

# ON THE RELATIVE CONTRIBUTION OF VISCOUS FLOW VS. DIFFUSIONAL (FRICTIONAL) FLOW TO THE STATIONARY STATE FLOW OF WATER THROUGH A "TIGHT" MEMBRANE

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**ABSTRACT** The practice of calculating the diffusion contribution to the total pressure-driven flow of water through a tight membrane by using the self-diffusion coefficient for tritiated water is examined by a theoretical analysis. Equations of motion for water and membrane in pressure-driven water flow and water, membrane, and tritiated water in self-diffusion of tritiated water are adapted from Bearman and Kirkwood (1958). These equations of motion are used to develop an equation for the pressure-driven flow of water. Because of the lack of specific information about the detailed structure of most membranes, as well as considerations of the need to eliminate some of the mathematical difficulties, an "equivalent capillary" model is used to find a solution to the equation of motion. The use of the equivalent capillary model and possible ambiguities in distinctions between diffusion and hydrodynamic flow are discussed

## INTRODUCTION

*"Viscous flow is a relative motion of adjacent portions of a liquid. Diffusion is a relative motion of its different constituents.*

*Strictly speaking, the two are inseparable; for the 'hydrodynamic' velocity in a diffusion mixture is merely an average determined by some arbitrary convention."* (Onsager, 1945)

The objective of this paper is to examine the relationship between the viscous and diffusional contributions to flow of water through a membrane having spaces of dimensions not much larger than molecular dimensions, say, less than 10 Å across at any given point between those parts which can be considered the membrane matrix. The reason for concentrating on "tight" membranes of this kind is that in more open membranes the relative contribution of the friction between the fluid and the mem-

brane matrix can be accurately modeled by considering the fluid to be stationary at the fluid-matrix interface. This is equivalent to considering the membrane-fluid frictional interaction as being infinite at the interface and negligible elsewhere (Kobatake and Fujita, 1964; Mikulecky and Caplan, 1966). Once the distance across fluid spaces between adjacent regions of membrane matrix becomes small enough, the above assumption breaks down and the membrane-fluid frictional interaction may be "felt" over a significant portion of the fluid region. It is this latter case that is to be studied here.

Since the work of Onsager (1945), the question of the relationship between the two types of flow has been dealt with by other workers (Mauro, 1957; Robbins and Mauro, 1960; Ticknor, 1958; Longuet-Higgins and Austin, 1966; Lakshminarayanaiah, 1967) from both the theoretical and experimental points of view. In the main these authors were concerned with the possibility of determining the relative contributions of the two types of flow by comparing the results of two experiments: (a) measurement of the water flow per unit of pressure difference across the membrane and (b) measurement of the flow of tritiated water per unit concentration difference of tritiated water in the absence of any hydrostatic pressure difference. The idea is that, by determining the frictional coefficient from the diffusion coefficient in the latter experiment, the contribution due to diffusion in the former can be calculated. Two questions arise here, the first being whether or not an unambiguous distinction between the two flows can be made, and, second, whether the methodology outlined above can indeed be used to make the distinction. This paper will attempt to deal with both these questions.

### *The Equation of Motion*

We wish to calculate the relative contributions of the two types of flow for the flow of water through a membrane for the case where the spaces in the membrane material are small enough to make the frictional terms significant in the equation of motion of water. After obtaining this relation, we wish to examine the validity of evaluating the frictional contribution by measurement of the diffusion rate of tritiated water in the absence of a pressure gradient. We begin with the equations of motion for the water and for the membrane according to Bearman and Kirkwood (1958):

$$\eta_w \nabla^2 \bar{u} - c_w \nabla \mu_w - c_w \xi_{wm} c_m \bar{u}_w = 0, \quad (1)$$

$$-c_m \nabla \mu_m + c_m \xi_{mw} c_w \bar{u}_w + c_m \bar{X}_m = 0, \quad (2)$$

where  $\eta_w$  is the viscosity of the water;  $\xi_{wm}$ ,  $\xi_{mw}$  are the frictional coefficients between water and membrane, and  $\xi_{mw} = \xi_{wm}$ ;  $\bar{X}_m$  is the body force due to the membrane clamps transmitted through the membrane matrix to each local volume element in order to hold the membrane stationary;  $\bar{u}$  is the velocity of the local center of mass

and is equal to

$$\frac{c_m \bar{u}_m + c_w \bar{u}_w}{c_m + c_w} = \frac{c_w}{\rho} \bar{u}_w \quad (3)$$

since the membrane is stationary;  $\bar{u}_i$  is the velocity of component  $i$  relative to some fixed frame of reference (i.e. the laboratory);  $\nabla \mu_w$  is the chemical potential gradient of water and is equal to  $\bar{v}_w \nabla p$  [referred to below as equation (4)] since the concentration of water does not vary across the membrane;  $\nabla \mu_m$  is the chemical potential gradient of membrane and is equal to  $\bar{v}_m \nabla p$  [referred to below as equation (5)] for a random distribution of membrane;  $p$  is the hydrostatic pressure;  $c_w$  is the concentration of water in grams per milliliter;  $c_m$  is the concentration of membrane in grams per milliliter; and  $\rho$  is the density of the water plus membrane system ( $\rho = c_w + c_m$ ).

We also note that

$$\bar{v}_w c_w + \bar{v}_m c_m = 1, \quad (6)$$

where the  $\bar{v}_i$  are the specific molar volumes.

Adding equations (1) and (2) and using equations (3)–(6) we obtain

$$\eta_w \nabla^2 \bar{u} - \nabla p + c_m \bar{X}_m = 0, \quad (7)$$

which is the appropriate form of the Navier-Stokes equation for this system. The next equation, which is the form of the equation of motion for the water flow we wish to examine, can be obtained directly from equation (1) or from equations (2) and (7), making use of the conditions (3)–(6).

$$\eta_w \nabla^2 \bar{u} - c_m \xi_{mw} \rho \bar{u} = c_w \nabla \mu_w. \quad (8)$$

### *The Equivalent Capillary Model*

The problem now reduces to the appropriate choice of geometry and boundary conditions, i.e. “model,” to impose on equation (8) in solving it. For simplicity we adopt the conventional procedure of solving the equation for a model which is a system of right circular cylinders which represent “equivalent” pathways to the actual pathways through the membrane. To preserve the contribution of frictional forces to the net force, we replace the frictional coefficients with “equivalent” or “effective” coefficients, which are a function of the radial distance,  $r$ , from the center of the equivalent capillary. This, in a sense, “smears out” the effect of the presence of membrane network throughout the equivalent capillary system. We assume that the capillaries are uniformly of radius  $a$ . The implications of this model will be examined further in the discussion.

We look for a solution of the form  $\bar{u} = \bar{u}' + \bar{u}_d$ , which represents a diffusion

flow superimposed on a hydrodynamic flow. Such a solution obtains if we require that  $\bar{u}'$  be a function of  $r$  alone, that  $c_m$ ,  $c_w$ ,  $\nabla p$ ,  $\rho$ , and  $\bar{u}_d$  not be functions of  $r$ , and that the quantity

$$c_m \xi_{mw}^*(r) \rho \bar{u}(r) \quad (9)$$

also be independent of  $r$ , where  $\xi_{mw}^*(r)$  is the effective frictional coefficient.

Equation (8) now has the form

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \bar{u}}{\partial r} \right) = \frac{1}{\eta_w} (c_w \nabla \mu_w + c_m \xi_{mw}^*(r) \rho \bar{u}). \quad (10)$$

The boundary conditions corresponding to the conditions mentioned above are

$$\bar{u} = \bar{u}_d \quad \text{at} \quad r = a$$

and

$$\frac{\partial \bar{u}}{\partial r} = 0 \quad \text{at} \quad r = 0.$$

The solution to equation (10) which corresponds to these conditions is

$$\bar{u} = \bar{u}_d + \frac{(r^2 - a^2)}{4\eta_w} [c_w \nabla \mu_w + c_m \xi_{mw}^*(r) \rho \bar{u}].$$

Rearranging this results in the explicit equation for  $\bar{u}$ ,

$$\bar{u} = \frac{4\eta_w \bar{u}_d + (r^2 - a^2) c_w \nabla \mu_w}{4\eta_w - (r^2 - a^2) c_m \xi_{mw}^*(r) \rho}. \quad (11)$$

Next we wish to examine the frictional coefficient which is measured in the experiment determining the diffusion of tritiated water through the membrane in the presence of ordinary water. This frictional coefficient is the one which is ordinarily associated with the self-diffusion of water. Once more following Bearman and Kirkwood (1958), the equations of motion for this case, in which we assume that there are no pressure gradients or velocity gradients present, are

$$-c_w \nabla \mu_w - c_w \xi_{wm} c_m \bar{u}_w - c_w \xi_{wT} c_T (\bar{u}_w - \bar{u}_T) = 0, \quad (12)$$

$$-c_T \nabla \mu_T - c_T \xi_{Tm} c_m \bar{u}_T - c_T \xi_{Tw} c_w (\bar{u}_T - \bar{u}_w) = 0, \quad (13)$$

$$-c_m \nabla \mu_m - c_m \xi_{mw} c_w (-\bar{u}_w) - c_m \xi_{mT} c_T (-\bar{u}_T) = 0, \quad (14)$$

where the subscript T refers to the tritiated water. These equations sum to yield the condition  $\nabla p = 0$ . Since there is no pressure gradient and the membrane is randomly distributed, i.e.  $\nabla \mu_m = 0$ .

$$c_w \nabla \mu_w + c_T \nabla \mu_T = 0. \quad (15)$$

We assume

$$\xi_{wm} = \xi_{mw}, \quad \xi_{Tw} = \xi_{wT}, \quad \xi_{mT} = \xi_{Tm}. \quad (16)$$

If there is no isotope separation, i.e. if  $\xi_{mw} = \xi_{mT}$ , equation (14) reduces to

$$c_T \bar{u}_T = -c_w \bar{u}_w \quad (17)$$

and there is only one independent equation. Substituting equation (17) into equation (13), the diffusion flow is

$$c_T \bar{u}_T = - \frac{c_T}{[c_m \xi_{Tm} + (c_T + c_w) \xi_{Tw}]} \nabla \mu_T. \quad (18)$$

Equation (18) shows that the diffusion coefficient measured in this experiment contains a contribution from the interaction between tritium and water. Although the same physical interaction between water molecules occurs in pure H<sub>2</sub>O, it manifests itself in another way because all the water molecules are indistinguishable. In that case  $\eta_w$  contains such interactions and it has been suggested (Spangler and Snell, 1966) that  $\xi_{Tw}$  and  $\eta_w$  are related by

$$c_w^2 \xi_{Tw} \delta_w^2 = \eta_w, \quad (19)$$

where  $\delta_w$  is a characteristic interaction distance for water. (It is assumed here that  $\xi_{Tw} = \xi_{Tm} = \xi_{wm}$ , i.e. that the isotopes behave the same.) To use equation (18) to evaluate the diffusion flow in the case of pure H<sub>2</sub>O, we must then set  $\xi_{Tw} = 0$  since it has no physical significance under these circumstances. This means that using information from the tritiated water diffusion experiment in the pure H<sub>2</sub>O experiment would imply that  $c_m \xi_{Tm} \gg (c_T + c_w) \xi_{Tw}$  in the former case. By such reasoning, the term  $\bar{u}_d$  in equation (11) should be

$$\bar{u}_d = - \frac{1}{c_m \xi_{Tm}} \nabla \mu_w, \quad (20)$$

where we have now used equation (18), which applies to the tritiated water experiment to calculate the diffusion in the pure water experiment as was done by other authors (Mauro, 1957). Equation (11) becomes

$$\bar{u} = - \frac{[4\eta_w - (r^2 - a^2)c_m \xi_{Tm} c_w]}{[4\eta_w - (r^2 - a^2)c_m \xi_{wm}^*(r)\rho]} \frac{1}{c_m \xi_{Tm}} \nabla \mu_w. \quad (21)$$

The nondiffusional flow is

$$\bar{u} - \bar{u}_d = - \frac{(r^2 - a^2)c_m [\xi_{wm}^*(r)\rho - \xi_{Tm} c_w]}{[4\eta_w - (r^2 - a^2)c_m \xi_{wm}^*(r)\rho]} \frac{1}{c_m \xi_{Tm}} \nabla \mu_w. \quad (22)$$

From the above equations the relative contributions of diffusional and nondiffusional flow can be expressed in terms of the relation of  $\xi_{wm}^*(r)\rho$  to  $\xi_{Tm}c_w$ . If they are equal, the flow is entirely diffusional, while if  $\xi_{wm}^*(r)$  and  $\bar{u}_d = 0$ , the flow is entirely nondiffusional and follows Poiseuille's law.

The analysis has been carried only to the point of describing flows along a given streamline through the membrane, where  $r$  is the position of that streamline relative to the center of the equivalent pore. To bring the analysis to the macroscopic level, the equations need to be integrated and averaged over the area of the capillary and then integrated along  $x$ . All flows are thus treated as flows per unit area.

The average center of mass velocity for the entire capillary is obtained by integration over the cross-sectional area of the equivalent capillary (Kobatake and Fujita, 1964; Mikulecky and Caplan, 1966).

$$\langle \bar{u} \rangle = \int_0^a \bar{u} 2\pi r dr / \int_0^a 2\pi r dr. \quad (23)$$

The resulting expression,

$$\langle \bar{u} \rangle = \left\{ - \int_0^a \frac{[4\eta_w - (r^2 - a^2)c_m \xi_{Tm} c_w]}{[4\eta_w - (r^2 - a^2)c_m \xi_{wm}^*(r)\rho]} r dr \right\} \frac{2}{c_m \xi_{Tm} a^2} \nabla \mu_w, \quad (24)$$

is rather complicated, but could be evaluated for certain functional dependences of  $\xi_{wm}^*(r)$  on  $r$ , which must be obtained for specific molecular models from statistical mechanical considerations. Alternatively, one could estimate the  $r$  dependence of  $\xi_{wm}^*(r)$  and calculate the macroscopic coefficient. The explicit form of this integral coefficient is not essential for this discussion and will be left for future work. It is important to note, however, that the functional form of  $\xi_{wm}^*(r)$  will determine the frictional contribution to the macroscopic flow.

One alternative model arises if the averaging is performed in a particular manner. First, by setting  $\xi_{wm}^*(r) = 0$  in equation (21),

$$\bar{u} = - \frac{1}{c_m \xi_{Tm}} \nabla \mu_w + \frac{c_w (r^2 - a^2)}{4\eta_w} \nabla \mu_w. \quad (25)$$

This equation, which is the sum of a diffusion term and a hydrodynamic term, makes sense only if the averaging is performed as follows:

$$\langle \bar{u} \rangle = \frac{2}{a^2} \int_0^a \frac{C_w (r^2 - a^2)}{4\eta_w} \nabla \mu_w r dr - \frac{2}{(a^2 - \alpha^2)} \int_\alpha^a \frac{1}{c_m \xi_{Tm}} \nabla \mu_w r dr, \quad (26)$$

which is the following expression when all the variables are independent of  $r$ :

$$\langle \bar{u} \rangle = \left[ \frac{c_w (\alpha^2/2 - a^2)}{4\eta_w} - \frac{1}{c_m \xi_{Tm}} \right] \nabla \mu_w. \quad (27)$$

This model assumes that an annular fraction of the capillary cross section of thickness  $(a - \alpha)$  corresponds to the diffusion flow and the remaining, central portion of the capillary has only hydrodynamic flow occurring in it.

The final step would be an integration of equation (24) or (27) over the  $x$  coordinate. This integration should be carried out over limits which correspond to some average path length through the membrane. In that case  $\nabla\mu_w$  would be replaced by  $\Delta\mu_w/\Delta x$ , where  $\Delta x$  is the effective membrane thickness and is related to the actual thickness by some tortuosity factor (Kedem and Katchalsky, 1961). This, of course, assumes a uniform membrane structure as before, so that  $\mu_w$  is the only variable dependent on  $x$ .

## DISCUSSION

Without an exact description of the geometrical pattern of the membrane matrix and a molecular theory for obtaining the function dependence of  $\xi_{wm}$  on position within the matrix, an equivalent capillary model seems to be a suitable way to approach this problem. Even if it were possible to have the information that is lacking, for most membranes the situation would be so complex as to prohibit an analytical solution to any of the pertinent equations. For these reasons there is a large measure of arbitrariness in the choice of model used to obtain a solution to equation (8). This very arbitrariness suggests that there is, at present, no unambiguous way to split the flow measured in the pressure-driven water flow experiment into components which are uniquely attributable to different physical mechanisms. The attempts to do this by bringing in data from the self-diffusion experiment might be questioned because the latter data include information about the interaction between the tritiated and ordinary water. In a tight membrane, however, the contribution of the tritiated water-water interaction can be expected to become negligible (Kedem and Katchalsky, 1961), so that this method should be applicable as long as the nature of the frictional interaction in the self-diffusion experiment is indicative of that in the case where viscous flow is occurring. It is this latter condition which is open to question and relates to the ambiguity in the choice of models for the theoretical description. It would seem that some independent confirmation of the assumption that the same interaction occurs in both experiments is necessary before this method can be considered as a reliable way of estimating the contributions of the two physical mechanisms to the total flow. Also, a theoretical determination of the manner in which the friction coefficient depends on position in the two different experiments would be useful.

Consideration must be given to the relation between the parameters describing the actual membrane and the equivalent capillary model used to approximate the real situation. The construction of an equivalent capillary model for any given membrane should be done in such a way as to preserve the maximum number of parameters characterizing the actual membrane. Thus it would be required that the

number and size of the capillaries leave such quantities as  $c_w$ ,  $c_m$ , and  $\rho$  unchanged. The equivalent capillary radius might be estimated from the results of the two experiments we have been discussing by a well-known technique (Solomon, 1961). The assumption that the membrane matrix is random is compatible with the equivalent capillary model, since we ultimately are only interested in the variation of quantities along the direction of flow through the membrane. Thus in either case statements such as  $\nabla c_m = 0$  apply. The use of an effective frictional coefficient is an attempt to map an irregular pattern of membrane matrix and interstitial spaces into a regular pattern. Whether such a mapping is indeed possible and, if not, how great an error is introduced are empty questions unless we have some means of experimentally evaluating the model. This might be done by attempting to fit it to a number of different experimental situations, but a criterion for using a given functional form of  $\xi_{wm}^*(r)$  must be decided upon, and this criterion also would need experimental verification. It may turn out that there is no equivalent capillary model which will be compatible with a given membrane under all circumstances. However, even if the model should prove to fail under certain other conditions, it does illustrate clearly the problem encountered in attempting to theoretically justify the method being used for experimental determination of the different physical mechanisms involved in the pressure-driven flow of water through a membrane.

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