

Full Analytical Description of Graviostmotic Volume Flows

M. KARGOL

*Institute of Physics, Pedagogical University,
Ul. Leśna 16, 25-509 Kielce, Poland*

Abstract. A full analytical description of graviostmotic volume flows is presented. This was done with the use of theoretical models earlier developed on the basis of interferometric studies of graviostmotic systems. The description includes both stationary and non-stationary graviostmotic flows induced with solutions whose density decreases as well as increases with increasing concentration. The obtained equations that describe the fluxes may prove especially useful in studies on water transport in plants which occurs by graviostmotic mechanisms.

Key words: Water — Membrane — Gravitational force — Graviostmosis — Volume flows — Equations of transport

Introduction

The graviostmotic phenomenon was first noticed in 1971 (Kargol 1971; Przestalski and Kargol 1972). Its essence consists in osmotic polarization of 2-membrane systems that are properly positioned with respect to the vertical. As a result of the polarization induced by the force of gravity, definite volume flows are generated which are called graviostmotic flows. This phenomenon has been the subject of numerous studies performed by the volume-flow measurement method (Kargol 1971, 1978, 1980, 1985, 1992; Kargol et al. 1979; Przestalski and Kargol 1972, 1976, 1987; Ślęzak 1983) and also the interferometric method (Dworecki 1984; Kargol et al. 1986; Kargol and Dworecki 1993). The main purpose was to give the graviostmotic phenomenon a physical interpretation and to try to develop a mathematical description of the generated volume flows. Already the first attempt to do so was based on the postulate raised by Kargol and Przestalski (Kargol 1971; Przestalski and Kargol 1972), which says that fundamental for graviostmosis is effect of gravity on the state of the near-membrane diffusive layers which are generated in graviostmotic systems. By the state of the layers are meant their thickness and concentration gradients in them. In later studies that concept was developed (Kargol 1978, 1980, 1992; Kargol et al. 1976, 1979; Przestalski and Kargol 1987; Ślęzak 1983).

Recently, we presented (Kargol and Dworecki 1993) some systematic interferometric studies on diffusive near-membrane layers generated in graviosmotic systems. These studies provided direct information on the layers such as their thickness and solution concentration gradients within them. Based on this, two theoretical models of graviosmotic systems have been developed. One of them is concerned with systems filled with solutions whose densities increase with increasing concentration, the other with systems whose densities decrease with increasing concentration.

In the present work the models have been supported by the results of experiments performed by the method of volume flow and solute flow measurement. Then, with the use of the models, suitable equations were derived that describe both stationary and non-stationary graviosmotic flows. They were derived on the basis of the so-called practical Kedem-Katchalsky equations (1958) which have the form:

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

$$J_s = -\omega \cdot \Delta\Pi + (1 - \sigma) \cdot \bar{C} \cdot J_v \quad (2)$$

where J_v is the volume flux, J_s is the flux of solute, L_p is the filtration coefficient, σ is the reflection coefficient, ω is the permeability coefficient, $\Delta\Pi$ is difference in osmotic pressures and ΔP is difference in mechanical pressures.

The quantity $\bar{C}$ is given by the expression:

$$\bar{C} = \frac{C_1 - C_2}{\ln(C_1/C_2)}$$

where C_1 and C_2 are concentrations.

It can be shown that for the small concentration's difference ($C_1 - C_2$) the last formula reduced to:

$$\bar{C} = 0.5 \cdot (C_1 + C_2) \quad (3)$$

The last formula is obtained by disintegrating function $\ln x$ into a series:

$$\ln x = 2 \left(\frac{x-1}{x+1} \right) + \frac{2}{3} \left(\frac{x-1}{x+1} \right)^2 + \dots,$$

and next by reducing calculations to the first member of this series (Katchalsky and Curran 1965, Podolak 1978).

The equations obtained in the present work describe fully graviosmotic flows. We assume that they can be especially useful in biophysical studies on water transport in plants which occurs with the graviosmotic mechanisms. Mainly, the xylem water transport is meant that occurs in agreement with the graviosmotic hypothesis (Kargol 1978, 1992).

The graviosmotic phenomenon. Theoretical models of graviosmotic systems

The essence of the graviosmotic phenomenon, which is observed in 2-membrane systems, consists in osmotic polarization of the systems due to the force of gravity. As a result of this polarization, definite volume flows called graviosmotic flows are generated. In order to present that phenomenon in most plain terms, let us consider the simplest graviosmotic system, i.e. a system composed of two membranes M_1 and M_2 with equal coefficients of filtration ($L_{p1} = L_{p2} = L_p$), reflection ($\sigma_1 = \sigma_2 = \sigma$) and permeability ($\omega_1 = \omega_2 = \omega$).

The membranes partition the system into three compartments A , B and C . Let the side compartments (A and C) be filled with pure water (or solution of low concentration $C_0 = C_A = C_C$) and the middle compartment (B) with solution of concentration $C_B > C_0$. It is obvious that this system in position (a) with respect to the vertical, as shown in Fig. 1a, is osmotically symmetrical. Differences in the effective osmotic pressures $\sigma\Delta\Pi_1$ and $\sigma\Delta\Pi_2$ on each membrane are equal and compensate one another ($\sigma\Delta\Pi_1 = \sigma\Delta\Pi_2$). No volume flow occurs in the system ($J_v = 0$) which is confirmed experimentally.

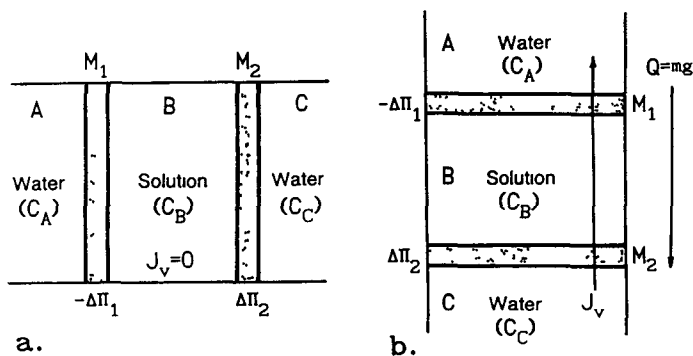


Figure 1. Two-membrane system in position (a) and (b) (Kalogol 1992). M_1 , M_2 – membranes; A , B , C – compartments; C_A , C_B , C_C – concentrations.

After reorientation of the system with respect to the vertical position (b), in which the membranes are situated horizontally (Fig. 1b), it becomes polarized osmotically due to the force of gravity. A certain resulting osmotic force, $\Delta\Pi = \sigma\Delta\Pi_2 - \sigma\Delta\Pi_1$, develops in the system and induces a volume flow J_v , called graviosmotic flow. This flow is directed upwards if the system contains solutions whose densities increase with concentration. In case the solutions density decreases with concentration, the graviosmotic flow is directed downwards. If the membranes

M_1 and M_2 of a graviosmotic system differ in their reflection coefficients ($\sigma_1 \neq \sigma_2$), there will be a volume flow even if the system is in position (a). The flow J_{va} occurs in position (a) because differences in the effective osmotic pressures $\sigma_1 \Delta \Pi_1$ and $\sigma_2 \Delta \Pi_2$ will not fully compensate (in spite of $\Delta \Pi_1 = \Delta \Pi_2$). Upon reorienting the system to position (b) the volume flow will change assuming value J_{vb} . In that case the graviosmotic flow will be equal to the difference between J_{va} and J_{vb} . Experimental investigations (Kargol 1978, 1980; Przestalski and Kargol 1987; Ślęzak 1983) have shown that graviosmotic flows may occur not only if $C_A = C_C$ but also if $C_A \neq C_C$. It has been also found (Kargol 1978) that they can be generated if $C_A < C_B$ and $C_C < C_B$ as well as if $C_A > C_B$ and $C_C > C_B$. In general, it can be said that graviosmotic flows can occur if $C_A \neq C_B \neq C_C$.

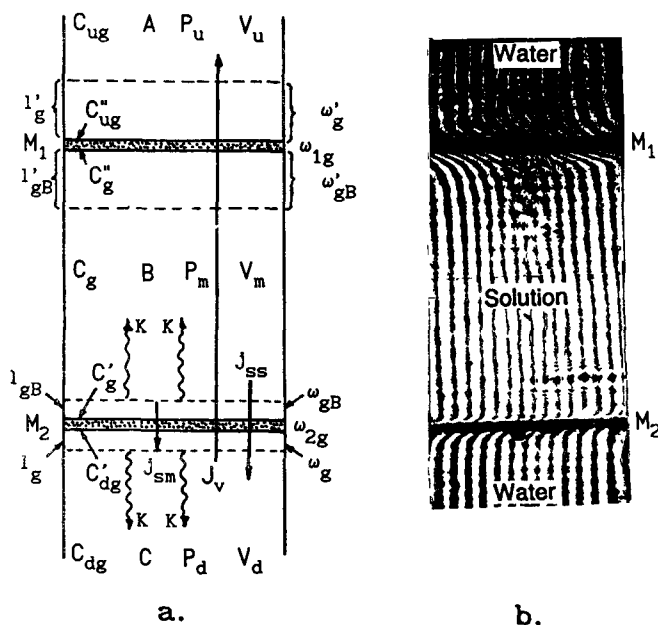


Figure 2. a: Theoretical model of graviosmotic system filled with solution of density increasing with increasing concentration. b: Exemplary interferogram performed with the use of aqueous solutions of glucose in the graviosmotic system (Kargol and Dworecki 1993).

In order to give a physical explanation of the graviosmotic phenomenon, let us consider two theoretical models of graviosmotic systems which are shown in Figs. 2a and 3a. They have been based mainly on the results of interferometric studies (Kargol and Dworecki 1993). The first of the models is for systems filled

with solutions whose density increases with concentration, the second is for systems filled with solutions whose density decreases with concentration.

Let us now take a closer look at the model of the system in Fig. 2a, i.e. a system filled with a solution whose density increases with concentration. Let us assume that the concentrations satisfy the conditions: $C_g > C_{ug}$ and $C_g > C_{dg}$, where C_g is the concentration in the middle compartment (B), C_{ug} is the concentration in the upper compartment (A) and C_{dg} is the concentration in the lower compartment (C). In the situation shown, in the vicinity of the upper membrane (M_1) there will develop stable diffusive layers l'_g and l'_{gB} , whereas in the vicinity of the lower membrane (M_2) unstable layers l_g and l_{gB} will develop. This is illustrated in greater detail by a model of the system shown in Fig. 2a and a sample interferogram in Fig. 2b (Kargol and Dworecki 1993).

From a number of interferometric studies (Dworecki 1984; Kargol et al. 1986; Kargol and Dworecki 1993) it follows that the stable layers (l'_g and l'_{gB}) are of relatively large thickness that increases in time. Large are also the falls in concentration occurring on them. Thus the concentration difference $\Delta C''_{ug} = C''_g - C''_{ug}$ on membrane M_1 is not great (C''_g and C''_{ug} are concentrations of the solutions at that membrane surface, Fig. 2a). This indicates also that the difference in osmotic pressure on that membrane is not great:

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

In order to further explain that situation, let us consider diffusion of a solute near the upper membrane (M_1). The solute's molecules, when leaving the layer l'_{gB} cause its density to become smaller than that of the solution C_g . So the layer remains stable, this being favoured by the force of gravity. Upon crossing the M_1 membrane, the molecules accumulate in the l'_g layer. The density of that layer becomes thus greater than the solution density C_{ug} of the upper compartment. That layer is thus also stable in the field of gravity. The thicknesses of those layers, and also the concentration falls on them, will increase in time. Meanwhile, the concentration difference and thus the osmotic pressure difference on membrane M_1 will decrease to a small value (within a relatively short time).

Different is the situation in the vicinity of the lower membrane (M_2). There the molecules leaving the layer l_{gB} cause its density to become smaller than that of the solution C_g of the middle compartment. Hence the layer is unstable to destruction due to gravity-induced convective flows K, K (Fig. 2a).

Solute molecules which left the layer diffuse through the membrane and then permeate layer l_g (under the membrane) creating a solution whose density is greater than that of the lower compartment solution C_{dg} . That layer is also unstable, and generates convective flows K, K . The flow generated insures that the layers remain thin and the concentration falls on them are not great. In general one can say that

the solutions separated by membrane M_2 are appreciably stirred by the convective flows. This has been confirmed by interferometric studies (Kargol and Dworecki 1993), for instance the interferogram shown in Fig. 2b. It should be added that the areas of the near-membrane layers are determined on interferogram proper curves of interferometric lines.

In the situation discussed, on membrane M_2 there is a relatively large concentration difference ($\Delta C'_{dg} = C'_g - C'_{dg}$) and thus a large osmotic pressure difference:

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

where C'_g and C'_{dg} are concentrations at the faces of membrane M_2 .

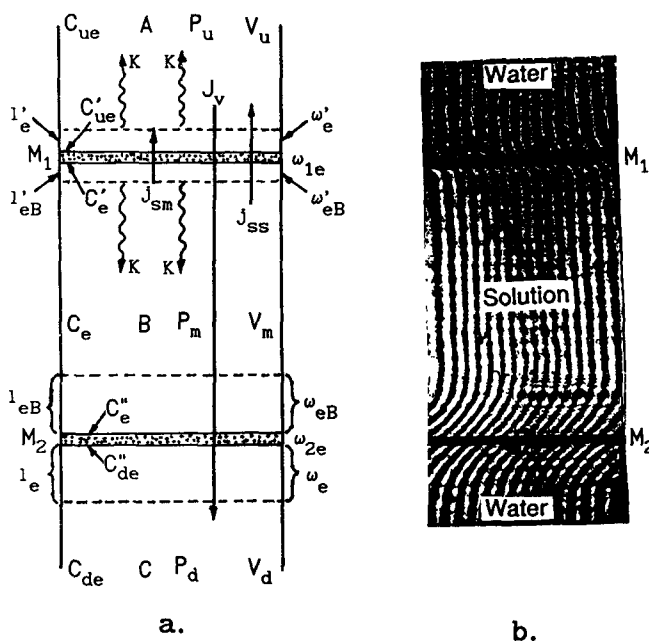


Figure 3. a. Theoretical model of graviosmotic system filled with solution of density decreasing with increasing concentration. b. Exemplary interferogram performed with the use of water solutions of ethanol in the graviosmotic system (Kargol and Dworecki 1993).

The model shown in Fig. 3a refers to graviosmotic systems with solutions of densities decreasing with concentration. One can easily apply the discussion performed above to this model. Further, in the case when concentrations of such solutions satisfy the conditions: $C_e > C_{ue}$ and $C_e > C_{de}$, in the vicinity of the

upper membrane (M_1) thin and unstable layers are formed (l'_e and l'_{eB}). On the other hand, in the vicinity of the lower membrane (M_2) stable layers (l_e and l_{eB}) of relatively large and increasing thickness are formed.

The model shown in Fig. 3a and the corresponding interferogram in Fig. 3b illustrate it in greater detail. It is easy to understand that there will be a large concentration difference $\Delta C'_{ue} = C'_e - C'_{ue}$ at the upper membrane, and thus also a large osmotic pressure difference:

$$\Delta \Pi'_{ue} = RT \cdot (C'_e - C'_{ue})$$

However, the concentration difference $\Delta C''_{de} = (C''_e - C''_{de})$ and the osmotic pressure difference at the lower membrane

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

will remain small. The quantities C'_e , C'_{ue} , C''_e and C''_{de} are concentrations at membrane faces. Volume flux J_v (the graviosmotic flux) generated in such systems will be directed downwards.

Analytical description of graviosmotic flows

a. Stationary graviosmotic flows

In order to describe mathematically stationary graviosmotic flows, let us consider a definite model of the system. Let it be the model shown in Fig. 2a. It is concerned with a graviosmotic system whose density increases with rising concentration. In that system we assumed that the concentrations C_g , C_{ug} and C_{dg} satisfy the concentrations: $C_g > C_{ug}$ and $C_g > C_{dg}$.

In order that the graviosmotic flow be constant in time, the volumes V_u , V_m and V_d of the compartments, and thus the volumes of solutions, must be sufficiently large, with definite active surfaces of the membranes and permeation parameters.

In the situation described, in vicinity of the upper membrane there will develop stable diffusive layers l'_g and l'_{gB} , while in the vicinity of the lower membrane unstable layers l_g and l_{gB} will develop. Hence the osmotic pressure difference $\Delta \Pi''_{ug} = RT \cdot (C''_g - C''_{ug})$ at the upper membrane will be negligibly small as compared to the difference $\Delta \Pi'_{dg} = RT \cdot (C'_g - C'_{dg})$ which occurs at the lower membrane. Let us further assume that the membrane's active surfaces are equal ($S_1 = S_2 = S$) but differ in their coefficients of filtration ($L_{p1} \neq L_{p2}$), reflection ($\sigma_{1g} \neq \sigma_{2g}$) and permeability ($\omega_1 \neq \omega_2$). Now we can, according to the Kedem and Katchalsky formalism (1958), for each membrane of the system write the following equations for volume flows:

$$J_{v1} = L_{p1} \cdot \sigma_{1g} \cdot RT \cdot (C''_{ug} - C''_g) + L_{p1} \cdot (P_m - P_u) \quad (4)$$

$$J_{v2} = L_{p2} \cdot \sigma_{2g} \cdot RT \cdot (C'_g - C'_{dg}) - L_{p2} \cdot (P_m - P_d) \quad (5)$$

where: P_m , P_u and P_d are mechanical pressures in the respective compartments (Fig. 2a), σ_{1g} , σ_{2g} are reflection coefficients for glucose.

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

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

Since the concentrations C'_g and C'_{dg} formula (5) are most known, we have to modify that formula in such a way as to replace those concentrations with C_g and C_{dg} . Equation (2) can be used as follows:

$$j_{sm} = -\omega_{2g} \cdot RT \cdot (C'_g - C'_{dg}) + (1 - \sigma_{2g}) \cdot \bar{C} \cdot J_{v2} \quad (7)$$

where: $\bar{C} = 0.5 \cdot (C'_g + C'_{dg})$, j_{sm} is the solute flux that permeates membrane M_2 , and ω_{2g} is permeability coefficient. We shall treat membrane M_2 together with layers l_g and l_{gB} as a triple membrane. Assigning to the layers their respective permeability coefficients ω_g and ω_{gB} , we obtain the following permeability coefficient for the triple membrane:

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

since, as follows from Kedem and Katchalsky (1963), the relation is fulfilled:

$$\frac{1}{\omega_{sg}} = \frac{1}{\omega_g} + \frac{1}{\omega_{2g}} + \frac{1}{\omega_{gB}}$$

Hence we can write the following equation for the transport of solute across the triple membrane:

$$j_{ss} = -\omega_{sg} \cdot RT \cdot (C_g - C_{dg}) + (1 - \sigma_{2g}) \cdot \bar{C}_s \cdot J_{v2} \quad (9)$$

where $\bar{C}_s = 0.5 \cdot (C_g + C_{dg})$.

If the concentration drops in the layers l_g and l_{gB} are equal, or differ only slightly, then it is easy to show that $\bar{C}$ and $\bar{C}_s$ are equal or almost equal ($\bar{C} \approx \bar{C}_s$) which results from the interferogram given in Fig. 2b and also from other interferometric investigations (Kargol and Dworecki 1993). Taking this into account, and knowing that in stationary state $j_{sm} = j_{ss}$, we obtain, using equations (7) and (9), the following:

$$C'_g - C'_{dg} = \frac{\omega_{sg}}{\omega_{2g}} \cdot (C_g - C_{dg}) \quad (10)$$

With this relationship equation (5) assumes the form:

$$J_{v2} = L_{p2} \cdot \sigma_{2g} \cdot \frac{\omega_{sg}}{\omega_{2g}} \cdot RT \cdot (C_g - C_{dg}) - L_{p2} \cdot (P_m - P_d)$$

or

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

where

$$\sigma_{sg} = \frac{\omega_{sg}}{\omega_{2g}} \cdot \sigma_{2g} \quad (12)$$

can be treated as a reflection pseudo-coefficient of the triple membrane.

The coefficient σ_{sg} can be determined in the same way as the coefficient σ_{2g} , provided the solutions are well stirred during measurement of σ_{2g} .

Solving now the set of equations (4), (6) and (11), the following expression for the stationary graviosmotic flow can be obtained:

$$J_v = \mathcal{L} \cdot [\sigma_{sg} \cdot RT \cdot (C_g - C_{dg}) - \sigma_{1g} \cdot RT \cdot (C_g'' - C_{ug}'') - (P_u - P_d)] \quad (13)$$

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

From interferometric studies (Kargol and Dworecki 1993) and from studies performed with the method of volume flow and solute flow measurement (Kargol 1978) it follows that:

$$C_g - C_{dg} \gg C_g'' - C_{ug}''$$

If so, then the second term on the right side of equation (13) can be left out as negligibly small, and the following expression is obtained:

$$J_v = \mathcal{L} \cdot \sigma_{sg} \cdot RT \cdot (C_g - C_{dg}) - \mathcal{L} \cdot (P_u - P_d) \quad (14)$$

Abandoning this member is an essential simplification in the mathematical description of graviosmotic flow because we do not know concentrations C_g'' and C_{ug}'' and we cannot modify equation (4) in the same way as it was done in relation to equation (5). The last difficulty results from the fact that the dissolved substance penetrates into layer l'_g (Fig. 2a), but it does not leave the layer; it is cumulated in it. It means that the coefficient of penetration ω'_g of this layer equals zero. In accord with equation (8) it also means that equal to zero is coefficient ω_{sg} of the triple membrane consisting of membrane M_1 and layers l'_g and l'_{gB} (Fig. 2a).

If we assume that $P_u = P_d$, then the last equation can be written:

$$J_v = \mathcal{L} \cdot \sigma_{sg} \cdot RT \cdot (C_g - C_{dg}) \quad (15)$$

It is easy to demonstrate that, based on the theoretical model shown in Fig. 3a, in the case of applying solutions of decreasing density with increasing concentration in the graviosmotic system, an adequate equation of transport has the form:

$$J_v = \mathcal{L} \cdot \sigma_{se} \cdot RT \cdot (C_e - C_{ue}) - \mathcal{L} \cdot (P_u - P_d) \quad (16)$$

where: $\sigma_{se} = \frac{\omega_{se}}{\omega_{1e}} \cdot \sigma_{1e}$ is reflection pseudo-coefficient, C_e , C_{ue} are concentrations (Fig. 3a).

b. Non-stationary graviosmotic flows

Let the subject of our considerations further be a graviosmotic system whose model is presented in Fig. 2a.

Let us now assume that the volumes of solutions V_u , V_m and V_d are adequately small with given surfaces of active membranes M_1 and M_2 and given parameters of penetration. In the presented situation the difference of concentrations ($C_g - C_{dg}$) occurring on the lower membrane will markedly disappear in time due to the existence of flux j_{gs} of solute (Fig. 2a). Therefore, graviosmotic transport will also decay. Thus, in this case we observe non-stationary graviosmosis. Having in mind an analytical description of this transport, let us assume still that concentration difference ($C_g'' - C_{ug}''$) occurring on membrane M_1 is also negligible in this case in relation to concentration difference ($C_g' - C_{dg}'$) as well as to concentration difference ($C_g - C_{dg}$). This phenomenon is confirmed among others by the results of experimental research presented in the next section of this paper. Our problem will be thus mainly reduced to finding an overt form of the dependence:

$$(C_g - C_{dg}) = f(t)$$

In order to obtain it, let us assume initially that at the start ($t = 0$) the difference of concentrations of compartments B and C is:

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

Let in time dt dm moles of solute penetrate membrane M_2 and layers l_g and l_{gB} . In consequence, solution concentration in compartments B and C of the graviosmotic system will have the values:

$$\begin{aligned} C_g &= C_{g0} - \frac{dm}{V_m} \\ C_{dg} &= C_{dg0} + \frac{dm}{V_d} \end{aligned}$$

Substrating the above equation by sides and assuming that $V_m = V_d = V = \text{const}$, one gets

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

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

On the basis of the above equation we can write:

$$d\Delta C_{dg} = \Delta C_{dg0} - \Delta C_{dg} = \frac{2dm}{V} \quad (17)$$

where $d\Delta C_{dg}$ is change in time of the concentration difference of solutions at intervals B and C .

In order to simplify our considerations, let us assume that the active surfaces of both membranes are equal: $S_1 = S_2 = S$. Under this assumption, using the definition:

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

we can write equation (9) in the form

$$dm = -\omega_{sg} \cdot RT \cdot \Delta C_{dg} \cdot Sdt + (1 - \sigma_{2g}) \cdot \bar{C}_s \cdot J_{v2} \cdot Sdt \quad (18)$$

As volume flux J_{v2} is equal to the graviosmotic volume flux J_v , then the above expression (after considering equation (15)) assumes the form:

$$dm = S[\Delta C_{dg} (-\omega_{sg} RT + (1 - \sigma_{2g}) \cdot \bar{C}_s \cdot \sigma_{sg} RT \cdot \mathcal{L}) - (1 - \sigma_{2g}) \cdot \bar{C}_s \cdot \mathcal{L} \cdot (P_u - P_d)] dt$$

After multiplying this equation by $\frac{2}{V}$, we get:

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

where a and b are given by formulas:

$$a = -\omega_{sg} RT + (1 - \sigma_{2g}) \cdot \bar{C}_s \cdot \sigma_{sg} \cdot RT \cdot \mathcal{L} \quad (20)$$

$$b = -(1 - \sigma_{2g}) \cdot \bar{C}_s \cdot \mathcal{L} \cdot (P_u - P_d) \quad (21)$$

On the basis of equations (17) and (19) we can write:

$$\frac{d\Delta C_{dg}}{a \cdot \Delta C_{dg} + b} = \frac{2S}{V} dt \quad (22)$$

After integrating the last equation, we get:

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

Assuming that for $t = 0$, $\Delta C_{dg} = \Delta C_{dg0}$, we find an integration constant:

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

Substituting the above expression into the formula (23) we get:

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

From it we obtain the sought expression for ΔC_{dg} as the function of time (t):

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

Next substituting this equation into formula (14) we finally get:

$$J_v = \mathcal{L} \cdot \sigma_{sg} \cdot RT \left[\left(\Delta C_{dg0} + \frac{b}{a} \right) \cdot \exp \left(\frac{2Sat}{V} \right) - \frac{b}{a} \right] - \mathcal{L} \cdot (P_u - P_d) \quad (25)$$

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

The above equation is the sought expression which describes non-stationary graviosmotic flows in the system whose model is shown in Fig. 2a. If we assume that $(P_u - P_d) = 0$, then this equation is reduced to the form:

$$J_v = \mathcal{L} \cdot \sigma_{eg} \cdot RT \cdot \Delta C_{dg0} \cdot \exp \left(\frac{2Sat}{V} \right) \quad (26)$$

It should be added to the above presented considerations that if solution concentration of the graviosmotic system is satisfied by the conditions:

$$C_g < C_{ug} \quad \text{and} \quad C_g < C_{dg},$$

then a considerable concentration difference will occur on the upper membrane (M_1) because solutions C_{ug} and C_g separated by this membrane will be mixed convectively. However, the difference of solution concentrations on the lower membrane (M_2) will be negligible. In the surrounding of this membrane stable near-membrane layers will be formed.

Assuming that

$$|-\omega_{sg} RT \cdot \Delta C_{dg}| \gg |(1 - \sigma_{2g}) \cdot \bar{C}_s \cdot J_v| \quad (27)$$

we can abandon member $(1 - \sigma_{2g}) \cdot \bar{C}_s \cdot J_v$ in equation (9). Then we will write:

$$dm = -\omega_{sg} \cdot RT \cdot \Delta C_{dg} \cdot S \, dt$$

Taking this into consideration, we get that constants expressed by equations (20) and (21) are:

$$a = -\omega_{sg} \cdot RT \quad \text{and} \quad b = 0 \quad (28)$$

In connection with the above, equation (26) assumes the following simplified form:

$$J_v = \mathcal{L} \cdot \sigma_{sg} \cdot RT \cdot \Delta C_{dg0} \cdot \exp \left(-\frac{2S}{V} \cdot \omega_{sg} \cdot RT \cdot t \right) \quad (29)$$

Considerations analogous to those presented above with reference to the graviosmotic system presented in Fig. 2a can also be made for a system whose theoretical model is shown in Fig. 3a.

Adequate equation of non-stationary graviosmotic transport has the form:

$$J_v = \mathcal{L} \cdot \sigma_{se} \cdot RT \cdot \Delta C_{ue0} \cdot \exp\left(-\frac{2S}{V} \cdot \omega_{se} \cdot RT \cdot t\right) \quad (30)$$

where: $\sigma_{se} = \frac{\omega_{se}}{\omega_{2e}} \cdot \sigma_{2e}$, $\Delta C_{ue0} = C_e - C_{ue}$ (Fig. 3a).

Exemplary results of the experimental investigation

Having in mind the aim to prove the correctness of the equations of graviosmotic transport which occurs both stationarily and non-stationarily, a proper experimental investigation was performed. Some selected results of this investigation, obtained by a standard method (Kargol 1978) are presented in Figs. 4, 5, 6 and 7. The results of the investigation represented in Figs. 4 and 5 concern stationary graviosmosis. They were obtained using a graviosmotic system built on two nephrophe membranes of identical coefficient of filtration ($L_{p1} = L_{p2} = L_p = 5 \cdot 10^{-12} \text{ m}^3 \text{N}^{-1} \text{s}^{-1}$) and equal active surface ($S_1 = S_2 = S$) which were 3.36 cm^2 each. The volume of compartments A, B and C of the system and therefore the volumes of solutions were sufficiently high and amounted to $V_u = V_m = V_d = 200 \text{ cm}^3$. Compartments A and C were filled with pure water, whereas the middle interval (B) with an aqueous solution of glucose of concentration $C_g = 0.3 \text{ mol/l}$, i.e. a solution of density increasing with increasing concentration. The previously determined pseudo-coefficient of reflection σ_{sg} of these membranes (for glucose) was $\sigma_{sg1} = \sigma_{sg2} = \sigma_{sg} = 0.035$.

The above presented experimental conditions secured stationarity of the process of graviosmosis for sufficiently long durations. This was confirmed by the exemplary results of the investigation shown in Fig. 4. Plot 1 in this figure is an experimental plot obtained through direct measurements of flux J_v . Plot 2 is a theoretical plot made on the basis of equation (15), i.e. the following equation:

$$J_v = \mathcal{L} \cdot \sigma_{sg} \cdot RT \cdot (C_g - C_{dg})$$

where: $\mathcal{L} = 0.5 \cdot L_p$, $T = 300 \text{ K}$.

Plot 2 is located in a given set of coefficient a little higher than plot 1. This is due to the existence of some negligible difference of osmotic pressures $\Delta \Pi''_{ud}$ on the upper membrane (M_1). In spite of this it can be assumed that equation (15) describes stationary graviosmotic flows with a sufficiently good approximation.

An analogous experimental investigation has been performed for different concentrations of C_g of the glucose solution. On this basis a plot of dependences

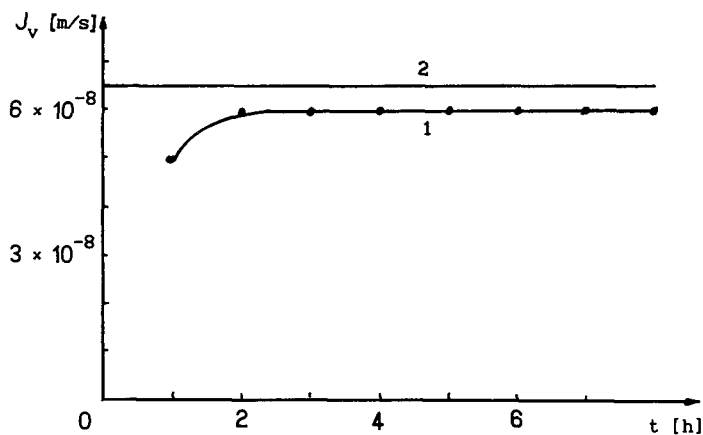


Figure 4. Stationary graviosmotic flows (1 – experimental plot, 2 – theoretical plot).

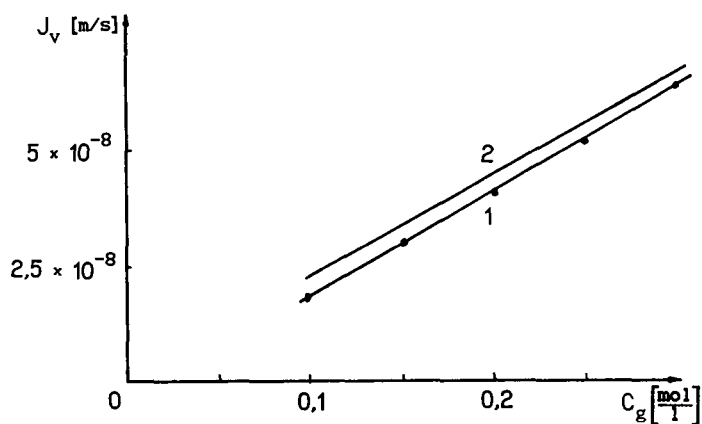
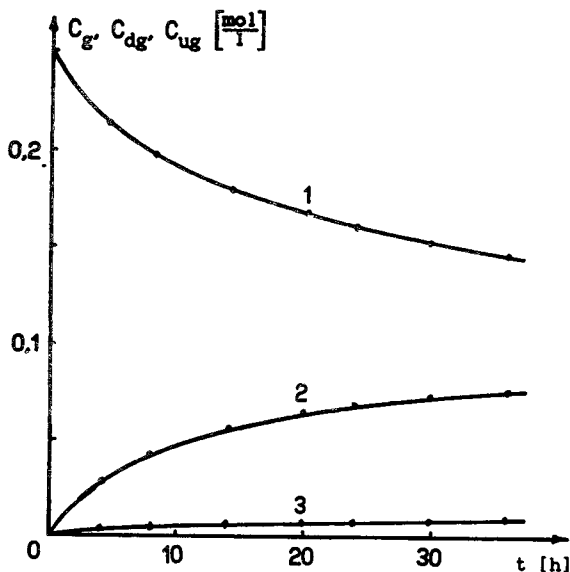


Figure 5. Dependence of stationary graviosmotic flow on concentration C_g mol/l of glucose solution.

was made $J_v = f(C_g)$. It is represented by straight line 1 in Fig. 5. Plot 2 in this figure represents a dependence obtained from calculations performed on the basis of equation (15). This plot is also located in a given set of coefficients, a little above plot 1. In spite of this fact, also in this case equation (15) is sufficiently adequate in relation to the real state. Practically, the same conformity of the theoretical and experimental investigation was obtained in relation to equation (16) concerning graviosmotic flows of solutions of density decreasing with increasing concentration. A proper investigation was performed using the example of

Figure 6. Dependences:
 $C_g(t)$ – plot 1, $C_{dg}(t)$ – plot
 2 and $C_{ug}(t)$ – plot 3.



aqueous solutions of ethanol (Kargol 1978). As far as non-stationary graviosmosis is concerned, first measurements of concentrations of solutions in the particular compartments were made in the function of time, i.e. $C_g(t)$, $C_{dg}(t)$ and $C_{ug}(t)$. The exemplary results of this investigation are presented in Fig. 6. They were obtained on a graviosmotic system based on two cellophane membranes M_1 and M_2 of equal filtration coefficient ($L_{p1} = L_{p2} = L_p = 0.85 \cdot 10^{-12} \text{ m}^3 \text{N}^{-1} \text{s}^{-1}$), pseudo-coefficient of reflection ($\sigma_{sg1} = \sigma_{sg2} = \sigma_{sg} = 0.1$) and equal coefficient of penetration ($\omega_{sg1} = \omega_{sg2} = \omega_{sg} = 1.7 \cdot 10^{-10} \text{ mol N}^{-1} \text{s}^{-1}$). These membranes of active surfaces $S_1 = S_2 = S = 3.36 \text{ cm}^2$ were separated by compartments A, B and C of relatively small volumes which equalled 20 cm^3 each. The middle compartment was filled with the solution of glucose of concentration $C_g = 0.25 \text{ mol/l}$ (i.e. a solution of density increasing with increasing concentration). Compartments A and C were filled with pure water. Curve 1 expresses dependence $C_g(t)$ which illustrates decay in time of the solution concentration in the middle compartment. Curve 2 is a dependence $C_{dg}(t)$ and curve 3 a dependence $C_{ug}(t)$. The last dependence indicates that increase in the solution concentration on the upper compartment is negligibly small. It means that there must be a small difference of solution concentrations on the upper membrane. It is understandable because in the surrounding of this membrane so-called stable diffusion layers are generated. On the other hand, curve 2 ($C_{dg}(t)$) is the evidence that on the lower membrane a high difference of solution concentration occurs which decreases in time. In the surrounding of this membrane intramembrane layers are formed. This investigation confirms the correctness of a theoretical model constructed on the

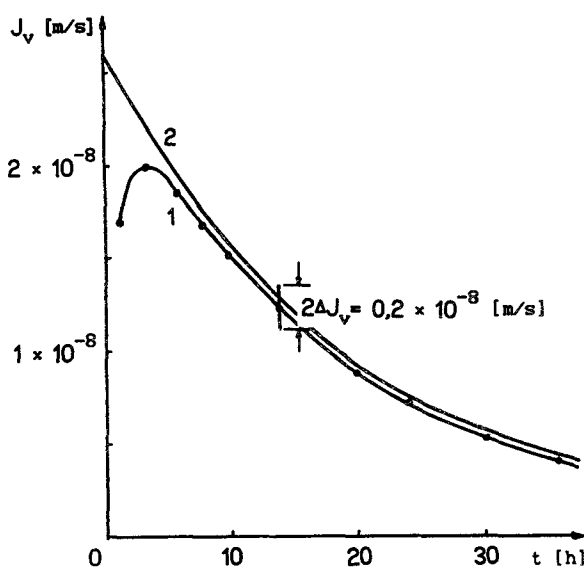


Figure 7. Dependence $J_v(t)$: 1 – experimental plot, 2 – theoretical plot.

basis of the interferometrical investigation as shown in Fig. 2a. Using the same set of membranes, measurements were done of graviosmotic flow J_v in the function of time. A graphic representation of this function is plot in Fig. 7. Plot 2 in the same figure is dependence $J_v(t)$ obtained theoretically on the basis of equation (29), i.e. the following equation:

$$J_v = \mathcal{L} \cdot \sigma_{sg} \cdot RT \cdot \Delta C_{dg0} \cdot \exp\left(-\frac{2S}{V} \cdot \omega_{sg} \cdot RT \cdot t\right)$$

where: $\mathcal{L} = 0.5 \cdot L_p$, $T = 300$ K, $S = \text{const.}$, and $V = \text{const.}$ Analyzing both plots it is easy to notice quite a good conformity of the results of the experimental and theoretical investigation. It means that equation (29) is applicable with the exception of some (relatively small) initial time of graviosmosis. Analogously, good conformity of the results of the experimental and theoretical investigation was obtained for other graviosmotic systems and other solutions, including a solution of ethanol whose density decreases with increasing concentration.

Conclusion

1. Taking into consideration the results of the investigation of graviosmosis carried out by the interferometrical method and the method of measurement of volume streams and concentration measurements, a full physical interpretation of this phenomenon was presented in this study. Within this interpretation two theoretical models of graviosmotic systems were constructed. One concerns systems filled with

solutions of density increasing with increasing concentration and the other with systems in which solutions of density decreasing with increasing concentration were applied.

2. Using these models and thermodynamical formalism of Kedem and Katchalsky (1958), definite equations were developed in order to describe in a comprehensive way graviosmotic flows. These equations describe both stationary and non-stationary flows and graviosmotic flows of solution of density increasing and decreasing with increasing concentration.

3. Furthermore, experimental verification of these equations was presented in the paper. It was shown that they describe graviosmotic flows with fairly good approximation.

4. Our interest in graviosmosis is mainly due to biophysical aspects. It has led us to the development of the so-called graviosmotic hypothesis (Kargol 1978, 1992, Przestalski and Kargol 1987). According to this hypothesis water in plants could be transported through xylem vessels using graviosmotic mechanisms. Speaking about these mechanisms we mean graviosmotic pumping of water against gravitation force, circulation of water as well as asymmetry and reinforcement of graviosmotic transport (Kargol 1978, 1992, Przestalski and Kargol 1987).

5. We also notice a need to call attention to this phenomenon in a number of technological membrane processes. (Strathmann 1981) in which a significant effect of gravitation force can be seen on the state of near membrane diffusion layers.

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