DILUTE SOLUTION APPROXIMATION AND GENERALIZATION OF THE REFLECTION COEFFICIENT METHOD OF DESCRIBING VOLUME AND SOLUTE FLOWS

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ABSTRACT Kedem and Katchalsky introduced an approximation for dilute solutions which requires that the quantity $(\Delta\pi/\Delta\pi_i)\phi_i$ be much less than one. Zelman attempted to generalize the reflection coefficient concept to apply to solutions of multiple solutes, both penetrable and impenetrable, of concentrations sufficiently high for the approximation not to work. By simple algebraic manipulation, Zelman introduced a pair of new reflection coefficients, and a third new parameter γ which he misleadingly calls the "deviation from the dilute solution approximation." It is shown here that the original Kedem-Katchalsky form for the flow equations can be preserved in such a way that no new coefficients need be introduced and an explicit statement of the effect of the dilute solution approximation can be made. There is an option of using a new set of conjugate driving forces for the solute flows or, alternatively, incorporating the nondilute solution correction in the coefficients in a clear way.

INTRODUCTION

Zelman (1) has shown that it is possible to formulate generalized reflection coefficients for multiple solute transport through membranes. He introduced a new coefficient γ which he calls the "deviation from the dilute solution approximation" and related it to the reflection coefficients he derived. One of his main conclusions was that the reflection coefficients in the volume flow equation were *not* the same as those in the solute flow equations. This work will show that Zelman's γ is not a full measure of the effect of the dilute solution approximation and that if the reflection coefficients are formulated after the Kedem-Katchalsky formulation, no new coefficients need be introduced.

LIST OF SYMBOLS

$\bar{c}_i$ Logarithmic mean concentration of solute across the membrane according to Eq. 6.
J_v Volume flow according to Eq. 4.

J_i	Flow of *i*th component across membrane, per unit area, from compartment I to compartment II.
L_{ij}	Phenomenological coefficient relating the *i*th flow to the *j*th force, all other forces set equal to zero.
P	Mechanical pressure.
$\bar{V}_i$	Partial molar volume of the *i*th component.
μ_i	Chemical potential of the *i*th component.
π	Total osmotic pressure of a solution according to Eq. 8.
π_i	Separate contribution of the *i*th solute to the total osmotic pressure.
ϕ_i	Volume fraction of the *i*th component.
L_p	Filtration coefficient.
σ_i	Reflection coefficient of the *i*th solute.
ω_{ii}	Permeability coefficient of the *i*th solute.
ω_{ij}	Coupling coefficient between the *i*th and *j*th solutes.
Δ	Difference operator: $\Delta y = y^{\text{I}} - y^{\text{II}}$ for any parameter y where y^{I} is its value in compartment I which bathes the membrane on one side and y^{II} is its value in compartment II which bathes the other side. Note that the definition of the positive direction for the flows has been chosen so that the difference operator has the opposite sign from that appearing in Zelman's paper. This is the reason for the difference in sign in all the equations.

THE VOLUME FLOW EQUATION

We will consider, as Zelman did, a membrane bathed by aqueous solutions with N chemical species, M of which penetrate the membrane ($M - 1$ solutes species + water) and $N - M$ of which do not. Zelman wrote a volume flow equation of the form

$$J_v = L_p\left(\Delta P - \sum_{i=1}^{N-1} \sigma_i \Delta\pi_i\right) \tag{1}$$

after Katchalsky and Curran (2). An alternative to this is to generalize an equation introduced by Kedem and Katchalsky (3). (In this equation i denotes both permeable and impermeable species.)

$$J_v = L_p\left(\Delta P - \Delta\pi + \sum_{i=1}^{M-1} (1 - \sigma_i^v)\Delta\pi_i\right) \tag{2}$$

(here i denotes permeable species).

There is a major difference between the two equations. In Eq. 2 the reflection coefficient of the impermeable species is essentially defined to be unity. In Eq. 1 this is not the case, and in general, the reflection coefficient can be less than one for impermeant species.

It can be shown, however that both equations can be derived from the same starting point, and thus, the reflection coefficients have different composition. The existence of two such sets of coefficients, both valid, and merely algebraic transformations of each other, illustrates their arbitrariness.

The starting point is the relation between the flux of each permeable species J_i and its chemical potential difference across the membrane, $\Delta\mu_i$.

$$J_i = \sum_{j=1}^{M} L_{ij}\Delta\mu_j\,. \tag{3}$$

To obtain the volume flow, each J_i must be multiplied by the partial molar volume of the *i*th species $\bar{V}_i$, and the sum of these products is the volume flow J_v.

$$J_v = \sum_{i=1}^{M} \bar{V}_i J_i = \sum_{i=1}^{M}\sum_{j=1}^{M} \bar{V}_i L_{ij}\Delta\mu_j\,. \tag{4}$$

Using the following transformations

$$\Delta\mu_i = \bar{V}_i\Delta P + \Delta\mu_i^{c}\,, \tag{5}$$

$$\Delta\mu_i^{c} = \Delta\pi_i/\bar{c}_i \quad \text{for solutes,} \tag{6}$$

$$\Delta\mu_w^{c} = -\bar{V}_w\Delta\pi\,, \tag{7}$$

$$\Delta\pi = \sum_{i=1}^{N-1} \Delta\pi_i\,. \tag{8}$$

The chemical potential differences for water and solutes can be written

$$\Delta\mu_w = \bar{V}_w(\Delta P - \Delta\pi), \tag{9}$$

$$\Delta\mu_i = \bar{V}_i\Delta P + (\Delta\pi_i/\bar{c}_i). \tag{10}$$

Zelman used transformations 5–8, but never put $\Delta\mu_w$ in the form of Eq. 9. Thus, he arrived at an equation that had the form of Eq. 1 and defined a set of reflection coefficients accordingly. The volume flow equation (Eq. 4) can be written in the form of Eq. 2 in the following manner: substituting Eqs. 9 and 10 in Eq. 4 and rearranging

$$J_v = \left(\sum_{i=1}^{M}\sum_{j=1}^{M} \bar{V}_i L_{ij} \bar{V}_j\right)(\Delta P - \Delta\pi) + \sum_{j=1}^{M-1}\left(\sum_{i=1}^{M} \bar{V}_i L_{ij}\right)[1 + (\Delta\pi/\Delta\pi_j)\phi_j](\Delta\pi_j/\bar{c}_j), \tag{11}$$

where $\phi_j = \bar{V}_j\bar{c}_j$ is the volume fraction of solute in the membrane. Kedem and Katchalsky (3) pointed out that for dilute solutions $\phi_i(\Delta\pi/\Delta\pi_i) \ll 1$ and they dropped this term in their dilute solution approximation. If we retain the term to treat cases where the approximation introduces errors too large to be ignored and preserve the form of Eq. 2 the coefficients L_p and σ_j^v are defined as follows

$$L_p = \sum_{i=1}^{M} \sum_{j=1}^{M} \bar{V}_i L_{ij} \bar{V}_j, \tag{12}$$

$$\sigma_j^v = 1 - (1/L_p) \left[\sum_{i=1}^{M} (\bar{V}_i L_{ij}/\bar{c}_j) \right] [1 + (\Delta\pi/\Delta\pi_j)\phi_j], \tag{13}$$

and since σ_j^v now depends on the forces $\Delta\pi$ and $\Delta\pi_j$ the flow-force equations appear to be nonlinear. That this is an apparent nonlinearity is obvious if in the nondilute case we called the force conjugate to the solute flow

$$\chi_i = [1 + (\Delta\pi/\Delta\pi_i)\phi_i](\Delta\pi_i/\bar{c}_i) = (\Delta\pi_i/\bar{c}_i) + \Delta\pi \cdot \bar{V}_i. \tag{14}$$

It will be shown that recognizing this as the conjugate force will eliminate most of the apparent discrepancies brought out by Zelman. In order to further understand his analysis we will proceed using Eqs. 12 and 13 above to define Lp and σ_j^v in the remainder of the calculations.

The next step is to derive the solute flow equation. This will allow a comparison between the two forms of the reflection coefficient σ_j^v and σ_j^s.

SOLUTE FLOW EQUATIONS

Starting with Eq. 3 once more and using the transformations 5–8 the solute flow equation becomes

$$J_i = \left(\sum_{j=1}^{M} L_{ij} \bar{V}_j \right) (\Delta P - \Delta\pi) + \sum_{j=1}^{M-1} L_{ij} [1 + (\Delta\pi/\Delta\pi_j)\phi_j](\Delta\pi_j/\bar{c}_j). \tag{15}$$

Solving Eq. 11 for $(\Delta P - \Delta\pi)$ and substituting in Eq. 15 using the definitions in Eqs. 12 and 13

$$J_i = \bar{c}_i(1 - \sigma_i^s) J_v + \sum_{j=1}^{M-1} \omega_{ij} [1 + (\Delta\pi/\Delta\pi_j)\phi_j](\Delta\pi_j/\bar{c}_j), \tag{16}$$

where $\omega_{ij} = L_{ij} - (\sum_{k=1}^{m} L_{ik}\bar{V}_k)(\sum_{k=1}^{m} \bar{V}_k L_{kj})$. Again we deviate from the procedure Zelman used, which was to substitute for ΔP from the volume flow equation. Once more we have the option of recognizing

$$[1 + (\Delta\pi/\Delta\pi_i)\phi_i](\Delta\pi_i/\bar{c}_i) \tag{17}$$

as the conjugate force to J_i or defining an apparently nonlinear permeability

$$\omega_{ij}^* = \omega_{ij}[1 + (\Delta\pi/\Delta\pi_j)\phi_j]. \tag{18}$$

If we do the latter we can compare the reflection coefficient in the volume flow equation and the solute flow equations.

$$\sigma_i^s = 1 - (1/L_p) \sum_{k=1}^{M} (\bar{V}_k L_{ki}/\bar{c}_i). \tag{19}$$

A comparison between the two reflection coefficients yields

$$(1 - \sigma_i^v) = (1 - \sigma_i^s)[1 + (\Delta\pi/\Delta\pi_i)\phi_i] \tag{20}$$

or

$$\sigma_i^v = \sigma_i^s[1 + (\Delta\pi/\Delta\pi_i)\phi_i] - (\Delta\pi/\Delta\pi_i)\phi_i \tag{21}$$

which leads to $\sigma_i^s = \sigma_i^v$ for the dilute solution approximation. It should be pointed out that the σ_i^s and σ_i^v are not equivalent to the σ_r^v, σ^{v}_{pj} and σ^{sv}_{pj} derived by Zelman nor is ω_{ij} of the same form as Zelman's ω_{ik} although the Lp is identical in the two derivations. Zelman's reflection coefficients and γ can be compared with σ_i^v and σ_i^s as follows:

$$\sigma^{sv}_{pi} = \sigma_i^s, \tag{22}$$

$$\sigma^{v}_{pi} = \sigma^{sv}_{pi} - \gamma = \sigma_i^s - \gamma, \tag{23}$$

$$\sigma_r^v = 1 - \gamma = \sum_{j=1}^{M-1} \sigma_j^s\phi_j + \phi_w , \tag{24}$$

$$\gamma = 1 - \sum_{j=1}^{M-1} \sigma_j^s\phi_j - \phi_w . \tag{25}$$

CASE OF A SINGLE PERMEABLE SOLUTE AND A SINGLE IMPERMEABLE SOLUTE

In the case of a single permeable solute and a single impermeable solute bathing the membrane, the equations for volume flow and solute flow become

$$J_v = L_p[(\Delta P - \Delta\pi) - (1 - \sigma^v)\Delta\pi_s , \tag{26}$$

$$J_s = \bar{c}_s(1 - \sigma^s)J_v + \omega^*\Delta\pi^s , \tag{27}$$

where the coefficients are defined by

$$L_p = \bar{V}_w^2 L_{ww} + \bar{V}_w\bar{V}_s L_{ws} + \bar{V}_s^2 L_{ss} ,$$

$$\sigma^s = 1 - (1/L_p\bar{c}_s)(\bar{V}_w L_{ws} + \bar{V}_s L_{ss}),$$

$$\omega^* = \omega[1 + (\Delta\pi/\Delta\pi_s)\phi_s],$$

$$\sigma^v = \sigma^s[1 + (\Delta\pi/\Delta\pi_s)\phi_s] + (\Delta\pi/\Delta\pi_s)\phi_s ,$$

$$\omega = L_{ws} - (L_{ww}\bar{V}_w + L_{ws}\bar{V}_s)(\bar{V}_w L_{ws} + \bar{V}_s L_{ss}).$$

When the dilute solution approximation holds, the coefficients σ^v and ω^* become identical with σ^s and ω, respectively, and these are the original Kedem-Katchalsky coefficients. The identity of these coefficients is preserved in the general treatment and is clearer if Eq. 17 is used to define the solute flow's conjugate driving force.

DISCUSSION AND CONCLUSIONS

A number of things can be said about this derivation. First of all γ which arose as the difference between two of Zelman's reflection coefficients is dependent on the Kedem-Katchalsky reflection coefficients (Zelman's σ_{pi}^{sv}) and the volume fractions of the various chemical species. Although the dilute solution approximation involves a term of the form

$$(\Delta\pi/\Delta\pi_i)\phi_i$$

it has been obscured by the transformations made and a number of new coefficients which are simple linear combinations of well-known coefficients have been introduced. It is obvious that had the driving force for solute flow in the absence of volume flow been taken as the force in Eq. 17 the entire problem would have been avoided.

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