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Hydrodynamic Models for Diffusion in Microporous Membranes *

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Abstract

The hydrodynamic theory of diffusion is extended to describe osmotic flow of binary solutions in microporous membranes. It is shown that the one-dimensional microscopic rate equations of irreversible thermodynamics are completely consistent with creeping flow hydrodynamic analyses. It is further shown how one may determine the one-dimensional coefficients from the results of hydrodynamic analysis and how one may obtain macroscopic descriptions by integrating the microscopic equations over the diffusion path. In this way a complete and self-consistent means is developed for interpreting macroscopic behavior in terms of a molecular model. By way of example, a scheme is presented and implemented for estimation of reflection coefficients, σ , from the hydrodynamic analysis of P. M. Bungay and H. Brenner (*Journal of Fluid Mechanics* 1973, 60, 81). The resulting σ 's are sensitive to the solute radial probability density; for a uniform distribution the present values are larger than those reported recently by other workers.

INTRODUCTION

Increasing interest in the nature of membrane transport by both biologists and engineers requires going beyond the formal descriptions provided by linear irreversible thermodynamics. We are now in need of physical models for interpreting experimental data and for predicting the properties of proposed synthetic membranes. The need for such models has been widely recognized and was recently discussed by Anderson and Quinn (1974). It has furthermore been recognized by many past workers, e.g., Kobatake (1964), that realistic physical models should be consistent with irreversible thermodynamic arguments.

One of the simplest models of membrane transport which appears realistic for interpretive purposes is that of parallel cylindrical pores with the pore wall and diffusing solute particles behaving as macroscopic hydrodynamic bodies, and with the solvent behaving as a Newtonian fluid. The simplest of such systems in turn contains but one solute species. Such a system is ternary from a diffusional point of view since it contains three diffusing species:

w = solvent, usually water,

s = solute, e.g., a hydrophilic molecule,

m = matrix or pore wall.

From a thermodynamic standpoint, however, the system is binary, since the internal state of the pore at equilibrium is determined only by that of the external binary solution. The solute is insoluble in the matrix substance.

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To describe such a system formally we need three microscopic continuity relations, two rate equations to relate transport rates to the appropriate driving forces, and suitable boundary conditions. These requirements are summarized by Lightfoot (1974, Sects. III. 1.2, 1.4, and 2.1) and are reviewed briefly below. To obtain numerical descriptions one needs, in addition, equations of state for the transport and thermodynamic properties appearing in the formal description. The primary purpose of this paper is to show how these may be obtained via hydrodynamic analysis for the specialized but useful pore model. To obtain the macroscopic numerical descriptions of primary practical interest one must then proceed to integrate the microscopic equations across the diffusion path and to take into account the concentration, pressure, and potential inequalities at the interfaces between the membrane and the surrounding fluid phases. It is a secondary purpose of this paper to illustrate this procedure, and we choose as an example the calculation of reflection coefficients for selected situations.

FORMULATION OF THE DIFFUSION PROBLEM

For the thin membranes of most current interest diffusional transients are unimportant, and we may write the continuity equations in the form

$$N_m=0, \quad (1)$$

$$N_s=\text{constant}, \quad (2)$$

$$N_w=\text{constant}. \quad (3)$$

Here the N_i are molar fluxes of the species i relative to coordinates fixed in the membrane, as described by Bird *et al.* (1960, Sect. 16.1).

The rate equations may be written in a variety of ways, among them that developed systematically by Lightfoot (1974, Sects. III. 1.2, 1.4, and 2.1) from the basic Onsager relationships as specialized by Scattergood and Lightfoot (1968). These are quite compact, and we therefore begin our analysis with them in the form

$$d_s=cR_{sw}x_sx_w(u_w-v_s)-cr_{sm}x_su_s, \quad (4)$$

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$$d_w=cR_{ws}x_wx_s(u_s-v_w)-cr_{wm}x_wu_w. \quad (5)$$

Here the d_i are normalized driving forces tending to produce diffusional motion of the species i ; for our situation they may be defined by

$$d_i=x_i\left(\frac{d}{dz}\ln\alpha_i\right)_{T,p}+\left(x_i\bar{V}_i/RT\right)\frac{dp}{dz}-x_i\frac{\tilde{g}_i}{RT}. \quad (6)$$

In Eqs. (4) to (6),

v_i = observable velocity of species i , with v_m taken equal to zero,

x_i = observable mole fraction of species i (s or w) in the binary solution contained within the pore

c = total molar concentration of the solution contained within the pore,

$R_{sw} = R_{ws}$ = an inverse diffusivity, or frictional coefficient, describing the diffusional interaction between solute and solvent,

r_{im} = corresponding frictional coefficient for interaction of species i with the matrix,

a_i = the thermodynamic activity of species i , defined for existing composition but at fixed, arbitrary, temperature T and pressure p ,

z = the direction of observable motion,

T = absolute temperature,

p = hydrostatic pressure,

$\bar{V}_i$ = partial molal volume of species i ,

R = international gas constant,

$\tilde{g}_i$ = sum of all body forces, per mole, acting on species i , in the z direction.

The above formulation is very closely related to the frictional model of Spiegler (1958). It is, however, based on rigorous thermodynamic analysis rather than a plausibility argument, and it has several particularly convenient features:

- i. Concentrations are defined for the mobile solution within the matrix so that $x_s + x_w = 1$ and

$$x_s \left(\frac{d}{dz} \ln \alpha_s \right) + x_w \left(\frac{d}{dz} \ln \alpha_w \right) = 0.$$

- ii. The membrane matrix concentration is incorporated directly into the frictional coefficients r_{im} and need not be specified.

¹The observable mole fractions and velocities are defined by the equations

$$x_s = \int_0^{R_0} \rho(r) r dr / \left(c \tilde{N} \int_0^{R_0} r dr \right), \quad (i)$$

$$v_s = \int_0^{R_0} \rho(r) (v_s)_{loc} r dr / \int_0^{R_0} \rho(r) r dr. \quad (ii)$$

Here $\tilde{N}$ is Avogadro's number and ρ is the probability density of a particle center occurring at radial position r . The term $(v_s)_{loc}$ is the local solute velocity at any given radial position.

$$x_w = 1 - x_s, \quad (iii)$$

$$v_w = [(Q/\pi R_0^2) - c_s \bar{V}_s v_s] / c_w \bar{V}_w, \quad (iv)$$

where Q is the total volumetric flow rate through the pore cross section.

iii. The $\tilde{g}_i$ comprise all body forces, including that of gravitational attraction.

All these features will be used to advantage below.

Our microscopic diffusional formulation is now complete, but it is not in the most convenient form for obtaining macroscopic descriptions. Rather, it is desirable to separate the diffusional driving forces from those of pressure and body forces, to obtain analogs to Poiseuille's and Fick's laws.

We begin simply by adding Eqs. (4) and (5) and putting in Eq. (6) for the d_i to obtain

$$(r_{sm}N_s + r_{wm}N_w) = (cr_{sm}x_s v_s + cr_{wm}x_w v_w) = -[(dp/dz) - (cx_s \tilde{g}_s + cx_w \tilde{g}_w)]/cRT \quad (7)$$

or

$$v^f = -\kappa(dP/dz), \quad (8)$$

where

$$\begin{aligned} v^f &\equiv \frac{(r_{sm}x_s v_s + r_{wm}x_w v_w)}{(r_{sm}x_s + r_{wm}x_w)} \\ &= \text{frictional velocity of the solution,} \end{aligned} \quad (9)$$

$$\kappa = [c^2 RT (r_{sm}x_s + r_{wm}x_w)]^{-1}, \quad (10)$$

$$dP/dz = dp/dz - (cx_s \tilde{g}_s + cx_w \tilde{g}_w). \quad (11)$$

It may be noted that dP/dz is just the total force per unit volume acting on the solution in the pore and that P is identical with that of Bird *et al.* (1960), as generalized to a multicomponent solution. The quantity κ is analogous to a hydraulic permeability. However, the velocity v^f in Eq. (9) is not the familiar mass-average velocity but a mixture velocity weighted with respect to the $x_i r_{im}$. The difference between v^f and the mass-average velocity will be small for dilute solutions ($x_s \ll x_w$), but it is important conceptually. Equation (11) appears to be new, in the use of *motive pressure* P in place of p , but it corresponds very closely to Lightfoot's equation (1974, Eq. (III. 3.16), p. 249). In the limit as x_s approaches zero we may write

$$v_w \doteq -(1/r_{wm}c^2 RT)(dP/dz) \quad (x_s \rightarrow 0). \quad (12)$$

We shall use this result later.

We would now like to put Eq. (6) into (4) and (5) and add the results in such a way as to eliminate P , and thus obtain an analog of Fick's law. This is unfortunately impossible for the general case, but it can be done if either pressure gradients or body forces can be neglected. Thus, if hydraulic gradients predominate we may write

$$N_s = -cD_{sm}(dx_s/dz) + x_s N \left(\tilde{g}_i \ll \bar{V}_i \frac{dp}{dz} \right), \quad (13)$$

where

$$\begin{aligned} N_i &= c_i v_i = \text{the molar flux of species } i, \\ cD_{sm} &= (\partial \ln \alpha_s / \partial \ln x_s)_{T,p} / (R_{sw} + r_{sm}), \end{aligned} \quad (17)$$

$$N = [R_{sw}(N_s + N_w) + c\bar{V}_s(r_{wm}N_w + r_{sm}N_s)] / (R_{sw} + r_{sm}). \quad (18)$$

² Equations (8) and (13), along with their definitions, are now ready to integrate over the diffusion path. Before proceeding to such a macroscopic description, however, we show how R_{sw} , r_{sm} , and r_{wm} , may be determined from hydrodynamic parameters.

COMPARISON OF DIFFUSIONAL AND HYDRODYNAMIC FORMULATIONS

We base this part of our development on the analysis of Bungay and Brenner (1973) who provide a very powerful general formulation of pore hydrodynamics as well as specific results of practical interest. This analysis deals with isolated spheres moving at vanishing Reynolds number through a Newtonian continuum in a duct of circular cross section; the geometry of this situation is shown in Fig. 1. The spheres then correspond to large³ solute molecules in dilute solution, the continuum to solvent, and the pore wall to the membrane matrix. Note that we have already ensured a complete analogy in defining our diffusing system to include only the mathematical surface of the matrix and the binary solution contained within it. We may therefore use Eqs. (4) to (6) without substantial change. Bungay and Brenner permit the sphere to take any physically possible position within the duct so that one can construct a proper model for arbitrary spatial distribution of solute. We return to this point later. These authors consider

²Equation (13) bears a superficial resemblance to Eqs. (6) and (7) of Anderson and Quinn (1974), but it is much to be preferred. First, Eq. (13) is independent of physical model and hence more general. Second, Eqs. (6) and (7) of Anderson and Quinn appear to be inconsistent even with hydrodynamic models in the use of the volume-average velocity v^0 as their reference velocity. This inconsistency arises because the diffusivity D_{im} and the reference velocity cannot be chosen independently. This can perhaps best be seen by writing Eq. (18) in the form

$$N = [(R_{sw} + c\bar{V}_s r_{sm})c_s v_s + (R_{sw} + c\bar{V}_s r_{wm})c_w v_w] / (R_{sw} + r_{sm}) \quad (14)$$

and comparing this with the volume-average velocity

$$v^0 = c_s \bar{V}_s v_s + c_w \bar{V}_w v_w. \quad (15)$$

Use of the volume-average velocity can then be justified for our D_{sm} only if

$$(R_{sw} + c\bar{V}_s r_{sm}) / (R_{sw} + c\bar{V}_s r_{wm}) = \bar{V}_s / \bar{V}_w, \quad (16)$$

which is unlikely. Consistent choices of D_{sm} and reference velocity can only be made if one starts with a proper ternary diffusional formulation.

³Bungay and Brenner's analysis is limited to large solutes through use of a no-slip boundary condition at the sphere surface. (See Bird *et al.*, (1960, Sect. 16.5, for a discussion of this point.)

as driving forces for diffusion only pressure gradients in the solution and body forces, e.g., of gravity, on the spheres. Equation (6) then takes the forms

$$d_s = [x_s \bar{V}_s (dp/dz) - x_s \tilde{g}_s] / RT, \quad (19)$$

$$d_w = [x_w \bar{V}_w (dp/dz)] / RT. \quad (20)$$

As we shall see, however, these are entirely sufficient to determine R_{sw} , r_{sm} , and r_{wm} , which can then be used to describe more complex situations.

We begin our comparison by noting that Eqs. (19) and (20) can be combined with (4) and (5) to obtain

$$\bar{V}_s (dp/dz) - \tilde{g}_s = -cRT[(r_{sm} + R_{sw}x_w)u_s - R_{sw}x_w u_w] \quad (21)$$

and

$$\bar{V}_w (dp/dz) = -cRT[-R_{sw}x_s u_s + (r_{wm} + R_{sw}x_s)u_w]. \quad (22)$$

These are now to be compared with the Bungay and Brenner formulation [1973, Eq. (2.13)], given in its most general form.

For the zero-torque condition of interest to us, that relation takes the form⁴

$$\tilde{g}_s = \tilde{N} [A_{11}u_s - A_{12}(\phi_s u_s + \phi_w u_w)], \quad (23)$$

$$dp^\dagger/dz = cx_s \tilde{N} [A_{21}u_s - A_{22}(\phi_s u_s + \phi_w u_w)]. \quad (24)$$

Here $\tilde{N}$ is Avogadro's number, and $dp^\dagger/dz$ is the change in pressure gradient resulting from the presence of solute; $\phi_i = c_i \bar{V}_i$ is the volume fraction of species i present.

The A_{ij} are phenomenological coefficients dependent only on relative size a/R_0 and position a/h of solute in the duct and subject to the restraint that

⁴The following relations exist between the Bungay and Brenner notation and ours:

$$\begin{aligned} -F &= \tilde{g}_s / \tilde{N}, \\ -A\Delta p^\dagger &= \left(\bar{V}_s / \tilde{N} \phi_s \right) (dp^\dagger/dz) = (dp^\dagger/dz) / c \tilde{N} x_s, \\ U_0 &= u_s, \\ V_m &= u^0 = (\phi_s u_s + \phi_w u_w) = \text{volume average velocity}, \\ A_{11} &= \mu [K^l - K^r (L^l/L^r)], \\ A_{12} &= A_{21} = \mu [K^s - K^r (L^s/L^r)], \\ A_{22} &= \mu [P^s - P^r (L^s/L^r)]. \end{aligned}$$

$$A_{12}=A_{21}. \quad (25)$$

Here a is the radius of the sphere, R_0 is the radius of the duct, and h is the distance of the sphere center from the duct wall. Equations (23) and (24) may now be put into Eqs. (19) and (20) with the aid of the relation⁵

$$dp/dz = dp^{\dagger}/dz - 8\mu v^0/R_0^2. \quad (26)$$

The second term on the right side of Eq. (26) is the pressure gradient in the absence of solute as given by Poiseuille's law. If we then collect terms in v_s , and v_w , we find by comparison with Eqs. (21) and (22) that⁶

$$\begin{aligned} R_{sw}=R_{ws} &= \left(A_{21} - \frac{32}{3}\pi\mu\frac{a^3}{R_0^2} - A_{22}cx_s\bar{V}_s \right) (\bar{V}_w/KT) \\ &= \left(A_{21} - \frac{32}{3}\pi\mu\frac{a^3}{R_0^2} \right) \frac{1}{cKT} + O(x_s) \end{aligned} \quad (27)$$

and similarly

$$r_{sm} = \left(A_{11} - A_{12} + \frac{32}{3}\pi\mu\frac{a^3}{R_0^2} \right) \frac{1}{cKT} + O(x_s), \quad (28)$$

$$r_{wm} = 8\mu/c^2 R_0^2 RT + O(x_s). \quad (29)$$

There is therefore, as expected, a complete one-for-one correspondence between the general irreversible-thermodynamic formulation and the specific creeping-flow hydrodynamic model.

Equations (27) through (29) complete the reformulation of the hydrodynamic analysis in diffusional terms, and this comparison is valuable in itself. Thus, even in the absence of numerical values for the A_{ij} , these results suggest that (i) R_{sw} , r_{sw} , and r_{wm} , are concentration independent in the first approximation, and (ii) r_{wm} is given directly by Poiseuille's law. These conclusions should also hold for nonspherical particles, so long as they are rigid and reasonably compact; they thus permit integration of Eqs. (4) through (6) over the pore length to obtain the macroscopic descriptions of the next section.

Equations (27) through (29) also provide numerical values for R_{sw} , r_{sm} , and r_{wm} , for situations described by Bungay and Brenner (1973), and other hydro-dynamists. We will discuss these numerical aspects elsewhere and only note here that

$$A_{12} = 6\pi\mu\alpha(y_3/y_2) \quad (30)$$

and

⁵Use of v^0 in Eq. (26) is required for consistency with Bungay and Brenner.

⁶Here advantage is taken of the relations $\bar{V}_s = \frac{4}{3}\pi\alpha^3 \tilde{N}$ and $\lim_{x_s \rightarrow 0} \{c\} = V_w^{-1}$. The Bungay and Brenner analysis was developed for isolated spheres so terms of order x_s , should not be retained relative to those of order unity.

$$A_{11}=6\pi\mu\alpha/y_2, \quad (31)$$

where y_2 and y_3 are the ordinates of Figs. 2 and 3, respectively, of Bungay and Brenner (1973).

It should also be noted that Eqs. (23) through (29) are valid only for a solute at a given position relative to the duct wall. For solutes distributed over the entire accessible space—the usual situation of interest—the frictional coefficients of Eqs. (27) to (29) must be replaced by the probability weighted values of the Appendix.

One simple example is

$$\rho(r)=\text{constant}, \quad 0 < r < (R_0 - \alpha), \quad (32)$$

$$=0, \quad r > (R_0 - \alpha). \quad (33)$$

Here $\rho(r)$ is the probability density of a solute molecule center existing at radial position r . This is a commonly used model in which solute concentration is considered uniform except for a region of thickness a adjacent to the wall, from which centers are excluded by simple steric considerations. The solute concentration to be used in Eqs. (4) through (6) is then the macroscopically observable ratio of moles of solute to total pore volume.

Equation (32) can also be used for nonuniform solute distribution *provided that the axial body forces on solute and solvent are position independent*, as assumed in the hydrodynamic analysis. Adsorbed molecules, for example, can be treated simply as residing at $r = R_0 - a$ where hydrodynamics requires them to be stationary.

If the radial distribution is affected by a radial potential, as in a diffuse double layer, one may write

$$\partial P / \partial r = \sum_{i=1}^n \left[\bar{V}_i (\partial p / \partial r) - c x_i \tilde{g}_{ir} \right] = 0, \quad (34)$$

where $\tilde{g}_{ir}$ is the radially directed body force acting on species i , and n refers to the total number of mobile species present. It follows that $\partial P / \partial z$ is independent of radial position,⁷ as required by Eq. (6). Our analysis then remains valid.

For most systems of biological interest, however, body forces result from electrical charges and this requires n to be at least 3: co-ion, counter-ion, and water. Such a situation is not adequately described either by our diffusional formulation or the corresponding hydrodynamic analysis. A one-dimensional self-consistent formal diffusional treatment is sketched out by Lightfoot (1974, Sect. III. 2.4, p. 222, and Sect. III. 3.4, p. 257), but this is still very cumbersome. Essentially all usable treatments of diffusional processes in charged membranes, like that of Kobatake (1964), rely on simplified transport relations. This is clearly still a research area.

⁷Anderson and Malone (1974) make a conceptual error in this regard, in their Eqs. (8)-(13) and the corresponding text. Equation (34) is this requirement for radial equilibrium at an impermeable wall.

DEVELOPMENT OF MACROSCOPIC DESCRIPTIONS

The most convenient starting point for macroscopic descriptions is provided by Eq. (7) in the form

$$cRT(r_{sm}N_s + r_{wm}N_w) = -dP/dz$$

and Eq. (13). It may be seen from Eqs. (2) and (3) and the hydrodynamic results of the previous section that N_s , N_w , and N are independent of z , and experience suggests that D_{sm} should be very nearly so for most situations described by the hydrodynamic model.

We may then integrate Eqs. (7) and (13) over the pore length δ (see Fig. 1) to obtain

$$(r_{sm}N_s + r_{wm}N_w) = (P_0 - P_\delta)/cRT\delta \quad (35)$$

and

$$\ln [(N_s - x_{s0}N)/(N_s - x_{s0}N)] = N\delta/cD_{sm}. \quad (36)$$

One may also obtain the axial concentration profile by partial integration of Eq. (13); this result may be conveniently written in the form

$$(x_s - x_{s0})/(x_{s\delta} - x_{s0}) = (e^{zN/cD_{sm}} - 1)/(e^{\delta N/cD_{sm}} - 1), \quad (37)$$

which is reminiscent of film theory in binary fluid systems (see, for example, Bird *et al.*, 1960, Sect. 21.5).

It must, however, be remembered that intramembrane concentrations and pressures are not directly accessible in most biologically interesting situations. It is thus necessary to relate P and x_s to their counterparts outside the membrane through appropriate distribution relations [for example Lightfoot, 1974, Eq. (1.5.3), p. 178]. For uncharged systems we may replace P by the hydrostatic pressure p and write

$$x_s/x'_s \equiv \lambda(c'/c) = (\gamma'_s/\gamma_s)e^{(p-p')\bar{V}_s/RT}, \quad (38)$$

$$p - p' = (RT/\bar{V}_w) \ln(\alpha_w/\alpha'_w). \quad (39)$$

Here λ is the equilibrium ratio of internal to external solute concentrations, and the primes (') refer to conditions in the external solutions. The γ_i and γ'_i are the mole-fraction-based activity coefficients for the internal and external solutions, respectively. In these equations for interphase distribution equilibria the partial molar volumes are assumed constant. This is not strictly necessary, but further refinement does not presently seem worth while.

It may now be noted that Eqs. (38) and (39) could have been written in the same form; there are, however, good reasons for not doing this:

- i. For dilute systems of usual biological interest $(p - p')$ is typically small relative to $(RT/\bar{V}_s)$ and λ is to a good approximation pressure independent. Furthermore for the nondissociating particles required by our hydrodynamic analysis (γ'_s/γ_s) is normally concentration independent. Then λ may usually be considered as constant; i.e., Henry's law may be assumed.
- ii. Once the constancy of λ is accepted for solute one may use Raoult's law for the solvent and write Eq. (39) as

$$(p - p') = (RT/\bar{V}_w) \ln (x_s/x'_s). \quad (40)$$

Use of these two approximations provides a simple explicit means for relating membrane phase composition and pressure to those in the external solution.⁸

We may now write Eqs. (35) and (36) directly in terms of conditions in the bounding external phases. Where Henry's law is valid for the solute we obtain

$$r_{sm}N_s + r_{wm}N_w = \left[(p'_0 - p'_\delta)/cRT \right] + \ln \left[\frac{1 - x'_{s0}}{1 - x'_{s\delta}} \cdot \frac{1 - x'_{s\delta}}{1 - x'_{s0}} \right], \quad (41)$$

$$\ln \left[\frac{N_s - (\lambda c'/c) x'_{s\delta} N}{N_s - (\lambda c'/c) x'_{s0} N} \right] = \frac{N\delta}{cD_{sm}}. \quad (42)$$

These two equations are sufficient to describe macroscopic behavior.⁹ These results are, however, more cumbersome than is often necessary. Some limiting behavior of interest is discussed by Lightfoot (1974, Sect. 111. 3.2).

This completes our formal development, and it remains only to consider numerical examples, and to compare the above results with other formulations. These tasks we leave largely to a later paper since the available numerical results of hydrodynamic analysis are not yet sufficient to provide a balanced picture of pore diffusion. However, it is possible to obtain rough estimates of the Staverman reflection coefficient σ from Fig. 3 of Bungay and Brenner (1973, Fig. 3), and we consider this possibility briefly by way of illustration.

In our notation σ is defined by the equation¹⁰

$$\sigma = 1 - (v_s/v^0) (\lambda c'/c) \quad (43)$$

for

$$\Delta c'_s = \tilde{g}_s = 0. \quad (44, 45)$$

⁸A more complete treatment was provided many years ago by Gregor. (1951) but its use is not normally justified by available data.

Here $\Delta c'_s$ is the difference between solute concentrations in the external solutions and λ is the equilibrium ratio of internal to external solute concentrations. The requirement that the former quantity be zero ensures that concentration gradients inside the pore vanish.

This is a degenerate case for which it is preferable to return to Eq. (13), rather than to its integrated form, Eq. (36). We may thus write

$$N_s = x_s N \quad (46)$$

or

$$\frac{v_s}{v^0} = \frac{R_{sw} + c \bar{V}_s r_{wm}}{R_{sw} + r_{sm}} + O(x_s). \quad (47)$$

Insertion of Eqs. (27) to (29) into this equation yields

$$\sigma = 1 - \lambda (\bar{A}_{21}/\bar{A}_{11}), \quad (48)$$

which is a very simple result. Note that it is not necessary here to calculate interfacial pressure distributions in order to evaluate Eq. (48), but it is of course necessary to know both the interfacial concentration distribution and the radial solute distribution $\rho(r)$.

In practice, the evaluation of σ from Eq. (48) can be accomplished using the averaging provided in the Appendix. However, by using a more direct method taking advantage of the

⁹Note that the expanded forms of (36) and (37) are

$$r_{sm}N_s + r_{wm}N_w = \left(\frac{\partial \ln \alpha_s}{\partial \ln x_s} \right) \ln \left\{ \frac{\left(\frac{x'_{s\delta}}{1-x'_{s\delta}} \right) - (\lambda c'/c) x'_{s\delta} \frac{N}{N_w}}{\left(\frac{x'_{s\delta}}{1-x'_{s\delta}} \right) - (\lambda c'/c) x'_{s\delta} \frac{N}{N_w}} \right\} / D, \quad (i)$$

$$D = \delta c \bar{V}_s \left\{ 1 + \left(\frac{R_{sw}}{r_{wm}} \right) / \left[1 + x'_{s\delta} \left(\frac{r_{sm}}{r_{wm}} - 1 \right) \right] \right\}, \quad (ii)$$

$$\frac{z}{\delta} = \ln \left\{ \frac{\left(\frac{x'_{s\delta}}{1-x'_{s\delta}} \right) - (\lambda c'/c) x'_{s\delta} (N/N_w)}{\left(\frac{x'_{s\delta}}{1-x'_{s\delta}} \right) - (\lambda c'/c) x'_{s\delta} (N/N_w)} \right\} / \ln \left\{ \frac{\left(\frac{x'_{s\delta}}{1-x'_{s\delta}} \right) - (\lambda c'/c) x'_{s\delta} (N/N_w)}{\left(\frac{x'_{s\delta}}{1-x'_{s\delta}} \right) - (\lambda c'/c) x'_{s\delta} (N/N_w)} \right\}, \quad (iii)$$

which corrects some serious typographical errors in Lightfoot (1974, p. 251).

¹⁰The velocities appearing in Eq. (43) may be written as $v_s = \lambda J_s / \varepsilon c'_s$ and $v^0 = J_v / \varepsilon$, where J_s and J_v are the solute and volumetric fluxes of Kedem and Katchalsky (1958), and ε is the void fraction of the membrane, Equation (43) is therefore identical to the definition of Staverman (1951).

hydrodynamic calculations of Bungay and Brenner (1973), Eq. (48) can be directly expressed in terms of $y_3(r)$, the ordinate in their Fig. 3:

$$\sigma = 1 - \lambda \bar{y}_3, \quad (49)$$

where

$$\bar{y}_3 = \int_0^{R_0} \rho(r) y_3 r dr / \int_0^{R_0} \rho(r) r dr. \quad (50)$$

Accurate tabulated values for $y_3(r)$ at specific values of a/R_0 and a/h were supplied by Bungay (1975) and $\bar{y}_3$ was evaluated using a third-order, least-squares polynomial approximation in the reduced radial coordinate $e = (r/R_0)/(1 - a/R_0)$ (for eight or more of these values) for a/R_0 of 0.05, 0.13, and 0.23. Values for the independent variable, a/h , had first to be converted to appropriate values for e (see legend of Fig. 2).

The estimated values of σ appear in the second column of Table 1 and are shown by the “X’s” in Fig. 2. These values tend to be lower than those obtained by Durbin (1960) using an equation by Renkin (1954), but higher than those obtained by Bean (1972), Curry (1974), or Anderson and Malone (1974), whose calculations are based on less complete theories.

It should be noted that particles near the pore center in a fully developed flow (parabolic velocity profile) would yield negative reflection coefficients, tending to cancel the strongly positive values exhibited by particles with low velocity near the wall. These are given in the third column of Table 1. As a/R_0 approaches zero the positive and negative contributions cancel exactly to produce an observable reflection coefficient of zero. This extreme sensitivity of σ to the distribution of particle velocities suggests a corresponding sensitivity to the radial probability density $\rho(r)$, hence to degree of attraction or repulsion near the wall. Further numerical analysis is clearly indicated.

APPENDIX

The averaging of the frictional coefficients may be obtained as follows, noting that x_s , and x_w , being macroscopically observable quantities as previously defined, are not functions of radial position. Similarly, v_w is not a function of r once the position of the single particle treated by Bungay and Brenner is fixed. Finally we note that the diffusional driving forces d_s and d_w are considered by Bungay and Brenner to be uniform over the cross section.

We now begin the averaging process by solving the basic flux equations for v_s and v_w . Thus if we begin with Eqs. (21) and (22) we obtain

$$(v_s)_{loc} = (b_{ww}/B) S - (b_{sw}/B) W, \quad (i)$$

$$(v_w)_{loc} = - (b_{ws}/B) S + (b_{ss}/B) W, \quad (ii)$$

where $S, W = d_s/x_s, d_w/x_w$,

$$b_{ss} = - (r_{sm} + x_w R_{sw})_{loc}, \quad b_{sw} = x_w (R_{sw})_{loc}, \quad (iii, iv)$$

$$b_{ws} = x_s(R_{sw})_{loc}, \quad b_{ww} = -(r_{wm} + x_s R_{sw})_{loc}, \quad (\text{v, vi})$$

$$B = b_{ss}b_{ww} - b_{sw}b_{ws}. \quad (\text{vii})$$

The subscript (loc) is a reminder that these velocities and frictional coefficients, which are those of Eqs. (27) to (29), refer to *localized* solute particles. (These are *not*), however, point values of the respective quantities.)

The velocities observed for particles distributed over a finite range of r must be obtained from those for localized solute by weighting with respect to the probability of any given solute position. Thus

$$v_i = \int_0^{R_0} \rho(r) (v_i)_{loc} r dr / \int_0^{R_0} \rho(r) r dr. \quad (\text{viii})$$

Note that $(v_w)_{loc}$ is the observable water velocity corresponding to a solute velocity $(v_s)_{loc}$ for all particles at the same distance r from the tube axis. [See also Footnote 1, Eq. (iv).]

It then follows that

$$v_s = \overline{(b_{ww}/B)} S - \overline{(b_{sw}/B)} W, \quad (\text{ix})$$

$$v_w = -\overline{(b_{ws}/B)} S + \overline{(b_{ss}/B)} W, \quad (\text{x})$$

where for any quantity q ,

$$\bar{q} = \int_0^{R_0} \rho(r) q r dr / \int_0^{R_0} \rho(r) r dr. \quad (\text{xi})$$

Note that in carrying out this averaging x_s and x_w are constants, as stated above.

It now only remains to solve the probability weighted equations for S and W , to return to the original Stefan–Maxwell form. We thus obtain

$$d_s/x_s = \left[\overline{(b_{ss}/B)}/B' \right] v_s + \left[\overline{(b_{sw}/B)}/B' \right] v_w, \quad (\text{xii})$$

$$d_w/x_w = \left[\overline{(b_{ws}/B)}/B' \right] v_s + \left[\overline{(b_{ww}/B)}/B' \right] v_w, \quad (\text{xiii})$$

where

$$B' = \overline{(b_{ss}/B)(b_{ww}/B)} - \overline{(b_{sw}/B)(b_{ws}/B)}. \quad (\text{xiv})$$

We now define the coefficients in Eq. (xii) as the probability weighted frictional coefficients of Eqs. (4) and (5) :

$$d_s/x_s = -(r_{sm} + x_w R_{sw}) v_s + x_w R_{sw} v_w, \quad (\text{xv})$$

$$d_w/x_w = x_s R_{sw} v_s - (r_{wm} + x_s R_{sw}) v_w. \quad (\text{xvi})$$

It is clear from the nature of the weighting process that the symmetry relation $R_{sw} = R_{ws}$ is retained. Equations (xv) and (xvi) may be rearranged to

$$d_s = c R_{sw} x_s x_w (v_w - v_s) - x_s r_{sm} v_s, \quad (\text{xvii})$$

$$d_w = c R_{ws} x_s x_w (v_s - v_w) - x_w r_{wm} v_w, \quad (\text{xviii})$$

which are identical to Eqs. (4) and (5). The equivalence of the hydrodynamic and diffusional formulations then extends to arbitrary distribution of solute particles, as it should.

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Fig. 1.
System analyzed. $v_w(r)$ is water velocity profile in the absence of solute particles.

Fig. 2.

Estimations of reflection coefficient, σ , according to various theories. The values from the present study (X) were based on Eq. (49), using the uniform radial probability distribution given by Eqs. (32) and (33). For simplification, $\alpha = a/R_0$. Calculations were carried out using the dimensionless relation $\sigma = 1 - 2 \int_0^{R_0 - \alpha} y_3(\alpha, r) r dr = 1 - 2(1 - \alpha)^2 \int_0^1 y_3(e) e de$, where $e = (r/R_0) / (1 - \alpha) = [1 - \alpha/(a/h)] / [1 - \alpha]$, and h is the distance of sphere center from the wall. The expressions recently developed by Bean [1972, Eqs. (22) and (63)] ($\circ$), Anderson and Malone (1974; $\sigma = [1 - (1 - \alpha)^2]^2$) (light solid line), and Curry [1974, Eq. (22), Table 1, Col. 8] (+) provide values comparable to one another. The heavy solid line is given by applying Renkin's

(1954) Eq. (19) for solute S and water W as suggested by Durbin (1960): $\sigma = 1 - S_s/S_w$, where S_x is an effective fractional surface area for filtration, and is given for molecule x by $S_x = [2(1 - \alpha)^2 - (1 - \alpha)^4] \cdot [1 - 2.104\alpha + 2.09\alpha^3 - 0.95\alpha^5]$.

TABLE 1Influence of Solute Radial Probability Density on Estimation of σ^a

(a/R_0)	Uniform distribution	Nearly on-axis location
0.01	<0.002	-0.962
0.05	0.019	-0.803
0.13	0.083	-0.512
0.23	0.224	-0.182

^aUniform distribution defined by Eqs. (32) and (33). Nearly on-axis location is defined by $\rho(r) = (1 - \alpha)^2/\varepsilon^2$, $0 \leq r \leq \varepsilon R_0 \ll a$, $\rho(r) = 0$, $\varepsilon R_0 \leq r \leq R_0$, the value given being for the limit as $\varepsilon \rightarrow 0$. For both cases, c'/c [Eq. (43)] is unity. For simplification, $\alpha = a/R_0$.