Permeability of porous membrane

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The permeability of porous membrane is determined by the size of pores, membrane structure, and magnitude and character of driving forces. The value of ionic flow is predominantly governed by ionic radius and hydration radius of ions. The gradients of electric potential, osmotic as well as hydrostatic pressure, and temperature work as driving forces. The permeability with respect to ions decreases with increasing diameter of membrane pores because of increasing osmotic flow of solute.

Проницаемость пористой мембраны определяется размером пор, строением мембраны, величиной и характером движущих сил. Величина ионного потока зависит, прежде всего, от ионного радиуса и гидратационного радиуса ионов. Движущими силами ионного потока являются градиенты электрического потенциала, осмотического и гидростатического давления и температуры. С увеличением диаметра пор мембраны ее проницаемость для ионов понижается вследствие возрастания осмотического давления растворенного вещества.

The permeability properties of porous membranes may be characterized by membrane potential, rate of electroosmosis [1], and ionic current through membrane. The value of transmembrane potential E_T as well as the ionic current through porous membrane may be measured by the method described in papers [2, 3]. The coefficient of permeability P_j characterizing the rate of ionic permeation through porous membrane may be determined by using the expression derived from the Goldman equation

$$P_j = G_j \frac{RT}{z_j^2 F^2} \frac{\exp(-z_j F E_T / RT) - 1}{[c_j]_0 - [c_j]_i \exp(-z_j F E_T / RT)} \qquad (1)$$

where z_j, F, R, T, G_j, $[c_j]_0$, $[c_j]_i$ are charge number, Faraday constant, universal gas constant, absolute temperature, electric conductivity of membrane, concentration of ions on the external side of membrane, and concentration of ions on the internal side of membrane, respectively.

The functioning of selective membranes is to be elucidated by investigating the changes in electric conductivity and coefficient of permeability P_j. That may be achieved by applying a known physiological stimulator to the system solution

—membrane—solution. An electric field of known intensity is the most convenient stimulator of this kind. The problem of electric conductivity of porous membranes was the topic of our preceding investigations [3]. This paper is concerned with permeability properties of these membranes.

Experimental

The permeability properties of porous membrane were investigated in an equipment containing two pairs of the Ag/AgCl electrodes [2—4] by using the method described in preceding paper [3]. We used synthetic nitrocellulose membranes Synpor 9 and 10 (size of pores (0.17 ± 0.03) μm and (0.12 ± 0.02) μm, respectively; catalogue of the producer Barvy a laky, Uhřiněves). The permeability of porous membrane was appreciated by means of the coefficient of permeability calculated from eqn (1) for the measured transmembrane potential E_T and the ionic current at given concentration differences $[c_j]_0 - [c_j]_i$ and applied external electric voltage E_0.

Results and discussion

The results presented in Figs. 1 and 2 show that the permeability of porous membrane proportionally increases for different sizes of pores with the growth of concentration difference and negative voltage applied to the system solution—membrane—solution. At a constant concentration gradient and applied negative or positive voltage, the permeability of membranes with larger diameter of pores is smaller than that of membranes with smaller diameter of pores.

If we separately appreciate the permeability (values of P_j) for a membrane with pore size of 0.12 μm and maximum applied negative voltage, we can observe that it corresponds to the known sequence of the values of diffusion coefficient, hydration entropy, enthalpy, Gibbs energy, Helmholtz energy, and mole conductance (Table 1). This observation confirms the fact that potassium ions pass the membrane more rapidly than the sodium ions and much more rapidly than those of calcium or magnesium. On the other hand, for a membrane with pore size of 0.17 μm the values of P_j do not correspond to the sequence of the values of diffusion coefficient but exhibit similar character as the sequence of the values of ionic radius (Table 1). In this case, the ions of calcium display higher permeability than the ions of sodium. We are going to interpret this observation later on.

As all these processes take place in aqueous solutions, we assume that the solvation properties of individual cations play a significant role. These properties may be described by hydration radius and pertinent thermodynamic potentials of the investigated cations, such as hydration entropy, enthalpy, Gibbs

energy, and Helmholtz energy, *i.e.* by the quantities which are related with the above-mentioned forces. The series of inequalities in Table 1 give a certain information. Nevertheless, the interactions between the water molecules bound to cations or anions and other water molecules in volume and pores of membrane are not known.

The great ability of potassium ions to pass porous membranes is consistent with the fact that the potassium ion exhibits the greatest mobility, hydration entropy, enthalpy, and Gibbs energy and the smallest hydration radius of all investigated ions. On the other hand, firstly, the sodium ion has the largest hydration radius and smallest relative atomic mass and, secondly, it exhibits smaller hydration entropy, enthalpy, Gibbs energy and mole conductance when compared with the potassium ion. It results from these facts that the sodium ion manifests the lowest ionic mobility (Table 1).

The lowest permeation ability of magnesium ions consists in their relatively large hydration radius, small hydration entropy, enthalpy, Gibbs energy, and mole conductance. Their diffusion ability is also small in spite of the fact that the ionic mobility is relatively high and ionic radius very small. The order of calcium ions is due to equal circumstances..

This interpretation of permeability properties of ions as well as membranes is in line with the existence of the electroosmotic phenomenon in this system.

The results presented in Figs. 1 and 2 show that the permeability of potassium ions is greater for a membrane with smaller pores than for membranes with

Table 1

Confrontation of the physical quantities characterizing K^+, Na^+, Ca^{2+}, and Mg^{2+} ions with the permeability coefficient of porous membranes with different pore diameters for K^+, Na^+, Ca^{2+}, and Mg^{2+} ions

Quantity		Sequence of magnitudes	Ref.
Ionic radius		$K^+ > Ca^{2+} > Na^+ > Mg^{2+}$	[5]
Hydration ionic radius		$Na^+ > Mg^{2+} > Ca^{2+} > K^+$	[6]
Ionic mobility		$K^+ > Mg^{2+} > Ca^{2+} > Na^+$	[7]
Mole conductance		$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$	[8]
Diffusion coefficient		$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$	[7]
$S_{hydr.}$		$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$	[9, 10]
$H_{hydr.}$		$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$	[9, 10]
$G_{hydr.}$		$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$	[9, 10]
Relative atomic mass		$Ca > K > Mg > Na$	
	Diameter of pores		
Permeability	$0.12 \ \mu m$	$P(K^+) \gg \quad > P(Na^+) > P(Ca^{2+}) > P(Mg^{2+})$	
coefficient	$0.17 \ \mu m$	$P(K^+) \gg P(Ca^{2+}) > P(Na^+) > P(Mg^{2+})$	

a

b
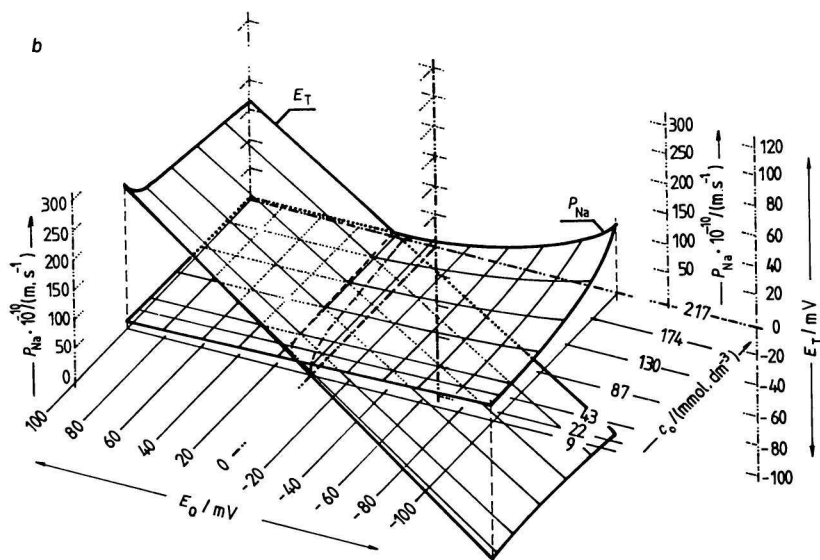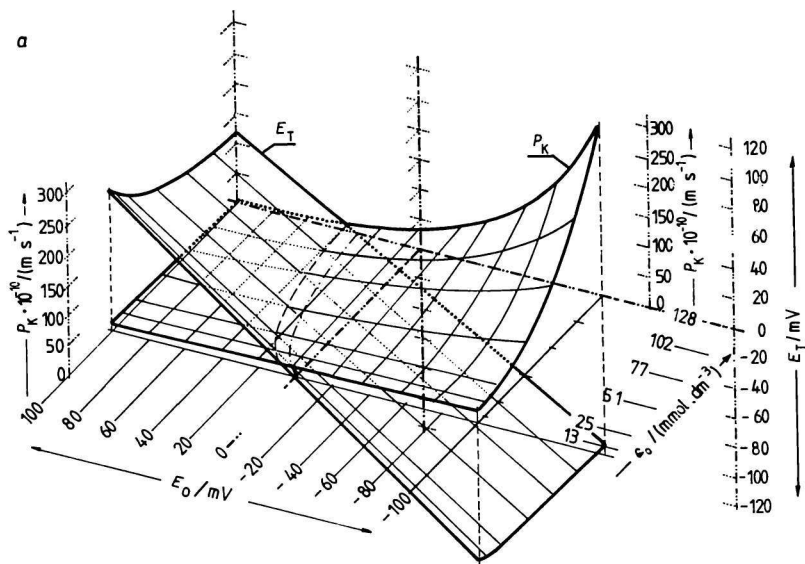
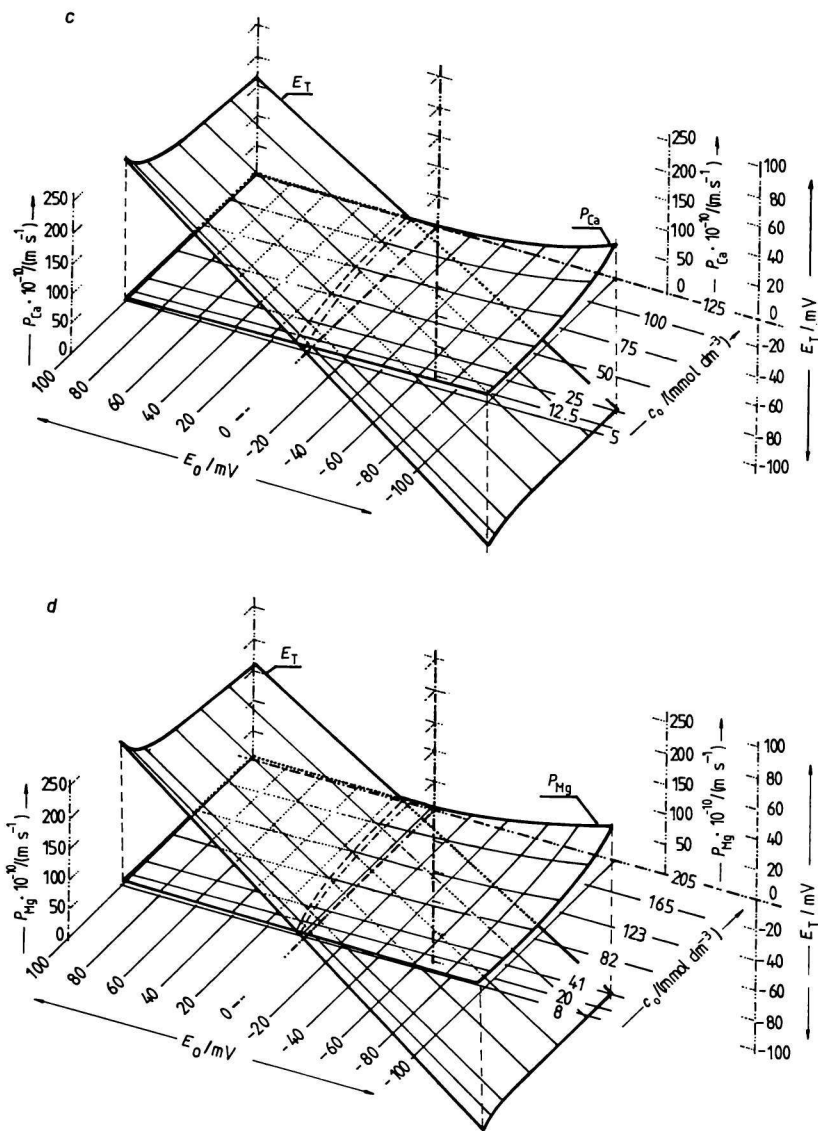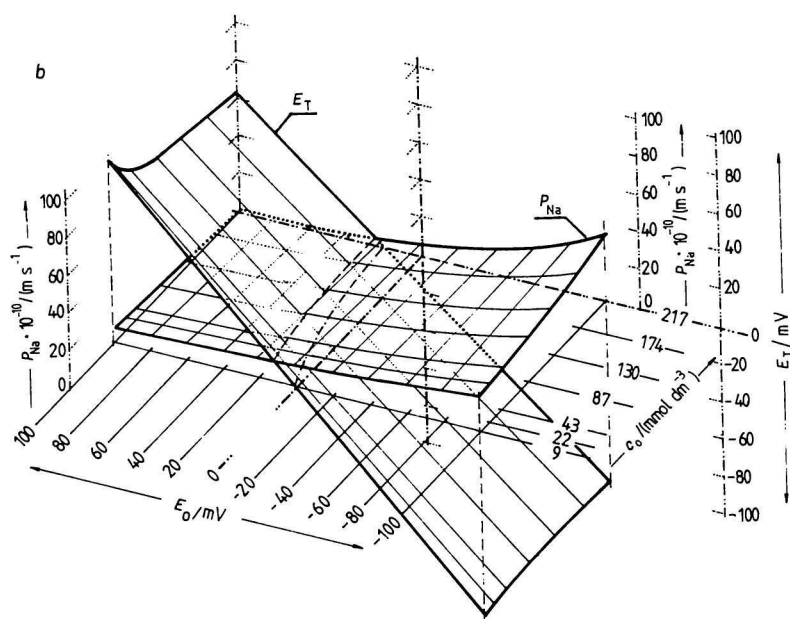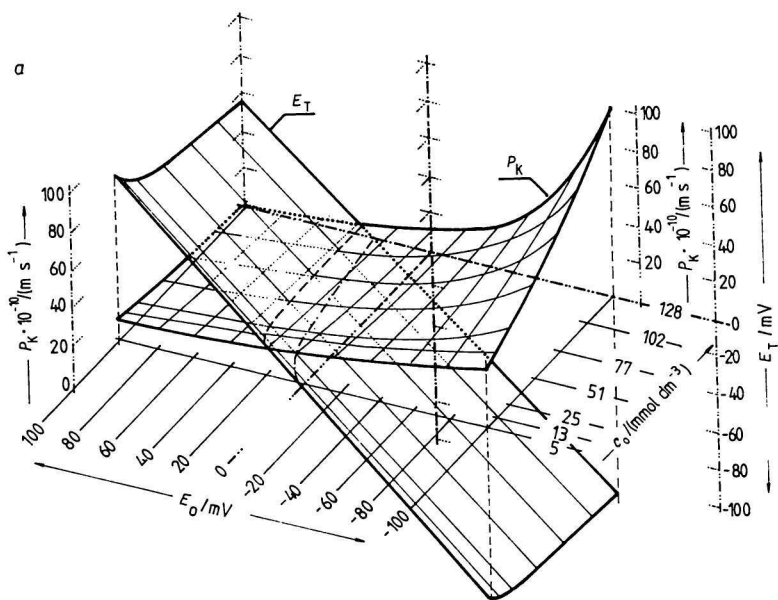*Fig. 1.* Variation of permeability coefficient P of synthetic porous membranes (pore diameter 0.12 µm) and overall transmembrane potential E_T with concentration gradient in membrane c_0 and applied electric voltage E_0. Membrane permeability for K^+ (*a*); Na^+ (*b*); Ca^{2+} (*c*); Mg^{2+} (*d*) ions. c_0 — concentration of pertinent ions in compartment corresponding to external medium of membrane (c_i — concentration of pertinent ions in compartment corresponding to internal medium of membrane was constant and very small with respect to external concentration; therefore only c_0 is denoted.)
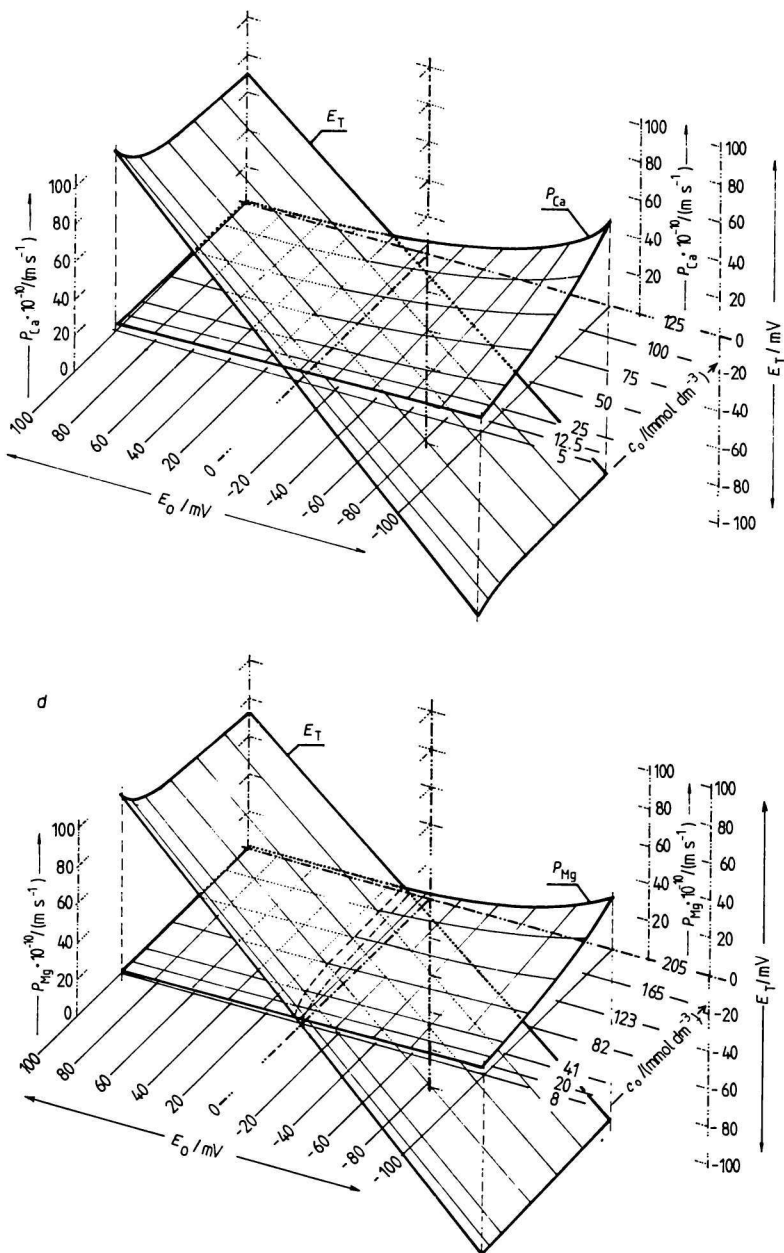
Fig. 2. Varia:ion of permeability coefficient P of synthetic porous membranes (pore diameter 0.17 μm) and overall transmembrane potential E_T with concentration gradient in membrane and applied electric voltage E_0. Membrane permeability for K^+ (*a*); Na^+ (*b*); Ca^{2+} (*c*); Mg^{2+} (*d*) ions. Other data as in Fig. 1.

larger pores. That is likely to be due to great differences between the values of hydration radius and ionic mobility which may be caused by the energy value of the pertinent ion with respect to water molecules [11, 12]. From the viewpoint of ionic mobility, that may be in connection with the friction forces in pores operating among the potassium ions and water molecules. Moreover, we cannot neglect the interaction of the potassium ions with possibly existing electric charges in membrane pores as well as the electroosmotic flow of water proceeding against the ionic flow which is greater for the pores of diameter 0.17 μm than for the pores of 0.12 μm [13]. Similar causes may play a part in the permeation of sodium and calcium ions through a membrane with larger pores. The series of inequalities P (for pore diameter of membrane 0.12 μm) confirms the fact that potassium ions in aqueous solution are more movable than the sodium ions.

Irrespective of increasing concentration gradient, the values of the permeability coefficient decrease to a minimum if a positive electric voltage E_0 is applied. It means that the applied increasing positive electric voltage prevents the cations from passing the membrane.

The origin of this phenomenon consists in polarization of the membrane [13]. A membrane is able to function as a plate condenser [3, 14, 15] that can, as known, regulate the ionic current. An increase in the external positive voltage applied to the system gives rise to a voltage barrier which gradually reduces the gradient of electrochemical potential functioning as driving force of the ions going through membrane and thus prevents the cations from passing the membrane pores. Provided an external negative voltage is applied, the overall measured transmembrane potential E_T increases and the ionic current decreases, which is fully confirmed in papers [2, 3].

The response to the question how the selective filters distinguish the ions able to pass a canal is related, according to [15], with the group of "mechanical" factors which result from chemical medium. On the basis of the results presented in papers [2, 3] and in Figs. 1 and 2, we may state that it has more to do with electrochemical factors than the mechanical ones. The essence of permeability is mainly governed by the choice of ions and the ability of ions to get over the energetic barrier in the course of going through membrane [4, 14].

All these considerations and facts suggest that a door phenomenon is involved. According to [14], the door flow itself represents the slow and nonlinear component of capacity current. A condenser with dielectric loss is not charged instantaneously when a voltage is applied and the current cannot go through membrane before a certain time after generation of a stationary voltage. That also results from the comparison of the values of the Nernst potential, transmembrane potential E_T, and permeability coefficient of membranes with smaller pore diameter for all four investigated ions [2].

It ensues from the presented analysis and the obtained results that some of the quantities characterizing the energy of passing ions, water molecules, and membrane or changes in this energy play a decisive role in both cases.

We may come to equal conclusion if we appreciate our results merely from the view-point of the thermodynamics of irreversible processes. By applying an external negative electric voltage, a transfer of molecules of solvent and ions sets in. This transfer can be measured by means of volume flow J_V and electric current I. Provided the gradient of hydrostatic pressure and temperature in the system is equal to zero, only the gradient of osmotic pressure Π and electric potential E, i.e. the dissipation function $\Phi = J_V \nabla \Pi + I \nabla E$ is in operation. Then the volume flow J_V is proportional to the gradient of osmotic pressure at the boundary of concentrations $(\nabla \Pi = RT \nabla c)$, i.e. to the change in concentration gradient while the current flow is proportional to the gradient of electric potential, i.e.

$$J_V = L_1 \nabla \Pi, \qquad I = L_2 \nabla E \qquad (2)$$

where L_1 and L_2 are filtration coefficient and electric conductivity of membrane, respectively [16].

The values of ionic radius, hydration ionic radius, hydration entropy, enthalpy, Helmholtz energy, Gibbs energy [17] as well as concentration ($\equiv$ osmotic) gradient, temperature gradient, gradient of hydrostatic pressure and (in the presence of electrolytes) gradient of electric potential play a significant part in the transport of ions and water molecules. The permeability of porous membrane, too, depends on these quantities.

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