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GRAVIOSMOTIC EFFECTS

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We present a physical interpretation of graviosmosis. Our analysis is based on various experimental studies, mostly by means of volume flux measurements or interferometric studies. We describe the graviosmotic effect within the framework of the Kedem-Katchalsky formalism. We discuss various related phenomena like: graviosmotic water uptake against the gravity, graviosmotically induced water circulation and the asymmetry of graviosmotic transport.

INTRODUCTION

In membrane systems different transport processes, called the membrane phenomena, may be observed depending on physical and chemical properties of the membranes and solutions they separate, as well on existing stimuli (such as concentration gradient, temperature difference, mechanical pressure or electric potential difference). Some of them are: diffusion, thermodiffusion, osmosis, thermoosmosis, electroosmosis, anomalous osmosis, filtration, reverse osmosis, dialysis and generation of electric membrane potentials.

There is also a group of membrane phenomena generated by the gravity force, such as are the gravielectric effects (Brauner, 1959; Custard & Faris, 1965; Kargol, Ornal & Kosztołowicz, 1995) and the graviosmosis (Kargol, 1971; 1978; 1992, Przestalski & Kargol, 1972; 1987). When a system is properly oriented relative to the direction of the gravity force we observe certain polarization of concentration. As a result so-called gravielectric potentials (in case of the gravielectric effects) or volume flows called the graviosmotic flows (in case of graviosmosis) are generated.

This work is concerned with the graviosmotic effects. In particular, we consider graviosmosis in two-membrane systems and related effects such as pumping of water to a certain height (against the gravity), water circulation, asymmetry of graviosmotic transport or its amplification.

Graviosmosis was first observed in 1971 (Kargol, 1971; Przestalski & Kargol, 1972). From a physical point of view the effect has been since then a subject of several papers (Kargol, 1971; 1978; 1980; 1992; 1994, Przestalski & Kargol, 1972; 1976; 1987; Kargol, Ludwików & Przestalski, 1976; Kargol, Dworecki & Przestalski, 1979, Kargol & Dworecki, 1994; Ślęzak, 1983). It also laid a foundation for so-called graviosmotic hypothesis of xylem transport of water in tall plants developed by Kargol and Przestalski (Kargol, 1971; 1978; 1992; Przestalski & Kargol, 1987). This hypothesis postulates that water transport along tracheal elements of xylem is generated not only by transpiration-cohesion principle (as the Dixon-Renner theory says) (Wilkins. 1970; Ziegler, 1977; Zimmermann & Brown, 1971) or by the root pressure (Wilkins, 1970; Ziegler, 1977; Zimmermann & Brown, 1971), but also by graviosmotic effects (Kargol, 1971; 1978; 1992; Przestalski & Kargol, 1972; 1987).

GRAVIOSMOSIS. EXPERIMENTAL RESULTS

In order to give a simple illustration of graviosmosis we consider a membrane system consisting of two membranes M_1 and M_2 with identical transport properties. In the Kedem-Katchalsky (Katchalsky & Curran, 1965) formalism the properties of membranes are described by the filtration (L_p), reflection (σ), and permeation (ω) coefficients. In the system considered $L_{p1}=L_{p2}=L_p$, $\sigma_1=\sigma_2=\sigma$, and $\omega_1=\omega_2=\omega$. The membranes M_1 and M_2 separate three compartments A, C, and B, the latter of which(B) is filled with a solution of concentration C_B while the former two (A and C) with pure water. It is clear that when the system is horizontal (Fig. 1a) it is in an osmotic equilibrium. The effective osmotic pressures on both membranes ($-\sigma\Delta\Pi_1$ and $\sigma\Delta\Pi_2$) are equal in magnitude and henceforth compensate each other. There are no net volume flows (J_v=0) as observed experimentally. Once we turn the system to a vertical position (b), the equilibrium is distorted and the system becomes osmotically polarized by the gravity. A net osmotic pressure difference $\Delta\Pi=\sigma\Delta\Pi_2-\sigma\Delta\Pi_1$ appears, thus

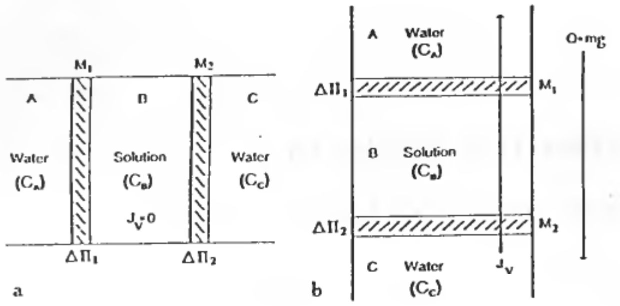

Fig.1. Two-membrane system in position (a) and (b): M_1, M_2 - membranes, A, B, C - compartments, C_A, C_B, C_C - concentrations.

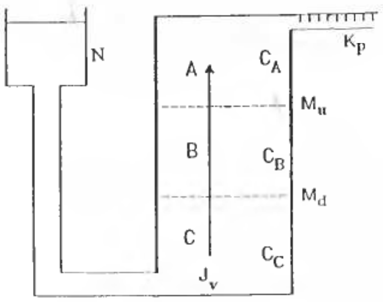

Fig.2. Experimental setup: M_1, M_2 - membranes, A, B, C - compartments, C_A, C_B, C_C - concentrations, J_v - graviosmotic flux, K_p - capillary (scaled), N - auxilliary vessel.

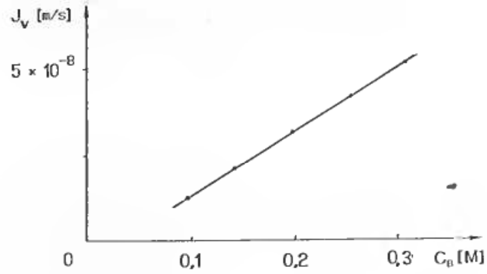

Fig.3. Dependence $J_v(C_B)_{C_A=C_C=0}$ - description in text.

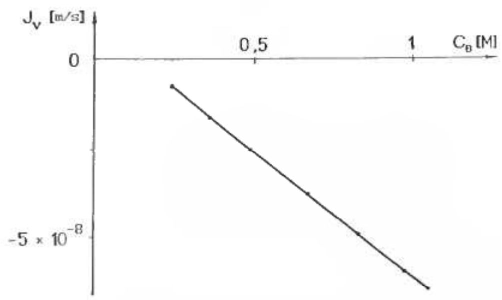

Fig.4. Dependence $J_v(C_B)_{C_A=C_C=0}$ - description in text.

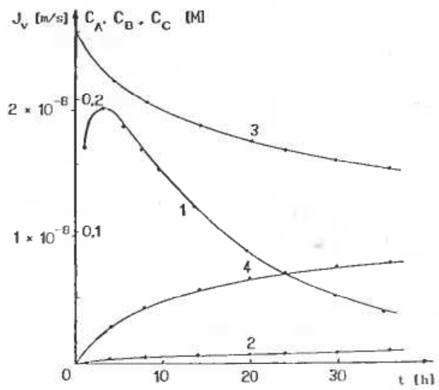

Fig.5. Nonstationary graviosmosis - description in text.

inducing a certain net volume flow J_v, called the graviosmotic flux.

If the membranes M_1 and M_2 differ in the reflection coefficient ($\sigma_1 \neq \sigma_2$) then there is a non-zero net volume flow J_{va} even in position (a) (see Fig. 1a). In that case the osmotic pressures on both membranes ($-\sigma_1 \Delta\Pi_1$ and $\sigma_2 \Delta\Pi_2$) do not fully compensate (even if $\Delta\Pi_1 = \Delta\Pi_2$). If the system is turned to position (b) (see Fig. 1b) the volume flux changes to a new value J_{vb}. The difference $J_{vb} - J_{va}$ is now called the graviosmotic flux. It has been shown experimentally (Kargol, 1971; 1978) the graviosmotic fluxes appear also when $C_A \neq C_C$.

Graviosmotic fluxes can be relatively easily measured by an experimental setup shown schematically in Fig. 2. The measurement reduces then to finding (by means of the capillary K_p) the volume ΔV of solution that permeated in time Δt through membranes M_1 and M_2, with active surfaces ($S_1 = S_2 = S$). The flux can be found as:

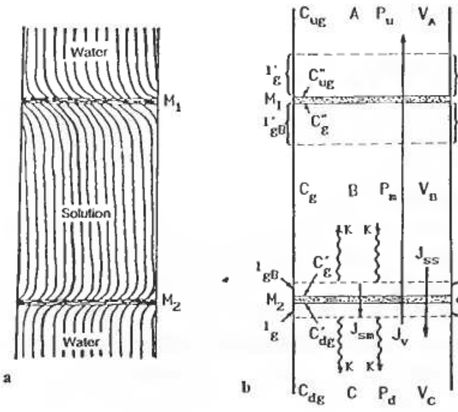

Fig.6. a. Interferogram (Kargol & Dworecki, 1994), b. Model of a graviosmotic system (solutions with densities increasing with concentration) - description in text.

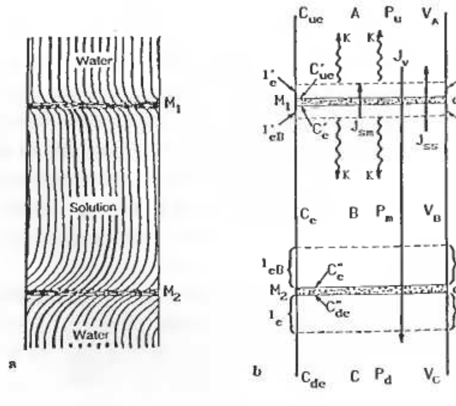

Fig.7. a. Interferogram (Kargol & Dworecki, 1994), b. Model of a graviosmotic system (solutions with densities decreasing with concentration) - description in text.

$$J_v = \frac{\Delta V}{S \Delta t}.$$

If the volumes of compartments A, B, and C are sufficiently large, for given membrane active surfaces, the value of flux J_v can remain constant over a period of hours. We observe then a stationary graviosmosis (Kargol, 1978).

Experimental results for the graviosmotic flux J_v obtained for different values of the concentration C_B in the middle compartment show a simple proportionality between J_v and C_B. It is illustrated in Fig. 3 plotted for a system of two nephrophan membranes and water solution of glucose (Kargol, 1978). Concentrations are given in moles per liter [M].

One might add here that the flux J_v is directed upwards if the density of the solution used grows with increasing concentration as happens, for instance, for glucose solutions. On the other hand if the density decreases with increasing concentration (e.g. ethanol solution) the graviosmotic flux is directed downwards, but its magnitude is still proportional to the concentration c_B in the middle compartment. An example is shown in Fig. 4 for two nephrophan membranes and water solution of ethanol (Kargol, 1978).

Experimental results mentioned above were obtained for systems with compartment volumes $V_A = V_B = V_C = 200\ \text{cm}^3$ and active surfaces of membranes $S_1 = S_2 = 3.36\ \text{cm}^2$. These values guarantee that the observed graviosmosis is stationary.

A graviosmotic flux generated in a system wwhre the compartments A, B, and C are relatively small (for given membrane active surfaces) slowly decays in time ($J_v(t)$). That means the graviosmosis in nonstationary. This is illustrated by experimental graphs in Fig. 5 (Kargol, 1978).

The data was taken on a system of two identical cellophane membranes with active surfaces $S_1 = = S_2 = 3.36\ \text{cm}^2$, separating water solutions of glucose, that is solutions with densities increasing with concentration. Volumes of all three compartments were here relatively small $V_A = V_B = = V_C = 20\ \text{cm}^3$. Curve 1 in the figure shows the dependence $J_v(t)$ of the graviosmotic flux on time. As can be seen the flux decays monotonically in time, apart from certain initial time interval after the system was filled with solutions and placed vertically. Additional measurements of concentrations $C_A(t)$, $C_B(t)$, and $C_C(t)$ were also taken and are shown as curves 2, 3, and 4 (respectively) in Fig. 5 (Kargol, 1978). One can notice that while concentrations C_B and C_C change significantly in time, the concentration C_A changes much slower. This observation is justified in the remainder of this work.

THEORETICAL MODELS. PHYSICAL INTERPRETATION

Already the first attempts at explanation of graviosmosis were based on the hypothesis of Kargol and Przestalski that the phenomenon is a result of the gravity force altering the so-called near-membrane layers (Kargol, 1971; Kargol, 1978; Przestalski & Kargol, 1972), that is their thickness and concentration difference across them. The idea has been subsequently developed. Recently thorough investigation of these layers formed in the vicinity of membranes was performed using interferometric technique (Kargol & Dworecki, 1994). Data concerning the layer thickness and the concentration profiles within the layers were obtained and sample results, reproduced from (Kargol, 1994; Kargol & Dworecki, 1994), are presented in Fig. 6a and 7a.

The former shows a system with the middle compartment filled with the water solution of glucose and the outer ones — with pure water. In the latter case the solution used in the middle compartment was that of ethanol (i.e. with density decreasing with concentration). As previously the outer parts were filled with pure water. Noticeable bending of the interference bands near membranes marks the extent of the near-membrane layers. Results of this study (Kargol, 1978) led to a development of two theoretical models for graviosmotic systems (shown in Fig. 6b and 7b) with solutions whose densities increase (Fig. 6b) or decrease (Fig. 7b) with concentration (Kargol, 1994; Kargol & Dworecki, 1994).

Let's consider the model in Fig. 6b first. We assume that $C_g > C_{ug}$ and $C_g > C_{dg}$, where C_g, C_{ug}, and C_{dg} denote concentrations in the middle (B), the upper (A), and the lower (C) compartments, respectively. The interferometric studies (Kargol & Dworecki, 1994) point to the existence of four near-membrane layers, two (l'_g and l'_{gB}) in the vicinity of the upper membrane (M_1) and two (l_g and l_{gB}) on the lower membrane (M_2). The layers formed on both sides of membrane M_1 are stable and their thickness grows in time (Kargol, 1978). This can be explained by looking at the diffusion of solute molecules from solution C_g, across membrane M_1, to solution C_{ug}. Since the solute molecules leave the layer l'_{gB} its density is lower than the bulk solution C_g in the middle compartment. Thus the layer is stable under the influence of the gravity force. On the other side, the molecules that left l'_{gB} and permeated across the membrane accumulate in the other layer l'_g above the membrane. The density here becomes higher than the bulk solution in compartment A. The layer is again gravitationally stable. The interferometric studies (Kargol & Dworecki, 1994) show that the thickness of both layers is relatively large and grows in time. As a result the concentration difference $\Delta C''_{ug} = C''_g - C''_{ug}$, (where C''_g and C''_{ug} are the concentrations on the surfaces — see Fig. 6b) on the membrane decreases to very small values. Similarly decays the osmotic pressure:

$$\Delta\Pi''_{ug} = RT(C''_g - C''_{ug}),$$

where R is the gas constant and T - the temperature.

Quite different is the situation in the vicinity of the lower membrane (M_2). Here, as the solute molecules leave the layer l_{gB}, the density within the layer becomes lower than the bulk region (B). The layer is henceforth unstable and is continuously being destroyed by upward convection currents generated by the gravity (see Fig.6b). The molecules, in turn, permeate across the membrane to layer l_g under the membrane, thus increasing density there. Since the density in layer l_g becomes larger than in the bulk solution in compartment (C), the layer is again unstable. Again, the gravity generates convection currents K,K, this time directed downward. These convection currents result in both layers l_{gB} and l_g being very thin and concentration profiles across them show very little variation. In other words, the solutions separated by membrane M_2 are well mixed by the convection currents. The concentration difference $\Delta C''_{dg} = C''_g - C''_{dg}$ (where C''_g and C''_{dg} are the concentrations on the membrane surfaces) across M_2 is therefore relatively large, so is the osmotic pressure:

$$\Delta\Pi'_{dg} = RT(C'_g - C'_{dg}).$$

Presented considerations are confirmed by recent interferometric studies (Kargol & Dworecki, 1994). In summary: formation of stable and unstable near-membrane diffusion layers in a graviosmotic system means that in the field of gravity the system becomes polarized in concentration. As a result graviosmotic flows are generated. They are directed upward as $\Delta\Pi'_{dg}$ is relatively large while $\Delta\Pi''_{ug}$ quickly decays to near zero (Kargol, 1979; Kargol & Dworecki, 1994).

Fig. 7b shows a model of a graviosmotic system with solutions whose densities decrease with concentration. It can be analyzed in an analogous way so we do not reproduce all details. Let's only say that if $C_e > C_{ue}$ and $C_e > C_{de}$, then two thin unstable layers (l'_e and l'_{eB}) form in a vicinity of the upper membrane M_1. On the other hand the lower membrane M_2 is surrounded by stable layers l_e and l_{eB} with relatively large and increasing in time thickness. Fig. 7b shows the details of the model and

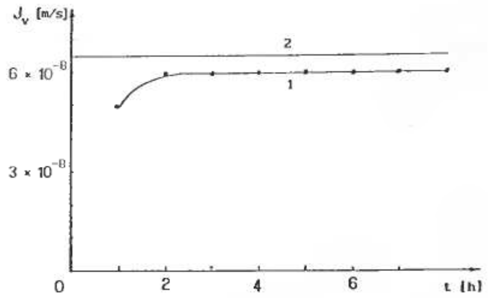

Fig.8. Relation $J_v(t)$: 1 - experimental data, 2 - theoretical prediction.

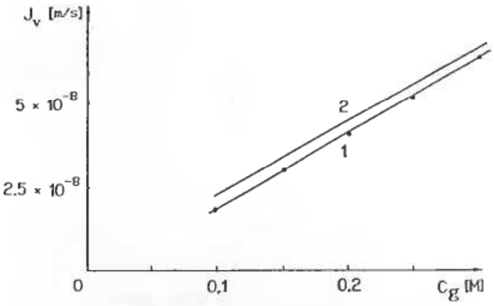

Fig.9. Dependence $J_v(C_g)$: 1 - experimental data, 2 - theoretical prediction.

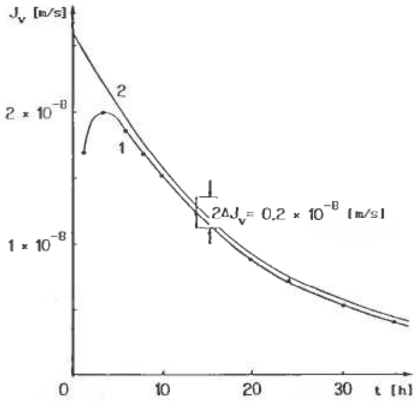

Fig.10. Dependence $J_v(t)$: 1- experimental data, 2 - theoretical prediction.

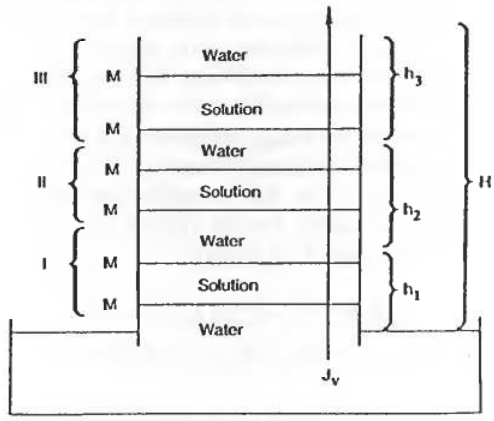

Fig.11. A column of three graviosmotic system connected in series: I, II, III - graviosmotic systems, H, h_1, h_2, h_3 - heights of water elevation ($H = h_1 + h_2 + h_3$).

Fig. 7a is the corresponding experimental interferogram.

Now it is easy to see that there is a significant concentration difference ($\Delta C''_{ue} = C''_e - C''_{ue}$), and henceforth a significant osmotic pressure $\Delta\Pi''_{ue} = RT(C''_e - C''_{ue})$, (where C''_e, C''_{ue} are the concentrations on both surfaces of the membrane) across the upper membrane. At the same time the concentration difference ($\Delta C''_{de} = C''_e - C''_{de}$) on the lower membrane is small, as is the osmotic pressure which can be written as:

$$\Delta\Pi''_{de} = RT(C''_e - C''_{de}),$$

where: C''_e, C''_{de} are the concentrations on both surfaces of the lower membrane.

Consequently, the graviosmotic flux is directed downward.

TRANSPORT EQUATIONS

Graviosmotic flows can be described quantitatively using the so-called practical Kedem-Katchalsky equations (Katchalsky & Curran, 1965). They have the form:

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

$$j_s = -\omega\Delta\Pi + (1-\sigma)\overline{C}J_v, \quad (2)$$

where: J_v is the volume flux, j_s - the solute flux, L_p – filtration coefficient, σ - reflection coefficient, ω- permeation coefficient, $\Delta\Pi$ - osmotic pressure, and ΔP - mechanical pressure difference.

Quantities $\Delta\Pi$ and $\overline{C}$ are given as:

$$\Delta\Pi = RT(C_2 - C_1) \text{ and}$$

$$\overline{C} = \frac{C_2 - C_1}{\ln\frac{C_2}{C_1}}, \quad (3)$$

where C_1 and C_2 are the concentrations, R - the gas constant, and T - temperature.

One can show that for small concentration differences (C_1-C_2) the latter formula simplifies (Kargol, 1996) to:

$$\overline{C} = 0.5(C_1 + C_2).$$

Stationary graviosmotic flows

We consider the model shown in Fig. 6b. It represents a graviosmotic system with solutions whose density grows with concentration. We assume $C_g > C_{ug}$ and $C_g > C_{dg}$. As remarked graviosmosis is stationary if the compartment volumes V_A, V_B, and V_C (and therefore solution volumes) are relatively large for given membrane active surfaces. We also assume that both membranes M_1 and M_2 have identical active surfaces $S_1 = S_2 = S$, but they differ in filtration $(L_{p1} \neq L_{p2})$, reflection $(\sigma_1 \neq \sigma_2)$, and permeation $(\omega_1 \neq \omega_2)$ coefficients.

According to the KK formalism we have the following equations for the volume fluxes across both membranes of the system:

$$J_{v1} = L_{p1}\sigma_1 RT(C''_{ug} - C''_g) + L_{p1}(P_m - P_u), \quad (4)$$

$$J_{v2} = L_{p2}\sigma_2 RT(C'_g - C'_{dg}) - L_{p2}(P_m - P_d), \quad (5)$$

where: P_m, P_u, and P_d are mechanical pressures (see Fig. 6b).

In a stationary state the fluxes J_{v1} and J_{v2} are constant in time and equal:

$$J_{v1} = J_{v2} = J_v = const. \quad (6)$$

We can eliminate the unknown concentrations C'_g and C'_{dg} from Eq. (5) and replace them by C_g and C_{dg} using Eq. (2) which, when written for membrane M_2, has a form:

$$j_{sm} = -\omega_2 RT(C'_g - C'_{dg}) + (1-\sigma_2)\overline{C} J_{v2}, \quad (7)$$

where j_{sm} is the solute flux through M_2, and $\overline{C} = 0.5(C'_g + C'_{dg})$.

We treat membrane M_2 and the adjacent layers l_g and l_{gB} as a triple membrane. If the layers are assigned the permeation coefficients ω_g and ω_{gB} then the composite triple membrane has a permeation coefficient given as (Kargol, 1994, 1996):

$$\omega_s = \frac{\omega_g \omega_{gB} \omega_{2g}}{\omega_g \omega_{gB} + \omega_g \omega_{2g} + \omega_{gB}\omega_{2g}}. \quad (8)$$

The solute transport equation across the triple membrane can be henceforth written as (Kargol, 1994):

$$j_{ss} = -\omega_s RT(C_g - C_{dg}) + (1-\sigma_2)\overline{C}_s J_{v2}, \quad (9)$$

where $\overline{C}_S = 0.5(C_g + C_{dg})$.

If the concentration drops within layers l_g and l_{gB} are equal or nearly equal, it is easy to show that the quantities $\overline{C}$ and $\overline{C}_S$ are equal or very close ($\overline{C}_S \approx \overline{C}$). Also noticing that in the stationary state $j_{sm}=j_{ss}$, from Eqs. (7) and (9) we get:

$$C'_g - C'_{dg} = \frac{\omega_s}{\omega_2}(C_g - C_{dg}). \quad (10)$$

Eq. (5) can then be rewritten as:

$$J_{v2} = L_{p2}\sigma_2 \frac{\omega_s}{\omega_2} RT(C_g - C_{dg}) - L_{p2}(P_m - P_d), \text{ or}$$

$$J_{v2} = L_{p2}\sigma_s RT(C_g - C_{dg}) - L_{p2}(P_m - P_d), \quad (11)$$

where

$$\sigma_s = \frac{\omega_s}{\omega_2}\sigma_2. \quad (12)$$

The quantity σ_s is called a pseudocoefficient of permeation for the triple membrane. It can be rather easily determined experimentally (Kargol, 1996).

Solving the system of Eqs. (4), (6), and (11) we get the following expression for the stationary graviosmotic flow:

$$J_v = \mathsf{L}[\sigma_s RT(C_g - C_{dg}) - \sigma_1 RT(C''_g - C''_{ug}) - (P_u - P_d)] \quad (13)$$

where $\mathsf{L} = L_{p1}L_{p2}(L_{p1} + L_{p2})^{-1}$.

Interferometric studies (Kargol & Dworecki, 1994) and measurements of volume flows (Kargol, 1978) indicate that $(C_g - C_{dg}) \gg G(C''_g - C''_{ug})$. Therefore the second term in Eq. (13) is negligible compared to the first and we get:

$$J_v = \mathsf{L}\sigma_s RT(C_g - C_{dg}) - \mathsf{L}(P_u - P_d)] \quad (14)$$

This approximation is crucial for the analysis since the concentrations C_g" and C_{ug}" are also unknown.

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but Eq. (4) cannot be modified as we did with Eq. (5).

Eq. (14) is the stationary graviosmotic flow equation sought after. If in addition, we put $P_u=P_g$, we get:

$$J_v = L\sigma_s RT(C_g - C_{dg}) \tag{15}$$

Experimental studies (Kargol, 1978, 1994) show that both the above equations satisfactorily describe the graviosmotic flux. It can be seen in Fig.8 and 9. Curve 1 in Fig.8 is experimental and curve 2 is obtained from Eq. (15). Similarly, curve 1 in Fig.9 shows the experimental dependence $J_v(c_g)$ while curve 2 is based on Eq. (15).

Finally, returning to the model system (Fig.7b) with solutions whose densities decrease with concentration, we can derive the following analogue of Eq. (14) (Kargol, 1994):

$$J_v = L\sigma_{se} RT(C_e - C_{ue}) - L(P_u - P_d)] \tag{16}$$

where $\sigma_{se} = \frac{\omega_{se}}{\omega_{le}}\sigma_1$ is the pseudocoefficient of membrane M_1.

Nonstationary graviosmotic flow

Our analysis of nonstationary graviosmotic flows is based on the model shown in Fig.6b. Contrary to the previous section we assume that the volumes V_A, V_B, and V_C are small for given active surfaces of membranes M_1 and M_2. In this case the concentration difference (C_g-C_{dg}) on the lower membrane M_2 and the adjacent near-membrane layers l_g and l_{gB} significantly decays in time as a result of the solute flow j_{ss} (see Fig.6b). Henceforth, the graviosmotic flow also decreases in time $(J_v(t))$. The observed graviosmosis is therefore nonstationary (Kargol, 1978, 1994). Our goal is to find an explicit dependence:

$$\Delta C_{dg} = f(t),$$

where $\Delta C_{dg} = C_g - C_{dg}$.

We assume that initially $(t = 0)$ the concentration difference between compartments B and C is:

$$\Delta C_{dg0} = C_{g0} - C_{dg0}$$

The amount of solute (in moles) that permeates across membrane M_2 and the layers l_g and l_{gB} in time dt equals dm. The corresponding changes in concentrations in compartments B and C are therefore:

$$C_g = C_{g0} - \frac{dm}{V_B},$$
$$C_{dg} = C_{dg0} + \frac{dm}{V_C}$$

Assuming $V_B = V_C = V$ we obtain:

$$\Delta C_{dg} = \Delta C_{dg0} - \frac{2dm}{V} \tag{17}$$

We can then write:

$$d(\Delta C_{dg}) = \Delta C_{dg0} - \Delta C_{dg} = \frac{2dm}{V}$$

where $d(\Delta C_{dg})$ is the change of concentration difference between B and C occurring in time dt.
Recall the definition:

$$j_{ss} = \frac{dm}{Sdt}$$

Then Eq. (9) can be rewritten as:

$$dm = -\omega_s RT\Delta C_{dg} Sdt + (1-\sigma_2)\overline{C}_s J_{v2} Sdt. \tag{18}$$

As the flux J_{v2} is nearly equal to the graviosmotic flux J_v, then after taking into account Eq. (14), the above Eq. (18) has the following form:

$$dm = S[\Delta C_{dg}(-\omega_s RT + (1-\sigma_2)\overline{C}_s\sigma_s RTL - (1-\sigma)\overline{C}_s L(P_u - P_d)dt.$$

From this:

$$\frac{2dm}{V} = \frac{2S}{V}(a\Delta C_{dg} + b)dt, \tag{19}$$

where:

$$a = -\omega_s RT + (1-\sigma_2)\overline{C}_s\sigma_s RTL \ \mathrm{L}, \tag{20}$$
$$b = -(1-\sigma_2)\overline{C}_s L(P_u - P_d). \tag{21}$$

From Eqs. (17) and (19) we get:

$$\frac{d\Delta C_{dg}}{a\Delta C_{dg} + b} = \frac{2S}{V}dt \tag{22}$$

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Integration of (22) yields:

$$\frac{1}{a}\ln(a\Delta C_{dg0}+b)=\frac{2St}{V}+G \qquad (23)$$

With the above mentioned initial condition the integration constant equals:

$$G=\frac{1}{a}\ln(a\Delta C_{dg0}+b)$$

i.e.

$$\frac{a\Delta C_{dg}+b}{a\Delta C_{dg0}+b}=\exp\left(\frac{2Sat}{V}\right)$$

From this formula we can find an expression for ΔC_{dg} as a function of time. Explicitly:

$$\Delta C_{dg}=(C_g-C_{dg})=\left(\Delta C_{dg0}+\frac{b}{a}\right)\exp\left(\frac{2Sat}{V}\right)-\frac{b}{a}. \qquad (24)$$

Substituting Eq. (24) to Eq. (14) we finally get (Kargol, 1994):

$$J_V = \mathrm{L}\sigma_s RT\left[\left(\Delta C_{dg0}+\frac{b}{a}\right)\exp\left(\frac{2Sat}{V}\right)-\frac{b}{a}\right] - L(P_u-P_d), \qquad (25)$$

where $\mathrm{L}=L_{p1}L_{p2}(L_{p1}+L_{p2})^{-1}$.

The above equation describes quasistationary graviosmotic flows. If for simplicity we put $(P_u-P_d)=0$ then it reduces to:

$$J_V=\mathrm{L}\sigma_s RT\Delta C_{dg0}\exp\left(\frac{2Sat}{V}\right) \qquad (26)$$

If we also assume (Kargol, 1994):

$$\left|-\omega_s RT\Delta C_{dg}\right| \gg \left|(1-\sigma_2)\overline{C}_s J_v\right|, \qquad (27)$$

then the term $(1-\sigma_2)\overline{C}_s J_v$ in Eq. (9) can be neglected. Therefore formulas (20) and (21) become:

$$a=-\omega_s RT \text{ and } b=0.$$

Thus we obtain the following simplified form of Eq. (25) (Kargol, 1978, 1994):

$$J_V=\mathrm{L}\sigma_s RT\Delta C_{dg0}\exp\left(-\frac{2S}{V}\omega_s RTt\right) \qquad (28)$$

Eqs. (25) and (28) give a fairly good description of graviosmotic flows as confirmed by experimental data (Kargol, 1978, 1994). Sample results are presented in Fig.10. Curve 1 in Fig.10 shows the experimental results obtained using the setup as in Fig.2, while curve 2 was calculated using Eq. (28). Both graphs refer to a graviosmotic system of two identical cellophane membranes with the middle compartment (B) filled with the water solution of glucose and the outer ones (A and C) - with pure water. The compartment volumes are $V_A=V_B=V_C=20\ \mathrm{cm}^3$ and the active surfaces $S_1=S_2=S=3.36\ \mathrm{cm}^2$.

Graviosmotic effects

Graviosmotic water uptake. Experimental studies (Kargol, 1978, 1992, Przestalski & Kargol, 1987) show that a graviosmotic system is capable of pumping water up to a certain height h. The height can be measured or calculated from Eq. (14). If we put $J_v=0$ and $(P_u-P_d)=\rho gh$, where ρ is the density and g - the acceleration of gravity, we get:

$$h=\frac{\sigma_s RT}{\rho g}(C_g-C_{dg}). \qquad (29)$$

As can be seen, the height h is determined by the concentration difference (C_g-C_{dg}). It has been shown that a column of such systems connected in series can pump water up to a total height:

$$H=h_1+h_2+h_3+\dots .$$

where h_1, h_2, h_3,... are pumping heights for individual systems in the column, respectively.

Fig.11 shows such a column composed of three graviosmotic systems. It is worth noticing that such graviosmotic transport, albeit generated by the gravity, is directed opposite to the gravity force.

Graviosmotically generated water circulation. Graviosmotic circulation of water can be observed if the outer compartments (A and C) of the graviosmotic system are connected by a pipe R (Kargol, 1978, Przestalski & Kargol, 1987). It is shown in Fig. 12 where the arrows mark the direction of water transport. Volume of circulating water $\Delta V_w'$ (in volume units) is given as:

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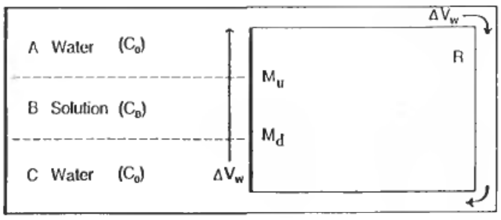

Fig.12. Graviosmotic circulation of water. M_u, M_d - membranes, A, B, C - compartments, J_v - volume flux, R - tube.

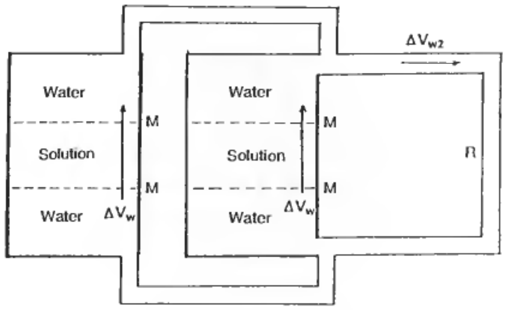

Fig.13. A system of two graviosmotic units connected in parallel.

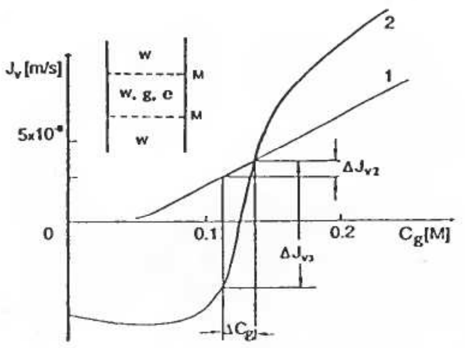

Fig.14. Plats of relationships: $J_{v1}(C_g)_{C_e=0}$ — curve 1 and $J_{v2}(C_g)_{C_e}$ — curve 2.

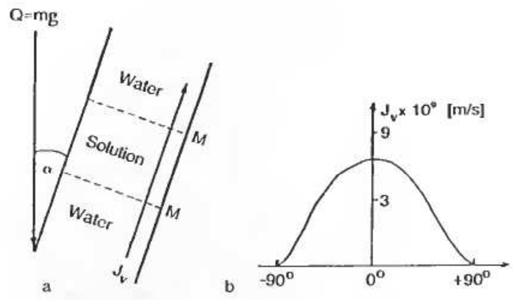

Fig.15. a. Graviosmotic system positioned at angle α with respect to the vertical, b. Dependence $J_v(\alpha)$.

$$\Delta V_w = \mathrm{L} RT\sigma_s (C_B - C_0) S\Delta t, \qquad (30)$$

where: $\mathrm{L} = L_{p1}L_{p2}(L_{p1}+L_{p2})^{-1}$, C_B, C_0 — concentrations, S — active surface of both membranes, Δt — time, σ_s — pseudocoefficient of reflection.

Eq. (30) as well as experimental studies (Kargol, 1978, 1992, Przestalski & Kargol, 1987) show that a parallel connection of two such graviosmotic systems as shown in Fig.13 (which effectively increases the active surfaces S of membranes) results in appropriate increase in the amount of circulating water. If the two connected systems are identical then $\Delta V_{w2}=2\Delta V_w$.

Amplification of graviosmotic transport. Amplification of the graviosmotic transport occurs if a three-component solution is used instead (Kargol, 1978, Kargol *et al.*, 1979). Specifically we mean here a solution whose density increases with concentration of one of the solutes but decreases with the concentration of the other. A good example is the water solution of glucose and ethanol.

I order to explain this phenomenon let us consider a graviosmotic system where the middle compartment (B) is filled with the water solution of glucose (i.e. a two-component solution) and the two outer compartments (A and C) - with pure water. As mentioned earlier in this work the graviosmotic flux J_{v2} depends linearly on the concentration C_g of glucose in compartment B, as illustrated by curve 1 in Fig.14. That is: the change of graviosmotic flux ΔJ_{v2} generated by a small change in concentration ΔC_g is relatively small and the same in the entire range of concentrations.

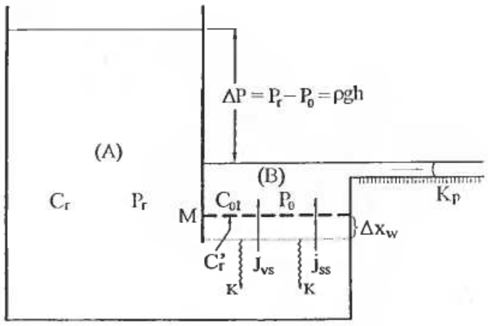

Fig.16. The membrane system: M - membrane, A, B - vessels, C_{01}, C_r, C_r' - concentrations, P_0, P_r - mechanical pressures, K_p - capillary, J_{vm}, j_{sm} - fluxes, KK - convection flows.

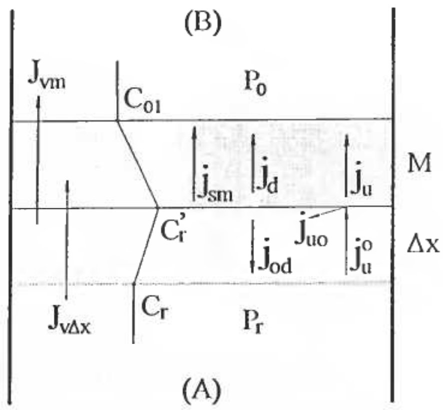

Fig.17. The fluxes through a membrane M and near-membrane layers Δx - description in text.

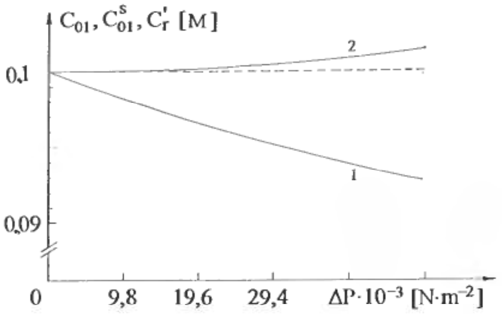

Fig.18. Relations: $C_{01}(\Delta P)$ - curve 1 and $C_r'(\Delta P)$ - curve 2, for the cuprophan membrane and vitamin B-12.

The situation is quite different if the solution of glucose in compartment B also contains a certain constant amount of ethanol (its concentration C_e = const.). An analogous relation between the graviosmotic flux (J_{v3}) and the glucose concentration C_g is shown as curve 2 in Fig.14. One can notice that changes ΔJ_{v3} of the flux caused by similar concentration changes ΔC_g vary in different concentration ranges. Moreover, ΔJ_{v3} can be many times larger than ΔJ_{v2}. In other words, the system has amplifying properties. As a measure of these properties we introduce an amplification coefficient K defined as:

$$K = \frac{\Delta J_{v3}}{\Delta J_{v2}}. \qquad (31)$$

It has been shown that in a system of two nephrophan membranes a maximal value of this coefficient can reach $K \cong 5$.

Curve 2 also indicates that not only the value but also the direction of the graviosmotic flux J_{v3} may be changed by a monotonical variation of concentration C_g. This observation is important for the graviosmotic hypothesis of xylem transport of water in plants (Kargol, 1992). Such regulatory and amplification affects also apply to water circulation and uptake mentioned earlier.

Transport asymmetry. Graviosmotic transport in systems of membranes differing in transport parameters ($L_p \neq L_p$, $\sigma_1 \neq \sigma_2$, $\omega_1 \neq \omega_2$) may exhibit certain asymmetry. Let us consider a system filled with solutions of concentrations such that $C_g > C_u = C_d = C_0$ and whose density grows with concentration. If in the system the membrane M_1 is above M_2 then a flux J_{va} will be generated. When the system is reoriented so that M_1 is below M_2 then we will observe a flux J_{vb} of different magnitude. In both cases, nevertheless, the flux is directed upwards. If the mechanical pressures are kept the same for both positions of the system we can write, according to Eq. (15):

$$J_{va} = L\sigma_{s2} RT(C_g - C_0) \qquad (32)$$

and

$$J_{vb} = L\sigma_{s1} RT(C_g - C_0), \qquad (33)$$

where σ_{s1}, σ_{s2} are the pseudocoefficients of reflection for the lower membrane (membrane M_2 in position (a) and membrane M_1 in position (b)). One can immediately see:

$$N = \frac{J_{va}}{J_{vb}} = \frac{\sigma_{s2}}{\sigma_{s1}} \neq 1. \qquad (34)$$

This quantity N is called an asymmetry coefficient and is determined by the values of reflection pseudocoefficients σ_{s1} and σ_{s2} (Kargol, 1980).

Graviosmotic transport as a function of inclination of the system. Graviosmotic flux J_v (as well as the amount of circulating water) depends on the inclination α of the system to the direction of the gravity force. A system, shown in Fig. 15a, was placed at different angles and the graviosmotically generated flux J_v was measured. A sample plot of the relation $J_v = f(\alpha)$ is presented in Fig.15b.

The flux J_v is maximal for $\alpha = 0$ and decays to zero as α goes to ±90°. This fact has some significance for the graviosmotic hypothesis (Kargol, 1992). It also leads to certain conclusions concerning possibility of graviosmotic mechanisms in biological systems (Kargol, 1992).

Reverse osmosis modified by the gravity force. A process in which a mechanical pressure difference forces solute transport across a membrane against the osmotic pressure is called reverse osmosis. It can be realised both for solution well mixed by some mechanical devices and for solutions weakly mixed. In the latter case we can distinguish within the solutions separated by a membrane relatively large regions which are well mixed and rather thin layers adjacent to the membrane where mixing does not occur (Dworecki, 1995, Kargol, 1994, 1996, Kargol & Dworecki, 1994). If there are concentration gradients across the layers we treat them as the near-membrane diffusion layers and assign permeation coefficients to them. In the present work we consider such case of reverse osmosis in a system with solutions weakly mixed, or precisely, mixed only by convection flows generated by the gravity. Hence the title of this section.

A model system is shown in Fig. 16 (Kargol 1999). It consists of a horizontal membrane M with transport parameters L_p, σ, and ω, separating two compartments: A (the lower) and B (the upper).

We assume that the former is relatively large and is filled with a solution of concentration C_r, the density of which increases with the concentration. The latter vessel (relatively small) is initially empty. Since there is a volume flux J_{vm} caused by the hydrostatic pressure difference $\Delta P = P_r - P_o = \rho g h$, this small compartment B fills with a solution of concentration C_{01} at some later time. We consider the case when the solution in A is not stirred mechanically.

If the reflection coefficient σ of the membrane is larger than zero ($\sigma > 0$) then we get $C_r > C_{01}$. Moreover, as the process continues, the concentration of the solution near the lower surface of the membrane increases. On the membrane surface it reaches a certain value $C_r' > C_r$. The concentration gradient across the membrane equals then $\Delta C_m = C_r' - C_{01}$, or in other words there appears the osmotic pressure difference:

$$\Delta\Pi_m = RT(C_r' - C_{01}) < \Delta P.$$

The above inequality means that the reverse osmosis occurs in the considered system.

As a result of the increase in concentration on the lower surface of the membrane a solution layer with density larger than c_r forms there. This layer is unstable in the gravitational field. Once its thickness exceeds a certain value Δx, convection flows K,K are generated, as shown in Fig.16. These convection flows tend to destroy the layer, but at the same time it is rebuilt by the continuing reverse osmosis. A stationary state is eventually reached, where the thickness of the layer is relatively small ($\Delta x \approx 0.5 \cdot 10^{-3}$ m), as found in experimental studies of such layers done using the laser interferometry technique (Dworecki, 1995, Kargol, 1996).

Fig.17 represents a "close-up" of the membrane M and its near-membrane layer Δx, with the arrows indicating the fluxes permeating through the system. We now concentrate on those fluxes.

There are fluxes J_{vm} and j_{sm} through the membrane due to the hydrostatic pressure difference ΔP, and the osmotic pressure difference $\Delta\Pi = RT(C_r' - C_{01})$ across the membrane. In the Kedem-Katchalsky formalism they are given by:

$$J_{vm} = L_p[\Delta P - \sigma RT(C_r' - C_{01})], \qquad (35)$$

$$j_{sm} = \omega RT(C_r' - C_{01}) + (1-\sigma)\frac{C_r' + C_{01}}{2} J_{vm}. \qquad (36)$$

There is also a volume flux across the near-membrane layer, denoted $J_{v\Delta x}$. In the stationary state both volume fluxes are equal:

$$J_{vm} = J_{v\Delta x}. \qquad (37)$$

The symbol j_u^0 denotes the flux of the solute carried by $J_{v\Delta x}$ within the layer. It equals:

$$j_u^0 = \frac{C_r' + C_r}{2} J_{v\Delta x} \qquad (38)$$

or

$$j_u^0 = \frac{C_r' + C_r}{2} J_{vm}.$$

A part of this flux, denoted j_{sm}, permeates across the membrane M. The remainder is "reflected" from the membrane, provided its reflection coefficient σ is larger than 0. We have then:

$$j_u^0 = j_{sm} + j_{uo}, \qquad (39)$$

where j_{uo} is the rejected flux.
Since there is a concentration gradient $\Delta C_x = (C_r' - C_r)$ within the layer Δx, then the diffusion flux j_{od} in the layer (see Fig.17) is given by the equation:

$$j_{od} = \frac{D}{\Delta x}(C_r' - C_r), \qquad (40)$$

where D is the diffusion constant.

This flux is equal in value to the flux j_{uo}. Therefore:

$$j_{uo} = \frac{D}{\Delta x}(C_r' - C_r). \qquad (41)$$

From Eqs. (35) and (36) we get:

$$\frac{j_{sm}}{j_{vm}} = \frac{\omega RT(C_r' - C_{01})}{L_p\left[\Delta P - \sigma RT(C_r' - C_{01})\right]} + (1-\sigma)\frac{C_r' + C_{01}}{2}. \qquad (42)$$

This ratio has a physical interpretation. Namely let's write, following (Katchalsky & Curran, 1965):

$$J_v = j_w \overline{V}_w + j_s \overline{V}_s, \qquad (43)$$

where: j_w, j_s are the fluxes, $\overline{V}_w$ and1 $\overline{V}_s$ — the molar volumes of water and the solute. In our notation (cf. Fig.17) this equation has a form:

$$J_{vm} = j_{wm}\overline{V}_w + j_{sm}\overline{V}_s. \qquad (44)$$

The fluxes j_{wm} and j_{sm} can be written as:

$$j_{wm} = \frac{\Delta m_w}{S\Delta t}, \qquad (45)$$

$$j_{sm} = \frac{\Delta m_s}{S\Delta t}, \qquad (46)$$

where: Δm_w, Δm_s are the masses of water and the solute, S — the membrane active surface, and Δt — the time.

One then finds (Kargol, 1997):

$$\frac{j_{sm}}{j_{vm}} = \frac{\Delta m_s}{\Delta m_w \overline{V}_w + \Delta m_s \overline{V}_s} = \frac{\Delta m_s}{V} = C_{01}, \qquad (47)$$

where V denotes the total volume.

Taking the above equation into account we can rewrite Eq. (42) as:

$$C_{01} = \frac{\omega RT(C_r' - C_{01})}{L_p[\Delta P - \sigma RT(C_r' - C_{01})]} + (1-\sigma)\frac{C_r' + C_{01}}{2}. \qquad (48)$$

Moreover, from the Eqs. (35), (36), (38), (39), and (41) we get:

$$\omega RT(C_r' - C_{01}) + (1-\sigma)\frac{C_r' + C_{01}}{2} L_p[\Delta P - \sigma RT(C_r' - C_{01}')] = \frac{C_r' + C_r}{2} L_p[\Delta P - \sigma RT(C_r' - C_{01})] - \frac{D}{\Delta x}(C_r' - C_r). \qquad (49)$$

The Eqs. (48) and (49) constitute a system of two coupled quadratic equations in variables C_r' and C_{01}. Values of Δx can be measured using the interferometric technique. As finding an analytical solution proved to be too cumbersome, we solved it numerically for different values of the mechanical pressure gradient ΔP (from the interval $0 < \Delta P < 50 \times 10^3$ Pa). Sample results are shown in Fig. 18. Curve 1 is the relation $C_{01}(\Delta P)$ while curve $2 - C_r'(\Delta P)$. Both were obtained for a cuphrophan membrane and solutions of vitamin B-12.

CONCLUSION

In this work we presented results of our experimental and theoretical studies of graviosmosis and related effects. The main conclusions are the equations describing stationary and nonstationary graviosmotic transport. These equations open new possibilities for further research. Namely, they allow study of graviosmosis from a point of view of energy conversion. Our interest in this stems from the fact that graviosmotic transport takes place against dissipative forces (viscosity forces) but also against external forces. A graviosmotic system is therefore capable of doing both dissipative and utility work. Hence, graviosmosis can be viewed as one of methods for conversion of free energy of solutions with different concentrations into useful work (Kargol, 1990). One might emphasize that graviosmosis, which is generated by the gravity, in fact generates volume flows (graviosmotic flows) which can be directed against the gravity. One might suspect that a gravisomotic system could satisfy criteria for an anti-gravity machine (Myślicki, 1963).

Equations presented in this work allow analysis of energetic aspect of graviosmosis (following an analytical procedure for osmotic-and-diffusive free energy conversion (Kargol, 1990)), and in particular validation of the above hypothesis. Our interest in energetic aspects of graviosmosis is however restricted to biophysical considerations. In particular, a new biophysical theory (graviosmotic theory) of xylem water uptake in tall plants was developed based on graviosmosis (Kargol 1978, 1992, Przestalski & Kargol 1987).

REFERENCES

Brauner L. (1959). Neue Versuche zur Analyse das Geoelektrischen Effekts. *Planta* **53**, 449-483.

Custard H. C. & Faris S. R. (1965). Observation of the „geoelectric effect" in electrochemical concentration cells using ion-exchange membranes. *Planta (Berlin)* **65**, 83-101.

Dworecki K. (1995). Interferometric investigation near-membrane diffusion layers. *J. Biol. Phys.* **21**, 37-49.

Kargol A. (1997). A description of reverse osmosis using practical Kedem-Katchalsky equation. *J. Biol. Phys.* **23**, 111-120.

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

Kargol M. (1971). Non-electrolytes and electrolytes transport through membrane systems. *Thesis, WSP Opole*, 79-88.

Kargol M. (1978). The effect of the gravitational field on substance transport in membrane systems. *D. Sc. Thesis, Wyd. WSP Kielce*, 3-60.

Kargol M. (1980). Assymmetry of graviosmotic transport. *Stud. Biophys.* **80**, 111-114.

Kargol M. (1990a) A practical method for the analysis of osmotic-and-diffusive energy conversion, *Gen. Physiol. Biophys.* **9**, 19-28.

Kargol M. (1990b). Effect of gravity force upon osmotic transport in 2-membrane systems. *Kieleckie Studia Fizyczne* **3**, 37-46.

Kargol M. (1992). The graviosmotic hypothesis of xylem transport of water in plants. *Gen. Physiol. Biophys.* **11**, 469-487.

Kargol M. (1994). Full analytical description of graviosmotic volume flows. *Gen. Physiol. Biophys.* **13**, 109-126.

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

Kargol M. & Dworecki K. (1994). Interferometric studies of diffusive unstirred layers generated in graviosmotic systems. *Current Topics in Biophysics* **18**, 99-104.

Kargol M., Dworecki K. & Przestalski S. (1979). Graviosmotic flow amplification effect in a series membrane system. *Stud. Biophys.* **76**, 137-142.

Kargol M., Ludwików F. & Przestalski S. (1976). Non-stationary graviosmotic transport of nonelectrolytes in a system of two membranes. *Stud. Biophys.* **58**, 131-146.

Kargol M., Ornal B. & Kosztołowicz T. (1995). A study on gravielectric polarization in 1-membrane systems. *Current Topics in Biophysics* **18**, 105-111.

Katchalsky A. & Curran P. F. (1965). *Nonequilibrium thermodynamics in biophysics*, Harvard Univ. Press, Cambridge, Massachusetts.

Malinowski E. (1978). *Anatomia roślin*, PWN Warszawa, pp. 138-190.

Myślicki A. (1963). Is the Newton's third principle always valid? *Zesz. Nauk. WSP Opole, Fizyka II*, 57-65.

Przestalski S. & Kargol M. (1972). Graviosmotic volume flow through membrane systems. *Stud. Biophys.* **34**, 7-14.

Przestalski S. & Kargol M. (1976). Composite membranes, *Third Winter School on Biophysics of Membrane Transport, Karpacz, 17-26 February*, 53-69.

Przestalski S. & Kargol M. (1987). Graviosmosis. *Comments Mol. Cell. Biophys.* **4**, 249-264.

Ślęzak A. (1983). Osmotic flows in a two-membrane system arrangements in a horizontal plane. *Post. Fiz. Med.* **18**, 225-233.

Wilkins M. B. (1970). *The physiology of plant growth development*, MacGrow-Hill Company, pp. 389-417.

Ziegler H. (1977). Flüssigkeitsströme in pflanzen, in *Biophysik*, (eds.) Hoppe W., Lohman W., Markl H. & Ziegler H., Springer-Verlag, Berlin, Heidelberg, New York, pp. 561-577.

Zimmermann M. H. & Brown C. L. (1971). *Trees. Structure and function*, Springer-Verlag, New York pp. 213-267.

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