

Mechanistic Formalism for Membrane Transport Generated by Osmotic and Mechanical Pressure

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Abstract. Since the physical interpretation of practical Kedem–Katchalsky (KK) equations is not clear, we consider an alternative, mechanistic approach to membrane transport generated by osmotic and hydraulic pressure. We study a porous membrane with randomly distributed pore sizes (radii). We postulate that reflection coefficient (σ_p) of a single pore may equal 1 or 0. From this postulate we derive new (mechanistic) transport equations. Their advantage is in clear physical interpretation and since we show they are equivalent to the KK equations, the interpretation of the latter became clearer as well. Henceforth the equations allow clearer and more detailed interpretation of results concerning membrane mass transport.

This is especially important from the point of view of biophysical studies on permeation processes across biological membranes, cell membranes including.

Key words: Porous membranes — Substance transport — Mechanistic equations — Thermo-dynamic equations

Introduction

Thermodynamic formalism of nonelectrolyte transport across membranes elaborated by Kedem and Katchalsky (1958, 1961, 1963); Katchalsky and Curran (1965) is a convenient and widely used as a scientific tool. Its main tools are the so-called practical equations describing membrane transport processes generated simultaneously by osmotic pressure $\Delta\Pi$ and mechanical pressure ΔP . The equations were derived from principles of linear thermodynamics of irreversible processes. Their standard form is:

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

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

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where: J_v, j_s – fluxes; L_p, σ, ω – coefficients (of filtration, reflection, and permeation, respectively); \bar{c} – a suitably defined mean concentration. The equations hold for membrane systems with sufficiently diluted, well-mixed solutions. In biophysics the equations were used mainly in studies of passive transport processes across biological membranes (Katchalsky and Curran 1965; Sha'afi et al. 1970; Tyree 1970; Ginsburg 1971; Fiscus 1975, 1977, 1986; Sha'afi and Gary-Bobo 1976; Steudle et al. 1987; Steudle and Brinckmann 1989; Tyree et al. 1994; Kargol and Kargol 2000 and others).

The phenomenological parameters appearing in these equations are defined as follows (Kedem and Katchalsky 1958, 1961, 1963; Katchalsky and Curran 1965):

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

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

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

These formulae express the physical meaning of the parameters and to some extent they determine experimental techniques for measurement of parameters (Kedem and Katchalsky 1961; Katchalsky and Curran 1965; Grygorczyk 1978). Since its inception the Kedem-Katchalsky (KK) formalism has been in various ways modified, expanded and complemented (Kedem and Katchalsky 1961; Patlak et al. 1963; Siegler and Kedem 1966; Zelman 1972; Levitt 1974; Monticelli and Celentano 1983; Kargol and Ślęzak 1985; Del Castillo and Mason 1986; Imai 1989; Kargol and Kargol 1989; Ślęzak and Turczyński 1992; Kargol 1994, 1996; Kargol et al. 1997; Kleinhans 1998; Kargol 1999; Katkov 2000 and others) with the goal of expanding its scope as well as interpretation of processes already included. Several attempts are also known (Kedem and Katchalsky 1961; Katchalsky and Curran 1965; Zelman 1972; Levitt 1974; Sha'afi and Gary-Bobo 1976; Kargol et al. 1997; Kleinhans 1998; Katkov 2000) aimed at reducing the number of phenomenological parameters from three to two.

In general one could say that the interpretation of KK equations is not entirely clear. In particular this issue concerns the solute flux equation. E.g. it is believed that the term $(1 - \sigma)\bar{c}J_v$ in this equation represents the convective flux carried by J_v . As we show this term should be understood differently. Moreover, one could also question the interpretation of coefficient ω . These issues are discussed in more detail in the appendix.

Considering known issues with the interpretation of these thermodynamic transport equations in this paper we present an alternative mechanistic analysis of processes of membrane substances transport generated by osmotic and hydraulic pressures.

We consider a generic porous membrane having a number N of pores permeable to the solvent. Typically the pores vary in their size and spatial distribution. We

assume that their permeability to the solute is determined by the relative pore and solute molecules' sizes and assign each pore a coefficient σ_p equal either 1 (impermeable pores) or 0 (permeable pores) (Kargol and Kargol 2000; Kargol 2001; Kargol et al. 2001). Hence a number n_a of smallest pores form an ideal barrier to this solute, while the remaining pores ($n_b = N - n_a$) are permeable. Based on this postulate we derive transport equations (for fluxes J_v and j_s) with three phenomenological parameters, i.e. L_p , σ and ω_d , where the latter is a coefficient of diffusive solute permeation. We call them the mechanistic equations after the derivation method.

The interpretation of transport equations obtained in this work is entirely clear, contrary to the KK equations. We show, however, that the mechanistic equations are equivalent to the KK equations. Henceforth the latter gained in clarity of their interpretation. We also found correlation relations for membrane transport parameters. Consequently, both the KK and mechanistic equations were rewritten in reduced form involving not two but three transport parameters.

In this work we also show a comparative analysis of functioning of the KK and mechanistic equations. The authors believe that this work opens new possibilities for application of both KK and mechanistic equations in studies of nonelectrolyte transport in artificial and biological membranes. The two sets of equations together become a more sophisticated and better understood scientific tool.

Owing to the mechanistic transport equations obtained in this work, new and radically more favourable research possibilities have now developed, concerned with passive transport processes in biological membranes, cell membranes including. Moreover, results of former studies obtained on the basis of the KK equations, which were not amenable to clear interpretation before, can now be interpreted. The number of such research results is relatively large, as seen for instance in the papers (Katchalsky and Curran 1965; Sha'afi et al. 1970; Tyree 1970; Ginsburg 1971; Levitt 1974; Fiscus 1975, 1977, 1986; Sha'afi and Gary-Bobo 1976; Steudle et al. 1987; Steudle and Brinckmann 1989; Tyree et al. 1994). Their hitherto interpretation is most often fragmentary and ambiguous (at times wrong). It follows especially from the fact that the KK equations apply for homogenous membranes, a criterion, which is not met by cell membranes. Those membranes have their water and solute transporting channels differentiated geometrically. Hence follows a special utility of the mechanistic equations, which are concerned just with substance transport across membranes of differentiated pore sizes.

Mechanistic analysis of membrane substances transport processes generated by osmotic and hydraulic pressures

Model membrane system with a generic porous membrane

We consider the problem of membrane transport generated by mechanical and osmotic pressure differently from the method developed by KK. Our approach, initiated in our papers (Kargol and Kargol 2000; Kargol 2001; Kargol et al. 2001)

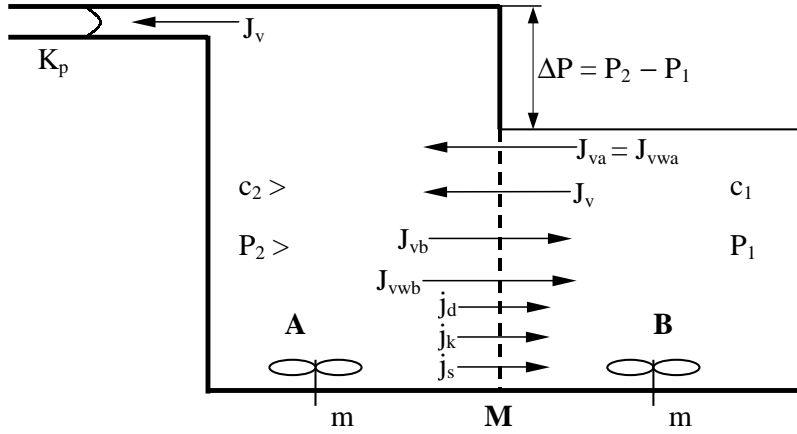


Figure 1. The model membrane system with well-mixed solutions (M – membrane; A, B – compartments; K_p – capillary; m – stirrer; c_1, c_2 – concentrations; P_1, P_2 – mechanical pressures). Fluxes are described in text.

is of mechanistic nature. The starting point for the analysis is a membrane system shown schematically in Fig. 1. Two compartments A and B filled with solutions c_1 and c_2 (respectively) of the same solute are separated by a generic selective porous membrane M . The solutions are well mixed by mechanical devices (stirrer m) and $c_1 < c_2$. The former compartment is subject to mechanical pressure P_1 , and the latter – P_2 , where $P_1 < P_2$. In such case there is an osmotic pressure:

$$\Delta\Pi = RT\Delta c = RT(c_2 - c_1)$$

as well as mechanical pressure $\Delta P = P_2 - P_1$ across the membrane.

We assume the membrane has a number N of pores permeable to the solvent. Typically the pores are modeled as being approximately cylindrical and normal to the membrane surface. For a typical porous membrane, like cellophane, nephropthane, or collodion membranes, the pores vary randomly in their dimensions, i.e. the cross-section radii. Their spatial distribution in the membrane is random as well. For biological membranes the pores (if we treat certain types of channels, e.g. water channels, as such) are typically more uniform in size. The pores can be however ordered in a series according to their radii, from the smallest (r_1^{\min}) to the largest (r_N^{\max}):

$$r_1^{\min} < r_2 \cdots < r_i < \cdots < r_N^{\max}$$

For such a membrane one can select a solute (with a molecular radius r_s) for which a number n_a of the smallest pores (with radii r such that $r_1^{\min} \leq r < r_s$) form an ideal barrier. The remaining pores, a total of $n_b = N - n_a$, are permeable. This fact can be described by assigning a parameter σ_p to each pore. The parameter can be only assume integer values either 1 (for impermeable pores) or 0 (for permeable

ones) and as we show later this postulate is closely related to the membrane reflection coefficient. As a justification of the postulate, let us assume that there is a relatively small number ΔN of unstable pores (with radii close to r_s), i.e. pores that change their solute permeability properties. This could be caused e.g. by a transient blockage of a pore to solute by a passing molecule or a transient decrease in pore radius due to a conformational change of molecule complex forming the pore (e.g. proteins forming a channel). However, it seems reasonable to assume that at any given moment the number of pores regaining their permeability to solute equals the number of pores becoming impermeable. Henceforth, there is a clear and stable division of pores into permeable ($\sigma_p = 0$) and impermeable ($\sigma_p = 1$).

It follows that if a membrane as a whole (a complex of N pores) has all pores impermeable to the solute, its reflection coefficient $\sigma = 1$ and the membrane is called semipermeable. On the other hand, if all pores are permeable to solvent as well as solute, then $\sigma = 0$ and the membrane is permeable (non selective). If only a fraction n_a (of the total of N pores) is impermeable, while the remaining pores (n_b) allow solute flow, the membrane reflection coefficient has a fractional value $0 < \sigma < 1$. Such a membrane is called selective and is a subject of our study. We might add that osmosis is understood as the solvent (water) transport across a semipermeable membrane driven by the osmotic pressure. This definition implies that in selective membranes osmosis takes place through pores n_a only, for which the total reflection coefficient is 1.

Equation for the volume flux

We begin our analysis of transport processes taking place in a system shown in Fig. 1, with an observation that as a result of pressures $\Delta\Pi$ and ΔP on the membrane M , there is a solvent volume flux ($J_{va} = J_{vwa}$) in membrane pores n_a (for which $\sigma_p = 1$). In pores n_b (with $\sigma_p = 0$) there is a solution volume flux. The fluxes are given by the following equations:

$$J_{va} = L_{pa}\Delta P - L_{pa}\Delta\Pi \quad (6)$$

$$J_{vb} = L_{pb}\Delta P \quad (7)$$

where L_{pa} (resp. L_{pb}) is the filtration coefficient of pores n_a (resp. n_b) defined as:

$$L_{pa} = \left(\frac{J_{va}}{\Delta P} \right)_{\Delta\Pi=0}$$

resp.

$$L_{pb} = \left(\frac{J_{vb}}{\Delta P} \right)_{\Delta\Pi=0}$$

The fluxes flow in opposite directions as those indicated by arrows in Fig. 1. The net of the two, denoted J_v :

$$J_v = J_{va} + J_{vb} \quad (8)$$

is called a volume flux.

One can easily notice in the above three equations that there is a value of pressure $\Delta P = \Delta P_m$ for which $J_v = 0$. Henceforth from equations (5) and (6) we get:

$$\Delta P_m = \frac{L_{pa}}{L_p} \Delta \Pi \quad (9)$$

where

$$L_p = L_{pa} + L_{pb} \quad (10)$$

is the total membrane filtration coefficient. Introducing the following notation:

$$\sigma_k = \frac{L_{pa}}{L_{pa} + L_{pb}} = \frac{L_{pa}}{L_p} \quad (11)$$

we obtain from equation (8):

$$\Delta P_m = \sigma_k \Delta \Pi$$

This relation holds if $J_v = 0$. Thus:

$$\sigma_k = \left(\frac{\Delta P_m}{\Delta \Pi} \right)_{J_v=0} \quad (12)$$

The above formula is identical with a definition of reflection coefficient σ given in the KK formalism (i.e. equation (4)), what implicates, that $\sigma_k \equiv \sigma$. Its physical interpretation is however different. In our framework the parameter σ is a ratio of the filtration coefficient L_{pa} (of pores N_a) to the total membrane filtration coefficient L_p , as shown by equation (11). Therefore if $L_{pa} = 0$, then according to equation (11) we get $\sigma = 0$. Such a membrane is permeable (non selective). On the other hand if $L_{pb} = 0$, then for $L_{pa} > 0$ we obtain $\sigma = 1$ meaning the membrane is semipermeable. For $0 < L_{pa} < L_p$ the reflection coefficient has a value $0 < \sigma < 1$ and the membrane is selective.

Parameters L_{pa} and L_{pb} are easy to determine provided L_p and σ are known. Namely, equation (11) yields:

$$L_{pa} = \sigma L_p \quad (13)$$

and recalling that $L_p = L_{pa} + L_{pb}$, we get also:

$$L_{pb} = (1 - \sigma)L_p \quad (14)$$

When $\Delta P \neq \Delta P_m$ a volume flux is induced in the system and using equations (6) and (7) we obtain from equation (8):

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

Substituting (10) and (11) we finally get:

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi \quad (15)$$

The equation has the same form as the KK equation for a volume flux. However, interpretation of the coefficient σ is somewhat different. In our framework it is given by equation (10), while in the KK formalism it is described by the Stavermann relation (Katchalsky and Curran 1965):

$$\sigma = -\frac{L_{pD}}{L_p}$$

where L_{pD} is the so-called osmotic flux coefficient. We note that both in our approach and in the KK formalism the coefficient L_p is defined by the same formula:

$$L_p = \left(\frac{J_v}{\Delta P} \right)_{\Delta \Pi=0} \quad (16)$$

Equation for the solute flux

In this section we consider the solute flux across a membrane. The KK equation for the solute flow j_s has a form:

$$j_s = \omega \Delta \Pi + (1 - \sigma) \bar{c} J_v$$

It can also be written as:

$$j_s = j_{sk} + j_{kk} \quad (17)$$

where

$$j_{sk} = \omega \Delta \Pi \quad (18)$$

and the term:

$$j_{kk} = (1 - \sigma) \bar{c} J_v \quad (19)$$

is treated as a convective flux, i.e. the solute flux carried in membrane pores by J_v . Let us now analyze the fluxes in the mechanistic framework. Again, our considerations are based on a system shown in Fig. 1. All fluxes induced either by mechanical pressure ΔP or osmotic pressure $\Delta \Pi$ are shown as arrows in Fig. 1. They are denoted by J_{va} , J_{vb} , j_s , j_d , j_k and J_{vwb} , where $J_{va} = J_{vwa}$ is the solvent flux permeating pores n_a (impermeable to the solute), J_{vb} denotes the volume flux flowing in pores n_{0b} permeable to the solute as well, j_s is the solute flux, j_d – the diffusive solute flux, and j_k – the convective solute flux. We use a sign convention where fluxes directed to the right (J_{vb} , j_s , j_d , and j_k) are positive, and the others (J_v and J_{va}) – negative. One might add that J_v is negative if $|J_{va}| > |J_{vb}|$. We also recall that if $\Delta P \neq \Delta P_m$ then there is a nonzero 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 (6) and (7). The former refers to pores n_a (permeable to the solvent only). It follows that if both osmotic $\Delta \Pi$ and mechanical ΔP pressures are applied to the membrane, then the total volume flux J_{va} generated within these pores equals the

solvent flux J_{vwa} . No solute flow takes place in these pores ($j_{\text{sa}} = 0$ since $\sigma_{\text{a}} = 1$). As for equation (6), it is concerned with pores n_{b} , i.e. pores permeable to both the solvent and the solute molecules. With the osmotic $\Delta\Pi$ and mechanical ΔP pressures across the membrane the equation can be rewritten as:

$$J_{\text{vb}} = L_{\text{pb}}\Delta P - L_{\text{pb}}\sigma_{\text{b}}\Delta\Pi = L_{\text{pb}}\Delta P$$

since the reflection coefficient σ_{b} of pores n_{b} equals 0. We note that the volume flux J_{vb} has two components:

$$J_{\text{vb}} = J_{\text{vwb}} + J_{\text{vsb}} > 0 \quad (20)$$

where J_{vwb} is the solvent (e.g. water) volume flux, and J_{vsb} is the solute volume flux. Both fluxes are generated by simultaneous processes of filtration (induced by ΔP) and diffusion (since $\Delta\Pi > 0$). In its full generality the problem is rather complex and we consider a simpler case when $\Delta P = 0$ and $\Delta\Pi > 0$ first. In this case only the solute and solvent diffusion in opposite directions takes place and the analogue of equation (20) has the form:

$$J_{\text{vb}}^{\Delta\Pi} = J_{\text{vwb}}^{\Delta\Pi} + J_{\text{vsb}}^{\Delta\Pi} = 0 \quad (21)$$

where as before $J_{\text{vwb}}^{\Delta\Pi}$ is the solvent volume flux and $J_{\text{vsb}}^{\Delta\Pi}$ – the solute volume flux. They satisfy the condition:

$$|J_{\text{vb}}^{\Delta\Pi}| = |J_{\text{vsb}}^{\Delta\Pi}| \neq 0 \quad (21a)$$

where $J_{\text{vwb}}^{\Delta\Pi} < 0$ and $J_{\text{vsb}}^{\Delta\Pi} > 0$, and can be expressed as:

$$J_{\text{vwb}}^{\Delta\Pi} = j_{\text{wb}}^{\Delta\Pi} \bar{v}_{\text{w}} \quad (22)$$

and

$$J_{\text{vsb}}^{\Delta\Pi} = L_{\text{pb}} \bar{c} \bar{v}_{\text{s}} \Delta\Pi \quad (23)$$

where: $\bar{c} = \frac{1}{2}(c_1 + c_2)$, \bar{c} is the mean solute concentration, and \bar{v}_{w} , \bar{v}_{s} are partial molar volumes of the solvent (w) and the solute (s). Denoting the $J_{\text{vsb}}^{\Delta\Pi}$ by J'_{vs0} we get:

$$J'_{\text{vs0}} = L_{\text{pb}} \bar{c} \bar{v}_{\text{s}} \Delta\Pi$$

Since $J'_{\text{vs0}} = j'_{\text{s0}} \bar{v}_{\text{s}}$, we can write:

$$J'_{\text{s0}} = L_{\text{pb}} \bar{c} \Delta\Pi \quad (24)$$

Taking into account equation (14), i.e. $L_{\text{pb}} = (1 - \sigma)L_{\text{p}}$, we obtain the following expression for the solute flux generated under condition $\Delta P = 0$:

$$j'_{\text{s0}} = \omega'_0 \Delta\Pi \quad (25)$$

where

$$\omega'_0 = \bar{c}L_p(1 - \sigma) \quad (26)$$

We note that $j'_{s0} = j_d$, where j_d is the diffusive solute flux, and thus $\omega'_0 = \omega_d$ is the coefficient of diffusive solute permeation. The above equations can then be written as:

$$j_d = \omega_d \Delta \Pi \quad (27)$$

where

$$\omega_d = \bar{c}L_p(1 - \sigma) \quad (28)$$

The last step can be justified by revisiting equations (21), (21a), (22) and (23). From these equations we get:

$$j_{wb}\bar{v}_w = j_{sb}\bar{v}_s$$

where $j_{wb}^{\Delta \Pi} = j_{wb}$, and $j_{sb}^{\Delta \Pi} = j_{sb} = L_{pb}\bar{c}\Delta \Pi$. Noting that $j_{wb} = \bar{c}_w v_w$, and $j_{sb} = \bar{c}_s v_s$ (where v_w and v_s are velocities of the solvent and the solute, respectively), we get:

$$\bar{c}_w \bar{v}_w \nu_w = \bar{c}_s \bar{v}_s \nu_s \quad (29)$$

If the membrane separates diluted solutions, and this is the case we consider here, then we assume $\bar{c}_w \approx 1$. Moreover, in this case $\bar{c}_w \gg \bar{c}$ as well. Therefore for solutes for which \bar{v}_s does not differ significantly from \bar{v}_w equation (29) yields $\nu_w \ll \nu_s$. In other words in pores n_b the velocity ν_w of solvent molecules is negligible compared to the velocity ν_s of the solute molecules. We conclude that the velocity of solute convection by the solvent flow is negligible as well. This justifies putting $j'_{s0} \approx j_d$. We emphasize that equation (28) represents a correlation relation among parameters L_p , σ and ω_d . It allows computation of any of the parameters if the other two are known. We elaborate this formula further later in the paper. For now let us only mention that, when equations (10) and (11) are substituted, this equation has a form:

$$\omega_d = \frac{(L_{pa}L_{pb} + L_{pb}^2)\bar{c}}{L_p}$$

Let us consider now the convection flux j_k . In our framework this flux is generated in pores n_b only and can be written as:

$$j_k = \bar{c}J_{vb} \quad (30)$$

Equations (7) and (14) yield:

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

hence we finally get:

$$j_k = (1 - \sigma)\bar{c}L_p\Delta P \quad (31)$$

This flux is generated by pressure ΔP ; it is practically not affected by the osmotic pressure $\Delta\Pi$ as we argued in the preceding paragraph. In summary, the total solute flux (which we for now denote j_s) generated by both ΔP and $\Delta\Pi$ equals:

$$j'_s = j_d + j_k$$

Considering equations (27) and (34) we get:

$$j'_s = \omega_d \Delta\Pi + (1 - \sigma) \bar{c} L_p \Delta P \quad (32)$$

The above expression and equation (15) constitute the mechanistic transport equations.

Functional comparison of mechanistic equations with the thermodynamic Kedem-Katchalsky equations. Formalism equivalence

In this section we compare both sets of equations, mechanistic and Kedem-Katchalsky (KK), first the volume flux equation and then the solute flux equation. We show their equivalence and derive a correlation relation for the transport parameters appearing in the KK formalism.

Equations for the volume flux

Comparing the mechanistic equation for the volume flux (i.e. equation (15)) with the corresponding KK equation (i.e. equation (1)) we immediately notice they have identical form. Moreover, parameters L_p and σ have analogous definitions. Namely, in both equations the filtration coefficient is defined as:

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

Similarly for the reflection coefficient – given as:

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

It comes therefore as no surprise that both formalisms suggest similar experimental methods for measurements of both parameters. The equations are thus equivalent, even despite the fact that the interpretation of the reflection coefficient is somewhat different. In KK approach it is given as (Kedem and Katchalsky 1958, 1961, 1963; Katchalsky and Curran 1965):

$$\sigma = -\frac{L_{pD}}{L_p}$$

where L_{pD} is called an osmotic flux coefficient. In our mechanistic formalism the same coefficient is interpreted as:

$$\sigma = \frac{L_{pa}}{L_p}$$

where, let us recall, L_{pa} is the filtration coefficient of pores n_a (i.e. impermeable to the solute). That suggests that parameters L_{pD} and L_{pa} should be treated as the same.

We want to emphasize that measurements of parameters L_p and σ are quite simple, even on biological membranes. We return to this point in section entitled: *Measurements of transport parameters. Sample results*, dealing with measurements of parameters ω and ω_d .

Solute flux equation. Correlation relation for transport parameters

The solute flux is described in our mechanistic formalism by equation (25). Taking into account correlation relation for parameters L_p , σ and ω_d , i.e. equation (21):

$$\omega_d = (1 - \sigma)\bar{c}L_p$$

the solute flux can be written as:

$$j'_s = (1 - \sigma)\bar{c}L_p\Delta\Pi + (1 - \sigma)\bar{c}L_p\Delta P \quad (33)$$

In the KK formalism the solute flux is given by equation (2), i.e.:

$$j_s = \omega\Delta\Pi + (1 - \sigma)\bar{c}J_v$$

where ω is the solute permeation coefficient and J_v – the volume flux (equation (1)).

We want to show that both expressions are equivalent. To that end, let us assume that a mechanical pressure:

$$\Delta P = \Delta P_m = \sigma\Delta\Pi$$

is applied to the membrane. The above equations thus assume the forms:

$$j'_s = j_{sm} = (1 - \sigma)\bar{c}L_p(1 + \sigma)\Delta\Pi \quad (34)$$

and

$$j_s = j_{sm} = \omega\Delta\Pi \quad (35)$$

respectively. Here $j_{sm} = j'_s = j_s$ denotes the value of solute flux permeating in the membrane under this particular mechanical pressure $\Delta P = \Delta P_m = \sigma\Delta\Pi$. From equations (34) and (35) it follows:

$$\omega = (1 - \sigma)\bar{c}L_p(1 + \sigma) = (1 - \sigma^2)\bar{c}L_p = \omega_d(1 + \sigma) \quad (36)$$

This is a correlation relation for parameters L_p , σ and ω introduced in KK equations.

Returning now to the general case of equations (33) and (2), we substitute relation (36) to (2). We obtain:

$$\begin{aligned} j_s &= (1 - \sigma)\bar{c}L_p(1 + \sigma)\Delta\Pi + (1 - \sigma)\bar{c}L_p\Delta P - (1 - \sigma)\bar{c}L_p\sigma\Delta\Pi = \\ &= \omega_d\Delta\Pi + (1 - \sigma)\bar{c}L_p\Delta P = j'_s \end{aligned}$$

Thus the KK equation is indeed equivalent to the mechanistic equation and the fluxes predicted by both equations are the same ($j_s = j'_s$). Hence the mechanistic equation can finally be written as:

$$j'_s = \omega_d\Delta\Pi + (1 - \sigma)\bar{c}L_p\Delta P \quad (37)$$

Parameter ω_d ought to be determined from condition:

$$\omega_d = \left(\frac{j_d}{\Delta\Pi} \right)_{\Delta P=0} \quad (38)$$

since for $\Delta P = 0$ we have $j_s = j_d$

Reduced equations

Using relation (28) we can rewrite the mechanistic equations ((15) and (37)) in a reduced (using equation (36)) form containing only two phenomenological parameters:

$$\begin{aligned} J_v &= L_p\Delta P - L_p\sigma\Delta\Pi \quad (39) \\ j'_s &= (1 - \sigma)\bar{c}L_p\Delta\Pi + (1 - \sigma)\bar{c}L_p\Delta P = (1 - \sigma)\bar{c}L_p(\Delta P + \Delta\Pi) \end{aligned}$$

Similarly, the KK equations (1) and (2) can be reduced to a form:

$$\begin{aligned} J_v &= L_p\Delta P - L_p\sigma\Delta\Pi \quad (40) \\ j_s &= (1 - \sigma^2)\bar{c}L_p\Delta\Pi + (1 - \sigma)\bar{c}J_v \end{aligned}$$

Measurements of transport parameters. Sample results

Transport parameters L_p and σ introduced in KK equations, as well as in our mechanistic equations, can be conveniently measured based on the following equations:

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

and

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

The situation is quite different for the permeation coefficient ω (in KK formalism) and ω_d (introduced in the mechanistic formalism). They are defined as:

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

and

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

Let us recall that according to equation (28) they are related:

$$\omega = \omega_d(1 + \sigma)$$

Accordingly, the coefficient ω_d ought to be measured with $\Delta P = 0$. On the other hand, the definition of ω requires condition $J_v = 0$, i.e. a situation when there is a nonzero mechanical pressure $\Delta P = \sigma\Delta\Pi$ on the membrane. In our mechanistic model such mechanical pressure drives a volume flux J_{vb} in pores n_b (permeable to the solute). It can be written as (Kargol and Kargol 2000; Kargol 2001):

$$J_{vb} = J_{vwb}^{\Delta P} + J_{vwb}^{\Delta\Pi} + J_{vd} + J_{vk} \quad (41)$$

where: $J_{vwb}^{\Delta P}$ – solvent flux driven by ΔP , $J_{vwb}^{\Delta\Pi}$ – solvent flux driven by $\Delta\Pi$, J_{vd} – solute volume flux generated diffusively, and J_{vk} – convective solute volume flux. In this case, in order to determine the value of parameter ω we need to find j_s first. The flux is measured as:

$$j_s = \frac{\Delta m}{S\Delta t}$$

where Δm is the solute mass permeating across the membrane (with the active surface area S) during time Δt . Mass Δm can be found as:

$$\Delta m = \Delta c_t V$$

where: Δc_t is the change of concentration of solution on either side of the membrane occurring in time Δt , and V – volume of that solution. From equation (31) we can see that the concentration change Δc_t , and therefore flux j_s is affected by fluxes $J_{vwb}^{\Delta P}$, $J_{vwb}^{\Delta\Pi}$, J_{vd} and J_{vk} . In other words parameter ω is determined under fairly complex conditions.

The case is somewhat clearer for coefficient ω_d . However, still if $\Delta P = 0$ then fluxes J_{vd} and J_{vwa} affect the measured value of ω_d . We conclude that experimental measurements of parameters ω and ω_d are difficult and sometimes impossible. In such cases of particular importance the correlation relations among transport parameters are derived in this paper, i.e. equations (21) and (28).

We illustrate these relations on selected membranes and solutes shown in Table 1. For all of these systems transport parameters L_p , σ and $\omega = \omega_{ex}$ were

Table 1. Values of transport parameters

| Membrane Solution | σ | $L_p \times 10^{12}$ [m ³ /Ns] | $\omega_{\text{ex}} \times 10^{10}$ [mol/Ns] | \bar{c} [mol/m ³] | $\omega \times 10^{10}$ [mol/Ns] | $\omega_d \times 10^{10}$ [mol/Ns] |
|---------------------------|----------|--|---|------------------------------------|-------------------------------------|---------------------------------------|
| Nephropane Ethanol | 0.025 | 5.0 | 21.0 ± 3.0 | 400 | 19.9 | 19.5 |
| Nephropane Glucose | 0.065 | 5.0 | 8.0 ± 1.5 | 200 | 9.95 | 9.35 |
| Cellophane Ethanol | 0.02 | 2.23 | 6.3 ± 1.3 | 300 | 6.68 | 6.55 |
| Cellophane Glucose | 0.1 | 2.23 | 2.3 ± 1.2 | 150 | 3.31 | 3.01 |
| Dialysis membrane Glucose | 0.13 | 1.09 | 2.3 ± 1.2 | 300 | 3.21 | 2.84 |

measured using standard methods (Kedem and Katchalsky 1961; Katchalsky and Curran 1965; Grygorczyk 1978; Kargol 1994). Parameters σ and ω_{ex} were measured for $J_v = 0$. The value of ω_{ex} is a mean of several measurements and the error reported – the average deviation from the mean. The last two columns in Table 1 show coefficients ω and ω_d (computed from equations (28) and (21)). The computed results show satisfactory agreement with the experiment. Also, values of ω_d are noticeably smaller than the corresponding ω 's, as the difference in thermodynamic and mechanistic equations for the solute flux suggests.

Conclusion

1. We considered membrane transport processes generated by osmotic and mechanical pressure difference. New model and a new interpretation has been proposed for transport across a typical porous membrane having a number N of pores of varying sizes. We assumed (Kargol and Kargol 2000; Kargol 2001; Kargol et al. 2001) that a single pore has a reflection coefficient (suitably re-defined) equal to 0 or 1.

2. We derived mechanistic transport equations which we believe have a clear physical interpretation. They have the form:

$$J_v = J_{vM} = L_p \Delta P - L_p \sigma \Delta \Pi$$

$$j'_s = j_{sM} = \omega_d \Delta \Pi + (1 - \sigma) \bar{c} L_p \Delta P$$

3. We showed that the mechanistic equations are equivalent to the KK equations, assuming:

$$\omega = (1 - \sigma) \bar{c} L_p (1 + \sigma)$$

and

$$\omega_d = (1 - \sigma)\bar{c}L_p$$

These equations show correlation relations among the transport parameters L_p , σ , and ω (for the KK formalism) and L_p , σ , and ω_d (for the mechanistic approach). Accordingly, one of the parameters from each set can be computed if only the other two are known. In particular we refer here to parameters ω and ω_d , measurements of which are typically rather difficult.

4. Considering the correlation relations, the mechanistic and KK equations were reduced to a form involving only two, as opposed to usual three, phenomenological transport parameters.

5. We believe that because of this work, the results concerning membrane mass transport (generated by osmotic and mechanical pressure) can be analyzed and interpreted in a clearer and more detailed way.

In particular, here we have in mind studies directed towards understanding the passive transport processes of water and solutes across cell membranes. It is sufficient to say that each cell has to exchange water and various substances with its medium in order to live. In other words it must take up water and solutes and excrete them with products of its metabolism. This exchange goes on across the cell membrane and with its active participation. Processes of this exchange belong to fundamental ones from the biological point of view. It is impossible to gain knowledge of them using only the KK equations. Radically more useful in this respect are the mechanistic transport equations. This is also substantiated by our recent result (in preparation).

Appendix

In general the KK equations (1) and (2) lack clarity of interpretation (Kargol and Kargol 2000; Kargol 2001). It concerns the solute flux (eq. (2)) in particular:

$$j_s = \omega\Delta\Pi + (1 - \sigma)\bar{c}J_v$$

Parameter ω in the first term of the right hand side is given by:

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

It expresses the magnitude of the solute flux generated by unit osmotic pressure, when $J_v = 0$, i.e. when there are both the osmotic pressure $\Delta\Pi$ and hydraulic pressure $\Delta P = \Delta P_m = \sigma\Delta\Pi$. It means that the flux j_s is generated jointly by the pressures $\Delta\Pi$ and ΔP_m . Hence it cannot be simply the diffusive flux and parameters ω should not be regarded as a measure of purely diffusive solute permeation. Frequently it is treated as such (Spiegler and Kedem 1966; Sha'afi et al. 1970; Steudle et al. 1987; Ślęzak 1989; Ślęzak et al. 1989; Ślęzak and Turczyński 1992;

Waniewski 1994; Kargol 1996 and others). We conclude that it is not clear what transport mechanisms the coefficient ω describes.

It is commonly stated that the second term in equation (2), i.e. the term $(1 - \sigma)\bar{c}J_v$ represents the convective solute flux (the flux carried by flow J_v). Although such interpretation may seem convincing, if we rewrite the equation into the form:

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

then certain difficulties in the interpretation of the last two terms arise (i.e. terms $(1 - \sigma)\bar{c}L_p\Delta P$ and $(1 - \sigma)\bar{c}L_p\sigma\Delta\Pi$).

In the framework of mechanistic analysis (as performed in this work) one might notice that the above mentioned issues with interpretation of the KK solute flux equation result from a misleading form in which the equation is typically presented. If we rewrite it as:

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

and taking into account equations (28) and (36), i.e. $\omega_d = (1 - \sigma)\bar{c}L_p$ and $\omega = \omega_d(1 + \sigma)$, we obtain:

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

where ω_d is the coefficient of the solute diffusive permeation across the membrane.

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