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Theoretical Estimation of Differential Coefficients of Ion-Exchange Membrane Diffusion Permeability

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Abstract—It has been shown that the differential coefficients of the diffusion permeability of MK-40 and Nafion 425 sulfonic cation-exchange membranes to solutions of diverse electrolytes can be calculated within the framework of the theory of generalized conductivity of structurally inhomogeneous membranes with the use of model transport-structural parameters. The calculation has been performed on the basis of experimentally measured concentration dependences of the specific electrical conductivities and diffusion fluxes of electrolytes through membranes into water. The results of the model calculation are in satisfactory agreement with the data obtained by an independent method without resorting to notions of the structural organization of a membrane.

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INTRODUCTION

When solving boundary-value problems relevant to diffusion transfer in electromembrane systems, one needs information on the differential coefficients of diffusion permeability of ion-exchange membranes. These coefficients cannot be determined experimentally, but can be calculated without resorting to the ideas of the structural organization of a membrane by the equation that relates the integral (P_m) and differential (P_m^*) coefficients of diffusion permeability [1]:

$$P_m^* = \frac{j_m l}{C}\beta_j = P_m\beta_j, \tag{1}$$

where j_m is the diffusion flux density, l is the membrane thickness, C is the concentration of an electrolyte that diffuses into water, and β_j is an empirical constant characterizing the slope of the concentration dependence of the diffusion flux in logarithmic coordinates $\left(\beta_j = \frac{d\log j_m}{d\log C}\right)$. In spite of the fact that the diffusion flux of an electrolyte through a membrane into water is always intensified with a rise in solution concentration, the integral permeability coefficient may not only increase, but also decrease or remain unchanged [1]. This is related to the shape of the concentration profile in a membrane during the diffusion of an electrolyte and reflected in the value of parameter β_j. At $\beta_j = 1$, the concentration profile is linear and P_m is independent of concentration. At $\beta_j > 1$, the concentration profile is convex and P_m increases with the concentration. Finally, at $\beta_j < 1$, the concentration profile is concave and P_m decreases with a rise in the concentration of a diffusing solution.

The generalized conductivity theory presents another possibility to estimate the P_m^* value. In this case, a structurally inhomogeneous membrane is simulated by a two-phase system composed of a gel phase and a phase of an intergel solution, the properties of which are identical to the properties of an equilibrium solution [2–4]. The gel phase contains polymer chains with a high concentration of ionogenic groups and inert fragments of a membrane (crystallites and polyethylene in Nafion and MK-40 membranes, respectively, as well as a reinforcing textile).

To calculate the value of P_m^* by the equation [4]

$$P_m^* C = [f_1(\bar{D}_-\bar{C}_-)^\alpha + f_2(DC)^\alpha]^{1/\alpha}, \tag{2}$$

it is necessary to know the volume fractions of the phases of the gel (f_1) and the intergel solution (f_2), the diffusion coefficients of an electrolyte in a solution (D) and cations in the gel phase ($\bar{D}_-$), the concentration of cations ($\bar{C}_-$) in the gel phase, and the relative arrangement of the phases with respect to the direction of the electric current or diffusion flux, the character of which is reflected in parameter α.

The diffusion coefficient and concentration of cations in the gel phase cannot be measured experimentally, while the calculation of the $\bar{C}_-$ value requires knowing the Donnan constant (K_D), which is rather difficult to determine; therefore, the authors of [4] proposed to introduce complex parameter G, which characterizes the diffusion permeability of the gel phase of a membrane. The following relation is valid for a cation-exchange membrane:

$$G = \frac{K_\mathrm{D}\bar{D}}{(-z_-)\bar{Q}^{-\frac{z_-}{z_+}}}, \tag{3}$$

where $\bar{Q}$ is the concentration of groups fixed in the gel phase, this concentration being related to exchange capacity Q of the membrane as follows:

$$\bar{Q} = \frac{Q}{f_1}. \tag{4}$$

Then, the equation for P_m^* takes the form of

$$P_\mathrm{m}^* = [f_1(GC)^\alpha + f_2 D^\alpha]^{1/\alpha}. \tag{5}$$

In [4, 5], a method was proposed for determining parameter G from the concentration dependence of the diffusion permeability of a membrane by the equation

$$G = \frac{P_\mathrm{m}^*}{C_0}\left(\frac{\beta_j - 1}{f_1}\right)^{1/\alpha}, \tag{6}$$

where C_0 is the solution concentration at the middle point of a studied range.

Parameter α, which may vary from −1 in the case of a series arrangement of conducting phases to +1 in the case of their parallel arrangement, is calculated by the following equation:

$$\alpha = \frac{\ln\left(\frac{1 - f_1}{2 - \beta_j}\right)}{\ln\left(\frac{P_\mathrm{m}^*}{D}\right)}. \tag{7}$$

Volume fractions f_1 and f_2 of the conducting phases are found from the concentration dependence of membrane specific conductivity. Thus, to find the parameters required for calculating the value of P_m^* by Eq. (5), it is necessary to determine experimentally two concentration dependences—namely, the dependences of the diffusion flux of an electrolyte through a membrane into water and the specific conductivity of the membrane. It should be noted that, up to the present, the P_m^* value has been calculated by Eq. (5) only for ion-exchange membranes in NaCl solutions. The applicability of this approach to the determination of P_m^* in solutions of simple binary electrolytes of other natures and asymmetric electrolytes has not yet been studied.

Therefore, this work had two goals. The first goal was to study experimentally the regularities of the diffusion transfer of diverse electrolytes through sulfonic cation-exchange membranes with different structures. The second goal was to calculate the differential coefficients of diffusion permeability of the ion-exchange membranes by two methods, i.e., from the concentration dependence of the diffusion flux of an electrolyte through a membrane into water and by the equation of the generalized conductivity theory using model parameters of the membranes.

EXPERIMENTAL

The objects of study were sulfonic cation-exchange membranes with polystyrene (MK-40) and perfluorinated (Nafion 425) matrices and close values of specific moisture capacity. For comparison, the properties of analogous membranes were also studied, i.e., a heterogeneous CR 67-HMR sulfonic cation-exchange membrane with a matrix based on vinyl monomers and a homogeneous MF-4SK-101 membrane with a perfluorinated matrix. The physicochemical characteristics of all these membranes, i.e., thickness l, exchange capacity Q, and specific moisture capacity n in a 0.1 M NaCl solution are presented in Table 1.

The diffusion permeability and conductivity of the membranes were studied in solutions of electrolytes of different natures and concentrations. The diffusion flux values were determined in a two-chamber cell during electrolyte diffusion through a membrane into water. The increase in the electrolyte concentration in the water-containing chamber during electrolyte diffusion was recorded by conductometry. Membrane specific conductivity κ_m was calculated from the data on sample resistance, which was measured as the active component of the impedance of a mercury-contact cell. The experiments were performed at 25°C, and their error was no larger than ±5%.

RESULTS AND DISCUSSION

1. 1 : 1 Electrolytes

Solutions of HCl, LiCl, NaCl, KCl, NH_4Cl, CsCl, NaOH, $NaHCO_3$, $NaHSO_4$, and NaH_2PO_4 were used as simple binary electrolytes. The results of studying the integral diffusion permeability coefficients of the membranes in 0.1 M solutions of alkali metal chlorides are presented in Fig. 1a as dependences of this characteristic on crystallographic radius r_+ of a counter-ion, which, for ions bearing the same charge, determines their radii in the hydrated state, and, consequently, their mobilities and diffusion coefficients. Table 2 shows that a reduction in the hydrated-ion radius in the series Li^+–Na^+–K^+–NH_4^+–Cs^+ leads to a regular decrease in moisture contents W and specific moisture capacities n of both homogeneous and heterogeneous membranes. However, the diffusion of ions that have smaller radii in the hydrated state proceeds more easily. Therefore, the integral diffusion permeability coef-

Table 1. Physicochemical characteristics of sulfonic cation-exchange membranes

Membrane (manufacturer)	Polymer matrix	Reinforcing textile	l, cm	Q, $\frac{\text{mmol}}{\text{g}}$	n, $\frac{\text{mol H}_2\text{O}}{\text{mol SO}_3^-}$
MK-40 (Shchekinoazot, Russia)	Heterogeneous membrane based on KU-2 cation-exchange resin (sulfonated polystyrene cross-linked by divinylbenzene) and polyethylene	Polycaproamide	0.0495	2.18	12.1
Nafion 425 (Dupont de Nemoure, United States)	Homogeneous membrane based on poytetrafluoroethylene and perfluorovinyl ether	Teflon	0.0366	0.81	12.9
CR 67-HMR (Ionics, United States)	Heterogeneous membrane based on vinyl monomers and polyacrylate fiber	Polycaproamide	0.0600	1.94	16.7
MF-4SK-101 (Plastpolimer, Russia)	Homogeneous membrane based on polytetrafluorethylene and perfluorovinyl ether	Teflon	0.0320	0.80	9.9

ficient of the membranes increases in the same series (Fig. 1).

For heterogeneous membranes, which, according to the data of reference contact porosimetry [3], contain heterogeneities between particles of a resin and an inert binder with a diameter of about 1 μm, a correlation is observed between variations in the values of P_{m}, diffusion coefficients D_+^0 of cations in infinitely dilute solutions, and diffusion coefficients of corresponding chlorides (Table 2). A similar increase in the diffusion characteristics of heterogeneous sulfonic cation-exchange membranes with the polystyrene matrix was also observed in [8, 9]. To confirm the increase in the diffusion permeability of the heterogeneous membranes with a rise in the crystallographic radius of a counter-ion, Fig. 1a (curve *3*) shows such a dependence for a CR 67-HMR sulfonic cation-exchange membrane, which has been made on the basis of vinyl monomers and acryl fiber and, therefore, have a higher level of the heterogeneity than the MK-40 membrane has.

For the perfluorinated membranes, which have a cluster–channel structure, this regularity remains preserved only until the effect of membrane dehydration begins to prevail. For example, a substantial decrease in moisture content *W* of the Cs^+-form Nafion 425 membrane (Table 2) leads to a reduction in the cluster diameters [11]. As a result, the P_{m} value of this membrane with respect to a CsCl solution is lower than that for a KCl solution (Fig. 1a, curve *1*).

Both the conductivity and diffusion permeability of the membranes also increase with the crystallographic radius of a counter-ion (Table 3). The conductivities of the MK-40 membrane in the K^+ and Cs^+ forms

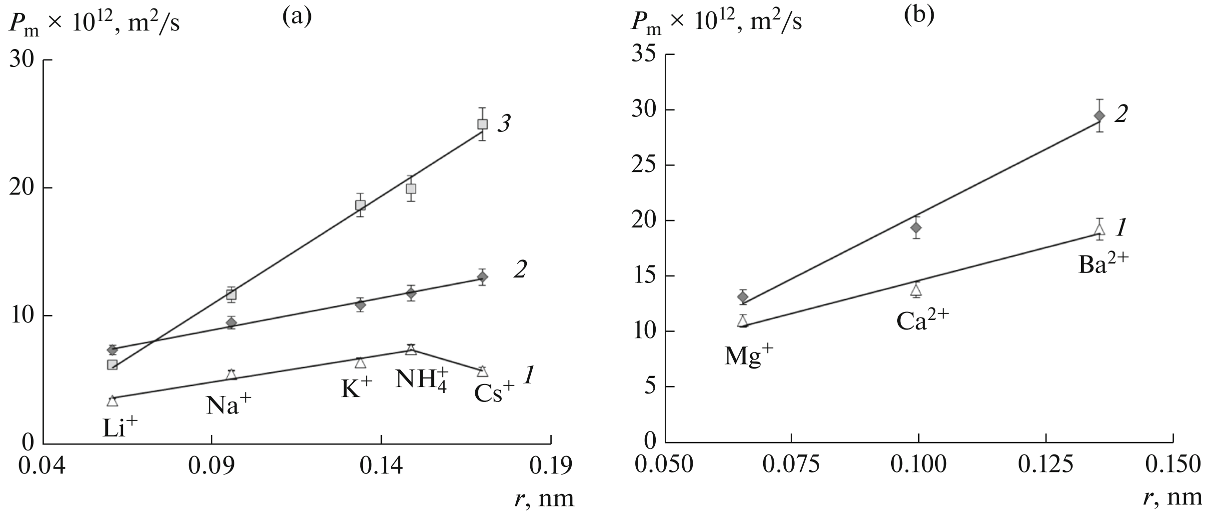

Fig. 1. Diffusion permeabilities of membranes in (a) 0.1 M solutions of alkali metal chlorides and (b) 0.05 M solutions of alkali-earth metal chlorides as functions of Pauling crystallographic radii of counter-ions: (*1*) Nafion 425, (*2*) MK-40, and (*3*) CR 67-HMR.

Table 2. Physicochemical characteristics of MK-40 and Nafion 425 membranes and electrolyte solutions

Electrolyte	MK-40		Nafion 425		Electrolyte solution	
	W, %	n, $\frac{\text{mol } H_2O}{\text{mol } SO_3^-}$	W, %	n, $\frac{\text{mol } H_2O}{\text{mol } SO_3^-}$	$D \times 10^9$, m^2/s [6]	$D_+^0 \times 10^9$, m^2/s [7]
0.1 M HCl	37.2	14.0	17.0	13.9	3.050	9.34
0.1 M LiCl	36.7	13.4	16.1	13.2	1.269	1.033
0.1 M NaCl	32.2	12.1	15.8	12.9	1.483	1.338
0.1 M KCl	29.4	10.7	8.9	7.3	1.844	1.962
0.1 M NH_4Cl	30.7	11.2	9.0	7.4	1.838	1.968
0.1 M CsCl	26.8	9.8	8.7	7.1	1.871	2.06
0.05 M $MgCl_2$	25.6	9.6	11.5	9.4	1.249	0.71
0.05 M $CaCl_2$	32.0	12.0	16.6	13.6	1.335	0.79
0.05 M $BaCl_2$	26.0	9.8	11.0	9.0	1.385	0.85

equilibrated with 0.1 M KCl and CsCl solutions are almost equal. This is due to the close values of conductivity κ of the solutions of these electrolytes. However, in the case of the perfluorinated membrane, its dehydration and, as a consequence, decrease in its specific conductivity take place even in a KCl solution. This agrees with the data on membranes of the Nafion type [11].

Figure 2 shows data on the diffusion flux through the sulfonic cation-exchange membranes for solutions of 1 : 1 electrolytes of different natures and concentrations. It is known that the nature of a co-ion has a determining influence on the diffusion permeability of ion-exchange membranes. Therefore, the highest j_m values have been obtained for the diffusion of NaOH solutions through both membranes [12, 13]. The close values of the diffusion characteristics of the MK-40 with respect to solutions of acidic sodium salts may be due to the fact that HCO_3^-, HSO_4^-, and $H_2PO_4^-$ anions have similar structures and almost the same mobility, and, according to the data of [14], the second-step dissociation of these anions does not take place.

The counter-ion nature, the influence of which may be monitored with the reference to the diffusion of NaCl and HCl, has a stronger effect on the diffusion permeability of heterogeneous membranes. Owing to the presence of large electrolyte-solution-filled intergel gaps and microdefects in their structure, in the course of HCl diffusion, the protons that move

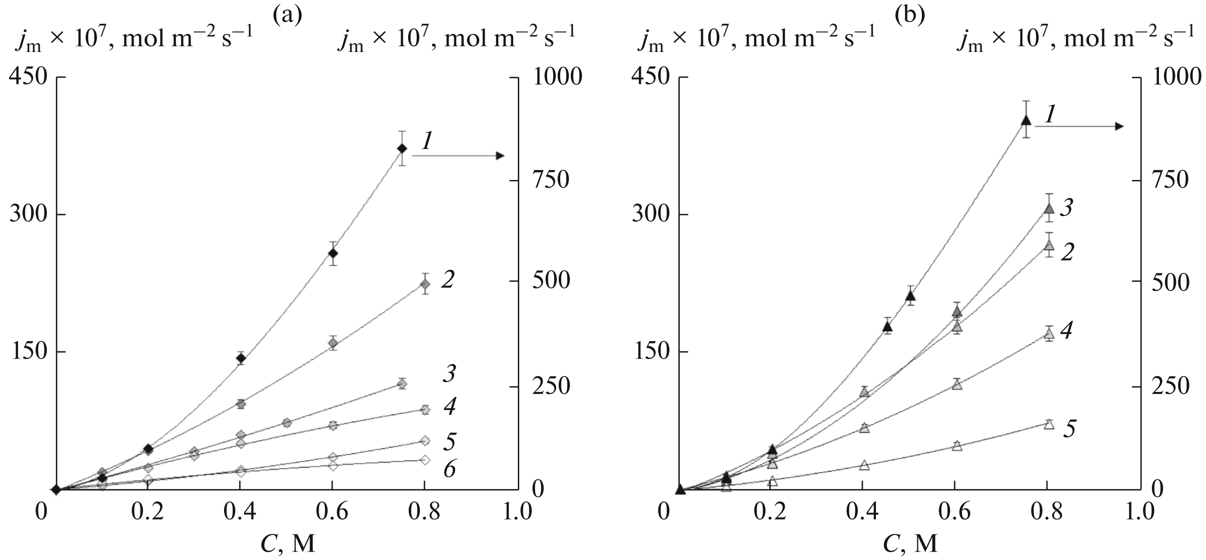

Fig. 2. Concentration dependences for diffusion fluxes through (a) MK-40 and (b) Nafion 425 membranes in solutions of binary electrolytes (*1*) NaOH, (*2*) NaCl, (*3*) HCl, (*4*) $NaHCO_3$, (*5*) $NaHSO_4$, and (*6*) NaH_2PO_4.

Table 3. Conductivity of electrolyte solutions and MK-40 and Nafion 425 membranes in these solutions

Electrolyte	r_+, nm [10]	κ_m, S/m		κ, S/m [10]
		MK-40	Nafion 425	
0.1 M HCl	0.208	3.081	1.782	3.91
0.1 M LiCl	0.060	0.380	0.351	0.96
0.1 M NaCl	0.095	0.440	0.459	1.07
0.1 M KCl	0.133	0.655	0.278	1.29
0.1 M CsCl	0.169	0.667	0.089	1.28
0.05 M $MgCl_2$	0.065	0.144	0.120	0.97
0.05 M $CaCl_2$	0.099	0.154	0.097	1.02
0.05 M $BaCl_2$	0.135	0.062	0.074	1.05

together with the Cl^- ions are seemingly transferred as components of hydronium complex ions, $H_7O_3^+ = H^+ \cdot 3H_2O$. As a result, the j_m value for HCl solutions is lower than that for NaCl solutions throughout the studied concentration range. The same regularity remains for perfluorinated membranes in dilute and moderately concentrated solutions. However, at $C >$ 0.5 M, the dependence reverses and the j_m value for HCl becomes higher than that for NaCl. A similar effect was observed in the experimental and theoretical study of the diffusion permeability of perfluorinated MF-4SK membranes [15] cast from a solution of the polymer in isopropanol. This may be due to the rearrangement of the hydronium complex ion, $H_7O_3^+ = H^+ \cdot 3H_2O$ into $H_5O_2^+ = H^+ \cdot 2H_2O$, which is caused by a decrease in the moisture capacity of the perfluorinated membrane with an increase in the solution concentration [14].

The processing of the concentration dependences of electrolyte fluxes in logarithmic coordinates yields parameter β_j, which is necessary for calculating model parameters G and α by Eqs. (6) and (7), respectively. The transport-structural parameters calculated using a specially developed software [16] for MK-40 and Nafion 425 membranes in solutions of diverse electrolytes are listed in Table 4. It can be seen that the configuration of the concentration profile developing inside a membrane and, hence, the value of β_j, are affected by the nature of both counter- and co-ions. In the case of heterogeneous MK-40 membranes, the value of this parameter depends to a larger extent on the nature and mobility of the co-ion than the counter-ion.

It is of interest that, for the MK-40 membrane in NaH_2PO_4 solutions, the values of parameter β_j is lower than unity (Table. 4). Hence, parameter G cannot be calculated by Eq. (6), thus indicating the limited applicability of the generalized conductivity theory to describing the diffusion permeability of membranes, in which concave concentration profiles develop. In the case of the homogeneous Nafion 425 membrane, parameter β_j is higher than that of the MK-40 membrane for all electrolytes. Hence, the shape of the concentration profile developing inside a membrane is affected by not only the nature of the counter- and co-ions, but also the structural inhomogeneity of an ion-exchange material.

To determine the transport-structural parameters of the membranes, it was necessary to obtain the concentration dependences of their specific conductivities (Fig. 3) in addition to the concentration dependences of the electrolyte diffusion fluxes. As follows from the data presented in Fig. 3, the conductivities of both heterogeneous and homogeneous membranes are determined by their ionic forms. The higher conductivities of the MK-40 and Nafion 425 in a $NaHSO_4$ solution are related to the partial dissociation of HSO_4^- ions in the solution (dissociation constant is $K_2 = 1 \times 10^{-2}$), as a result of which the membranes occur in a mixed Na^+–H^+ form.

Analysis of structural parameters f_1 and f_2 shows that the volume fraction of the intergel-solution phase in the homogeneous Nafion 425 perfluorinated membrane is substantially smaller than that in the heterogeneous MK-40 membrane occurring in the same ionic form. Attention is drawn by an increase in parameter f_2 upon the passage of the membranes from the Na^+ to the H^+ form. A similar effect was observed in [17, 18]. It may be surmised that the increase in this parameter is "apparent" and caused by different mechanisms of Na^+ and H^+ transfer in an external electric field. Seemingly, proton transfer does not involve all of the gel phase water contained in the fixed

Table 4. Transport-structural parameters of MK-40 and Nafion 425 membranes in solutions of 1 : 1 electrolytes

Membrane	Solution	β_j	$G \times 10^{16}$, m^5/(mol s)	f_2	α
MK-40	NaOH	1.68	470.0	0.15	0.24
	NaCl	1.19	8.02	0.14	0.37
	HCl	1.14	0.10	0.26	0.19
	LiCl	1.22	4.34	0.16	0.35
	KCl	1.21	8.44	0.16	0.34
	NH_4Cl	1.17	5.16	0.16	0.33
	CsCl	1.24	17.2	0.15	0.36
	$NaHCO_3$	1.10	0.32	0.10	0.43
	$NaHSO_4$	1.16	0.14	0.17	0.14
	NaH_2PO_4	0.78	–	0.16	0.28
Nafion 425	NaOH	1.75	553.54	0.08	0.27
	NaCl	1.36	50.51	0.06	0.48
	HCl	1.69	79.13	0.16	0.12
	LiCl	1.31	13.40	0.07	0.43
	KCl	1.47	56.60	0.06	0.42
	$NaHCO_3$	1.25	15.52	0.05	0.53
	$NaHSO_4$	1.48	7.07	0.12	0.25

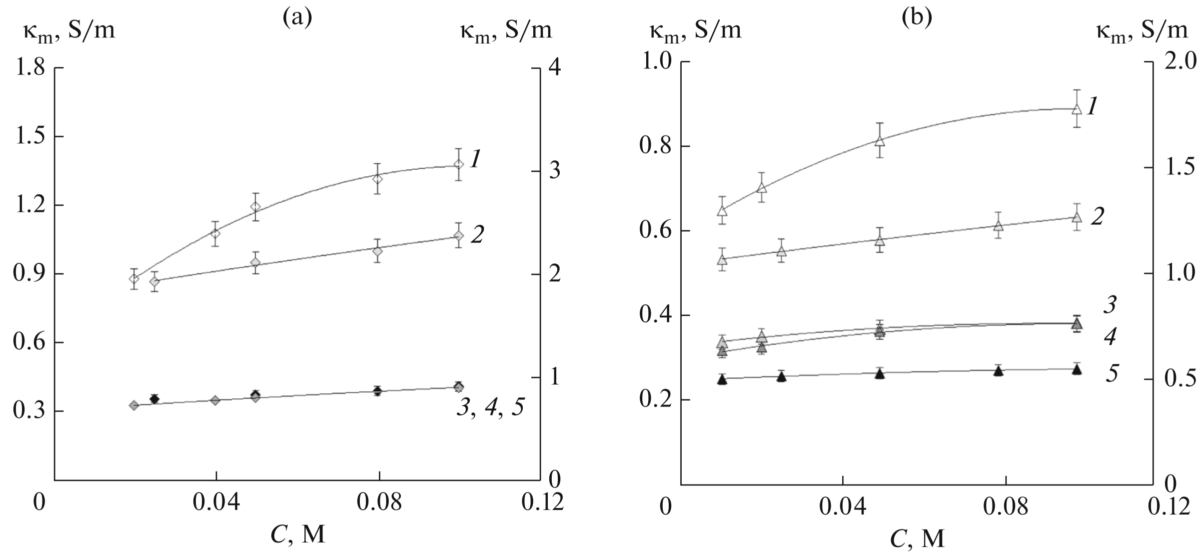

Fig. 3. Concentration dependences for conductivities of (a) MK-40 and (b) Nafion 425 membranes in solutions of binary electrolytes: (*1*) HCl, (*2*) $NaHSO_4$, (*3*) NaCl, (*4*) NaOH, and (*5*) $NaHCO_3$.

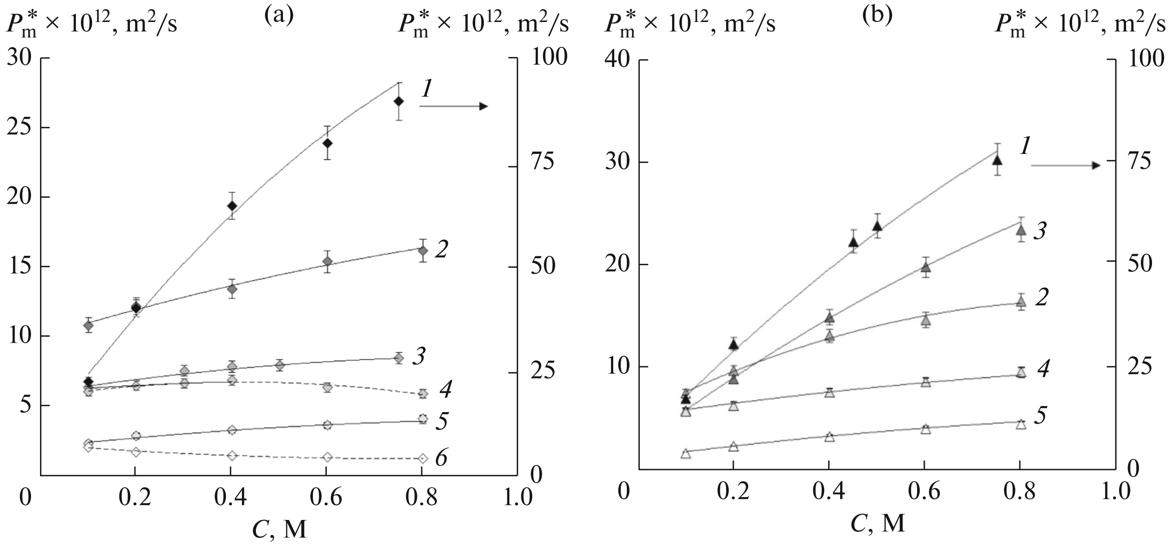

Fig. 4. Concentration dependences for differential coefficients of diffusion permeabilities in solutions of binary electrolytes calculated by Eq. (6) (solid lines) and (1) (dots connected by dashed lines) for (a) MK-40 and (b) Nafion 425 membranes: (*1*) NaOH, (*2*) NaCl, (*3*) HCl, (*4*) $NaHCO_3$, (*5*) $NaHSO_4$, and (*6*) NaH_2PO_4.

ion–counter-ion complexes, thereby leading to formally overestimated values of the volume fraction of the intergel solution when determining parameter f_2 from the data on the membrane conductivity. This explains the higher values of parameter f_2 for membranes with structures of different types in the $NaHSO_4$ solution to compare with solutions of other salts and confirms that the membranes are in the mixed Na^+–H^+ form in this solution.

As follows from the data in Table 4, the value of parameter G, which characterizes the diffusion permeability of the gel phase in a membrane, depends on not only the nature of the co-ion, but also the type of the counter-ion, the structural type of the membrane, and the exchange capacity of the latter. Since the heterogeneous MK-40 membrane has a higher exchange capacity, the diffusion permeability of its gel phase is markedly lower than that of the Nafion 425 membrane. Hence, the electrolyte diffuses in the heterogeneous membrane mainly through the intergel gaps, the volume fraction of which is three times higher than that in the Nafion 425 membrane.

The transport-structural parameters listed in Table 4 were used to calculate the differential coefficients of the diffusion permeabilities of the studied membranes by Eq. (5). The obtained P_m^* values are presented in Fig. 4 by solid lines. In the same figure, the points connected by dashed lines show the P_m^* values calculated by Eq. (1).

As follows from Fig. 4, the results of the calculations in terms of the model coincide (with an error of no higher than 5%) with the data calculated on the basis of the experimental concentration dependence of electrolyte diffusion flux through a membrane into water. The value of P_m^* could not be calculated by Eq. (5) for the MK-40 membrane in the solutions of NaH_2PO_4, because, in this case, the value of parameter β_j is smaller that unity (Table 4).

2. Asymmetric Electrolytes

Solutions of $MgCl_2$, $CaCl_2$, $BaCl_2$, Na_2CO_3, Na_2SO_4, Na_2HPO_4, and Na_3PO_4 were used as asymmetric electrolytes. As in the case of single-charged ions, a decrease in the radius of a hydrated ion in the series Mg^{2+}–Ca^{2+}–Ba^{2+} leads to a regular decrease in hydration parameters W and n of both homogeneous and heterogeneous membranes (Table 2). Therewith, the integral coefficients of the diffusion permeability of the membranes linearly grow in the same series of the alkali-earth metal chlorides (Fig. 1b). A correlation between variations in the values of P_m, D, and D_+^0 and a decrease in the radius of a hydrated ion is observed for both the heterogeneous membrane with the polystyrene matrix and the homogeneous perfluorinated membrane.

The specific conductivity of the heterogeneous membrane, as well as the conductivity of the solutions, slightly changes upon passage from Mg^{2+} to Ca^{2+} (Table 3). At the same time, the conductivity of the perfluorinated membrane decreases due to the dehydration of the membrane occurring in the form of

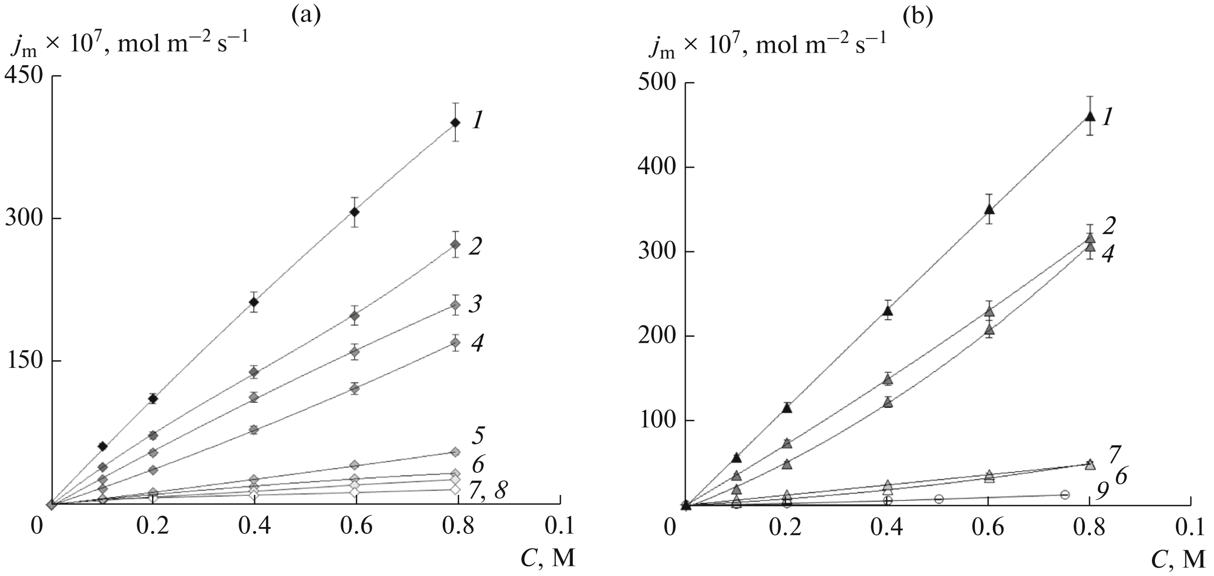

Fig. 5. Concentration dependences for diffusion fluxes through (a) MK-40 and (b) Nafion 425 membranes in solutions of asymmetric electrolytes: (*1*) $BaCl_2$, (*2*) $CaCl_2$, (*3*) $MgCl_2$, (*4*) NaCl, (*5*) Na_3PO_4, (*6*) Na_2SO_4, (*7*) Na_2CO_3, and (*8*) Na_2HPO_4; (*9*) MF-4SK-101 membrane in a Na_2SO_4 solution. Molar concentration of equivalents is counted in the abscissa axis.

bivalent ions. A substantial decrease in the conductivity of both membranes is observed in a $BaCl_2$, solution because of the formation of sulfo-group–barium counter-ion ion–dipole associates in the membrane structure.

The regularities revealed for variations in P_m and κ_m as depending on the radius and charge of a counter-ion (Fig. 1, Table 3) confirm that the counter-ion nature has a substantial effect on both the specific conductivity and diffusion permeability of the ion-exchange membranes with different structures.

Figure 5 illustrates the concentration dependences of the diffusion flux for solutions of different asymmetric electrolytes through the MK-40, Nafion 425, and MF-4SK-101 sulfonic cation-exchange membranes. As might be expected, the lowest j_m values are observed for the diffusion of solutions containing be- and trivalent co-ions. Especially low diffusion characteristics are characteristic for the MF-4SK membrane, which is designed to be used in the chlorine–alkali electrolysis. Lower values of the diffusion permeability of this membrane than those of the Nafion 425 were also reported in [19].

The values of parameter β_j found from the concentration dependences of the fluxes of asymmetric electrolytes are presented in Table 5. As can be seen from the presented data, parameter β_j is lower than unity for the diffusion of asymmetric electrolytes through the MK-40 membrane in almost all cases, with the exception of $MgCl_2$ and Na_3PO_4 solutions. Hence, the diffusion of these electrolytes inside the heterogeneous membrane is accompanied by the development of a concave concentration profile, while the integral coefficient of its diffusion permeability decreases with a rise in the solution concentration. Moreover, values $\beta_j \leq 1$ make impossible the calculation of model parameters G and α by Eqs. (6) and (7), respectively, for the subsequent determination of the diffusion permeability coefficients for these electrolytes in terms of the generalized conductivity theory. Such effects were not observed for the perfluorinated membranes: for all studied electrolytes, $\beta_j > 1$.

The concentration dependences of the specific conductivity of the membranes, which are necessary for determining their transport-structural parameters, are presented in Fig. 6. It can be seen that the conductivities of both heterogeneous and homogeneous membranes are, as in the case of simple electrolytes, determined to greater extent by the nature of a counter-ion and are almost independent of the cation nature.

The solid lines and dots in Fig. 7 show the results of calculating P_m^* by Eq. (5) with the use of the found transport-structural parameters and by Eq. (1), respectively. It can be seen that the results are in good agreement. However, for the MK-40 heterogeneous membrane, calculation of P_m^* by Eq. (5) was performed only for the electrolytes, in which the integral coefficient of membrane diffusion permeability increases with the concentration. In the case of the asymmetric electrolytes, the decreasing character of the concentration dependence of the integral coefficient of the diffusion permeability of this membrane is

Table 5. Transport-structural parameters of MK-40 and Nafion 425 membranes in solutions of asymmetric electrolytes

Membrane	Solution	β_j	$G \times 10^{16}$, m^5/(mol s)	f_2	α
MK-40	$MgCl_2$	1.05	0.21	0.18	0.37
	$CaCl_2$	0.93	–	0.16	0.43
	$BaCl_2$	0.91	–	0.17	0.46
	Na_2CO_3	0.88	–	0.21	0.25
	Na_2SO_4	0.87	–	0.20	0.27
	Na_2HPO_4	0.56	–	0.15	0.30
	Na_3PO_4	1.09	0.05	0.16	0.30
Nafion 425	$CaCl_2$	1.05	2.25	0.07	0.58
	$BaCl_2$	1.01	0.43	0.07	0.64
	Na_2CO_3	1.01	5×10^{-5}	0.13	0.32
	Na_2SO_4	1.31	0.60	0.17	0.22
MF-4SK-101	Na_2SO_4	1.34	2.24	0.01	0.55

observed much more frequently [20]. For the Nafion 425 perfluorinated membrane in solutions of both binary and asymmetric electrolytes, the results of the calculations in terms of the model and the data calculated by Eq. (1) without resorting to the ideas of the structural organization of a membrane coincide with each other with an error of no larger than 5%.

Thus, the generalized conductivity theory is applicable to determining the differential coefficients of diffusion permeability of ion-exchange membranes when the slope of the concentration dependence of the diffusion flux in bilogarithmic coordinates is larger than unity and the integral coefficient of the diffusion permeability increases with the concentration of a diffusing electrolyte solution.

CONCLUSIONS

It has been shown that the differential coefficients of the diffusion permeability of MK-40 and

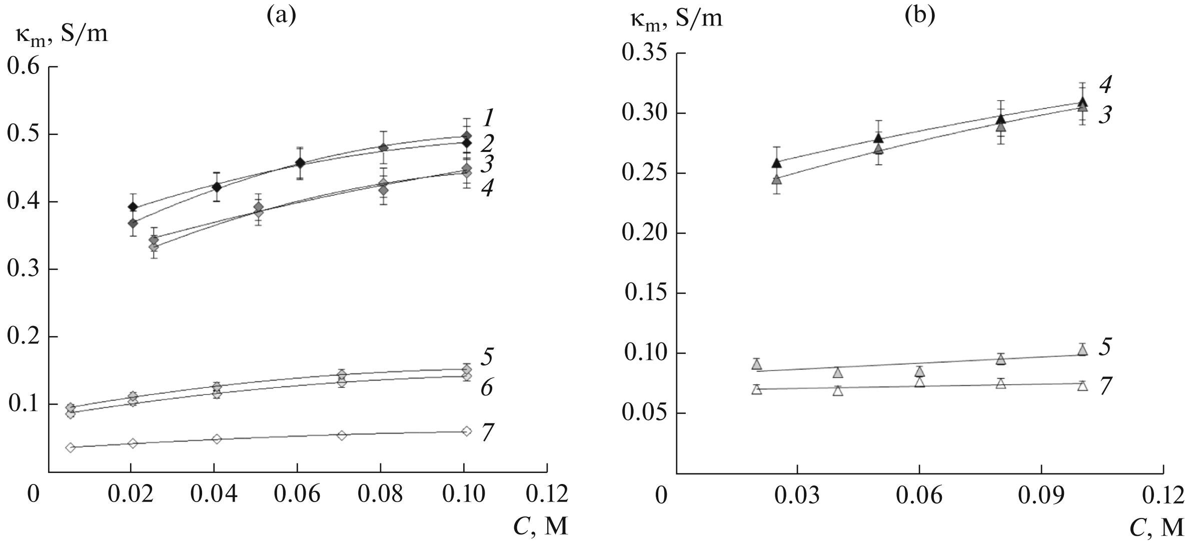

Fig. 6. Concentration dependences for conductivities of (a) MK-40 and (b) Nafion 425 membranes in solutions of asymmetric electrolytes: (*1*) Na_2HPO_4, (*2*) Na_3PO_4, (*3*) Na_2SO_4, (*4*) Na_2CO_3, (*5*) $CaCl_2$, (*6*) $MgCl_2$, and (*7*) $BaCl_2$.

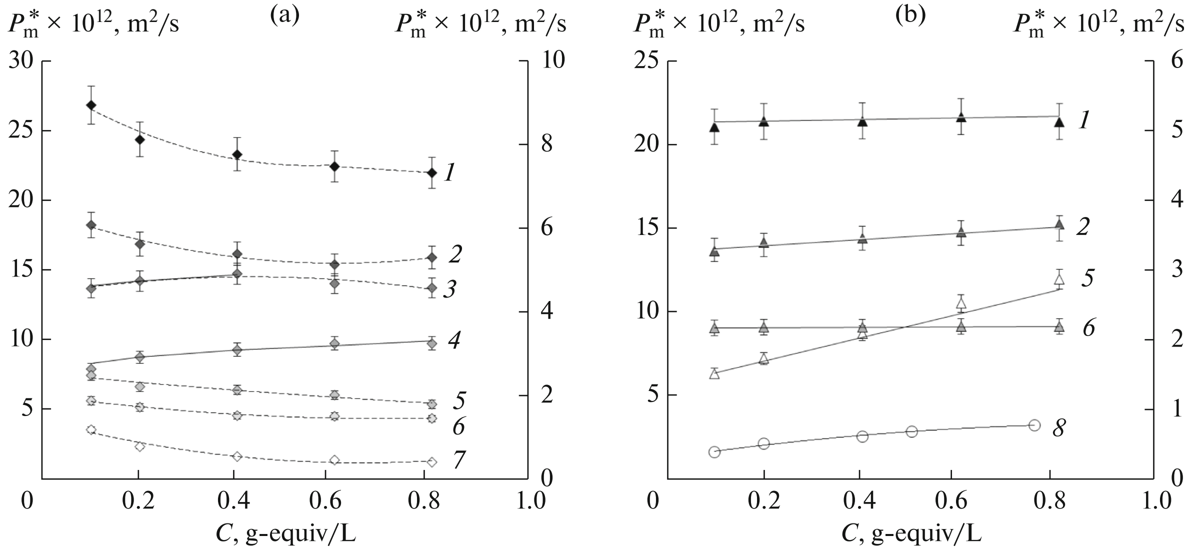

Fig. 7. Concentration dependences for differential coefficients of diffusion permeability in solutions of asymmetric electrolytes calculated by Eqs. (6) (solid lines) and (1) (dots connected by dashed lines) for (a) MK-40 and (b) Nafion 425 membranes: (*1*) $BaCl_2$, (*2*) $CaCl_2$, (*3*) $MgCl_2$, (*4*) Na_3PO_4, (*5*) Na_2SO_4, (*6*) Na_2CO_3, and (*7*) Na_2HPO_4; (*8*) MF-4SK membrane in a Na_2SO_4 solution. Molar concentration of equivalents is counted in the abscissa axis.

Nafion 425 sulfonic cation-exchange membranes with respect to both simple binary and asymmetric electrolytes may be calculated within the framework of the theory of the generalized conductivity of structurally heterogeneous membranes with the use of model transport-structural parameters. The calculation can be performed only when the integral coefficient of diffusion permeability increases with the concentration of a diffusing electrolyte solution. Experimental concentration dependences of the specific conductivity and diffusion fluxes of these electrolytes through the membranes into water have been employed for the calculation. The results of the model calculations are in satisfactory agreement with the data obtained by an independent method without resorting to the concepts of the structural organization of the membranes. It has been established that the degree of the influence of the counter-ion and co-ion nature on the differential characteristics of an ion-exchange membrane depends on its structural organization and the degree of heterogeneity. In the heterogeneous membrane, the decisive role is played by the co-ion nature, while, in the Nafion 425 perfluorinated membrane, which has a cluster–channel structure, a more convex concentration profile develops, and the values of the diffusion characteristics depend on the natures of both counter-ions and co-ions.

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