

Theoretical and Experimental Investigation of Interdiffusion in MF-4SC Sulfonated Cation-Exchange Membranes

A. N. Filippov^{a,*}, E. Yu. Safronova^b, and A. B. Yaroslavtsev^b

^aGubkin Russian State University of Oil and Gas, Leninskii pr. 65/1, Moscow, 119991 Russia

*e-mail: filippov.a@gubkin.ru

^bKurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

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Abstract—Theoretical approaches to describe the interdiffusion of aqueous solutions of inorganic 1 : 1 electrolytes having a common anion across a cation-exchange membrane have been discussed. A new method to characterize the interdiffusion of cations across an MF-4SC sulfonated cation-exchange membrane in terms of the “fine-pore membrane” homogeneous model taking into account the physicochemical properties of the membrane has been proposed. It has been theoretically found that the interdiffusion coefficient of the membrane with respect to a pair of electrolytes is inversely proportional to the difference in the reciprocals of the diffusion coefficients of the cations and depends on the ratio between the fixed charge density and the electrolyte concentration and on the equilibrium distribution coefficients of the cation–anion ionic pairs in the membrane matrix. The adequacy of the proposed approach has been confirmed via comparing theoretical calculations and experimental results on the interdiffusion permeability of the MF-4SC membranes.

Keywords: cation interdiffusion, diffusion permeability, MF-4SC perfluorinated sulfonated cation-exchange membrane, interdiffusion model

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INTRODUCTION

The study and description of the properties of ion-exchange membrane materials is an important and urgent problem of modern science because these materials are widely used in various technologies (purification, filtration, and liquid separation systems; hydrogen power engineering; catalysis; sensor systems; etc.) [1–4]. In recent decades, scientists have paid particular attention to the simulation of the ion and molecular transport across that sort of membranes because it is these processes that involve practical application of these materials [5–11]; most of the studies are focused on the electromigration processes. At the same time, the use of ion-exchange membranes is quite frequently based on the diffusion processes occurring therein. To describe these processes, a mathematical model of diffusion permeability of a 1 : 1 electrolyte across single-layer and bilayer membranes has been previously proposed and favorably tested for ion-exchange membranes, including those based on polystyrene and perfluorinated matrices [7]. This mathematical model has been successfully applied to study the effect of asymmetry of the diffusion permeability of an MF-4SC membrane containing polyaniline nanoparticles in the surface layer [12]. The authors of the cited study have estimated the modified-layer thickness and revealed the determining

effect of the difference in the absolute values of the effective exchange capacities of the layers on the development of an asymmetry effect in the diffusion permeability. Methods for estimating diffusion coefficients and effective ion-exchange constants from the data on the ionic conductivity and interdiffusion of mixed cation membranes have been proposed in [13]. The use of these methods makes it possible to predict the efficiency of transport processes at different ion concentration ratios.

Of no less importance is the development of approaches to describe the interdiffusion of cations across membranes. In this study, the interdiffusion of the cations of aqueous solutions of electrolytes has been first theoretically examined in terms of the fine-pore membrane model and compared with experimental data using the example of an MF-4SC perfluorinated sulfonated cation-exchange membrane.

THEORETICAL

Using the Nernst–Planck transport equations, formulate the stationary boundary problem of the interdiffusion of aqueous solutions of 1 : 1 electrolytes that have the same concentration C_0 and a common anion (here, NaCl and HCl) and are located on opposite sides of a cation-exchange membrane and occupy

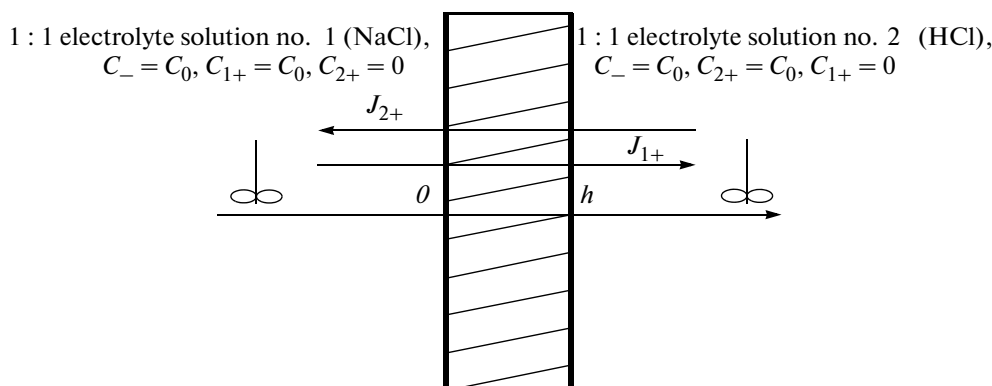


Fig. 1. Schematic interdiffusion of cations across a uniformly charged membrane.

semi-infinite regions (Fig. 1). It is assumed that the cation interdiffusion does not change the concentration on the other side of the membrane owing to the assumption that the electrolyte has an infinite volume and the process is quasi-equilibrium. The membrane is characterized by thickness h , coefficients of diffusion (mobility) D_{1+} , D_{2+} , D_- and equilibrium distribution γ_{1+} , γ_{2+} , γ_- of the two cations and the anion, respectively (γ_i represents the level of interaction of the ions with the membrane material), and fixed group concentration (exchange capacity) ($-\rho$), which is constant throughout the membrane thickness, $\rho > 0$. For simplicity, the presence of diffusion layers is neglected. In particular, this condition is almost satisfied under vigorous stirring of the solution. Take subscripts 1 and 2 for the metal cation and the proton, respectively. Let $\gamma_1 = \sqrt{\gamma_{1+}\gamma_-}$ and $\gamma_2 = \sqrt{\gamma_{2+}\gamma_-}$ be the equilibrium distribution coefficients of the $\text{Na}^+\text{-Cl}^-$ and $\text{H}^+\text{-Cl}^-$ ion pairs, respectively, in the membrane ($\gamma_i = \exp(\Phi_i)$, Φ_1 and Φ_2 are the averaged dimensionless interaction potentials for the ion pairs and the membrane pore walls expressed in terms of $k_B T$, k_B is the Boltzmann constant and T is the absolute temperature) and C_0 be the initial electrolyte concentration. In this case, in the membrane region of $0 < x < h$, the transport equations for the ions of the three types are written in the following standard form:

$$J_{1+} = -D_{1+}(C'_{1+} + C_{1+}\varphi'), \quad (1)$$

$$J_{2+} = -D_{2+}(C'_{2+} + C_{2+}\varphi'), \quad (2)$$

$$J_- = -D_-(C'_- - C_-\varphi'), \quad (3)$$

where the prime symbol denotes differentiation with respect to the x coordinate and φ is the dimensionless electric potential expressed in terms of F/RT (F is the Faraday constant and R is the universal gas constant). Here, J_{1+} , J_{2+} , J_- are the flux densities and C_{1+} , C_{2+} , C_- are the ion concentrations.

At the $x = 0$ and $x = h$ interfaces, the boundary conditions for the equality of chemical potentials are as follows [7, 12]:

$$C_0 = C_{1+}(+0)\gamma_{1+}\exp(\Delta\varphi_0), \quad (4)$$

$$0 = C_{2+}(+0)\gamma_{2+}\exp(\Delta\varphi_0), \quad (5)$$

$$C_0 = C_-(+0)\gamma_-\exp(-\Delta\varphi_0), \quad (6)$$

$$\gamma_{1+}C_{1+}(h-0)\exp(-\Delta\varphi_h) = 0, \quad (7)$$

$$\gamma_{2+}C_{2+}(h-0)\exp(-\Delta\varphi_h) = C_0, \quad (8)$$

$$\gamma_-\cdot C_-(h-0)\exp(\Delta\varphi_h) = C_0, \quad (9)$$

where $\Delta\varphi_0$ and $\Delta\varphi_h$ are the electric potential jumps at the respective interfaces. To close system (1)–(9), it should be supplemented with the conditions of electroneutrality

$$C_{1+} + C_{2+} = C_- + \rho \quad (10)$$

and the absence of an electric current

$$J_{1+} + J_{2+} = J_- \quad (11)$$

Since the 1 : 1 electrolytes on the two sides of the membrane have the same concentration and a drop of electric potential is supposed being equal to zero, the total flux of anions in this system is zero as well, while the fluxes of cations in a quasi-stationary process are equal in magnitude and opposite in sign ($J_{1+} = -J_{2+}$). In this context, by analogy with the case of diffusion permeability [7, 12], the H^+/Na^+ interdiffusion coefficient in the membrane can be introduced:

$$P \equiv \frac{J_{1+}h}{C_0} = -\frac{J_{2+}h}{C_0} > 0. \quad (12)$$

Boundary value problem (1)–(11) implies an exact analytical solution (this solution is described in detail in [14]). Note that, in this study, an algebraic expression for coefficient P as a function of electrolyte concentration on both sides of the membrane has been first derived:

$$P = \frac{\frac{\rho}{C_0}}{\frac{1}{D_{1+}} - \frac{1}{D_{2+}}} \times \left(-\ln \frac{\sqrt{1 + \frac{D_{1+}}{D_{2+}} \left(\frac{2C_0}{\rho\gamma_1} \right)^2} - 1}{\sqrt{1 + \left(\frac{2C_0}{\rho\gamma_2} \right)^2} - 1} + \sqrt{1 + \left(\frac{2C_0}{\rho\gamma_1} \right)^2} - \sqrt{1 + \left(\frac{2C_0}{\rho\gamma_2} \right)^2} \right), \quad (13)$$

It is evident from Eq. (13) that the H^+/Na^+ interdiffusion coefficient in the membrane is inversely proportional to the difference in the reciprocals of the diffusion coefficients of the cations in the membrane and does not depend on the diffusion coefficient of the anion. This means that this difference scales the $P(C_0)$ plot along the axis of ordinates. At the same time, P depends on the equilibrium distribution coefficients of both ion pairs.

In addition, according to Eq. (13), the interdiffusion coefficient tends to infinity and to a value characteristic of the uncharged membrane with a decrease in the electrolyte concentration C_0 to zero on both sides of the membrane and with an increase in the concentration, respectively:

$$\lim_{C_0 \rightarrow 0} P(C_0) = +\infty, \quad \lim_{C_0 \rightarrow +\infty} P(C_0) = 2 \left(\frac{1}{\gamma_1} - \frac{1}{\gamma_2} \right) / \left(\frac{1}{D_{1+}} - \frac{1}{D_{2+}} \right) \equiv P^\infty. \quad (14)$$

Thus, for an interdiffusion coefficient value known from experiment, at high (compared to the exchange capacity of the membrane) electrolyte concentrations, using Eq. (14), it is possible to find a relationship between the diffusion coefficients of the cations and the equilibrium distribution coefficients; this feature greatly simplifies subsequent calculations. It is evident from Eqs. (13) and (14) that the interdiffusion coefficient $P(C_0)$ decreases with increasing electrolyte concentration because the effect of the exchange capacity of the membrane on the process is suppressed since the right-hand side of Eq. (13) is defined, particularly, by the $\frac{\rho}{C_0}$ ratio between the exchange capacity of the membrane to the initial electrolyte concentration.

Equation (13) allows for simplification in two practice-significant cases:

(i) If $\left(\frac{2C_0}{\rho\gamma_{1,2}} \right)^2 \ll 1$ (fulfilled, e.g., provided that $\gamma_{1,2} \gg 1$), then

$$P \approx D_s \left(-\frac{\rho}{C_0} \ln \frac{(D_{1+}/D_{2+})\gamma_2^2}{\gamma_1^2} + 2 \frac{C_0}{\rho} \left(\frac{1}{\gamma_1^2} - \frac{1}{\gamma_2^2} \right) \right), \quad (15)$$

where a new notation is introduced for convenience:

$$D_s \equiv \frac{1}{\frac{1}{D_{1+}} - \frac{1}{D_{2+}}} = \frac{D_{1+}D_{2+}}{D_{2+} - D_{1+}}; \quad (16)$$

(ii) If $\left(\frac{2C_0}{\rho\gamma_{1,2}} \right)^2 \gg 1$ (fulfilled, e.g., provided that $\gamma_{1,2} \ll 1$), then

$$P \approx D_s \left(-\frac{\rho}{C_0} \ln \frac{(D_{1+}/D_{2+})\gamma_2}{\gamma_1} + 2 \left(\frac{1}{\gamma_1} - \frac{1}{\gamma_2} \right) \right). \quad (17)$$

EXPERIMENTAL

An MF-4SC ion-exchange membrane (Plast-polymer, St. Petersburg) with a thickness of $\sim 170 \mu\text{m}$ was used in the experiment. To standardize the conditions, the membrane was conditioned by the sequential exposure to a 5% solution of hydrochloric acid and deionized water at 80°C under constant stirring for 3 h. The cycle was conducted twice.

Ion-exchange capacity (EC, mmol/g) was determined as follows. A weighted portion (0.5–1 g) of the membrane held at a relative humidity of 95% was exposed to 50 mL of a 0.5 M NaCl solution (V_{NaCl} , L) under constant stirring for 24 h. After that, the salt solution was separated from the membrane and titrated with a NaOH solution of known concentration. The EC value was calculated by the formula

$$\text{EC} = \frac{C_{\text{H}^+} V_{\text{NaCl}}}{m} \times 10^{-3}, \quad (18)$$

where C_{H^+} is the proton concentration in the NaCl solution after holding the membrane in the solution (mol/L) and m is the mass of the membrane sample (g). To convert EC (mol/g) to ρ (mol/L), the density of the swollen membrane sample was taken to be 1.65 g/cm^3 .

To determine the interdiffusion coefficients, equal volumes of HCl and NaCl solutions with an equivalent concentration ($0.1 \text{ mol/L} \leq C_0 \leq 1 \text{ mol/L}$) were placed in cells separated by a membrane with an effective area of $S = 3.9 \text{ cm}^2$. In the experiment, the change in the pH value in the cell with the NaCl solution was measured using an Econix-Expert pH meter every 3 s. The pH meter was calibrated using standard buffer solutions. The end of the experimental run was determined from the stabilization of the pH values of the solution. Before each experiment, the membrane was converted into the hydrogen form by holding it in a 5% HCl solution and subsequent washing with deionized water to remove Cl^- ions. The interdiffusion coefficient was determined with the equation

$$P = \frac{dc}{dt} \frac{Vh}{S\Delta c}, \quad (19)$$

where V is the volume of the solution in the cells, cm^3 ; h is the membrane thickness, cm; Δc is the hydrogen ion concentration gradient, mol/cm^3 ; and t is the time, s (the error in the determination of P of less than

1%). The rate of change in the concentration $\frac{dc}{dt}$ was determined as the change in the H^+ ion concentration in the cell initially containing the NaCl solution within a given time.

COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

The adequacy of the proposed theory can be verified using Eq. (13). The curve in Fig. 2 shows the results derived by the least-square method from the best match of the theoretical dependence of the coefficient $P(C_0)$ (Eq. (13)) and experimental coefficient values. In the calculations, the value of exchange capacity ρ of the membrane found in an independent experiment was used ($\rho = 1.3$ M).

According to the calculations conducted using the FindFit procedure of the Wolfram Mathematica 9 software package, all the three physicochemical parameters of the membrane system were determined: equilibrium distribution coefficients γ_1 and γ_2 of the ion pairs of sodium chloride and hydrochloric acid, respectively, and the diffusion coefficient of the pair of cations in the membrane: $\gamma_1 = 0.1222$, $\gamma_2 = 0.1223$, and $D_s = 9.1 \times 10^{-9}$ m²/s.

The points and the curve in Fig. 2 show the results of the experiments and the calculations that are in good agreement with each other.

Note that the following pairs of parameters were determined in [15]: $D_1 = 12 \times 10^{-12}$ m²/s, $\gamma_1 = 0.30$ for the diffusion of NaCl and $D_2 = 30 \times 10^{-12}$ m²/s, $\gamma_2 = 0.65$ for the diffusion of HCl across the MF-4SC membrane in deionized water, where the averaged diffusion coefficients of the ion pairs are designated as follows [7]:

$$D_i = \frac{2D_-D_{i+}}{D_- + D_{i+}} \quad (i = 1, 2). \quad (20)$$

The calculation of the D_s value from these data in terms of the easily verified equality

$$\frac{D_{1+}D_{2+}}{D_{2+} - D_{1+}} \equiv \frac{D_1D_2}{2(D_2 - D_1)} (= D_s), \quad (21)$$

yields a value of $D_s = 9.4 \times 10^{-12}$ m²/s, which is 60 times lower than the D_s value resulting from processing of the data on interdiffusion (Fig. 2). In this case, the equilibrium distribution coefficients decrease by a factor of 3–5 and the positive ion sorption inside the membrane pores increases.

In fact, a change in the equilibrium distribution coefficients of the ion pairs compared to the case of individual diffusion of the two electrolytes across the membrane in water can be indicative of a modification of the MF-4SC cation-exchange membrane in the event of interdiffusion of the pair of electrolytes across the membrane, which leads to a change in the distribution coefficients and the diffusion coefficients of the

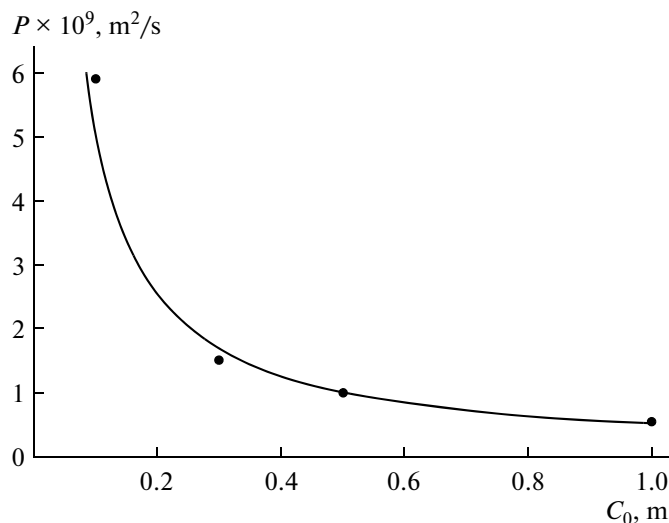


Fig. 2. H^+/Na^+ interdiffusion coefficient of the MF-4SC membrane for $\gamma_1 = 0.1222$, $\gamma_2 = 0.1223$, and $D_s = 9.1 \times 10^{-9}$ m²/s: (points) experiment and (curve) calculation by Eq. (13).

cations. Note that D_s is extremely sensitive to the difference in the diffusion coefficients of cations—the smaller the difference, the higher the D_s value—and to the value thereof: the higher the coefficients, the more significant the increase in D_s (see Eq. (21)).

Analysis of the ion concentration profiles with respect to the studied electrolytes and MF-4SC membrane using the general solution of the problem [14] yields a pattern schematically shown in Fig. 3 for the case of $C_0 < \rho$.

It is evident that the sodium cation concentration decreases from a maximum value of $\frac{\sqrt{\rho^2 + 4C_0^2/\gamma_1^2} + \rho}{2} \approx$

$\rho + \frac{C_0^2}{\rho\gamma_1^2}$ (at $\gamma_1 \gg \frac{C_0}{\rho}$) on the left side of the membrane to zero on the right side. The proton concentration, conversely, monotonically increases from zero on the

left side to a maximum value of $\frac{\sqrt{\rho^2 + 4C_0^2/\gamma_2^2} + \rho}{2} \approx$

$\rho + \frac{C_0^2}{\rho\gamma_2^2}$ (at $\gamma_2 \gg \frac{C_0}{\rho}$) on the right side. The chlorine anion concentration is close to zero everywhere inside the membrane and slightly decreases from $\frac{\sqrt{\rho^2 + 4C_0^2/\gamma_1^2} - \rho}{2} \approx \frac{C_0^2}{\rho\gamma_1^2}$ to $\frac{\sqrt{\rho^2 + 4C_0^2/\gamma_2^2} - \rho}{2} \approx \frac{C_0^2}{\rho\gamma_2^2}$.

The abrupt changes in the concentration at the interfaces are associated with jumps of the electric potential, which is negative and monotonically decreases

from a value of $\ln\left(\gamma_- \frac{\sqrt{\rho^2 + 4C_0^2/\gamma_1^2} - \rho}{2C_0}\right) \approx \ln\left(\frac{C_0}{\rho\gamma_{1+}}\right)$ at

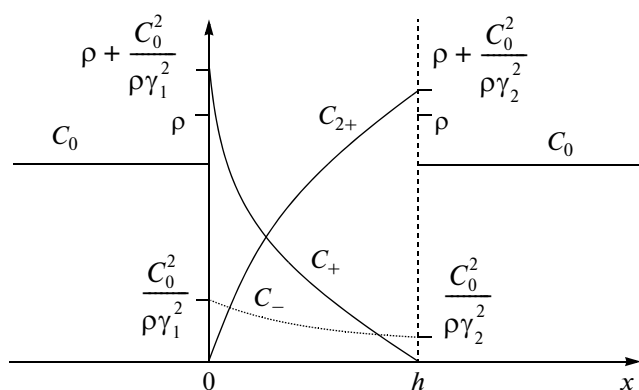


Fig. 3. Schematic ion concentration profiles during the interdiffusion of 1 : 1 electrolytes across a membrane provided that $\max\{\gamma_1, \gamma_2\} \gg \frac{C_0}{\rho}$.

the left interface of the membrane ($x = 0$) to a value of $\ln\left(\gamma_- \frac{\sqrt{\rho^2 + 4C_0^2/\gamma_2^2} - \rho}{2C_0}\right) \approx \ln\left(\frac{C_0}{\rho\gamma_{2+}}\right)$ at the right interface ($x = h$). It is also of interest to note that under accepted assumptions about null current density and null electric potential, according to the general solution [14], the profile of the electric potential in the membrane is entirely determined by the profile of the relative concentration and equilibrium partition coefficient of the coion (chlorine):

$$\varphi = \ln\left(\frac{C_- \gamma_-}{C_0}\right). \quad (22)$$

The last-mentioned fact suggests that the distribution coefficients of the anions also change during interdiffusion, although there is no anion flux across the membrane.

CONCLUSIONS

In this study, a new method for estimating the physicochemical parameters (the equilibrium distribution coefficients of ion pairs and the difference in the reciprocals of diffusion coefficients of cations) of the ion-exchange membrane–1 : 1 electrolyte solution system has been proposed; this method makes it possible to determine quantitative changes in the above param-

eters under the modification of ion-exchange membranes using experimental data on interdiffusion. These changes, in turn, provide the possibility of estimating the extent of modification and select optimum modes for the process.

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