ELSEVIER

Biophysical Chemistry 103 (2003) 117–127

Biophysical Chemistry

www.elsevier.com/locate/bpc

Mechanistic equations for membrane substance transport and their identity with Kedem–Katchalsky equations

M. Kargol[a],*, A. Kargol[b]

[a]*Institute of Physics, Świętokrzyska Academy, 25-406 Kielce, Świętokrzyska 15, Poland*
[b]*Department of Physics, Tulane University, 2001 Percival Stern Hall, New Orleans, LA 70118, USA*

Received 17 April 2002; received in revised form 16 August 2002; accepted 16 August 2002

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. Hence the equations allow clearer and more detailed interpretation of results concerning membrane substances transport.

Keywords: Membrane; Substance transport; Thermodynamics equations; Mechanistic equations

1. Introduction

It is convenient to describe membrane transport of non-electrolytes, generated by osmotic pressure difference $\Delta\Pi$ and mechanical pressure difference ΔP, using the so-called practical equations of Kedem and Katchalsky [1–4]. So it is no wonder that these equations have been broadly applied in studies on substance permeation across artificial and biological membranes. The equations describe four transport processes, i.e. filtration, osmosis, diffusion and convection. Those practical Kedem–Katchalsky equations (KK) were derived on the basis of the linear thermodynamics of irreversible processes, and thus we shall treat them as thermodynamical equations.

It should be stressed that application of the classical version of the KK equations is limited to membrane systems with two-component solutions, sufficiently diluted and well stirred. Moreover, the equations are not transparent when it comes to interpretation. For those reasons the equations were (since their first formulation) developed and completed in various ways. They were modified to make them suitable for membrane systems with weakly stirred solutions [10,11,13,16,31], multi-component solutions [6,9,15,23] and for multi-membrane systems (especially two-membrane systems) [2,8,11,19–21], and also to write them

---

*Corresponding author. Tel.: +48-41-362-64-52; fax: +48-41-362-64-52.

E-mail address: kargol@pu.kielce.pl (M. Kargol).

0301-4622/03/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0301-4622(02)00250-8

in a reduced form (containing not three but two transport parameters) [3,4,14,17,23].

In the present work an attempt has been made to solve the interpretational difficulties concerning the KK equations, and in particular those concerning the various terms and parameters in the equations. For that purpose, first, an overall interpretational analysis of the equations has been made in the realm of the formalism they were created.

Next, membrane transport processes were considered (generated by simultaneous presence of the pressures $\Delta\Pi$ and ΔP) based on mechanical considerations, which were started in our previous papers [18,22,24]. Such considerations were conducted for a typical porous membrane having a statistical number N of pores with randomly differentiated linear dimensions (i.e. radii of their cross-sections). In the considerations it was assumed that a single pore has a reflection coefficient equal either $\sigma_p = 1$ or $\sigma_p = 0$.

From these considerations were derived new transport equations, which were called mechanistic due to the character of the considerations. They describe, like the KK equations, volume transport J_v and solute transport j_s. Their special advantage consists in total interpretational transparency—something that the thermodynamic KK equations are lacking.

In this work we were able to show that the KK equations and the mechanistic transport equations we derived are identical. That finding made the KK equations easy to interpret. So now we can say that the KK equations and the mechanistic equations (taken together) constitute a more clear-sighted and lucid research tool (than the KK equations alone). This fact assumes an added importance from the biophysical point of view, because now one can interpret deeper and with greater clarity new results on substance transport across biological membranes. Moreover, one can also reinterpret the results of studies performed on the basis of the KK equations only. It should be added that there are a great many of such studies, as one can see from the papers ([1,12,18,25–30,32–36] and others).

2. Interpretational analysis of the Kedem–Katchalsky equation

The so-called practical KK equations are most often written in the form:

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi, \tag{1}$$

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

where J_v—volume flux, j_s—solute flux, ΔP and $\Delta\Pi$—pressure difference (mechanical and osmotic), L_p, σ and ω—coefficients (of filtration, reflection and permeation) and $\bar{c}$—mean concentration.

These equations were derived on the basis of linear irreversible thermodynamics [1–4]. They describe four transport processes generated by simultaneous action of the pressure differences ΔP and $\Delta\Pi$. Those processes are: filtration, osmosis, diffusion and convection.

The utility of the equations is restricted (as mentioned in Section 1) to membrane systems with two-component solutions, sufficiently diluted and well stirred. Volume flux J_v can be expressed as:

$$J_v = j_s \bar{v}_s + j_w \bar{v}_w, \tag{3}$$

where j_s and j_w—solute (s) and water (w) fluxes, $\bar{v}_s$ and $\bar{v}_w$—molar volumes. So, in general, one can say that flux J_v is the net flux of both $J_{vs} = j_s \bar{v}_s$ and $J_{vw} = j_w \bar{v}_w$.

The transport parameters occurring in Eqs. (1) and (2) are defined by the formulae:

$$L_p = \left(\frac{J_v}{\Delta P}\right)_{\Delta\Pi = 0}, \tag{4}$$

$$\sigma = \left(\frac{\Delta P}{\Delta \Pi}\right)_{J_v = 0}, \tag{5}$$

and

$$\omega = \left(\frac{j_s}{\Delta \Pi}\right)_{J_v = 0}. \tag{6}$$

These formulae express the physical sense of the parameters, and also suggest methods for their determination [1–5].

In the light of Eq. (4), the filtration coefficient L_p expresses the value of volume flow across the membrane induced by a unit pressure difference, at $\Delta\Pi = 0$. In other words, it expresses the overall filtration properties of all pores within a given membrane. So the interpretation here is quite clear.

In turn, the reflection coefficient σ represents (according to Eq. (5)) the ratio of mechanical pressure ΔP (measured osmometrically at $J_v = 0$) to osmotic pressure difference $\Delta\Pi$ given by the van't Hoff's formula

$$\Delta\Pi = RT\Delta c$$

where R and T—gas constant and temperature, and Δc—concentration difference. This parameter may express the full measure of membrane selectivity. If its value is unity,

$$\sigma = \left(\frac{\Delta P}{\Delta\Pi}\right)_{J_v = 0} = 1,$$

it means that the membrane is semipermeable. All pores of such a membrane (permeable for the solvent) do not allow through the solute molecules, reflecting them.

In the case $\sigma = 0$, we have to deal with permeable (unselective) membrane. It means that each pore of such a membrane is as permeable for the solvent as for the solute. In both the cases the situation is clear from the physical point of view.

However, some interpretational problems appear when the parameter σ is within the range $0 < \sigma < 1$. It is commonly assumed that such membrane is simply selective; it lets the solvent pass better than the solute. Such understanding of the parameter, though correct, is too general; especially when it refers to membranes with differentiated pore diameters, and just such membranes we have it to investigate. The problem of 'reflecting' solute molecules by membrane pores cannot be solved within the limits of KK formalism.

The last of the parameters, i.e. the reflection coefficient ω, expresses (according to Eq. (6) the value of solute flux induced by a unit osmotic pressure difference $\Delta\Pi$, when $J_v = 0$. It means that solute flux is here generated by a simultaneous presence of osmotic pressure difference and mechanical pressure difference $\Delta P = \sigma\Delta\Pi$. Hence it follows that in the case of membrane with differentiated pore diameters the coefficient ω should not be treated as only a coefficient of diffusive solute permeation. It is, however, often treated in such a way ([7,10,25,30,31,36] and others). So, a question arises: what processes does that parameter include?

There are also problems with interpretation of some of the terms in the KK equations. As far as Eq. (1) is concerned, the situation is clear. The first term of the equation (i.e. $L_p\Delta$P) refers to filtration, whereas the second (i.e. $L_p\sigma\Delta\Pi$)—to the osmotic process. With reference to the second term, one can have some doubts resulting from the difficulties with understanding of the reflection coefficient σ.

Basic interpretational difficulties refer to the terms of Eq. (2). Because of problems with understanding of the coefficient ω, it is not clear what processes are described by the first term (i.e. $\omega\Delta\Pi$) of the equation. Concerning the second term ($(1-\sigma)\bar{c}J_v$), it is thought to be a solute flux due to convection, i.e. carried by the volume flux J_v, and this seems convincing. However, the matter becomes complicated when Eq. (2) is transformed to the form:

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

Now, there are two terms expressing oppositely directed convection fluxes and one does not know how to interpret them, especially when the membrane has pores of differentiated linear dimensions.

In order to remove the above-mentioned difficulties and interpretational doubts referring to the KK equations, we are going now to present the so-called mechanistic formalism of membrane substance transport. Some preliminary information about that formalism was given in our previous papers [18,22,24]. Equations of that formalism, describing volume flow J_v and solute flow j_s, offer a quite clear interpretation. They are also identical with the KK equations. Owing to that fact, the KK equations became also quite transparent.

3. Mechanistic equations of transport

3.1. Model membrane system with a generic porous membrane

We consider the problem of membrane transport generated by mechanical and osmotic pressure

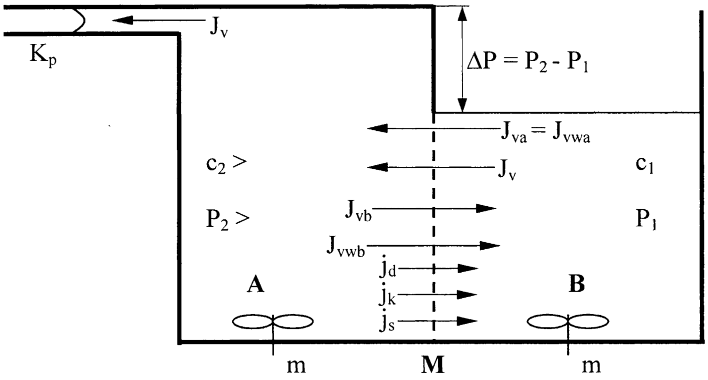

Fig. 1. The model membrane system with well-mixed solutions (M—membrane; A, B—compartments; K_p—capillary; m, m—stirrers; c_1, c_2—concentrations; P_1, P_2—mechanical pressures). Fluxes are described in text.

differently from the method developed by Kedem and Katchalsky. Our approach, initiated in our papers [18,22,24] 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 (stirrers m, 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 $\Delta P = P\ - P_1$ 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, nephrophane, 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 ($r_N^{\min}$):

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

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 $r_1^{\min} \leqslant r < r_s$) 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 assume only integer values 1 (for impermeable pores) or 0 (for permeable ones) and as we show in what follows 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 equals unity $\sigma = 1$ 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 (nonselective). 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.

3.2. 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:

$$J_{va} = L_{pa}\Delta P - L_{pa}\Delta\Pi, \tag{7}$$

$$J_{vb} = L_{pb}\Delta P, \tag{8}$$

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

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

and

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

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

$$J_v = J_{va} + J_{vb} \tag{9}$$

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 $J_v = 0$. Hence from Eqs. (7) and (8) we get:

$$\Delta P_m = \frac{L_{pa}}{L_p}\Delta\Pi, \tag{10}$$

where

$$L_p = L_{pa} + L_{pb} \tag{11}$$

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

$$\sigma_k = \frac{L_{pa}}{L_{pa} + L_{pb}} = \frac{L_{pa}}{L_p} \tag{12}$$

we obtain from Eq. (10):

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

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

$$\sigma_k = \left(\frac{\Delta P_m}{\Delta\Pi}\right)_{J_v = 0}. \tag{13}$$

The above formula is identical with a definition of reflection coefficient σ given in the KK formalism (i.e. Eq. (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 Eq. (12). Therefore if $L_{pa} = 0$, then, according to Eq. (12), we get $\sigma = 0$. Such a membrane is permeable (nonselective). 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, Eq. (12) yields:

$$L_{pa} = \sigma L_p, \tag{14}$$

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

$$L_{pb} = (1 - \sigma)L_p. \tag{15}$$

When $\Delta P \neq \Delta P_m$ a volume flux is induced in the system and by using Eqs. (7) and (8) we obtain from Eq. (9):

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

Substituting Eqs. (11) and (12) we finally get:

$$J_v = L_p\Delta P - L_p\sigma\Delta\Pi. \tag{16}$$

The equation has the same form as the KK equation for a volume flux. However, an interpretation of the coefficient σ is somewhat different. In our framework it is given by Eq. (12), while in the KK formalism it is described by the Stavermann relation [1]:

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

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:

$$L_p = \left(\frac{J_v}{\Delta P}\right)_{\Delta\Pi=0}. \tag{17}$$

3.3. 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:

$$j_s = j_{sk} + j_{kk} \tag{18}$$

where

$$j_{sk} = \omega\Delta\Pi \tag{19}$$

and the term:

$$j_{kk} = (1-\sigma)\bar{c}J_v \tag{20}$$

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_b 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 Eqs. (7) and (8). 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 ($j_{sa} = 0$ since $\sigma_a = 1$). As for Eq. (8), 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:

$$J_{vb} = L_{pb}\Delta P - L_{pb}\sigma_b\Delta\Pi = L_{pb}\Delta P,$$

since the reflection coefficient σ_b of pores n_b equals 0. We note that the volume flux J_{vb} has two-components:

$$J_{vb} = J_{vwb} + J_{vsb} > 0, \tag{21}$$

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 Eq. (21) has a form:

$$J_{vb}^{\Delta\Pi} = J_{vwb}^{\Delta\Pi} + J_{vsb}^{\Delta\Pi} = 0, \tag{22}$$

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

$$|J_{vb}^{\Delta\Pi}| = |J_{vsb}^{\Delta\Pi}| \neq 0, \tag{22a}$$

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

$$J_{vwb}^{\Delta\Pi} = -L_{pb}\bar{c}_w\bar{v}_w\Delta\Pi, \tag{23}$$

and

$$J_{vsb}^{\Delta\Pi} = L_{pb}\overline{cv}_s\Delta\Pi. \tag{24}$$

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

$$J'_{vs0} = L_{pb}\bar{c}\,\bar{v}_s\Delta\Pi.$$

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

$$J'_{s0} = L_{pb}\bar{c}\Delta\Pi. \tag{25}$$

Taking into account Eq. (15), i.e. $L_{pb} = (1-\sigma)L_p$, we obtain the following expression for the solute flux generated under condition $\Delta P = 0$:

$$j'_{s0} = \omega'_0\Delta\Pi, \tag{26}$$

where

$$\omega'_0 = \bar{c}L_p(1-\sigma). \tag{27}$$

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:

$$j_d = \omega_d\Delta\Pi, \tag{28}$$

where

$$\omega_d = \bar{c}L_p(1-\sigma). \tag{29}$$

The last step can be justified by revisiting Eqs. (22), (22a), (23) and (24). From these equations we get:

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

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

$$\bar{c}_w\bar{v}_w\nu_w = \bar{c}\,\bar{v}_s\nu_s. \tag{30}$$

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 $\bar{v}_w$ Eq. (30) 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 Eq. (29) represents a correlation relation among parameters L_p, σ and ω_d.

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:

$$j_k = \bar{c}J_{vb}. \tag{31}$$

Eqs. (8) and (15) yield:

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

hence we finally get:

$$j_k = (1-\sigma)\bar{c}L_p\Delta P. \tag{32}$$

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 Eqs. (28) and (32) we get:

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

The above expression and Eq. (16) constitute the mechanistic transport equations.

4. Functional comparison of mechanistic equations with the thermodynamic KK equations: formalism equivalence

In this section we compare both sets of equations, mechanistic and 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.

4.1. Equations for the volume flux

Comparing the mechanistic equation for the volume flux (i.e. Eq. (16)) with the corresponding KK equation (i.e. Eq. (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 [1–4]:

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

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 comment in a later section dealing with measurements of parameters ω and ω_d.

4.2. Solute flux equation: correlation relation for transport parameters

The solute flux is described in our mechanistic formalism by Eq. (33). Taking into account correlation relation for parameters L_p, σ and ω_d, i.e. Eq. (29):

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

the solute flux can be written as:

$$j'_s = (1-\sigma)\bar{c}L_p\Delta\Pi + (1-\sigma)\bar{c}L_p\Delta P. \qquad (34)$$

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

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

where ω is the solute permeation coefficient and J_v is the volume flux (Eq. (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 assume then forms:

$$j'_s = j_{sm} = (1-\sigma)\bar{c}L_p(1+\sigma)\Delta\Pi \qquad (35)$$

and

$$j_s = j_{sm} = \omega\Delta\Pi, \qquad (36)$$

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 Eqs. (35) and (36) it follows:

$$\begin{aligned}\omega &= (1-\sigma)\bar{c}L_p(1+\sigma)\\ &= (1-\sigma^2)\bar{c}L_p = \omega_d(1+\sigma).\end{aligned} \qquad (37)$$

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

Returning now to the general case of Eqs. (34) and (2), we substitute relation Eq. (37) to Eq. (2). We obtain:

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

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

$$j_s = \omega_d\Delta\Pi + (1-\sigma)\bar{c}L_p\Delta P. \qquad (38)$$

Parameter ω_d ought to be determined from condition:

$$\omega_d = \left(\frac{j_d}{\Delta\Pi}\right)_{\Delta P=0}, \qquad (39)$$

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

4.3. 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 Eq. (37) 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 [18,22]:

$$J_{vb} = J_{vwb}^{\Delta P} + J_{vwb}^{\Delta\Pi} + J_{vd} + J_{vk}, \tag{40}$$

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:

$$j_s = \frac{\Delta m}{S\Delta t}, \tag{41}$$

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:

$$\Delta m = \Delta c_t V, \tag{42}$$

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 Eq. (40) 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 are correlation relations among transport parameters derived in this paper, i.e. Eqs. (29) and (37).

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 measured using standard methods [1,5,10]. 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 Eqs. (37) and (29)). 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.

5. Conclusion

(1) We considered membrane transport processes generated by osmotic and mechanical pressure difference. A 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 [18,22,24] that a single pore has a reflection coefficient (suitably re-defined) equal 0 or 1.

Table 1
Values of transport parameters (own results)

Membrane Solution	σ	$L_p \times 10^{12}$ (m^3/Ns)	$\omega_{ex} \times 10^{10}$ (mol/Ns)	$\bar{c}$ (mol/m^3)	$\omega \times 10^{10}$ (mol/Ns)	$\omega_d \times 10^{10}$ (mol/Ns)
Nephrophane Ethanol	0.025	5.0	21.0 ± 3.0	400	19.9	19.5
Neprophane 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

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

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi,$$

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

(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) 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 non-electrolyte transport in artificial and biological membranes. The two sets of equations together become a more sophisticated and better understood scientific tool.

References

[1] A. Katchalsky, P.F. Curran, Non-equilibrium Thermodynamics in Biophysics, Harvard University Press, Cambridge, MA, 1965.

[2] O. Kedem, A. Katchalsky, Permeability of composite membranes, Trans. Faraday Soc. 59 (Part 1–3) (1963) 1918–1953.

[3] O. Kedem, A. Katchalsky, Thermodynamics analysis of the permeability of biological membranes to non-electrolytes, Biochim. Biophys. Acta 27 (1958) 229–246.

[4] O. Kedem, A. Katchalsky, A physical interpretation of the phenomenological coefficients of membrane permeability, J. Gen. Physiol. 45 (1961) 143–179.

[5] Cz. Grygorczyk, Measurement of practical phenomenological coefficients at membranes, Curr. Top. Biophys. 3 (1978) 5–19, in Polish.

[6] A. Zelman, Membrane permeability. Generalisation of the reflection coefficient method of describing volume and solute flows, Biophys. J. Membr. 12 (1972) 414–419.

[7] K.S. Spiegler, O. Kedem, Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes, Desalination 1 (1966) 311–326.

[8] Y. Imai, Membrane transport system modeled by network thermodynamics, J. Membr. Sci. 41 (1989) 3–21.

[9] L.F. Del Castillo, E.A. Mason, Generalisation of membrane reflection coefficients for nonideal, nonisothermal, multicomponent systems with external forces and viscous flow, J. Membr. Sci. 28 (1986) 229–267.

[10] M. Kargol, A more general form of Kedem and Katchalsky's practical equations, J. Biol. Phys. 22 (1996) 15–26.

[11] M. Kargol, Full analytical description of graviosmotic volume flows, Gen. Physiol. Biophys. 13 (1994) 109–126.

[12] D.G. Levitt, A new theory of transport for cell membrane pores (General theory and application to red cell), Biochim. Biophys. Acta 373 (1974) 115–131.

[13] M. Kargol, A. Ślęzak, Modification of the Kedem–Katchalsky practical equations, Technical University Kielce, Zesz. Nauk. 16 (1985) 5–12, in Polish.

[14] F.W. Kleinhans, Membrane permeability modeling: Kedem–Katchalsky vs. a two-parameter formalism, Cryobiology 37 (1998) 271–289.

[15] A. Ślęzak, B. Turczyński, Generalisation of the Spiegler–Kedem–Katchalsky frictional model equations of the transmembrane transport for multicomponent nonelectrolyte solutions, Biophys. Chem. 44 (1992) 139–142.

[16] A. Kargol, Effect of boundary layers on reverse osmosis through a horizontal membrane, J. Membr. Sci. 159 (1999) 177–184.

[17] A. Kargol, M. Kargol, S. Przestalski, Correlation relation for the membrane transport parameters L_{p}, σ and ω, J. Biol. Phys. 23 (1997) 233–238.

[18] A. Kargol, M. Kargol, Membrane transport generated by the osmotic and hydraulic pressure. Correlation relation for parameters L_{p}, σ and ω, J. Biol. Phys. 26 (2000) 307–320.

[19] C.S. Patlak, D.A. Goldstein, I.F. Hoffman, The flow of solute and solvent across a two-membrane system, J. Theoret. Biol. 5 (1963) 426–442.

[20] G. Monticelli, F. Celentano, Further properties of the two-membrane model, Bull. Math. Biol. 45 (1983) 1073–1096.

[21] M. Kargol, A. Kargol, Full analysis of lifting-and-forcing properties of two-membrane osmotic pump dealing with well mixed solutions, Kieleckie Studia Fizyczne 2 (1989) 35–50, in Polish.

[22] A. Kargol, A mechanistic model of transport processes in porous membranes generated by osmotic and hydraulic pressures, J. Membr. Sci. 191 (2001) 61–69.

[23] J.J. Katkov, A two-parameter model cell membrane permeability for multisolute systems, Cryobiology 40 (2000) 64–83.

[24] M. Kargol, A. Kargol, S. Przestalski, Studies on the structural properties of porous membranes: measurement of linear dimensions of solutes, Biophys. Chem. 91 (2001) 263–271.

[25] R.J. Sha'afi, G.T. Rich, D.C. Mikulecky, A.K. Solomon, Determination of urea permeability in red cells by minimum method, J. Gen. Physiol. 55 (1970) 427–450.

[26] R.J. Sha'afi, C.M. Gary-Bobo, Water and non-electrolytes permeability in mammalian red cell membranes, in: J.A.V. Butler, D. Noble (Eds.), Progress in Biophysics and Molecular Biology, vol. 26, Pergamon Press, Oxford and New York, 1976, pp. 105–144.

[27] H. Ginsburg, Model for iso-osmotic water flow in plant root, J. Theoret. Biol. 32 (1971) 147–159.

[28] M.T. Tyree, The symplast concept. A general theory of symplastic transport according to the thermodynamics of irreversible processes, J. Theoret. Biol. 26 (1970) 181–214.

[29] E.L. Fiscus, The interaction between osmotic-and-pressure induced water flow in plant roots, Plant Physiol. 55 (1975) 917–922.

[30] E. Steudle, R. Oren, E.D. Schulze, Water transport in maize roots, Plant Physiol. 84 (1987) 1220–1232.

[31] A. Ślęzak, B. Turczyński, Modification of the Kedem–Katchalsky equations, Biophys. Chem. 24 (1986) 173–178.

[32] M.T. Tyree, S. Yang, P. Cruiziat, B. Sindair, Novel method of measurement hydraulic conductivity of tree root systems and interpretation using AMAIZED, Plant Physiol. 104 (1994) 189–199.

[33] E.L. Fiscus, Diurnal changes in volume and solute transport coefficients of Phaseolus roots, Plant Physiol. 80 (1986) 752–759.

[34] E.L. Fiscus, Determination of hydraulic and osmotic properties of soybean root systems, Plant Physiol. 59 (1977) 1013–1020.

[35] E. Steudle, E. Brinckmann, The osmometer model of the root; water and solute relations of roots of Phaseolus coccineus, Botanica Acta 102 (1989) 85–95.

[36] J. Waniewski, Linear approximations for the description of solute flux through permselective membranes, J. Membr. Sci. 95 (1994) 179–184.