Membrane Transport Generated by the Osmotic and Hydrostatic Pressure. Correlation Relation for Parameters L_p , σ , and ω

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Abstract. Standard approach to membrane transport generated by osmotic and hydrostatic pressures, developed by Kedem and Katchalsky, is based on principles of thermodynamics of irreversible processes. In this paper we propose an alternative technique. We derive transport equations from few fairly natural assumptions and a mechanistic interpretation of the flows. In particular we postulate that a sieve-type membrane permeability is determined by the pore sizes and these are random within certain range. Assuming that an individual pore is either permeable or impermeable to solute molecules, the membrane reflection coefficient depends on the ratio of permeable and impermeable pores. Considering flows through permeable and impermeable pores separately, we derive equations for the total volume flux, solute flux and the solvent flux across the membrane. Comparing the mechanistic equations to the Kedem-Katchalsky equations we find the former easier to interpret physically. Based on the mechanistic equations we also derive a correlation relation for the membrane transport parameters L_p , σ , and ω . This relation eliminates the need for experimental determination of all three phenomenological parameters, which in some cases met with considerable difficulties.

Key words: Irreversible processes, Kedem-Katchalsky equations, membrane transport

1. Introduction

Passive membrane transport of nonelectrolytes across porous (sieve-type) membranes generated by hydrostatic (ΔP) and osmotic ($\Delta \Pi$) pressure can be described by Kedem-Katchalsky formalism [1–4, 7]. The formalism is based on the so-called practical transport equations derived by these authors. The equations have the form:

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi, \quad (1)$$

$$j_s = \omega \Delta \Pi + (1 - \sigma) \bar{c} L_p (\Delta P - \sigma \Delta \Pi), \quad (2)$$

where: J_s , j_s are the fluxes, L_p , σ , ω – coefficients of filtration, reflection and permeation, respectively, and $\bar{c}$ – the average concentration in membrane pores. The parameters L_p , σ , and ω are defined as:

$$L_p = \left(\frac{J_v}{\Delta P} \right)_{\Delta \Pi=0} \quad (3)$$

$$\sigma = \left(\frac{\Delta P}{\Delta \Pi} \right)_{J_v=0} \quad (4)$$

$$\omega = \left(\frac{j_s}{\Delta \Pi} \right)_{J_v=0}. \quad (5)$$

The above definitions capture the physical meaning of the parameters and to some extent determine techniques for their experimental measurements [1, 4–6]. The volume flux J_v is defined as:

$$J_v = j_w \overline{v_w} + j_s \overline{v_s} = J_{vw} + J_{vs}, \quad (6)$$

where: j_w , j_s are the solvent and solute fluxes, $\overline{v_w}$, $\overline{v_s}$ – molar volumes of the solvent and the solute, and J_{vw} , J_{vs} – the solvent and solute volume fluxes.

The Kedem-Katchalsky formalism has been and still is an important tool in physico-chemical as well as technological and biophysical studies of membrane transport processes. Since its conception it has been expanded and modified in different ways [6–17]. This is also the subject of the present work.

We present a new approach to transport of nonelectrolytes across porous membrane generated both osmotically and hydraulically. It is based on a postulate that among all pores in a membrane, a certain number n_a has radii sufficiently small to become totally impermeable to the given solute. The remaining $n_b = n - n_a$ pores are permeable. If we extend the notion of the reflection coefficient to a patch of a membrane, or even a single pore, we postulate that a single membrane pore has the reflection coefficient for a given solute equal to either 1 or 0. Our analysis led to three equations for: the volume flux J_v , the solute flux j_s , and the solvent volume flux J_{vw} . We reinterpret the classical Kedem-Katchalsky equations (1)–(2) and also present a new derivation of our previous result on the correlation relation of the membrane transport parameters L_p , σ , and ω .

2. Analysis and interpretation. Transport equations

2.1. POROUS MEMBRANE. AN EQUIVALENT MEMBRANE MODEL

We consider transport processes across porous membranes generated by hydrostatic and osmotic pressure gradients. A typical sieve-type membrane has a number n of pores with random radii, from very small to a certain maximal value. The pores are distributed randomly in the entire membrane area. Examples of such membranes are: cellophane, colloid, or nephrophane membranes. We assume that all pores are permeable to the solvent, however a certain number, say n_a , is too small to allow the flow of solute molecules. These pores are then totally impermeable to the solute, while the remaining $n_b = n - n_a$ pores are permeable to both the solvent and the solute. Using the notion of the reflection coefficient, this postulate can be rephrased by saying that a single pore has the reflection coefficient equal either 1 or 0. Fractional values of σ_p are not allowed. In other words, the membrane as a

Figure 1. The equivalent membrane system (M – the equivalent membrane, c_1 , c_2 – concentrations, P_1 , P_2 – hydrostatic pressures, J_{va} , J_{vb} , J_v , j_d , j_k , j_s , J_{vwa} , J_{vwb} – fluxes).

whole (a complex of n pores) has the reflection coefficient equal $\sigma = 1$ if all of its pores are impermeable for a given solute. The membrane reflection coefficient equals $\sigma = 0$ if all the pores are permeable to the solute. If only part of the total of n pores is permeable and the rest form an ideal barrier to the solute molecules, the reflection coefficient of the entire membrane has a fractional value from the interval $0 < \sigma < 1$.

Of course one can allow also unstable pores that change their properties, i.e. randomly become permeable or impermeable to a given solute. However, if the membrane as a whole has fixed properties, we can assume that there is a state of equilibrium when the number of pores ‘opening’ at a given moment is equal to the number of pores ‘closing’ at the same time. In any case, one can divide all pores into permeable ($\sigma_p = 0$) and impermeable ($\sigma_p = 1$) and for a membrane with sufficiently large n the number of pores in each category is constant.

Let us now consider an equivalent model membrane where all the pores are ordered according to their sizes. For a given solute a part of the membrane (part (a)) has pores that are impermeable, while the other part of the membrane (part (b)) has only permeable pores. In the following sections such an equivalent membrane is used to analyze hydraulically and osmotically generated transport.

2.2. FILTRATION AND REFLECTION COEFFICIENTS. VOLUME TRANSPORT EQUATION

In the preceding section we described an equivalent membrane, such as the one presented in Figure 1. Part (a) of the membrane has only pores impermeable to a given solute, therefore its reflection coefficient is $\sigma_a = 1$. On the other hand part (b)

consists only of permeable pores, hence the reflection coefficient here is $\sigma_b = 0$. The filtration coefficients for both parts of the membrane are L_{pa} and L_{pb} .

The membrane separates well-mixed solutions of concentrations c_1 and c_2 ($c_1 < c_2$). Hydrostatic pressures on both sides are P_1 and P_2 , respectively. For concreteness we assume $P_1 < P_2$. Then there are both the osmotic pressure $\Delta\Pi = RT\Delta c = RT(c_2 - c_1)$ and the hydrostatic pressure $\Delta P = P_2 - P_1$, where R is the gas constant and T – the absolute temperature. The pressure gradients generate volume fluxes J_{va} and J_{vb} in parts (a), respectively (b), of the membrane. The fluxes can be described as:

$$J_{va} = L_{pa}\Delta P - L_{pa}\Delta\Pi \quad (7)$$

$$J_{vb} = L_{pb}\Delta P, \quad (8)$$

since $\sigma_b = 0$. The fluxes have opposite directions as indicated in Figure 1. The total volume flux across the membrane is the net of the two:

$$J_v = J_{va} + J_{vb}. \quad (9)$$

From Equation (7) and (8) one can see that $J_{va} + J_{vb} = J_v = 0$ for the pressure $\Delta P = \Delta P_m$ equal:

$$\Delta P_m = \frac{L_{pa}}{L_{pa} + L_{pb}} \Delta\Pi \quad (10)$$

or

$$\Delta P_m = \frac{L_{pa}}{L_p} \Delta\Pi \quad (11)$$

where: $L_p = L_{pa} + L_{pb}$ is the total filtration coefficient of membrane M. Denoting:

$$\sigma = \frac{L_{pa}}{L_{pa} + L_{pb}} = \frac{L_{pa}}{L_p} \quad (12)$$

we get the relation known from [1–4]:

$$\Delta P_m = \sigma \Delta\Pi. \quad (13)$$

This equation can also be written as:

$$\sigma = \left(\frac{\Delta P}{\Delta\Pi} \right)_{J_v=0}, \quad (14)$$

which is the same as the previous definition of the reflection coefficient (Equation (4)). However, the above considerations give the reflection coefficient a new meaning. According to Equation (12) it is a ratio of the filtration coefficient L_{pa} of the part of the membrane including impermeable pores to the total filtration coefficient $L_p = L_{pa} + L_{pb}$, where L_{pb} is the filtration coefficient of the permeable part of the equivalent membrane. If, for instance, $L_{pa} = 0$ then $\sigma = 0$, or if $L_{pb} = 0$ then $\sigma = 1$. Both parameters L_{pa} and L_{pb} are easy to determine if L_p and σ are known. Equation (12) can also be written as:

$$L_{pa} = \sigma L_p \quad (15)$$

$$L_{pb} = (1 - \sigma)L_p. \quad (16)$$

If the value of ΔP is different from this ΔP_m then there is a net volume flux J_v resulting from J_{va} and J_{vb} in this membrane system. Since both fluxes are generated by pressures ΔP and $\Delta \Pi$ they are given by Equations (7) and (8). From (7), (8), and (9) we get:

$$J_v = J_{va} + J_{vb} = (L_{pa} + L_{pb})\Delta P - \frac{L_{pa}(L_{pa} + L_{pb})}{L_{pa} + L_{pb}}\Delta \Pi. \quad (17)$$

Using (12) the last equation can be rewritten as:

$$J_v = L_p\Delta P - L_p\sigma\Delta \Pi \quad (18)$$

i.e. in a form identical with Equation (1), that is the Kedem-Katchalsky equation.

2.3. SOLUTE TRANSPORT EQUATION. PERMEATION COEFFICIENT ω

In this section we consider the solute transport. The standard form of the solute transport equation is given as Equation (2). It can be also written as:

$$j_s = j_d + j_k \quad (19)$$

where:

$$j_d = \omega\Delta \Pi \quad (20)$$

is the diffusive flux, and

$$j_k = (1 - \sigma)\bar{c}(L_p\Delta P - L_p\sigma\Delta \Pi) \quad (21)$$

is the convective flux.

We consider the two fluxes in the system with the equivalent membrane shown in Figure 1. Arrows in the figure indicate all fluxes generated by $\Delta \Pi$ and ΔP , i.e. J_{va} , J_{vb} , J_v , j_s , j_d , j_k and J_{vwb} (the latter is the solvent volume flux permeating across part (b) of the equivalent membrane). We use a sign convention where all fluxes directed to the right (J_{vb} , j_d , j_k , j_s and J_{vwb}) are positive. The total volume flux J_v is positive if $|J_{va}| > |J_{vb}|$. Let us recall that if $\Delta P \neq \Delta P_m$ then there is a nonzero net volume flux $J_v \neq 0$ in the system.

We begin our analysis of fluxes j_d and j_k with a more detailed discussion of Equations (7) and (8). The former refers to part (a) of the membrane, that is the part impermeable to the solute molecules. If both osmotic and hydrostatic pressures are applied to the membrane ($\Delta P > 0$ and $\Delta \Pi > 0$), then the total volume flux J_{va} equals the solvent flux J_{vwa} since the solute flux is zero (J_{sa}) in the part of the membrane where $\sigma_a = 1$.

As for Equation (8), it is concerned with part (b) of the membrane containing pores permeable also to solute molecules. The osmotic and hydrostatic pressures are the same as in part (a) ($\Delta P > 0$ and $\Delta \Pi > 0$) and the equation can be written as:

$$J_{vb} = L_{pb}\Delta P - L_{pb}\sigma_b\Delta \Pi = L_{pb}\Delta P \quad (22)$$

since $\sigma_b = 0$ for this part of the membrane. The total volume flux has two components.

$$J_{vb} = J_{vwb} + J_{vsb} > 0 \quad (23)$$

where J_{vwb} is the solvent (water) volume flux, and J_{vsb} is the solute volume flux. Both fluxes are generated by concurrent processes of filtration (since $\Delta P > 0$) and diffusion ($\Delta \Pi > 0$). In general the problem is rather complex and we postpone the analysis. Instead we consider a simpler case when $\Delta P = 0$. Only solute and solvent diffusion in opposite directions takes place then and the equivalent of Equation (23) has a form:

$$J_{vb}^{\Delta \Pi} = J_{vwb}^{\Delta \Pi} + J_{vsb}^{\Delta \Pi} = 0 \quad (24)$$

where the superscript $\Delta \Pi$ emphasizes the fact that the osmotic pressure only is driving the flows. Both fluxes $J_{vwb}^{\Delta \Pi}$ and $J_{vsb}^{\Delta \Pi}$ are nonzero and:

$$|J_{vwb}^{\Delta \Pi}| = |J_{vsb}^{\Delta \Pi}| \neq 0 \quad (25)$$

while $J_{vwb}^{\Delta \Pi} < 0$ and $J_{vsb}^{\Delta \Pi} > 0$. The fluxes can be written as:

$$J_{vwb}^{\Delta \Pi} = -L_{pb}\overline{c_w v_w} \Delta \Pi \quad (26)$$

and

$$J_{vsb}^{\Delta \Pi} = L_{pb}\overline{c_s v_s} \Delta \Pi \quad (27)$$

where $\overline{c_w}$ is the mean solvent (water) concentration in pores in part (b) of the membrane (note that for diluted solutions $\overline{c_w} \approx 1$) and $\overline{c_s} = \bar{c} = \frac{c_1+c_2}{2}$ is the mean solute concentration in the same pores. Denoting the diffusion flux $J_{vsb}^{\Delta \Pi}$ by J_{vd} we get:

$$J_{vd} = L_{pb}\overline{c_s v_s} \Delta \Pi. \quad (28)$$

Since $J_{vd} = j_d \overline{v_s}$ we write:

$$j_d = L_{pb}\bar{c} \Delta \Pi. \quad (29)$$

Recalling relations: $L_p = L_{pa} + L_{pb}$, $\sigma = \frac{L_{pa}}{L_{pa}+L_{pb}}$, and $L_{pb} = (1 - \sigma)L_p$ we finally obtain:

$$j_d = \omega \Delta \Pi \quad (30)$$

where the coefficient ω is given as:

$$\omega = (1 - \sigma)\bar{c}L_p = \frac{(L_{pa}L_{pb} + L_{pb}^2)\bar{c}}{L_p}. \quad (31)$$

Let us consider now the convection flux j_k . In our equivalent model membrane this flux is generated only in part (b) of the membrane and can be written as:

$$j_k = \bar{c}J_{vb}. \quad (32)$$

Since $J_{vb} = L_{pb}\Delta P = (1 - \sigma)L_p\Delta P$ we get:

$$j_k = (1 - \sigma)\bar{c}L_p\Delta P. \quad (33)$$

We emphasize the fact that part (a) of the membrane contains only pores impermeable to the solvent hence no solvent convection takes place there. The convective flux is generated by the hydrostatic pressure gradient ΔP while the effective osmotic pressure $\sigma_b\Delta\Pi$ has no effect on convection since $\sigma_b = 0$.

Taking into account Equations (19), (30), and (33) we can write:

$$j_s = \omega\Delta\Pi + (1 - \sigma)\bar{c}L_p\Delta P. \quad (34)$$

The parameter ω can be therefore defined as:

$$\omega = \left(\frac{j_d}{\Delta\Pi} \right)_{\Delta P=0} \quad (35)$$

and should be measured with $\Delta P = 0$. Equation (34) can be rewritten as:

$$J_{vs} = j_s\bar{v}_s = \omega\bar{v}_s\Delta\Pi + (1 - \sigma)\bar{c}\bar{v}_sL_p\Delta P \quad (36)$$

where J_{vs} is the solute volume flux and $\bar{v}_s$ – the solute molar volume.

2.4. EQUATION FOR THE SOLVENT VOLUME FLUX j_{vw}

In the Kedem-Katchalsky formalism the membrane transport is usually expressed in terms of the volume flux J_v and the solvent flux j_s . The flow of the solvent itself is included in the volume flux. However, in some applications the knowledge of the solvent flux could be helpful. We mean here for instance the concentration changes due to osmosis, analysis of time course of concentration with the aim of determining the membrane permeation coefficient or transport studies in biological membranes where passive solute transport is accompanied by some form of active transport. With this in mind we write a separate equation for the solvent flux. Moreover, in the preceding sections we have written two separate expressions for the volume flux (Equations (6) and (9)). A simple argument shows that they are indeed the same.

Within the framework of the Kedem-Katchalsky formalism the total volume flux can be expressed as (Equation (6)): $J_v = j_w\bar{v}_w + j_s\bar{v}_s = J_{vw} + J_{vs}$ where $\bar{v}_w$

and $\bar{v}_s$ are the molar volumes of the solvent (w) and the solute (s). On the other hand we expressed the volume flux as (cf. Equation (9)): $J_v = J_{va} + J_{vb}$. As we described earlier in the paper the flux J_{va} equals the solvent flux J_{vwa} generated in part (a) of the equivalent membrane by the osmotic pressure $\Delta\Pi > 0$ and the hydrostatic pressure $\Delta P > 0$. The same pressures exist in part (b) of the membrane and the flux generated there equals (cf. Equation (8)):

$$J_{vb} = L_{pb}\Delta P. \quad (37)$$

According to Equation (23) it consists of two components:

$$J_{vb} = J_{vwb} + J_{vsb} \quad (38)$$

where the latter can be written as: $J_{vsb} = J_{vs} = J_{vd} + J_{vk}$ (where: $J_{vd} = j_d\bar{v}_s$ and $J_{vk} = j_k\bar{v}_s$). Based on the previous subsection we write the flux J_{vwb} as:

$$J_{vwb} = J_{vwb}^{\Delta\Pi} + J_{vwb}^{\Delta P} \quad (39)$$

where: $J_{vwb}^{\Delta P}$ is the solvent volume flux for $\Delta\Pi = 0$ and $J_{vwb}^{\Delta\Pi}$ is the diffusive volume solvent flux for $\Delta P = 0$. Hence Equation (23) has a form:

$$J_{vb} = J_{vwb}^{\Delta P} + J_{vwb}^{\Delta\Pi} + J_{vd} + J_{vk}. \quad (40)$$

It is easy to show that the expressions (6) and (9) are simply different groupings of all the volume fluxes across the membrane. In particular we can write:

$$J_v = J_{va} + J_{vb} = \overbrace{J_{vwa} + J_{vwb}^{\Delta P} + J_{vwb}^{\Delta\Pi}}^{J_{vw}} + \overbrace{J_{vd} + J_{vk}}^{J_{vs}} = J_{vw} + J_{vs}. \quad (41)$$

Substituting (16) and (28) to (31) we obtain an expression for the volume solvent flux:

$$J_{vw} = J_v - J_{vs} = -\left(\sigma + \frac{\omega\bar{v}_s}{L_p}\right) L_p\Delta\Pi + [1 - (1 - \sigma)\bar{c}\bar{v}_s] L_p\Delta P. \quad (42)$$

3. Correlation relation for the transport parameters L_p , σ , and ω

Analysis of available experimental data suggests that the membrane transport parameters, although measured independently, show a certain degree of correlation. This was a subject of our previous paper [21]. In this section we present a new derivation of the correlation relation from the transport equations obtained in the previous parts of the paper. We begin with Equation (42) rewritten as:

$$J_{vw}^c = |J_{vw}| = J_{vs} - J_v = \left(\sigma + \frac{\omega\bar{v}_s}{L_p}\right) L_p\Delta\Pi - [1 - (1 - \sigma)\bar{c}\bar{v}_s] L_p\Delta P \quad (43)$$

where J_{vw}^c denotes the absolute value of the volume solvent flux. Dividing sidewise by $L_p\Delta\Pi$ we obtain an equation for the normalized solvent volume flux, i.e. the magnitude of the flux per unit hydrostatic conductivity and unit osmotic pressure:

Figure 2. Relation $\frac{J_{vw}}{L_p \Delta \Pi} = f(\sigma)$. Dots correspond to experimental data sets from Table I.

$$\frac{J_{vw}^c}{L_p \Delta \Pi} = \sigma + \frac{\omega \bar{v}_s}{L_p} - [1 - (1 - \sigma) \bar{c} \bar{v}_s] \frac{\Delta P}{\Delta \Pi}. \quad (44)$$

For simplicity we consider the case $\Delta P = 0$. Then:

$$\frac{J_{vw}^c}{L_p \Delta \Pi} = \sigma + \frac{\omega \bar{v}_s}{L_p}. \quad (45)$$

This equations has been previously derived in [21]. The derivation shown there was based on the standard Kedem-Katchalsky equations and involved certain approximations.

One can immediately notice that Equation (45) has certain constraints built in. Namely, for $\sigma = 1$ we get:

$$\frac{J_{vw}^c}{L_p \Delta \Pi} = \frac{J_{vwa}^c}{L_p \Delta \Pi} = 1 \quad (46)$$

since for $\sigma = 1$ the coefficient $\omega = 0$ and $J_{vwa}^c = L_p \Delta \Pi$. On the other hand $\sigma = 0$ yields:

$$\frac{J_{vw}^c}{L_p \Delta \Pi} = \frac{J_{vwa}^c}{L_p \Delta \Pi} = \frac{\omega \bar{v}_s}{L_p} = \frac{\omega_0 \bar{v}_s}{L_p} > 0 \quad (47)$$

since $\omega = \omega_0 > 0$.

We use Equation (45) to find the correlation relation. From the available literature [1, 10, 14, 20, 22–27] we selected 52 sets of parameters L_p , σ , and ω measured

Table I. Experimental transport parameter sets

No.	Membrane	Solute	$L_p \times 10^{12}$ [m ³ /Ns]	σ	$\omega \times 10^{10}$ [mol/Ns]	$v_s \times 10^3$ [m ³ /mol]	$\omega_t \times 10^{10}$ [mol/Ns]
1	Toad skin	Acetamide	0.4	0.89	0.0041	0.052	0.17
2	<i>Nitella translucens</i>	Methanol	1.1	0.5	11	0.04	2.8
3	<i>Nitella translucens</i>	Ethanol	1.1	0.44	11	0.058	2.2
4	<i>Nitella translucens</i>	Isopropanol	1.1	0.4	7	0.076	1.8
5	Human red blood cell	Urea	0.92	0.62	17	0.042	1.7
6	Human red blood cell	Ethylene glycol	0.92	0.63	8	0.056	1.27
7	Visking dialysis tubing	Urea	3.2	0.013	20.8	0.042	16
8	Visking dialysis tubing	Glucose	3.2	0.123	7.2	0.115	5.1
9	Visking dialysis tubing	Sucrose	3.2	0.163	3.9	0.2	2.8
10	DuPont 'wet gel'	Urea	9.7	0.0016	31.6	0.042	48
11	DuPont 'wet gel'	Glucose	9.7	0.024	12.2	0.115	17
12	DuPont 'wet gel'	Sucrose	9.7	0.036	7.7	0.2	9.8
13	Dialysis membrane	Glucose	1.09	0.13	2.95	0.115	1.7
14	Nephrophane	Ethanol	5	0.025	20	0.058	17.6
15	Nephrophane	Glucose	5	0.065	8	0.115	8.5
16	Cuprophane	Sucrose	2.88	0.28	6.7	0.2	2.17
17	GSRII	NaCl	0.6	0.62	25.25	0.027	1.7
18	Cuprophane	Sucrose	5.5	0.157	6.89	0.2	4.8
19	Cuprophane	Urea	3.96	0.015	46.1	0.042	19.5
20	Cuprophane	Glucose	3.96	0.08	15	0.115	6.6
21	Cuprophane	Sucrose	3.96	0.157	7.05	0.2	3.5
22	Maize root	Ethanol	0.055	0.27	0.188	0.058	0.14
23	Maize root	Sucrose	0.055	0.54	0.048	0.2	0.026
24	Maize root	NaCl	0.055	0.64	0.228	0.027	0.15
25	<i>Phaseolus coccineus</i> root (1)	Ethanol	0.023	0.28	0.017	0.058	0.059
26	<i>Phaseolus coccineus</i> root (1)	KCl	0.023	0.43	0.0028	0.037	0.074
27	<i>Phaseolus coccineus</i> root (1)	NaCl	0.023	0.59	0.00084	0.027	0.073
28	<i>Phaseolus coccineus</i> root (1)	NaNO ₃	0.023	0.54	0.0015	0.037	0.06
29	<i>Phaseolus coccineus</i> root (2)	Ethanol	0.076	0.34	0.026	0.058	0.18
30	<i>Phaseolus coccineus</i> root (2)	KCl	0.076	0.54	0.0036	0.037	0.19
31	<i>Phaseolus coccineus</i> root (3)	Ethanol	0.032	0.47	0.028	0.058	0.06
32	<i>Phaseolus coccineus</i> root (4)	Methanol	0.025	0.16	0.01	0.04	0.11
33	<i>Phaseolus coccineus</i> root (5)	Ethanol	0.054	0.15	0.029	0.058	0.16
34	<i>Phaseolus coccineus</i> root (5)	Urea	0.054	0.41	0.002	0.042	0.159
35	<i>Phaseolus coccineus</i> root (6)	Methanol	0.058	0.34	0.0248	0.04	0.2
36	<i>Phaseolus coccineus</i> root (7)	Urea	0.058	0.51	0.0044	0.042	0.14
37	Nephrophane	Glucose	5	0.068	8	0.115	8.5
38	Nephrophane	Ethanol	5	0.025	20	0.058	17.6

Table I. (continued)

No.	Membrane	Solute	$L_p \times 10^{12}$ [m ³ /Ns]	σ	$\omega \times 10^{10}$ [mol/Ns]	$v_s \times 10^3$ [m ³ /mol]	$\omega_t \times 10^{10}$ [mol/Ns]
39	Nephrophane	NaCl	5	0.06	14.3	0.027	36
40	Ultra-Flo 145 dialyser	NaCl	0.85	0.167	5.5	0.027	5.5
41	GSRI IV	NaCl	0.27	0.8	6.9	0.027	0.42
42	Nephrophane	Glucose	5	0.068	8	0.115	8.5
43	Cellulose RA	Glucose	1.6	0.094	3	0.115	2.6
44	Cellulose RB	Glucose	0.85	0.112	1	0.115	1.37
45	Nephrophane	H ₂ SO ₄	5	0.11	38	0.053	17.6
46	Nephrophane	HCl	5	0.08	33.2	0.023	42
47	Nephrophane	KCl	5	0.04	25.4	0.037	27
48	Nephrophane	Ethanol	5	0.016	18.9	0.058	17.8
49	<i>Nitella translucens</i>	Urea	1.1	1	0.0008	0.042	
50	Nephrophane	Glucose	5	0.076	7.82	0.115	8.4
51	Cellulose	Ethanol	2.21	0.017	6.28	0.058	7.8
52	Cellulose	Glucose	2.21	0.09	2.21	0.115	3.6

for various membranes and solutes. Data is presented in Table I. For each set we computed the normalized solvent volume flux (Equation (45)) and plotted against σ in Figure 2. Each point corresponds to one data set from Table I. As the figure shows a linear form of the function $\frac{J_{vw}^c}{L_p \Delta \Pi} = f(\sigma)$ is strongly suggested. As we mention above the function $f(\sigma)$ is constrained to pass through a point A(1,1). A linear function satisfying this condition has a form:

$$\frac{J_{vw}^c}{L_p \Delta \Pi} = (1 - K)\sigma + K. \quad (48)$$

Comparing (48) and (45) we get:

$$\omega = \omega_t = K \frac{L_p}{v_s} (1 - \sigma). \quad (49)$$

Using the least squares fit we find $K = 0.021 \pm 0.015$ where the error is the standard deviation. The value $K = 0.03$ reported in [21] stays within the error bounds.

Parameter sets labeled 3, 5, 6, 17, 41, and 49 from Table I were rejected from calculations on the grounds that they deviate too far from the pattern showed by other sets. We are convinced that they suffered from large measurement errors due to, for instance, a presence of transport mechanisms other than considered here. All of the rejected data (with the exception of set no. 41) were taken from biological membranes for which such errors are difficult to avoid. If we consider only our own

experimental data (sets 13, 14, 48, 50, 51, and 52) then we obtain $K = 0.0217 \pm 0.005$.

Having determined the constant $K = 0.021$ we computed the theoretical value of the permeation coefficient ω_i from Equation (48) for each data set (shown in the last column in Table I). For a majority of membranes there is a very good agreement between the experimental and theoretical values of ω . A significant deviation is observed for data sets 1, 5, 17, 27, 28, 30, and 34. Again, we note that all of these (with the exception of no. 17) are for biological membranes. For such systems transport measurements and determination of the membrane parameters (in particular the permeation coefficient) are more difficult than for artificial membranes and present much more opportunities for significant systematic errors.

4. Conclusions

We consider the passive membrane transport generated by osmotic pressure $\Delta\Pi$ and hydrostatic pressure ΔP . Our analysis is based on the assumptions that a typical membrane has a number of pores of different radii. Introducing a local interpretation of the reflection coefficient we postulate that an individual pore can have either $\sigma_p = 1$ or $\sigma_p = 0$ while for the membrane as a whole $0 \leq \sigma \leq 1$. If $\sigma = 1$ then each and every pore is an ideal barrier for the solute molecules and only the solvent permeates through the membrane. This solvent flow can be generated either osmotically (due to $\Delta\Pi$) or hydraulically (ΔP). In the case $\sigma = 0$ there is a volume flux J_v determined by the hydrostatic pressure ΔP . If there is an osmotic pressure $\Delta\Pi$ across the membrane the total volume flux J_v includes the diffusive flux J_{vd} . If $\Delta P = 0$ and $\Delta\Pi \neq 0$ then the flux J_{vd} is nonzero while the total flux $J_v = 0$. For a generic membrane the reflection coefficient is $0 < \sigma < 1$. This reflects the fact that a fraction of the pores is open to the solute while the others are not. The paper deals with this situation in detail.

In this generic situation and in the presence of both the osmotic and hydrostatic driving forces the membrane transport can be summarized in a form of three equations:

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi \quad (50)$$

$$j_s = \omega \Delta \Pi + (1 - \sigma) \bar{c} L_p \Delta P \quad (51)$$

$$J_{vw} = j_w \bar{v}_w = L_p [1 - (1 - \sigma) \bar{c} \bar{v}_s] \Delta P - L_p \left(\sigma + \frac{\omega \bar{v}_s}{L_p} \right) \Delta \Pi. \quad (52)$$

The first equation is identical with the volume flux equation derived by Kedem and Katchalsky. The second (the solute flux equation) is simpler than the corresponding Kedem-Katchalsky equation (it doesn't contain the term $(1 - \sigma) \bar{c} L_p \sigma \Delta \Pi$ present in the Kedem-Katchalsky equation). The last equation for the solvent volume flux is new.

We also present a derivation of the correlation relation for the membrane transport parameters (L_p , σ , and ω) based on the transport equation developed in the paper. Our previous analysis of the transport parameters correlation was based on the Kedem-Katchalsky equation and involved certain approximations. The correlation relation has a form:

$$\omega = K \frac{L_p}{v_s} (1 - \sigma) \quad (53)$$

where $K = 0.0021 \pm 0.015$. The relation allows computation of one of the parameters if the other two are known. In biophysical studies it is the permeation coefficient ω that is notoriously difficult to measure and thus can be computed if L_p and σ are measured.

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