Biophysical Chemistry 24 (1986) 173–178
Elsevier

BPC 01066

MODIFICATION OF THE KEDEM-KATCHALSKY EQUATIONS

A. SLEZAK and B. TURCZYNSKI

Department of Biophysics, Silesian Medical Academy, K. Marxa 19, 41-808 Zabrze 8, Poland

Received 16th May 1985
Revised manuscript received 5th April 1986
Accepted 10th April 1986

Key words: Kedem-Katchalsky equations; Membrane transport

The presented modification of the transport equations of Kedem-Katchalsky resulted in the introduction of (ω_s/ω) and $\omega/\{\omega - L_p\sigma[(1-\sigma)\bar{C}_1 - (1-\sigma_s)\bar{C}_2]\}$ factors into the Kedem-Katchalsky equations. The above factors determine the influence of boundary layers on transport across the membrane. The modified Kedem-Katchalsky equations were verified for synthetic membranes and it was shown that the value of the (ω_s/ω) factor depended on the type of membrane and the membrane configuration system. This modification facilitated a wider range of application of the Kedem-Katchalsky equations to systems in which the solutions were stirred or unstirred.

1. Introduction

The so-called practical Kedem-Katchalsky equations are used in the quantitative description of the transport of a substance across an optional membrane (semipermeable, selective and permeable) separating solutions of various concentrations [1,2]:

$$J_v = L_p[\sigma RT\Delta C \pm \Delta P], \tag{1}$$

$$j_s = J_v(1-\sigma)\bar{C} - \omega RT\Delta C, \tag{2}$$

where J_v is the volume flux, j_s solute flux, RT product of gas constant and absolute temperature, ΔC concentration difference, ΔP hydrostatic pressure difference, $\bar{C}$ average concentration, L_p filtration coefficient, σ reflection coefficient and ω membrane permeability coefficient.

These equations are valid for solutions which are sufficiently diluted and well stirred, and this indicates that these conditions must be fulfilled when the coefficients σ and ω are determined. Good solution stirring may be provided by the application of suitable mechanical stirrers [3,4].

When the solutions are not stirred mechanically on both sides of the membrane the diffusion boundary layers are formed [5–10]. These layers are the direct reason for the occurrence of gravity-induced membrane phenomena, including asymmetry and amplification of osmotic transport [4] of graviosmotic transport [11–13]. A 'membrane version of Rayleigh-Taylor instability' was noted, and described in ref. 14 on the basis of hydrodynamics.

The problem of the modification of the Kedem-Katchalsky equations has been undertaken in order to determine the formalism which forms the basis of an analytical description of the above-mentioned membrane phenomena.

The aim of this paper is to present a modification of the Kedem-Katchalsky equations, so that they can be applied with reference to membrane systems in which the solutions are stirred weakly or unstirred.

2. The modification of the Kedem-Katchalsky equations

The membrane system presented in fig. 1 will be considered. It is composed of a symmetric membrane of thickness d and two unstirred solutions of the same nonelectrolyte substance at concentrations C_1 and C_2. In this system water and the dissolved substance diffusing across the membrane will lead to the formation of boundary layers of thickness δ_1 and δ_2. These layers, which are in fact diffusion layers, can be treated as membranes characterized by the permeability coefficients ω_1 and ω_2. Thus, we are dealing with a complex of three membranes sticking together, i.e., two boundary layers (l_1, l_2) and the membrane (M).

Let us determine the flux, j_{sm} of dissolved substance diffusing from layer l_2 across the membrane M (whose permeability coefficient is ω) to layer l_1 as well as that of dissolved substance diffusing from the solution of concentration C_2 across the complex of the diffusion boundary layers and the membrane to the solution of concentration C_1 by j_{ss}. The permeability coefficient of this complex will be indicated by ω_{s}.

On the basis of eq. 2 we can write

$$j_{\mathrm{sm}} = J_{\mathrm{v}}^*(1-\sigma)\bar{C}_1 - \omega RT(C_{\mathrm{b}} - C_{\mathrm{a}}), \tag{3}$$

$$j_{\mathrm{ss}} = J_{\mathrm{v}}^*(1-\sigma_{\mathrm{s}})\bar{C}_2 - \omega_{\mathrm{s}} RT(C_2 - C_1). \tag{4}$$

In the steady state the following condition is fulfilled

$$j_{\mathrm{sm}} = j_{\mathrm{ss}} = j_{\mathrm{s}}^*. \tag{5}$$

In such a case the solution of the system of equations results in

$$C_{\mathrm{b}} - C_{\mathrm{a}} = \frac{\omega_{\mathrm{s}}}{\omega}(C_2 - C_1) + \frac{J_{\mathrm{v}}^*\left[(1-\sigma)\bar{C}_1 - (1-\sigma_{\mathrm{s}})\bar{C}_2\right]}{\omega RT}. \tag{6}$$

The volume flux in the membrane system shown in fig. 1 can be expressed by the following equation:

$$J_{\mathrm{v}}^* = L_{\mathrm{p}}\left[\sigma RT(C_{\mathrm{b}} - C_{\mathrm{a}}) \pm \Delta P\right]. \tag{7}$$

Taking into consideration eq. 6 in eq. 7 we obtain

$$J_{\mathrm{v}} = L_{\mathrm{p}}\xi\left[\sigma\frac{\omega_{\mathrm{s}}}{\omega}RT(C_2 - C_1) \pm \Delta P\right], \tag{8}$$

where

$$\xi = \frac{\omega}{\omega - L_{\mathrm{p}}\sigma\left[(1-\sigma)\bar{C}_1 - (1-\sigma_{\mathrm{s}})\bar{C}_2\right]}.$$

The classical definition of the membrane reflection coefficient, $\sigma = (\Delta P/\Delta\pi)_{J_{\mathrm{v}}=0}$, and eq. 8 show that the reflection coefficient of the boundary layer-membrane-boundary layer complex (pseudo-reflection coefficient) is expressed by

$$\sigma_{\mathrm{s}} = \sigma\frac{\omega_{\mathrm{s}}}{\omega}. \tag{9}$$

This formula is in accord with the results of Kedem and Katchalsky [15] for series of membranes, and with the results of Jonsson [16] for asymmetric membranes.

Using the expression [6,17]:

$$\frac{1}{\omega} = \frac{1}{\omega_{\mathrm{s}}} - \frac{RT}{D}(\delta_1 + \delta_2), \tag{10}$$

where ω_{s} is the permeability coefficient of the membrane-boundary layer system, ω the membrane permeability coefficient, D the diffusion constant, and δ_1 and δ_2 the thickness of the boundary layers, eqs. 8 and 9 can be written in the following way:

$$\sigma_{\mathrm{s}} = \sigma\left[1 - \frac{\omega_{\mathrm{s}}RT}{D}(\delta_1 + \delta_2)\right], \tag{11}$$

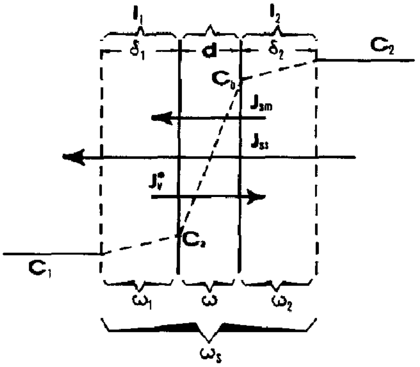

Fig. 1. Membrane system (M, membrane; l_1, l_2, diffusion boundary layers; C_1, C_2, total solution concentration; C_{a}, C_{b}, local solution concentration; j_{sm}, j_{ss}, solute flux; J_{v}^*, volume flux; ω_1, ω_2, permeability coefficients of the boundary layers; ω, membrane permeability coefficient; ω_{s}, permeability coefficient of the complex of membrane and boundary layers).

Table 1

Membrane thickness and membrane permeability parameters for glucose

Membrane	d (μm)	L_p (m^3 N^{-1} s^{-1}) (×10^{12})	σ (×10^2)	ω (mol N^{-1} s^{-1}) (×10^{10})
Nephron *	200	5.0	6.8	8.0
Cellulose RA	600	1.6	9.4	3.0
Cellulose RB	800	0.85	11.2	1.0

* The properties of the Nephron membrane are similar to those of the Visking dialysis tubing used by Ginzburg and Katchalsky [6].

Table 3

Values of the pseudo-reflection coefficient σ_s

Membrane	Configuration	σ_s		
		Expt.	Eq. 9	Eq. 11
Nephron	vertical a	0.03	0.029	0.029
	horizontal b	0.031	0.031	0.030
	horizontal c	0.0024	0.0023	0.0031
Cellulose RA	vertical a	0.056	0.056	
	horizontal b	0.06	0.064	
	horizontal c	0.007	0.0069	
Cellulose RB	vertical a	0.09	0.09	
	horizontal b	0.10	0.101	
	horizontal c	0.01	0.014	

$$J_v^* = L_p\xi\left\{\sigma RT\left[1-\frac{\omega_s RT}{D}(\delta_1+\delta_2)\right]\times(C_2-C_1)\pm\Delta P\right\}. \qquad (12)$$

By analogy we obtain

$$j_s^* = J_v^*(1-\sigma_s)\bar{C}-\omega_s RT(C_2-C_1). \qquad (13)$$

Eqs. 8, 12 and 13 are a simple modification of the Kedem-Katchalsky transport equations.

3. Experimental verification of the obtained dependences

3.1. Materials and methods

Studies upon osmotic and diffusive transport through membranes were carried out by means of the measuring system whose detailed description has been given in the previous papers [4,18]. The measuring system was set in three configurations. In configuration a the membrane was put in the vertical plane, and in configurations b and c in the horizontal plane. In configuration b the solution of concentration C_2 was found above the membrane, but in configuration c under the membrane.

In the afore-mentioned papers the methods of determination of the volume flux (J_v^*), solute flux (j_s^*), and permeability coefficient ω_s were described. The parameters of the membrane, i.e., filtration coefficient (L_p), reflection coefficient (σ), and permeability coefficient (ω), were determined according to the methods in ref. 2. Their values for three membranes and the membrane

Table 2

Value of coefficients ω_s and the (ω_s/ω) factor

Membrane	Configuration	ω_s (mol N^{-1} s^{-1})(×10^9)	ω_s/ω)		
			Expt.	Eq. 14	Eq. 15
Nephron	vertical a	0.37	0.462	0.465	0.46
	horizontal b	0.40	0.503	0.503	0.490
	horizontal c	0.03	0.0375	0.04	0.039
Cellulose RA	vertical a	0.18	0.60	0.607	0.602
	horizontal b	0.20	0.67	0.668	0.663
	horizontal c	0.022	0.073	0.07	0.071
Cellulose RB	vertical a	0.08	0.80	0.809	0.803
	horizontal b	0.09	0.90	0.914	0.907
	horizontal c	0.013	0.13	0.11	0.12

thickness (d) are listed in table 1. All experiments were performed for aqueous glucose solutions.

3.2. Results and discussion

Our investigations indicate that the values of the coefficients L_p, σ and ω are not governed by the configuration of the membrane system, whereas the values of coefficients σ_s and ω_s do depend upon the membrane system configuration as shown in tables 2 and 3.

The results obtained on the osmotic and diffusive transport are presented in figs. 2–5. The graphs illustrating the dependence $J_v = f(\Delta C)$ for various synthetic membranes are shown in figs. 2 and 3. The results presented in fig. 2 were obtained when the solutions were stirred mechanically at 500 rpm, whereas those in fig. 3 were obtained with the solutions being left unstirred. The graphs of the $j_s = f(\Delta C)$ dependence obtained under conditions similar to those for the $J_v = f(\Delta C)$ dependence are shown in figs. 4 and 5. In connection with the above we found that J_v and j_s obtained under conditions of intensive stirring did not depend upon the configuration of the membrane system, but upon the membrane type. J_v^* and j_s^* obtained without mechanical stirring depended on the configuration of the membrane system and the type of the membrane as shown in the graphs in figs. 3 and 5.

On the basis of interferometric studies made upon the interface regions of membrane layers [14], it was found that a hydrodynamically stable system of layers was observed in configuration c. For this configuration the concentration-gradient Rayleigh number (R_C) was smaller than its critical value (R_C^*), and in this case the solutions were not stirred. In configurations a and b, $R_C > R_C^*$, and in this respect convective flow perpendicular to the membrane surface was present. Therefore, the stirring was weak. The thickness of the diffusive boundary layers was determined on the basis of the interferograms obtained for a 0.1 M aqueous glucose solution. The results were as follows: for configuration a, $\delta_a = 200$ μm [18]; configuration b, $\delta_b = 180$ μm; and for configuration c, $\delta_c = 420$ μm [14].

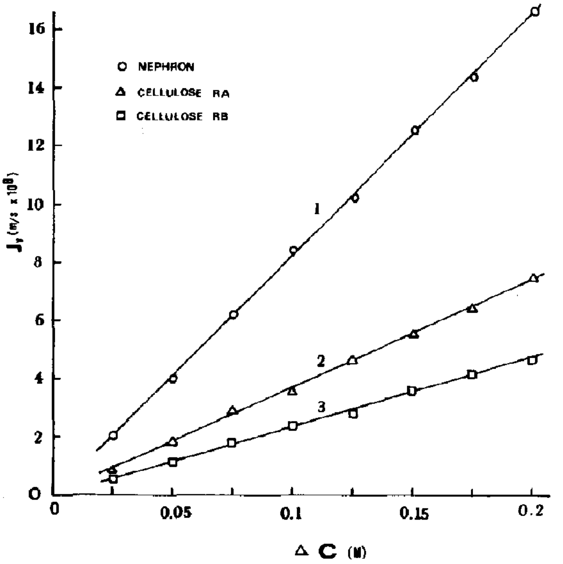

Fig. 2. Dependences $J_v = f(\Delta C)$ of solutions obtained under good stirring conditions by mechanical means. Traces: 1, Nephron; 2, cellulose RA; 3 cellulose RB.

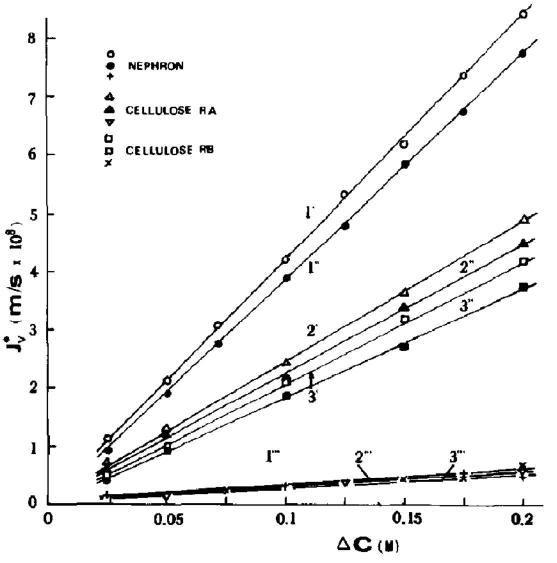

Fig. 3. Dependences $J_v^* = f(\Delta C)$ of solutions obtained without any mechanical stirring. Traces: 1′–1‴, Nephron; 2′–2‴, cellulose RA; 3′–3‴, cellulose RB. 1′–3′, configuration a; 1″–3″, configuration b; 1‴–3‴, configuration c.

Let us consider eqs. 1 and 8. It is clear that

$$\frac{\omega_s}{\omega} = 1 - \frac{J_v - J_v^* \xi^{-1}}{L_p \sigma R T \Delta C}. \tag{14}$$

Since the expression $L_p\sigma[(1-\sigma)\bar{C}_1 - (1-\sigma_s)\bar{C}_2]$ occurring in eq. 8 was smaller than ω by two orders of magnitude (on average), we assume that $\xi \approx 1$. Because J_v and J_v^* are linear functions of ΔC for $T=$ constant, and L_p and σ are constant for the studied membranes, then $(\omega_s/\omega)=$ constant. In the same way, j_s and j_s^* are linear functions of ΔC. Hence, from the expression

$$\frac{\omega_s}{\omega} = \frac{\bar{C}(1-\sigma_s)J_v^* - j_s^*}{\bar{C}(1-\sigma)J_v - j_s}, \tag{15}$$

which is obtained from eqs. 2 and 13, it is evident that $(\omega_s/\omega)=$ constant. The constant value should also be obtained when the values of coefficients ω and ω_s are determined experimentally. Their values are presented in tables 1 and 2. In fact, the tabulation of (ω_s/ω) values for the three membranes and three configurations of the membrane system indicate that the value of (ω_s/ω) is constant for a given configuration of the membrane system. The following condition results from dependences of eqs. 14 and 15:

$$0 \leqslant \frac{\omega_s}{\omega} \leqslant 1. \tag{16}$$

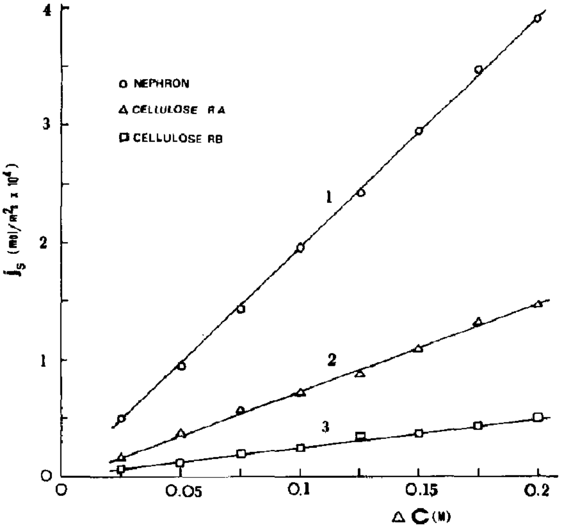

Fig. 4. Dependences $j_s = f(\Delta C)$ were obtained under conditions analogous to those for dependences $J_v = f(\Delta C)$.

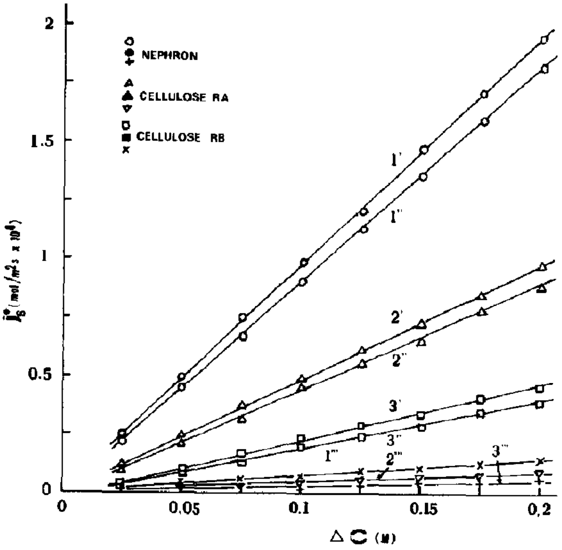

Fig. 5. Dependences $j_s^* = f(\Delta C)$ were obtained under conditions analogous to those for dependences $J_v^* = f(\Delta C)$.

4. Conclusions

The Kedem-Katchalsky equations were derived on the basis of linear thermodynamics of irreversible processes for well-stirred solutions. The usefulness of these equations for descriptions of membrane transport processes has been confirmed [1–3,5,6,17,20,23,24].

In the case of weakly stirred (i.e., convectionally) or unstirred solutions the usefulness of these equations is limited by parameters σ and ω. The coefficients determined under such conditions do not refer to the membrane but to the complex of membrane and diffusion boundary layers, and they should be expressed by the pseudo-reflection coefficient (σ_s) and coefficient ω_s. The problem of biomembrane parameters discussed in several papers [5,8,10,17,21,22,24–26] concerns biological systems in which it is very difficult to provide conditions for good stirring. The paper by Barry and Diamond [10] reviews the effects of boundary layers on membrane phenomena.

The proposed modification of the Kedem-Katchalsky equations expands the range of their application to weakly stirred and unstirred systems.

References

1 O. Kedem and A. Katchalsky, Biochim. Biophys. Acta 27 (1958) 229.
2 A. Katchalsky and P.F. Curran, Nonequilibrium thermodynamics in biophysics, Harvard University Press, Cambridge (1965).
3 N. Lakshminarayanaiah, Transport phenomena in membranes, Academic Press, New York (1969).
4 A. Slezak and K. Dworecki, Stud. Biophys. 100 (1984) 41.
5 J. Dainty, Protoplasma 57 (1963) 220.
6 B.Z. Ginzburg and A. Katchalsky, J. Gen. Physiol. 47 (1963) 403.
7 K. Inenaga and N. Yoshida, J. Membrane Sci. 6 (1980) 271.
8 D. Lerche, J. Membrane Biol. 27 (1976) 193.
9 A. Rejou-Michel, M. Villardi and M. Delmotte, Bioelectrochem. Bioenerg. 6 (1979) 289.
10 P.H. Barry and J.M. Diamond, Physiol. Rev. 64 (1984) 763.
11 M. Kargol, K. Dworecki and S. Przestalski, Stud. Biophys. 76 (1979) 137.
12 M. Kargol, Stud. Biophys. 80 (1980) 111.
13 A. Slezak, Stud. Biophys. 88 (1982) 179.
14 A. Slezak, K. Dworecki and J.E. Anderson, J. Membrane Sci. 23 (1985) 71.
15 O. Kedem and A. Katchalsky, Trans. Faraday Soc. 59 (1963) 1941.
16 G. Jonsson, Desalination 34 (1980) 141.
17 C.R. House, Water transport in cells and tissues, Edward Arnold, London (1974).
18 A. Slezak, Postepy Fiz. Med. 18 (1983) 235.
19 S. Przestalski and M. Kargol, Stud. Biophys. 34 (1972) 7.
20 C.S. Patlak, D.A. Goldstein and J.F. Hoffman, J. Theor. Biol. 5 (1963) 426.
21 J.M. Diamond, J. Physiol. 161 (1962) 503.
22 L.E. Segel, J. Theor. Biol. 29 (1970) 233.
23 J. Jagur-Grodzinski and O. Kedem, Desalination 1 (1966) 327.
24 O. Kedem, Proceedings of the XIXth Symposium of the Society for Experimental Biology, Held at Swansea (Cambridge University Press, Cambridge, 1964) p. 61.
25 R. Hingson and J.M. Diamond, J. Membrane Biol. 10 (1972) 93.
26 A.P. Smulders and E.M. Wright, J. Membrane Biol. 5 (1971) 297.