Electric character of driving forces of ionic transport

J. MICHALOV

Institute of Experimental Biology and Ecology, Centre for Biological and Ecological Research, Slovak Academy of Sciences, CS-814 34 Bratislava

Received 7 April 1987

The transport of ions through a membrane as well as the participation of membrane in this process was investigated by observing the effect of external electric field on the membrane separating the electrolytes with different concentrations of the corresponding ions. The results confirmed the presence of polarizable particles in the system, their participation in transport and the function of the electric field regulating the activity not only of the membrane itself but also of the whole transport system.

С помощью действия внешнего электрического поля на мембрану, разделяющую электролит с различной концентрацией соответствующих ионов, исследовался перенос ионов через мембрану, а также ее роль в этом процессе. Результаты подтвердили присутствие поляризуемых частиц в системе, их участие в переносе и функцию электрического поля как регулятора действия не только мембраны, но и всей транспортной системы.

The mechanism of the transport phenomenon through membranes has been studied for a few decades. There are different theories and hypotheses, more or less justified for its explanation. It is clear that the concentration gradient between two electrolyte solutions separated by a permeable membrane changes with quantity of the ions of a certain substance transported through this membrane and is proportional to the transmembrane electric potential.

Every membrane present in the electric field is polarized. The polarization manifests itself by dipole formation or orientation of permanent dipoles in the membrane space or in the boundary between membrane and solution. The orientation appears if the membrane or the membrane—solution boundary contains polar molecules with permanent dipole. The polar molecules may be orientated chaotically but in the presence of electric field, they are orientated in the direction of the lines of force according to intensity of the electric field and thermal excitability of the structure of membrane [1—4].

The effect of external electric field of the same or opposite polarity on a polarized membrane consists in intensification of existing polarization or in inversion of polarity of the membrane, respectively.

If the membrane is porous and exhibits properties of an electric insulant, it represents an analogue of electric conductor. The ionic current going through

the pores of membrane induces in their neighbourhood magnetic field which gives rise to an electric current of opposite direction. These induced electric and magnetic fields as well as the electric flows produced by them represent components of the driving forces of the transport of ions.

As the electric field is considered to be the factor regulating the membrane function as well as the concentration of ions in the membrane and its proximity [5—10], it is convenient to use the electric field for studying the transport of ions through membranes as well as the influence of the membranes themselves on this transport. The possibility of influencing the polarized membrane by an external electric field of a known intensity and the study of conductivity properties of this membrane provide access to the aim of this paper.

Experimental

The influence of external electric field on the transport of ions through porous membranes was investigated with an equipment containing the system of two pairs of the Ag/AgCl electrodes [8, 11, 12]. The external constant unidirectional (positive or negative) voltage (U/mV = 5, 10, 20, 30, 40, 50, 60, 80, and 100) was applied to each concentration difference by means of one pair of electrodes. The junction between solutions of different concentration of ions consisted of a synthetic porous nitrocellulosic membrane Synpor 9 or 10 (size of pores 0.17 μm and 0.12 μm) which had the properties of electric insulant [8]. The combinations of the used concentration differences for measuring the transmembrane potential, ohmic resistance, and ionic current are given in Table 1. The measurements were carried out at room temperature (20 °C).

Table 1

The applied concentrations at the outside (c_0) and inside (c_i) of the membrane in the measurement of the changes of E_T (transmembrane potential) and R (ohmic resistance)

K^+	Na^+	Ca^{2+}	Mg^{2+}
c_i/(mmol dm^{-3}): constant values			
2.55	4.35	2.50	4.11
c_0/(mmol dm^{-3}): changing values			
5.11	8.70	4.98	8.22
12.78	21.75	12.47	20.55
25.57	43.50	24.95	41.12
38.36	65.20	36.93	61.10
51.15	86.90	48.90	82.24
76.73	130.48	74.85	123.36
102.30	173.98	99.80	164.47
127.87	217.47	124.75	205.59

In order to estimate the influence of the applied electric field on the transport of ions through the membrane, the electric polarization $\boldsymbol{P}$ and conductivity G of the membrane were determined under different experimental conditions. Both quantities were determined from the measured values of intensity of the electric current I, transmembrane potential E, and time t for which the current I flowed through membrane of the width d. For this determination the following expression was used

$$\boldsymbol{P} = \varkappa \mathscr{E} \qquad G = \frac{I}{E}$$

where $\mathscr{E}$ is the intensity of electric field (E/d), the electric susceptibility $\varkappa$ is given by the expression $(\varepsilon_r - 1)/4\pi$, the absolute permittivity ε is equal to $4\pi dC/S$ (S is area of the membrane functioning as a condenser and the electric capacity C is equal to $(It)/E$).

Results and discussion

Fig. 1 illustrates the differences of the effect of external electric field at a given concentration gradient (only the varying concentration c_0 is given in figures; the concentration c_i is constant and essentially smaller than c_0). The thick dashed line starting from the point $E_0 = 0$ shows the change of transmembrane poten-

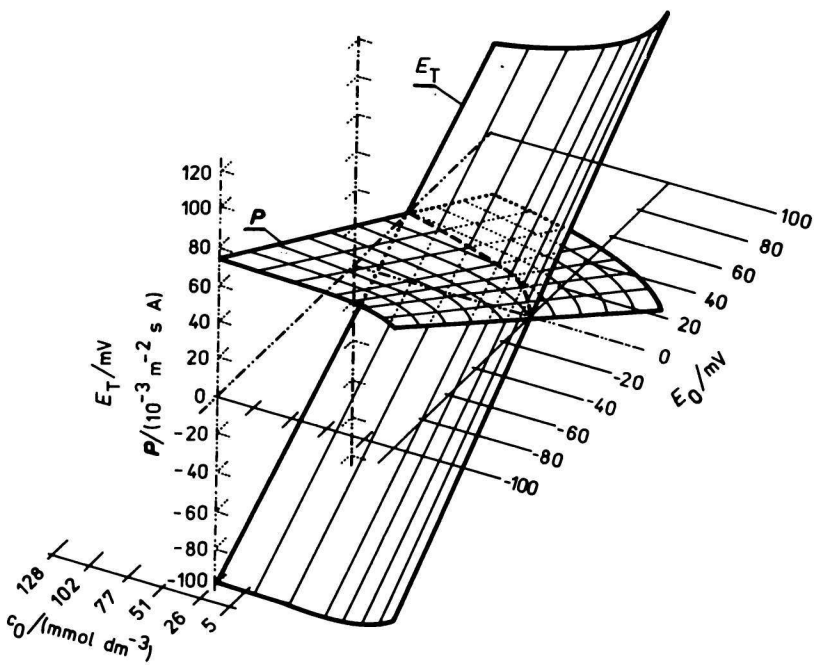

Fig. 1. Variation of intensity of the resulting electric field E_T and polarization $\boldsymbol{P}$ with the applied external electric field and external concentration of K^+ ions. The dashed line represents the conditions under which these two factors intersect themselves (temperature 20 °C).

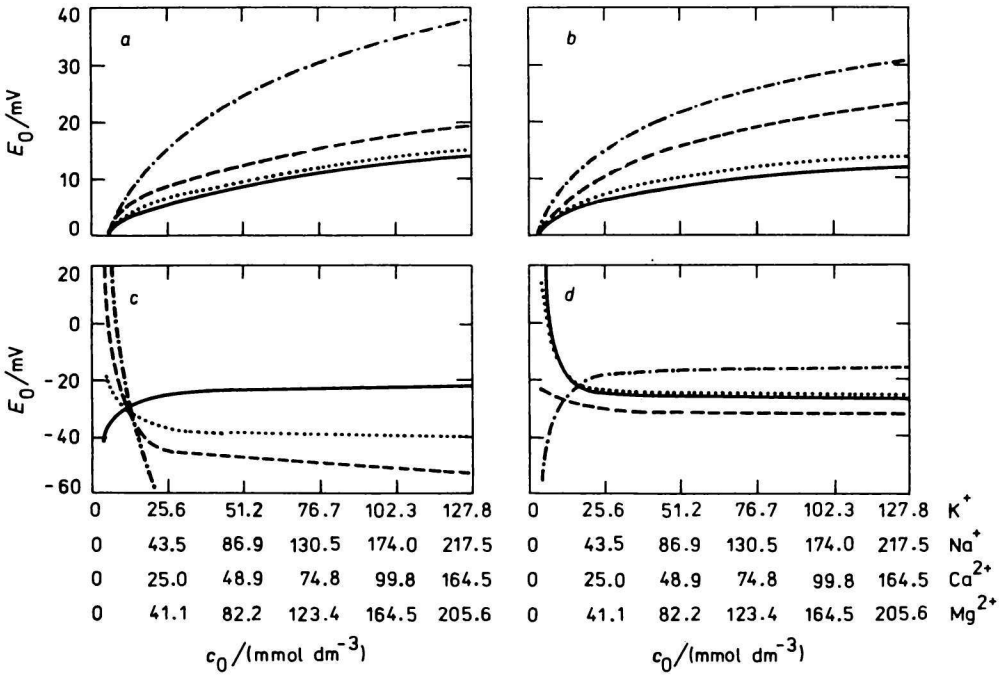

Fig. 2. Boundary of polarization reversal of the resulting electric field E_T (pore size 0.12 μm (*a*), pore size 0.17 μm (*b*)), flow of ions I_i (pore size 0.12 μm (*c*), pore size 0.17 μm (*d*)) as a function of the applied voltage E_0 and concentration gradient.
—·—· K^+; ——— Na^+; ····· Ca^{2+}; ——— Mg^{2+}.

tial E_T when the applied external voltage $E_0 = 0$ and E_T depends only on concentration gradient. The boundaries of the inversion of polarity of transmembrane potential and electric polarization as a function of concentration gradient and voltage of the applied electric field are represented in Fig. 2. We may state that the size of pores of membrane has influence on the inversion of polarity of transmembrane potential and especially on the change of direction of the flow of ions.

The Synpor membranes (in contrast to the biological ones) do not contain any polar molecules [8]. Therefore they can hold only induced dipoles and are liable to inversion of polarity by the effect of external electric field. The determined vector of polarization ***P*** (Fig. 1) confirms this statement. If we apply the external electric field to an already polarized membrane and membrane—solution boundary, the resulting polarization indicates the character of the forces causing the transport of ions through a membrane and the part of the membrane in this process. Figs. 1 and 2 show that the value of polarization depends not only on the external electric field but also on the value of concentration gradient.

It results that the major forces causing the transport of ions are electric forces. This fact is demonstrated by the dependence of membrane conductance on the concentration gradient of electrolyte and applied electric field (Figs. 3 and 4). The membrane conductance significantly decreases by the effect of negative electric field. For a small concentration gradient and strong negative electric field, the conductance is almost equal to zero. The conductance also decreases by the effect of positive electric field, but this decrease is considerably dependent on the magnitude of concentration gradient of the pertinent cations. The relationships involving conductance demonstrate that the membrane permeability significantly depends on size of the transported ions as well as on size of the solvation sphere of these ions and size of the membrane pores.

The dependence of conductance of the membrane on size of the pores is demonstrated by Figs. 3 and 4 where pictures *a*, *b*, *c*, and *d* describe conductance of the membrane for potassium, sodium, calcium, and magnesium ions, respectively. The differences in membrane conductance due to different size of the pores are also represented in these figures (Fig. 3 — size of pores 0.12 μm, Fig. 4 — size of pores 0.17 μm).

The conductance of the membrane for Mg^{2+} ions with pore size of 0.12 μm and the conductance of the membrane for K^+ ions with pore size of 0.17 μm are remarkable. In the first case, the external negative or positive voltage significantly affects the conductance of the membrane for Mg^{2+} ions when compared with the conductance of other cations at equal or still larger pores. In the second case, the conductance of the membrane for K^+ ions is very small not only for the negative field but also for small voltage of the positive external field. The increase in the conductance of the membrane for K^+ ions by the effect of positive electric field of voltage exceeding 10 mV which is proportional to the increase in concentration gradient is interesting. Furthermore, the results show that the membrane conductance for both sizes of pores and bivalent cations is smaller than for univalent cations except for the conductance of the membrane for K^+ ions which has been already mentioned.

The combed (in Figs. dotted) curves ought to describe the membrane conductance as a function of pore size when an external electric field is not in operation and the transport ought to proceed only owing to the forces of concentration gradient of electrolyte. However, it is not the case.

It is obvious from Figs. 3 and 4 that the effect of a small electric field exists and this effect increases with concentration gradient. This increase is different for K^+, Na^+, Ca^{2+}, and Mg^{2+} ions and different sizes of pores. In ideal case, this combed line should go through the wall of the space (G — conductance, c — concentration gradient). The cause of the shift in optimum membrane conductance to the conditions under which the membrane polarized by the electric field of the concentration gradient of electrolyte comes into domain of

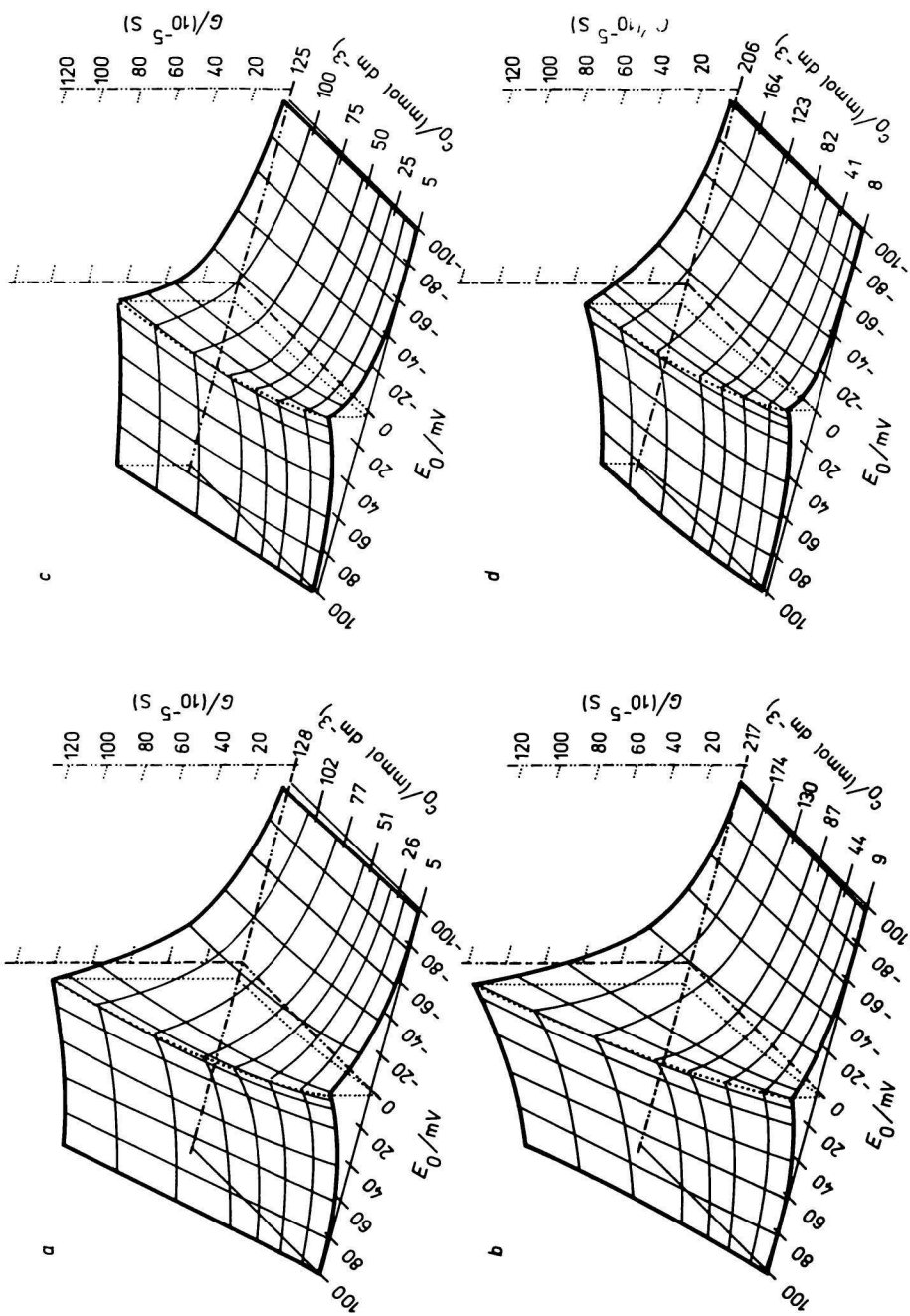

Fig. 3. Variation of conductance G of membranes (pore size 0.12 μm) with concentration gradient and voltage of the applied electric field E_0. (The conductance of the membrane for K^+ (*a*), Na^+ (*b*), Ca^{2+} (*c*), and Mg^{2+} (*d*) ions.)

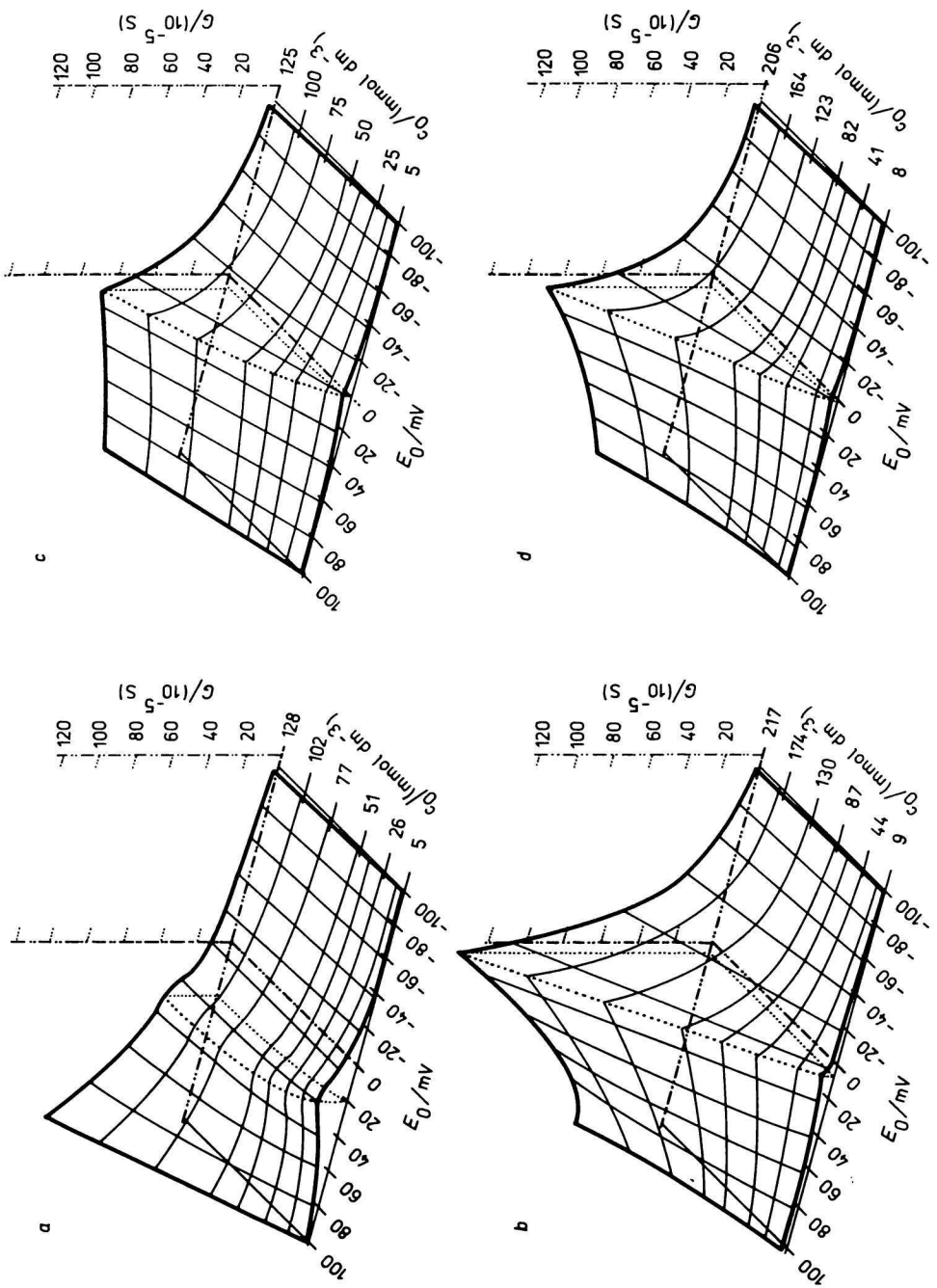

Fig. 4. Variation of conductance G of membranes (pore size 0.17 μm) with concentration gradient and voltage of the applied electric field E_0. (The conductance of the membrane for K^+ (*a*), Na^+ (*b*), Ca^{2+} (*c*), and Mg^{2+} (*d*) ions.)

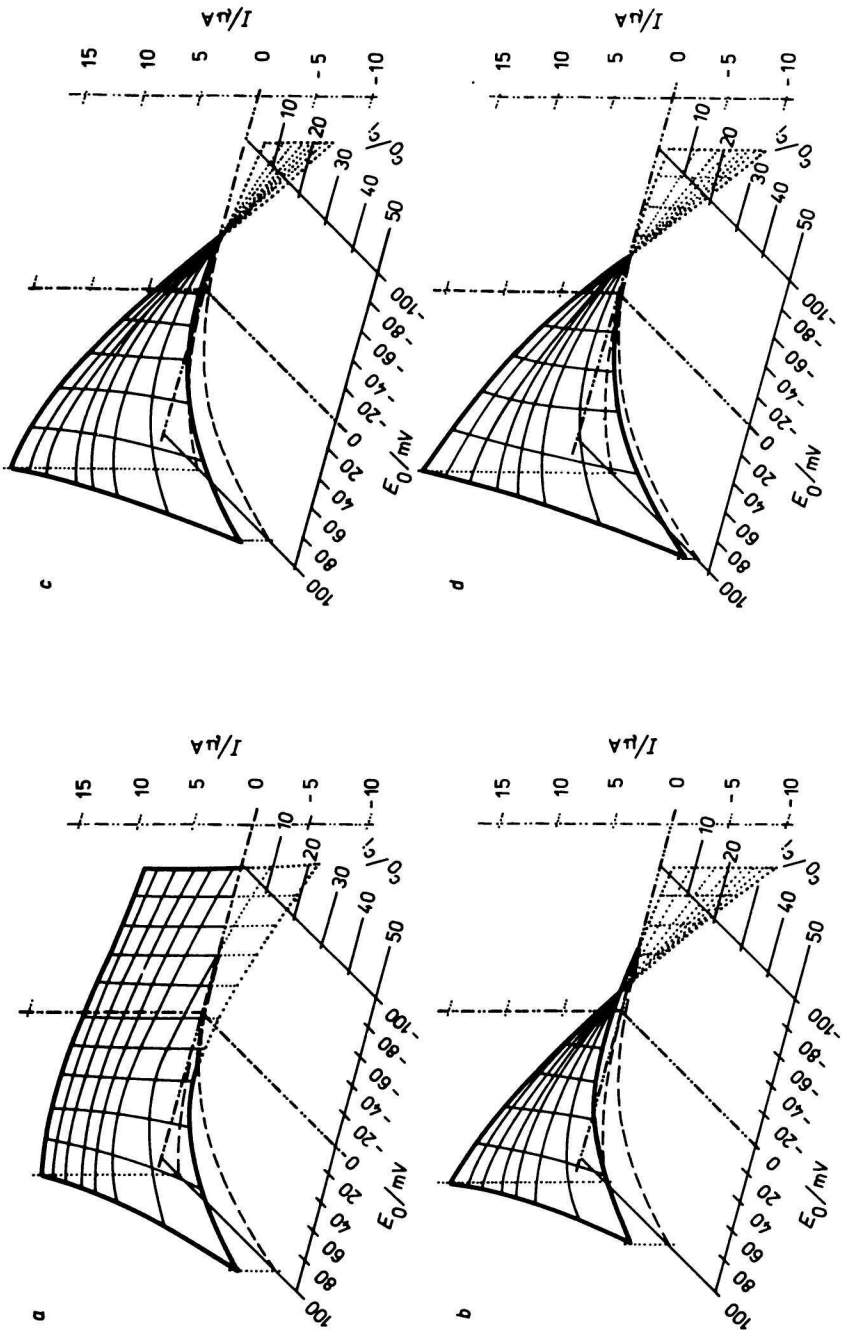

Fig. 5. Variation of ionic current I with concentration gradient c_0/c_i (external concentration: internal concentration) and voltage of the applied electric field E_0 (pore size 0.17 μm). (Potassium (*a*), sodium (*b*), calcium (*c*), and magnesium (*d*) ionic current.)

the positive external electric field consists in the fact that the membrane behaves as a condenser with electric charge of such polarity that it prevents the passage of ions through the membrane and by the effect of the external positive electric field the ways are unblocked for the transport of ions. The curves illustrate the specificity of membrane conductance with respect to individual cations.

The influence of the applied electric field on magnitude and direction of the ionic current is shown in Fig. 5 where the dependence of the ionic current I on voltage of the applied electric field E_0 and concentration gradient c_0/c is represented.

The dependence of the potassium ionic current I on E_0 and c_0/c_i clears up the disparity in the conductance of the membrane for K^+ ions. Only a small part of this current is negative (dotted part of curves). As for the sodium, calcium, and magnesium ionic current, the joining line of the points (thick dashed line) in which the values of ionic currents become negative is considerably shorter than for the potassium current and the reversal from positive values (full lines) to negative values (dotted lines) is more distinct.

The results of this study evidence the presence of polarizable particles in the system, their participation in transport, the role of the membrane in transport of ions and the fact that the electric field is the regulating factor of membrane function.

References

1. Sollner, K., *J. Macromol. Sci., Chem. A3*, 1 (1969).
2. Zimmermann, U., Pilwat, G., Beckers, F., and Riemann, F., *Bioelectrochem. Bioenerg. 3*, 58 (1976).
3. Zimmermann, U., *Biochim. Biophys. Acta 694*, 227 (1982).
4. Schwarz, G., *J. Membrane Biol. 43*, 127 (1978).
5. Forsyth, P. A., Marcelja, S., Mitchell, D. J., and Ninham, B. W., *Biochim. Biophys. Acta 469*, 335 (1977).
6. Glaser, R., Bernhardt, I., and Donath, E., *J. Electroanal. Chem. 116*, 281 (1980).
7. Kennedy, S. J., *J. Membrane Biol. 42*, 265 (1978).
8. Michalov, J., *Chem. Papers 42*, 559 (1988).
9. Pethig, R., *Dielectric and Electronic Properties of Biological Materials*. J. Wiley and Sons, Chichester—New York, 1979.
10. Reinhart, H., Gaestel, M., and Glaser, R., *J. Theor. Biol. 96*, 211 (1982).
11. Bureš, J., Petráň, M., and Zachar, J., *Electrophysiological Methods in Biological Research*. Academia, Prague, 1967.
12. Lakshminarayanaiah, N., *Membrane Electrodes*. Academic Press, New York, 1976.

Translated by R. Domanský