

A STUDY ON GRAVIELECTRIC POLARIZATION IN 1-MEMBRANE SYSTEMS

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In the present paper are presented the results of an experimental study on the gravelectric effect generated in a 1-membrane system. The results indicate that the gravelectric potential strongly depends on the concentrations of the solutions and on the inclination angle of the system with respect to the vertical. An attempt has also been made to explain and describe the effect analytically by constructing a theoretical model of the system, making use of the Goldman equation.

INTRODUCTION

The influence of the field of gravity on electrolyte transport in membrane systems may appear mainly as the effect of graviosmotic polarization and gravelectric polarization. In reality the effects obtained by proper reorientation of the membrane system in the field of gravity.

The first of the effects, called graviosmosis, was discovered in 2-membrane systems in 1971 (Kargol, 1971; Przestalski & Kargol, 1972). It consists in the generation of volume flows, which are called graviosmotic flows (Kargol 1978, 1992).

The second effect (gravelectric), called also gcoelectric effect, consists in generation of gravelectric potential in a membrane system.

The studies of the effect conducted so far with artificial membrane systems were concerned mainly with attempts to explain the physical mechanism of gravelectric potential generation (Brauner, 1926, 1959; Custard & Faris, 1965; Kargol, 1981). One of the first interpretations was made by Brauner back in 1926. According to him the potential of the polarization is connected with the effect of gravitation forces on ion transport within the membrane. It results in a separation of positive and negative ions and thus in creation of electric potential difference on the membrane. This interpretation was questioned even by Brauner because the gravitational interaction is by many orders of magnitude weaker than the electrostatic one (Brauner, 1926, 1959).

Custard and Faris (1965) suggest various interpretations. Eventually, it is postulated there that the gravelectric polarization is caused by the stable solution layer the stable solution layer that

forms above the upper surface of a horizontally situated membrane and destruction of this layer by tangential action of the force of gravity when the membrane is situated horizontally. This results in changed transference numbers of the ions.

According to the latest concepts (Kargol, 1981, 1988), fundamental for the creation of the gravelectric effect is the formation of the diffusive layers on both sides of the membrane. As a result it increases or decreases, depending on positioning of the system with respect to the force of gravity, the concentration difference on the membrane. This in turn results in changed concentration difference on the membrane thickness and altered diffusion potential.

All previous attempts to interpret the gravelectric effect are either not complete or not convincing. Therefore further studies of the effect are needed. In them, we think, special attention should be paid to gravidiffusion and convection Chandrasekhar, 1942; Etori, 1986, Hladyszowski *et al.* 1989; Kargol, 1988, 1992; Schatz *et al.* 1991). These phenomena are thought to be fundamental for the destruction of the near-membrane diffusive layers. The gravidiffusive factor refers mainly to systems that contain strongly diluted solutions.

In the present work some systematic experimental studies of the effect of gravelectric polarization in 1-membrane system have been made. Based on the results of the study, an attempt at physical interpretation and analytical description of the effect have been made. Our interest in the gravelectric effect has been mainly for biophysical reasons. These include in particular the problems of gravidiffusion of ions in biological sys-

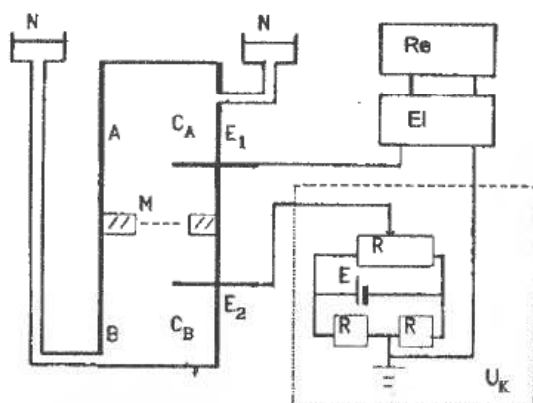


Fig. 1 Experimental system (C_A , C_B — solutions, M — membrane, E_1 , E_2 — electrodes, U_K — compensation system, EI — electrometer, Re — recorder).

tems, together with geoelectrical effects and geotropic issues in plants (Brauner, 1926, 1959; Grahm & Hertz, 1962; Kargol, 1978, 1988; Wilkins, 1969).

RESULTS AND DISCUSSION

The experimental studies of the gravielectric effect in a 1-membrane system were performed with a typical experimental setup. Its scheme is shown in Fig. 1. The setup is composed of a membrane system with reversible electrodes (E_1 and E_2) which have been made with copper wire, a compensating system (U_K), an electrometer (EI) together with a recorder (Re). The overall voltage U on electrodes E_1 and E_2 was the resultant of membrane voltage U_m , voltages U_A and U_B occurring within the solution between membrane M and the

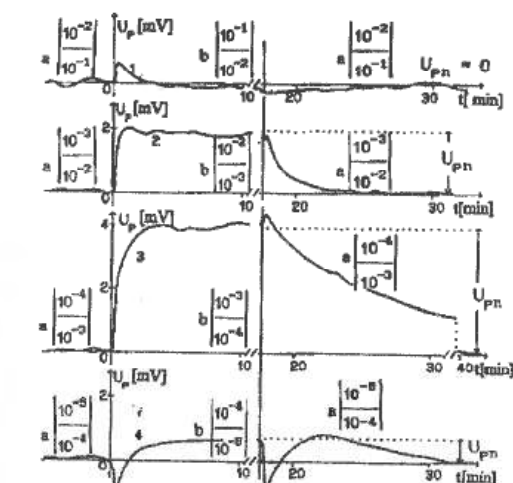


Fig. 2 Dependences $U_m = f(t)$ for different concentrations of solution CuSO_4 (for a more detail description see the text)

electrodes, and electrode potentials U_{E1} and U_{E2} :

$$U = U_m + U_A + U_B + U_{E1} + U_{E2}. \quad (1)$$

Robber tubes (G, G) were long enough for vertical rotation of the membrane system. Time dependence of the voltage $U = U_o$ was measured when the system was in position (a) (which was shown in Fig. 1a), and when the system was turned to position (b) (which was shown in Fig. 1b). In both positions of the system the membrane was positioned horizontally, and in position (a) the more concentrated solution (C_A) is under the membrane and the less concentrated (C_B) — above the membrane. The experiments were started with setting the system in position (a) and calibrating the electrometer (using a compensating system U_K). The electrometer was set to zero when the voltage stopped changing. Then the system was reoriented

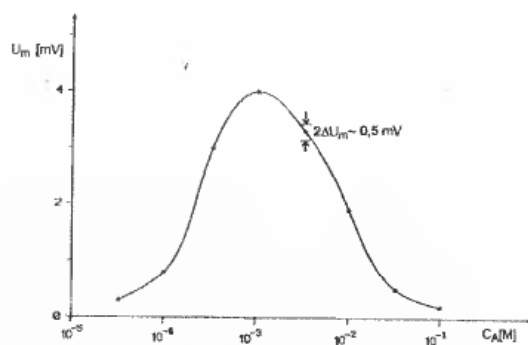


Fig. 3 Dependence $U_m = f(C_A)$.

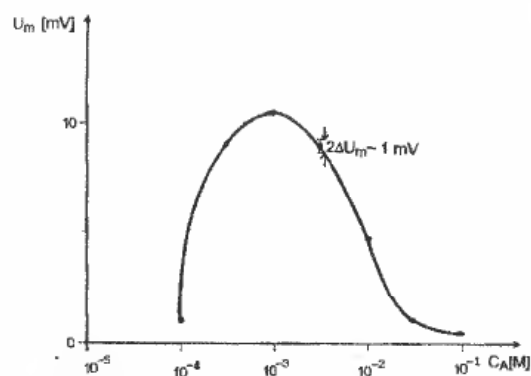


Fig. 4 Dependence $U_m = f(C_A)$.

to position (b) and time course of the voltage U_b measured until the voltage levelled off at the value (U_b^n). The curves in Fig. 2. illustrate that in detail. On reorienting the system again to the starting position (a) the system returned after a time to the state of zero voltage U_a . The voltage value $U_{pn} = U_b^n$ was taken as a measure of the gravielectric polarization, which is the voltage of system's saturation in position (b) (see Fig. 2). The studies described above were carried out with different membranes and solutions. In all cases the results obtained were analogous to those shown in Fig. 2 (taken as a sample).

The results shown in that figure refer to a nephropneumatic membrane (whose filtration coefficient $L_p = 5 \cdot 10^{-12} \text{ m}^3 \text{ N}^{-1} \text{ s}^{-1}$) which separates copper sulfate solutions (CuSO_4).

In each of the experiments there was a 10th-fold concentration difference ($C_A = 10 \cdot C_B$). The concentrations were expressed in moles per liter [M]. Based on such experiments, performed for various concentrations C_A in the range from $0.5 \cdot 10^{-1} \text{ M}$ to $0.5 \cdot 10^{-4} \text{ M}$ a plot was made of concentration dependence of the gravielectric polarization U_{pn} . That plot is shown in Fig. 3. From it one can see that potential U_{pn} depends strongly on concentration C_A . The potential rises from zero at $C_A = 0.5 \cdot 10^{-4} \text{ M}$ CuSO_4 to a maximum $C_{pn}^{\text{max}} = 4 \text{ mV}$ at $C_A = 10^{-3} \text{ M}$. With further increase in C_A the voltage U_{pn} decreases, reaching zero at $C_A \approx 10^{-1} \text{ M}$. It should be added here that for concentrations $C_A > 10^{-1} \text{ M}$ convective flows are generated on both sides of the membrane if the system is in position (a). The occurrence of the

flows (generated by the force of gravity) is confirmed, among others, by studies on irregular electric oscillations observed in l-membrane systems (Kargol, 1988). With concentrations $C_A < 10^{-1} \text{ M}$ we have to deal, due to great interionic distances, with gravidiffusion, i.e. diffusion of molecules (ions in our case) which is activated or inhibited by the force of gravity (Chandrasekhar, 1942; Etori, 1986; Hladyszowski *et al.*, 1989; Kargol, 1988, 1992; Schatz *et al.*, 1991).

Having in view physical interpretation of the gravielectric effect, measurements have been performed of the membrane potential U_m (diffusion potential) as dependent on concentration C_A , when solutions C_A and C_B of copper sulfate were well stirred (with mechanical stirrers). In the study the condition $C_A = 10 \cdot C_B$ was also satisfied. The relationships $U_m = f(C_A)$ thus obtained are shown in graphical form in Fig. 4. The course of the curve is similar to the one in Fig. 3. Potential U_m also reaches zero value for concentrations $C_A < 0.5 \cdot 10^{-4} \text{ M}$ and $C_A > 10^{-1} \text{ M}$. The maximal value of the potential is in this case greater and equal to $U_m^{\text{max}} = 10 \text{ mV}$. It is reached also at $C_A = 10^{-3} \text{ M}$. From comparison of the curves in Figs 3 and 4 it follows that there is a close relationship between potentials U_{pn} and U_m .

The dependence of potentials U_{pn} and U_m on inclination of the system with respect to the vertical was also investigated. It was found that potential U_m does not depend on the inclination angle, while potential U_{pn} depends on it markedly. That is shown in detail by the curve in Fig. 5, which was obtained for $C_A = 10^{-3} \text{ M}$ (at $C_B = 10^{-4} \text{ M}$).

The results presented above will be utilized for an attempt at physical interpretation of the effect

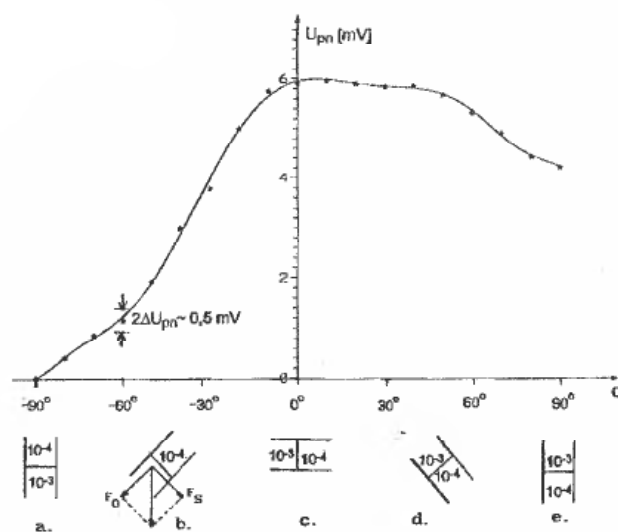


Fig. 5 Dependence $U_{pn} = f(\alpha)$.

of gravielectric polarization in 1-membrane systems. In addition to above, we have to add that if angle α belongs to interval $0 < \alpha < 90^\circ$ or to interval $0 > \alpha > -90^\circ$, then we take into consideration the component F_0 of gravitation force perpendicular to the membrane (*vide* Fig. 5b). The tangent component F_s is not taken into consideration here.

The essence of the gravielectric effect

In order to try to explain the essence of the gravielectric effect in a 1-membrane system, let us consider such a system in the two extreme positions (a) and (b) with respect to the vertical, as

shown in Fig. 6 a, b. In position (a) solution C_B (the less concentrated) is above and solution C_A (the more concentrated) under the membrane.

In the configuration shown the upwards transport of ions Cu^{++} and SO_4^{--} inhibited by the force of gravity (Chandrasekhar, 1942; Etori, 1986; Hladyszowski *et al.*, 1989; Schatz *et al.*, 1991; Kargol, 1992). Copper sulfate gives solutions of density rising with concentration. As a result of ion transport across the membrane, from solution C_A to C_B , a concentration distribution will develop (after a time t) as shown by plot α . It implies the existence around the membrane of diffusive layers l_a and l_a^* with large concentration gradients.

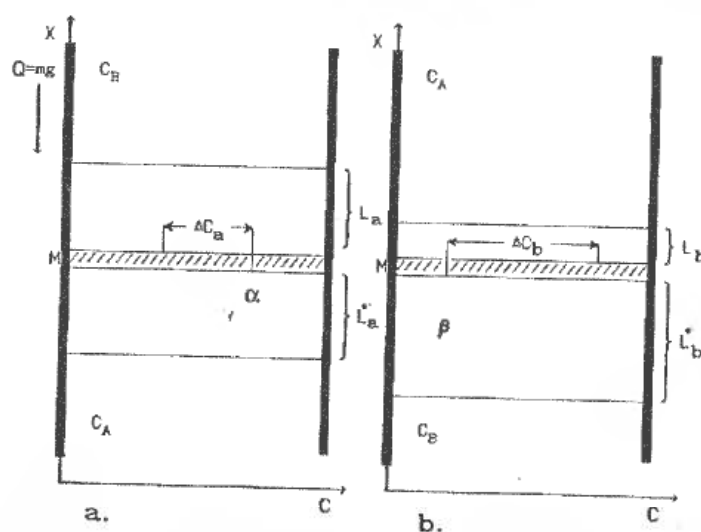


Fig. 6 The model of one-membrane system in configurations a and b with respect to the vertical.

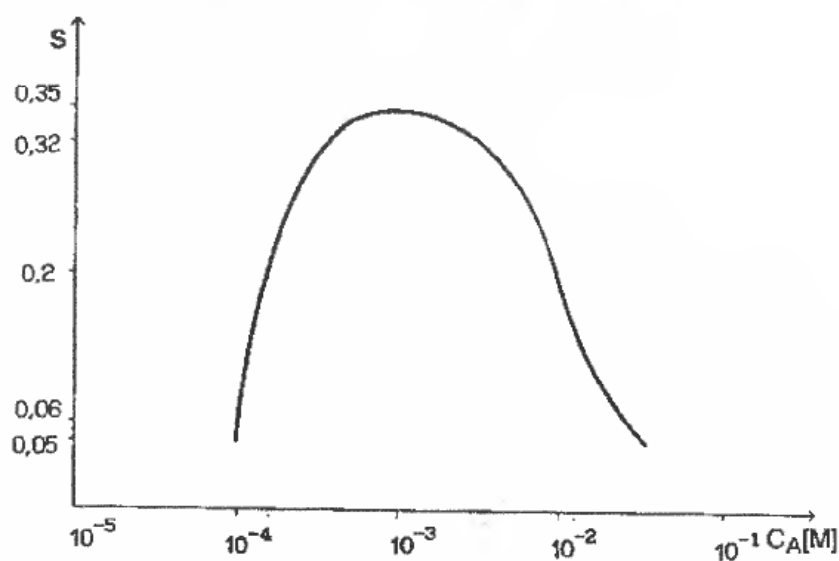


Fig. 7 Dependence $s = f(C_A)$.

Hence the concentration difference ΔC_a at the membrane is not great, as is the flux of ions across it.

Markedly different will be the distribution of concentration after the same time (t) since reorienting the system (by turning it) to position (b) (see Fig. 6b). Plot β illustrates that. In this case, due to diffusive transport being activated by gravity, a relatively thin diffusive layer l_b is formed above the membrane. Not great is also the drop in concentration. The diffusive layer l_b' developed under the membrane is however adequately broad. So it happens due to the gravity activated diffusive transport of ions Cu^{++} and SO_4^{--} (in solution C_B). The drop in concentration in this layer is however not great, as is also the concentration C_B' . This happens because the membrane permeability to ions is not great as compared to permeability of the diffusive layer l_b' . Throughout the membrane thickness there is, thus, a relatively great concentration difference ΔC_b (markedly greater than ΔC_a). Hence the membrane potential U_m^b is correspondingly great (with respect to potential U_m^a , when the system is in position (a)). On the basis of the above considerations we can generally postulate that the gravielectric polarization U_{pn} is the difference in membrane potentials U_m^b and U_m^a . From experimental studies it follows that the potentials U_A , U_B , U_{EF} and U_{ED} that appear in equation (1) are independent of the angle of system's inclination to the vertical.

Thus we can write:

$$U_{pn} = U_m^b - U_m^a,$$

where U_m^a and U_m^b are the measured potentials of the steady state. Since during the experiment the equality $U_m^a = U_m^b = 0$ was achieved, we can write that

$$U_{pn} = U_m^b = U_m^a.$$

From the experimental study discussed it follows that the gravielectric polarization potential is greatest at $C_A = 10^{-3}$ M. For lower concentrations the potential decreases due to hydrogen ions. In the case of concentrations C_A greater than 10^{-3} M the membrane selectivity for anions and cations decreases due to the accumulation of ions, which compensates the fixed charges in the membrane pores.

In order to quantitatively describe the gravielectric polarization in the membrane system studied, we will make use of Goldman equation (Giebisch, 1978). For CuSO_4 solution that equation has the form

$$U_m^b = 29[\text{mV}] \ln \frac{P^- C_B^- + P^+ C_A^+}{P^- C_A^- + P^+ C_B^+}, \quad (2)$$

where P^+ , P^- — permeability coefficients of positive and negative ions across membrane; C_A^+ , C_A^- — concentrations positive and negative ions in the solution C_A ; C_B^+ , C_B^- — concentrations positive and negative ions in the solution C_B (see Fig. 1).

Let us introduce the following mathematical

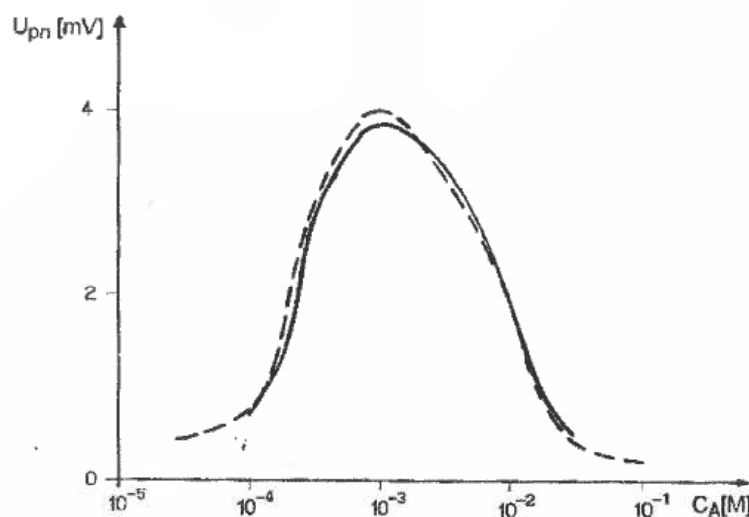


Fig. 8 Dependences $U_{pn} = f(C_A)$: the dashed line shows the experimental dependence and the continuous line shows the calculated one.

definition of membrane selectivity towards anions and cations:

$$s = 1 - \frac{P^-}{P^+} \quad (3)$$

From this definition it follows that $s = 0$ if $P^+ = P^-$ and $s = 1$ if $P^- = 0$.

With that definition of selectivity equation (2) can be written:

$$U_m^h = 29[\text{mV}] \ln \frac{(1-s)C_B^- + C_A^+}{(1-s)C_A^- + C_B^+} \quad (4)$$

or

$$\frac{U_m}{29[\text{mV}]} = \ln \frac{(1-s)C_B^- + C_A^+}{(1-s)C_A^- + C_B^+} \quad (5)$$

Since $C_A = 10 C_B$, the last equation results in:

$$s = \frac{11 \cdot [\exp(U_m/29[\text{mV}]) - 1]}{10 \cdot \exp(U_m/29[\text{mV}]) - 1} \quad (6)$$

Using U_m values from the plot in Fig. 4, the above equation gives us the relationship $s = f(C_A)$, which has been plotted in Fig. 7. It was obtained for solutions which are well stirred and there is a 10-fold concentration difference on the membrane. The quantity (s), which represents membrane selectivity for anions and cations of CuSO_4 , is seen to depend strongly on concentration C_A .

Thus we can write:

$$U_m = k \cdot s \quad (7)$$

The quantity k can be found from the equation

$$k = \frac{U_m}{s} \quad ,$$

putting $U_m = U_m^{\text{max}}$ and taking for (s) the selectivity at $U_m = U_m^{\text{max}}$. The value calculated in this way is $k \approx 29 \text{ mV}$.

Analyzing the results shown in Figs 3 and 4, we can notice that for the whole range of concentrations studied the following relationship is met to a good approximation:

$$\frac{U_{pm}}{U_m} = \frac{U_{pm}^{\text{max}}}{U_m^{\text{max}}} \equiv \text{const.} \quad (8)$$

where U_{pm}^{max} and U_m^{max} are maximal potentials (obtained at $C_A = 10^{-3} \text{ M}$). Finally, since $U_m = ks$, we get

$$U_{pm} = \frac{U_{pm}^{\text{max}}}{U_m^{\text{max}}} U_m = \frac{U_{pm}^{\text{max}}}{U_m^{\text{max}}} k \cdot s \quad (9)$$

where (s) is, as follows from the plot in Fig. 7, a function of C_A .

Based on this expression, and by way of calculation, a plot of the relationship $U_{pm}(C_A)$ was made. It has been as continuous line in Fig. 8. The dashed line shows the relationship $U_{pm} = f(C_A)$ obtained from experiment (see Fig. 3). Comparing the two curves one can see that equality (9) describes the dependence of the gravielectric polarization on concentration C_A in a satisfactory way. This makes the considerations performed in this paper, that include a physical interpretation of the gravielectric phenomenon, convincing enough.

CONCLUSION

The present work is a systematic study of the gravielectric polarization of 1-membrane systems, also called gravielectric effect. Keeping a 10-fold concentration difference on the membrane, it has been shown that, e.g., the gravielectric polarization in such a system depends strongly on concentration of the solutions and the angle of inclination of the system with respect to the vertical. A nephrophe membrane was used in the study, which in normal conditions is selective with respect to anions and cations. Based on the results of the measurements performed, an attempt has been made to formulate a physical interpretation of the graviosmotic effect. A use has been made of the gravidiffusion postulate (Chandrasekhar, 1942; Etori, 1986; Hładyszowski *et al.*, 1989; Kargol, 1978, 1988, 1992; Schatz *et al.*, 1991) saying that the force of gravity can induce or inhibit vertical transport of molecules (ions in this case) and thus affect the state of the near-membrane diffusive layers. By state of the layers we mean their thickness and concentration drops in them. A change in those drops implies a change in the concentration difference on the membrane thickness. This in turn induces a change in the diffusion potential on the membrane (if it is selective with respect to the ions, i.e. if permeability coefficients of anions and cations differ).

Our interest in the gravielectric effect is dictated mainly by biophysical aspects. To be precise, it is concerned with biophysical mechanisms which are responsible for the effects of geotropic bend in

plants (Brauner, 1926, 1959; Grahm & Hertz, 1962; Kargol, 1988, 1992; Wilkins, 1969 and others). It is connected also with graviosmotic and electro-graviosmotic transport of water in plants on long distances; the phloem transport of water and assimilates in particular (Wilkins, 1969).

REFERENCES

- Brauner L. (1926). Über des geo-elektrische Phänomen. *Kolloidchem. Beih.*, **23**, 143–152.
- Brauner L. (1959). Neue Versuche zur Analyse des geoelektrischen Effects. *Planta*, **53**, 449–483.
- Chandrasekhar S. (1942). Stochastic problems in physics and astronomy. *Rev. Modern Phys.*, **15**, 1–89.
- Custard H. C. & Faris S. R. (1965). Observation of the geoelectric effect in electrochemical concentration cells using ionexchange membranes. *Planta Berl.*, **65**, 83–101.
- Etori K. (1986). Statistical estimation of a nonlinear diffusion system in a gravitational field. *Phys. Fluids*, **29**, 879–880.
- Giebisch G., Testeson D. C. & Ussing H. H. (1978). *Membrane transport in Biology*. Springer Verlag, Berlin, Heidelberg, New York, pp. 5–113.
- Grahm L. & Hertz C. H. (1962). Measurement of the geoelectric effect in coleoptiles by a new technique. *Physiol. Plantarum*, **15**, 96.
- Iljadyszowski J., Kargol M. & Przestalski S. (1989). Graviosmotic polarity of capillary membrane systems. *Stud. Biophys.*, **133**, 43–48.
- Kargol M. (1971). *Nonelectrolytes and electrolytes transport through membrane systems*. Master Thesis, WSP Opole (in Polish).
- Kargol M. (1978). *The effect of the gravitational field on substance transport in membrane systems*. D. Sc. Thesis, Wyd. WSP Kielce (in Polish).
- Kargol M. (1981). *O mechanizmie polaryzacji grawi-elektrycznej układów I-membranowych*. XXVII Zjazd PTF, Lublin, 21–25 września, p. 113.
- Kargol M. (1988). Graviosmotic polarisation of one-membrane systems. Generation of irregular electric oscillations. *Post. Fiz. Med.*, **23**, 169–177.
- Kargol M. (1992). The graviosmotic hypothesis of xylem transport of water in plants. *Gen. Physiol. Biophys.*, **11**, 469–487.
- Przestalski S. & Kargol M. (1972). Graviosmotic volume flow through membrane systems. *Stud. Biophys.*, **34**, 7–14.
- Schatz A., Reitschetter R., Briegleb W. & Linke-Hommers A. (1991). Gravity effects on biological systems. *Adv. Space Res.*, **12**, 51–53.
- Wilkins M. B. (1969). *The physiology of plant growth development*. MacGraw-Hill Co., New York.