127. *Transport of Non-electrolytes through Ion-selective Membranes by Electro-osmosis.*

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Removal of sodium chloride from aqueous solutions of D-glucose and glycerol by electrodialysis through Permaplex C-10 and A-10 ion-selective membranes is accompanied by transport of some non-electrolyte through the membranes. At current densities of $\nless 10$ mA/cm.^{2} the transport of non-electrolyte is almost entirely due to electro-osmosis; at lower densities, provided reverse osmotic flow is small, the transport of non-electrolytes per faraday is larger owing to an increased contribution from diffusion.

An equation expressing total transport in terms of electro-osmosis and diffusion is deduced, whence it follows that the transport of non-electrolyte by electro-osmosis depends only on the concentration of the non-electrolyte in the solution donating the counter-ions to the membrane. Further, the percentage loss of non-electrolyte during electrodialytic desalting is shown to be independent of the non-electrolyte concentration but dependent on the reduction in salt concentration.

Comparison of the quantities of D-glucose and water transported by electro-osmosis with those present in the donating solution shows that water is transported preferentially.

Electrodialysis in a cell containing ion-selective membranes has been used to remove electrolytes from aqueous solutions containing non-electrolytes or amphoteric substances at their isoelectric points.[1] An important aspect that has received little attention is the extent to which the non-electrolyte is lost by passage through the ion-selective membranes into the waste stream.

Transport of non-electrolyte through the membranes can, in principle, occur by diffusion and by electro-osmosis. The diffusion, through cation-selective membranes, of acetone, formaldehyde, and acetic acid,[2] and of ethanol[3] has been studied. However, apart from a brief mention by Peers[1] and a little work by Lightfoot and Friedman,[1] the possibility that non-electrolytes can be transported by electro-osmosis does not seem to have been generally appreciated.

The object of the present work is to assess the importance of non-electrolyte transport by electro-osmosis through Permaplex C-10 and A-10 membranes.

EXPERIMENTAL

Materials.—The cation- and anion-selective membranes were Permaplex C-10 and A-10 (The Permutit Co., Ltd.) respectively, which have been described previously.[4] Sodium chloride, D-glucose, and glycerol were of laboratory-reagent grade (B.D.H. Ltd.).

Apparatus.—The cell is shown in Fig. 1. The body *B* is of Perspex and consists of 5 compartments separated by alternate cation-selective *C* and anion-selective *A* membranes, the effective area of each membrane being 100 cm.^{2}. The whole is clamped together by lengths of 2BA brass studding, terminated by nuts. Gaskets *G* of plasticised polyvinyl chloride ensure water-tight joints between membranes and compartments. All compartments are provided with lids *L* and drainage holes *J*. The anode *D* is a carbon block ½" thick and the cathode *E* a sheet of $\frac{1}{32}$" flattened expanded stainless steel (Expanded Metal Co., Ltd.). The electrode compartments contain glass cooling-coils *W*, and were continuously flushed with 1·0N-sodium chloride to remove electrode products, the solution entering at *K* and overflowing at *O*. Each of the central compartments 1, 2, and 3 holds 150 ml. of solution which was air-stirred.

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[1] Lightfoot and Friedman, *Ind. Eng. Chem.*, 1954, **46**, 1599; Anderson and Wylam, *Chem. and Ind.*, 1956, 191; Blainey and Yardley, *Nature*, 1956, **180**, 83; Wood, *Biochem. J.*, 1956, **62**, 611; Di Benedetto and Lightfoot, *Ind. Eng. Chem.*, 1958, **50**, 691; Peers, *J. Appl. Chem.*, 1958, **8**, 59; Payne, *Internat. Sugar J.*, 1957, **61**, 149; Dept. Sci. & Ind. Res., "Food Investigation, 1957," H.M.S.O., London, 1958, p. 51; Wingerd and Block, *J. Dairy Sci.*, 1954, **27**, 932.

[2] Manecke and Heller, *Discuss. Faraday Soc.*, 1956, **21**, 101.

[3] Mackie and Meares, *ibid.*, p. 111.

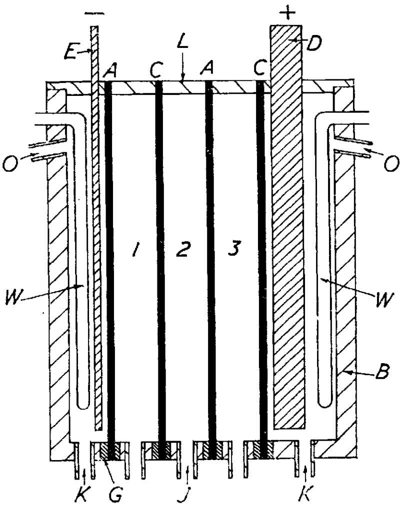
[4] Kressman and Tye, *ibid.*, p. 185.

A Crompton–Parkinson Universal Indicator (Pattern OLD, 8″ scale) with appropriate shunts was used to measure current. It was accurate to ±1%.

Analysis.—Sodium chloride solutions were titrated with standard silver nitrate, with potassium chromate as indicator. D-Glucose was estimated with Fehling's solution with Methylene Blue as indicator,[5] and glycerol by oxidation with periodic acid, the excess of periodic acid being back-titrated with sodium thiosulphate in the presence of potassium iodide.[6]

Procedure.—Each experiment was immediately preceded by an identical dummy run. The procedure for both was as follows. 150 ml. of solution containing known concentrations of sodium chloride and non-electrolyte were pipetted into compartment 2, and compartments 1 and 3 were filled with 0·1N-sodium chloride. A constant current was then passed for a measured interval of time, after which compartments 1, 2, and 3 were emptied, a constant drainage time of 90 sec. being allowed. After the run the drained contents of these compartments were analysed for glycerol and sodium chloride, while that from compartment 2 was also weighed.

FIG. 1. *Apparatus for electro-osmosis.*



The dummy run served a dual purpose. It ensured that the condition of each compartment just before an actual experiment was similar to its condition after it had been drained. Thus a true measure of the contents of a compartment was obtained without the need for additional rinsing, which would have caused errors by leaching absorbed solutes from the membranes. Secondly, the dummy run ensured that the appropriate concentration profiles of the non-electrolyte in the membranes were already established at the start of a run.

D-Glucose and glycerol, the non-electrolytes, were used at an average concentration of 1·03 ± 0·07M except for run 8 in which the average glycerol concentration was 5·2M. The change in non-electrolyte concentration in compartment 2 was kept less than 5%, and the final non-electrolyte concentrations in compartments 1 and 3 <0·1M. The average sodium chloride concentration in compartment 2 was 2·0 ± 0·2M except for runs 7 and 8 in which it was 1·4M and 0·5M respectively. The average sodium chloride concentration in compartments 1 and 3 varied between 0·2M and 0·6M. Current densities from 0 to 40 mA/cm.^{2} were used, the runs at zero current density giving the amounts of non-electrolyte diffusing through the membranes. The temperature was 20° ± 2°.

The following quantities were obtained from each experiment: (i) faradays of electricity passed, (ii) moles of non-electrolyte passing through the cation-selective membrane, (iii) moles of non-electrolyte passing through the anion-selective membrane, (iv) moles of non-electrolyte left in compartment 2, (v) moles of water lost from compartment 2, and (vi) moles of sodium chloride lost from compartment 2.

From the sum of (ii), (iii), and (iv) the average total recovery of non-electrolyte was found to be 98·8%. The sum of the counter-ion transport numbers through the anion and cation-selective membranes was calculated from (i) and (vi) and found to be 1·90, a value consistent with that obtained previously.[4]

RESULTS AND DISCUSSION

Symbols

The following symbols are used: $\bar{C}$, C = concentration of non-electrolyte inside and outside the membrane (mole/ml.); $\bar{t}$ = " observed " transport number (total moles of non-electrolyte or total g.-equiv. of ion passing through membrane per faraday); t° = " true " transport number of non-electrolyte (moles of non-electrolyte passing through membrane by electro-osmosis per faraday); A,K = proportionality constants ($t^\circ = A\bar{C} = KC$); D = diffusion coefficient of non-electrolyte (cm.^{2}/sec.); i = current density (A/cm.^{2}).;

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[5] Lane and Eynon, *Analyst*, 1923, **48**, 221.

[6] Miner and Dalton, " Glycerol," Reinhold Publ. Inc., New York, 1953, p. 206.

F = the faraday; l = membrane thickness (cm.). Subscripts C and A refer to cation- and anion-selective membranes. Subscripts D and R refer to the sides donating the counter-ions to, and receiving them from, the membranes. Superscripts $^\circ$ and ^{E} refer to non-electrolyte and electrolyte.

The results are shown in the Table.

Run no.	Non-electrolyte	Current density (mA/cm.^{2})	$\bar{t}_C^\circ$ Obs.	$\bar{t}_C^\circ$ Calc. from diffusion	$\bar{t}_A^\circ$ Obs.	$\bar{t}_A^\circ$ Calc. from diffusion
1	D-Glucose	40	0·025	0·00017	0·025	0·0013
2	D-Glucose	20	0·030	0·00035	0·027	0·0027
3	D-Glucose	10	0·026	0·00069	0·024	0·0053
4	D-Glucose	3	0·016	—	0·035	—
5	D-Glucose	2	0·014	—	0·040	—
6 *	D-Glucose	2	0·031	—	0·055	—
7	Glycerol	20	0·035	0·00115	0·047	0·0074
8	Glycerol	20	0·14	—	0·20	—

* Glycerol added to solutions in compartments 1 and 3 to reduce osmotic flow.

The observed transport numbers of the non-electrolyte are compared in runs 1, 2, 3, and 7 with the values if diffusion had been the only process causing transport. It is evident that the actual amounts of non-electrolyte passing through the membranes were 1—2 orders greater than that attributable to diffusion. Further, in runs 1—3 the amounts transported per faraday were independent of current density, whereas transport by diffusion would have been inversely proportional to current density. It is, therefore, concluded that for these runs the major process causing movement of non-electrolytes was electro-osmosis. At higher concentrations of non-electrolyte (run 8), electro-osmosis gave rise to even higher non-electrolyte transport numbers.

It might be expected that, at the low current densities used in runs 4 and 5, the observed transport numbers of the non-electrolyte would have risen owing to an increased contribution from diffusion. In fact, although $\bar{t}_A^\circ$ increased, $\bar{t}_C^\circ$ decreased. This discrepancy is attributed to osmotic flow of water through the membranes. The concentrations on both sides of the membranes were such that the osmotic flow was in the opposite direction to the movement of non-electrolyte and hence it could have reduced non-electrolyte transport. Osmotic flow in the expected direction was observed at zero current density. This explanation was confirmed by an experiment (run 6) in which glycerol was added to the solutions in compartments 1 and 3 to make their particle concentration identical with that in compartment 2. Thus the solutions on both sides of the membrane were approximately isotonic and flow of water by osmosis was reduced. Under these conditions at 2 mA/cm.^{2}, $\bar{t}_C^\circ$ was slightly greater than and $\bar{t}_A^\circ$ twice the value observed at the higher current densities. The greater increase in $\bar{t}_A^\circ$ was due to the higher rate of diffusion of D-glucose through the anion-selective membrane. This rate was eight times that through the cation-selective membrane.

In the absence of osmotic flow the total transport of non-electrolyte resulting from diffusion and electro-osmosis can be established by a simple theoretical treatment. Two assumptions are made: that Fick's law is applicable and that transport by electro-osmosis is directly proportional to concentration. Then, at a plane within the membrane situated a distance x from the donating-side surface and at which the concentration is $\bar{C}$, the total transport of non-electrolyte is given by

$$\bar{t}^\circ = AC - \frac{DF}{i}\frac{d\bar{C}}{dx}$$

Integrating for the stationary state and using the boundary conditions that $\bar{C} = \bar{C}_D$ when $x = 0$ and $\bar{C} = \bar{C}_R$ when $x = l$, we have:

$$\bar{t}^\circ = \frac{A[\bar{C}_D - \bar{C}_R \exp(-Ali/DF)]}{[1 - \exp(-Ali/DF)]}$$

Putting $\bar{C}_D = \alpha C_D$, $\bar{C}_R = \alpha C_R$ and $K = \alpha A$, the relationship becomes:

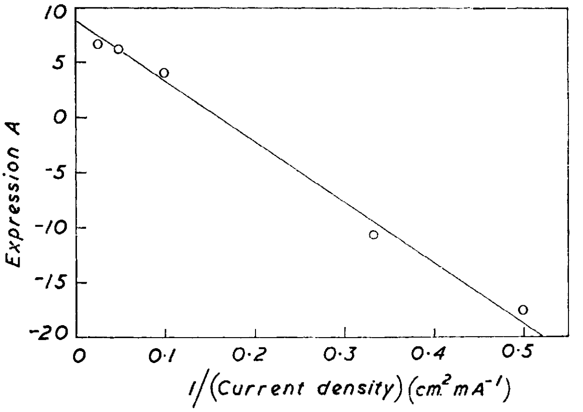
$$\bar{t}^{\circ} = \frac{K[C_D - C_R \exp(-Kli/\alpha D\boldsymbol{F})]}{[1 - \exp(-Kli/\alpha D\boldsymbol{F})]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It will be noted that the contributions from electro-osmosis and diffusion are not directly additive. Now when $Ai/\boldsymbol{F} \gg \alpha D/l$, the contribution of diffusion to the non-electrolyte transport is negligible, so that $\bar{t}^{\circ} = t^{\circ}$ and equation 1 simplifies to

$$t^{\circ} = KC_D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

C_R does not appear in equation (2); hence the true transport number of the non-electrolyte is independent of the receiving-side concentration and depends only upon the donating-side concentration. This conclusion holds even in the presence of significant flux of non-electrolyte by diffusion. In other words, if the total non-electrolyte flux consists of contributions from electro-osmosis and diffusion, then that part due to electro-osmosis is determined only by the donating-side concentration. This important conclusion is not dependent upon the initial assumption that t° is directly proportional to concentration: the sole requirement is that t° should increase as the concentration of non-electrolyte increases.[7]

FIG. 2. *Plot of* 1/*Current density against* $\bar{t}_C^{\circ}(H_2O) + \bar{t}_A^{\circ}(H_2O)$ (*expression A*).



In order to assess the importance of the loss of non-electrolyte by electro-osmosis in an electrodialysis process, consider a volume V(ml.) having a non-electrolyte concentration C_D. Let E equivalents of sodium chloride be removed by electrodialysis. The number of faradays required is $E/(t_C^E + t_A^E - 1)$ and the loss of non-electrolyte is therefore $E(t_C^{\circ} + t_A^{\circ})/(\bar{t}_C^E + \bar{t}_A^E - 1)$. Hence from equation (2) the percentage loss of non-electrolyte is $E(K_A + K_C)100/[V(\bar{t}_A^E + \bar{t}_C^E - 1)$. Now E/V is the change in electrolyte concentration ΔC^E so that the percentage loss of non-electrolyte is:

$$\frac{\Delta C^E(K_A + K_C)100}{\bar{t}_C^E + \bar{t}_A^E - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

that is to say, it is directly proportional to the change in electrolyte concentration. C_D does not appear in equation (3) and therefore the percentage loss of non-electrolyte must be independent of the non-electrolyte concentration.

By means of values of K_C and K_A calculated from runs 1, 2, and 3, and the appropriate value of 0·9 for $\bar{t}_C^E + \bar{t}_A^E - 1$, percentage losses of non-electrolyte are calculated to be 11·5,* 1·2, and 0·12 for changes in salt concentration of 2·0, 0·2, and 0·02N. Thus a significant loss can occur when the change in salt concentration is sufficiently large.

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* This value is appreciably underestimated since the solution volume is reduced considerably, owing to loss of water by electro-osmosis, when the salt concentration is changed by 2·0N.

[7] Cf. Kressman and Tye, *Trans. Faraday Soc.*, 1959, **55**, 1441.

Finally it is of interest to compare the quantities of D-glucose and water transferred electro-osmotically with the quantities present in the donating solution. The amount of water transferred per faraday is obtained from the experimental results but this cannot be directly equated to electro-osmotic flow since water is also transferred by simple osmosis. The two phenomena can be separated by extrapolation to infinite current density where the osmotic flow per faraday must be zero. Fig. 2 shows a suitable plot for runs 1—6, from which a value of $t_C{}^{\circ}(H_2O) + t_A{}^{\circ}(H_2O)$ of 8·8 is obtained. This is 170 times the average value, 0·052, of $t_C{}^{\circ}$(D-glucose) + $t_A{}^{\circ}$(D-glucose) obtained in runs 1—3. The average value of the molar ratio H_2O : D-glucose in the donating solution was 47 : 1. Thus considerably more water is transported electro-osmotically than would be expected from the composition of the donating solution. This effect could arise from three possible causes: (i) the non-electrolyte content of the movable pore fluid is different from that of the donating solution, (ii) D-glucose is subject to an extra restrictive force in the membrane on account of its size, (iii) water is transported by electro-convection and as water of hydration while D-glucose is transported by electro-convection only.[8] For (iii) to account for the observed results, the sum of the primary solvation numbers of Na^+ and Cl^- would have to be 7, a not unreasonable value.

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[8] Despic and Hills, *Discuss. Faraday Soc.*, 1956, **21**, 150, 204.