

Friction Coefficient Analysis of Multicomponent Solute Transport Through Polymer Membranes

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SYNOPSIS

A new analysis is presented of the relations between the multicomponent diffusion coefficients and the classical Kedem–Katchalsky coefficients which describe solute transport in membranes. This analysis is applied to binary and ternary systems and shows the importance of system nonideality in the calculation of solute diffusion coefficients. It is shown that the solute permeability coefficients can be calculated from independent knowledge of the nonideal thermodynamic activity coefficients and the multicomponent diffusion coefficients of the system. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Linear phenomenological laws combined with expressions from nonequilibrium thermodynamics provide accurate characterization of multicomponent transport in membranes.¹ It is thus possible to characterize a membrane for a particular separation without performing experiments on a wide variety of membranes.

In the following study, two methods were examined that are useful in the study of solute transport through membranes. First, the multicomponent Stefan–Maxwell equations² are compared to the Kedem–Katchalsky³ equations and new correlations between their parameters are derived. The importance of the friction coefficients in determining the response of the membrane suggests that a deeper look at the causes of the friction is necessary. New friction coefficient formalisms are analyzed. These analyses are applicable to dilute solute polymer systems, although the behavior of concentrated solutions cannot be satisfactorily explained.

EQUIVALENCE OF MULTICOMPONENT SOLUTE-TRANSPORT RELATIONS

Consider the multicomponent solute transport in a membrane. From the fundamental entropy dissi-

pation formalism for small departures from equilibrium, the use of equilibrium relations for thermodynamic quantities permits the recognition of all possible ways of entropy dissipation as the products of conjugate driving forces and resulting fluxes. Furthermore, for small gradients of these forces, linearity in the relation of forces to fluxes is assumed, with the material transport properties appearing as the symmetric coefficients in this force-flux relation. The symmetry of these coefficients is the major development of Onsager⁴ and allows the specification of the force on a particular component in a system such as multicomponent transport.

Neglecting temperature gradients since the systems of concern are largely isothermal, a set of equations, known as the Stefan–Maxwell equations, can be obtained.² These are eqs. (1) and (2a–c):

$$\mathbf{d}_i = \sum_{\substack{j=1 \\ j \neq k}}^n \frac{x_i x_j}{D_{ij}} (\mathbf{v}_j - \mathbf{v}_k) \quad (1)$$

$$D_{ij} = D_{ji} \quad (2a)$$

$$\sum_{i=1}^n \frac{x_i}{D_{ij}} = 0 \quad (2b)$$

$$\sum_{i=1}^n \mathbf{d}_i = 0 \quad (2c)$$

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Here, \mathbf{v}_k is a reference velocity arbitrarily chosen as the velocity of the membrane species; D_{ij} , the symmetric multicomponent diffusion coefficient, and \mathbf{d}_i , the force on the species i which has a molefraction x_i .

BINARY SYSTEMS

The first case of application of eqs. (1) and (2) is for the system consisting of three components, i.e., a single solute, water, and the membrane. Since $\mathbf{v}_k = \mathbf{v}_m$ and the membrane is fixed at zero, eq. (1) is written as

$$\nabla \ln a_i + \frac{\bar{V}_i}{RT} \nabla p = \sum_{j=S,W} \frac{N_j}{cD_{ij}} \quad (3)$$

Here, N_j is the flux of component j and is $cx_j\mathbf{v}_j$. The terms x_i in eq. (1) are canceled from both sides after expanding \mathbf{d}_i into the driving forces of chemical potential and pressure. The driving force due to an electrostatic potential can be included on the left-hand side of eq. (3). In eq. (3), a_i is the activity of component i ; \bar{V}_i , the specific volume of component i ; and p , the pressure. Before performing an integration of eq. (3) over the thickness of the membrane δ , the quantities a_i and p have to be averaged out or their dependencies on membrane position have to be specified. For pressure, it is assumed that the gradient across a thin membrane is given by the difference of pressure of the two bounding solutions.

For the solute activity, the activity coefficient is employed:

$$RT \frac{d}{dn} (\ln a_s) = \frac{RT}{\bar{c}_s} \left[1 + \frac{d \ln \gamma_s}{d \ln c_s} \right] \frac{dc_s}{dn} \quad (4)$$

Here, \bar{c}_s is an average concentration of solute which is defined by Kedem and Katchalsky³ as the mean logarithmic concentration based on the concentrations of the bounding solutions, i.e.:

$$\bar{c} = \frac{c_2 - c_1}{\ln(c_2/c_1)} \quad (5)$$

In our new analysis, by defining

$$\frac{d \ln \gamma_s}{d \ln c_s} = \Gamma \quad (6)$$

and using the Gibbs–Duhem relation, we obtain

$$\begin{aligned} RT d \ln a_w &= -RT \frac{\bar{c}_s}{\bar{c}_w} d \ln a_s \\ &= \frac{-(1 + \Gamma)}{\bar{c}_w} RT dc_s \quad (7) \end{aligned}$$

Equation (3) can now be integrated. For a binary system with stationary membrane species, the matrix expression is conveniently written as

$$\begin{bmatrix} \frac{(1 + \Gamma)}{\bar{c}_s} RT \bar{V}_s \\ -\frac{(1 - \Gamma)}{\bar{c}_w} RT \bar{V}_w \end{bmatrix} \begin{bmatrix} \Delta c_s \\ \Delta p \end{bmatrix} = RT \begin{bmatrix} r_{SS} & r_{SW} \\ r_{SW} & r_{WW} \end{bmatrix} \begin{bmatrix} N_S \\ N_W \end{bmatrix} \quad (8)$$

where r_{ij} are the binary resistance (friction) coefficients expressed by eq. (9):

$$r_{ij} = \int_0^d \frac{RT dx}{cD_{ij}} \quad (9)$$

By rearrangement, one obtains

$$\begin{bmatrix} \bar{V}_s \frac{(1 + \Gamma)}{\bar{c}_s} \\ \bar{V}_w \frac{-(1 + \Gamma)}{\bar{c}_w} \end{bmatrix} \begin{bmatrix} \Delta p \\ RT \Delta c_s \end{bmatrix} = [R] \begin{bmatrix} N_S \\ N_W \end{bmatrix} \quad (10)$$

Here, matrix $[R]$ is the *resistance (friction) coefficient matrix* which represents the interaction between the solutes and water in the presence of the membrane. The terms r_{ij} are elements of matrix $[R]$. To incorporate the nonideality in the original expressions of Kedem and Katchalsky³ as expressed by the terms r_{ij} , the following equations can be written for the entropy dissipation function Φ :

$$\Phi = (\mu_w^0 - \mu_w^i) N_w + (\mu_s^0 - \mu_s^i) N_s \quad (11)$$

Here, N_w and N_s are fluxes given by eq. (3) and $(\mu^0 - \mu^i)$ is the difference in chemical potential of the bounding solutions, which is given by

$$\mu^0 - \mu^i = \bar{V} \Delta p + RT \frac{[1 + \Gamma]}{\bar{c}} \Delta c \quad (12)$$

Writing eq. (12) for water and solute, we obtain

$$\begin{aligned}
 & (\mu_w^0 - \mu_w^i)N_w \\
 & = \bar{V}_w N_w \Delta p - \frac{(1 + \Gamma)}{\bar{c}_w} N_w RT \Delta c_s \quad (13)
 \end{aligned}$$

and

$$\begin{aligned}
 & (\mu_s^0 - \mu_s^i)N_s \\
 & = \bar{V}_s N_s \Delta p + (1 + \Gamma) \frac{N_s}{\bar{c}_s} RT \Delta c_s \quad (14)
 \end{aligned}$$

Hence,

$$\begin{aligned}
 \Phi & = (\bar{V}_w N_w + \bar{V}_s N_s) p \\
 & + (1 + \Gamma) \left(\frac{N_s}{\bar{c}_s} - \frac{N_w}{\bar{c}_w} \right) RT \Delta c_s \quad (15)
 \end{aligned}$$

Here, \bar{V}_i is the specific volume of component i . A comparison between the Stefan–Maxwell relations of eq. (10) and the above formulation which incorporates nonideality into the Kedem–Katchalsky framework³ can now be made using the definitions of volume flow, J_V , and exchange flow, J_D . Indeed,

$$J_V = \bar{V}_w N_w + \bar{V}_s N_s \quad (16)$$

and

$$J_D = \left(\frac{N_s}{\bar{c}_s} - \frac{N_w}{\bar{c}_w} \right) (1 + \Gamma) \quad (17)$$

Equations (15)–(17) imply that

$$\Phi = J_V \Delta p + J_D RT \Delta c_s \quad (18)$$

Therefore,

$$\begin{bmatrix} J_V \\ J_D \end{bmatrix} = \begin{bmatrix} \bar{V}_s & \bar{V}_w \\ \frac{(1 + \Gamma)}{\bar{c}_s} & -\frac{(1 + \Gamma)}{\bar{c}_w} \end{bmatrix} \begin{bmatrix} N_s \\ N_w \end{bmatrix} \quad (19)$$

Inversion of eq. (10) and substitution into eq. (19) yields

$$\begin{bmatrix} J_V \\ J_D \end{bmatrix} = \begin{bmatrix} \bar{V}_s & \bar{V}_w \\ \frac{1 + \Gamma}{\bar{c}_s} & -\frac{(1 + \Gamma)}{\bar{c}_w} \end{bmatrix} \times [R]^{-1} \begin{bmatrix} \bar{V}_s & \frac{1 + \Gamma}{\bar{c}_s} \\ \bar{V}_w & \frac{1 + \Gamma}{\bar{c}_w} \end{bmatrix} \begin{bmatrix} \Delta p \\ RT \Delta c_s \end{bmatrix} \quad (20)$$

where matrix $[R]^{-1}$ is the inverse of the friction coefficient matrix.

Thus, the phenomenological coefficients are identified as the matrix elements of $[X^T R^{-1} X]$, where the matrix $[X]$ contains terms representing the system nonideality and matrix $[R]^{-1}$ is symmetric and a function of species interactions. Equation (20) relates experimentally measurable fluxes as defined by Kedem–Katchalsky to experimentally measurable gradients due to differences in bounding solutions. The Onsager coefficients can be evaluated by suitably arranging an experiment whereby flows are measured for prescribed driving forces. This is usually achieved with either a zero concentration gradient and a fixed pressure differential or vice versa, since there are only two equations and three coefficients to be evaluated.

TERNARY SYSTEMS

For a ternary formulation, the Gibbs–Duhem expression must be reexamined. This expression is written as

$$\bar{c}_w d \ln a_w + \bar{c}_s d \ln a_s + \bar{c}_d \ln a_d = 0 \quad (21)$$

This can be rewritten as

$$d \ln a_w = -\frac{\bar{c}_S}{\bar{c}_w} d \ln a_S - \frac{\bar{c}_d}{\bar{c}_w} d \ln a_d \quad (22)$$

From eq. (4) it follows that

$$d \ln a_S = \frac{1}{\bar{c}_S} (1 + \Gamma_S) d\bar{c}_S \quad (23)$$

and

$$d \ln a_d = \frac{1}{\bar{c}_d} (1 + \Gamma_d) d\bar{c}_d \quad (24)$$

Therefore,

$$d \ln a_w = -\frac{(1 + \Gamma_S)}{\bar{c}_w} d\bar{c}_S - \frac{(1 + \Gamma_d)}{\bar{c}_w} d\bar{c}_d \quad (25)$$

Using the Kirkwood formulation as in Lightfoot et al.⁵ for the force balance in terms of resistance coefficients r_{ij} , we obtain

$$RT[1 + \Gamma_S] \frac{d\bar{c}_S}{dx} + \bar{V}_S \frac{dp}{dx} = [r_{SS}N_S + r_{SW}n_w + r_{Sd}N_d] \quad (26)$$

$$-\frac{RT}{\bar{c}_w} [1 + \Gamma_S] \frac{d\bar{c}_S}{dx} - \frac{RT}{\bar{c}_w} [1 + \Gamma_d] \frac{d\bar{c}_d}{dx} + \bar{V}_w \frac{dp}{dx} = [r_{SW}N_S + r_{WW}N_{WW} + r_{Wd}N_d] \quad (27)$$

and

$$\frac{RT}{\bar{c}_d} [1 + \Gamma_d] \frac{d\bar{c}_d}{dx} + \bar{V}_d \frac{dp}{dx} = [r_{Sd}N_S + r_{Wd}N_W + r_{dd}N_d] \quad (28)$$

Performing the integration across the differential thickness dx and using constant values for all the other quantities (since the process is at steady state, the values of N_j are constant), we obtain the matrix form

$$\begin{bmatrix} \bar{V}_S & \frac{1 + \Gamma_S}{\bar{c}_S} & 0 \\ \bar{V}_w & \frac{(1 + \Gamma_S)}{\bar{c}_w} & -\frac{(1 + \Gamma_d)}{\bar{c}_w} \\ \bar{V}_d & 0 & \frac{1 + \Gamma_d}{\bar{c}_d} \end{bmatrix} \begin{bmatrix} \Delta p \\ RT\Delta\bar{c}_S \\ RT\Delta\bar{c}_d \end{bmatrix} = [R] \begin{bmatrix} N_S \\ N_W \\ N_d \end{bmatrix} \quad (29)$$

where

$$R = \begin{bmatrix} r_{SS} & r_{SW} & r_{Sd} \\ r_{SW} & r_{WW} & r_{Wd} \\ r_{Sd} & r_{Wd} & r_{dd} \end{bmatrix} \quad (30)$$

The matrix $[R]$ is symmetric and is the *resistance coefficient matrix*. The Kedem-Katchalsky equations can be applied only if the total and exchange flows are defined correctly for the ternary system. The entropy dissipation function is

$$\Phi = (\mu_w^0 - \mu_w^i)N_w + (\mu_S^0 - \mu_S^i)N_S + (\mu_d^0 - \mu_d^i)N_d \quad (31)$$

Equation (25) gives the driving chemical potential as

$$\mu_w^0 - \mu_w^i = \bar{V}_w \Delta p - \frac{(1 + \Gamma_S)}{\bar{c}_w} RT d\bar{c}_S - \frac{(1 + \Gamma_d)}{\bar{c}_w} RT d\bar{c}_d \quad (32)$$

$$\mu_S^0 - \mu_S^i = \bar{V}_S \Delta p - \frac{(1 + \Gamma_S)}{\bar{c}_S} RT d\bar{c}_S \quad (33)$$

and

$$\mu_d^0 - \mu_d^i = \bar{V}_d \Delta p - \frac{(1 + \Gamma_d)}{\bar{c}_d} RT d\bar{c}_d \quad (34)$$

After integration and averaging, we obtain

$$\begin{aligned} \Phi &= (N_S \bar{V}_S + N_W \bar{V}_W + N_d \bar{V}_d) \Delta p \\ &+ RT(1 + \Gamma_S) \left(\frac{N_S}{\bar{c}_S} - \frac{N_W}{\bar{c}_W} \right) d\bar{c}_S \\ &+ RT(1 + \Gamma_d) \left(\frac{N_d}{\bar{c}_d} - \frac{N_W}{\bar{c}_W} \right) d\bar{c}_d \quad (35) \end{aligned}$$

or

$$\Phi = J_V \Delta p + J_{D1} RT \Delta c_S + J_{D2} RT \Delta c_d \quad (36)$$

Here, J_V is the total flow, and J_{D1} and J_{D2} are the two exchange flows. It must be noted here that the nonideality of the system appears as a multiplying factor $(1 + \Gamma)$ in each flow. Thus, we are free from the Kedem-Katchalsky assumption of a dilute state which would have necessitated ideality and, therefore, a value of Γ , defined in eqs. (4) and (6), that would have been zero. This approach is similar to the binary formalism of Friedman and Meyer.⁶ The following relations are obtained:

$$\begin{aligned} \begin{bmatrix} J_V \\ J_{D1} \\ J_{D2} \end{bmatrix} &= \begin{bmatrix} \bar{V}_S & \bar{V}_W & \bar{V}_d \\ \frac{1 + \Gamma_S}{\bar{c}_S} & -\frac{(1 + \Gamma_S)}{\bar{c}_W} & 0 \\ 0 & -\frac{(1 + \Gamma_d)}{\bar{c}_W} & \frac{(1 + \Gamma_d)}{\bar{c}_d} \end{bmatrix} \begin{bmatrix} N_S \\ N_W \\ N_d \end{bmatrix} \\ &\quad (37) \end{aligned}$$

Substituting for the fluxes from eq. (29) in eq. (37), we obtain

$$\begin{aligned} \begin{bmatrix} J_V \\ J_{D1} \\ J_{D2} \end{bmatrix} &= \begin{bmatrix} \bar{V}_S & \bar{V}_W & \bar{V}_d \\ \frac{(1 + \Gamma_S)}{\bar{c}_S} & -\frac{(1 + \Gamma_S)}{\bar{c}_W} & 0 \\ 0 & \frac{(1 + \Gamma_d)}{\bar{c}_W} & \frac{(1 + \Gamma_d)}{\bar{c}_d} \end{bmatrix} \\ &\times [R]^{-1} \begin{bmatrix} \bar{V}_S & \frac{1 + \Gamma_S}{\bar{c}_S} & 0 \\ \bar{V}_W & -\frac{(1 + \Gamma_S)}{\bar{c}_W} & -\frac{(1 + \Gamma_d)}{\bar{c}_d} \\ \bar{V}_d & 0 & \frac{1 + \Gamma_d}{\bar{c}_d} \end{bmatrix} \\ &\times \begin{bmatrix} p \\ RT \Delta \bar{c}_S \\ RT \Delta \bar{c}_d \end{bmatrix} \quad (38) \end{aligned}$$

Therefore, the Onsager coefficient matrix for this ternary system is

$$\begin{aligned} L_T &= \begin{bmatrix} \bar{V}_S & \bar{V}_W & \bar{V}_d \\ \frac{1 + \Gamma_S}{\bar{c}_S} & -\frac{(1 + \Gamma_S)}{\bar{c}_W} & 0 \\ 0 & -\frac{(1 + \Gamma_d)}{\bar{c}_W} & \frac{(1 + \Gamma_d)}{\bar{c}_d} \end{bmatrix} \\ &\times [R]^{-1} \begin{bmatrix} \bar{V}_S & \frac{1 + \Gamma_S}{\bar{c}_S} \\ \bar{V}_W & -\frac{(1 + \Gamma_S)}{\bar{c}_d} \\ \bar{V}_d & \frac{1 + \Gamma_d}{\bar{c}_d} \end{bmatrix} \quad (39) \end{aligned}$$

Comparison of this with the coefficient matrix of eq. (20) in the binary system allows an extension to other systems. For example, the binary and quaternary systems have coefficient matrices L_B and L_Q given by

$$\begin{aligned} L_B &= \begin{bmatrix} \bar{V}_S & \bar{V}_W \\ \frac{(1 + \Gamma_S)}{\bar{c}_S} & -\frac{(1 + \Gamma_S)}{\bar{c}_W} \end{bmatrix} \\ &\times [R]^{-1} \begin{bmatrix} \bar{V}_S & \frac{(1 + \Gamma_S)}{\bar{c}_S} \\ \bar{V}_W & \frac{(1 + \Gamma_S)}{\bar{c}_W} \end{bmatrix} \quad (40) \end{aligned}$$

$$L_Q = \begin{bmatrix} \bar{V}_S & \bar{V}_W & \bar{V}_{d1} & \bar{V}_{d2} \\ \frac{(1 + \Gamma_S)}{\bar{c}_S} & \frac{(1 + \Gamma_S)}{\bar{c}_W} & 0 & 0 \\ 0 & \frac{(1 + \Gamma_{d1})}{\bar{c}_W} & \frac{(1 + \Gamma_{d2})}{\bar{c}_d} & 0 \\ 0 & \frac{-(1 + \Gamma_{d2})}{\bar{c}_W} & 0 & \frac{(1 + \Gamma_{d2})}{\bar{c}_d} \end{bmatrix} \times [R''] \begin{bmatrix} \bar{V}_S & \frac{(1 + \Gamma_S)}{\bar{c}_W} & 0 & 0 \\ \bar{V}_W & \frac{(1 + \Gamma_S)}{\bar{c}_W} & \frac{-(1 + \Gamma_{d1})}{\bar{c}_W} & -(1 + \Gamma_{d2}) \\ \bar{V}_{d1} & 0 & \frac{(1 + \Gamma_{d1})}{\bar{c}_d} & 0 \\ \bar{V}_{d2} & 0 & 0 & \frac{(1 + \Gamma_{d2})}{\bar{c}_d} \end{bmatrix} \quad (41)$$

The major development of Kedem and Katchalsky³ was to specify relations between experimentally measured fluxes and pressure or concentration gradients for a system of a single solute. The coefficients in these relations are the membrane-related parameters, though they are also functions of solute properties. Consider the equations

$$J_V = -L_p \Delta p + (L_p \sigma_V) RT \Delta c_S \quad (42)$$

and

$$N_S = [L_p(1 - \sigma_S)\bar{c}_S] \Delta p + [L_p \sigma_V(1 - \sigma_S)\bar{c}_S \omega_p] RT \Delta c_S \quad (43)$$

Here, J_V is the volume flux, and N_S , the solute flux. The coefficients are functions of the hydraulic conductivity L_p , the phenomenological permeability ω_p , and the reflection coefficients σ_V and σ_S for flow volume and solute, respectively. Equations (42) and (43) can be compared to eqs. (10) and (20) to determine if the coefficients calculated from membrane diffusion experiments are really functions of the elements of the matrix $[R]$. However, eq. (20) represents conjugated fluxes and forces, whereas eqs. (42) and (43) do not.

It is clear that three coefficients are needed to determine the system for the case of a single solute with water and membrane as the other components. In the Kedem-Katchalsky framework, these are L_p ,

ω_p , and σ_V or σ_S . For a system with more components, the number of coefficients will increase. The two reflection coefficients are experimentally defined by

$$\sigma_S = 1 - \frac{N_S}{\bar{c}_S J_V} \Big|_{\Delta \bar{c}_S = 0} \quad (44)$$

$$\sigma_V = \frac{\Delta p}{RT \bar{c}_S} \Big|_{J_V = 0} \quad (45)$$

where the experiment is chosen so that concentration differences are zero for σ_S and there is no net flow for σ_V .

Equations (20) and (38) must be viewed in the light of their ability to specify the membrane. Experimentally, a system for pressure and concentration gradients can be set up using a diffusion cell and characterization of various membranes is possible.⁷ The experiments must be conducted with extreme care and there is a scarcity of reliable data where the effects of concentration polarization, among other adverse effects, are minimized. An example of such data was that of Kaufman and Leonard⁸ where cellophane is characterized for only three solutes at two temperatures.

From the coefficient matrices presented earlier, it is expected that the coefficients for a membrane in a binary system will be different from the coefficients for the same membrane in a ternary system.⁹ This is due to the increased competition for pore openings and a blocking of these openings. The pre-

vious analysis provides a clear method of calculation of all the coefficients needed for the determination of the solvent and solute fluxes in membranes, starting from first principles. Knowledge of the non-ideal thermodynamic behavior of the system is enough to achieve this calculation.

CONCLUSIONS

The previous analysis presented a potentially useful framework of correlation of solute permeabilities with the multicomponent diffusivities in multicomponent systems of membrane transport. Knowledge of the nonideal behavior of such systems can lead to an accurate analysis of solute transport. Unfortunately, with the exception of very special cases,⁷ the various nonideal terms are not always available for the necessary calculations.

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