The Relation between Salt
and Ionic Transport Coefficients

ORA KEDEM and ALEXANDER LEAF

From the Departments of Medicine, Harvard Medical School, and the Massachusetts General Hospital, Boston. Dr. Kedem's permanent address is the Polymer Department, Weizmann Institute of Science, Rehovoth, Israel

ABSTRACT The reflection coefficient was originally introduced by Staverman to describe the movement of nonelectrolytes through membranes. When this coefficient is extended to salts, one has a choice of defining this term for the whole salt moving as a single electrically neutral component or for the individual ions of the salt. The latter definition is meaningful only in the absence of an electric field across the permeability barrier. This condition may be achieved with the voltage clamp or short-circuit technique and is especially useful in dealing with biological systems in which one rarely has only a single salt or even equal concentrations of the major anion and cation. The relations between the transport coefficients for the salt and its individual ions are derived. The special conditions which may result in negative osmosis through a charged membrane in the presence of a salt are discussed.

The reflection coefficient was originally defined by Staverman (1) for nonelectrolytes. To extend this definition to electrolytes two approaches are possible and reasonable: (a) In the absence of an electric *current* a salt moves in solution as a single electroneutral component. It is possible to deal with a simple "salt flux" under these circumstances, if only a single salt is present in the solution, and to define transport coefficients for the salt (2). (b) In the absence of an electric *field* across the permeability barrier the forces acting on an ion are of the same kind as those acting on a neutral molecule and coefficients for single ions, analogous to those for nonelectrolytes, can be defined (3).

Both definitions are useful for different purposes. In biological systems one rarely deals with only ions of a single salt nor even with equal concentrations of the major anion and cation. The voltage clamp or short-circuit technique of Ussing and Zerahn (4), furthermore, has allowed the measurement of single ion mobilities across various epithelial structures. For these reasons the latter definition of the reflection coefficient for ions (in the absence of an electrical field) has practical advantages for the biologist. The relations between the two types of coefficients are derived in the following.

NOTATIONS (INCLUDING CONVENTIONS FOR SUBSCRIPTS)

The model discussed in this paper consists of a membrane or permeability barrier separating two solutions. Differences in hydrostatic pressure, ΔP, osmotic pressure, $\Delta \pi$, and electrical potential, $\Delta \psi$, across the membrane are possible. The following notations will be used in the text without further definition:

ν number of ions, positive or negative, per molecule of salt.

ω mobility of solute, defined in equation 2. Note that this differs from the usual definition of mobility as the linear dimension is omitted. With biological membranes one rarely has knowledge of the actual distance traversed by the penetrating species or even of the thickness of the permeability barrier.

P permeability coefficient in units of cm sec^{-1}. This also differs from a conventional permeability constant as the linear dimension is omitted.

I_s flow of electric current through the membrane which just reduces $\Delta \psi$ to zero; the short-circuit current

according to the usage of Ussing and Zerahn (4).

a chemical activity.

μ thermodynamic chemical potential.

$\Delta \psi$ electrical membrane potential as measured with balanced calomel electrodes.

$\bar{\mu}$ electrochemical potential

J net flux of solute (J_s) or of volume (J_v) across the membrane. J_v will be taken essentially equal to J_w, the flux of solvent.

τ transference number.

σ reflection coefficient, defined in equations (7) and (8).

$\bar{c}$ the average concentration across the barrier and has been defined previously (5) for nonelectrolytes in ideal solution as

$$\bar{c} = \frac{\Delta c}{\Delta \ln c} \quad \text{(see Appendix)}$$

Subscripts which may be used with the above symbols are:

$+, -$ indicating positive or negative ion

j, i, k species of solute

s, v pertaining to solute or solvent, respectively.

Permeability of a Salt

Defined previously (2). It is assumed here that only one electrolyte permeates the membrane and that the concentrations of the permeating cation and anion are matched:

$$c_+ = \nu_+ c_s \; ; \qquad c_- = \nu_- c_s \tag{1}$$

then

$$\omega = \left(\frac{J_s}{\Delta \pi_s}\right)_{I, J_v} \tag{2}$$

For ideal solutions this is equivalent to the permeability coefficient, P.

$$P = \frac{J_s}{\Delta c_s}$$

with

$$P = (\nu_1 + \nu_2)\omega RT$$

If another electrolyte with a common ion is present so that the concentrations of permeating anion and cation are not equal, the definition of $\Delta \pi_s$ is not straightforward. c_s is the concentration of the neutral salt defined by the ion not common with another electrolyte. $\Delta \mu_s$ contains, of course, via $\nu_+\bar{\mu}_+$ and $\nu_-\bar{\mu}_-$, the effect of the common ion. Hence no simple "P" in terms only of Δc can be given.

Permeabilities for Single Ions

(Single permeating salt, but $\nu_+c_+ \gtrless \nu_-c_-$ is possible.)

In the absence of an electric field ("short-circuit") across the membrane, and neglecting changes of the activity coefficients, the permeability coefficient for a single ion is usually defined as:

$$P_i = \frac{J_i}{\Delta c_i} \tag{4}$$

A more general definition which will reduce to (4) under simple conditions is:

$$\omega_j = \frac{J_j}{\bar{c}_j \Delta \mu_j} \tag{5}$$

Note, ω_j is defined for $J_k = 0$. This restriction is important if the ion fluxes interact with each other.

In this definition it is assumed implicitly that a change in chemical potential, $d\mu = RTd (\ln a_i)$, will cause the same response in J_i as an equivalent change of electrical potential $zFd\psi = RTd (\ln a_i)$; chemical and electrical forces are assumed to provide equivalent driving forces for the flow of ions. This assumption forms the basis of the theory of ion transport in solutions and has been amply verified there. It also applies in ion exchange membranes. A further experimental verification may, however, be necessary to establish its validity in biological membranes.

The permeability for single ions is clearly defined only if the concentrations of the ions examined are finite on both sides of the membrane. The average concentration of the ion, c_j, has been defined as:

$$\bar{c}_j = \frac{\Delta c_j}{\Delta \ln c_j},$$

so that $\bar{c}_j \Delta \mu_j = RT\Delta c_j$ in ideal solutions.

Clearly, if J_j is independent of J_k, if the electrical potential difference across the membrane, $\Delta\psi$, is zero, and if volume flow is zero

$$\omega_j = \frac{J_j}{RT\Delta c_j} \tag{6}$$

The relationship of the ionic mobilities determined in the absence of an electric field to the partial or individual ionic conductances (reference 6) may be mentioned. When an electric current passes through the membrane, the relative contribution of each ion to the flow of current, i.e. the partial ionic conductance, will be directly proportional to the product of its valence and mobility, ω_j of equation (6).

Reflection Coefficients

For the whole salt the reflection coefficient is defined by:

$$\bar{c}_s(1 - \sigma_s) = \left(\frac{J_s}{J_v}\right)_{\Delta\pi_s, I} \tag{7}$$

The coefficients for the single ions are formally completely analogous:

$$\bar{c}_j(1 - \sigma_j) = \left(\frac{J_j}{J_v}\right)_{x_j, J_i} \tag{8}$$

Despite the formal similarity these describe measurements made under quite different conditions: σ_s is derived from ultrafiltration or osmotic measurements in the absence of current. σ_j is measured while the membrane is short-circuited; i.e., $\Delta\psi$ is kept zero by the passage of a suitable current.

Flow Equations in Terms of σ_j and ω_j

For the derivation of ω and σ it is convenient to write the forces as functions of flows:

$$\Delta\bar{\mu}_+ = \frac{1}{\omega_+ \bar{c}_+} J_+ - \frac{(1 - \sigma_+)}{\omega_+} J_v - \alpha J_-$$

$$\Delta\bar{\mu}_- = \frac{1}{\omega_- \bar{c}_-} J_- - \frac{(1 - \sigma_-)}{\omega_-} J_v - \beta J_+ \tag{9}$$

α and β represent the interaction between J_+ and J_- and, according to Onsager's relation,

$$\alpha = \beta \tag{10}$$

The salt permeability, ω, is measured at $I = 0$, hence:

$$\frac{J_+}{\nu_+} = \frac{J_-}{\nu_-} \equiv J_s \tag{11}$$

The difference in the thermodynamic potential of the salt is:

$$\Delta\mu_s = \nu_+\Delta\bar{\mu}_+ + \nu_-\Delta\bar{\mu}_-$$

From equations (9), (10), and (11), and with $J_v = 0$:

$$\triangle\mu_s = \frac{\nu_+^2}{\omega_+\bar{c}_+} J_s + \frac{\nu_-^2}{\omega_-\bar{c}_-} J_s - 2\alpha\nu_+\nu_- J_s \tag{12}$$

$$\triangle\mu_s = \frac{\nu_+}{\omega_+} \frac{J_s}{\bar{c}_s} + \frac{\nu_-}{\omega_-} \frac{J_s}{\bar{c}_s} - 2\alpha\nu_+\nu_-\bar{c}_s \frac{J_s}{\bar{c}_s}$$

$$\frac{1}{\omega} = \frac{\bar{c}_s\triangle\mu_s}{J_s} = \frac{\nu_+}{\omega_+} + \frac{\nu_-}{\omega_-} - 2\alpha\nu_+\nu_-\bar{c}_s \tag{13}$$

Thus the resistance to the salt is smaller than the sum of the resistances to the individual ions if the ions drag each other along.

At equal salt activities, i.e. $\Delta\mu_s = 0$, the salt flow is:

$$J_s = (1 - \sigma)\bar{c}_s J_v$$

From equations (9), (10), and (11):

$$\nu_+\triangle\bar{\mu}_+ + \nu_-\triangle\bar{\mu}_- = 0$$

$$= J_s\left[\frac{\nu_+}{\omega_+\bar{c}_s} + \frac{\nu_-}{\omega_-\bar{c}_s} - 2\nu_+\nu_-\alpha\right] - J_v\left[\frac{\nu_+(1 - \sigma_+)}{\omega_+} + \frac{\nu_-(1 - \sigma_-)}{\omega_-}\right]$$

and hence, according to the equations (8) and (13):

$$(1 - \sigma) = (1 - \sigma_+)\frac{\nu_+\omega}{\omega_+} + (1 - \sigma_-)\frac{\nu_-\omega}{\omega_-} \tag{14}$$

as shown above (13), for interacting flows:

$$\frac{\nu_+}{\omega_+}\omega + \frac{\nu_-}{\omega_-}\omega \gtrless 1$$

Thus $(1 - \sigma)$ is not necessarily an average between $(1 - \sigma_+)$ and $(1 - \sigma_-)$. For mutual drag

$$\frac{\nu_+\omega}{\omega_+} + \frac{\nu_-\omega}{\omega_-} > 1$$

tending to decrease the reflection coefficient for the whole salt relative to the coefficients for the single ions.

Noninteracting Flows

Very simple relations are obtained if anion and cation permeate independently. Writing $\alpha = 0$, the flow equations give:

$$\frac{1}{\omega} = \frac{\nu_+}{\omega_+} + \frac{\nu_-}{\omega_-} \tag{15}$$

and

$$\sigma = \frac{\sigma_+ \nu_+}{\omega_+} \omega + \frac{\sigma_- \nu_-}{\omega_-} \omega \tag{16}$$

Thus both permeability and reflection coefficients for a salt are determined mainly by the less permeant ion.

For uni-univalent salts permeabilities are closely related to the electric transport numbers, τ. In a measurement of τ, with equal concentratons of the salt on both sides of a permeability barrier,

$$\Delta\bar{\mu}_+ = -\Delta\bar{\mu}_- \tag{17}$$

From equations (9), (15), and (17):

$$\tau_+ = \frac{J_+}{J_+ - J_-} = \frac{\omega_+}{\omega_+ + \omega_-} = \frac{\omega}{\omega_-} \tag{18}$$

and

$$\tau_- = \frac{\omega}{\omega_+}$$

Similarly, equation (16) in terms of the transport numbers reads:

$$\sigma = \tau_- \sigma_+ + \tau_+ \sigma_- \tag{19}$$

To illustrate equation (19), consider a highly porous, charged, homogeneous membrane. The reflection coefficients for the single ions measure the amount of the ions swept along with water flowing through the membrane, while the electric field across the membrane is kept at zero and the outside concentrations are equal. Neglecting the frictional resistance offered by the matrix to the passage of the ion, σ_i will be fully determined by the concentration of the ion in the channels. For the counter ion this will be larger than the salt concentration in the outside solutions and thus $(1 - \sigma_i)\bar{c}$ is expected to be larger than c, or σ_i of the counter ion will be negative. As long as the

outside salt concentration is not too high, the concentration of the co-ion in the channels of the membrane must be small, and σ_i for the co-ion close to 1. The over-all value of σ for the salt is usually closer to that of the co-ion, because its transport number is small. However, if the mobility of the co-ion in the channels of the membrane is much larger than that of the counterion, τ (co-ion) is increased and the over-all σ may be negative (2). Under the influence of an hydrostatic pressure or osmotic pressure gradient or in the presence of a concentration gradient of the salt in question, this will lead to negative osmosis and the transport of a solution in which the solute concentration is higher than that of the outside solution. Negative osmosis has been observed for acids permeating positively charged membranes in which the proton has a high mobility (7).

APPENDIX

The definition of $\bar{c}$ has been given for nonelectrolytes (5) as the average concentration across a permeability barrier,

$$\bar{c} = \frac{\Delta c}{\Delta \ln c} \tag{a}$$

for nonelectrolytes in ideal solutions. The concentration is thus an average, not with respect to distance through the barrier, but with respect to μ_s

$$\bar{c} = \frac{\int c_s \, d\mu_s}{\Delta \mu_s} \tag{b}$$

This definition may be applied also to nonideal solutions of either electrolytes or nonelectrolytes. In any case

$$c_s \, d\mu_s = d\pi_s$$

and (2)

$$\bar{c} = \frac{\Delta \pi_s}{\Delta \mu_s} \tag{c}$$

In terms of the activity coefficient, γ, in the whole range of concentrations (c) reads:

$$\bar{c} = \frac{\Delta c}{\Delta \ln c} \left(\frac{1 + \int_{c^{\mathrm{I}}}^{c^{\mathrm{II}}} \dfrac{c \, d \ln \gamma}{\Delta c}}{1 + \dfrac{\Delta \ln \gamma}{\Delta \ln c}} \right) \tag{d}$$

Both the numerator and denominator contain a correction term dependent on the change of γ with c. As long as $\Delta \ln \gamma / \Delta \ln c$ is small enough we may write instead of the last equation,

$$\bar{c} = \frac{\Delta c}{\Delta \ln c} \left(1 + \frac{\int_{c^{\mathrm{I}}}^{c^{\mathrm{II}}} c \, d \ln \gamma}{\Delta c} - \frac{\Delta \ln \gamma}{\Delta \ln c} \right) \tag{e}$$

In many cases $\bar{c}$ as given by equations (c) or (e) is practically identical with $\Delta c / \Delta \ln c$, although deviations from ideality may be considerable, because the last two terms in (c) largely cancel each other. Thus, for example, if the solutions contain NaCl at 0.1 and 0.01 M, respectively, the values for $\bar{c}$ according to the two definitions agree within 2%. If, however, the lower concentration is decreased to a very small value, the last term in (e) vanishes while the other correction term is practically unchanged.

In order to extend the corrected definition of $\bar{c}$ to single ions, one must accept the definability of single ion activity coefficients. As discussed, $\Delta c / \Delta \ln c$ will usually be a good approximation, except when the two concentrations c^{I} and c^{II} on opposite sides of the barrier differ too widely. For the measurement of the permeability to single ions it is advisable to avoid large concentration differences. In fact if the concentration of the ion considered is zero in one compartment and an electric field is present, then the permeability of the barrier to the ion is undefined. For measurements with single ions, therefore, the concentrations are assumed to be finite on both sides.

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