MEMBRANE PERMEABILITY

GENERALIZATION OF THE REFLECTION COEFFICIENT METHOD

OF DESCRIBING VOLUME AND SOLUTE FLOWS

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ABSTRACT   The reflection coefficient method for describing volume and solute fluxes through membranes is generalized to take into account the nonideality of the solutions bathing the membrane and/or multicomponent systems. The reflection coefficient of the impermeable species in these systems is less than unity by a coefficient γ. The reflection coefficient obtained solely from the volume flow equation, σ^V, will always be less than the reflection coefficient obtained from the solute flow equation, σ^{*V}. These two coefficients are related by $\sigma^{*V} = \sigma^V + \gamma$.

INTRODUCTION

The relationship between the volume flow through a membrane J_V and the osmotic pressure across the membrane was greatly illuminated by Staverman (1951). Through a treatment utilizing the linear theory of nonequilibrium thermodynamics, he was able to demonstrate that the differences in hydrostatic pressure ΔP and osmotic pressure $\Delta\pi$ across a membrane are not additive, but that the effect of these pressures differs by a coefficient σ which Staverman named the reflection coefficient. Staverman's original equations are written in their popular form from Katchalsky and Curran (1965) as

$$J_V = -L_P\left(\Delta P - \sum_{i=1}^{N-1} \sigma_i \Delta\pi_i\right) \quad \text{(for } N-1 \text{ solutes)} \tag{1}$$

for the volume flow, and

$$J_i = (1 - \sigma_i)\bar{C}_i J_V - \omega_i \Delta\pi_i \quad \text{(for a single permeable species)} \tag{2}$$

for the solute flow. The flows are taken positive left to right, and the differences are taken right minus left. The Nth term is the solvent, i.e. the sum is over all chemical species in the solutions bathing the membrane, excluding the solvent. L_P is the hydraulic permeability, ω is the solute permeability at zero volume flow, π_i

is the osmotic pressure of species i, and $\bar{C}_i$ is an average concentration defined by equation 7. Equation 1 was derived using the empirical relationship

$$RT \sum_{i=1}^{N-1} \Delta C_i = -\frac{\Delta \mu_w^c}{\bar{v}_w}.$$ (3)

$\bar{v}_w$ is the partial molar volume of the solvent, R is the gas constant, T is the temperature, C_i is the concentration of species i, and μ_w^c is the chemical potential of the solvent.

For a dilute system with a single solute, Staverman demonstrated that σ is unity for an impermeable solute and less than unity for a permeable solute. Physically, $(1 - \sigma_i)$ is the fraction of solute i carried through the membrane by the volume flow when $\Delta \pi_i = 0$. $(1 - \sigma_i)$ deviates from this meaning as $\Delta \pi_i$ increases from zero.

Equations 1 and 2 are inappropriate for concentrated or multicomponent systems, but can be easily generalized to cover *all* systems for which linear flux equations are applicable. The reflection coefficients are given the following notation. σ^V is a reflection coefficient obtained solely from a volume flow experiment, i.e., equation 1. σ^{sV} is a reflection coefficient obtained from a solute–volume flow experiment, i.e., equation 2. I will show from a general derivation based upon the linear theory of nonequilibrium thermodynamics that: (a) for systems with at least one permeable solute, σ^V for the impermeable species is always *less* than unity; (b) for the permeable species $\sigma^V \leq \sigma^{sV}$; (c) that reciprocity is not necessary in the derivation of any σ; and (d) σ^{sV} can be obtained from two separate volume flow experiments.

THE REFLECTION COEFFICIENT BY MEASUREMENT OF VOLUME FLOW

The linear theory of nonequilibrium thermodynamics assumes that the flux of each species i, J_i, through the membrane can be expressed as

$$J_i = -\sum_{j=1}^{M} L_{ij} \Delta \mu_j,$$ (4)

where L_{ij} is a phenomenological transport coefficient and the sum is over the M independent chemical species which are free to be transported across the membrane. Because partial molar volumes are nearly independent of concentration, for a steady state the volume flux through the membrane can be written

$$J_V = \sum_{i=1}^{M} \bar{v}_i J_i = -\sum_{i=1}^{M} \sum_{j=1}^{M} \bar{v}_i L_{ij} \Delta \mu_j.$$ (5)

Now

$$\mu_i = \mu_i^0 + \bar{v}_i P + \mu_i^c,$$ (6)

where μ_i^0 is the standard chemical potential of species i, $\bar{v}_i$ is its partial molar volume, $\mu_i^c = RT \ln a_i$, and a_i is its chemical activity. Following Katchalsky and Curran, a term is defined called the "average concentration," $\bar{C}_i$,

$$\bar{C}_i = \frac{\Delta \pi_i}{\Delta \mu_i^c}, \tag{7}$$

where

$$\sum_{i=1}^{N-1} \Delta \pi_i = -\frac{\Delta \mu_w^c}{\bar{v}_w}. \tag{8}$$

N is the total number of chemical species in the solutions bathing the membrane, i.e., there are $(N - M)$ nonpermeable species. In this notation both the Nth and the Mth species are solvent. $\bar{C}_i$ is simply the arithmetic mean concentration for dilute systems, but varies from this physical meaning in concentrated systems. By separating the pressure and concentration terms and introducing equation 7 into equation 5, I find

$$J_V = -\sum_{i=1}^{M} \sum_{j=1}^{M} \bar{v}_i \bar{v}_j L_{ij} \left[\Delta P + \frac{\sum_{i=1}^{M} \sum_{j=1}^{M} \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \Delta \pi_j}{\sum_{i=1}^{M} \sum_{j=1}^{M} \bar{v}_i \bar{v}_j L_{ij}} \right]. \tag{9}$$

The second term within the brackets can be split into two terms, one for impermeable solutes and one for permeable solutes, in the following way.

Let A denote the numerator; then

$$A = \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \Delta \pi_j = \sum_{i=1}^{M} \left[\frac{\bar{v}_i L_{iw}}{\bar{C}_w} \Delta \pi_w + \sum_{j=1}^{M-1} \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \Delta \pi_j \right], \tag{10}$$

where

$$\Delta \mu_w^c \equiv \frac{\Delta \pi_w}{\bar{C}_w}. \tag{11}$$

Introducing equation 8, I obtain

$$A = \sum_{i=1}^{M} \left[-\bar{v}_i L_{iw} \sum_{k=1}^{N-1} \bar{v}_w \Delta \pi_k + \sum_{j=1}^{M-1} \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \Delta \pi_j \right], \tag{12}$$

$$A = \sum_{i=1}^{M} \left[\underbrace{-\bar{v}_w \bar{v}_i L_{iw} \sum_{k=M+1}^{N-1} \Delta \pi_k}_{\binom{\text{impermeable}}{\text{species}}} + \underbrace{\sum_{j=1}^{M-1} \left[-\bar{v}_w \bar{v}_i L_{iw} + \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \right] \Delta \pi_j}_{\binom{\text{permeable}}{\text{species}}} \right]. \tag{13}$$

Reversing the order of the summation,

$$A = \underbrace{\sum_{k=M+1}^{N-1} \left[\sum_{i=1}^{M} -\bar{v}_w \bar{v}_i L_{iw} \right] \Delta \pi_k}_{\binom{\text{impermeable}}{\text{species}}} + \underbrace{\sum_{j=1}^{M-1} \left[\sum_{i=1}^{M} \left[-\bar{v}_w \bar{v}_i L_{iw} + \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \right] \right] \Delta \pi_j}_{\binom{\text{permeable}}{\text{species}}}. \tag{14}$$

By introducing equation 14 into equation 9, i.e. replacing the old numerator with the new and comparing coefficients with equation 1, I obtain for the reflection coefficients and the hydraulic permeability as would be calculated solely from a volume flow measurement

$$\sigma_r^V \left(\begin{smallmatrix}\text{impermeable}\\\text{solutes}\end{smallmatrix}\right) = \frac{\sum\limits_{j=1}^{M} \bar{v}_w \bar{v}_j L_{jw}}{L_P}, \tag{15}$$

where subscript r denotes the "reflected" species.

$$\sigma_{pj}^V \left(\begin{smallmatrix}\text{permeable}\\\text{solutes}\end{smallmatrix}\right) = \frac{\sum\limits_{i=1}^{M} \left(\bar{v}_w \bar{v}_i L_{iw} - \frac{\bar{v}_i L_{ij}}{\bar{C}_j} \right)}{L_P}, \tag{16}$$

where subscript p denotes the permeable species.

$$L_P = \sum_{i=1}^{M} \sum_{j=1}^{M} \bar{v}_i \bar{v}_j L_{ij}. \tag{17}$$

THE REFLECTION COEFFICIENT BY MEASUREMENT OF SOLUTE AND VOLUME FLOW

The reflection coefficients for the permeable species can also be obtained via the solute flow. Equation 4 can be written

$$J_i = -\sum_{j=1}^{M} L_{ij} \bar{v}_j \Delta P - \sum_{j=1}^{M-1} \frac{L_{ij} \Delta \pi_j}{\bar{c}_j} - L_{iw} \bar{v}_w \sum_{j=1}^{M-1} \Delta \pi_j. \tag{18}$$

Equation 1 is solved for ΔP, and this is placed in equation 18, and using relations 7 and 8 equation 2 can now be generalized to

$$J_i = (1 - \sigma_{pi}^{sV}) \bar{C}_i J_V - \sum_{h=1}^{N-1} \omega_{ih} \Delta \pi_h, \tag{19}$$

where

$$\sigma_{pi}^{sV} \left(\begin{smallmatrix}\text{permeable}\\\text{solutes}\end{smallmatrix}\right) = 1 - \frac{\sum\limits_{j=1}^{N} \frac{L_{ij} \bar{v}_j}{\bar{C}_i}}{L_P}, \tag{20}$$

and

$$\omega_{ih} = \sigma_h^V \sum_{j=1}^{N} L_{ij} \bar{v}_j - \frac{L_{ih}}{\bar{C}_i} + L_{iw} \bar{v}_w.$$

$$L_{ih} = 0 \quad \text{if} \quad h \geq M. \tag{21}$$

σ_{pi}^{sV} is the reflection coefficient which is obtained from a solute–volume flow meas-

urement and ω_{ii} is the solute permeability at zero volume flow when $\Delta\pi_h = 0$ for all $h \neq i$.

DISCUSSION

The coefficients which have been derived in equations 15, 16, and 20 may be used to characterize those membrane-solution systems where the partial molar volumes are nearly constant and linearity is an appropriate assumption. Reciprocity was not used in the derivation and neither validity nor invalidity of reciprocity would alter their basic form. Equations 15, 16, and 20 should fully characterize the reflection coefficients evaluated for biological systems, say, for example, red blood cells or glomeruli. In these systems application of the dilute solution approximation may introduce appreciable error; and since reciprocity has not been demonstrated, it is probably not a good basic assumption. The properties of these generalized reflection coefficients will now be explored.

Consider the situation of an ideal semipermeable membrane; only L_{ww} exists, all $L_{ij} = 0$ for i or $j \neq w$.

$$\sigma_r^V \, {}^{\text{ideal}}_{\text{membrane}} = \frac{\bar{v}_w^2 L_{ww}}{\bar{v}_w^2 L_{ww}} = 1, \tag{22}$$

$$\sigma_p^{sV} \, {}^{\text{ideal}}_{\text{membrane}} = 1 - 0 = 1. \tag{23}$$

σ_r^V and σ_p^{sV} have the same upper limit of unity for a single impermeable species.

Now consider one permeable solute i and one impermeable solute r, and obtain

$$\sigma_r^V = \frac{\bar{v}_w^2 L_{ww} + \bar{v}_w \bar{v}_i L_{iw}}{\bar{v}_w^2 L_{ww} + \bar{v}_w \bar{v}_i (L_{wi} + L_{iw}) + \bar{v}_i^2 L_{ii}}, \tag{24}$$

and

$$\sigma_{pi}^V = \frac{\bar{v}_w^2 L_{ww} + \bar{v}_w \bar{v}_i L_{iw} - (\bar{v}_w L_{wi} + \bar{v}_i L_{ii})(\bar{c}_i)^{-1}}{\bar{v}_w^2 L_{ww} + \bar{v}_w \bar{v}_i (L_{wi} + L_{iw}) + \bar{v}_i^2 L_{ii}}, \tag{25}$$

and

$$\sigma_{pi}^{sV} = 1 - \frac{(\bar{v}_w L_{iw} + \bar{v}_i L_{ii})(\bar{c}_i)^{-1}}{\bar{v}_w^2 L_{ww} + \bar{v}_w \bar{v}_i (L_{wi} + L_{iw}) + \bar{v}_i^2 L_{ii}}. \tag{26}$$

From equation 24, σ_r^V, will always be less than unity when even a single permeable species is present. Because the sum is over all j for σ_r^V, every impermeable species will have the same reflection coefficient. By adding an impermeable species to a system with permeable species, the effective osmotic pressure of the impermeable solute will always be less than that for a perfect semipermeable membrane.

In order to see clearly the relationship between σ_{pi}^{sV} and σ_{pi}^V, let us define a term for the "deviation from the dilute solution approximation," γ, and write for equa-

tion 15

$$\sigma_r^V = 1 - \gamma. \tag{27}$$

It is seen that

$$\sigma_{pi}^{*V} = \sigma_{pi}^V + \gamma. \tag{28}$$

The reflection coefficient obtained solely from a volume flow measurement σ_{pi}^V will always be less than the reflection coefficient obtained from a solute–volume flow measurement; however, σ_{pi}^{*V} can be obtained solely from a volume flow experiment in the following way. First, measure σ_r^V for any totally impermeable species; calculate γ from equation 27. Then measure σ_{pi}^V and calculate σ_{pi}^{*V} from equation 28. Without making questionable assumptions, I cannot speculate whether σ^V or σ^{*V} is closer in physical meaning to the dilute solution σ, i.e., the "Staverman reflection coefficient."

CONCLUSIONS

The reflection coefficient is an important parameter for characterizing membrane transport phenomena because of its ease of measurement and its simple physical meaning for systems which have a single solute and for which the dilute solution approximation is reasonable. In multicomponent systems and/or where nonideal conditions exist, as in most biological experiments, the reflection coefficient of the impermeable species is dependent upon the transport coefficients of the permeable species. The reflection coefficient of the permeable species, as obtained from a solute–volume flow experiment, will always be larger than that obtained solely from a volume flow experiment.

REFERENCES

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