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Coupling of Ion and Water Fluxes in Synthetic Membranes

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ABSTRACT

When the salt fluxes across a fixed charge membrane predicted by the Teorell-Meyer-Sievers (TMS) theory are compared with experiment it is found that in low-resistance ion-exchange membranes the coupling of ion and water fluxes should be taken into account. An examination of equivalent conductance and electro-osmotic data show that coupling occurs to different extents for counterions and co-ions. A satisfactory practical correction is achieved when all sorbed electrolyte, co-ions and counterions, is treated as fully coupled with the osmotic flux while those counterions that exactly balance the fixed charges are regarded as unaffected by the osmotic flux. This procedure can be shown to have a phenomenological justification in terms of the behaviour of pair-wise frictional coefficients.

INTRODUCTION

The Teorell (10), Meyer and Sievers (6) (TMS) theory of membrane fluxes and potentials was developed originally to interpret the properties of some biological membranes. It was found to apply also to synthetic membranes of high electrical resistance (9). When, about thirty years ago, synthetic membranes of low electrical resistance, commonly called ion-exchange membranes, were introduced for technological uses involving the transport of large fluxes it was natural to interpret their behaviour in terms of the TMS theory. Furthermore it became possible to measure with considerable precision membrane parameters such as ion mobilities and concentrations, including the fixed-charge concentration, which appear in the TMS equations. These parameters cannot usually be measured in biological membranes. Hence the introduction of these synthetic membranes has enabled the TMS theory to be subjected to rigorous testing. This paper is concerned with the consequences of flux coupling for the TMS equations.

THEORY

The TMS theory is founded on two principles (11): ionic distributions across the membrane/solution interfaces are at equilibrium and can be described by the ideal Donnan equations, fluxes of ions in the membrane occur due to diffusion down their concentration gradients and migration along electric potential gradients. Such fluxes are described in the theory by the Nernst-Planck flux equation. This can be written

$$J_i = -u_i c_i (RT\, d\, \ell n\, c_i + z_i F\, d\psi)/dx \qquad (1)$$

where J_i is the flux density, u_i the absolute mobility and c_i the molar concentration of ions i (valency z_i) at the plane distant x from one face of the membrane where the local electric potential is ψ. R, T and F are the gas constant, absolute temperature and Faraday's number respectively.

Equation (1) is a differential equation and to evaluate the flux or potential difference between a particular pair of solutions it must be integrated across the membrane with the appropriate boundary conditions which are the ion concentrations and potentials in the membrane at its faces (7). Conservation requirements connecting the concentrations and fluxes of the various ionic species with local electric neutrality and the net electric current simplify the problem.

An ion exchange membrane consists of a homogeneous crosslinked polymeric network to which ionizable groups are covalently bound and into which water penetrates dissociating the ionizable groups and hydrating the ions. When the sorption of electrolyte from a surrounding solution by such a membrane is measured it is found that to describe the concentration dependence of this sorption two non-ideality corrections θ and β have to be introduced into the ideal Donnan distribution expression (5). The corrected expression is

$$c_+^{\nu_+} c_-^{\nu_-} = (\theta\, C_s)^{\beta\nu} \qquad (2)$$

where ν_+ and ν_- are the stoichiometric numbers of cations and anions per mole of electrolyte, ν is their sum and C_s the molar concentration of the solution. θ is effectively a ratio of activity coefficients and is close to unity. β is a function of the dispersity of the distribution, at the molecular level, of the fixed charges in the macroscopically homogeneous membrane.

Once θ and β have been determined experimentally, the flux equation (1) can be tested. It is found that the flux of salt down a concentration gradient across the membrane is usually less than that predicted by equation (1). It has been recognized for a long time (2,8) that a part of this discrepancy is due to the omission from equation (1) of any terms relating to the coupling of fluxes in the membrane by, for example, molecular friction.

When salt diffuses through a membrane there is simultaneously an osmotic flow of solvent (although the reflection coefficient may be a good deal less than unity) usually in the opposite direction from the salt flux. This solvent flux is expected to interact frictionally with and so to reduce the salt flux. Thus the Nernst-Planck equation should be modified to

$$J_i = -u_i c_i (RT\, d\,\ell n\, c_i + z_i F\, d\,\psi)/dx + \alpha_i c_i v \qquad (3)$$

where v is the volume flux density in the membrane and α_i measures the strength of interaction between the ion and volume (mainly solvent) flows.

In the early uses (2,8) of equation (3) α_i was omitted, i.e. set at unity, which assumes in effect that the friction between ions and the membrane matrix equals the friction between water molecules and the membrane matrix. This is unlikely to be true because counterions are electrostatically attracted by and co-ions repelled by the matrix whereas its interaction with water is determined by Van der Waals forces of all kinds. It is to be expected that α_i will depend on the charge, size and polarizability of i.

ELECTRO-OSMOSIS

One of the most direct ways of observing coupling between ion and water flows is by the study of electro-osmosis. In the absence of any concentration difference across a fixed-charge membrane an electric current drives a considerable flux of water (exceeding in some cases 50 mol F^{-1}) usually in the direction of the counterion current.

When equation (3) is written for this electro-osmotic experiment it reduces readily to

$$\Lambda_i = |z_i|(F^2 D_i/RT + \alpha_i\, k\, t_w V_w/z_i) \qquad (4)$$

Here Λ_i is the equivalent conductance and D_i the tracer diffusion coefficient of i in the membrane at the constant concentration c_i, k is the specific conductance, t_w the transference number in mol F^{-1} and V_w the molar volume of water in the membrane.

Λ_i is obtained from data on the ionic concentrations and transport numbers together with the value of k. D_i and t_w can readily be measured with synthetic ion-exchange membranes. Thus equation (4) can be used to evaluate α_i from the data.

Such measurements have been made with NaBr and with $SrBr_2$ in the cation exchange membrane Zeo-Karb 315. This is a phenol sulphonate crosslinked with formaldehyde. Its principal properties are in Table 1.

TABLE 1 Properties of Zeo-Karb 315 membranes per kg of Na^+ form fully swollen in water

$\frac{\text{Fixed charge content}}{\text{equiv.}}$	$\frac{\text{Volume}}{m^3}$	$\frac{\text{Water content}}{\text{kg}}$
0.486	0.887×10^{-3}	0.665

The behaviour of α_i as a function of concentration for each ion is shown in Fig. 1. It is seen that $\alpha_i \approx 0.5$ for Na^+ and Sr^{2+} which means that the average interaction between the counterions and the matrix is a good deal stronger than that between water and the matrix; a consequence of the electrostatic attraction concentrating the counterions into the vicinity of the fixed charges.

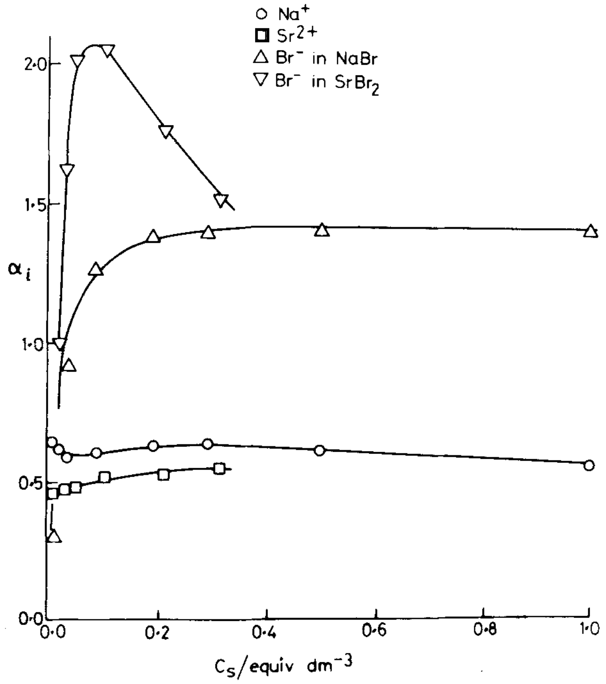

Fig. 1. The solvent drag coefficient α_i determined from conductance, electro-osmotic and tracer diffusion coefficients in Zeo-Karb 315 cation selective membrane in sodium and strontium bromide solutions at 25°C.

For the co-ions Br^-, which are repelled by the matrix and so prefer regions of high water content and low fixed charge density, α_i takes values greater than unity at the higher concentrations. At very low concentrations, when very few co-ions are present, they occupy only regions of abnormally low fixed-charge density and in which there will therefore be very little electro-osmotic activity. This probably explains the small values to which α_{Br} falls as C_s approaches zero.

DISCUSSION

Clearly it is not practicable to seek to introduce the effects of flux coupling or "osmotic drag" as it is sometimes called, into the original TMS theory by using instead of the Nernst Planck equation, equation (3) in which the value of α_i has to be determined as a function of concentration for each ion in each membrane.

A more thorough examination of the nature and effect of flux coupling has been made through the evaluation of pair-wise friction coefficients (4). A consideration of these leads to the concept of dividing the counterions into two populations. One group of counterions is always present in the membrane and serves to balance the charge carried by the ions covalently bound to the membrane. These counterions will normally be located in the general vicinity of the membrane matrix. The other group of counterions can be thought of as balancing or accompanying the co-ions absorbed from the aqueous solutions in contact with the membrane. These counterions may be expected to spend most of their time together with, but dissociated from, the co-ions in those volume elements of the membrane where water is most concentrated and where contact with the matrix is comparatively rare.

The effect of coupling with the osmotic flow on the flux of the former group of counterions can be disregarded. By setting α_i equal to unity for the latter group of counterions and for the co-ions i.e. for the "sorbed electrolyte", one can obtain a quantitatively satisfactory correction for the influence of ion and water flux coupling on the diffusion flux of salt while retaining all of the principles of the TMS theory.

This procedure was proposed twenty five years ago on intuitive grounds only (2). The results of subsequent experience and the growth of understanding about membrane processes have been to confirm that this approximate procedure has a genuine foundation. In the author's experience osmotic drag can reduce the salt flux by up to 10%. A more serious error and uncertainty is introduced into the prediction of fluxes from the TMS theory when one integrates the flux equation across the membrane while assuming that the ionic mobilities are independent of the local concentration. Although this assumption may be satisfactory in the case of the co-ions there is much data (3) which shows that the average mobility of the counterions may fall by a factor of up to two-fold as the ambient concentration is reduced from moderate values, comparable with the fixed charge concentration, towards zero.

REFERENCES

1. McHardy, W.J., Meares, P., Sutton, A.H. & Thain, J.F.: Electrical transport phenomena in a cation-exchange membrane Part II. Conductance and electro-osmosis. J. Colloid Interf. Sci. 29: 116-128, 1969.
2. Mackie, J.S. & Meares, P.: The diffusion of electrolytes in a cation-exchange resin membrane Parts I & II. Proc. Royal Soc. (London) A 232: 498-509, 510-518, 1955.
3. Meares, P.: Diffusion in ion-exchange polymers. In: Diffusion in Polymers (ed. J. Crank & G.S. Park) pp. 373-428. Academic Press, London, 1968.
4. Meares, P.: Some uses for membrane transport coefficients. In: Charged Gels and Membranes III.1 (ed. E. Selegny) pp. 123-146. Reidel, Dordrecht, 1976.
5. Meares, P.: The permeability of charged membranes. In: Transport Mechanisms in Epithelia (ed. H.H. Ussing & N.A. Thorn) pp. 51-67. Munksgaard, Copenhagen, 1973.
6. Meyer, K.J. & Sievers, J.-F.: La permeabilite des membranes I, II, IV & V. Helv. Chim. Acta 19: 649-664, 665;677, 987-995, 1936. 20: 634-644, 1937.
7. Schlögl, R.: Stofftransport durch Membranen. Steinkopf Verlag, Darmstadt, 1964.
8. Schlögl, R. & Schödel, U.: Über das Verhalten geladner Porenmembranen bei Stromdurchgang. 5: 372, 1955.
9. Sollner, K.: The early developments of the Electrochemistry of Polymer Membranes. In: Charged Gels and Membranes III.1 (ed. E. Selegny) pp. 3-55. Reidel, Dordrecht, 1976.
10. Teorell, T.: An attempt to formulate a Quantitative Theory of Membrane Permeability. Proc. Soc. Exptl. Biol. and Med. 33: 282-285, 1935. *Zur quantitaven Behandlung der Membran permeabilitat. Z. Elektrochem.* 55: 460-469, 1951.
11. Teorell, T.: Transport Processes and Electrical Phenomena in Ionic Membranes. In: Progress in Biophysics and Biophysical Chemistry III (ed. J.A.V. Butler & J.T. Randall) pp. 305-369. Pergamon, London, 1953.

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