

# Diffusion of Electrolytes of Different Natures through the Cation-Exchange Membrane

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Received October 3, 2016

**Abstract**—Diffusion of different electrolytes through a negatively charged (cation-exchange) membrane into distilled water has been studied. It has been established theoretically (with no regard to the presence of diffusion layers) that the integral diffusion permeability coefficient of an electrolyte depends on the diffusion coefficients and the ratio between the charge numbers of a cation–anion pair, the ratio between the density of charges fixed in the membrane and electrolyte concentration, and the averaged coefficient of equilibrium distribution of cation–anion ion pairs in the membrane matrix. It has been found that, when co-ions have a higher mobility, the dependence of diffusion permeability on electrolyte concentration passes through a maximum. Derived equations have been compared with experimental dependences of the diffusion permeability of an MC-40 membrane with respect to different solutions of inorganic 1 : 1 and 2 : 1 electrolytes. The developed method has been shown to be applicable for describing diffusion of any electrolytes (including asymmetric ones) through arbitrary uniformly charged membranes.

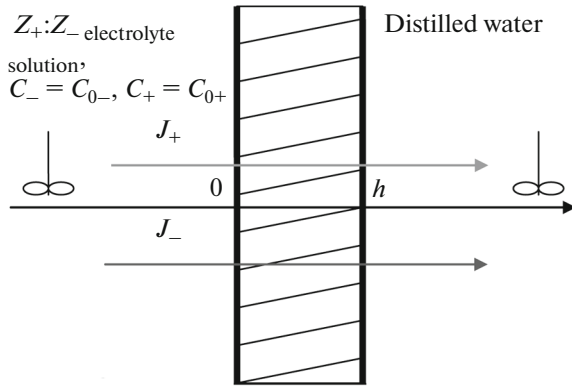
DOI: 10.1134/S1061933X17040044

## 1. INTRODUCTION

The determination of the diffusion permeability coefficients of charged membranes is of great importance for the characterization of new composite and hybrid ion-exchange materials produced by surface or bulk modification with polymers (e.g., polyaniline) or nanoparticles (in particular, metal-oxide nanoparticles), as well as inorganic materials (carbon nanotubes or halloysite). Previously, we have used solutions of different electrolytes to study the diffusion permeability of reverse-osmosis, bipolar, composite bilayer, and modified ion-exchange membranes based on polystyrene and perfluorinated matrices [1], as well as perfluorinated MF-4SC membranes, the surfaces of which were modified with polyaniline [2], and theoretically explained the asymmetric diffusion permeability at different orientations of a bilayer membrane in a measuring cell [3]. Work [4], which was devoted to the modification of layer-by-layer sulfated hydrophobic fluoroplast-4SF (F-4SF) films with polyaniline, has shown that the theoretical approach developed in [1] makes it also possible to explain the symmetry observed for the diffusion permeability of the obtained composite films. In [5], a new model has been developed for an ion-exchange membrane charged linearly along its thickness, and the asymmetry of the diffusion permeability has been proven for such a membrane. It has been noted that, while the bilayer model of an ion-exchange membrane adequately describes membranes

with modified surfaces, the new linear model is better applicable in the case of a gradient distribution of the density of charges fixed in a membrane subjected to bulk modification. We have elaborated a procedure for determining the main physicochemical parameters (diffusion coefficients and equilibrium distribution of ions in a membrane) of bulk-modified membranes. This procedure has been realized to advantage by the example of MF-4SC perfluorinated membranes modified with silica nanoparticles [6] and halloysite nanotubes [7–9].

However, we have failed to find models in the literature for diffusion of asymmetric electrolytes through charged membranes into water. At the same time, having experimental data on diffusion permeability of such membranes, we may try to explain previously unmentioned peculiarities of the curves for the diffusion as depending on electrolyte concentration. In this work, a model of a fine-porous membrane has, for the first time, been used to study theoretically diffusion of asymmetric electrolytes into water. Exact analytical solutions of corresponding boundary problems have been obtained for the case of 1 : 2 and 2 : 1 electrolytes to determine conditions under which maxima are observed in the concentration dependences of integral diffusion-permeability coefficients of membranes. The Mathematica® 11 software package has been employed to find the main physicochemical parameters (individual diffusion coefficients and equilibrium



**Fig. 1.** Schematic representation of asymmetric electrolyte diffusion through uniformly negatively charged (cation-exchange) membrane.

distribution coefficients of ions in a membrane matrix) for different membrane–electrolyte solution systems.

## 2. PROBLEM FORMULATION

Let us use the Nernst–Planck transfer equations to formulate the stationary boundary value problem concerning diffusion of aqueous solutions of  $Z_+ : Z_-$  electrolytes with equivalent concentration  $C_0 = Z_{\pm}C_{0\pm}$  through a cation-exchange membrane into water (Fig. 1). The case of an anion-exchange membrane is considered analogously. The membrane is characterized by thickness  $h$ ; diffusion coefficients  $D_{m+}, D_{m-}$  and equilibrium distribution coefficients  $\gamma_+, \gamma_-$  of cations and anions in the membrane matrix; and concentration of fixed groups (exchange capacity)  $\rho > 0$ , which is constant over the membrane thickness. Remember that  $\gamma_{\pm}$  reflects the level of the interaction between ions and membrane pore walls. The presence of diffusion layers is ignored for simplicity. Let us introduce the following denotation coefficients:  $\gamma = \gamma_+^{Z_-/Z} \gamma_-^{Z_+/Z}$  being the equilibrium distribution coefficient of ion pairs in the membrane;  $\gamma_{\pm} = \exp(\Phi_{\pm})$ , where  $\Phi_{\pm}$  denotes the dimensionless potentials of the interaction of ions with membrane pore walls in the  $k_B T$  units ( $k_B$  is Boltzmann's constant, and  $T$  is absolute temperature);  $C_{0\pm}$  denoting the concentrations of ions in an equilibrium solution to the left of the membrane (Fig. 1); and  $Z_{\pm}$  are the charge numbers of the ions with no regard to the signs ( $Z = Z_+ + Z_-$ ). Then, in the range of the membrane,  $0 < x < h$ , the equations for the diffusion and electromigration transfer of ions are written in the following standard manner:

$$J_+ = -D_{m+} \left( C_+' + Z_+ C_+ \Phi' \right), \quad (1)$$

$$J_- = -D_{m-} \left( C_-' - Z_- C_- \Phi' \right), \quad (2)$$

where the prime indicates differentiation over coordinate  $x$ , while  $\Phi$  is the dimensionless electric potential expressed in  $F/RT$  units ( $F$  is Faraday's constant, and  $R$  is the gas constant). Here,  $J_+, J_-$  are the flux densities and  $C_+, C_-$  are the concentrations of the ions.

At the interfaces,  $x = 0$  and  $x = h$ , the conditions for the equality of the chemical potentials have the following form [1–3]:

$$C_0 = Z_+ C_+ (+0) \gamma_+ \exp(Z_+ \Delta \Phi_0), \quad (3)$$

$$C_0 = Z_- C_- (+0) \gamma_- \exp(-Z_- \Delta \Phi_0), \quad (4)$$

$$C_-(h-0) = 0, \quad C_+(h-0) = \rho / Z_+, \quad (5)$$

where  $\Delta \Phi_0$  is the electric-potential drop at interface  $x = 0$  and  $C_0 = Z_{\pm} C_{0\pm}$  is the equivalent electrolyte concentration. In order to close the set of Eqs. (1)–(5), it must be supplemented with the conditions of electrical neutrality

$$Z_+ C_+ = Z_- C_- + \rho \quad (6)$$

and the absence of electric current

$$Z_+ J_+ = Z_- J_- \equiv J. \quad (7)$$

## 3. SOLUTION OF THE PROBLEM

Boundary value problem (1)–(7) implies an exact analytical solution. In order to obtain this solution, we introduce the following dimensionless variables and parameters:

$$\begin{aligned} y &= \frac{x}{h}, \quad \xi_{\pm} = \frac{Z_{\pm} C_{\pm}}{C_0}, \\ v_m &= \frac{D_{m-}}{D_{m+}}, \quad P = \frac{J_{\pm} h}{C_{0\pm}} \equiv \frac{Jh}{C_0}, \\ \vartheta_{\pm} &= \frac{P}{D_{m\pm}}, \quad \sigma = \frac{\rho}{C_0}, \quad u = \xi_- (+0), \end{aligned} \quad (8)$$

where  $P$  is the integral diffusion permeability coefficient of an electrolyte. Then, with allowance for the condition of electrical neutrality taken in the dimensionless form

$$\xi_+ = \xi_- + \sigma, \quad (6a)$$

Eqs. (1) and (2) are written as follows:

$$-\vartheta_+ = \frac{d\xi_-}{dy} + Z_+ (\xi_- + \sigma) \frac{d\Phi}{dy}, \quad (1a)$$

$$-\vartheta_- = \frac{d\xi_-}{dy} - Z_- \xi_- \frac{d\Phi}{dy}. \quad (2a)$$

By subtracting Eq. (2a) from Eq. (1a), we obtain

$$\frac{d\Phi}{dy} = \frac{\vartheta_- - \vartheta_+}{Z \xi_- + Z_+ \sigma}. \quad (9)$$

As can be seen from Eq. (9), the behavior of the potential depends on the relation between dimensionless fluxes  $\vartheta_{\pm}$ . At  $\vartheta_{-} > \vartheta_{+}$  or  $\nu_m < 1$ , the potential profile increases over the membrane thickness, while, at  $\vartheta_{-} < \vartheta_{+}$  or  $\nu_m > 1$ , it decreases. Assume that any of the described situations takes place. The case of  $\vartheta_{-} = \vartheta_{+}$  or  $\nu_m = 1$  is degenerate and not considered here. Then, because of the monotonic character of the electric potential, a one-to-one correspondence (bijection) exists between it and dimensionless coordinate  $y$ , which enables us to search for the solution of problem (1)–(7) for coordinate  $y(\varphi)$  and concentrations  $\xi_{\pm}(\varphi)$ ,  $\xi_{\pm}(\varphi)$  (all of them being dimensionless) as functions of the electric potential. Furthermore, rewriting Eq. (2a) with allowance for Eq. (9), we obtain the following differential equation for  $\xi_{-}(\varphi)$ :

$$\frac{d\xi_{-}}{d\varphi} + \lambda\xi_{-} = -\sigma \frac{Z_{+}\vartheta_{-}}{\vartheta_{-} - \vartheta_{+}},$$

the solution of which is

$$\xi_{-} = A \exp(-\lambda\varphi) - \frac{\sigma Z_{+}\vartheta_{-}}{Z_{-}\vartheta_{+} + Z_{+}\vartheta_{-}}. \quad (10)$$

Substituting expression (10) into Eq. (9) and integrating the result, we find the general solution for the electric potential in the form of the inverse function

$$y(\varphi) = -\frac{ZA}{Z_{+}\vartheta_{-} + Z_{-}\vartheta_{+}} \exp(-\lambda\varphi) - \frac{Z_{-}Z_{+}\sigma}{Z_{+}\vartheta_{-} + Z_{-}\vartheta_{+}} \varphi + B, \quad (11)$$

with the following denotation being introduced:

$$\lambda \equiv \frac{Z_{-}\vartheta_{+} + Z_{+}\vartheta_{-}}{\vartheta_{-} - \vartheta_{+}}. \quad (12)$$

Using boundary conditions (3) and (4) rewritten in the dimensionless form, we find the following equations for the concentration of anions and the electric potential drop in the membrane at interface  $y = 0$ :

$$\left(\frac{u}{\sigma} + 1\right)^{Z_{-}} \left(\frac{u}{\sigma}\right)^{Z_{+}} = \left(\frac{1}{\sigma\gamma}\right)^Z, \quad (13)$$

$$\Delta\varphi_0 = \varphi(+0) = \frac{1}{Z_{-}} \ln(u\gamma_{-}). \quad (14)$$

In the case of 1 : 2 and 2 : 1 electrolytes, Eq. (13) is reduced to a cubic one and implies an analytical solution, which will be presented below. For a binary (symmetric) electrolyte,  $Z_{-} = Z_{+}$ , Eq. (13) is reduced to a quadratic one. In the general case, Eq. (13) is an algebraic equation of an integral power with respect to dimensionless co-ion concentration  $\frac{u}{\sigma} = \frac{C_{-}(+0)}{\rho}$  at the left-hand interface from side of the membrane, and its solution can be found only numerically. Writ-

ing solutions (10) and (11) at  $y = +0$  and  $y = 1 - 0$  with allowance for boundary condition (5) rewritten in the dimensionless form and expression (14), we determine integration constants  $A$  and  $B$ , as well as the electrical potential at the right-hand interface of the membrane via unknown boundary concentration of anions  $u$ , which is independently determined from Eq. (13), and derive the following expression for the dimensionless flux of anions:

$$A = \frac{\sigma Z_{+}\vartheta_{-}}{\lambda(\vartheta_{-} - \vartheta_{+})} \times \exp\left(\lambda \frac{Zu - \lambda(\vartheta_{-} - \vartheta_{+})}{\sigma Z_{-}Z_{+}}\right) (u\gamma_{-})^{\frac{\lambda}{Z_{-}}}, \quad (15)$$

$$B = \frac{\sigma Z_{+}}{\lambda(\vartheta_{-} - \vartheta_{+})} \ln(u\gamma_{-}) + \frac{Z}{\lambda(\vartheta_{-} - \vartheta_{+})} \left(u + \frac{\sigma Z_{+}\vartheta_{-}}{\lambda(\vartheta_{-} - \vartheta_{+})}\right), \quad (16)$$

$$\varphi(1 - 0) = \frac{Zu - \lambda(\vartheta_{-} - \vartheta_{+})}{\sigma Z_{-}Z_{+}} + \frac{1}{Z_{-}} \ln(u\gamma_{-}), \quad (17)$$

$$\vartheta_{-} = \frac{\sigma}{\nu_m + Z_{+}/Z_{-}} \left( \left(1 + \frac{Z_{+}}{Z_{-}}\right) \frac{u}{\sigma} + \frac{\nu_m - 1}{(Z_{-}/Z_{+})\nu_m + 1} \ln\left(1 + \frac{u}{\sigma} \left(\frac{Z_{+}}{Z_{-}}\nu_m + 1\right)\right) \right). \quad (18)$$

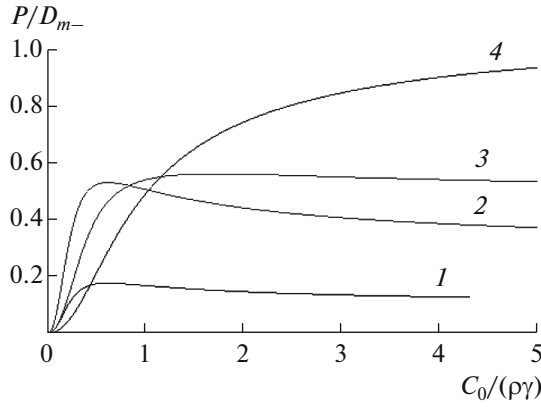
Note that condition (7) for the absence of electric current has been used when deriving Eq. (18), with this condition yielding the following relation between dimensionless fluxes of ions:

$$\vartheta_{+} = \nu_m \vartheta_{-}. \quad (19)$$

Integral coefficient  $P = D_m \vartheta_{-}$  of membrane diffusion permeability is determined by simple multiplication of Eq. (18) by the anion diffusion coefficient. In addition, Eq. (18) shows that  $P$  depends on the ratio between the charge numbers of the ions rather than on each of them; therefore, in the case of symmetric electrolytes, diffusion permeability is independent of ion charges. In order to analyze the behavior of permeability coefficient  $P$ , let us determine the derivative of the right-hand side of Eq. (18) over parameter  $\sigma$  and equate it to zero taking into account relation (13), from which we may find derivative  $\frac{du}{d\sigma}$ . Then, we obtain the following implicit equation:

$$\nu_m \frac{(Z_{-}/Z_{+} + 1)u/\sigma}{1 + ((Z_{-}/Z_{+})\nu_m + 1)u/\sigma} = \frac{\nu_m - 1}{(Z_{-}/Z_{+})\nu_m + 1} \ln(1 + ((Z_{-}/Z_{+})\nu_m + 1)u/\sigma). \quad (20)$$

It is clear that Eq. (20) has a positive solution  $(u/\sigma)_{*}$  (it may be shown that this solution is unique)



**Fig. 2.** Reduced integral diffusion permeability coefficients  $P/D_{m-}$  calculated by Eqs. (22) and (24) as functions of 1 : 2 electrolyte dimensionless equivalent concentration  $C_0/(\rho\gamma)$  at fixed parameters (1)  $v_m = 50$  and  $\gamma = 0.3$ , (2)  $v_m = 50$  and  $\gamma = 0.1$ , (3)  $v_m = 10$  and  $\gamma = 0.3$ , and (4)  $v_m = 0.95$  and  $\gamma = 0.95$ .

only at  $v_m > 1$ , because both sides of Eq. (20) are positive only in this case. This solution corresponds to the maximum in the dependence of diffusion permeability coefficient  $P$  on electrolyte concentration. At  $v_m \leq 1$ , Eq. (20) has no positive solution; hence, the  $P(C_0)$  dependence is, in this case, monotonically increasing.

#### 4. ANALYSIS OF THE RESULTS OBTAINED

Let us, initially, consider some particular cases.

##### 4.1. Symmetric Electrolyte ( $Z_- = Z_+ \equiv Z_0$ )

As has been mentioned above, Eq. (13) becomes, in this case, quadratic; therefore, substituting its positive solution into Eq. (18), we find the following explicit expression for the diffusion permeability of the membrane:

$$P = \frac{\sigma D_{m-}}{v_m + 1} \left( \sqrt{1 + \left(\frac{2}{\sigma\gamma}\right)^2} - 1 + \frac{v_m - 1}{v_m + 1} \times \ln \left( \frac{1}{2}(v_m + 1) \sqrt{1 + \left(\frac{2}{\sigma\gamma}\right)^2} - \frac{1}{2}(v_m - 1) \right) \right) \quad (21)$$

Note that, for the case of a 1 : 1 electrolyte, Eq. (21) was previously obtained in [6], and it has, now, been established that it is independent of the magnitude of ion charge  $Z_0$ , provided that an electrolyte is symmetric.

##### 4.2. Asymmetric 1 : 2 Electrolyte ( $Z_+ = 1, Z_- = 2$ )

In this case, the expression for diffusion permeability acquires the following form:

$$P = \frac{\sigma v_m D_{m-}}{2v_m + 1} \left( 3\omega + \frac{2v_m - 2}{2v_m + 1} \ln(1 + \omega(2v_m + 1)) \right), \quad (22)$$

while dimensionless value  $\omega \equiv \frac{u}{\sigma}$  is determined from the following cubic equation derived from relation (18):

$$\omega^3 + 2\omega^2 + \omega - \frac{1}{(\sigma\gamma)^3} = 0. \quad (23)$$

Analysis shows that Eq. (23) always has the only real root, which may be determined by the Cardano equation

$$\omega = \sqrt[3]{\frac{1}{2(\sigma\gamma)^3} \left( 1 + \sqrt{1 + \frac{4}{27}(\sigma\gamma)^3} \right)} + \frac{1}{27} + \sqrt[3]{\frac{1}{2(\sigma\gamma)^3} \left( 1 - \sqrt{1 + \frac{4}{27}(\sigma\gamma)^3} \right)} + \frac{1}{27} - \frac{2}{3}. \quad (24)$$

Figure 2 presents the dependences of the integral diffusion-permeability coefficient on electrolyte concentration for different sets of parameters  $v_m, \gamma$ , these dependences being calculated by Eqs. (22) and (24). It can be seen that a decrease in equilibrium distribution coefficient  $\gamma$  of electrolyte ion pairs (curves 1, 2), i.e., an increase in the positive sorption of the ions in membrane pores, leads to a growth in the diffusion permeability. The same takes place upon decreasing diffusion coefficient ratio  $v_m$  between anions and cations, i.e., an increase in the mobility of the cations (curves 1, 3). At  $v_m > 1$  (curves 1–3), a rather pronounced maximum is observed, in contrast to the case of  $v_m < 1$  (curve 4), in which the  $P(C_0)$  dependence is monotonic. Note that the existence of an extreme at  $v_m > 1$  is also characteristic of symmetric electrolytes [9]. As the concentration increases, diffusion permeability tends to limiting value  $P^\infty$ , which corresponds to the permeability of an uncharged membrane and is determined by the exact equation presented below.

##### 4.3. Asymmetric 2 : 1 Electrolyte ( $Z_+ = 2, Z_- = 1$ )

In this case, the expression for diffusion permeability acquires the form

$$P = \frac{\sigma D_{m-}}{v_m + 2} \left( 3\omega + \frac{2v_m - 2}{v_m + 2} \ln \left( 1 + \omega \left( \frac{v_m + 1}{2} \right) \right) \right), \quad (25)$$

while the values of  $\omega$  are determined from another cubic equation, which also follows from relation (18):

$$\omega^3 + \omega^2 - \frac{1}{(\sigma\gamma)^3} = 0. \quad (26)$$

Analysis shows that Eq. (26) always has only one real root, which is also easy to determine by the Cardano equation

$$\omega = \sqrt[3]{\frac{1}{2(\sigma\gamma)^3} \left( 1 + \sqrt{1 - \frac{4}{27}(\sigma\gamma)^3} \right) - \frac{1}{27}} + \sqrt[3]{\frac{1}{2(\sigma\gamma)^3} \left( 1 - \sqrt{1 - \frac{4}{27}(\sigma\gamma)^3} \right) - \frac{1}{27} - \frac{1}{3}}. \quad (27)$$

Figure 3 shows the concentration dependences of the integral coefficient of membrane diffusion permeability with respect to a 2 : 1 electrolyte at the same sets of the physicochemical parameters as in Fig. 2. The first thing to attract attention is the more distinctly pronounced extreme, as well as the higher values of the limiting permeability. In other respects, the behavior of the curves is similar to that in Fig. 2. It is clear that the diffusion permeability is, in this case, higher because of the larger size of the counterion (Fig. 3), the charge of which is twice as high.

#### 4.4. Limiting Cases

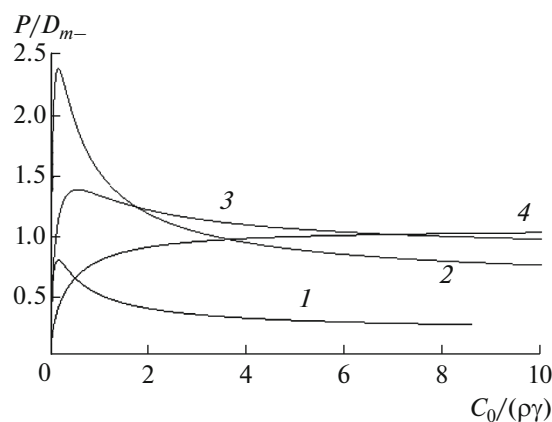
Two limiting cases may be distinguished. (1) When the equivalent electrolyte concentration tends to zero ( $C_0 \rightarrow 0 \Rightarrow \sigma \rightarrow \infty$ ), it follows from Eq. (13) that  $u \rightarrow 0$ , while relation (18) yields  $P \rightarrow 0$ . Hence, all diffusion curves originate from the coordinate origin of the  $(P, C_0)$  system. (2) If the equivalent electrolyte concentration infinitely increases, or the membrane exchange capacity tends to zero ( $C_0 \rightarrow \infty$ , or  $\rho \rightarrow 0 \Rightarrow \sigma \rightarrow 0$ ), Eq. (13) shows that  $u \rightarrow \frac{1}{\gamma}$ , which makes it possible to use relation (18) for determining the limiting value of the diffusion permeability as follows:

$$\lim_{C_0 \rightarrow \infty} P \equiv P^\infty = \frac{1 + Z_+/Z_-}{v_m + Z_+/Z_-} \frac{D_{m-}}{\gamma} \equiv \frac{D_m}{\gamma}, \quad (28)$$

where

$$D_m = \frac{(Z_- + Z_+) D_{m-} D_{m+}}{Z_- D_{m-} + Z_+ D_{m+}} = \frac{1/Z_+ + 1/Z_-}{1/(Z_+ D_{m+}) + 1/(Z_- D_{m-})} \quad (29)$$

is the diffusion coefficient of an electrolyte molecule. It follows from relation (28) that, in the case of a 2 : 1 electrolyte and  $v_m > 1$ , its limiting permeability



**Fig. 3.** Reduced integral diffusion permeability coefficients  $P/D_{m-}$  calculated by Eqs. (25) and (27) as functions of 2 : 1 electrolyte dimensionless equivalent concentration  $C_0/(\rho\gamma)$  at fixed parameters (1)  $v_m = 50$  and  $\gamma = 0.3$ , (2)  $v_m = 50$  and  $\gamma = 0.1$ , (3)  $v_m = 10$  and  $\gamma = 0.3$ , and (4)  $v_m = 0.95$  and  $\gamma = 0.95$ .

$$P_{2:1}^\infty = \frac{3}{v_m + 2} \frac{D_{m-}}{\gamma} \quad (\text{here, the electrolyte-molecule diffusion coefficient is } D_m = \frac{3D_{m-}}{v_m + 2})$$

is always higher (other conditions being equal) than the limiting diffusion permeability of a 1 : 2 electrolyte  $P_{1:2}^\infty = \frac{3}{2v_m + 1} \frac{D_{m-}}{\gamma}$  (here,

$$D_m = \frac{3D_{m-}}{2v_m + 1}), \text{ while, at } v_m < 1, \text{ it is, vice versa, lower.}$$

At  $v_m = 1$ , the limiting permeability is, as can be seen from relation (28), independent of the ion charges.

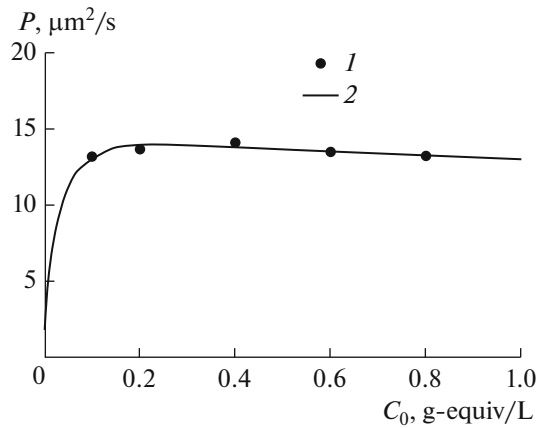
## 5. EXPERIMENTAL

A series of experiments were performed to determine integral diffusion-permeability coefficient  $P$  of the MC-40 heterogeneous membrane sample for solutions of different electrolytes. The exchange capacity of the membrane was 1.52 mmol/g, while its thickness in the swollen state was  $520 \pm 3 \mu\text{m}$ . Membrane moisture capacities  $W$  in the studied 1 : 1 and 2 : 1 electrolytes are presented in Table 1.

In order to calculate  $P$ , the integral diffusion flux was experimentally determined using a two-chamber

**Table 1.** Moisture capacity of MC-40 membrane in 0.1 N solutions of alkali and alkaline-earth metal chlorides and radii of cations

| Parameter                                 | Electrolyte |      |                    |      |       |                   |                   |                   |
|---|-------------|------|--------------------|------|-------|-------------------|-------------------|-------------------|
|   | LiCl        | NaCl | NH <sub>4</sub> Cl | KCl  | CsCl  | MgCl <sub>2</sub> | CaCl <sub>2</sub> | BaCl <sub>2</sub> |
| $W, \%$                                   | 36.7        | 32.2 | 30.7               | 29.4 | 26.8  | 25.6              | 32.0              | 26.0              |
| Cation Stokes radius, Å [10]              | 2.36        | 1.80 | 1.225              | 1.21 | 1.155 | 1.725             | 1.53              | 1.42              |
| Shannon physical radius of cation, Å [11] | 0.90        | 1.16 | —                  | 1.52 | 1.81  | 0.86              | 1.14              | 1.49              |



**Fig. 4.** (1) Experimental and (2) theoretical dependences of integral diffusion permeability coefficient of MC-40 membrane with respect to  $\text{MgCl}_2$  electrolyte on its equivalent concentration  $C_0$ .

cell in the course of electrolyte electrodiffusion through a membrane into water. The electrolyte flux through the membrane in a quasi-stationary state has constant value

$$J = P \frac{\Delta C}{h} \quad (30)$$

and is calculated by the following equation:

$$J = \frac{VdC}{Sd\tau}, \quad (31)$$

where  $V$  is a water-containing chamber volume equal to 100 mL,  $S = 19.5 \text{ cm}^2$  is membrane area, and  $\tau$  is time. Since diffusion proceeds from a solution into pure water, the concentration drop is  $\Delta C = C_0 - 0 = C_0$ .

An increase in electrolyte concentration in the water-containing chamber during its penetration through the membrane was recorded by conductometry using the following relation:

$$\frac{dC}{d\tau} = K \frac{d\left(\frac{1}{R_s}\right)}{d\tau}, \quad (32)$$

where  $K$  is the cell constant, which depends on the nature of an electrolyte and is determined for each specific case, and  $R_s$  is the electric resistance of a solution in the cell chamber that is initially filled with water (Fig. 1). With allowance for the aforementioned,  $P$  was calculated as follows:

$$P = \frac{hV}{SC_0} K \frac{d\left(\frac{1}{R_s}\right)}{d\tau}. \quad (33)$$

The experiments were carried out at  $25^\circ\text{C}$ , and their error, including that relevant to the ignorance of the growth of the electrolyte concentration in the

chamber initially filled with water, was no higher than 5% [12]. In the calculations and experiments, equivalent concentration (molar concentration of equivalents) was used. The electric-potential drop across the membrane for the initial membrane systems was not measured; the influence of diffusion layers on the integral diffusion permeability was ignored. The effects of the diffusion-layer thickness and the electrolyte concentration in the chamber to the right of the membrane will be described in Section 7.

## 6. RESULTS AND DISCUSSIONS

Figures 4–11 show the experimental and calculated data on the integral diffusion permeability coefficients, which are in satisfactory agreement with each other. Table 2 presents the numerical values of the physicochemical parameters obtained for the membrane systems by minimizing the root-mean-square deviations between the theoretical and experimental values of diffusion permeability with the use of a program written in the Mathematica<sup>®</sup> 11 computing environment. The minimization was performed in several stages. The calculations were carried out for three asymmetric 2 : 1 electrolytes using Eq. (25) and five symmetric 1 : 1 electrolytes by Eq. (21).

Initially, all three model parameters,  $v_m$ ,  $\gamma$ , and  $D_{m-}$ , were determined by the method of least squares from the experimental extremal  $P(C_0)$  dependence for  $\text{MgCl}_2$  electrolyte. In the case of the other seven electrolytes, the error was minimized only for two parameters,  $v_m$  and  $\gamma$ , assuming that the diffusion coefficient of chlorine co-ions was the same in the experiments:  $D_{m-} = 2.85 \mu\text{m}^2/\text{s}$ , which was 712 times lower than that in a dilute solution. Then, Eqs. (28) and (29) were used to calculate the asymptotic value of diffusion permeability  $P^\infty$  at high concentrations and the diffusion coefficient of electrolyte molecules in the membrane, respectively. It can be seen that the calculated diffusion coefficients of cations (as well as electrolyte molecules themselves) in the membrane decrease in the series Mg–Ca–Ba according to an increase in the Shannon physical radii of these bivalent cations (Table 1). This confirms the hypothesis that ions partly lose their hydration shells when entering a membrane. At the same time,  $P^\infty$  increases due to the enhancement of the positive sorption of electrolyte molecules in membrane pores in the aforementioned series, i.e., a reduction in equilibrium distribution coefficient  $\gamma$  (a rise in the absolute value of specific interaction potential  $\Phi$ ).

The data calculated for symmetric 1 : 1 electrolytes are presented in Table 2 also according to an increase in the Shannon radii of the cations (a decrease in the Stokes radius) listed in Table 1. The results presented in Table 2 show that the order of univalent cations  $\text{Li}^+ - \text{Na}^+ - \text{NH}_4^+$



**Table 2.** Calculated physicochemical parameters of heterogeneous MC-40 membrane

| Electrolyte        | $v_m = D_{m-}/D_{m+}$ | $D_{m-}, \mu\text{m}^2/\text{s}$ | $D_{m+}, \mu\text{m}^2/\text{s}$ | $D_m, \mu\text{m}^2/\text{s}$ | $P^\infty$ | $\gamma$ | $\Phi/k_B T = \ln \gamma$ |
|--------------------|-----------------------|----------------------------------|----------------------------------|-------------------------------|------------|----------|---------------------------|
| MgCl <sub>2</sub>  | 4.34                  | 2.85                             | 0.657                            | 1.350                         | 11.70      | 0.115    | -2.16                     |
| CaCl <sub>2</sub>  | 6.26                  | 2.85                             | 0.456                            | 1.036                         | 14.10      | 0.073    | -2.61                     |
| BaCl <sub>2</sub>  | 6.70                  | 2.85                             | 0.426                            | 0.985                         | 21.47      | 0.046    | -3.08                     |
| LiCl               | 2.60                  | 2.85                             | 1.099                            | 1.587                         | 10.82      | 0.147    | -1.92                     |
| NaCl               | 2.70                  | 2.85                             | 1.058                            | 1.544                         | 13.46      | 0.115    | -2.17                     |
| NH <sub>4</sub> Cl | 2.80                  | 2.85                             | 1.018                            | 1.500                         | 11.99      | 0.125    | -2.08                     |
| KCl                | 1.29                  | 2.85                             | 2.220                            | 2.498                         | 29.57      | 0.084    | -2.47                     |
| CsCl               | 2.19                  | 2.85                             | 1.305                            | 1.791                         | 18.20      | 0.098    | -2.32                     |

corresponds to an increase in the radii and a decrease in the diffusion coefficients of the ions. Later, the mobility of potassium cations doubles, while that of cesium cations decreases. This may be due to different degrees of hydration shell loss by the cations in the membrane. This is explained by, e.g., different moisture capacities of the membrane exposed to different electrolytes (Table 1) and supported by the higher integral diffusion permeabilities of potassium and cesium chlorides and, hence, their higher asymptotic values of integral diffusion permeability  $P^\infty$ .

As can be seen from Table 2, the MC-40 membrane is characterized by the positive sorption of all electrolytes under consideration. Therewith, the equilibrium distribution coefficient  $\gamma < 1$ , while dimensionless specific interaction potential  $\Phi/(k_B T) = \ln \gamma$  is negative (see the last column in Table 2). Note that the aforementioned property is, in general, typical of all ion-exchange materials. The comparison of a heterogeneous MC-40 membrane with a homogeneous MF-4SC membrane, for which the calculation has yielded  $\Phi = -1.78 k_B T$  in the case of NaCl diffusion [6], leads us to suppose that the interaction of the ions of this electrolyte with MC-40 matrix is 2.5 times stronger than with the matrix of the perfluorinated membrane.

According to the above-described model, all  $P(C_0)$  dependences for the electrolyte under consideration may reach a maximum upon increasing concentration, because the mobility of co-ions in a membrane matrix is higher than the mobility of counterions ( $v_m > 1$ ). The existence of the maximum is explained by the nonuniform contributions of the diffusion and electromigration components to the total flux with increasing electrolyte concentration. The higher the  $v_m$  ratio, the more pronounced this maximum; therefore, it is especially distinct for CaCl<sub>2</sub> and BaCl<sub>2</sub> electrolytes, which have the highest  $v_m$  values (Table. 2). Note that, previously, when calculating simultaneously three physicochemical parameters,  $v_m$ ,  $\gamma$ , and  $D_{m-}$ , for symmetric 1 : 1 electrolytes [6, 8, 9], we

encountered a poor conditioned system (nonuniqueness of the set of these parameters). For asymmetric electrolytes, this problem of the calculation is, in the considered case, absent, probably, due to the pronounced extremal character of the diffusion dependences. The poor conditioned system might also be related to a small number of experimental points or a large number (three) of the sought parameters. This difficulty may be overcome by reducing the number of the parameters to two by using the experimental values of the diffusion permeability at any high electrolyte concentration, when the  $P(C_0)$  dependence almost reaches the plateau (asymptotic value of the diffusion permeability). Then, using expression (28), parameter  $v_m$  may be excluded from Eqs. (21), (22), and (25) for diffusion-permeability coefficients of a membrane with respect to 1 : 1, 1 : 2 and 2 : 1 electrolytes, respectively, as follows:

$$P_{1:1} = \frac{P^\infty}{2} \left( \sqrt{\bar{\sigma}^2 + 4} - \bar{\sigma} + \bar{\sigma} \left( 1 - \frac{P^\infty}{\bar{D}_{m-}} \right) \right) \times \ln \left( 1 + \frac{\bar{D}_{m-}}{P^\infty} \left( \sqrt{1 + \frac{4}{\bar{\sigma}^2}} - 1 \right) \right), \quad (21a)$$

$$P_{1:2} = P^\infty \left( \omega_1 + \bar{\sigma} \left( 1 - \frac{P^\infty}{\bar{D}_{m-}} \right) \ln \left( 1 + 3 \frac{\omega_1 \bar{D}_{m-}}{\bar{\sigma} P^\infty} \right) \right), \quad (22a)$$

$$\omega_1 = \sqrt[3]{\frac{1}{2} \left( 1 + \sqrt{1 + \frac{4}{27} \bar{\sigma}^3} \right) + \frac{1}{27} \bar{\sigma}^3} + \sqrt[3]{\frac{1}{2} \left( 1 - \sqrt{1 + \frac{4}{27} \bar{\sigma}^3} \right) + \frac{1}{27} \bar{\sigma}^3} - \frac{2}{3} \bar{\sigma},$$

$$P_{2:1} = P^\infty \left( \omega_2 + \frac{2}{3} \bar{\sigma} \left( 1 - \frac{P^\infty}{\bar{D}_{m-}} \right) \right) \times \ln \left( 1 + \frac{3 \omega_2 \bar{D}_{m-}}{2 \bar{\sigma} P^\infty} \right), \quad (25a)$$

$$\omega_2 = \sqrt[3]{\frac{1}{2} \left( 1 + \sqrt{1 - \frac{4}{27} \bar{\sigma}^3} \right) - \frac{1}{27} \bar{\sigma}^3} + \sqrt[3]{\frac{1}{2} \left( 1 - \sqrt{1 - \frac{4}{27} \bar{\sigma}^3} \right) - \frac{1}{27} \bar{\sigma}^3} - \frac{1}{3} \bar{\sigma},$$

where denotations  $\bar{\sigma} = \sigma\gamma = \frac{\rho\gamma}{C_0}$  and  $\bar{D}_{m-} = D_{m-}/\gamma$  have been introduced. The two unknown physicochemical parameters of the model, i.e., effective exchange capacity  $\bar{\rho} = \rho\gamma$  and co-ion diffusion coefficient  $\bar{D}_{m-}$ , are determined by the aforementioned equations using the procedure of minimizing the root-mean-square deviation between experimental and theoretical data. Then, at experimentally determined exchange capacity  $\rho$  and limiting diffusion permeability  $P^\infty$ , we determine successively equilibrium electrolyte distribution coefficient  $\gamma = \bar{\rho}/\rho$  and diffusion coefficients of ions in the membrane,  $D_{m-} = \gamma\bar{D}_{m-}$  and  $D_{m+} = \gamma\bar{D}_{m-}P^\infty / (\bar{D}_{m-}(1 + Z_+/Z_-) - P^\infty Z_+/Z_-)$ . Note that Eqs. (21a), (22a), and (25a) are applicable only when an experiment distinctly shows that the curve for the diffusion permeability reaches an asymptotic value. In this respect, our experimental data do not meet this condition. The only way out is to use a large number of experimental points, thereby widening the range of variations in the concentration, or determine the physicochemical parameters in combination with the studies of other important characteristics of a membrane, e.g., the electrical conductivity [8, 9] and/or current–voltage curve [13, 14]. An alternative is the method that is used in this work and based on the investigation of the diffusion permeability of a membrane with respect to a number of electrolytes containing a common anion or cation.

It is worth noting that there are, so far, no reliable methods for exact determining individual diffusion coefficients of ions in membranes or other porous bodies. Due to the condition for the local electrical neutrality of a solution, the transfer of cations is accompanied by simultaneous transfer of anions; therefore, effective diffusion coefficient  $D_m$  of an electrolyte molecule has an important practical significance and a clear physical meaning. This coefficient is calculated by Eq. (29) and has been called an ambipolar or average coefficient [15]. It follows from Eq. (29) and Table 2 that the electrolyte diffusion coefficient is to a larger extent determined by an ion that has a lower diffusion coefficient and a charge. In addition to  $\gamma$ , this coefficient should be considered to be one of two main physicochemical parameters of a membrane system; therefore, the fifth column of Table 2 lists its values for the studied electrolytes. The calculations show that this diffusion coefficient inside a heterogeneous MC-40 membrane is, depending on the nature of an electrolyte, 3–3.5 orders of magnitude lower than that in a dilute solution. This decrease is much greater than that observed in the case of a homogeneous perfluorinated MF-4SC membrane, for which value  $D_m = 7.2 \mu\text{m}^2/\text{s}$  in the case of NaCl [6] is only one and a half order lower than that in a dilute solution. The perfluorinated membrane represents a noncross-

linked polymer; therefore, the diffusion coefficient of NaCl in it is higher.

## 7. ON THE CORRECTNESS OF BOUNDARY CONDITIONS

At first sight, boundary conditions (5) are incorrect, because they formally lead to an infinite transmembrane jump in the electric potential. Below, it will be shown that this apparently rough approximation has a weak effect on the values of the integral diffusion-permeability coefficient. As for the transmembrane electric-potential drop, it is not considered in this work and is intended to be studied in a subsequent communication. We have performed preliminary experiments on measuring the transmembrane potential difference for NaCl electrolyte in a two-chamber cell upon tangential stirring of the solutions on both sides of an MC-40 membrane. In particular, at electrolyte concentration  $C_0 = 0.1 \text{ M}$  and  $k = 100$ , the measured potential and that calculated by an analytical equation derived under boundary condition (33) (in this work, this equation is not presented) differed from each other by no more than 10%. Its value has appeared to be about 100 mV.

Let us show that the ignorance of the diffusion layers and the use of the condition for the zero concentration behind the right-hand diffusion layer do not affect significantly the value of integral diffusion-permeability coefficient  $P$ , and its variations are no larger than 5% that does not exceed the experiment error.

First, it should be noted that the solution of the boundary problem was obtained in terms of the traditional formulation taking into account both diffusion layers of equal thicknesses  $\delta$  and the standard boundary conditions relating the electric potential drops and the concentrations of ions at the near and far membrane surfaces. The concentration behind the membrane was taken low, however, nonzero and equal to  $C_0/k$  ( $k > 100$ ). Therewith, the boundary conditions imposed on the electric potential drops and ion concentrations at the right-hand side of the membrane were written as follows:

$$\gamma_{\pm} C_{\pm}(h-0) \exp(\mp Z_{\pm} \Delta\phi_h) = C_{\pm}(h+0), \quad (34)$$

where  $\Delta\phi_h$  is the (finite) electric potential drop upon the passage through the right-hand boundary of the membrane. Unfortunately, an exact equation for integral diffusion permeability coefficient  $P$  is, then, implicit and, in the case of an, e.g., 1 : 1 electrolyte, has the following form (see Eq. (13) in our work [7]):



$$\frac{2P}{\bar{D}_m} = \sqrt{\sigma^2 + \frac{4}{\gamma^2} \left(1 - \frac{P}{\bar{D}} \Delta\right)^2} - \sqrt{\sigma^2 + \frac{4}{\gamma^2} \left(\frac{1}{k} + \frac{P}{\bar{D}} \Delta\right)^2} \quad (35)$$

$$- \sigma v \ln \frac{\sigma v + \sqrt{\sigma^2 + \frac{4}{\gamma^2} \left(1 - \frac{P}{\bar{D}} \Delta\right)^2}}{\sigma v + \sqrt{\sigma^2 + \frac{4}{\gamma^2} \left(\frac{1}{k} + \frac{P}{\bar{D}} \Delta\right)^2}},$$

where the following new denotations have been introduced:  $v_0 = \frac{D_-}{D_+}$ ,  $v = \frac{1 - v_m}{1 + v_m}$ ,  $\Delta = \frac{\delta}{h}$ ,

$$\bar{D} = \frac{2D_- D_+}{D_- + D_+} \equiv \frac{2D_-}{1 + v_0}, \quad \text{and}$$

$$\bar{D}_m = \frac{2D_{m-} D_{m+}}{D_{m-} + D_{m+}} \equiv \frac{2D_{m-}}{1 + v_m}.$$

Since Eq. (35) determines the  $P$  value implicitly, it is inconvenient to use it for calculating physicochemical parameters via the error-minimization algorithm. Therefore, we have ignored (as well as in the experiment) the presence of diffusion layers and an increase in the electrolyte concentration in the region initially filled with distilled water. It is distinctly seen that, at  $\delta = 0$  ( $\Delta = 0$ ), expression (35) acquires the following explicit form:

$$P = \frac{D_{m-}}{v_m + 1} \left[ \sqrt{\sigma^2 + \frac{4}{\gamma^2}} - \sqrt{\sigma^2 + \frac{4}{\gamma^2 k^2}} - \sigma \frac{1 - v_m}{1 + v_m} \ln \frac{\sigma \frac{1 - v_m}{1 + v_m} + \sqrt{\sigma^2 + \frac{4}{\gamma^2}}}{\sigma \frac{1 - v_m}{1 + v_m} + \sqrt{\sigma^2 + \frac{4}{\gamma^2 k^2}}} \right]. \quad (36)$$

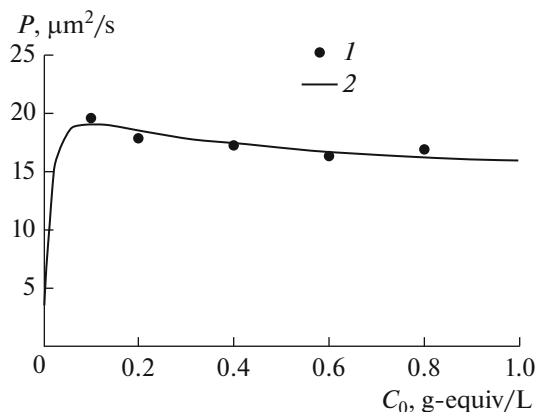


Fig. 5. The same as in Fig. 4 for  $\text{CaCl}_2$  electrolyte.

Table 3. Dependence of coefficient  $P$  on diffusion-layer thickness

| $\delta, \mu\text{m}$       | 0     | 50    | 100   | 200   | 400   | 520   | 1000  |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|
| $P, \mu\text{m}^2/\text{s}$ | 13.61 | 13.59 | 13.58 | 13.55 | 13.50 | 13.47 | 13.34 |

Table 4. Dependence of coefficient  $P$  on degree of NaCl-solution dilution to the right of MC-40 membrane ( $C_0 = 0.1 \text{ M}$ ),  $\delta = 100 \mu\text{m}$

| $k$                               | 10    | 100   | 1000  | 10000 |
|-----------------------------------|-------|-------|-------|-------|
| $P, \mu\text{m}^2/\text{s}, (35)$ | 9.617 | 9.758 | 9.759 | 9.759 |
| $P, \mu\text{m}^2/\text{s}, (36)$ | 9.595 | 9.738 | 9.740 | 9.740 |

Table 3 shows the values of  $P$  calculated by exact equation (35) at  $k = 100$ , these values attesting to a weak dependence of the diffusion permeability of MC-40 membrane with respect to NaCl electrolyte on diffusion-layer thickness in a very large range of its variations from 0 to 1000  $\mu\text{m}$  (membrane thickness is  $h = 520 \mu\text{m}$ , experimental permeability value is  $P = 13.0 \mu\text{m}^2/\text{s}$  at  $C_0 = 0.4 \text{ M}$ , while the value calculated by approximate Eq. (36) is  $P = 13.61 \mu\text{m}^2/\text{s}$ ). Diffusion coefficients of sodium and chlorine ions in an infinitely dilute solution,  $D_+ = 1350$  and  $D_- = 2030 \mu\text{m}^2/\text{s}$ , used in the calculations were taken from monograph [10].

As can be seen from Table 3, the scatter of diffusion permeability values at  $0 \leq \delta \leq 1000 \mu\text{m}$  is no higher than 2%, which is within the experiment error (5%). At  $k \rightarrow \infty$  and  $\delta = 0$ , boundary conditions (34) degenerate (with allowance for solution electrical neutrality) into conditions (5), which have already been derived in our work [1], while Eqs. (35) and (36) are transformed into Eq. (21) presented in this paper. As can be seen from the structure of Eq. (36), at high  $k$  values (which really take place in experiments), inte-

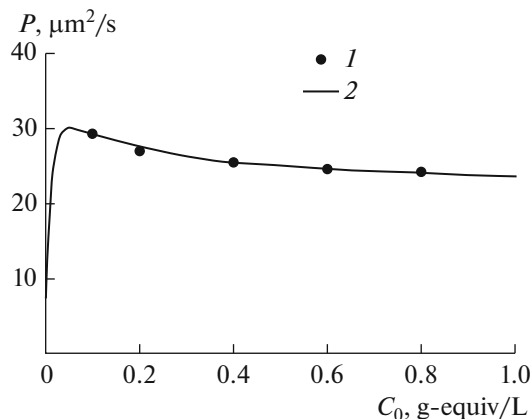


Fig. 6. The same as in Fig. 4 for  $\text{BaCl}_2$  electrolyte.

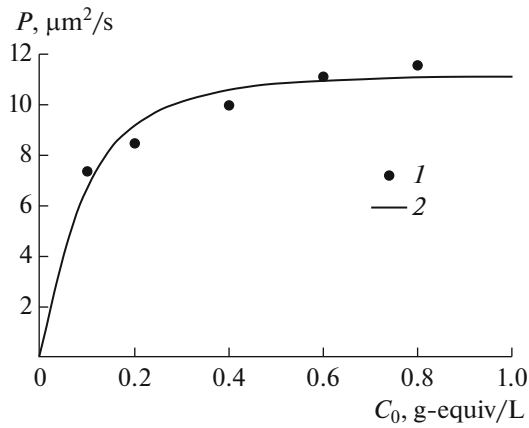


Fig. 7. The same as in Fig. 4 for LiCl electrolyte.

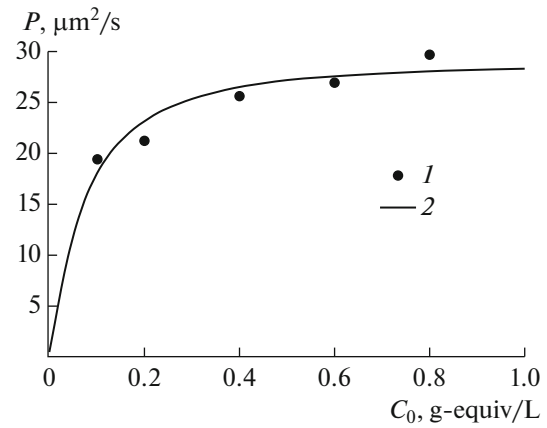


Fig. 10. The same as in Fig. 4 for KCl electrolyte.

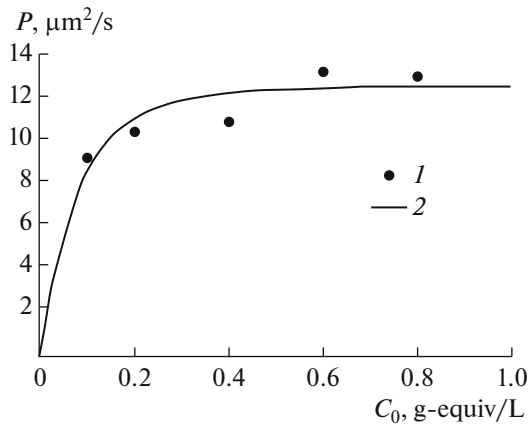


Fig. 9. The same as in Fig. 4 for NH<sub>4</sub>Cl electrolyte.

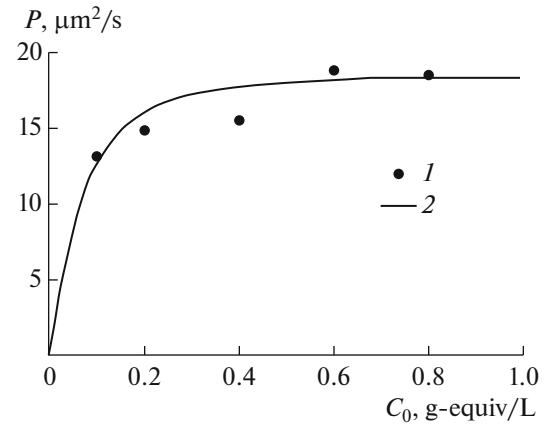


Fig. 11. The same as in Fig. 4 for CsCl electrolyte.

gral diffusion permeability  $P$  weakly depends on this parameter.

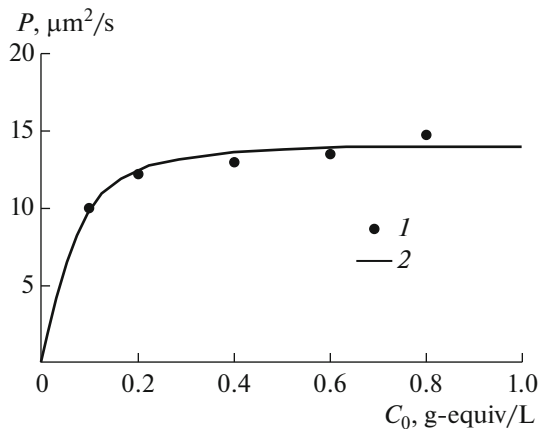


Fig. 8. The same as in Fig. 4 for NaCl electrolyte.

The  $P(k)$  dependences calculated for comparison by exact equation (35) and approximate equation (36) at sodium chloride concentration  $C_0 = 0.1$  M are presented in Table 4. Equation (21) yields  $P = 9.759$  at infinitely high  $k$  values (i.e., when the chamber to the right of the membrane contains pure water).

The data in Table 4 show that, at  $k \geq 100$ , the data calculated by any equation are almost identical, and the difference between the approximate and exact values is no larger than 0.5%. Under the experimental conditions, parameter  $k$  represents a function slightly increasing with time; i.e., the studied system is quasi-stationary.

### 8. CONCLUSIONS

In this work, on the basis of a homogeneous model of a fine-porous membrane, a general theory has been proposed for steady diffusion of an optional electrolyte

through a cation-exchange membrane into distilled water. Explicit algebraic equations have been derived for the determination of integral diffusion permeability coefficients of any symmetric  $Z_{0+} : Z_{0-}$  and asymmetric 1 : 2 and 2 : 1 electrolytes, as depending on the physicochemical parameters of a membrane system, such as the coefficients of equilibrium distribution of ion pairs, diffusion coefficients of ions involved in the process, and exchange capacity of a membrane. In the general case, to find the integral diffusion permeability coefficient, it is necessary to solve a set of two algebraic equations, with one of them being implicit. The derived equations enable one to find the aforementioned parameters from the comparison between calculated and experimental data. Such calculations have been performed with the use of the method of least squares and the Mathematica® 11 software for a heterogeneous MC-40 membrane. Diffusion coefficients of some inorganic ions in the MC-40 membrane matrix have for the first time been determined. It has been established theoretically and confirmed experimentally that, when the diffusion coefficient of a cation is higher, the concentration dependence of the integral diffusion-permeability coefficient exhibits a maximum. This maximum may be rather distinct (when ratio  $v_m$  of the diffusion coefficients of co- and counterions is rather high (Figs. 5, 6)), or weakly pronounced (Fig. 4). In the case of symmetric 1 : 1 electrolytes, the maximum also exists in the theoretical dependence but is difficult to find experimentally (Figs. 7–11).

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, projects nos. 15-08-03285 and 16-08-00642.

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*Translated by A. Kirilin*