

was supported on the low-pressure side by a sheet of $\frac{1}{8}''$ expanded polyvinyl chloride (Expanded Metal Co., Ltd.) resting against Perspex ribs which traversed the centre compartment.

Runs were carried out at current densities of 4·4 and 22 mA/cm.^{2} and, at each current density, pressure differentials across the cation-selective membrane of 0, 32, and 133 cm. of water head were used. The pressure head was always such that the flow of water through the membrane caused by the head was in a direction opposite to the movement of non-electrolyte. The solution donating the cations and non-electrolyte to the cation-selective membrane was initially 1·09M in glycerol and 2·3M in sodium chloride. The glycerol concentration changed by less than 8% during a run and the concentration of sodium chloride decreased to 2·06 $\pm$ 0·03M and 1·3 $\pm$ 0·15M in the low and high current-density runs, respectively. The average concentrations of the solution receiving the cations and glycerol from the cation-selective membrane were 0·22 $\pm$ 0·02M and 0·51 $\pm$ 0·05M with respect to sodium chloride in the low and high current-density runs and always less than 0·04M in glycerol.

The results are expressed as transport numbers (t) of glycerol, *i.e.*, moles of glycerol passing through the cation-selective membrane per faraday.

Results and Discussion.—The results, given in the Table, show that a pressure differential (Δp) has a very marked effect on the transport of glycerol through the membrane. Quite moderate pressure differentials reduced the glycerol transport more than ten-fold. The effect was due to the small liquid flow, caused by the pressure differential, which passed through the membrane in the direction opposite to that in which the glycerol was being transported. The liquid flow was not actually through the ion-exchange particles of the heterogeneous membrane but rather through paths between the exchange resin and the inert matrix. The glycerol was removed from the exchange resin through which it was being transported by partition with the liquid in the space between the resin particles and the inert matrix. In effect the resin was subjected to a countercurrent washing. The presence of interstices between the ion-exchange resin and the inert matrix has been demonstrated by Hale and McCauley [3] for membranes similar to that used in this study.

Transport numbers (t) for glycerol on electro-osmosis against a pressure differential (Δp; in cm. of H_2O).

Δp	0	32	133
(t at Δp)/(t at $\Delta p = 0$): at 4·4 milliamp./cm.^{2} ...	1·0	0·13	0·02
at 22 milliamp./cm.^{2} ...	1·0	0·42	0·04

Evidence for such a mechanism was obtained from experiments with a Permaplex C-20 membrane (The Permutit Co., Ltd.). This membrane is identical with Permaplex C-10 except that a reinforcing web of inert material is incorporated during manufacture. As a result when the membrane swells in water, the swelling is restricted in the plane normal to membrane thickness, and the development of paths right through the membrane between resin and matrix is considerably reduced. In consequence the water permeability of Permaplex C-20 is a power of ten less than that for Permaplex C-10. Further, the application of a pressure differential of 133 cm. of water head across a Permaplex C-20 membrane had no effect on the transport number of glycerol. This demonstrates that the reduction in transport number of glycerol in the case of the Permaplex C-10 membrane was due to liquid flow between the resin and inert matrix and not to a much smaller flow through the ion-exchange resin itself.

The effect of current density is qualitatively understandable. At the lower current density the rate at which glycerol was being transported was lower, so that a smaller liquid flow and hence a lower pressure differential was necessary to bring about a similar reduction in glycerol transport.

The use of a small flow from the receiving solution to the donating solution to reduce the transport number of glycerol must reduce the effective selectivity of the membrane by transporting salt in the direction opposite to that transported by the electric current. The sodium chloride transferred by liquid flow is VN g.-equiv. sec.$^{-1}$ cm.$^{-2}$ where V is the

[3] Hale and McCauley, *Trans. Faraday Soc.*, 1961, **57**, 135.

flow in l. sec.$^{-1}$ cm.$^{-2}$ and N is the normality of the sodium chloride in the receiving solution. The decrease in transport number of the counter-ion is thus $VN\mathbf{F}/i$, where $\mathbf{F}$ is the faraday and i is the current density in amp. cm.$^{-2}$. If the reduction in counter-ion transport number is to be limited to 0·1, then VN/i must be less than $1{\cdot}04 \times 10^{-6}$ g.-equiv. coulomb^{-1}. Separate experiments showed the flow through the Permaplex C-10 membrane to be proportional to the pressure differential and equal to $6{\cdot}7 \times 10^{-11}$ l. sec.$^{-1}$ cm.$^{-2}$ for a differential of 1 cm. of water head. From this it was calculated that the maximum value of VN/i in the present work was $0{\cdot}45 \times 10^{-6}$ g.-equiv. coulomb^{-1}. Therefore changes in the cation membrane selectivity should have been small and the experimental results confirmed that this was so.

The authors thank Dr. T. R. E. Kressman for his interest in the work.

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[*Received, April 24th,* 1961.]