CORRELATION OF ELECTRICAL AND PERMEABILITY PROPERTIES OF ION-SELECTIVE MEMBRANES

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ABSTRACT The linear phenomenological equations giving particle and practical fluxes of a single electrolyte across an ion-selective membrane are stated and interrelated. It is shown that the experimental measurements commonly made in biological and synthetic membrane studies may be used, with minor modification, to obtain the phenomenological transport coefficients and their concentration dependences. It is demonstrated that the electrical properties of a homogeneous membrane may be obtained as functions of the bathing solution concentration by combining fluxes measured under open and short circuit. Attention is paid to the use of radiotracers when measuring ionic fluxes. To obtain all the phenomenological coefficients at least one measurement must be made under a pressure gradient. The experimental difficulties in such measurements are discussed and the merits and demerits of various experiments considered. The problems of measuring potentials and concentrations at the low pressure face of a supported membrane make several mathematically simple approaches experimentally unattractive. The best methods appear to be either the measurement of a succession of "apparent osmotic pressures" under concentration differences sufficiently small that the membrane does not require support or the study of "reverse osmosis". Sets of equations are given which enable the phenomenological coefficients to be evaluated from convenient experiments. With a stable homogeneous membrane nine coefficients may be obtained thus enabling either the applicability of the reciprocal relations or the applicability of linear theory under the conditions of the experiments to be tested. For a discontinuous system the six independent coefficients may be obtained from experiments in a single membrane cell.

Introduction

The application of nonequilibrium thermodynamics to transport processes across ion-selective membranes has been explored in many theoretical discussions and criteria have been developed which permit an assessment of the validity of particular transport mechanisms. These theoretical developments have not been paralleled by experimental developments enabling the new theories to be widely exploited. The purpose of this paper is to draw attention to a number of relatively minor modifications to common experimental techniques which would permit a closer integration of the so called linear nonequilibrium thermodynamic theory and experiment.

We shall consider only the passive fluxes of water and a single salt, dissociating into two kinds of ions, across a membrane under isothermal conditions and in the steady state of flow.

Nonequilibrium thermodynamics permits the electrical and permeability properties, and the relations between them, to be set down rigorously subject usually to the restriction that the whole system is not too far from equilibrium. Because the electrical properties can be measured easily and accurately, whereas, the permeabilities can be measured only with difficulty and often with lower accuracy, information on permeabilities is frequently sought from electrical measurements. Even in chemically simple systems the exact relations between the electrical and permeability properties are often complex because of the interactions between the fluxes of different species.

To discuss a passive ion flux three independent driving forces are needed. These may conveniently be related to the gradients of electric potential, hydrostatic pressure, and concentration. The number of independent fluxes which have to be considered must equal the number of distinguishable substances transportable in the membrane. That is three (two ionic species and water) in the case being considered here.

In this simple case the minimum number of experimental coefficients needed to characterize the transport properties is six and usually these are strong and unknown functions of the concentrations. Because so many coefficients have to be measured to characterize completely each membrane plus solution system, a quantitative application of nonequilibrium thermodynamics to the interpretation of experimental data cannot readily be made a routine procedure. By choosing experimental situations in which some of the fluxes and forces equal zero the general relations take on simpler forms.

The choice of the definitions of the fluxes and forces is to some extent flexible, subject to the thermodynamic requirement that the sum of the products of fluxes and forces must give the rate of entropy production or the rate of dissipation of free energy due to the irreversible processes taking place in the system. In theoretical discussions it has been convenient to choose as fluxes the flows of the distinguishable molecular particles and as forces the gradients of the generalized electrochemical potentials of these particles. The relations and restrictions which result from setting some of these fluxes and forces at zero do not readily lend themselves to experimental study.

A choice of fluxes more closely related to experimental quantities and the identification of the appropriate forces to conjugate with them was made and its advantages demonstrated several years ago (Staverman, 1952; Michaeli and Kedem, 1961; Kedem and Katchalsky, 1963; Schlögl, 1964). Nevertheless, experimenters have not yet made wide use of these developments. We shall therefore briefly restate the basic principles before relating them to the design of experiments which can be readily performed.

The Practical System of Fluxes and Forces

The membrane system will be treated as discontinuous because flux measurements are made by observing changes in the phases outside the membrane. Later we shall discuss how far, in the case of a homogeneous and isotropic membrane, the results may also be interpreted in terms of the properties of a continuous system.

The dissipation function of the discontinuous system is given by

$$T\,dS_i/dt = A(\phi_1\Delta\eta_1 + \phi_2\Delta\eta_2 + \phi_w\Delta\mu_w). \tag{1}$$

dS_i/dt is the rate of entropy production due to the irreversible processes, T the absolute temperature, and A the membrane area. ϕ_1 and ϕ_2 are the molar fluxes per cm^2 of the cations and anions respectively and ϕ_w the molar flux per cm^2 of water. The fluxes are taken as positive in the direction opposite from that chosen for expressing the increases in potentials. $\Delta\eta_1$ and $\Delta\eta_2$ are the differences in the electrochemical potentials of the cations and anions between the two external solutions and $\Delta\mu_w$ the difference in the chemical potential of water.

Close to equilibrium the flows and forces are connected by linear relations and the following equations connect the particle flux densities ϕ_i and the forces $\Delta\eta_i$ and $\Delta\mu_w$

$$\phi_1 = L_{11}\Delta\eta_1 + L_{12}\Delta\eta_2 + L_{13}\Delta\mu_w \tag{2 a}$$

$$\phi_2 = L_{21}\Delta\eta_1 + L_{22}\Delta\eta_2 + L_{23}\Delta\mu_w \tag{2 b}$$

$$\phi_w = L_{31}\Delta\eta_1 + L_{32}\Delta\eta_2 + L_{33}\Delta\mu_w\,. \tag{2 c}$$

The number of independent phenomenological cross coefficients $L_{ik}(i \neq k)$ may be reduced from six to three by making use of the reciprocal relations $L_{ik} = L_{ki}$ of Onsager.

Because the individual fluxes and electrochemical potential gradients cannot be experimentally separately controlled equations 2 are transformed into a new set of forces and fluxes more suitable for describing experiments. Any linear transformation which leaves the value of the dissipation function unaltered is permissible and we follow in general a treatment given by Kedem and Katchalsky (1963).

The independent fluxes chosen are:

(i) the flux of cations per cm^2 ϕ_1

(ii) the defined flux of volume per cm^2 ϕ_v

(iii) the electric current density i

where ϕ_v and i are related to the particles fluxe by

$$\phi_v = V_s\phi_1/\nu_1 + V_w\phi_w \tag{3}$$

$$i = F(z_1\,\phi_1 + z_2\,\phi_2). \tag{4}$$

Here V_s and V_w are the partial molar volumes of the salt and water respectively, z_1 and z_2 are the valencies of the cation and anion respectively, including a negative sign for z_2, and ν_1 is the number of cations formed per mole of salt.

This liner transformation of the particle fluxes into the new fluxes is described by means of the matrix

$$\begin{pmatrix}\phi_1\\ \phi_v\\ i\end{pmatrix} = \begin{pmatrix}1 & 0 & 0\\ V_s/\nu_1 & 0 & V_w\\ z_1 F & z_2 F & 0\end{pmatrix} \cdot \begin{pmatrix}\phi_1\\ \phi_2\\ \phi_w\end{pmatrix}. \tag{5}$$

It may be shown that the new forces X_α which conjugate correctly with the new fluxes are obtained from the original forces by transformation with the inverse transpose of the matrix equation 5 (Fitts, 1963). Thus,

$$\begin{pmatrix}X_1\\ X_v\\ X_i\end{pmatrix} = \begin{pmatrix}1 & -z_1/z_2 & -V_s/\nu_1 V_w\\ 0 & 0 & 1/V_w\\ 0 & 1/z_2 F & 0\end{pmatrix} \cdot \begin{pmatrix}\Delta\eta_1\\ \Delta\eta_2\\ \Delta\mu_w\end{pmatrix} \tag{6}$$

$$X_1 = \Delta\eta_1 - z_1\Delta\eta_2/z_2 - \Delta\mu_w V_s/\nu_1 V_w \tag{7}$$

$$X_v = \Delta\mu_w/V_w \tag{8}$$

$$X_i = \Delta\eta_2/z_2 F. \tag{9}$$

The chemical potential difference of the salt $\Delta\mu_s$ is given by

$$\Delta\mu_s = \nu_1\Delta\eta_1 + \nu_2\Delta\eta_2\,. \tag{10}$$

To take account of a pressure difference p we must write

$$\Delta\mu_i = (\Delta\mu_i)_{p,T} + pV_i \qquad (i = s,\ w) \tag{11}$$

where the pressure dependence of V_i is neglected and $(\Delta\mu_i)_{p,T}$ is the concentration dependent part of $\Delta\mu_i$.

The difference in osmotic pressure π is

$$\pi = -(\Delta\mu_w)_{p,T}/V_w \tag{12}$$

which in view of equation 11 gives

$$\Delta\mu_w = V_w(p - \pi). \tag{13}$$

If the potential difference E between the outer solutions is recorded with electrodes reversible to the anions

$$E = \Delta\eta_2/z_2F. \tag{14}$$

Consideration of the Gibbs-Duhem equation shows that it is meaningful to define a mean salt concentration $\bar{c}_s$ by

$$\bar{c}_s = \pi/RT\Delta \ln a_s = \pi/(\Delta\mu_s)_{p,T} \tag{15}$$

where a_s is the activity of salt.

When equations 10–15 are substituted into equations 7–9 we find

$$X_1 = \pi(1 + \bar{c}_s V_s)/\nu_1\bar{c}_s \simeq \pi/\nu_1\bar{c}_s \tag{16}$$

$$X_v = p - \pi \tag{17}$$

$$X_i = E. \tag{18}$$

The approximate equality in equation 16 holds when the volume fraction of salt $\bar{c}_s V_s$ is very much less than unity.

The practical phenomenological flux equations are therefore

$$\phi_1 = L_\pi(\pi/\nu_1\bar{c}_s) + L_{\pi p}(p - \pi) + L_{\pi E}E \tag{19 a}$$

$$\phi_v = L_{p\pi}(\pi/\nu_1\bar{c}_s) + L_p(p - \pi) + L_{pE}E \tag{19 b}$$

$$i = L_{E\pi}(\pi/\nu_1\bar{c}_s) + L_{Ep}(p - \pi) + L_E E. \tag{19 c}$$

It is desirable that experiments intended to characterize the permeability properties of a membrane should give results which can be expressed as definite and simple functions of the $L_{\alpha\beta}$-coefficients in equations 19. ($L_{\alpha\beta}$ is used to distinguish the coefficients of equations 19 from the L_{ik}-coefficients of equations 2. The precise connections between these coefficients are given in appendix 3.)

Some Practical Considerations

The difference between the osmotic pressures of the solutions on opposite sides of the membrane π is straightforwardly evaluated in the case of solutions of a single salt whose thermodynamic properties are tabulated as functions of concentration. The measurement of a hydrostatic pressure difference across the membrane introduces no problems of principle. The potential E used here is the potential difference between a pair of standard electrodes reversible to the anions (e.g. silver/silver halide electrodes) immersed in the two solutions. If it is preferred to use instead electrodes reversible to the cations (e.g. Na^+-sensitive glass electrodes) equations 19 are still valid provided subscript 1 is read as referring to the anions and subscript 2 to the cations.

It has to be taken into account that the electromotive force (emf) of an Ag/AgCl electrode, and of most other electrodes, is a function of pressure. Thermodynamic analysis shows that in experiments where $p \neq 0$ a correction has to be applied to the observed potential difference E (obs) to obtain E. They are related by

$$E = E\,(\text{obs}) - p(V^{s}_{\text{AgCl}} - V^{s}_{\text{Ag}})\,F \tag{20}$$

where V^{s}_{AgCl} and V^{s}_{Ag} are the molar volumes of solid AgCl and Ag respectively.

The design and siting of the electrodes requires careful consideration when the potential has to be determined accurately across a low resistance membrane immersed in dilute solutions during the passage of an electric current. This problem is greatly simplified when the membrane is of high resistance.

The measurement of the electric current i requires no special comment. The ionic flux ϕ_1 may be measured in various ways. Frequently, instead of analyzing for concentration changes due to the flux (which are undesirable anyway since they produce changes in π) radiotracers are used to measure ϕ_1. Unless proper precautions are taken the use of tracers can introduce theoretical problems which are discussed below. The flux ϕ_v is defined in equation 3. Provided the electrodes supplying the current i are, like the potential determining electrodes, reversible to the anions (or the cations if ϕ_1 is replaced by the anion flux) ϕ_v is the rate of increase of volume of the solutions on the outgoing side per cm² of membrane. The volume change observed in, for example, a capillary tube attached to the membrane cell records as well the volume change due to the electrode reaction. Thus, if ϕ_v (obs) is the observed rate of volume increase per cm² of membrane, then when using, for example, Ag/AgCl electrodes

$$\phi_v = \phi_v\,(\text{obs}) + i(V^{s}_{\text{AgCl}} - V^{s}_{\text{Ag}})/F. \tag{21}$$

It must be strongly emphasized that the sets of linear flux equations 2 and 19 are not generally valid thermodynamic equations. They hold only over a range close to equilibrium where the transport properties of the membrane as expressed by the L_{ik}- and $L_{\alpha\beta}$-coefficients do not depend explicitly on the magnitudes of the applied forces. Thus, any electric potential gradient set up across the membrane must be insufficient to appreciably disturb the orientation of the molecular dipoles or to polarize the distribution of substances in the membrane. In studying a pressure force the applied pressures must not affect the local molecular Brownian motion inside the membrane by bulk compression so reducing the "free volume"[1] of the membrane material nor must they affect appreciably the composition of the membrane when at equilibrium with the bathing solutions.

In general, all the coefficients are functions of the concentrations of the substances present in the membrane and hence they will appear to be functions of π. This complicates the interpretation of fluxes measured when $\pi \neq 0$. It is important to distinguish between the circumstance that the $L_{\alpha\beta}$-coefficients are functions explicitly of the concentrations only so that their apparent dependence on π arises only from their dependence on the concentrations chosen to set up the osmotic pressure difference π and the circumstance that the $L_{\alpha\beta}$-coefficients are also explicit functions either of the osmotic force itself or of diffusion potentials caused by the concentration gradient. In the former case the restrictions inherent in the linear theory may still be obeyed, in the latter case they are not.

Even when the forces E, p, and π are each sufficiently small that the linear equations might be expected to hold, nonlinear phenomena may arise in certain circumstances in which two sets of steady fluxes may be observed corresponding with a given set of forces and external concentrations (Teorell, 1959; Franck, 1963).

In order to be useful the linear approximation must hold satisfactorily over a range of forces and concentrations wide enough to be of practical interest. This range of validity will vary from membrane to membrane. There is very little clear evidence at present to suggest how wide the range is likely to be in various types of membranes. Such evidence must be sought in experimental studies as well as in theoretical discussion of membrane structure and properties at the molecular level. The equations given in the remainder of this paper linking experimental quantities with $L_{\alpha\beta}$-coefficients have all been derived on the assumption that the linear approximation holds. It is our hope that experimental studies on many types of membranes may be carried out in such a way as to test these equations and determine their ranges of utility. From such studies we may discover whether the linear nonequilibrium thermodynamic theory of membrane phenomena has practical value or whether it is but a stepping stone on the way to developing a more elaborate and satisfactory nonlinear theory.

Experiments with $\pi = 0$ and $p = 0$

We shall deal first with the case of zero pressure and osmotic pressure differences. Equations 19 with $\pi = 0$ and $p = 0$ reduce to

$$\phi_1 = L_{\pi E} E \qquad (22\,a)$$

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[1] "Free volume" is used here in the sense in which it occurs in the kinetic theory of liquids and it does not refer to pore volume in the membrane.

$$\phi_v = L_{pE}E \tag{22 b}$$

$$i = L_E E. \tag{22 c}$$

From equations 22 we easily derive

$$(i/E)_{\pi,p=0} = L_E = \kappa \tag{23 a}$$

$$(\phi_1/i)_{\pi,p=0} = L_{\pi E}/L_E = t_1/z_1F \tag{23 b}$$

$$(\phi_v/i)_{\pi,p=0} = L_{pE}/L_E = W. \tag{23 c}$$

These well known relations identify L_E with κ the membrane conductance, and L_{pE} with κW where W is the rate of electroosmotic flow of volume at unit current. Both κ and W can be determined by simple experiments bearing in mind the need to correct for the volume of the electrode reaction (equation 21). $L_{\pi E}$ is seen to be directly related to the transport number t_1 of the cations.

The restriction $\pi = 0$ requires that the external solutions have equal concentrations c_s but the values of L_E, $L_{\pi E}$ and L_{pE} depend upon the particular value of c_s. By carrying out experiments at a series of concentrations c_s the variations of L_E, $L_{\pi E}$, and L_{pE} with c_s may be found. The range of linear behavior may be checked by confirming that L_E, $L_{\pi E}$ and L_{pE} are independent of E and i.

The Use of Radiotracer Ions

If it is desired to measure ϕ_1 with the help of radiotracers this may be done by measuring the tracer flux in the direction against the electric current and then in the direction of the current. The net flux ϕ_1 is given by

$$\phi_1 = \phi_1'(F) - \phi_1'(B) \tag{24}$$

where $\phi_1'(F)$ and $\phi_1'(B)$ are the whole unidirectional fluxes of species 1 in the direction of the electric current and in the direction against the electric current respectively. $\phi_1'(F)$ and $\phi_1'(B)$ are determined, as is usual in flux studies using radiotracers, by dividing the observed flux of tracer by the specific activity of tracer at the ingoing face of the membrane and correcting if necessary for effects due to nonzero activity at the outgoing face of the membrane (Meares and Sutton, 1968).

In an unsymmetrical system it may be convenient to label only one side with tracer and to pass the electric current in only one direction. The evaluation of t_1 from a single tracer flux is complicated by interaction between the fluxes of tracer and nontracer ions of the same species. This difficulty may be overcome by determining the tracer flux first with the current i passing and then with zero current i.e., $\phi_1'(0)$. $\phi_1'(0)$ is often called the "self-diffusion flux".

Theoretical analysis (Meares and Sutton, 1968) shows that provided i is small enough for the linear equations to be valid the effects due to interaction of tracer with nontracer may be eliminated and the transport number calculated from

$$t_1 = \frac{z_1 F\phi_1'(0)}{i} \ln\left(1 + \frac{i t_1}{z_1 F\phi_1'(B)}\right) \tag{25}$$

$$t_1 = \frac{z_1 F\phi_1'(0)}{i} \ln\left(1 - \frac{i t_1}{z_1 F\phi_1'(F)}\right) \tag{26}$$

depending on whether $\phi_1'(B)$ or $\phi_1'(F)$ was determined together with $\phi_1'(0)$.

Equations 25 and 26 cannot be solved conveniently. Instead the right-hand sides are calculated from the observed uni-directional fluxes for a series of values of t_1 and plotted against t_1. The true value of t_1 is obtained from the intersection of either of these plots with a plot of t_1 against t_1 on the same graph.

The use of equations 25 and 26 is demonstrated in Fig. 1. The transport number of the Br$^-$ co-ions in the homogeneous cation exchange membrane Zeo-Karb 315 has been measured by determining $\phi_{\mathrm{Br}}'(0)$, $\phi_{\mathrm{Br}}'(F)$ and $\phi_{\mathrm{Br}}'(B)$. From these data t_{Br} can be evaluated in three ways, from equations 23 *b* and 24, from equation 25 and from equation 26. It is seen that excellent agreement is obtained between the three methods. In these experiments it was found that no departures from linear

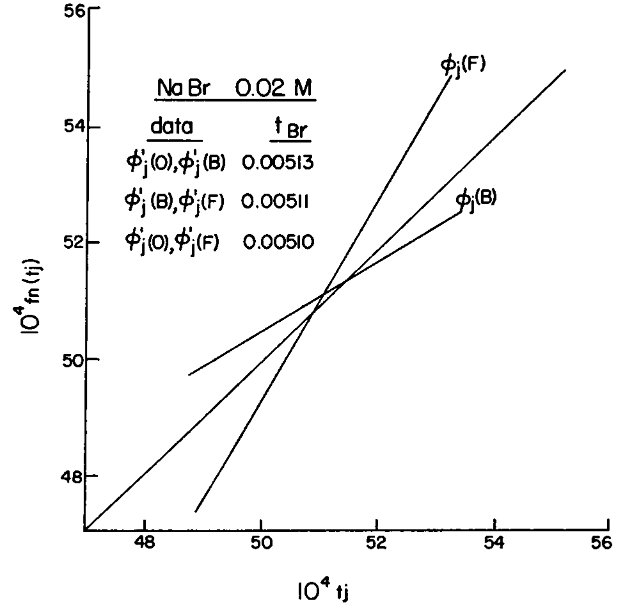

Figure 1 The evaluation of the transport number of Br$^-$ co-ions in a Zeo-Karb 315 cation exchange membrane in 0.02 M NaBr using radiotracer fluxes of Br$^-$ (Meares and Sutton, 1968). The unlabelled line is at 45° to the axes, that labelled $\phi_j'(B)$ is the right-hand side of equation 25 plotted against t_j, line $\phi_j'(F)$ is from equation 26.

behavior by the membrane were observed even at current densities of 10 ma/cm². The upper limits of study were set by the efficiency of stirring especially in dilute solutions.

Experiments with $\pi \neq 0$ and $p = 0$

We shall now consider the case when the solutions have different concentrations ($\pi \neq 0$) while retaining the restriction $p = 0$. Two classes of measurements can be conveniently performed. They are under open circuit conditions ($i = 0$) and under short circuit conditions ($E = 0$). Notice that this short circuit condition is defined relative to the potential between *reversible* electrodes. If other electrodes, for example normal calomels and connecting bridges, are used it is necessary to determine the value of the observed PD which corresponds with the condition $E = 0$.

Substituting the appropriate conditions into equations 19 under the restrictions $p = 0$ and $i = 0$ gives

$$(E/\pi)_{p=0}^{i=0} = (L_{Ep} - L_{E\pi}/\nu_1\bar{c}_s)/L_E \tag{27}$$

for the membrane potential and the following for the osmotic and salt diffusion fluxes

$$\left(\frac{\phi_v}{\pi}\right)_{p=0}^{i=0} = \frac{L_{pE}\,(L_{Ep} - L_{E\pi}/\nu_1\bar{c}_s)}{L_E} + \frac{L_{p\pi}}{\nu_1\bar{c}_s} - L_p \tag{28}$$

$$\left(\frac{\phi_1}{\pi}\right)_{p=0}^{i=0} = \frac{L_{\pi E}\,(L_{Ep} - L_{E\pi}/\nu_1\bar{c}_s)}{L_E} + \frac{L_\pi}{\nu_1\bar{c}_s} - L_{\pi p}. \tag{29}$$

When $p = 0$ and $E = 0$ we have the short circuit current given by

$$(i/\pi)_{p,E=0} = L_{E\pi}/\nu_1\bar{c}_s - L_{Ep} \tag{30}$$

while for the volume and cation fluxes under short circuit the relations are

$$(\phi_v/\pi)_{p,E=0} = L_{p\pi}/\nu_1\bar{c}_s - L_p \tag{31}$$

$$(\phi_1/\pi)_{p,E=0} = L_\pi/\nu_1\bar{c}_s - L_{\pi p}\,. \tag{32}$$

So far we have not used the reciprocal relations

$$L_{Ep} = L_{pE}\,; \qquad L_{E\pi} = L_{\pi E}\,; \qquad L_{p\pi} = L_{\pi p} \tag{33}$$

which reduce from nine to six the number of $L_{\alpha\beta}$-coefficients. It might be thought that the six equations 27–32 define six experiments from which the six independent $L_{\alpha\beta}$-coefficients could be determined. Unfortunately, when the reciprocal relations are introduced only five of the resulting equations are independent. It is readily confirmed that the relationship

$$\left(\frac{\phi_1}{\pi}\right)_{p,E=0} - \left(\frac{\phi_1}{\pi}\right)_{p=0}^{i=0} = \nu_1 \bar{c}_s \left[\left(\frac{\phi_v}{\pi}\right)_{p,E=0} - \left(\frac{\phi_v}{\pi}\right)_{p=0}^{i=0} - \left(\frac{E}{\pi}\right)_{p=0}^{i=0} \cdot \left(\frac{i}{\pi}\right)_{p,E=0}\right] \quad (34)$$

exists among the independent coefficients.

Because the linear flux equations were used to derive equation 34 the range of π over which linear behavior holds under both open and short circuit conditions may be studied by checking experimentally the validity of this equation. It may also be verified whether the linear relation, required by equation 19 *c*, holds by making small variations δi about the short circuit current and about $i = 0$, while holding π constant, and determining the variations of potential δE. For the combination of equations 28–32 to be valid, it is necessary that $(\partial i/\partial E)_{\pi,p}$ be independent of i over the range from zero up to the short circuit current. This will be true provided the concentration difference across the membrane, and consequently the short circuit current, are sufficiently small that changing from open to closed circuit conditions does not appreciably change the steady concentration profile in the membrane.

Average and Differential $L_{\alpha\beta}$-Coefficients

Before considering the development of another measurement in order to evaluate all the $L_{\alpha\beta}$-coefficients it is desirable to consider the nature of the coefficients which appear in equations 27–32. These coefficients are functions of the composition of the membrane system and consequently of the concentrations of the solutions. When $\pi \neq 0$ the coefficients in equations 27–32 are mean values averaged over the range between the concentrations c_1 and c_2 of the two solutions. The precise form of average is dictated by the concentration profile and hence by the unknown properties of the membrane. There is no reason to believe that the experimental values of the average coefficients are the true values for the membrane at the composition which is in equilibrium with a solution of the mean concentration $\bar{c}_s$ defined by equation 15.

If the experiments defined by equations 27–32 could be carried out with only a very small difference between the solution concentrations, say between c_s and $(c_s + dc_s)$, then the $L_{\alpha\beta}$-coefficients would refer to the membrane composition in equilibrium with solution at concentration c_s.

Coefficients determined under these conditions of a differential concentration gradient will be called the differential phenomenological coefficients of the discontinuous system and will be denoted by the script symbols $\mathcal{L}_{\alpha\beta}$.

If the membrane material is intrinsically homogeneous and uniform it may be shown that the $\mathcal{L}_{\alpha\beta}$-coefficients may be evaluated from a suitably chosen series of flux measurements made across finite concentration intervals. By intrinsically homogeneous and uniform it is meant that when the opposite sides are bathed by identical solutions the local transport properties of the membrane are the same at every point and when between two different solutions the local transport properties are functions only of the local concentrations. The necessary procedure is demonstrated below by considering the case of the osmotic permeability $(\phi_v/\pi)_{p=0}^{i=0}$ but analogous procedures can be used with the other fluxes and for the forces, in particular for the potential E.

Consider a set of experiments carried out at $p = 0$ and $i = 0$ and with the concentration c_s at one side of the membrane held constant at a reference concentration c_1 while that on the other side of the membrane c is varied. The volume flux will vary with c and a plot can be made of ϕ_v against c. The slope of this plot $(\partial\phi_v/\partial c)_{p=0,c_1}^{i=0}$ may be taken as defining a permeability coefficient $q_c(c)$.

This permeability coefficient is a function only of c and not of c_1 in a homogeneous membrane, as defined above, and under the linear conditions that the $L_{\alpha\beta}$-coefficients do not depend explicitly on the applied forces.

Under these restrictions we may write for the flux $\phi_v(c_1 \rightarrow c_3)$ from the reference solution c_1 into concentration c_3

$$\begin{aligned}\phi_v(c_1 \rightarrow c_3) &= \int_{c_1}^{c_3} q_c(c)\,dc = \int_{c_1}^{c_2} q_c(c)\,dc + \int_{c_2}^{c_3} q_c(c)\,dc \\ &= \phi_v(c_1 \rightarrow c_2) + \phi_v(c_2 \rightarrow c_3) \qquad (35)\end{aligned}$$

where $\phi_v(c_1 \rightarrow c_2)$ and $\phi_v(c_2 \rightarrow c_3)$ are the fluxes which would be observed from c_1 into c_2 and from c_2 into c_3 respectively.

Equation 35 demonstrates an additivity rule for ϕ_v which may readily be verified experimentally in order to confirm that measurements are being made under conditions to which the linear laws apply. By making a set of flux measurements with n solutions of different concentrations, increasing from c_1 to c_n, and studying these in adjacent and alternate pairs to check that the additivity of equation 35 always holds, a composite curve may be built up giving $\phi_v(c_1 \rightarrow c)$ versus c extending up to c_n since from equation 35

$$\phi_v(c_1 \rightarrow c_j) = \sum_{i=1}^{j-1} \phi_v(c_i \rightarrow c_{i+1}). \qquad (36)$$

The building up of such a curve does not imply that the linear flux equations would necessarily be obeyed if the membrane were interposed between a pair of solutions c_j and c_k if $|k - j| > 2$. The maximum intervals $(c_k \rightarrow c_j)$ over which the linear equations may be used have to be discovered by experiment.

We have confirmed that rules such as the one in equation 35 apply to ϕ_v, ϕ_1, and E under open circuit conditions in the homogeneous cation exchanger Zeo-Karb 315 over a wide concentration range. This is demonstrated for ϕ_v in sodium bromide in Table I. We have not tested the rule under closed circuit conditions.

A composite curve of flux versus concentration c relative to a reference concentration c_1 may readily be converted to the corresponding plot of flux versus $\pi(c_1, c)$, where $\pi(c_1, c)$ is the osmotic pressure difference between concentrations c_1 and c.

TABLE I

TEST OF EQUATION 35 FOR $(\phi_v)_{p=0}^{i=0}$ IN ZEO-KARB 315 HOMOGENEOUS CATION EXCHANGE MEMBRANE USING NaBr SOLUTIONS AT 25°C

c_1	c_2	c_3	$\phi_v(c_1 \rightarrow c_2)$	$\phi_v(c_2 \rightarrow c_3)$	$\phi_v(c_1 \rightarrow c_3)$	$[\phi_v(c_1 \rightarrow c_2) + \phi_v(c_2 \rightarrow c_3)]$
	molar			($cm^3\ cm^{-2}\ sec^{-1} \times 10^{-6}$)		
0.01	0.02	0.05	1.28	3.06	4.47	4.34
0.01	0.05	0.10	4.47	3.16	7.70	7.63
0.01	0.05	0.20	4.47	6.27	10.70	10.74
0.01	0.10	0.20	7.70	3.13	10.70	10.83
0.02	0.05	0.10	3.06	3.16	6.18	6.22
0.02	0.10	0.20	6.18	3.13	9.49	9.31
0.05	0.10	0.20	3.16	3.13	6.27	6.29
0.20	0.30	0.50	1.49	1.23	2.65	2.72
0.20	0.50	1.00	2.65	0.87	3.49	3.52
0.30	0.50	1.00	1.23	0.87	1.99	2.10

Continuing to consider for example ϕ_v the slope of the plot at concentration c may be found by a suitable graphical method. This slope may be written $[\partial\phi_v(c_1, \pi(c_1, c))/\partial\pi]_{p=0,c_1}^{i=0}$. By setting c_2 in equation 35 at c and c_3 at $(c + dc)$ it can be seen that

$$\left[\frac{\partial\phi_v(c_1, \pi(c_1, c))}{\partial\pi}\right]_{c_1} = \lim_{c_3 \to c}\left[\frac{\phi_v(c, \pi(c, c_3))}{\pi(c, c_3)}\right]_c \tag{37}$$

which is independent of the reference concentration c_1.

Expressions like equation 37 may be obtained for the other fluxes under open and closed circuit conditions. For brevity the right-hand side of equation 37 will in future be written as $(\partial\phi_v/\partial\pi)$, it being understood that it is a function explicitly of c, and similarly for the analogous quantities from other fluxes.

We now have to consider the relation of quantities such as $(\partial\phi_v/\partial\pi)$ to the $\mathcal{L}_{\alpha\beta}$-coefficients. If the forces and fluxes in equations 19 become infinitesimally small, the equations may be written in the differential forms

$$\partial\phi_1 = \mathcal{L}_\pi\partial(\pi/\nu_1 c_s) + \mathcal{L}_{\pi p}\partial(p - \pi) + \mathcal{L}_{\pi E}\partial E \tag{38 a}$$

$$\partial\phi_v = \mathcal{L}_{p\pi}\partial(\pi/\nu_1 c_s) + \mathcal{L}_p\partial(p - \pi) + \mathcal{L}_{pE}\partial E \tag{38 b}$$

$$\partial i = \mathcal{L}_{E\pi}\partial(\pi/\nu_1 c_s) + \mathcal{L}_{Ep}\partial(p - \pi) + \mathcal{L}_E\partial E. \tag{38 c}$$

The $\mathcal{L}_{\alpha\beta}$-coefficients are thus seen to conform to the general definition

$$\mathcal{L}_{\alpha\beta} = \lim_{\text{all } X \to 0}\left(\frac{\partial\phi_\alpha}{\partial X_\beta}\right)_{X_{\gamma \neq \beta}}. \tag{39}$$

The Onsager reciprocal relations hold for these $\mathcal{L}_{\alpha\beta}$-coefficients and, in addition, by arguments similar to those used to derive equations 27–32 a set of relations between quantities like $(\partial\phi_v/\partial\pi)^{i=0}_{p=0}$ and the $\mathcal{L}_{\alpha\beta}$-coefficients may be obtained from equation 38 *a*, *b*, and *c*.

These $\mathcal{L}_{\alpha\beta}$-coefficients may in many respects be interpreted as coefficients of the continuous membrane phase. We prefer however to denote them as differential phenomenological coefficients of the discontinuous system. They can be used to predict the fluxes which would occur across any given concentration interval between the solutions on opposite sides of the membrane provided the whole system continues to behave in accordance with the linear flux equations. The true phenomenological coefficients of the membrane regarded as a continuous system would give also the dependence of the coefficients on the space coordinates inside the membrane as well as on the ambient solution concentrations. These continuous coefficients could only be evaluated if the concentration profiles inside the membrane were determined separately under the conditions prevailing in the flux experiment.

Electrical Coefficients from Data at $\pi \neq 0$

In view of the foregoing argument we may rewrite equations 27–32 in the following differential forms

$$\left(\frac{\partial E}{\partial \pi}\right)^{i=0}_{p=0} = \frac{\mathcal{L}_{Ep} - \mathcal{L}_{E\pi}/\nu_1 c_s}{\mathcal{L}_E} \qquad (40)$$

$$\left(\frac{\partial \phi_v}{\partial \pi}\right)^{i=0}_{p=0} = \frac{\mathcal{L}_{pE}(\mathcal{L}_{Ep} - \mathcal{L}_{E\pi}/\nu_1 c_s)}{\mathcal{L}_E} + \frac{\mathcal{L}_{p\pi}}{\nu_1 c_s} - \mathcal{L}_p \qquad (41)$$

$$\left(\frac{\partial \phi_1}{\partial \pi}\right)^{i=0}_{p=0} = \frac{\mathcal{L}_{\pi E}(\mathcal{L}_{Ep} - \mathcal{L}_{E\pi}/\nu_1 c_s)}{\mathcal{L}_E} + \frac{\mathcal{L}_{\pi}}{\nu_1 c_s} - \mathcal{L}_{\pi p} \qquad (42)$$

$$(\partial i/\partial \pi)_{p,E=0} = \mathcal{L}_{E\pi}/\nu_1 c_s - \mathcal{L}_{Ep} \qquad (43)$$

$$(\partial \phi_v/\partial \pi)_{p,E=0} = \mathcal{L}_{p\pi}/\nu_1 c_s - \mathcal{L}_p \qquad (44)$$

$$(\partial \phi_1/\partial \pi)_{p,E=0} = \mathcal{L}_{\pi}/\nu_1 c_s - \mathcal{L}_{\pi p}\,. \qquad (45)$$

If equation 40 is compared with equation 23 it is seen that in view of the reciprocal relations $\mathcal{L}_{Ep} = \mathcal{L}_{pE}$ and $\mathcal{L}_{E\pi} = \mathcal{L}_{\pi E}$

$$(\partial E/\partial \pi)^{i=0}_{p=0} = W - t_1/z_1 F \nu_1 c_s \equiv A. \qquad (46)$$

Equation 46 is already well known; it is tested in Fig. 2 using data on Zeo-Karb 315. The very good agreement obtained is evidence that the experiments were carried out within the range of fluxes and forces to which the linear theory applies.

In the remainder of this section we shall use the reciprocal relations when required without comment. From equations 41–45 with the help of equation 23 it is

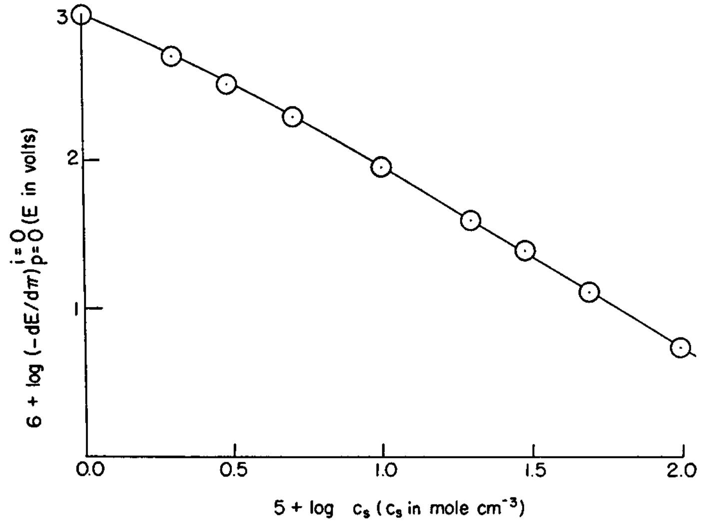

FIGURE 2 The differential cell potential $(\partial E/\partial \pi)_{p=0}^{i=0}$ of NaBr solutions and a Zeo-Karb 315 cation exchange membrane at 25°C. The points were calculated from equation 46 using measurements of the transport number and electroosmotic permeability made under constant concentration conditions at a number of concentrations c_s as in equations 23 *b* and *c* (Meares and Sutton, 1968; McHardy et al., 1968). The curve was obtained from a set of membrane potential measurements, made as defined by equation 27, and plotted as a composite curve built up by using an additivity rule like equation 36 relative to 0.01 M as reference concentration. A fifth order polynomial was fitted to this membrane potential curve and was then differentiated so as to enable $(\partial E/\partial \pi)$ to be calculated as a function of *c* (see equation 37). This $(\partial E/\partial \pi)$ is plotted here against $5 + \log c_s$ (c_s in mole cm^{-3}) to provide a clear display of the data.

straightforward to derive

$$(\partial i/\partial \pi)_{p,E=0} = -\kappa(W - t_1/z_1 F v_1 c_s) \equiv B \qquad (47)$$

$$\left(\frac{\partial \phi_1}{\partial \pi}\right)_{p=0}^{i=0} - \left(\frac{\partial \phi_1}{\partial \pi}\right)_{p,E=0} = \frac{t_1 \kappa}{z_1 F}\left(W - \frac{t_1}{z_1 F_1 c_s}\right) \equiv C \qquad (48)$$

$$\left(\frac{\partial \phi_v}{\partial \pi}\right)_{p=0}^{i=0} - \left(\frac{\partial \phi_v}{\partial \pi}\right)_{p,E=0} = W\kappa\left(W - \frac{t_1}{z_1 F_1 c_s}\right) \equiv D. \qquad (49)$$

Equations 46–49 define the four experimental quantities A, B, C, and D. It is easily verified that

$$-B/A = \kappa \qquad (50)$$

$$-D/B = W \qquad (51)$$

$$-z_1 F v_1 c_s(D/B + A) = t_1 \qquad (52)$$

$$-c_s B(D/B + A) = C \qquad (53)$$

and that

$$\mathfrak{L}_E = -B/A \tag{54}$$

$$\mathfrak{L}_{pE} = \mathfrak{L}_{Ep} = D/A \tag{55}$$

$$\mathfrak{L}_{\pi E} = \mathfrak{L}_{E\pi} = C/A\,. \tag{56}$$

Equations 50–52 show how the three electrical coefficients κ, W, and t_1 and their concentration dependence may be determined in an experimental system where the concentration can be varied on only one side of the membrane and the concentrations cannot be made equal. Indeed it is not necessary even to know the concentration on the inaccessible side provided it can be held constant.

If, for example, the membrane potential, short circuit current and the difference between the volume flows under open and short circuit conditions are measured, then the effect of short circuiting on the ion fluxes is given by equation 53. Other combinations of determined and derived quantities may readily be devised.

Equations 54–56 show that three of the $\mathfrak{L}_{\alpha\beta}$-coefficients at definite concentrations may be evaluated from these measurements made under concentration gradients, provided the experiments already commonly performed in membrane studies are carried out over appropriately chosen concentration ranges. The values of these $\mathfrak{L}_{\alpha\beta}$-coefficients should equal those of the corresponding $L_{\alpha\beta}$-coefficients determined from equations 22 *a*, *b*, and *c* at constant concentration.

Experiments with $p \neq 0$ *and* $\pi = 0$

In order to evaluate the remaining $\mathfrak{L}_{\alpha\beta}$-coefficients equations 44 and 45 may be used in combination with one additional equation. The experiments already described have exhausted the independent possibilities that exist with $p = 0$ and hence measurements are required with $p \neq 0$.

Many difficulties attend such experiments. In particular, if conditions such as $\pi = 0$ and $E = 0$ are to be met, immense care has to be taken in setting up the boundary conditions. For example, the thermodynamic force which results from a pressure difference of 1 atmosphere acting on a species of molar volume 20 cm^3/mole is equivalent to a potential difference of only 0.02 mv acting on a univalent ionic species or a difference between the mole fractions of the species at opposite faces of the membrane of 0.08% at 25°C. The problems of siting electrodes and stirring up to the surfaces of a membrane make such stringent requirements almost impossible to satisfy when the membrane has to be rigidly supported against the applied pressure. To overcome these experimental difficulties it has been suggested that the hydrostatic pressure difference may be replaced by an additional osmotic pressure π_i generated by a nonpermeating component added to the solution on one side of the membrane. This procedure, while superficially simple, introduces the complication that the thermodynamic properties i.e. activity coefficients, partial molar volumes etc. must be determined in the solution to which the nonpermeating component has been added. More serious is the fact that by lowering the activity of water in the solution the nonpermeating component may cause an osmotic deswelling of the membrane at one side and so alter its permeability properties. Applying a pressure to a supported membrane will have only little effect on its swelling unless the partial molar volume of water in the membrane is very different from that in the solution. The use of nonpermeating solutes to generate additional forces can be advocated in only those circumstances where sufficient data is collected to demonstrate that the procedure is valid.

Consider first that experiments can be conducted with $p \neq 0$ and $\pi = 0$ then from equations 19, 23, and 33 we readily find

$$(\phi_v/p)_{\pi=0}^{i=0} + W^2\kappa = L_p = (\phi_v/p)_{\pi,E=0} \tag{57}$$

for the volume flows under open and short circuit conditions. Experimentally the former is the simpler. The mechanical salt permeabilities give

$$(\phi_1/p)_{\pi=0}^{i=0} + Wt_1\kappa/z_1F = L_{\pi p} = (\phi_1/p)_{\pi,E=0}\,. \tag{58}$$

L_p and $L_{\pi p}$ determined in this way at constant concentration c_s are equal to $\mathcal{L}_p$ and $\mathcal{L}_{\pi p}$ evaluated at the same concentration.

Either equation 57 or 58 may be combined with equations 44 and 45 to determine $\mathcal{L}_p$, $\mathcal{L}_\pi$, and $\mathcal{L}_{p\pi}$. Probably L_p from $(\phi_v/p)_{\pi=0}^{i=0}$ is the easiest to measure.

The streaming potential $(E/p)_{\pi=0}^{i=0}$ and streaming current $(i/p)_{\pi,E=0}$ give $-L_{Ep}/L_E$ and L_{Ep} respectively. These can be compared with L_{pE} from the electroosmotic permeability either as a test of the reciprocal relation $L_{Ep} = L_{pE}$, which was used to derive equations 57 and 58, or, more realistically, to confirm that work is being carried out in the linear regime.

The electroosmotic pressure generated in a closed system ($\phi_v = 0$) by an electric current has often been discussed. If E is the PD we find from equations 19 and 23

$$-W\kappa(E/p)_{\pi=0}^{\phi_v=0} = L_p\,. \tag{59}$$

There are two problems in measuring Lp from the electroosmotic pressure. When a steady pressure is established there are fluxes of ions and water continuously flowing through the membrane. The problem of ensuring that $\pi = 0$ and that there is no concentration polarization at the supported face of the membrane has to be overcome. Secondly, when there is an electric current passing there is a volume change at the electrodes. Thus, from equation 21 $\phi_v \neq \phi_v(\text{obs})$. Experimentally one establishes $\phi_v(\text{obs}) = 0$ but equation 59 requires $\phi_v = 0$. Provided the volume change of the electrode reaction is small compared with W the error introduced in this way may not be important.

Experiments with $p \neq 0$ and $\pi \neq 0$

If the requirement $\pi = 0$ is dropped the determination of $\mathfrak{L}_p$ becomes in some respects simpler. We shall discuss two methods here. In the first two fluxes, ϕ_v and i, are kept at zero, π is chosen by the observer and p and E are measured. The value of p determined in this way is the "apparent osmotic pressure" used to determine the "reflection coefficient" p/π.

When the conditions $\phi_v = 0$ and $i = 0$ are imposed on equations 19 and E is eliminated we obtain

$$\left(\frac{p}{\pi}\right)^{\phi_v, i=0} = 1 + \left[\frac{L_E L_{p\pi} - L_{E\pi} L_{pE}}{\nu_1 \bar{c}_s (L_{Ep} L_{pE} - L_E L_p)}\right]. \qquad (60)$$

The problem that the $L_{\alpha\beta}$-coefficients in equation 60 are average values over the concentration range spanned by the osmotic pressure difference π has to be overcome as before by making a series of measurements of p while holding the concentration on one side of the membrane constant and varying that on the other. From the resulting curve of p versus π or c_s on the varying side we obtain $(\partial p/\partial \pi)^{\phi_v, i=0}$ by differentiation at any chosen c_s.

Introducing the reciprocal relations, substituting the electrical coefficients from equation 23 into equation 60 and differentiating subject to the restrictions discussed earlier gives

$$\left(\frac{\partial p}{\partial \pi}\right)^{\phi_v, i=0} = 1 + \left[\frac{z_1 \mathfrak{L}_{p\pi} - t_1 W_K}{z_1 F \nu_1 c_s (W^2{}_K - \mathfrak{L}_p)}\right]. \qquad (61)$$

By combining equation 61 with equation 41 $\mathfrak{L}_{p\pi}$ may be eliminated and

$$\mathfrak{L}_p = W^2{}_K - \left(\frac{\partial \phi_v}{\partial \pi}\right)^{i=0}_{p=0} \Big/ \left(\frac{\partial p}{\partial \pi}\right)^{\phi_v, i=0}. \qquad (62)$$

If instead of measuring the pressure difference at the "osmotic equilibrium" the potential difference is measured, by an analogous argument

$$\mathfrak{L}_p = \frac{W[(\partial \phi_v/\partial \pi)_{p,E=0} + W_K (\partial E/\partial \pi)^{\phi_v, i=0}]}{[(\partial E/\partial \pi)^{\phi_v, i=0} - 1]} \qquad (63)$$

is obtained. Equation 62 is of more practical value than equation 63.

It must be remembered that the "osmotic equilibrium" represents a quasi-steady state in which salt and water are diffusing across the membrane between relatively large sources and sinks. If the membrane requires to be supported against the pressure developed the control or measurement of the interfacial concentrations remains a problem. It is desirable, therefore, to work with a succession of small concentration intervals so that the membrane does not require support and to build up the p versus π curve as described in connection with ϕ_v by using the additivity rule of equation 36.

Finally we may consider a procedure to be called "reverse osmosis". In this procedure the membrane may be supported on a porous frit or similar material which should preferably be electrically nonconducting. Solution at a known and constant concentration is circulated under pressure on the unsupported side of the membrane. This causes fluxes of volume ϕ_v and salt ϕ_1. The experiment is carried out with $i = 0$ and hence the apparatus must be constructed in such a way that there is no metallic interconnection through the apparatus itself between the high and low pressure side solutions.

The apparatus volume on the low pressure side of the membrane is kept to a minimum and it fills with a solution of molar concentration given by ϕ_1/ϕ_v. Provided the upstream pressure and concentration are held constant the fluxes, and hence the downstream concentration, remain constant. Thus, no interfacial polarization problems arise. One measures ϕ_v and the downstream or effluent solution concentration ϕ_1/ϕ_v. From these data ϕ_1 is readily obtained.

If the upstream pressure is changed then ϕ_1 and ϕ_v will both change and a new steady condition will be established after a delay long enough to refill the downstream cell volume with the new effluent.

From equations 19 with the sole restriction $i = 0$ we obtain

$$\phi_v = \frac{\pi}{\nu_1 \bar{c}_s}\left(L_{p\pi} - \frac{L_{pE} L_{E\pi}}{L_E}\right) + (p - \pi)\left(L_p - \frac{L_{pE} L_{Ep}}{L_E}\right) \tag{64}$$

$$\phi_1 = \frac{\pi}{\nu_1 \bar{c}_s}\left(L_\pi - \frac{L_{\pi E} L_{E\pi}}{L_E}\right) + (p - \pi)\left(L_{\pi p} - \frac{L_{Ep} L_{\pi E}}{L_E}\right). \tag{65}$$

Introducing equation 28 into equation 64 and equation 29 into equation 65 gives

$$\left(\frac{\phi_v}{\pi}\right)^{i=0} = \left(\frac{\phi_v}{\pi}\right)_{p=0}^{i=0} + \frac{p}{\pi}\left(L_p - \frac{L_{pE} L_{Ep}}{L_E}\right) \tag{66}$$

$$\left(\frac{\phi_1}{\pi}\right)^{i=0} = \left(\frac{\phi_1}{\pi}\right)_{p=0}^{i=0} + \frac{p}{\pi}\left(L_{\pi p} - \frac{L_{\pi E} L_{Ep}}{L_E}\right). \tag{67}$$

Since the concentration is held constant on the high pressure side and ϕ_1/ϕ_v is measured on the low pressure side π may be obtained from the thermodynamic properties of these solutions. ϕ_v and ϕ_1/ϕ_v are measured for various upstream pressures. ϕ_1, ϕ_v, and p are plotted against π. Differentiation of these curves at a chosen π defines also the concentration c_s since c_s is the concentration of a solution which would have an osmotic pressure π when placed against the constant concentration on the high pressure side. These differential values together with the Onsager reciprocal relations enable equations 66 and 67 to be transformed into

$$\mathfrak{L}_p = W^2\kappa + [(\partial\phi_v/\partial\pi)^{i=0} - (\partial\phi_v/\partial\pi)_{p=0}^{i=0}](\partial\pi/\partial p)^{i=0} \tag{68}$$

$$\mathfrak{L}_{\pi p} = Wt_1\kappa/z_1F + [(\partial\phi_1/\partial\pi)^{i=0} - (\partial\phi_1/\partial\pi)_{p=0}^{i=0}](\partial\pi/\partial p)^{i=0} \tag{69}$$

respectively, from which $\mathfrak{L}_p$ and $\mathfrak{L}_{\pi p}$ may be obtained as functions of c_s. $\mathfrak{L}_\pi$ then follows from equation 42.

This "reverse osmosis" method is experimentally relatively straightforward. The absence of polarization complications and the simplicity of the measurements required should lead to accurate values of $\mathfrak{L}_p$ and $\mathfrak{L}_{\pi p}$ being obtained, despite the greater mathematical complication of equations 68 and 69 relative to equations 57 and 58.

APPENDIX I

When a stable and strong membrane is studied the following well defined experimental quantities permit the nine differential phenomenological $\mathfrak{L}_{\alpha\beta}$-coefficients to be evaluated without recourse to the Onsager reciprocal relations

Electric conductance

$$\kappa = (i/E)_{p,\pi=0} = \mathfrak{L}_E \tag{i}$$

Hydraulic permeability

$$q_p = (\phi_v/p)_{E,\pi=0} = \mathfrak{L}_p \tag{ii}$$

Electric transference number

$$t_1 = (z_1 F \phi_1/i)_{p,\pi=0} = z_1 F \mathfrak{L}_{\pi E}/\mathfrak{L}_E \tag{iii}$$

Streaming current

$$i_p = (i/p)_{E,\pi=0} = \mathfrak{L}_{Ep} \tag{iv}$$

Electroosmotic permeability

$$W = (\phi_v/i)_{p,\pi=0} = \mathfrak{L}_{pE}/\mathfrak{L}_E \tag{v}$$

Cell potential

$$E_\pi = (\partial E/\partial \pi)_{p=0}^{i=0} = (\mathfrak{L}_{Ep} - \mathfrak{L}_{E\pi}/\nu_1 c_s)/\mathfrak{L}_E \tag{vi}$$

Salt permeability

$$j_\pi = (\partial \phi_1/\partial \pi)_{p=0}^{i=0} = (\mathfrak{L}_{Ep}\mathfrak{L}_{\pi E} - \mathfrak{L}_{E\pi}\mathfrak{L}_{\pi E}/\nu_1 c_s)/\mathfrak{L}_E + \mathfrak{L}_\pi/\nu_1 c_s - \mathfrak{L}_{\pi p} \tag{vii}$$

Osmotic permeability

$$q_\pi = (\partial \phi_v/\partial \pi)_{p=0}^{i=0} = (\mathfrak{L}_{Ep}\mathfrak{L}_{pE} - \mathfrak{L}_{E\pi}\mathfrak{L}_{pE}/\nu_1 c_s)/\mathfrak{L}_E + \mathfrak{L}_{p\pi}/\nu_1 c_s - \mathfrak{L}_p \tag{viii}$$

Mechanical salt permeability

$$j_p = (\phi_1/p)_{\pi=0}^{i=0} = \mathfrak{L}_{\pi p} - \mathfrak{L}_{Ep}\mathfrak{L}_{\pi E}/\mathfrak{L}_E \tag{ix}$$

Measurements i-v inclusive and ix must all be made at the same uniform concentration c_s and the differential coefficients in vi, vii, and viii must be evaluated at this same concentration from experimental data determined over a range of concentrations extending above and below c_s.

The $\mathcal{L}_{\alpha\beta}$-coefficients can be expressed in terms of these experimental coefficients as follows

$$\mathcal{L}_{\pi} = \nu_1 c_s (j_\pi + j_p) + \nu_1 c_s (i_p - \kappa E_\pi) t_1 / z_1 F \tag{x}$$

$$\mathcal{L}_{p} = q_p \tag{xi}$$

$$\mathcal{L}_{E} = \kappa \tag{xii}$$

$$\mathcal{L}_{\pi p} = j_p + i_p t_1 / z_1 F \tag{xiii}$$

$$\mathcal{L}_{p\pi} = \nu_1 c_s (q_\pi + q_p - \kappa E_\pi W) \tag{xiv}$$

$$\mathcal{L}_{\pi E} = t_1 \kappa / z_1 F \tag{xv}$$

$$\mathcal{L}_{E\pi} = \nu_1 c_s (i_p - \kappa E_\pi) \tag{xvi}$$

$$\mathcal{L}_{pE} = \kappa W \tag{xvii}$$

$$\mathcal{L}_{Ep} = i_p \tag{xviii}$$

APPENDIX II

If, accepting the validity of the reciprocal relations, it is desired to determine the six $\mathcal{L}_{\alpha\beta}$-coefficients for a discontinuous system in which the membrane separates a particular pair of solutions this may be done via the coefficients in equations 27–32 and 60. The requisite equations are set down in compact form by using the following shorthand notation

$$(E/\pi)_{p=0}^{i=0} \equiv (E)_p^i \, , \; (i/\pi)_{p,E=0} \equiv (i)_{pE}$$

$$(\phi_v/\pi)_{p,E=0} \equiv (\phi_v)_{pE} \, , \; (\phi_1/\pi)_{p,E=0} \equiv (\phi_1)_{pE}$$

$$[(\phi_v/\pi)_{p=0}^{i=0} - (\phi_v/\pi)_{p,E=0}] \equiv \Delta\phi_v$$

$$[(\phi_1/\pi)_{p=0}^{i=0} - (\phi_1/\pi)_{p,E=0}] \equiv \Delta\phi_1$$

$$(p/\pi)^{\phi_v, i=0} \equiv (p)^{\phi_v i}.$$

The $L_{\alpha\beta}$-coefficients are given by

$$L_E = -(i)_{pE}/(E)_p^i$$

$$L_{pE} = \Delta\phi_v/(E)_p^i$$

$$L_{\pi E} = \Delta\phi_1/(E)_p^i$$

$$L_p = \left[\frac{L_{pE}}{L_E}\left(L_{pE} + \frac{L_{\pi E}}{\nu_1 \bar{c}_s (p)^{\phi_v i}}\right) - \frac{(\phi_v)_{pE}}{(p)^{\phi_v i}}\right]$$

$$L_{p\pi} = \nu_1 \bar{c}_s[(\phi_v)_{pE} + L_p]$$

$$L_\pi = \nu_1 \bar{c}_s[(\phi_1)_{pE} + L_{p\pi}].$$

The open circuit and short circuit fluxes, potential and pressure might be determined in a single well designed membrane cell. The relation

$$\Delta\phi_1 = \nu_1\bar{c}_s\Delta\phi_v - \nu_1\bar{c}_s(E)_p^i(i)_{pE}$$

may be tested experimentally to discover whether the linear flux equations are valid over the range being studied.

APPENDIX III

The $L_{\alpha\beta}$-coefficients used throughout most of this paper are related to the L_{ik}-coefficients of the particle flux equations 2 by the matrix equation

$$(L_{ik}) = \Gamma^{-1}(L_{\alpha\beta})\Gamma^{-1T}$$

where

$$\Gamma = \begin{pmatrix} 1 & 0 & 0 \\ V_s/\nu_1 & 0 & V_w \\ z_1F & z_2F & 0 \end{pmatrix}.$$

Thus, a determination of the $L_{\alpha\beta}$-coefficients permits a unique evaluation of the L_{ik}-coefficients. The algebraic expressions for the nine L_{ik}-coefficients are set out below

$$L_{11} = L_\pi$$

$$L_{12} = (L_{\pi E} - z_1FL_\pi)/z_2F$$

$$L_{13} = (\nu_1L_{\pi p} - V_sL_\pi)/\nu_1V_w$$

$$L_{21} = (L_{E\pi} - z_1FL_\pi)/z_2F$$

$$L_{22} = (L_E/F - z_1L_{E\pi} - z_1L_{\pi E} + z_1^2FL_\pi)/z_2^2F$$

$$L_{23} = (z_1FV_sL_\pi - z_1F\nu_1L_{\pi p} + \nu_1L_{Ep} - V_sL_{E\pi})/z_2F\nu_1V_w$$

$$L_{31} = (\nu_1L_{p\pi} - V_sL_\pi)/\nu_1V_w$$

$$L_{32} = (z_1FV_sL_\pi - z_1F\nu_1L_{p\pi} + \nu_1L_{pE} - V_sL_{\pi E})/z_2F\nu_1V_w$$

$$L_{33} = (\nu_1^2L_p - \nu_1V_sL_{p\pi} - \nu_1V_sL_{\pi p} + V_s^2L_\pi)/\nu_1^2V_w^2\,.$$

These equations written above for the average discontinuous coefficients apply also between the differential $\mathcal{L}_{\alpha\beta}$-coefficients and analogously defined differential $\mathcal{L}_{ik}$-coefficients.

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