

The use of electric current for enhancing the efficiency of pressure-driven membrane processes

Yu. I. Dytnerskii

Mendeleev Institute of Chemical Technology, Moscow, USSR

Abstract - The effect of direct, alternating and asymmetric electric current on the technological characteristics of reverse osmosis, ultrafiltration and microfiltration have been investigated. The properties of the ion separation were determined and the ion transfer through a membrane as a result of combined pressure and electric potential gradients was described.

INTRODUCTION

The transport of substances through a membrane and its separation properties change significantly when pressure-driven membrane processes are carried out in an electric field (ref. 1-5). The associated effects depend on the system being separated, the membrane structure, the nature of the electric field (d.c. or a.c.) and on other factors*.

In reverse osmosis the ions are transferred through the membrane in practically equivalent amounts (ref. 1). This means that it is extremely difficult to separate multicomponent electrolyte mixtures by means of this technique. However, such problems are often encountered in industrial practice (for instance, in the isolation of valuable components from naturally occurring or waste water, in the production of high purity materials, etc.).

EFFECT OF ELECTRIC CURRENT ON PRESSURE-DRIVEN MEMBRANE PROCESSES

It has been shown experimentally (ref. 1-5) that such problems can be solved, if a constant electric current is passed through the system solution undergoing separation/reverse osmosis membrane (Fig. 1). We employed various types of membranes (acetyl cellulose, ethyl cellulose, nitrocellulose, polyacrylonitrile) and aqueous solutions of NaCl, KCl, LiCl, CsCl, CaCl₂, K₂SO₄, CaSO₄, etc., and their mixtures. It was established that, when a d.c. voltage is

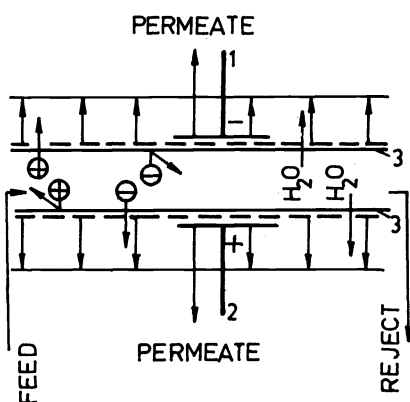


Fig. 1. Schematic diagram of electro-osmotic filtration:
1,2 - porous electrodes,
3 - membrane.

*Yu. V. Karlin, E. P. Morgunova and G. D. Sukhov participated in the investigation.

applied to a reverse-osmosis membrane, the basic characteristics of ion transfer through the membrane are changed: the transfer rate increases for some ions and decreases for others. This produces a drastic increase in the separation factor - by one, two, or even more orders of magnitude.

The process resulting from the joint application of pressure and electric potential gradients is called electro-osmotic filtration (EOF). In EOF, cations passing through the membrane at the cathode are removed in the permeate in the form of bases, and anions that permeate through the anodic membrane are removed as acids. The ions held back by the membranes accumulate in the initial solution. If the system to be separated contains several cations or anions, the separation degree can be controlled by changing the current density (see Fig. 2): an increase in the current density sharply reduces the selectivity of the membrane with respect to Na^+ and K^+ cations (since it raises the rate of their transfer through the membrane), whereas the selectivity decreases only slightly for Ca^{2+} ions; up to a current density

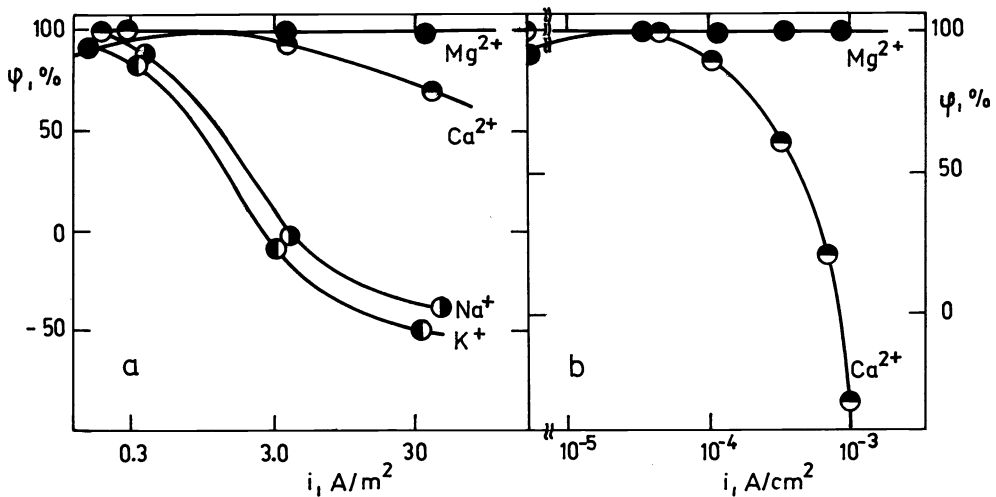


Fig. 2. Cation selectivity of the cathodic membrane versus current density (MGA-100 acetate cellulose membrane, $P=3$ MPa, $t=20\pm 3^\circ\text{C}$). Aqueous solutions: (a) $\text{KCl}+\text{NaCl}+\text{CaCl}_2+\text{MgCl}_2$ and (b) $\text{CaCl}_2+\text{MgCl}_2$.

of about $3\text{A}/\text{m}^2$, the magnitude of ϕ remains practically constant, while for Mg^{2+} ions it even increases. Here, a definite relation is observed between selectivity (or separation degree) and the values of the ionic heat of hydration - the greater the difference in the hydration heats, the higher the degree of separation of the ions (see Fig. 3).

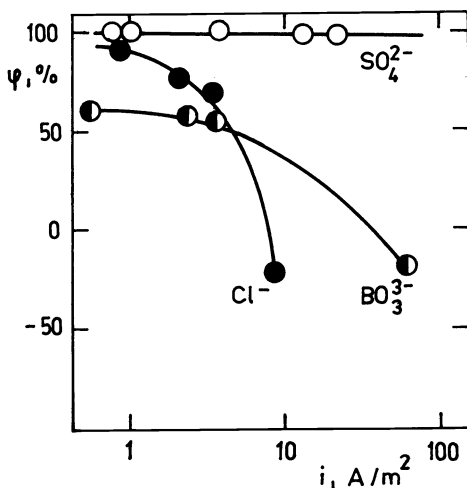


Fig. 3. Anode-membrane anion selectivity versus current density (MGA-100 membrane, $P=3$ MPa, $t=20\pm 3^\circ\text{C}$).

In addition to ions of the original solution, in all the EOF experiments H^+ (or OH^-) ions produced at the electrodes by electrolysis also were transferred through the membranes. The flow of H^+ (OH^-) ions through the membranes occurred from the respective permeate to the original solution, counter to the flow of the solvent, and hence it is called "ion counterflow". The ion counterflows increase with the current density (5). Its fraction in the electric current transfer through a membrane amounts to 60 or 70 percent. The ion counterflows change the pH value of the original solution in the vicinity of the membranes: the solution becomes more alkaline near the cathode membrane and more acidic near that at the anode. Alkalization of the solution near the cathode leads to precipitation of metal hydroxides (tending to hydrolysis) on this membrane.

In addition to these features of the EOF process, it should be mentioned that the electric current passing through a membrane does not alter its water permeability over the investigated range of ionic strengths of the solutions (0.01-0.04 g-ion/l), and current densities (0-50 A/m²).

An investigation of the influence of external factors (pressure, hydrodynamic conditions, temperature, concentration, etc.) on the EOF process showed that its efficiency depends on them in the same way as the selectivity of reverse osmosis carried out under identical conditions. It follows that the conditions under which EOF is possible are directly related to the reverse-osmotic flow of water through the pores of the reverse-osmosis membranes to which the electric field is applied. Hence, EOF can only be carried out at pressures that exceed the osmotic pressure of the solution.

Similarly to reverse osmosis, electro-osmotic filtration is intimately associated with surface and electrocapillary phenomena and is a very complex process. It should be noted that the study of EOF is of interest for the investigation of processes in biological membranes.

The transfer of ions and molecules through the membrane is also significantly altered when an a.c. electric field is imposed on an electro-osmotic system (3,5). Thus, for example, the ionic selectivity of a reverse-osmosis membrane is reduced at low frequencies; the lower the frequency and the higher the current, the greater the reduction (see Fig. 4). The selectivity of the membrane with respect to saccharose remains unchanged. Thus, it becomes possible to control the separation process, for instance, the separation of a non-electrolyte from an electrolyte.

When the current imposed on the process has both an a.c. and a d.c. component (asymmetric current), the separation is even more efficient. Thus, in separating a binary KCl + LiCl solution, the separation factor K_S increases markedly at a frequency of about 500 Hz (see Fig. 5), compared with its value when there is no a.c. component ($K_S = (C_{pi}/C_{bi})/(C_{pj}/C_{bj})$, where C_{pi} and C_{pj} are the concentrations of i and j ions in the permeate, respectively, and C_{bi} and C_{bj} are the respective concentrations of ions in the original solution). At other frequencies no such drastic change in K_S was observed. For the a.c. component of the asymmetric current, the system evidently has an inherent frequency interval in which the K_S value is enhanced.

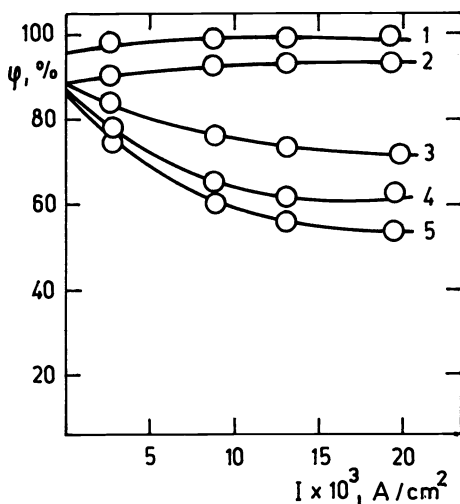


Fig. 4. The reverse-osmotic membrane selectivity vs. the frequency and magnitude of the a.c. current (MGA-100 membrane, $P=3.0$ MPa, saccharose + NaCl solution). 1 saccharose; 2-5 NaCl at $f=2000, 500, 50$ and 20 Hz, respectively.

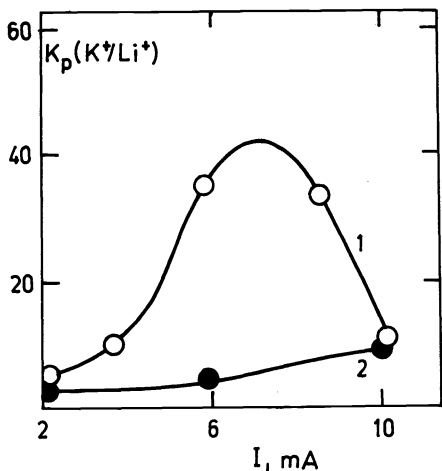


Fig. 5. The separation factor of the cathode membrane vs. the d.c. component of an $f=500$ Hz (1) asymmetric a.c. current. (1) and d.c. current strength (2) for a 0.005 M LiCl+KCl solution ($P=3$ MPa, MGA-100 membrane).

Ultrafiltration in an electric field has been employed in the laboratory for many years, but not yet in industrial practice, although the associated effects are very interesting. Thus, for example, the results of ref.(4) (Fig.6) indicate that in the separation of solutions of charged proteins, an increase in the current density raises the rate of protein permeation through the membrane, which is however different for different proteins. This can serve as the basis for controlling the separation and purification of proteins by varying the current density.

In the case where the particles of a system separated by microfiltration carry a charge, the efficiency of the process can be raised significantly by passing the electric current through the microfilter, using electrodes for this purpose (see Fig. 1). As follows from our experiments (Fig.11), the selectivity of the cathode membrane is enhanced, since the cationogenic surfactant ($ABDMCl^-$) contained in the original system is negatively charged and is repelled from the cathode membrane. On the other hand, the selectivity of the anode membrane is naturally decreased in this case. Hence, for such systems the membrane apparatus should be designed for either cathode or anode membranes. It should be noted that an appreciable effect can be achieved at much lower current densities in microfiltration than in reverse osmosis or ultrafiltration.

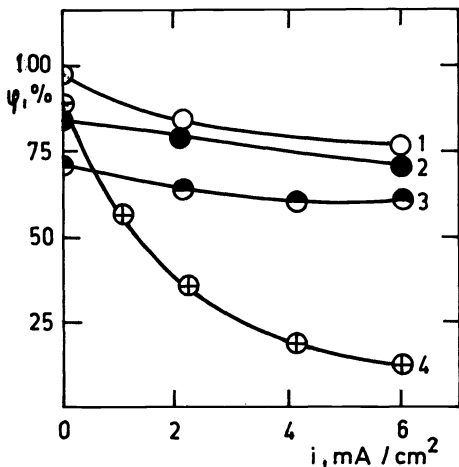


Fig. 6. Selectivity of ultrafiltration membranes vs. current density ($P=0.2$ MPa pH=6.8): (1) albumin, (2) myoglobin, and (3) cytochrome solutions; (4) trypsin inhibitor.

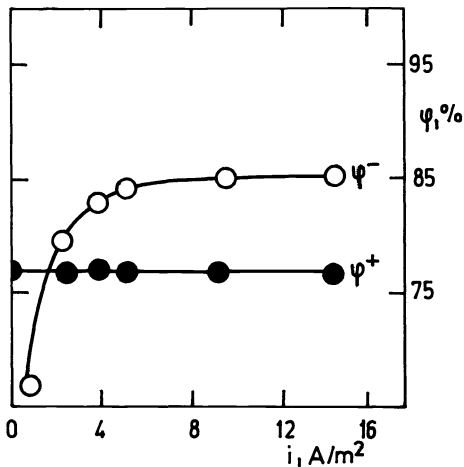


Fig. 7. Selectivity of microfiltration separation of aqueous surfactant ($ABDMCl^-$ C₁₄-C₁₇) solutions vs. current density. Surfactant concentration 0.9 g/l, MFA-MA N1 membrane, $P=0.05$ MPa, $t=20 \pm 1^\circ C$.

ION TRANSPORT THROUGH MEMBRANES IN REVERSE OSMOSIS AND ELECTRO-OSMOTIC FILTRATION (refs. 5,6)

The following basic stages of the ion transport through reverse-osmosis membranes can be distinguished: 1. ion transfer from the bulk of the original solution to the membrane surface; 2. ion transfer across the interface between the initial solution and the membrane; 3. ion transfer through the active (selective) membrane layer; 4. ion transfer in the large-pore membrane layer, and 5. ion transfer in the porous support (if there is one).

The ion transfer in stages 1, 3 and 4 represents transfer in diffusion zones adjacent to the active layer of the membrane. The determination of the ion-concentration profiles in the zones in question reduces to solving a system of equations that describe the convective electrodiffusion of ions in a layer of the electrolyte mixture solution. We assume that the solution and its components are independent of concentration and are determined by their limiting values. This approach is not entirely correct, but in some cases it yields a general description of the process by a relatively simple procedure. For this purpose, we shall also employ concentrations of the solution components instead of their activities. We will assume that the diffusion layer has finite dimensions and that the convective flow through the layer is in the direction normal to its surface and is approximately equal to the water penetrability of the membrane (m/s). A similar problem is formulated in ref. (7). The author gives the following system of equations, which must be solved to determine the ion-concentration profile in a layer:

$$j_n = C_n G - D_n (dC_n/dy) - z_n C_n D_n (d\psi/dy) \quad (1)$$

$$\sum z_n C_n = 0 \quad (2)$$

$$i = F \sum z_n j_n \quad (3)$$

Here, j_n is the flow of ions of a species n through the layer, C_n is the ion concentration, z_n and D_n are, respectively, the ion charge and diffusion coefficients, i is the current density in the layer, F is the Faraday constant, y is the coordinate normal to the surface layer, $\psi = F\phi/RT$ is the dimensionless electric potential, R is the universal gas constant, T is temperature, and G is the rate of the convective flow through the layer, equal to the water permeability of the membrane ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$).

The thickness δ_D of the diffusion layer on the original solution side of the membrane has been found as follows. The approximate Dresner equations for the laminar flow of a solution in a plane-parallel channel with suction through porous walls were employed to determine the concentration polarization, $CP = (C_{ms}/C_b) - 1$, of the membrane in reverse osmosis of a NaCl solution at various distances from the channel entrance (here, C_{ms} is the salt concentration at the membrane surface and C_b is the salt concentration in the bulk of the original solution). We arbitrarily assume the membrane selectivity to be unity. From the calculated CP values, we find the thickness of a diffusion layer that would produce a similar change in the NaCl concentration at the membrane surface. We will assume, approximately, that the thickness of the diffusion layer changes very little with the magnitude of the ion flows and also with the ion species. We employ the δ_D values thus found to plot the diffusion-layer thickness vs. the longitudinal coordinate of the channel. Graphic integration yields the average thickness $\bar{\delta}_D$ of the diffusion layer in the channel, in our experiments estimated at 130-150 μm . By this procedure, $\bar{\delta}_D$ can only be evaluated for channel regions not very far from the entrance, where the diffusion layers of the symmetrically located membranes do not yet overlap one another.

For a number of cases, the equation system (1)-(3) related to EOP of NaCl and CaCl_2 solutions and their mixtures was solved on a computer by the method of finite differences. When evaluating the ion-concentration profiles in the porous layer, we took into account the decrease in the diffusion coefficients of the ions owing to the porosity of the medium.

The calculated ion concentrations in the original solution and in permeates are the boundary conditions. Some results are presented in Fig.8. In the calculation of the ion-concentration profiles in the porous layer, at a certain point (B in Fig.8) the concentration of the OH^- or H^+ ions formed at the electrodes reaches zero, and becomes negative during further motion to the active layer. Taking into account that there are no other sources of ions, we concluded that at point B the flow of OH^- or H^+ ions from the electrode is neutralized by an equal, but opposite flow of H^+ or OH^- ions from the active layer; in evaluating the ion-concentration profiles between point B and the

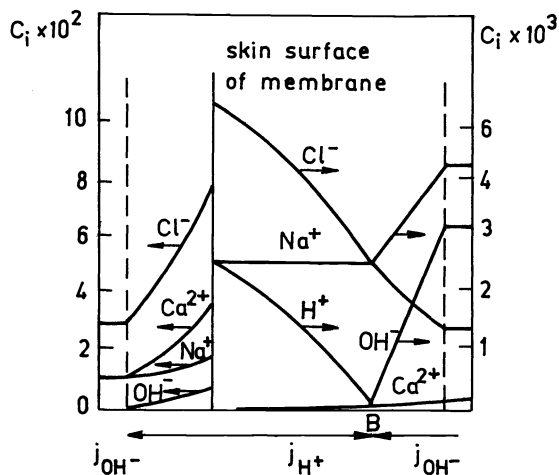


Fig. 8. Ion-concentration profiles in near-membrane layer at EOF of NaCl (0.01 M) + $CaCl_2$ (0.01 M) solution; MGA-80 membrane; $i = 20 \text{ A/m}^2$, cathodic membrane. Concentration C_i expressed in gram-ions per hour

active layer, we introduced corresponding changes in the overall pattern of the ion flows. The generation of large H^+ and OH^- ion flows in the active layer, which are equal in size and oppositely directed, can only be explained by dissociation of water in the region of the original solution/membrane interface. The dissociation may result from the following. It is known that the permeability of a reverse-osmosis membrane differs for different ions. The higher the hydration heat of an ion the more difficult its transport through the membrane (ref. 1). Hence, when separating electrolyte solutions at the interface between the original solution and the membrane, an electric potential jump appears that results in a balance between the rates of anion and cation entrance into the membrane. If an external electric field is applied, the equilibrium established is shifted, and instantaneous, high-strength electric fields arise at the original solution/membrane interface, owing to local deviations from electroneutrality of the solution. The strong electric fields give rise to dissociation of water. The H^+ and OH^- ions formed balance the deviation from electroneutrality of the solution in the membrane. When the current density and, consequently, the applied potential increase, the deviation from equilibrium also increases, and the dissociation of water becomes more intense.

The proposed explanation has a certain consequence: the active layer of a reverse-osmosis membrane is structurally nonuniform, the pores in the active layer and the hydrated ions are commensurable, and hence local deviations from electroneutrality of the solution in the pore are possible even in the absence of an applied potential, and consequently of electric current through the membrane. This means that, in principle, if the membrane permeability differs significantly for the cations and anions in the original solution, dissociation of water should occur even in the case of the usual reverse-osmotic separation. Here, the larger the difference in membrane permeability for the anions and the cations, the higher the degree of water dissociation. The pH values of the permeate measured in the reverse-osmotic separation of solutions of various metal chlorides confirm such inference (ref. 5). Hence, the known phenomenon of changes in the permeate pH is explained primarily by water dissociation at the boundary between the original solution and membrane.

We consider the ion transport across the original solution/membrane interface from positions of the capillary-filtration model (ref. 5). The concept of bound water which represents an individual phase implies that there exists an interphase boundary at the membrane surface where the properties of the water change drastically. Since the thermodynamic equilibrium at the boundary between solution and membrane is not compatible with the established fact that water is dissociated at this interface, we employ the activated complex theory to describe the ion transfer across the original solution/membrane interface. According to this theory, the flow of ions of species n across the

interphase boundary can be represented as the difference between the entering (+) and leaving (-) ion flows:

$$j_n = kC_{ib} \exp(-\vec{\Delta E}_n^*/RT) - \vec{k}C_n^* \exp(-\overleftarrow{\Delta E}_n^*/RT) \quad (4)$$

where $k = RT\vec{k}/N_A h$ and $\vec{k} = RT\overleftarrow{k}/N_A h$ are factors, R is the universal gas constant, T is temperature, N_A is the Avogadro number, h is Planck's constant, \vec{k} and \overleftarrow{k} are the transmission coefficients, C_{ibn} and C_n^* are the ion concentrations at the interphase boundary, respectively, on the solution and active-layer sides, and $\vec{\Delta E}_n^{\#}$ and $\overleftarrow{\Delta E}_n^{\#}$ are the activation energies of ion transfer across the interphase boundary. $\vec{\Delta E}_n^{\#}$ and $\overleftarrow{\Delta E}_n^{\#}$ are related to the free energy difference, ΔG_n , of the ion in the original solution and the membrane, using the Brønsted-Polanyi-Semenov relationship:

$$\begin{aligned} \vec{\Delta E}_n^{\#} &= \Delta E_{On}^{\#} + \vec{\alpha} \Delta G_n \\ \overleftarrow{\Delta E}_n^{\#} &= \Delta E_{On}^{\#} - \overleftarrow{\alpha} \Delta G_n \end{aligned} \quad (5)$$

Here, $\Delta E_{On}^{\#}$ is the activation energy of ion transfer at $\Delta G_n = 0$, $\vec{\alpha}$ and $\overleftarrow{\alpha}$ are the transfer coefficients, which in most cases are 0.5.

The change in the free energy of the ion can be represented as the sum of two terms:

$$\Delta G_n = \Delta \Delta G_{On} + z_n RT \Delta \Psi_m \quad (6)$$

Here, z_n is the ion charge, $\Delta \Psi_m = F \Delta \phi_m / RT$ is the dimensionless jump in the electric potential at the interphase boundary, F is the Faraday number, and $\Delta \Delta G_{On}$ is a change of the free energy of secondary hydration of the ion, which can be evaluated using the Born equation

$$\Delta \Delta G_{On} = \frac{(z_n e)^2 N_A}{4\pi \epsilon_0 r_{cn}} \left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon} \right) \quad (7)$$

Here, ϵ^* and ϵ are the permittivity of water in the pores of the active layer and in the original solution, respectively, and r_{cn} is the radius of the primary aquacomplex of the ion. The second term on the righthand side of Eq. (6) describes a change in the electrostatic energy of the ion associated with transport across the interphase boundary. The solvent flow through the membrane must sharply reduce the flow of ions from the membrane to the original solution ($\overleftarrow{k} \approx 0$); then the second term on the right side of Eq. (4) can be neglected. Upon substituting $\vec{\Delta E}_n^{\#}$ and $\overleftarrow{\Delta E}_n^{\#}$ from Eq. (5) into Eq. (4), we obtain the equation for the ion flow into the membrane:

$$j_n = \vec{k} \exp(-\vec{\Delta E}_{On}^{\#}/RT) \times \exp(-\Delta \Delta G_{On} \vec{\alpha}/RT) \times \exp(-z_n \vec{\alpha} \Delta \Psi) \times C_{ibn} \quad (8)$$

In principle, the proposed model of ion transport into the membrane allows the stage of ion transfer to the active layer of the membrane to be omitted, since according to Eq. (8) the ion flow into the membrane is determined exclusively by the transport conditions in the boundary layer on the original solution side of the membrane and by the transfer conditions across the original solution/membrane interface.

At present, Eq. (8) cannot be tested directly, since it is not known how ϵ^* and $\Delta \phi_m$ depend on the separation conditions. Nevertheless, it can be shown that the dependence of j_n on the interphase jump in the electric potential is indeed exponential. We now consider EOF with an externally applied sinusoidal electric field.

We neglect the supplementary membrane polarization and the change in the time-average jump, $\Delta \Psi_{Om}$, of the interphase electric potential, produced by the alternating component of the electric field, and evaluate the change $\Delta \Psi_m$, using the equation

$$\Delta \Psi_m = \Delta \Psi_{Om} + \beta F \Delta U_{\sim} / RT \sin(2\pi \nu \tau) \quad (9)$$

Here, ΔU_{\sim} and ν are, respectively, the amplitude and frequency of the alternating electric field, β is the fraction of the potential drop at the interphase boundary, and τ is time. We substitute the expression for $\Delta \Psi_m$ given by Eq. (9) into Eq. (8):

$$j_n = \bar{K} C_{ibn} \exp(-\Delta E_{on}/RT) \times \exp(\Delta \Delta G_{on} \vec{\alpha}/RT) \times \exp(-z_n \vec{\alpha} \Delta \Psi_{om}) \times \exp(-z_n \vec{\alpha} \beta F \Delta U_{\sim}/RT) \times \sin(2\pi \nu \tau) \quad (10)$$

$$j_{on} = j_{on} \times \exp(-z_n \alpha \beta F \Delta U_{\sim}/RT) \times \sin(2\pi \nu \tau) \quad (11)$$

Here,

$$j_{on} = \bar{K} C_{ibn} \exp(-\Delta E_{on}^{\#}/RT) \times \exp(-\Delta \Delta G_{on} \vec{\alpha}/RT) \times \exp(-z_n \vec{\alpha} \Delta \Psi)$$

is the ion flow into the membrane in reverse osmosis or electroosmotic filtration in the absence of an alternating electric field. In this case the time-average ion flow into the membrane is given by

$$j_n = \int_0^{1/\nu} j_n d\tau / \int_0^{1/\nu} d\tau = j_{on} \int_0^{1/\nu} \exp(-z_n \alpha \beta F \Delta U_{\sim} \sin(2\pi \nu \tau)/RT) \times d\tau \quad (12)$$

An analysis of Eq. (12) shows that the ion flow into the membrane increases, when an external sinusoidal electric field is imposed, and that the increase is greater with the ion charge and the amplitude of the alternating component. The experimental data presented in Fig. 9 are in a satisfactory agreement with such conclusions, which indicates that the approach employed in describing the ion transport through reverse-osmosis membranes is qualitatively correct. The ionic specificity of a membrane is characterized by the ion-separation factor. A distinction should be made between the formal separation factor $K_{i/jf}$ for ions i and j , which does not take into account the concentration polarization of the membranes, and the real separation factor $K_{i/jr}$ for the ions. $K_{i/jf}$ and $K_{i/jr}$ and their ratio can be found by using the following expressions:

$$K_{i/jf} = j_i C_{oj} / j_j C_{oi} \quad (13)$$

$$K_{i/jr} = j_i C_{ibj} / j_j C_{ibi} \quad (14)$$

$$K_{i/jf} = K_{i/jr} (C_{ibi} C_{oj} / C_{ibj} C_{oi}) \quad (15)$$

We substitute the expressions from Eq. (8) for the flows into Eq. (14):

$$K_{i/jr} = \exp\left(-\frac{\Delta E_{oi}^{\#} - \Delta E_{oj}^{\#}}{RT}\right) \exp\left(-\frac{N_A e^2 \vec{\alpha}}{4\pi \epsilon_0 RT}\right) \left(\frac{z_i^2}{r_{ci}} - \frac{z_j^2}{r_{cj}}\right) \left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon}\right) \times e^{-\vec{\alpha} \Delta \Psi_m (z_i - z_j)} \quad (16)$$

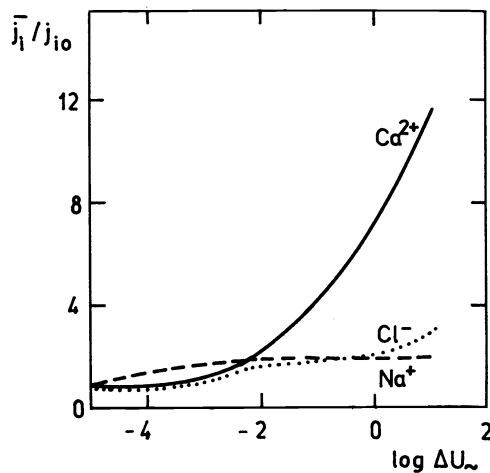


Fig. 9. Plots for the analysis of Eq. (12); 0.01 M NaCl + 0.01 M CaCl₂ solution, MGA-80 membrane.

Since the first term of Eq. (16) is directly proportional to the diffusion coefficient D_n , we write:

$$K_{i/jr} = \frac{D_i}{D_j} \times \exp\left(-\frac{N_A e^{2\alpha}}{4\pi\epsilon_0 RT} \left(\frac{z_i^2}{r_{ci}} - \frac{z_j^2}{r_{cj}}\right) \left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon}\right) \times e^{-\alpha(z_i - z_j)} \Delta\psi_m\right) \quad (17)$$

From an analysis of Eqs. (8) and (17) we have that the membrane selectivity for an ion increases with decreasing radius of the primary aquacomplex of the ion, increasing ion charge, and decreasing permittivity of water in the pores of the membrane active layer (associated with a decrease in the pore radius, an increase in the hydrophily of the membrane surface, or more structured bound water). Information concerning the magnitude of the interphase potential jump and its dependence on the current density and on the permittivity of water bound in the pores of the active layer can be obtained by transforming Eq. (17) to

$$A\left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon}\right) + B\Delta\phi_m = \ln\left(\frac{D_i}{D_j K_{i/jr}}\right) \quad (18)$$

Here, $A = \frac{N_A e^{2\alpha}}{4\pi\epsilon_0 RT} \left(\frac{z_i^2}{r_{ci}} - \frac{z_j^2}{r_{cj}}\right)$ and $B = \frac{\alpha(z_i - z_j)F}{RT}$

are constants for ions i and j , which can be approximated by assuming $\alpha = 0.5$. The diffusion coefficients of the ions on the right-hand side of Eq. (18) are known. $K_{i/jr}$ can be found using Eq. (14). The flows of the ions i and j through the membranes are:

$$j_n = G C_{n,perm}; n = i, j \quad (19)$$

Here, G is the membrane permeability ($m^3 m^{-2} m^{-1}$), and $C_{n,perm}$ is the n -ion concentration in the permate. If the original solution contains $K \geq 3$ ion species, the experimental data give $k-1$ independent equations of the type, from which ϵ^* and $\Delta\phi_m$ in Eq. (18) can be found. Figure 10 shows the dependences of ϵ^* and $\Delta\phi_m$ on the current density calculated from the data on electro-osmotic filtration of a 0.01 M NaCl + 0.01 M CaCl₂ solution on MGA-80 membranes. The r_{cn} values were borrowed from ref. 9. The linear dependence found for the interphase jump in the electric potential as a function of the current density is an indication that the resistance at the original solution/membrane interface depends very little on the ratio between the ion flows through it, but changes with the sign of the electric potential jump.

This may be connected with the orientation of water molecule dipoles at the entrance to the pores in the active layer. The dependence of permittivity ϵ^* of bound water in pores of the active layer on the current density is similar to that of the change in the pH jump at the original-solution/membrane interface (see Fig.10). The correlation observed between ϵ^* and ΔpH^* can be explained as follows. H^+ and OH^- ions have a different structuring effect on water: excess H^+ ions strengthen the water structure more than excess OH^-

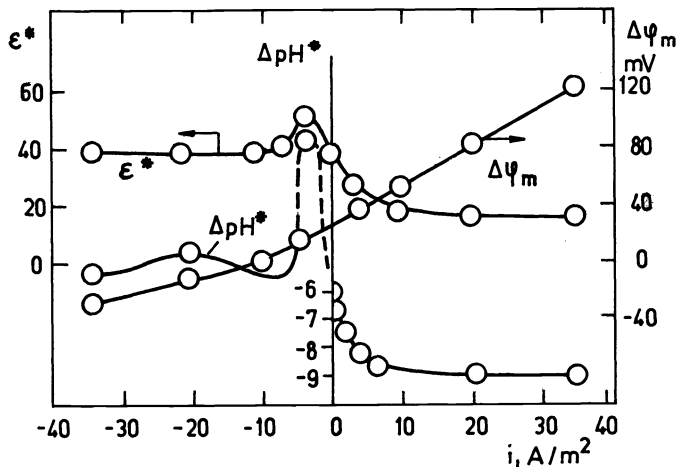


Fig. 10. ϵ^* , ΔpH and $\Delta\phi_m$ vs. the current density in EOF of a 0.01 M NaCl + 0.01 M CaCl₂ solution using an MGA-80 membrane.

ions, since their free energy of hydration is higher. Hence, when $\Delta p H^* < 0$ (more H^+ ions in the pores of the active layer), the gradient of the water structuring degree near the boundary between the original solution and the membrane is steeper than when $\Delta p H^* > 0$ (more OH^- ions in the pores than in the original solution at the boundary with the membrane). This is reflected in the ϵ^* value, related to the rearrangement energy of the secondary hydrate envelope of the ion. A more specific explanation can probably be obtained by means of experiments, specially designed to study the properties of the boundary layer of water on hydrophilic surfaces in electrolyte solutions.

The experimental dependence of ϵ^* and $\Delta\phi_m$ on the electric current density in the membrane reveal causes of the increase in the separation factor of similarly charged ions with current density. Fig. 11 shows the separation factors for Na^+ and Ca^{2+} ions in EOF for a solution of a mixture of chlorides of these metals. The increase in $K_{Na^+/Ca^{2+}r}$ on the cathodic membrane is related primarily to the decrease in ϵ^* ; the increase in the electric potential jump at the interphase boundary has an opposite effect. On the other hand, the rise in the $K_{Na^+/Ca^{2+}r}$ value on the anodic membrane is due mainly to the reduction, and even change in the sign of $\Delta\phi_m$ ($\epsilon^* \approx \text{const.}$). Let it be noted that the concentration polarization on the membrane has a negative influence: the $C_{Na^+}/C_{Ca^{2+}}$ ratio is lower at the membrane surface than in the bulk of the original solution. Due to this, $K_{Na^+/Ca^{2+}f} < K_{Na^+/Ca^{2+}r}$. Thus, according to the nature of ion-retention, a reverse-osmosis membrane is in many ways similar to a liquid organic membrane. Its principal distinction from an organic membrane is its high water permeability, which is due to the similarity between the solvent molecules in solution and the separating liquid film.

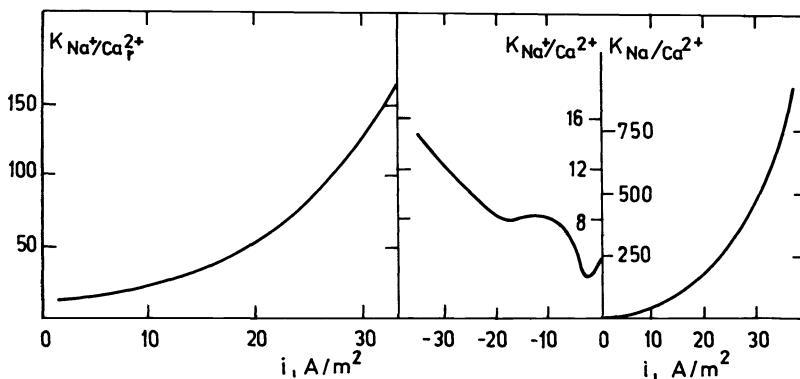


Fig. 11.
Separation factor vs.
current density.

To sum up, we have considered the mechanism of all the transport stages of ion transfer through the membrane in reverse osmosis and electro-osmotic filtration. In order to determine the ion flow through a reverse-osmosis membrane, it is necessary to evaluate mass transfer to the membrane surface and across the original solution/membrane interface, having fitted the boundary conditions of transport zones with each other. However, even with simplifying assumptions, an analytical solution can only be obtained for the case of reverse osmotic separation of a binary electrolyte solution. However, the ion transfer through a membrane in electro-osmotic filtration is complicated by an intensive dissociation of water at the boundary between the original solution and the membrane; the phenomenon was detected, but has not yet been investigated. In spite of this, however, the suggested description of ion transfer and some methods for determination of factors which affect ion separation derived from it help us obtain methods for calculating the ion flow through the membrane in a general case.

REFERENCES

1. Yu.I. Dytnerskii, *Reverse Osmosis and Ultrafiltration* (in Russian), Khimiya, Moscow (1978).
2. Yu.I. Dytnerskii, G.D. Sukhov and E.P. Morgunova, *Khim. Prom.* 5, 32(1982).
3. Yu.I. Dytnerskii, A.E. Savkin, V.D. Sobolev and N.V. Churaev, *Teor. Osnovy Khim. Tekhnol.* 6, 349 (1981).
4. Yu.I. Dytnerskii, V.V. Chechina, V.P. Chemkov and A.N. Cherkasov, *Kolloidnyi Zhurn.* 42, 748 (1986).
5. Yu.I. Dytnerskii, *Pressure Driven Membrane Processes Theory and Calculations* (Khimiya, Moscow (1986)).
6. Yu.I. Dytnerskii, *Kolloidnyi Zhurn.*, 48, 421 (1986).
7. G. Newman, 463 c, *Electrochemical Systems*, Mir, Moscow (1977).
8. Yu.I. Dytnerskii, G.V. Polaykov and L.S. Lukavii, *Teor. Osnovy Khim. Tekhnol.* 15, 628 (1972).
9. S.I. Drakin, *Zhurn. Strukturn. Khimii* 4, 514 (1963).