The Frictional Coefficients of the Flows of Non-Electrolytes Through Artificial Membranes

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ABSTRACT The phenomenological permeation coefficients were determined for two artificial cellulose membranes of known thickness and water content. Transport of non-electrolytes was studied with tagged water, urea, glucose, and sucrose. The effect of the unstirred layers on the experimental determination of the coefficients is discussed. Frictional coefficients between membrane matrix and solutes, and between solvent and solutes in the membrane are calculated. It was shown that the geometrical tortuosity does not correspond to a physical tortuosity.

INTRODUCTION

The phenomenological coefficients used in the thermodynamic description of permeation through membranes are functions of the membrane structure and the properties of the permeating species; in general there is also a dependence on solute concentration. An attempt was made by Spiegler (1) to translate these coefficients into frictional terms of the type used by Einstein in his well known theory of Brownian motion and diffusion. This approach was extended by Kedem and Katchalsky (2) who derived a set of equations in which the phenomenological coefficients are expressed as explicit functions of frictional and distribution coefficients as well as of some membrane characteristics such as membrane thickness, water content, and the tortuosity of the capillaries. Although the expressions thus obtained have the advantage of physical concreteness and can be compared with other known properties of the permeants and the membrane, they are less general than the proper thermodynamic coefficients. Moreover, it is realized that the frictional expressions are based on several assumptions which apply to dilute solutions and to membranes which may be regarded as phases in a thermodynamic sense. To what extent these assumptions apply to biological membranes is open to further investigation. It is reasonable, however, to expect that synthetic membranes of

known thickness, structure, and water content, would fulfil the requirements of the theory and could serve as suitable material for the testing of its validity. This paper is devoted to the study of two synthetic, highly swollen membranes through which several solutions of non-electrolytes were transported either by an osmotic gradient or by the action of a mechanical pressure head. The experimental results of the study were analyzed by means of the theoretical equations of Kedem and Katchalsky (2) and frictional coefficients evaluated. The following discussion is devoted to the analysis of the physical meaning of the coefficients and their dependence on membrane and solution factors. Although the frictional description of the membranes leads in general to a consistent interpretation of membrane behavior, there remain even in the simple cases studied below a number of obscure points awaiting elucidation.

MATERIALS AND METHODS

1. *Membranes*

Two commercial cellulose membranes, investigated earlier by Renkin (3) and Durbin (4) were used in this work: these are the Visking dialysis tubing (denoted in the following as D.T.) and the Sylvania wet gel of 300 weight (denoted W.G.). The membranes are relatively stable for several months and gave the same permeability coefficients throughout the testing period. A prolonged storage for several years shows, however, a definite decrease in the filtration coefficient, L_p; thus for fresh D.T. membranes $L_p = 3.4 \times 10^{-11}$ while for membranes kept at room temperature for 12 months $L_p = 2.4 \times 10^{-11}$ cm³/sec. dyne. Measurements extending over shorter periods gave reproducible and consistent results.

The thickness of the wet membranes (Δx) was measured by two methods, first, with a vernier-micrometer (3) equipped with a ratchet to ensure uniform pressure, second, microscopically, between two spots marked on opposite surfaces of the membrane. The second method gave in all cases a result higher by about 10 per cent. It seems that the micrometer exerts some pressure and squeezes the membrane slightly so that the second method was chosen as the more reliable.

The thicknesses used in the calculation were:

Δx for D.T. $\quad 45.2 \times 10^{-4}$ cm $\pm 0.5 \times 10^{-4}$ cm (SE)

Δx for W.G. $\quad 84.2 \times 10^{-4}$ cm $\pm 0.4 \times 10^{-4}$ cm (SE)

The water content of the wet membranes is expressed as the volume fraction φ_w of water of the total membrane volume. It is numerically identical with the fraction of the membrane surface available for the permeation of water-soluble substances (2) and plays an important role in subsequent calculations. The volume fraction of water was determined as follows:—

The wet membrane is blotted seven times and weighed. After some practice the weight of the wet-blotted membranes can be obtained constant to within 1 per cent. The membrane is then dried at 105°C for 2 to 4 hours to constant weight. It is

assumed that the decrease in weight is entirely due to water loss and that it may be used for the evaluation of the water imbibed in the membrane.

The results obtained were:

φ_w for D.T. 0.68 ± 0.02 (SE)

φ_w for W.G. 0.77 ± 0.03 (SE)

2. *Solutes*

The permeating substances were sucrose, glucose, urea (Fisher Chemicals) of analytical reagent grade, and tritiated water. They were dissolved in distilled water.

3. *Determination of Volume Flow*

Both the method and apparatus for measuring volume flow have been described by Durbin *et al.* (4, 5). The apparatus consisted of two lucite chambers separated by the membrane to be studied. A capillary tube was sealed into the smaller of the two chambers, the so called "volume chamber." The larger chamber contained 13 ml of water while the volume chamber contained 2 ml of solution. Changes in volume of fluid in this latter chamber could be determined to 0.1 microliter by observing the level of fluid in the capillary tube through a cathetometer.

During measurements in an osmotic flow experiment, the membrane was supported by a piston of perforated lucite, and pressure was applied to return the membrane to its original position. The reproducibility of the volume measurements was checked by using water on both sides of the membrane. The volume deviated at the most by 0.3 μl from one measurement to another, and there was no one direction of deviation. A check series of five measurements gave the same volume with an accuracy of 0.1 μl; this includes variation due to the measuring apparatus.

To measure the flow of water due to a pressure gradient across the membrane, both chambers were filled with distilled water. A perforated lucite disk was clamped in place to support the membrane, the disk having been covered with thick filter paper (Whatman No. 3) so that the whole area of the membrane was available for filtration.

Routine checks for the stability of the system (i.e. leaks or variation due to temperature etc.) were made by using a saran wrap membrane which is impermeable to water. The system was judged to be stable enough for use when the volume changed by less than 0.1 μl/hr.; this introduced an error of 1 per cent into our smallest volume flow measured.

All experiments were performed in an air-conditioned room at 24 ± 1°C.

Stirring was accomplished by means of a circulating pump in the big chamber, and by a glass-enclosed iron wire driven by an external magnetic stirrer in the small chamber.

4. *Solute Flow*

The apparatus described above was found to be unsatisfactory for solute flow measurement as the stirring was inadequate, and as the total fluid volume could not be

measured with sufficient accuracy. Two large lucite chambers with good access to the inside were therefore used, and the membrane was clamped between them without any support to minimize as far as possible the influence of unstirred regions. The volume of the fluids could be kept constant even if there was some slight movement of the membrane during the experiments. Care was taken to eliminate bubbles accumulating on the surface of the membrane.

Vigorous stirring was achieved by two big glass-enclosed iron bars, on either side of the membrane, driven at the same rate by external magnetic stirrers.

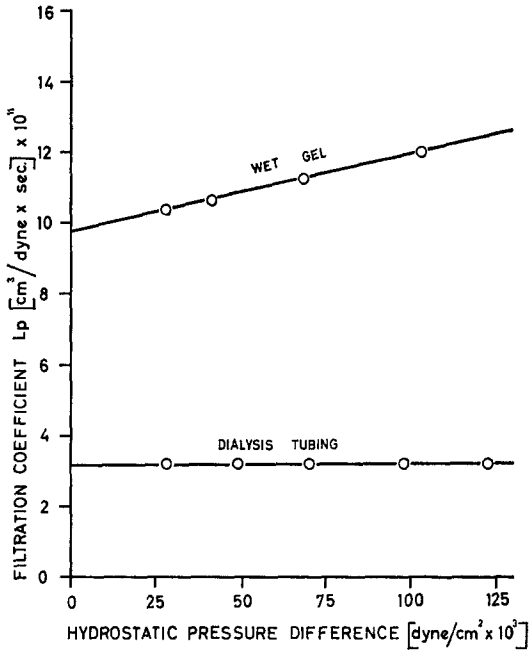

FIGURE 1. Filtration coefficient (L_p) as a function of hydrostatic pressure, in dialysis tubing and wet gel membranes.

The measurements of solute flows were done with radioactive isotopes of C^{14} or H^3. Each measurement consisted of a single sample of 100 μl withdrawn by a micropipette and transferred to 10 ml of scintillation liquid. For all experiments, one micropipette was used; it was rinsed with water and dried with acetone. The samples were counted with a Packard liquid scintillation spectrometer until at least 10,000 counts were obtained.

RESULTS

1. *The Filtration Coefficient L_p*

The thermodynamic equation for volume flow (J_v) as a function of the applied pressure head (Δp) and osmotic difference ($\Delta \pi$) across the membrane is:

$$J_v = L_p \Delta p - \sigma L_p \Delta \pi \qquad (1)$$

It is convenient to determine the filtration coefficient L_p at $\Delta \pi = 0$ or at

equal solute concentration on both sides of the membrane:

$$L_p = \left(\frac{J_v}{\Delta p}\right)_{\Delta\pi=0} \tag{2}$$

The experiments show that with dialysis tubing the volume transported per unit time is linearly proportional to the pressure head, so that L_p is a characteristic property of the dialysis tubing membrane.

In the case of the wet gel, increased pressure on one side of the membrane causes a stretch in the membrane and a corresponding increase in the value of L_p. Both cases are represented in Fig. 1.

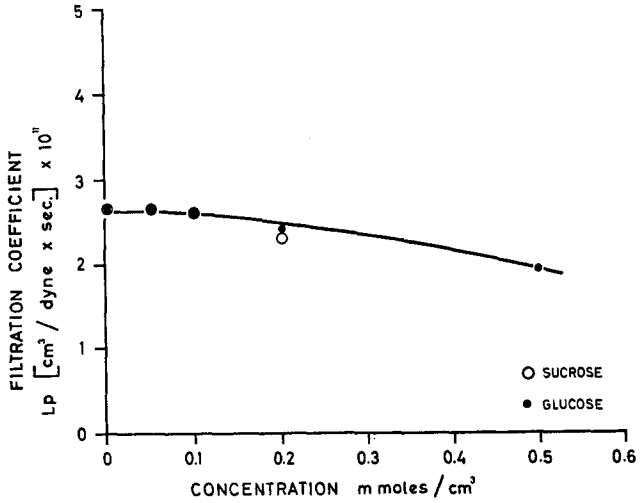

FIGURE 2. Filtration coefficient (L_p) as a function of solute concentration.

L_p is only slightly dependent on solute concentration and may be taken to be equal to the L_p of pure water flow for concentrations smaller than 0.1 M. At higher concentrations, however, a definite decrease in L_p is observable for sucrose and glucose solutions at $\Delta\pi = 0$ (see Fig. 2). This decrease in L_p can be readily explained by the increase in solution viscosity with concentration.

2. *The Solute Permeability Coefficient ω and Its Dependence on Rate of Stirring*

The thermodynamic equation for the determination of ω relates the rate of solute flow J_s with the osmotic pressure difference $\Delta\pi_s$ and with the volume flow J_v

$$J_s = \bar{c}_s(1 - \sigma)J_v + \omega\Delta\pi_s \tag{3}$$

where $\bar{c}_s$ is an average concentration defined in reference 2.

By working with radioactive solute and on assuming solute flow to be represented by the flow of radioactive isotope, it is possible to achieve a condition in which $J_v = 0$ so that

$$\omega = \left(\frac{J_s}{\Delta\pi_s}\right)_{J_v=0} \tag{4}$$

It is difficult to determine ω experimentally because for a given $\Delta\pi_s$, J_s is markedly dependent on the rate of stirring of the solution. The effective permeability coefficient ω' increases with the rate of stirring and approaches a limiting value for a high number of rotations per minute.

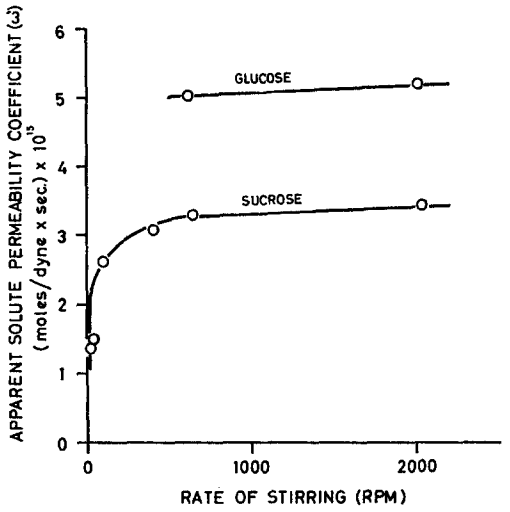

FIGURE 3. The apparent solute permeability (ω') in dialysis tubing as a function of rate of stirring.

The results of some measurements are given in Figs. 3 and 4.

With glucose and sucrose a limiting value was approached which might be regarded as the "true" value for the permeability. In contrast the permeability of HTO does not approach a limiting value and clarification of the dependence of ω' on the rate of stirring is required. In order to understand why ω' changes with stirring, we assume the existence of an *unstirred layer* in the direct neighborhood of the membrane. The existence of such a layer is well known from hydrodynamic studies, and was invoked as early as 1905 by Nernst for the explanation of heterogeneous reactions. The effect of the unstirred layer on membrane permeability was studied *inter alia* by Peterson and Gregor (6).

Denoting the thickness of the unstirred layer by δ, we consider, instead of the net membrane of thickness Δx and permeability ω, a complex membrane of variable thickness $\Delta x + 2\delta$ and effective permeability ω'. As shown in the Appendix, the relation between ω', ω, and δ is given by the expression

$$\frac{1}{\omega'} = \frac{1}{\omega} + \frac{2RT}{D}\delta \tag{5}$$

where D is the solute diffusion coefficient in free solution.

In view of equation (5) the data in Figs. 3 and 4 were replotted as $\frac{D}{2\omega' RT}$ *versus* the rotations per minute of the stirring bar in the cells (see Fig. 5). It will be observed that here, too, a limiting value is reached at velocities of over 500 RPM. Since the thickness of the unstirred layer is essentially a hydro-

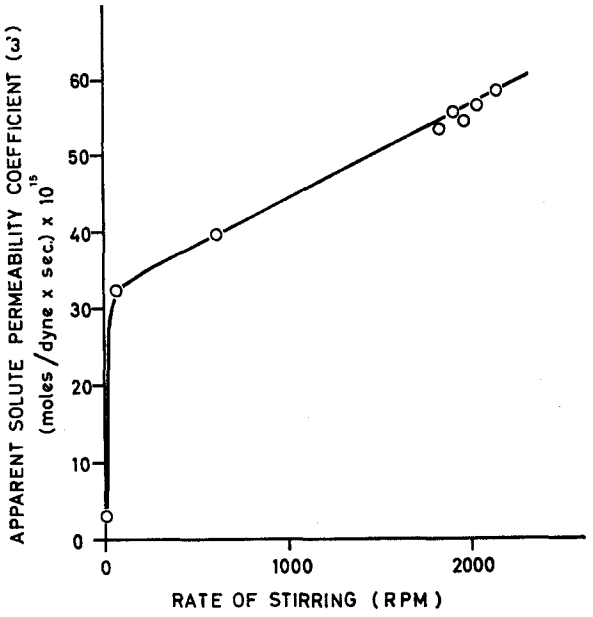

FIGURE 4. The apparent permeability of tritiated water (ω') in wet gel as a function of rate of stirring.

dynamic quantity and therefore independent of solute and membrane, it may be assumed that in all cases the same value of δ_{limiting} is reached and the limiting value of $\frac{D}{2RT\omega'}$ is given by $\frac{D}{2RT\omega} + \delta_{\text{limiting}}$. An estimate of the value of δ_{limiting} is therefore of primary importance for the evaluation of ω—the true permeability of the membrane.

The magnitude of the value of δ_{limiting} can be estimated from Fig. 5 in the following manner; the permeability coefficient ω of tritiated water can be approximated by use of equation 3-16 of the paper of Kedem and Katchalsky (2), namely

$$\omega_o = \frac{\vartheta \varphi_w D_{\text{HTO}}}{\Delta x \cdot RT} \tag{6}$$

where ϑ is the tortuosity factor of the capillaries in the membrane.

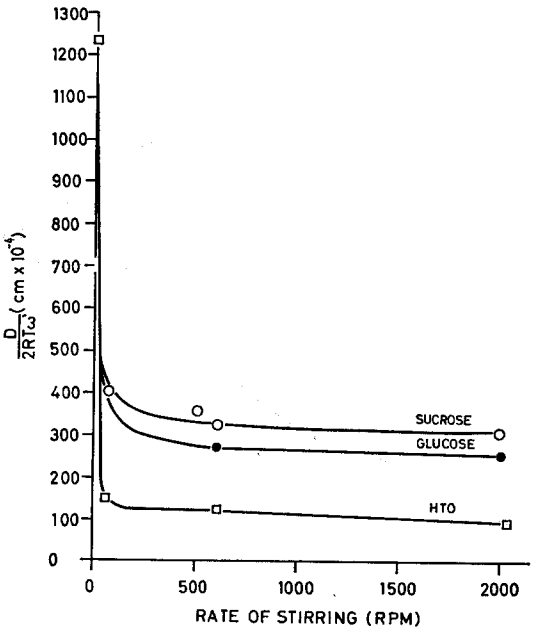

FIGURE 5. $\frac{D}{2RT\omega'}$ (obtained by calculation) as a function of rate of stirring.

TABLE I

PERMEABILITY OF SOLUTES (ω) AS FUNCTION OF CONCENTRATION

Concentration	D.T.	W.G.
moles/cm³	*mole/sec.* × *dyne*	*mole/sec.* × *dyne*
Sucrose		
0.2×10^{-5}	$3.92\times10^{-15}\pm0.13$	
2.5×10^{-5}	$3.67\times10^{-15}\pm0.23$	$7.65\times10^{-15}\pm0.32$
20.0×10^{-5}	$3.50\times10^{-15}\pm0.23$	$7.55\times10^{-15}\pm0.27$
Glucose		
0.5×10^{-5}	$7.18\times10^{-15}\pm0.09$	$12.2\times10^{-15}\pm0.05$
5.0×10^{-5}	$7.14\times10^{-15}\pm0.07$	$11.3\times10^{-15}\pm0.12$
50.0×10^{-5}	$5.91\times10^{-15}\pm0.12$	$10.3\times10^{-15}\pm0.12$
Urea		
30.0×10^{-5}	$20.8\times10^{-15}\pm0.6$	$31.6\times10^{-15}\pm0.7$
200.0×10^{-5}	$19.6\times10^{-15}\pm0.5$	$30.0\times10^{-15}\pm0.65$
HTO		
	$44.7\times10^{-15}\pm1.8$	$78.7\times10^{-15}\pm2.3$

Table I shows that the average value of ω is characteristic for both solute and membrane. Its magnitude is, however, clearly concentration-dependent, decreasing with increasing concentrations. This concentration dependence will be considered in more detail below.

Introducing (6) into (5) we get

$$\frac{D_{\text{HTO}}}{2RT\omega'} = \frac{D_{\text{HTO}}}{2RT\omega_0} + \delta_{\text{limiting}} = \frac{\Delta x}{2\vartheta\varphi_w} + \delta_{\text{limiting}}$$

From Fig. 5 we find that $\left(\frac{D_{\text{HTO}}}{2RT\omega'}\right)_{\text{limiting}} = 100\ \mu$

while for the wet gel $\frac{\Delta x}{2\varphi_w} = \frac{84.2}{2 \times 0.8} = 52.5\ \mu$

so that

$$\delta_{\text{limiting}} = 100\ \mu - \frac{52.5\ \mu}{\vartheta}$$

The value of ϑ for the wet gel is unknown but since the membrane is highly swollen, ϑ must be rather high, say $0.6 < \vartheta < 1$ and hence δ_{limiting} varies from 12μ to 47.5μ.

The value of δ_{limiting} is significant in the study of permeation of highly penetrating substances such as water and urea,[1] while its exact magnitude plays only a minor role in determining permeability of less penetrating substances such as glucose or sucrose.

The failure to recognize the importance of δ and its contribution to ω produced a number of contradictory results. In the following section we assign to δ_{limiting} an arbitrary value of 25μ, with the aid of which the values of ω shown in Table I were obtained.

[1] For membranes with small ω, of the order of magnitude of 10^{-15}, the term δ_{limiting} may be neglected (D is of the order of magnitude of 5×10^{-6}; $2RT = 50 \times 10^{9}$; $\omega \sim 10^{-15}$; $\frac{D}{2RT} = \frac{5 \times 10^{-6}}{5 \times 10^{-5}}$ $= 0.1$ cm so that δ_{limiting} which varies from 10^{-5} to 10^{-3} cm can be neglected).

A direct method for the determination of δ_{limiting} is given by the study of solute permeating through two membranes. The permeability coefficients for the two membranes, ω_1' and ω_2', are first determined independently. The membranes are then arranged in series and the over-all ω_{12}' is measured. For separate membranes we have according to equation (5)

$$\frac{1}{\omega_1'} = \frac{1}{\omega_1} + \frac{2RT\delta_{\text{lim}}}{D} \qquad \frac{1}{\omega_2'} = \frac{1}{\omega_2} + \frac{2RT\delta_{\text{lim}}}{D}$$

The equation for the composite membrane (reference 9) is:

$$\frac{1}{\omega_{12}'} = \frac{1}{\omega_1} + \frac{1}{\omega_2} + \frac{2RT\delta_{\text{lim}}}{D}$$

$$\frac{1}{\omega_{12}'} - \left(\frac{1}{\omega_1'} + \frac{1}{\omega_2'}\right) = -\frac{2RT\delta_{\text{lim}}}{D}$$

Hence,

$$\delta_{\text{lim}} = \frac{D}{2RT}\left(\frac{1}{\omega_1'} + \frac{1}{\omega_2'} - \frac{1}{\omega_{12}'}\right)$$

3. The Reflection or Coupling Coefficient σ

The coupling coefficient, σ, is again evaluated by means of equation (1). Operating at zero pressure difference ($\Delta p = 0$) and using a known concentration difference across the membrane ($\Delta c_s \rightarrow 0$), we obtain a volume flow given by

$$(J_v)_{\Delta p=0} = -\sigma L_p \Delta \pi_s = -\sigma L_p RT \Delta c_s \qquad (7)$$

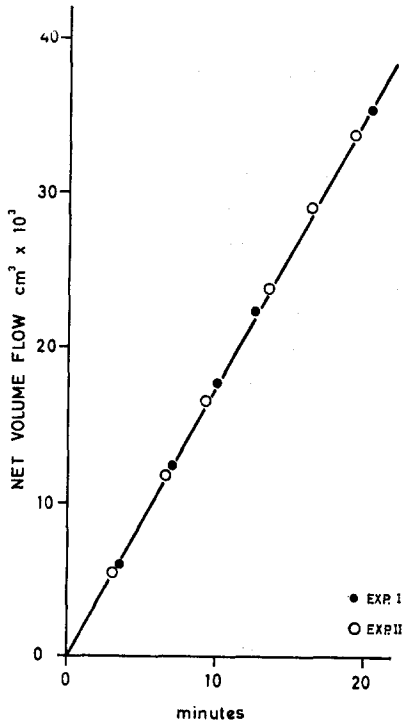

FIGURE 6. Net volume flow across dialysis tubing membrane with sucrose solution (0.1 M) in the volume chamber and distilled water in the large chamber (details in the text).

Since L_p was determined earlier we obtain

$$\sigma = -\left(\frac{J_v}{L_p RT \Delta c_s}\right)_{\Delta p=0} \qquad (8)$$

The volume flow was measured during a period of 10 to 20 minutes starting from the introduction of the solutions into the measuring chambers. During this time interval a quasi steady-state flow was reached as seen in Fig. 6. As shown by Ginzburg and Durbin (7), the concentration difference across the membrane decreases with a rate coefficient k given by:

$$k = RTA\left\{L_p(1 - \sigma)\sigma c^o/V_2 - \omega \frac{V_1 + V_2}{V_1 \cdot V_2}\right\}$$

From the values of k obtained in our experiments the half-time of concentration equilization is about 3 hours. We can therefore assume that during the initial 15 minutes Δc_s remains constant. This assumption is supported by the observation that the rate of flow remains constant during that time. The assignment of a known and constant value to Δc_s enables us to calculate σ.

The values of σ obtained during the period of steady flow are independent of the rate of stirring.

TABLE II

REFLECTION COEFFICIENTS (σ) AS FUNCTIONS OF SOLUTE CONCENTRATION

Concentration $\bar{c}_s$	Dialysis tubing	Wet gel
mole/cm³		
Sucrose		
1.25×10^{-5}	0.163±0.09	
2.50	0.142±0.12	0.036±0.03
5.00	0.122±0.04	0.036±0.02
10.00	0.114±0.01	0.036±0.01
20.00	0.114±0.01	
Glucose		
1.25×10^{-5}	0.123±0.02	
2.50	0.112±0.09	
3.75	0.087±0.01	
5.00	0.083±0.02	0.024±0.05
10.00	0.072±0.04	0.024±0.04
25.00	0.061±0.01	0.019±0.03
Urea		
1.5×10^{-4}	0.013±0.01	
5.0	0.0059±0.01	0.0016±0.008

An inspection of Table II shows that the values of σ are relatively low. This is to be expected for highly swollen membranes of low selectivity. The more swollen wet gel is characterized by lower σ's than the dialysis tubing and the more permeable urea has values of σ closer to zero than those attributed to the sugars. Table II demonstrates the strikingly strong dependence of σ on solute concentration; σ drops by a half as the concentration of glucose in contact with D. T. increases from 1.25×10^{-5} to 25×10^{-5} moles/cm³ and as the concentration of urea rises from 1.5×10^{-4} to 5.0×10^{-4} moles/cm³. As will be shown in the Discussion, this unexpected behavior is fully explained by the strong dependence of the solute diffusion coefficient on concentration in the concentration range of our measurements.

DISCUSSION

The "translation" of the permeability coefficients L_p, ω, and σ into frictional coefficients is based on the assumption that both solute and water encounter

three types of friction in the membrane: the frictional interaction of the solute with its surrounding solvent characterized by the coefficient f_{sw}; the friction of solute with the membrane described by f_{sm}; and that of water and membrane given by the coefficient f_{wm}. In addition, a coefficient K, for the distribution of solute between membrane and surroundings, appears in the expressions for ω and σ. However, in highly swollen membranes, which may be regarded as capillary systems, K may be equated to the water content of the membrane φ_w or $K = \varphi_w$.

As may be shown from the equations of Kedem and Katchalsky (2) the relation between the two sets of coefficients is:

$$L_p = \frac{\varphi_w}{\Delta x\left\{\frac{f_{wm}}{\bar{V}_w} + f_{sm}(1-\sigma)\bar{c}_s\right\}}$$

$$\sigma = 1 - \frac{\omega\bar{V}_s}{L_p} - \frac{f_{sw}}{f_{sw}+f_{sm}} \tag{9}$$

$$\omega = \frac{\varphi_w}{\Delta x(f_{sw}+f_{sm})}$$

By rearranging equations (9), we obtain an equivalent set which permits the evaluation of f_{sw}, f_{sm}, and f_{wm} from the measured permeability coefficients:

$$f_{sw} = \frac{\left\{1 - \sigma - \frac{\omega\bar{V}_s}{L_p}\right\}\varphi_w}{\omega\Delta x}$$

$$f_{sm} = \frac{\sigma + \frac{\omega\bar{V}_s}{L_p}}{1 - \left(\sigma + \frac{\omega\bar{V}_s}{L_p}\right)} f_{sw} \tag{10}$$

$$f_{wm} = \frac{\varphi_w\bar{V}_w}{\Delta x}\left\{\frac{1}{L_p} - \frac{(1-\sigma)\left(\sigma + \frac{\omega\bar{V}_s}{L_p}\right)\bar{c}_s}{\omega}\right\}$$

The coefficients thus calculated are summarized in Table III.

An inspection of Table III reveals a series of interesting facts. First it will be observed that the values of f_{sw} for solute transport in the D.T. membrane increase with concentration of solute. Moreover, Table IV shows that they are higher by an order of magnitude than the corresponding frictional coefficients f°_{sw} derived from the diffusion in free solution $f^{\circ}_{sw} = \frac{RT}{D}$. Table IV shows too that f°_{sw} is not constant but increases with concentration in the

TABLE III

FRICTION COEFFICIENTS $\frac{dyne.\ sec.}{moles.\ cm}$ IN DIALYSIS TUBING AND WET GEL MEMBRANES AS FUNCTION OF CONCENTRATION

	Dialysis tubing			Wet gel		
$\bar{c}_s$	f_{sw}	f_{sm}	f_{wm}	f_{sw}	f_{sm}	f_{wm}
mole/cm³						
Sucrose						
1.25×10^{-5}	3.12×10^{16}	0.73×10^{16}	8.43×10^{13}			
2.50	3.25	0.65	8.55	1.12×10^{16}	0.066×10^{16}	1.72×10^{13}
5.00	3.43	0.59	8.72	1.13	0.067	1.74
10.00	3.57	0.57	8.95	1.14	0.068	1.79
Glucose						
1.25×10^{-5}	1.79×10^{16}	0.31×10^{16}	8.35×10^{13}			
2.50	1.82	0.29	8.45			
3.75	1.88	0.24	8.47			
5.00	1.89	0.23	8.52	0.78×10^{16}	0.030×10^{16}	1.71×10^{13}
10.00	1.97	0.21	8.65	0.78	0.031	1.72
25.00	2.12	0.20	9.85	0.82	0.026	1.76
Urea						
5.00×10^{-4}	0.66×10^{16}	0.065×10^{16}	8.30×10^{13}	0.282×10^{16}	0.0046×10^{16}	1.68×10^{13}
HTO						
	0.328×10^{16}			0.114×10^{16}		

TABLE IV

THE RATIOS OF FRICTION COEFFICIENTS f°_{sw}/f_{sw} AND f_{sw}/f_{sm} IN THE DIALYSIS TUBING AND WET GEL MEMBRANES AS A FUNCTION OF CONCENTRATION

		Dialysis tubing		Wet gel	
$\bar{c}_s$	f°_{sw}	$\vartheta = (f^{\circ}_{sw}/f_{sw})$	f_{sw}/f_{sm}	$\vartheta = f^{\circ}_{sw}/f_{sw}$	f_{sw}/f_{sm}
mole/cm³					
Sucrose					
1.25×10^{-5}	0.482×10^{16}	0.154	4.3		
2.50	0.487	0.150	5.0	0.43	16.8
5.00	0.500	0.145	5.8	0.44	16.8
10.00	0.521	0.146	6.2	0.45	16.8
Glucose					
1.25×10^{-5}	0.368	0.206	5.8		
2.50	0.370	0.203	6.3		
3.75	0.371	0.198	7.9		
5.0	0.373	0.197	8.2	0.48	26.0
10.00	0.380	0.193	9.3	0.49	26.0
25.00	0.400	0.189	10.8	0.49	31.0
Urea					
5.0×10^{-4}	0.172	0.261	10.2	0.61	61.0
HTO					
	0.101	0.308		0.89	

same way as f_{sw}. The ratio of f^{o}_{sw}/f_{sw}, however, is constant for any one substance, and therefore practically independent of concentration.

To a first approximation, the tortuosity is a geometrical factor characterizing the membrane (MacKay and Meares (8). From the study of sugar permeation, we find that tortuosity for the less swollen D.T. membrane is 0.15 to 0.20; it is higher for the more swollen W.G. and ranges from 0.4 to 0.5. A closer study of the data shows that even with the same membrane ϑ changes markedly with different solutes. For instance in D.T. the readily permeable HTO has a high ϑ value of 0.31 while, for sucrose, ϑ is 0.15. In other words, when the membrane capillaries approach the size of the molecules of the permeating substance, the tortuosity factor decreases with increasing dimensions of the molecules of the permeant. This may indicate that the physical tortuosity is not a simple expression of the geometrical tortuosity of capillaries but depends on the collision probability of the solute with the macromolecular network of the membrane.

Using Equation 5.21 of Kedem and Katchalsky (2) we have calculated the pore radii of the membranes used (*cf.* also references 3 and 4). The radii are 23 A for the D.T. and 31 A for the W.G.

With these radii and with known f_{sm}'s, it was possible to evaluate the values of ϑ for permeation of water. The values we obtained by Equation 5.20 are $\vartheta = 0.336$ for D.T. and $\vartheta = 0.875$ for W.G. These values agree very well with the values of ϑ for water which have been calculated by use of the ratio f^{o}_{sw}/f_{sw}; $\vartheta = 0.308$ for D.T. and $\vartheta = 0.89$ for W.G.

Another important conclusion from Table IV is that the frictional coefficient f_{sm} is at least an order of magnitude smaller than f_{sw}. This indicates that in the present case the main resistance to transport of the permeants is not from the matrix of the membrane but from the friction between solute and solvent. It should also be noticed that f_{wm} is smaller by two orders of magnitude than f_{sm}.

The present work shows that the frictional model of permeability leads to a consistent and meaningful representation of the processes in highly swollen membranes. It should, however, be borne in mind that the membranes considered above differ appreciably from dense biological membranes. The magnitudes of the frictional coefficients, their dependence on concentration and membrane structure, and even their usefulness for the explanation of the behavior of natural membranes, require further investigation.

APPENDIX

Effect of Unstirred Layer on Measurement of Permeability Coefficient (ω')

Well stirred solution	Unstirred layer	Membrane	Unstirred layer	Well stirred solution
	δ_1 ω_o	Δx ω	δ_3 ω_o	
	$\Delta\pi_1$	$\Delta\pi_2$	$\Delta\pi_3$	

We denote the permeability coefficients of the membrane and the unstirred layers by ω and ω_o respectively. Let us consider a measurement done in a system in the steady state, when the volume flow is zero ($J_v = 0$). We assume that the two unstirred layers are of equal thickness ($\delta_1 = \delta_3$). Under these conditions we find:

$$J_s = \omega_o\Delta\pi_1 = \omega\Delta\pi_2 = \omega_o\Delta\pi_3 \tag{1}$$

$$\therefore \Delta\pi_1 = \Delta\pi_3 \tag{2}$$

and

$$\Delta\pi = \Delta\pi_1 + \Delta\pi_2 + \Delta\pi_3 = \Delta\pi_2 + 2\Delta\pi_1 \tag{3}$$

From (1)

$$\Delta\pi_1 = \frac{J_s}{\omega_o} \tag{4}$$

On introducing (3) into (4) and rearranging:

$$\Delta\pi_2 = \Delta\pi - \frac{2J_s}{\omega_o} \tag{5}$$

From (5) and (1)

$$J_s = \omega\Delta\pi - \frac{2\omega J_s}{\omega_o} \tag{6}$$

or

$$\omega\Delta\pi = J_s\left(1 + \frac{2\omega}{\omega_o}\right) \tag{7}$$

Let us denote the measured (apparent) permeability coefficient by ω'.

$$J_s = \omega'\Delta\pi \tag{8}$$

On equating (7) and (8) we get

$$\omega' = \frac{\omega}{1 + \frac{2\omega}{\omega_o}} \tag{9}$$

or

$$\frac{1}{\omega'} = \frac{1}{\omega} + \frac{2}{\omega_o} \tag{10}$$

The permeability of the unstirred water layer is given by

$$\omega_o = \frac{D^o}{RT\delta} \tag{11}$$

Where D^o is the diffusion coefficient in water, and hence

$$\frac{1}{\omega'} = \frac{1}{\omega} + \frac{2RT}{D^o}\,\delta \tag{12}$$

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