Mechanistic Equations for Membrane Transport of Multicomponent Solutions

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Abstract. In the present article, mechanistic equations for membrane transport of $N+1$-component solutions have been derived. The major specific investigation result is the introduction – for ternary solutions – of two diffusion coefficients ω_{d1} and ω_{d2} for solutes, as well as two cross coefficients ω_{d12} and ω_{d21} for these solutes. The latter parameters may be treated as coefficients of interdiffusion. The expansion of the description of substance transport to include the $N+1$-component solutions does not formulate any additional physical phenomena other than those which are formulated by the transport equations for three-component solutions.

Key words: Porous membranes — Multi-component solutions — Transport processes — Transport equations

Introduction

The Kedem–Katchalsky (KK) equations describe the transport of a solvent and a single solute across a membrane which is in the literature referred to as a "black box" (Kedem and Katchalsky 1958; Katchalsky and Curran 1965). This label means that, with the use of the phenomenological thermodynamic formalism (which provides the basis for the KK equations) it is impossible to obtain or write any information pertaining to the internal structure of the model membrane. Due to this, the KK equations are mainly applied to membranes which are homogeneous in terms of their transport properties. However, in order to describe the transport across membranes of specified structure, mechanistic phenomenon models are built, thus putting the KK equations in the role of a thermodynamic standard to serve the purposes of verification of already-existing mechanistic equations (Katchalsky and Curran 1965).

In recent years, several papers on the so-called mechanistic equations for porous membrane transport have been published (Kargol and Kargol 2000, 2003a,b, c; Kargol 2001, 2002). These equations have been derived on the way of mechanistic considerations. They are based on the model of a porous heterogeneous membrane,

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i.e. a membrane whose pores differ in their cross-section radiuses. (If a membrane contains pores of the same radiuses, it is to be treated as homogeneous in terms of transport properties.) With a view to the internal membrane structure, these equations enable a more profound interpretation of membrane transport processes than the very general KK formalism.

Owing to the fact that the practical KK equations and the mechanistic equations offer different interpretations of the diffusion permeability coefficient ω (ω_d) (Kargol and Kargol 2000, 2003a,b,c; Kargol 2001, 2002) both of these descriptions have been for a long time treated as alternatives. In the recent paper (Suchanek 2005), I have demonstrated that both of the above equation systems are equivalent; moreover, that the mechanistic equations may be derived from the phenomenological KK equations, given certain conditions. This result enables the solution of another problem – the one signalled in the title of the present paper.

Because in research practice (in biology in particular) we deal with membrane systems with complex solutions, it seems reasonable to extend the mechanistic equations in such a way that they can be used for investigations into transport properties of these very systems. The solution of the arising problems on the way of mechanistic considerations, in a manner analogous to the papers (Kargol and Kargol 2000, 2003a,b,c; Kargol 2001, 2002), is a difficult task (if at all possible). That is because, in the case of occurrence of many components in the solutions, numerous concentration stimuli are generated on the membrane, and – consequently – processes, conjugated and cross, occur.

However, it is possible to derive the mechanistic transport equations for complex solutions from the thermodynamic phenomenological equations. As has already been suggested, a similar procedure has been used with reference to binary solutions (Suchanek 2005). As we know, the linear phenomenological equations can bind any number (N) of forces and thermodynamic flows (Katchalsky and Curran 1965; Kargol et al. 1987). An increase in the number of solution components brings a corresponding increase in the number of thermodynamic stimuli and flows in the system, as well as the number of the coefficients which bind them.

The extended equations ought to also include the phenomenon of mutual diffusion (Kargol et al. 1987; Slezak and Turcznski 1992), which results from the presence of two or more solutes in the solution. Below, starting from the phenomenological equations (in their adjusted form (Suchanek et al. 2005a,b)), we shall derive mechanistic equations for complex solutions. First of all, transport across the membrane which separates ternary solutions will be discussed.

Basic phenomenological equations

Phenomenological equations which describe transport across the membrane which separates binary solutions may be written in the following form (Kedem and Katchalsky 1958; Katchalsky and Curran 1965):

$$J_\mathrm{v} = L_\mathrm{p}\Delta P + L_\mathrm{pD}\Delta\Pi \tag{1a}$$

$$J_\mathrm{D} = L_\mathrm{Dp}\Delta P + L_\mathrm{D}\Delta\Pi \tag{1b}$$

or, alternatively, in their "adjusted" form (Suchanek 2005; Suchanek et al. 2005a,b):

$$J_v = L_p \Delta P - L_{pD} \Delta \Pi \tag{2a}$$

$$J_D = -L_{Dp} \Delta P + L_D \Delta \Pi \tag{2b}$$

In both of the above equation systems, L_p, L_{pD}, L_{Dp} and L_D denote coefficients (of filtration, osmotic transport, ultrafiltration and diffusion, respectively), while cross coefficients satisfy Onsager's law: $L_{pD} = L_{Dp} \cdot \Delta P$ and $\Delta \Pi$ denote pressure differences (mechanical and osmotic).

In the Eqs. (1a) and (1b) for membranes whose $\sigma > 0$, the cross coefficient L_{pD} is a negative value ($L_{pD} < 0$). This fact follows from the arbitrary decision of Staverman (Kedem and Katchalsky 1958; Katchalsky and Curran 1965), who defined the membrane's reflection coefficient as $\sigma = -\dfrac{L_{pD}}{L_p}$.

However, in the formulas (2a) and (2b), referred to in the literature (Suchanek 2005; Suchanek et al. 2005a,b) as adjusted equations, the cross coefficient is positive ($L_{pD} = L_{Dp} \geq 0$ for $\sigma > 0$), while the reflection coefficient is defined as $\sigma = \dfrac{L_{pD}}{L_p}$.

Both of the above possibilities result from the conditions imposed on the signs of phenomenological coefficients by thermodynamics of irreversible processes. These conditions have the following form (Kedem and Katchalsky 1958; Katchalsky and Curran 1965):

$$L_p \geq 0, \ L_D \geq 0 \text{ and } L_{pD}^2 \leq L_p L_D$$

As can be seen, they are unambiguous only in their determination of the $+$ sign of single coefficients, but they do allow both the $+$ and $-$ signs of the coefficient L_{pD}.

Taking as a starting point the phenomenological equations (either in the form (1a), (1b), or in the form (2a), (2b)), as a result of the procedure offered by Kedem and Katchalsky (1958), Katchalsky and Curran (1965) and Kargol et al. (1987), it is possible to arrive at the well-known practical form of the KK equations:

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi \tag{3a}$$

$$j_s = \omega \Delta \Pi + L_p (1 - \sigma) \bar{c} J_v \tag{3b}$$

As has been shown in the paper (Suchanek 2005), in order to derive the mechanistic equations (for solutions with any number of components), it is convenient to start from the equations written in the form (2a) and (2b).

Mechanistic equations pertaining to ternary solutions

We shall begin the derivation procedure of mechanistic equations for membrane transport for ternary solutions (consisting of solvent and two solutes) with the notation of the adjusted phenomenological equations for three components. In the light of Eqs. (2a) and (2b), they will take the following obvious form:

$$J_v = L_p \Delta P - L_{pD1} \Delta \Pi_1 - L_{pD2} \Delta \Pi_2 \tag{4a}$$

$$J_{D1} = -L_{D1p} \Delta P + L_{D1} \Delta \Pi_1 + L_{D12} \Delta \Pi_2 \tag{4b}$$

$$J_{D2} = -L_{D2p} \Delta P + L_{D21} \Delta \Pi_1 + L_{D2} \Delta \Pi_2 \tag{4c}$$

in which ΔP denotes the mechanical pressure difference, $\Delta \Pi_1$ is the osmotic pressure difference generated by the s_1, and $\Delta \Pi_2$ is the osmotic pressure difference for the substance s_2, J_v in turn is a volume flow here, J_{D1} is a diffusion flow of the substance s_1 and J_{D2} is a diffusion flow of the substance s_2.

In the above equations, the flows and forces are linked by means of nine phenomenological coefficients, denoted in the above equations by the letter L. According to Onsager's law (Kedem and Katchalsky 1958; Katchalsky and Curran 1965), cross coefficients of these equations are subject to the following relations:

$$L_{pD1} = L_{D1p}, \quad L_{pD2} = L_{D2p} \quad \text{and} \quad L_{D12} = L_{D21} \tag{5}$$

The number of independent phenomenological coefficients in Eqs. (4a), (4b) and (4c) decreases, as a result of the validity of the relation (5), to six.

The coefficients $L_{pD1} = L_{D1p}$, $L_{pD2} = L_{D2p}$ may be defined by means of Eqs. (2a) and (2b) for the substances s_1 and s_2, respectively, while the parameter $L_{D12} = L_{D21} = L_{DW}$ denotes the mutual interaction of both solutes, and is defined by Eqs. (4a), (4b) and (4c). Due to the physical interpretation of this coefficient (resulting from the analysis of the above-mentioned equations), it has been called the coefficient of inter-diffusion (Kargol et al. 1987).

At this stage of reasoning, it must be stressed that Eqs. (4a), (4b) and (4c) still pertain to the homogeneous membrane whose transport parameters are constant at each point.
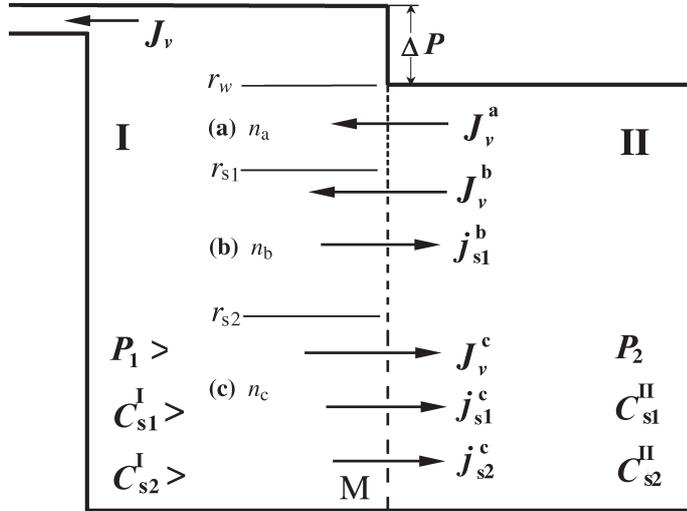

Figure 1. Model membrane system: M, heterogeneous membrane; I, II, compartments; P_1, P_2, mechanical pressures; $C_{s1}^{I}, C_{s2}^{I}, C_{s1}^{II}, C_{s2}^{II}$, concentrations; J_v^a, J_v^b, J_v^c, volume flows permeating across Parts (a), (b), (c) of the membrane, respectively; $j_{s1}^b, j_{s1}^c, j_{s2}^c$, "net" solute flows.

Let us now consider a membrane system as presented in Fig. 1, which contains a heterogeneous porous membrane M, characterised by the properties discussed in Introduction to the present article.

We assume that all the coefficients which appear in the phenomenological Eqs. (4a), (4b) and (4c) (i.e. L_p, $L_{pD1} = L_{D1p}$, $L_{pD2} = L_{D2p}$ and $L_{D12} = L_{D21}$), may only be positive or equal to zero because they describe a mechanistic porous membrane now. In order to facilitate our considerations, let us assume here that individual pores have been – for the sake of a model – arranged in one direction, starting with the smallest pores (at the top), down to the largest pores r_N (at the bottom). In a real membrane of this kind, pores are randomly arranged.

With regard to the membrane of the system, it is possible to find two such solutes s_1 and s_2 with molecule radiuses r_{s1} and r_{s2}, respectively ($r_{s1} < r_{s2}$), which satisfy the relations: $r_1 < r_{s1} < r_N$, $r_{s1} < r_{s2} < r_N$. Consequently, the relation $r_1 < r_2$ is also valid.

In view of these assumptions, the membrane may be divided into the Parts (a), (b) and (c). Naturally, only the solvent can flow across the Part (a), which contains n_a pores whose radiuses $r < r_{s1} < r_{s2}$, (cf. Fig. 1). Across the Part (b) of the membrane which contains n_b pores whose radiuses $r_{s2} > r > r_{s1}$, both the solvent and the solute s_1 permeate. Finally across the Part (c) of the membrane which contains n_c pores whose radiuses $r > r_{s2}$, all the three substances which make up the solution can pass.

The above presented membrane may, in fact, be formally treated as three parallell connected membranes (a), (b) and (c) with various filtration coefficients L_{pa}, L_{pb} and L_{pc}, respectively. In the situation at issue, the total volume flow across the membrane amounts to:

$$J_v = J_v^a + J_v^b + J_v^c \tag{6a}$$

The total diffusion flows of the solutes across the membrane equal, respectively,

$$J_{D1} = J_{D1}^a + J_{D1}^b + J_{D1}^c \tag{6b}$$
$$J_{D2} = J_{D2}^a + J_{D2}^b + J_{D2}^c \tag{6c}$$

Our analysis of this system will begin with the application of the phenomenological Eqs. (4a), (4b) and (4c) to the description of individual Parts of the membrane (a), (b) and (c).

The Part (a) of the membrane is semi-permeable. It is obvious that for this Part of the membrane $\Delta P = \Delta\Pi_1 + \Delta\Pi_2$, if $J_{va} = 0$.

In view of the above, in accordance with Eq. (4a), the equality $L_p^a = L_{pD1}^a = L_{pD2}^a$ must be satisfied. However, due to the fact that solutes do not diffuse across this part of the membrane, the diffusion flows of the substances s_1 and s_2 equal zero. Consequently, Eqs. (4a), (4b) and (4c) which describe the transport across the Part (a) of the membrane, are reduced to the form:

$$J_v^a = L_p^a(\Delta P - \Delta\Pi_1 - \Delta\Pi_2) \tag{7a}$$

and

$$J_{D1}^a = 0 \tag{7b}$$
$$J_{D2}^a = 0 \tag{7c}$$

In the Part (b) of the membrane, due to the fact that only the substance s_1 permetates across the pores, (which are impermeable to the substance s_2), Eqs. (4a), (4b) and (4c) shall be reduced to the following forms:

$$J_v^b = L_p^b \Delta P - L_p^b \Delta \Pi_2 \tag{8a}$$
$$J_{D1}^b = L_{D1}^b \Delta \Pi_1 \tag{8b}$$
$$J_{D2}^b = 0 \tag{8c}$$

In Eq. (10b), the cross coefficients $L_{pD1}^b = L_{D1p}^b$ (which are linked to the membrane selectivity for the solute s_1 and the solvent) equal zero, since the membrane in its Part (b) is non-selective. Also, the coefficient of interdiffusion L_{D1D2}^b of both solutes obviously equals zero.

The Part (c) of the membrane is permeable to both the two solutes and the solvent. In this case, the cross coefficients, which satisfy the relation $L_{pD1}^c = L_{D1p}^c$, $L_{pD2}^c = L_{D2p}^c$ also equal zero, due to reasons specified above. Diffusion coefficients L_{D1}^c, L_{D2}^c and interdiffusion coefficients $L_{D1D2}^c = L_{D2D1}^c$ are nonzero.

This means that Eqs. (6a), (6b) and (6c) for the Part (c) of the membrane assume to the following form:

$$J_v^c = L_p^c \Delta P \tag{9a}$$
$$J_{D1}^c = L_{D1}^c \Delta \Pi_1 + L_{D12}^c \Delta \Pi_2 \tag{9b}$$
$$J_{D2}^c = L_{D2}^c \Delta \Pi_2 + L_{D21}^c \Delta \Pi_1 \tag{9c}$$

The total volume flow across the membrane, according to Eq. (6a) as well as the expressions (7a), (8a) and (9a), amounts to:

$$J_v = (L_p^a + L_p^b + L_p^c)\Delta P - L_p^a \Delta \Pi_1 - L_p^a \Delta \Pi_2 - L_p^b \Delta \Pi_2 =$$
$$= (L_p^a + L_p^b + L_p^c)\Delta P - (L_p^a + L_p^b)\Delta \Pi_2 - L_p^a \Delta \Pi_1$$

By introducing the following notation:

$$L_p = L_p^a + L_p^b + L_p^c \qquad \sigma_1 = \frac{L_p^a}{L_p} \qquad \sigma_2 = \frac{L_p^a + L_p^b}{L_p} \tag{10}$$

the above equation may be written as

$$J_v = L_p \Delta P - L_p \sigma_1 \Delta \Pi_1 - L_p \sigma_2 \Delta \Pi_2 \tag{11a}$$

Let us note that, in both cases, σ is the ratio of the filtration coefficient of the membrane part which is impermeable to the given substance, to the total filtration coefficient of the membrane. The expression (13a) has the form of a mechanistic equation (Kargol and Kargol 2000, 2003a,b,c; Kargol 2001, 2002), analogous to the equation quoted in the Introduction.

The total diffusion flow of the substance s_1, in view of the formulas (6b) as well as (7b), (8b) and (9b), may be written as

$$J_{D1} = (L_{D1}^{b} + L_{D1}^{c})\Delta\Pi_1 + L_{D12}^{c}\Delta\Pi_2 \tag{11b}$$

In like manner, from the formulas (8c) as well as (7c), (8c) and (9c), it follows that the diffusion flow of the substance s_2 across the membrane amounts to

$$J_{D2} = L_{D2}^{c}\Delta\Pi_2 + L_{D21}^{c}\Delta\Pi_1 = L_{D2}^{c}\Delta\Pi_2 + L_{D21}^{c}\Delta\Pi_1 \tag{11c}$$

These are the formulas for diffusion flows of both solutes with regard to the membrane whose pores vary in linear dimensions (Fig. 1).

Following in KK's footsteps, let us also assume that, for the sake of experiment, it is more convenient to have equations in which "net" solute flows j_{s1} and j_{s2} occur. Hence, after appropriate transformations (Suchanek 2005), we obtain the equations:

$$j_{s1} = L_p(1 - \sigma_1)\bar{c}_{s1}\Delta P + \bar{c}_{s1}(L_{D1}^{b} + L_{D1}^{c})\Delta\Pi_1 + \bar{c}_{s1}(L_{D12}^{c} - L_p^{b})\Delta\Pi_2 \tag{12a}$$
$$j_{s2} = L_p(1 - \sigma_2)\bar{c}_{s2}\Delta P + \bar{c}_{s2}L_{D2}^{c}\Delta\Pi_2 + \bar{c}_{s2}L_{D21}^{c}\Delta\Pi_1 \tag{12b}$$

By introducing the following notation:

$$L_{D1} = L_{D1}^{a} + L_{D1}^{b} + L_{D1}^{c} = L_{D1}^{c} + L_{D2}^{b} \qquad (\text{since } L_{D1}^{a} = 0) \tag{13a}$$
$$L_{D2} = L_{D2}^{a} + L_{D2}^{b} + L_{D2}^{c} = L_{D2}^{c} \qquad (\text{since } L_{D2}^{a} = 0 \text{ and } L_{D2}^{b} = 0) \tag{13b}$$
$$\omega_{d1} = \bar{c}_{s1}L_{D1}^{c} = \bar{c}_{s1}L_{D1} \quad \omega_{d2} = \bar{c}_{s2}(L_{D2}^{b} + L_{D2}^{c}) = \bar{c}_{s2}L_{D2} \tag{13c}$$
$$\omega_{d12} = \bar{c}_{s1}(L_{D12}^{c} - L_p^{b}) \qquad \omega_{d21} = \bar{c}_{s2}L_{D21}^{c} \tag{13d}$$

Eqs. (12a) and (12b) may be thus written:

$$j_{s1} = L_p(1 - \sigma_1)\bar{c}_{s1}\Delta P + \omega_{d1}\Delta\Pi_1 + \bar{c}_{s1}\omega_{d12}\Delta\Pi_2 \tag{14a}$$

and

$$j_{s2} = L_p(1 - \sigma_2)\bar{c}_{s2}\Delta P + \omega_{d2}\Delta\Pi_2 + \bar{c}_{s2}\omega_{d21}\Delta\Pi_1 \tag{14b}$$

where $\omega_{d12} = \omega_{d21}$.

Eqs. (11a), (14a) and (14b) are mechanistic equations which describe any homogenous or heteogeneous porous membrane which separates ternary solutions.

With this notation, the coefficients ω_{d1}, ω_{d2} have the nature of diffusional coefficients of substances s_1 and s_2, respectively, whose diffusion flows are generated by the activity of conjugate forces ($\Delta\Pi_1$, $\Delta\Pi_2$), while the cross coefficients ω_{d12}, ω_{d21} are the coefficients of interdiffusion.

The case of heterogeneous membrane separating $N + 1$-component solutions

While expanding on Eqs. (11a), (14a) and (14b) to include the case of $N + 1$ substances in the solution (water $+ N$ solutes), we can write the reflection coefficient for any (i) solute:

$$\sigma_i = \frac{L_p^{ai}}{L_p} \tag{15a}$$

and the diffusive permeability coefficient:

$$\omega_{di} = \bar{c}_{si} L_{Di}^{bi} \tag{15b}$$

in which a generally denotes the part of the membrane which is impermeable to the substance s_i, and bi denotes the membrane part across which the given s_i can permeate freely. For any diffusion coefficient L_{Di} for the i-th solute, the identity $L_{Di} = L_{Di}^{bi}$ is valid because it is only in the permeable parts of the membrane that these coefficients are nonzero.

For any i and j (where $i \neq j$), L_{Dij} (interdiffusion coefficients) are nonzero only for those parts of the membrane across which the substances s_i, s_j permeate jointly. These parts of the membrane shall be denoted by cij. In accordance with these assumptions, the diffusive convection coefficients ω_{dij} and ω_{dji} shall be written as

$$\omega_{dij} = (L_{Dij}^{cij} - L_p^{(bi-cij)}) \qquad \omega_{dji} = (L_{Dji}^{cij} - L_p^{(bj-cji)}) \tag{15c}$$

where $L_{Dij}^{cij} = L_{Dji}^{cij}$ and $\omega_{dij} = \omega_{dji}$.

Due to the assumption concerning the random distribution of the pores in the membrane, the equality $L_{Dij}^{cij} = L_{Dji}^{cij} = L_{Dij}$ is valid, which means that each interdiffusion coefficient defined for the area cij of the membrane simultaneously pertains to this membrane as a whole.

The Kargol's mechanistic equations for the $N + 1$-component solution, written by means of the above-defined coefficients (Eqs. (15a), (15b) and (15c)), shall have the following form (equivalent to Eqs. (14a) and (14b), written for three components):

$$J_v = L_p \Delta P - L_p \sum_{i=1}^{N} (\sigma_i \Delta \Pi_i) \tag{16a}$$

$$j_{si} = (1 - \sigma_i) L_p \bar{c}_{si} \Delta P + \omega_{di} \Delta \Pi_i + \sum_{j=1, j \neq i}^{N-1} (\bar{c}_{si} \omega_{dij} \Delta \Pi_j) \tag{16b}$$

in which i, $j = 1, 2, \ldots N$.

As has been demonstrated, the addition of subsequent components to a solution causes some complication to the equations, the complication being of quantitative nature. New thermodynamic forces and flows appear, and the number of independent practical coefficients increases. The expanded Eqs. (16a) and (16b) do not describe additional physical phenomena beyond these which have been formulated in Eqs. (11a) as well as (14a) and (14b), which described ternary solutions.

Discussion

In the present paper, I have derived equations for transport across a porous membrane, which separates multi-component solutions. A practical (convenient for measurement) form of these equations has been obtained by starting the considerations from the KK phenomenological equations (Kedem and Katchalsky 1958; Katchalsky and Curran 1965). These equations, based on the general thermodynamic formalism (for a "black box" membrane), have been applied herein to the description of the membrane which is subject to certain mechanistic limitations. Consequently, the above results require some commentary, in particular with reference to transport coefficients which characterise the above-mentioned porous membrane (both phenomenological and practical ones).

At the beginning of our considerations, it has been assumed that the coefficients L_{p}, $L_{\mathrm{pD}i} = L_{\mathrm{Dp}i}$, $L_{\mathrm{D}ij} = L_{\mathrm{D}ji}$, in the phenomenological Eqs. (4a), (4b) and (4c) (where i, j = 1, 2) may only be positive or equal to zero because they describe a mechanistic porous membrane. This assumption pertains in particular to the phenomenological coefficients which characterise individual Parts (a), (b) and (c) of the membrane, marked in Fig. 1. These areas are sets of pores with particular diameters, which can be either permeable or impermeable to particular substances. Consequently, the cross coefficients $L_{\mathrm{pD}i} = L_{\mathrm{Dp}i}$, which are connected with membrane pore selectivity, equal zero. The interdiffusion coefficients of the solutes s_i and s_j ($L_{\mathrm{D}ij}^{cij} = L_{\mathrm{D}ji}^{cij} = L_{\mathrm{D}ij}$) are non-zero (and positive) in those membrane pores across which they permeate jointly (i.e. in the parts "cij").

An unambiguous attribution of the sign + to the coefficients $L_{\mathrm{D}ij}$ renders it necessary to determine, equally unambiguously, the orientations of the flows $J_{\mathrm{D}i}$ and thermodynamic forces $\Delta\Pi_j$ with respect to each other in Eqs. (4b) and (4c). There is no reason to introduce into the mechanistic model (Fig. 1) any arbitrary assumptions related to that issue, hence the latter remains unresolved at this stage of our considerations. In view of the above, the notation $+L_{\mathrm{D}12}\Delta\Pi_2$ and $+L_{\mathrm{D}21}\Delta\Pi_2$ in these equations, which denotes the agreement of flow and thermodynamic force orientations, has been accepted arbitrarily. Yet there exists a possibility of verifying this notation through measurement and on the basis of the following line of reasoning.

It is true that the mechanistic practical Eqs. (14a) and (14b) also do not determine the direction in which any flow j_{si} moves when driven by the osmotic pressure difference $\Delta\Pi_j$. This issue may be resolved experimentally, by means of measurement of the practical coefficients ω_{dij} (always positive). On the other hand, it is known that the coefficient ω_{dij} may also be expressed with (positive as well) phenomenological coefficients, as their differences ($\omega_{dij} = (L_{\mathrm{D}ij}^{cij} - L_{\mathrm{p}}^{(bi-cij)})$). The sign of any such difference is negative when $L_{\mathrm{D}ij}^{cij} < L_{\mathrm{p}}^{(bi-cij)}$. If, in any particular case, this is what happens, that fact is to be interpreted as a signal that the given thermodynamic force has been incorrectly attributed the sign (orientation) in the input phenomenological equations. Nonetheless, it is not to be concluded that the

coefficient ω_{dij} is negative. For example, in the case of finding that in the formula (13d) the difference $(L_{D12}^c - L_p^b)$ is negative, the input phenomenological Eqs. (4b) and (4c) are to be thus adjusted:

$$J_{D1} = -L_{D1p}\Delta P + L_{D1}\Delta\Pi_1 - L_{D12}\Delta\Pi_2$$

$$J_{D2} = -L_{D2p}\Delta P - L_{D21}\Delta\Pi_1 + L_{D2}\Delta\Pi_{21}$$

where all phenomenological coefficients are larger than (or equal to) zero.

The question of phenomenological equations notation is then directly resolved by the experiment as a result of which it is possible to determine the signs of the terms $\bar{c}_i\omega_{dij}\Delta\Pi_j$ and $\bar{c}_j\omega_{dji}\Delta\Pi_i$ in Eqs. (14a), (14b) and (15b).

All practical coefficients in mechanistic equations (as well as the general KK equations) are defined through measurement. By determining the mechanistic practical coefficients L_p, σ_i and ω_{di}, it is possible (and advisable) to employ the well-known methods, developed on the basis of the classic KK equations and tested in numerous cases. For the measurement of the reflection coefficients σ_i and diffusive permeability coefficients ω_{di} for individual solutes, a membrane system filled with a binary solution (water + selected substance s_i) may be used. The measurement of interdiffusion coefficients ω_{dij} is defined by means of the following formulas:

$$\bar{c}_{si}\omega_{dij} = \left(\frac{j_{si}}{\Delta\Pi_j}\right)_{\Delta P=0} \quad \text{or} \quad \bar{c}_{sj}\omega_{dji} = \left(\frac{j_{sj}}{\Delta\Pi_i}\right)_{\Delta P=0} \quad \text{while} \quad \omega_{dij} = \omega_{dji}$$

(Due to the random distribution of all pores within the membrane, we assume that these confidents are subject to Onsager's law both within the parts cij and the entire membrane).

The measurement of any coefficient ω_{dij} for two substances (s_i and s_j) may be performed by using an appropriate ternary solution (water + s_i + s_j). It is to be stressed that the measurement of the coefficients ω_{dij} is difficult because these are secondary cross coefficients (extremely small).

The "regional" filtration coefficients for the solutions of various substances L_p^{ai}, L_p^{bi} and $L_p^{(bi-cij)} = L_p^{(bi-bj)}$ (when $i < j$) may be calculated from the formulas $\sigma_i = \dfrac{L_p^{ai}}{L_p}$ and $L_p = L_p^{ai} + L_p^{bi}$, if the previously measured values of the practical coefficients L_p and σ_i are known.

There also exists a possibility of estimating the phenomenological coefficients L_{Di}^{bi} and L_{Dij}^{cij} by means of the formulas (13d). Nevertheless, in my opinion, the most significant is the possibility of "insight" into the practical coefficients, i.e. a possibility of their more detailed interpretation, characteristic of mechanistic models.

Finally, it must be stressed once again that the expansion of the description of the substance transport across the heterogeneous porous membrane to include $N + 1$-component solutions does not cover any additional physical phenomena beyond these which are formulated by transport equations for ternary solutions (a solvent + two solutes).

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