

A Cell Model of an Ion-Exchange Membrane. Capillary-Osmosis and Reverse-Osmosis Coefficients

A. N. Filippov*

National University of Oil and Gas “Gubkin University”, Moscow, 119991 Russia

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

Received March 2, 2022; revised March 18, 2022; accepted March 21, 2022

Abstract—The capillary-osmosis and reverse-osmosis coefficients of an ion-exchange membrane have been calculated as the kinetic coefficients of the Onsager matrix within the thermodynamics of nonequilibrium processes and on the basis of the cell model proposed previously by the author for charged porous layers. The membrane is assumed to consist of an ordered set of spherical completely porous charged particles placed into spherical shells filled with a binary electrolyte solution. Boundary value problems have been analytically solved to determine the capillary-osmosis and reverse-osmosis coefficients of such a membrane under the Kuwabara boundary condition imposed on the cell surface. The consideration has been implemented within the framework of small deviations of system parameters from their equilibrium values under the action of external fields. Different particular cases of the obtained exact analytical equations have been studied including the case of a binary symmetric electrolyte and an ideally selective membrane. It has been shown that, for the considered cell model of an ion-exchange membrane, the Onsager reciprocity theorem is violated; i.e., the found kinetic cross coefficients are unequal to each other. The violation is explained by the fact that the reciprocity theorem is valid only for systems implying the linear thermodynamics of irreversible processes, for which generalized flows are equal to zero at nonzero thermodynamic forces.

DOI: 10.1134/S1061933X2203005X

DENOTATIONS			
Roman Symbols			
a	Is the particle radius	$m = \mu^i / \mu^o$	Is the viscosity ratio between a liquid in a Brinkman medium the pure liquid
b	Is the cell radius	$m_0 = 1 - \gamma^3$	Is the membrane macroscopic porosity
d	Is the electrical double layer thickness	L_{ij}	Are the kinetic coefficients of the Onsager matrix
k	Is the Brinkman constant	r	Is the radial coordinate
$k_D = \mu^o / k$	Is the Brinkman specific hydrodynamic permeability of an ion exchanger grain	R	Is the gas constant
C	Is the electrolyte concentration	T	Is the absolute temperature
C_0	Is the equivalent concentration of an electrolyte occurring at equilibrium with a membrane	p	Is the pressure
D and D_0	Are the diffusion coefficient and characteristic diffusion coefficient, respectively	$p_0 = RTC_0$	Is the characteristic osmotic pressure
I	Is the flux density of mobile charges (electric current density)	$Pe = \frac{aU_0}{D_0}$	Is the Peclet number
J	Is the diffusion flux density	$R_b = \sqrt{\mu^o / k} = \sqrt{k_D}$	Is the Brinkman radius (width of a filtration zone in a porous medium)
j	Is the dimensionless diffusion flux density	$s^2 = a^2 k / \mu^i$	Is a dimensionless parameter
F_0	Is the Faraday constant	$s_0^2 = ms^2 = a^2 / R_b^2$	Is a dimensionless parameter
h	Is the membrane thickness		

$U_0 = ap_0/\mu^0$	Is the characteristic filtration velocity
U	Is the solvent (water) flux density;
\mathbf{v}	Is the velocity vector
Z_{\pm}	Is the ion charge number (without a sign)

Greek Symbols

$\gamma = a/b$	Is a dimensionless parameter
$\delta = d/a$	Is the dimensionless thickness of an electrical double layer
∇	Is the gradient operator
ϵ_0 and ϵ	Are the dielectric constant and the relative dielectric permittivity of a medium, respectively
μ^0	Is the viscosity of a pure liquid
μ^i	Is the viscosity of a liquid in a Brinkman medium
μ	Is the chemical potential
μ_0	Is the standard chemical potential
φ	Is the electric potential
$-\rho_V$	Is the volume density of the fixed charge of a porous skeleton (ion exchanger)
$\bar{\rho} = \frac{\rho_V}{F_0}$	Is the exchange capacity of an ion exchanger grain (absolute value)
$\sigma = \frac{\rho_V}{F_0 C_0}$	Is the dimensionless exchange capacity
$\bar{\rho}_0 = \frac{\mu^0 D_+}{k_D RT}$	Is the characteristic exchange capacity
Φ_i	Denotes the gradients of external forces applied to a cell and a membrane

Indices

“1”	Indicates a physical value of deviation from its equilibrium magnitude
“e”	Indicates an equilibrium value
“o”	Indicates a value that refers to the liquid shell of a cell
“i”	Indicates a value that refers to a porous particle in a cell
~	Indicates a dimensionless value
“1” and “2”	Indicate the left- and right-hand sides, respectively, of a membrane located in a measuring cell
m	Indicates a value that refers to a membrane
±	Indicates a value that refers to cations/anions

INTRODUCTION

The cell method described in detail by Happel and Brenner in their well-known monograph [1] is widely and efficiently employed to study concentrated disperse systems, including membranes. A cell model of, e.g., an ion-exchange membrane implies, in particular, replacement of a real set of chaotically arranged ion exchanger grains by a periodic array of identical porous charged spheres enclosed by concentric spherical shells, which are filled with an electrolyte and form a porous layer. In the cell method, the effects of adjacent particles are taken into account by imposing specific boundary conditions on the surface of the liquid shell. It is assumed that the gradients of external forces applied to the porous layer coincide with the local gradients for the cells. The described approach is advantageous in the fact that all parameters, such as thermodynamic fluxes and forces, included in the equations for transport through the porous layer may be directly measured in experiments. In [2], a cell model of an ion-exchange membrane was formulated; a problem concerning the determination of kinetic coefficients was set and solved in the general form, and an exact algebraic expression was, for the first time, derived for hydrodynamic permeability L_{11} of a charged membrane. The model formulated in [2] was then used to determine electroosmotic permeability L_{12} and specific conductivity L_{22} of a cation-exchange membrane, while, in [3], diffusion permeability L_{33} and electrodiffusion coefficient L_{23} were found. The proposed cell model was successfully verified using the experimental data obtained for a cast perfluorinated MF-4SC membrane and that modified with halloysite nanotubes functionalized with platinum and iron nanoparticles in aqueous HCl solutions, as well as for an extruded MF-4SC membrane and a number of 1 : 1 electrolytes (HCl, NaCl, KCl, LiCl, and CsCl). To determine the physicochemical and geometric parameters of the model, a special computational algorithm and a program were developed within the framework of the Mathematica® computing shell for the simultaneous optimization of specific conductivity and electroosmotic permeability with respect to experimental dependences.

In this work, the gradients of pressure, electric potential, and chemical potential $\mu(C) = \mu_0 + RT \ln(C/C_0)$: $\Phi_1 = \nabla p \approx (p_{20} - p_{10})/h$, $\Phi_2 = \nabla \varphi \approx (\varphi_{20} - \varphi_{10})/h$, $\Phi_3 = \nabla \mu(C) \approx RT(C_{20} - C_{10})/(C_0 h)$, respectively, have been selected as independent thermodynamic forces, which are preset in the experiments. Here, C_0 is the equivalent concentration of an electrolyte brought in contact with a membrane, μ_0 is the standard chemical potential, h is the membrane thickness, R is the gas constant, T is the absolute temperature, and subscripts “1” and “2” indicate, respectively, the left- and

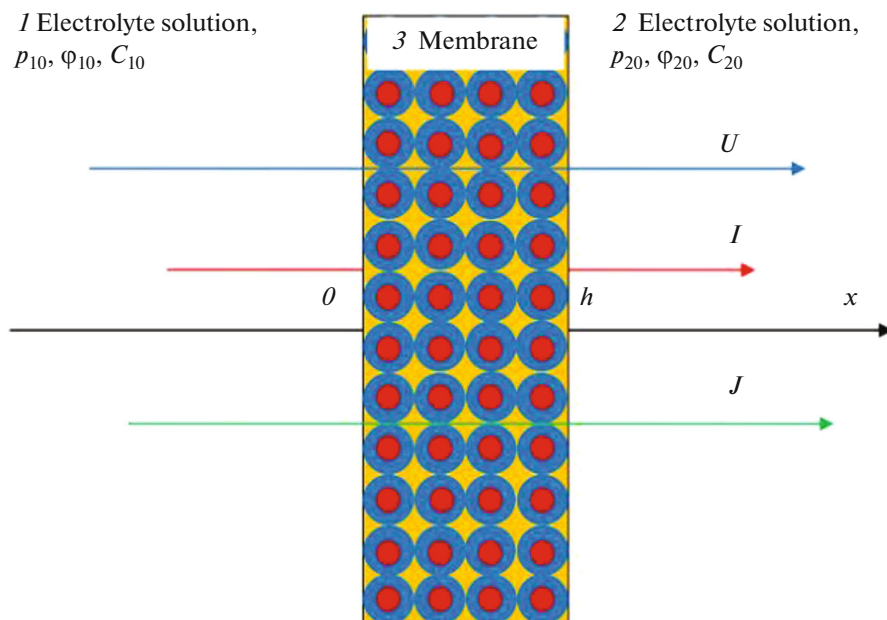


Fig. 1. Membrane cell used to study nonequilibrium processes: (1, 2) donor and acceptor chambers, respectively, and (3) membrane.

right-hand sides of a membrane located in a measuring cell filled with a binary electrolyte solution (Fig. 1). In contrast to [2], the chemical potential gradient rather than the concentration gradient is used here to correctly derive the equations for the kinetic coefficients related to the existence of a concentration drop across the membrane, as in [3].

Flux densities of a solvent (e.g., water), U ; mobile charges (electric current density), I ; and a solute (electrolyte diffusion flux density), J , have been taken as dependent thermodynamic parameters determined in the experiments. Then, the phenomenological transport equations for isothermal processes may be written as the following set linear equations:

$$\begin{cases} U = -(L_{11}\nabla p + L_{12}\nabla\varphi + L_{13}\nabla\mu), \\ I = -(L_{21}\nabla p + L_{22}\nabla\varphi + L_{23}\nabla\mu), \\ J = -(L_{31}\nabla p + L_{32}\nabla\varphi + L_{33}\nabla\mu). \end{cases} \quad (1)$$

According to the Onsager reciprocity theorem, the matrix of kinetic coefficients must be symmetric: $L_{ik} = L_{ki}$ ($i \neq k$). However, as will be shown below, this property becomes invalid in our case. Here, we shall discuss the calculation of capillary-osmosis L_{13} and reverse-osmosis L_{31} coefficients of an ion-exchange membrane, with these coefficients being found by expressions that follow from Eq. (1):

$$L_{13} = -\frac{U}{\nabla\mu}\Big|_{\nabla p=0, \nabla\varphi=0}, \quad (2a)$$

$$L_{31} = -\frac{J}{\nabla p}\Big|_{\nabla\mu=0, \nabla\varphi=0}. \quad (2b)$$

Relations (2) indicate that coefficient L_{13} may be correctly measured only in the absence of drops of the pressure and electric potential and at preset constant chemical potential drop $\mu_{20} - \mu_{10} \approx h\nabla\mu = \text{const}$ across the membrane, while coefficient L_{31} may be found in the absence of drops of the chemical and electric potentials and at preset constant pressure drop $p_{20} - p_{10} \approx h\nabla p = \text{const}$.

GENERAL FORMULATION OF THE PROBLEM

We shall simulate a charged membrane by a periodic array of porous spherical charged particles of the same radius a enclosed by liquid spherical shells of radius b , which is selected in a manner such that the particle-to-cell volume ratio is equal to the volume fraction of particles in the disperse system:

$$\gamma^3 = (a/b)^3 = 1 - m_0, \quad (3)$$

where m_0 is the macroscopic porosity, which depends of the character of packing porous particles in a charged layer (membrane) (Fig. 2).

The mathematical formulation of the problem has been presented in [2]; here, it is not repeated for short. The denotations of the variables and parameters coincide with those in [2]. For the convenience of a reader, the list of the main denotations is presented at the

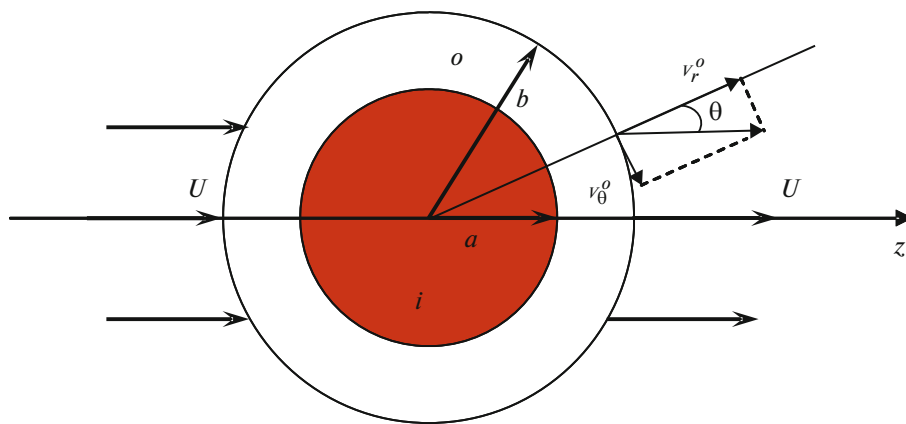


Fig. 2. Unit cell of the membrane: (*o*) outer region (electrolyte solution) and (*i*) inner region (charged porous particle).

beginning of the article. The flow of an incompressible liquid (electrolyte) at small Reynolds numbers (“creeping flow”) in the outer region ($a < r < b$) is described by the Stokes vector differential equation supplemented with the spatial electric force. The flow of the liquid in the inner region ($0 \leq r < a$) obeys the Brinkman vector differential equation [4], complicated by the same spatial electric force. Traditionally, a “Brinkman liquid” is assumed to be incompressible [5]. The electric potential satisfies the Poisson equation inside and outside of the particles, while the Nernst–Planck representation is used for the flux density of ions. Therewith, sources and sinks of charges are absent in the system, and the problem is considered under stationary conditions. Let, as in [2], $-\rho_v$ be the volume density of the porous skeleton fixed charge. To be more specific, the particle charge is taken to be negative (a cation-exchange membrane is simulated); then, $\rho_v > 0$. To make the analysis more convenient, we use dimensionless variables and values the same as in [2]:

$$\begin{aligned} \tilde{r} &= r/a, \quad \tilde{\mathbf{v}} = \mathbf{v}/U_0, \quad \tilde{p} = p/p_0, \quad \tilde{\sigma}_{r\theta} = \sigma_{r\theta}/p_0, \\ \tilde{\sigma}_{rr} &= \sigma_{rr}/p_0, \quad \tilde{C}_{\pm} = C_{\pm}/C_0, \quad \tilde{\varphi} = \frac{\varphi F_0}{RT}, \\ \mathbf{j}_{\pm} &= \frac{\mathbf{J}_{\pm}}{U_0 C_0}, \quad v_{\pm} = D_0/D_{\pm}, \quad v_{m\pm} = D_0/D_{m\pm}, \\ \text{Pe} &= \frac{aU_0}{D_0}, \quad \sigma = \frac{\rho_v}{F_0 C_0}, \quad p_0 = RTC_0, \\ U_0 &= ap_0/\mu^o, \quad \delta = d/a, \quad m = \mu^i/\mu^o, \\ s^2 &= a^2 k/\mu^i, \quad s_0^2 = ms^2 = a^2/R_b^2, \end{aligned} \quad (4)$$

where $R_b = \sqrt{\mu^o/k}$ is the characteristic thickness of a filtration layer (Brinkman radius), D_0 is the scale of diffusion coefficients, $d = \left(\frac{C_0 F_0^2}{\varepsilon \varepsilon_0 RT} \right)^{-1/2}$ is the Debye

radius, Pe is the Peclet number, and F_0 is the Faraday constant. Below, the tilde symbol will be omitted for convenience. Assuming the Debye radius to be negligibly small as compared with the particle radius, the electrical double layers (EDLs) are adequately displaced by jumps of the electric potential and ion concentrations across geometric interface $r = 1$ [2, 3]. In the absence of external forces Φ_i ($i = 1, 2, 3$), each cell of the membrane is at equilibrium with an ambient quiescent electrolyte solution; i.e., the velocities and ion flux densities are equal to zero in this state. At the same time, equilibrium distributions of ions $C_{e\pm}^o$, $C_{e\pm}^i$ and electric potential φ_e^o , φ_e^i are established in the system. The problem concerning the determination of the equilibrium concentrations and the potential was solved in [2] (see Eqs. (28)–(32)). Assuming that the imposition of an external field causes small deviations of the sought functions from their equilibrium values and linearizing all equations and boundary conditions of the boundary problem for the cell with respect to these small deviations (they have subscript 1), we arrive at the Laplace equations for the unknown potential and unknown nonequilibrium equivalent electrolyte concentration $C_1 = Z_+ C_{1+} = Z_- C_{1-}$ [2]:

$$\Delta \varphi_1 = 0, \quad \Delta C_1 = 0. \quad (5)$$

These equations are valid throughout the cell.

The general solutions of Eqs. (5) were presented in [2]:

$$\varphi_1^o = \left(G^o r + \frac{H^o}{r^2} \right) \cos \theta, \quad C_1^o = \left(L^o r + \frac{M^o}{r^2} \right) \cos \theta \quad (6)$$

at $1 < r \leq 1/\gamma$,

$$\varphi_1^i = G^i r \cos \theta, \quad C_1^i = L^i r \cos \theta, \quad (7)$$

at $0 \leq r < 1$,

where integration constants $G^{o,i}$, $L^{o,i}$, H^o , and M^o are to be determined from the boundary conditions.

DETERMINATION OF CAPILLARY-OSMOSIS COEFFICIENT

Let us initially formulate the boundary conditions imposed on unit cell for this boundary value problem. The linearization of the conditions for the equality of electrochemical potentials of ions at the interface enables us to write the following [2, 3]:

$$C_1^o = \alpha^o (\varphi_1^i - \varphi_1^o), \quad C_1^i = \alpha^i (\varphi_1^i - \varphi_1^o) \quad \text{at } r = 1, \quad (8)$$

$$\alpha^o = \frac{Z_+ \beta_+ + Z_- \beta_-}{\sigma}, \quad \alpha^i = \frac{Z_+ + Z_-}{\sigma} \beta_+ \beta_-, \quad (9)$$

$$\beta_{\pm} = \frac{\exp(\mp Z_{\pm} \varphi_e^i)}{\gamma_{\pm}},$$

γ_{\pm} , $\gamma_m = \sqrt{\gamma_+ \gamma_-}$ are the coefficients of the equilibrium distributions for ions and molecules of the electrolyte in an ion exchanger grain (gel), respectively; and φ_e^i is the equilibrium dimensionless electric potential in the grain, with this potential being found by equation $\beta_+ - \beta_- = \sigma$ [2].

At interface $r = 1$, the conditions for equality between the radial components of ion fluxes must be fulfilled, with these conditions leading to the following set of equations relative to the unknown constants (see Eq. (43a) in [2]):

$$\text{Pe} u_{11} (\beta_+ - 1) = \frac{L^i + Z_+ \beta_+ G^i}{v_{m+}} - \frac{L^o - 2M^o + Z_+ (G^o - 2H^o)}{v_+}, \quad (10)$$

$$\text{Pe} u_{11} (\beta_- - 1) = \frac{L^i - Z_- \beta_- G^i}{v_{m-}} - \frac{L^o - 2M^o - Z_- (G^o - 2H^o)}{v_-}.$$

Here, taking into account the form of the general solution for radial velocity component u_1 , the following denotation has been introduced:

$$u_{11} \equiv \frac{u_1|_{r=1}}{\cos \theta}. \quad (11)$$

Cell pressure gradient Φ_1 was previously determined as $\nabla p = -F/V$, where $V = 4\pi b^3/3$ is the cell volume, while $F = -4\pi B a \mu^o U_0$ is the force applied from the side of a liquid to a porous charged particle [1, 2], this leading to

$$\Phi_1 = \nabla p = 3B\gamma^3 \frac{\mu^o U_0}{a^2}. \quad (12)$$

Cell electric potential gradient Φ_2 was determined in [3] as

$$\nabla \varphi = \frac{RT}{aF_0} \frac{\varphi_1^o|_{r=1/\gamma; \theta=0} - \varphi_1^o|_{r=1/\gamma; \theta=\pi}}{2/\gamma}. \quad (13)$$

Analogously to [3], let us introduce cell chemical potential gradient Φ_3 as follows:

$$\nabla \mu(C) = \frac{RTZ_0}{a} \frac{C_1^o|_{r=1/\gamma; \theta=0} - C_1^o|_{r=1/\gamma; \theta=\pi}}{2/\gamma}, \quad (14)$$

where $Z_0 = (Z_+ + Z_-)/Z_+ Z_-$. As follows from Eq. (2a), when calculating capillary-osmosis coefficient L_{13} , the gradients of the electric potential and pressure across the membrane must be absent, while the chemical potential gradient must be constant:

$$\Phi_3 = \frac{RTZ_0}{a} \text{const}_3. \quad (15)$$

With allowance for Eq. (13), first condition $\Phi_2 = 0$ nullifies the electric potential on the cell surface:

$$\varphi_1^o = 0 \quad \text{at } r = 1/\gamma. \quad (16)$$

Substituting general solution (6) for the potential into Eq. (16), we obtain

$$G^o = -\gamma^3 H^o. \quad (17)$$

Taking into account Eq. (12), second condition $\Phi_1 = 0$ yields $B = 0$, thus allowing us to use the set of algebraic equations (45a) and (47a), which were obtained in [2] by imposing the Kuwabara condition (absence of vorticity) on the cell surface, for determining some constants that are necessary for solving the hydrodynamic problem (see relations (23) and (24) in [2]):

$$A = B = D = E = 0, \quad C = F = -\frac{\sigma G^i}{ms^2} = u_{11}. \quad (18)$$

With regard to Eq. (14), third condition (15) imposes the following boundary condition on the concentration:

$$C_1^o|_{r=1/\gamma} = \frac{\text{const}_3}{\gamma} \cos \theta, \quad (19)$$

which, being substituted into Eq. (6), leads to relation

$$L^o = \text{const}_3 - \gamma^3 M^o. \quad (20)$$

Taking into account the pattern of solutions (6) and (7), boundary conditions (8), (17), and (19) yield two algebraic equations for the integration constants:

$$G^i = \frac{\text{const}_3}{\alpha^o} + (1 - \gamma^3) (H^o + M^o / \alpha^o), \quad (21)$$

$$L^i = \frac{\alpha^i}{\alpha^o} (\text{const}_3 + (1 - \gamma^3) M^o).$$

Substituting Eqs. (17), (18), (20), and (21) into set (10), we find explicit expressions for constants H° and M° :

$$\begin{aligned}
 H^\circ &= -\frac{3\text{const}_3}{\alpha^\circ \Delta_0} h^\circ, \quad M^\circ = -\frac{\text{const}_3}{\alpha^\circ \Delta_0} m^\circ, \quad \text{where} \\
 h^\circ &= \frac{\delta_+}{v_-} + \frac{\delta_-}{v_+} + \alpha^i \left(\frac{1}{v_- v_{m+}} - \frac{1}{v_+ v_{m-}} \right), \\
 m^\circ &= (1 - \gamma^3) \left(\alpha^i \left(\frac{\delta_+}{v_{m-}} + \frac{\delta_-}{v_{m+}} \right) - \alpha^\circ \left(\frac{\delta_+}{v_-} + \frac{\delta_-}{v_+} \right) \right) \\
 &\quad + (2 + \gamma^3) \left(\frac{Z_- \delta_+}{v_-} - \frac{Z_+ \delta_-}{v_+} + \alpha^i \right. \\
 &\quad \times \left. \left(\frac{Z_+}{v_+ v_{m-}} + \frac{Z_-}{v_- v_{m+}} \right) - \frac{\alpha^\circ}{v_+ v_-} (Z_+ + Z_-) \right), \\
 \Delta_0 &= (2 + \gamma^3) (1 - \gamma^3) \\
 &\quad \times \left(\frac{1}{\alpha^\circ} \left(\frac{Z_- \delta_+}{v_-} - \frac{Z_+ \delta_-}{v_+} \right) + \left(\frac{\delta_+}{v_-} + \frac{\delta_-}{v_+} \right) \right) \\
 &\quad + \frac{(Z_+ + Z_-) (2 + \gamma^3)^2}{v_- v_+} + \frac{\alpha^i}{\alpha^\circ} (1 - \gamma^3) \\
 &\quad \times \left((1 - \gamma^3) \left(\frac{\delta_+}{v_{m-}} + \frac{\delta_-}{v_{m+}} \right) \right. \\
 &\quad \left. + (2 + \gamma^3) \left(\frac{Z_+}{v_+ v_{m-}} + \frac{Z_-}{v_- v_{m+}} \right) \right). \quad (22)
 \end{aligned}$$

The following denotations have been introduced here and below:

$$\begin{aligned}
 \delta_\pm &= \frac{Z_\pm \beta_\pm \pm \sigma \text{Pe} (\beta_\pm - 1)}{v_{m\pm} ms^2}, \\
 v &= \frac{Z_+ v_- + Z_- v_+}{v_+ - v_-}, \quad Z = \frac{Z_+}{v_+} + \frac{Z_-}{v_-}. \quad (24)
 \end{aligned}$$

Capillary-osmosis coefficient L_{13} (2a) is found as the ratio between cell filtration velocity U and cell chemical potential gradient (14):

$$\begin{aligned}
 L_{13} &= -\frac{U}{\Phi_3} = -\frac{aU}{RTZ_0 \text{const}_3} \\
 &= -\frac{au_{11}U_0}{RTZ_0 \text{const}_3} = \frac{a\sigma G^i U_0}{s_0^2 RTZ_0 \text{const}_3}, \quad (25)
 \end{aligned}$$

where $u_{11} = U/U_0$ is the dimensionless filtration velocity, whose value is found from relations (18), (21)–(24):

$$u_{11} = -\frac{\sigma G^i}{ms^2} = -\frac{\sigma \text{const}_3}{ms^2 \alpha^\circ} \left(1 - \frac{1 - \gamma^3}{\Delta_0} \left(3h^\circ + \frac{m^\circ}{\alpha^\circ} \right) \right). \quad (26)$$

The following exact expression for the capillary-osmosis coefficient follows from relations (25) and (26):

$$L_{13} = \frac{R_b^2 \rho_V}{\mu^\circ F_0 Z_0 \alpha^\circ} \left(1 - \frac{(1 - \gamma^3)}{\alpha^\circ \Delta_0} (3\alpha^\circ h^\circ + m^\circ) \right). \quad (27)$$

ANALYSIS OF CAPILLARY-OSMOSIS COEFFICIENT AND DISCUSSION OF RESULTS

The passage to important particular cases makes it possible to simplify exact equation (27) obtained for the capillary-osmosis coefficient. This equation is equally applicable to both a porous charged membrane and a concentrated dispersion of charged particles. This coefficient determines the osmotic transport of a solvent (water) through membrane pores. This transport develops in a membrane system under the action of an external concentration drop imposed on it. In the case of a highly concentrated dispersion of porous charged particles, expression (27) for the capillary-osmosis coefficient is essentially simplified:

$$L_{13}|_{\gamma=1} = \frac{R_b^2 \rho_V}{\mu^\circ F_0 Z_0 \alpha^\circ} = \frac{R_b^2 \rho_V^2}{\mu^\circ Z_0 F_0^2 (Z_+ \beta_+ + Z_- \beta_-) C_0}. \quad (28)$$

In the case of a 1:1 electrolyte and ideally selective ion exchanger grains ($\gamma_m = +\infty$), expression (28) gives the following dimensional capillary-osmosis coefficient for a dispersion:

$$L_{13}|_{\gamma=1} = \frac{k_D \rho_V}{2\mu^\circ F_0}, \quad (29)$$

where $k_D = \mu^\circ/k$ is the Brinkman specific hydrodynamic permeability of an ion exchanger grain. This coefficient is independent of the electrolyte concentration.

Symmetric 1:1 Electrolyte

This is the most interesting case, because namely 1:1 electrolytes are most often used in experiments. In this case, we, from Eqs. (32a) presented in [2] and relations (9) and (24), obtain:

$$\begin{aligned}
 \alpha^\circ &= \frac{\sqrt{\sigma^2 + 4/\gamma_m^2}}{\sigma}, \quad \alpha^i = \frac{2}{\sigma \gamma_m^2}, \\
 v &= \frac{v_+ + v_-}{v_+ - v_-}, \quad Z = \frac{1}{v_+} + \frac{1}{v_-}, \quad (30)
 \end{aligned}$$

$$\delta_\pm = v \frac{\beta_\pm \pm \sigma \text{Pe} (\beta_\pm - 1)}{v_{m\pm} ms^2}, \quad \beta_\pm = \frac{\sqrt{\sigma^2 + 4/\gamma_m^2} \pm \sigma}{2}.$$

Substituting expressions (30) into Eq. (27) and taking into account definitions (23) and (24), we, after corresponding transformations carried out with regard to denotations (3) and (4), arrive at the following expressions:

$$L_{13} = \frac{k_D \rho_V}{2\mu^0 F_0 \alpha^0} \left(1 - \frac{m_0}{\Delta_0} \left(\frac{m^0}{\alpha^0} + 3h^0 \right) \right), \quad (31)$$

where

$$\begin{aligned} & \frac{m^0}{\alpha^0} + 3h^0 = (3 - m_0) \\ & \times \left[\frac{1}{\alpha^0} \left(\frac{\delta_+}{v_-} - \frac{\delta_-}{v_+} \right) + \frac{\alpha^i}{\alpha^0} \left(\frac{1}{v_+ v_{m-}} + \frac{1}{v_- v_{m+}} \right) - \frac{2}{v_+ v_-} \right] \\ & + 3 \left(\frac{\delta_+}{v_-} + \frac{\delta_-}{v_+} + \alpha^i \left(\frac{1}{v_- v_{m+}} - \frac{1}{v_+ v_{m-}} \right) \right) \\ & + m_0 \left[\frac{\alpha^i}{\alpha^0} \left(\frac{\delta_+}{v_{m-}} + \frac{\delta_-}{v_{m+}} \right) - \left(\frac{\delta_+}{v_-} + \frac{\delta_-}{v_+} \right) \right], \\ & \Delta_0 = (3 - m_0) m_0 \left(\frac{1}{\alpha^0} \left(\frac{\delta_+}{v_-} - \frac{\delta_-}{v_+} \right) + \left(\frac{\delta_+}{v_-} + \frac{\delta_-}{v_+} \right) \right) \\ & + \frac{2(3 - m_0)^2}{v_- v_+} + \frac{\alpha^i}{\alpha^0} m_0 \\ & \times \left(m_0 \left(\frac{\delta_+}{v_{m-}} + \frac{\delta_-}{v_{m+}} \right) + (3 - m_0) \left(\frac{1}{v_+ v_{m-}} + \frac{1}{v_- v_{m+}} \right) \right). \end{aligned} \quad (32)$$

Ideally selective membrane for pressure-driven membrane processes. In this case, we have

$$\begin{aligned} \gamma_m &= +\infty, \quad \beta_- = 0, \quad \beta_+ = \sigma, \quad \alpha^0 = 1, \\ \alpha^i &= 0, \quad \delta_+ = \frac{\sigma}{v_{m+}} + \frac{\sigma \text{Pe} (\sigma - 1)}{s_0^2}, \quad \delta_- = \frac{\sigma \text{Pe}}{s_0^2}. \end{aligned} \quad (30a)$$

At the same time, expressions (31)–(33) are markedly simplified and yield the following dimensional expression for coefficient L_{13} :

$$L_{13} = \frac{3k_D \rho_V}{2\mu^0 F_0} \frac{1}{m_0 \delta_+ v_+ + (3 - m_0)}, \quad (34)$$

or

$$L_{13} = \frac{3k_D}{2\mu^0} \frac{\bar{\rho} C_0}{m_0 \bar{\rho} \left(\frac{D_{m+}}{D_+} + \frac{\bar{\rho}}{\rho_0} \right) + \left(3 - m_0 \left(1 + \frac{\bar{\rho}}{\rho_0} \right) \right) C_0}, \quad (35)$$

where it has been taken into account that $\sigma \text{Pe} = \frac{s_0^2 \bar{\rho}}{v_+ \bar{\rho}_0}$, $\bar{\rho} = \frac{\rho_V}{F_0}$, while $\bar{\rho}_0 = \frac{\mu^0 D_+}{k_D RT}$ is the characteristic scale of the exchange capacity. In the absence of macroporosity ($m_0 = 0$), Eq. (35) gives the following expression for the constant value of the capillary-osmosis coefficient: $L_{13}|_{m_0=0} = \frac{k_D \bar{\rho}}{2\mu^0}$, this expression coinciding with Eq. (29).

It is seen that expression (35) for the capillary-osmosis coefficient is directly proportional to the hydrodynamic permeability of a cation exchanger grain (gel) and inversely proportional to the solution viscosity. Note that, as follows from Eq. (35), the sign

of coefficient L_{13} , is always positive at physically acceptable values of the key parameters of the system; i.e., the osmotic flux of the solvent is directed oppositely to the electrolyte concentration gradient, and the liquid penetrating through the membrane “tries” to dilute a more concentrated solution.

It should also be noted that the equation of the specific conductivity obtained previously for the case under consideration has the pattern structurally similar to Eq. (35):

$$\begin{aligned} L_{22} &= \frac{F_0^2 D_+ C_0}{RT (3 - m_0)} \left(2m_0 \left(1 + \frac{D_-}{D_+} \right) \right. \\ &+ \frac{9(1 - m_0) \left(\frac{D_{m+}}{D_+} + \frac{\bar{\rho}}{\rho_0} \right) \bar{\rho}}{m_0 \bar{\rho} \left(\frac{D_{m+}}{D_+} + \frac{\bar{\rho}}{\rho_0} \right) + \left(3 - m_0 \left(1 + \frac{\bar{\rho}}{\rho_0} \right) \right) C_0} \left. \right). \end{aligned} \quad (36)$$

It follows from Eq. (35) that all curves for the capillary-osmosis coefficient of an ideally selective cation-exchange membrane have rectilinear asymptotics at low electrolyte concentrations

$$L_{13}|_{C_0 \rightarrow 0} = \frac{3k_D}{2\mu^0} \frac{C_0}{m_0 \left(\frac{D_{m+}}{D_+} + \frac{\bar{\rho}}{\rho_0} \right)} \equiv b_0 C_0, \quad m_0 \neq 0, \quad (37)$$

and, at high electrolyte concentrations, they become constant:

$$L_{13}|_{C_0 \rightarrow \infty} = \frac{3k_D}{2\mu^0} \frac{\bar{\rho}}{3 - m_0 \left(1 + \frac{\bar{\rho}}{\rho_0} \right)} \equiv a_\infty. \quad (38)$$

As is seen from expressions (37) and (38), the slope of straight line (37) is always positive; i.e., $b_0 > 0$. At the same time, $a_\infty > 0$, provided that $\bar{\rho}/\bar{\rho}_0 < 3/m_0 - 1$ and $a_\infty < 0$, if $\bar{\rho}/\bar{\rho}_0 > 3/m_0 - 1 > 2$. The latter case is not realized in practice, because $\bar{\rho}_0 > \bar{\rho}$. Hence, for an ideally selective membrane, the $L_{13}(C_0)$ dependence monotonically increases from zero to an asymptotic value represented by relation (38). The nonideality of an ion exchange membrane qualitatively “deforms” the $L_{13}(C_0)$ dependence, and a maximum arises in it. Figure 3 shows the behavior of normalized capillary-osmosis coefficient $\bar{L}_{13} \equiv (\mu^0/k_D) L_{13}$ calculated by exact equation (31) (curve 1, $\gamma_m = 0.527$) and approximate equation (35) (curve 2, $\gamma_m = +\infty$) for an ideally selective cation-exchange membrane at the same values of the physicochemical parameters which are characteristic of the cast perfluorinated MF-4SC cation-exchange membrane in a NaCl solution [11]: $D_{m+} = D_{m-} = 23.68 \mu\text{m}^2/\text{s}$, $\bar{\rho} = 1.08 \text{ mol}/\text{dm}^3$, $\bar{\rho}_0 = 2.18 \text{ mol}/\text{dm}^3$, and $m_0 = 0.2$. It is seen that, at

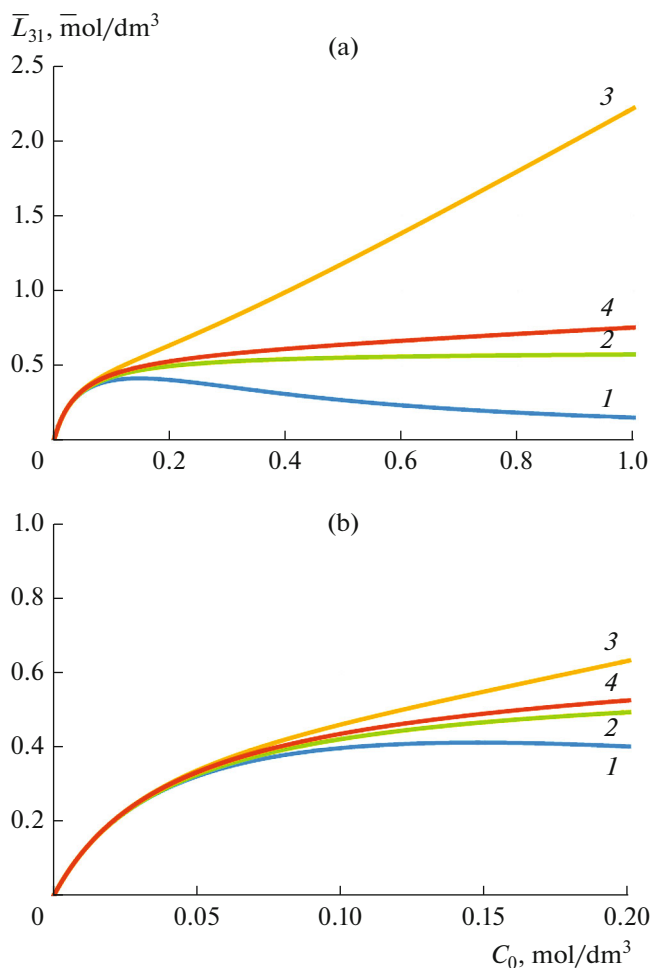


Fig. 3. Calculated dependences of normalized (1, 2) capillary-osmosis $\bar{L}_{13} = (\mu^\circ/k_D)L_{13}$ (mol/dm³) and (3, 4) reverse-osmosis $\bar{L}_{31} = (\mu^\circ/k_D)L_{31}$ (mol/dm³) coefficients on aqueous NaCl solution concentration C_0 (mol/dm³) for a cast perfluorinated MF-4SC membrane at (1, 3) $\gamma = 0.527$ and (2, 4) $\gamma = +\infty$; ideally selective cation-exchange membrane. See text for other parameters.

$C_0 = 0.15$ mol/dm³, an extreme is present in exact curve 1. This means a decrease in the osmotic permeability of the system at electrolyte concentrations above the aforementioned one probably due to a substantial (by a factor of 1.5) excess of the mobility of chlorine anions over the mobility of sodium cations. At the same time, if an ideally selective membrane with the same properties existed, no decrease in L_{13} would be observed, and the coefficient would reach a marked positive value (curve 2). This may be explained by the fact that no flux of coions through an ideal membrane takes place.

Ideal cation-exchange membrane (the case of excluded coions, $\gamma_m = 0$). In this case, the capillary-

osmosis coefficient is equal to zero: $L_{13}(C_0)|_{\gamma_m=0} = 0$. This is intuitively understandable, because there is no transport of coions through the membrane in this case; hence, they cannot transport solvent molecules through it in the absence of a pressure drop.

DETERMINATION OF REVERSE-OSMOSIS COEFFICIENT OF A CATION-EXCHANGE MEMBRANE AND DISCUSSION OF RESULTS

As follows from Eq. (2b), reverse-osmosis coefficient L_{31} must be calculated in the absence of the electric and chemical potential gradients ($\Phi_2 = \Phi_3 = 0$) and under a constant pressure gradient ($\Phi_1 = \nabla p = 3B\gamma^3 \frac{\mu^\circ U_0}{a^2}$). This leads to the same boundary problem for a cell, the solution of which was found previously when calculating coefficient L_{11} [2]. This solution can now be used to calculate coefficient L_{31} . The cell flux density of the salt is determined by the standard method [3]:

$$J = C_0 U_0 \frac{j_{1r}^\circ|_{r=1/\gamma}}{\cos\theta}, \quad (39)$$

where $j_{1r}^\circ = \frac{1}{Z_0}(j_{1r+}^\circ + j_{1r-}^\circ)$ is the radial component of the dimensionless local flux density of the salt, with this component being found on the cell surface by expressions (34a) presented for ion flux density in [2] taking into account Eqs. (6), (11), and (17), as well as relation $L^\circ = -\gamma^3 M^\circ$, which is a consequence of condition $\Phi_3 = 0$:

$$\begin{aligned} \frac{j_{1r}^\circ|_{r=1/\gamma}}{\cos\theta} &= u_{1\gamma} - \frac{1}{Z_0 \text{Pe} \cos\theta} \\ &\times \left(\left(\frac{1}{v_+ Z_+} + \frac{1}{v_- Z_-} \right) \frac{\partial C_1^\circ}{\partial r} \Big|_{r=1/\gamma} + \left(\frac{1}{v_+} - \frac{1}{v_-} \right) \frac{\partial \Phi_1^\circ}{\partial r} \Big|_{r=1/\gamma} \right) \\ &= \frac{U}{U_0} + \frac{3\gamma^3}{Z_0 \text{Pe}} \left(\left(\frac{1}{v_+ Z_+} + \frac{1}{v_- Z_-} \right) M^\circ + \left(\frac{1}{v_+} - \frac{1}{v_-} \right) H^\circ \right). \end{aligned} \quad (40)$$

Here, we have taken into account the expression for the radial velocity at cell boundary $r = 1/\gamma$. This expression may be found in [2]: $u^\circ(r = 1/\gamma) = u_{1\gamma} \cos\theta = U/U_0 \cos\theta$, i.e., $u_{1\gamma} = U/U_0$.

When calculating the electroosmotic permeability coefficient, constants M° and H° were found from the conditions of equal normal components of ion fluxes at the interface:

$$\begin{aligned}
M^o &= \frac{Pe u_{11}}{Z_- + Z_+} \left(\frac{Z_- (\beta_+ - 1) v_{m+}}{(1 - \gamma^3) \beta_+ + (2 + \gamma^3) m_+} \right. \\
&\quad \left. + \frac{Z_+ (\beta_- - 1) v_{m-}}{(1 - \gamma^3) \beta_- + (2 + \gamma^3) m_-} \right), \\
H^o &= \frac{Pe u_{11}}{Z_- + Z_+} \left(\frac{(\beta_+ - 1) v_{m+}}{(1 - \gamma^3) \beta_+ + (2 + \gamma^3) m_+} \right. \\
&\quad \left. - \frac{(\beta_- - 1) v_{m-}}{(1 - \gamma^3) \beta_- + (2 + \gamma^3) m_-} \right).
\end{aligned} \tag{41}$$

Let us substitute Eq. (41) into Eq. (40) and take into account the expression for velocity u_{11} at interface $r = 1$ (this expression was also found in [2]):

$$-u_{11}/B = 3/(ms^2 + n\sigma Pe(1 - \gamma^3)), \tag{42}$$

where

$$B = -\frac{U/U_0}{f(\gamma; s) + \frac{3}{ms^2 + n\sigma Pe(1 - \gamma^3)}}, \tag{43}$$

$$\begin{aligned}
f(\gamma; s) &\equiv 1 - \frac{6\gamma}{5} + \frac{\gamma^6}{5} \\
&\quad - \frac{m\omega_3(s)(1 - \gamma^3)^2}{3(2\omega_1(s) - 4\omega_2(s) + m\omega_3(s))},
\end{aligned} \tag{44}$$

$$\begin{aligned}
n &= \frac{1}{Z_+ \beta_+ + Z_- \beta_-} \left[\frac{\beta_+ (\beta_+ - 1) v_{m+}}{(1 - \gamma^3) \beta_+ + (2 + \gamma^3) m_+} \right. \\
&\quad \left. - \frac{\beta_- (\beta_- - 1) v_{m-}}{(1 - \gamma^3) \beta_- + (2 + \gamma^3) m_-} \right], \quad m_{\pm} = \frac{v_{m\pm}}{v_{\pm}},
\end{aligned} \tag{45}$$

$$\begin{aligned}
\omega_1(x) &= 30 \left(\frac{\cosh x}{x^4} - \frac{\sinh x}{x^5} - \frac{1}{3x^2} \right), \\
\omega_2(x) &= -\frac{15}{2} \left(\frac{\cosh x}{x^4} - \frac{\sinh x}{x^5} (1 + x^2) + \frac{2}{3x^2} \right), \\
\omega_3(x) &= -90 \left(\frac{\cosh x}{x^4} \left(1 + \frac{x^2}{6} \right) - \frac{\sinh x}{x^5} \left(1 + \frac{x^2}{2} \right) \right).
\end{aligned} \tag{46}$$

For liquids with equal viscosities ($m = 1$), Eq. (44) acquires a simpler form with regard to Eq. (46):

$$\begin{aligned}
f(\gamma; s)|_{m=1} &\equiv 1 - \frac{6\gamma}{5} + \frac{\gamma^6}{5} \\
&\quad - 2 \left(\frac{1}{s_0^2} + \frac{1}{6} + \frac{1}{3} \frac{\tanh s_0}{\tanh s_0 - s_0} \right) (1 - \gamma^3)^2.
\end{aligned} \tag{44a}$$

It may be shown that the multiplier before the term $(1 - \gamma^3)^2$ in expression (44a) decreases from $-1/5$ at $s_0 = a/R_b = 0$ to $-1/3$ at $s_0 \rightarrow \infty$; i.e., it does not change significantly. The case of $s_0 = 0$ corresponds to a high permeability of a porous grain (large Brinkman

radius), while $s_0 \rightarrow \infty$ is consistent with a low permeability (small Brinkman radius). Then, identity (44a) yields:

$$\begin{aligned}
\lim_{s=s_0 \rightarrow 0} f(\gamma; s)|_{m=1} &\equiv 1 - \frac{6\gamma}{5} + \frac{\gamma^6}{5} - \frac{1}{5} (1 - \gamma^3)^2 \\
&= \frac{4}{5} - \frac{6\gamma}{5} + \frac{2\gamma^3}{5} \in \left[0; \frac{4}{5} \right],
\end{aligned} \tag{44b}$$

$$\begin{aligned}
\lim_{s=s_0 \rightarrow \infty} f(\gamma; s)|_{m=1} &\equiv 1 - \frac{6\gamma}{5} + \frac{\gamma^6}{5} - \frac{1}{3} (1 - \gamma^3)^2 \\
&= \frac{2}{3} - \frac{6\gamma}{5} + \frac{2\gamma^3}{3} - \frac{2\gamma^6}{15} \in \left[0; \frac{2}{3} \right].
\end{aligned} \tag{44c}$$

Note that both functions (44b) and (44c) are monotonically decreasing. Taking into account Eqs. (39) and (12), as well as relations (42)–(46), we, from Eq. (2b), found the reverse-osmosis coefficient as

$$\begin{aligned}
&L_{31} \\
&\left(\frac{ms^2 f(\sqrt[3]{1 - m_0}; s)}{3(1 - m_0)} + \frac{1}{1 + n \frac{m_0 \bar{\rho}}{v_{\pm} \bar{\rho}_0}} \right) \\
&= \frac{k_D C_0}{\mu^o} \times \left(\frac{1}{1 - m_0} + \frac{3}{Z_0} \left(\frac{m_+ (\beta_+ - 1)}{Z_+ m_0 \beta_+ + (3 - m_0) m_+} \right. \right. \\
&\quad \left. \left. + \frac{m_- (\beta_- - 1)}{Z_- m_0 \beta_- + (3 - m_0) m_-} \right) \right).
\end{aligned} \tag{47}$$

The first and second terms in Eq. (47) determine the transmembrane salt transport due to the convective water transfer and electrodiffusion of ions, respectively. When the permeability of ion exchanger grains is rather high ($k_D \gg a^2$, i.e., $s \rightarrow 0$), the first term in Eq. (47) may be ignored; when it is low ($k_D \ll a^2$, i.e., $s \rightarrow \infty$), the second term may be ignored.

In the case of zero macroporosity ($m_0 = 0$), Eq. (47) gives the following expression:

$$L_{31}|_{\gamma=1} = \frac{k_D C_0}{\mu^o Z_0} \left(\frac{\beta_+}{Z_+} + \frac{\beta_-}{Z_-} \right) = \frac{k_D C_0}{\mu^o} \left(\frac{\beta_+ Z_- + \beta_- Z_+}{Z_- + Z_+} \right).$$

Let us present the expression of the capillary-osmosis coefficient under the same conditions for comparison:

$$L_{13}|_{\gamma=1} = \frac{k_D \rho v}{\mu^o F_0 Z_0 \alpha^o} = \frac{k_D \bar{\rho}^2}{\mu^o Z_0 (Z_+ \beta_+ + Z_- \beta_-) C_0}.$$

These equations are seen to be substantially different. Thus the Onsager reciprocity theorem is not fulfilled here. This fact has been confirmed by the data obtained in [6], where it was phenomenologically proven that, in the case of nonequilibrium thermodynamics, the matrix of kinetic coefficients is symmetric only in a particular case, in which the generalized thermodynamic fluxes are equal to zero, while the thermodynamic forces are unequal to zero. Note that we

have revealed inequality $L_{ij} \neq L_{ji}$ for all cross coefficients calculated in terms of the cell model of an ion-exchange membrane. This question will be considered in detail in the next work of the author.

In the case of an ideally selective membrane, for pressure-driven processes ($\gamma_m = +\infty$) and a 1:1 electrolyte, we have:

$$L_{31} = \frac{k_D C_0}{\mu^0} \left(\frac{ms^2 f(\sqrt[3]{1-m_0}; s)}{3(1-m_0)} + \frac{1}{1 + \frac{(\sigma-1)v_{m+}}{m_0\sigma v_+ + (3-m_0)v_{m+}} \frac{\bar{\rho}}{\rho_0} m_0} \right) \times \left(\frac{1}{1-m_0} + \frac{3}{2} \left(\frac{(\sigma-1)v_{m+}}{m_0\sigma v_+ + (3-m_0)v_{m+}} - \frac{1}{(3-m_0)} \right) \right) \quad (48)$$

In the case of zero macroporosity, Eq. (48) yields relation $L_{31}|_{m_0=0} = \frac{k_D \bar{\rho}}{2\mu^0}$, which coincides with

expression (29). After identical transformations, expression (48) acquires the following form:

$$L_{31} = \frac{k_D C_0}{\mu^0} \left(\frac{ms^2 f(\sqrt[3]{1-m_0}; s)}{3(1-m_0)} + \frac{m_0 \frac{D_{m+}}{D_+} + (3-m_0) \frac{C_0}{\bar{\rho}}}{m_0 \left(\frac{D_{m+}}{D_+} + \frac{\bar{\rho}}{\rho_0} \right) + \left(3-m_0 \left(1 + \frac{\bar{\rho}}{\rho_0} \right) \right) \frac{C_0}{\bar{\rho}}} \right) \times \left(\frac{1}{1-m_0} + \frac{3}{2} \left(\frac{\left(1 - \frac{C_0}{\bar{\rho}} \right)}{m_0 \frac{D_{m+}}{D_+} + (3-m_0) \frac{C_0}{\bar{\rho}}} - \frac{1}{(3-m_0)} \right) \right) \quad (49)$$

In the case of an ideal cation-exchange membrane (the case of excluded coions, $\gamma_m = 0$), 1:1 electrolyte, and coinciding viscosities of liquids, $m = 1$, we have:

$$L_{31} = \frac{k_D C_0}{\mu^0} \left(\frac{\left(1 - \frac{6\sqrt[3]{1-m_0}}{5} + \frac{(1-m_0)^2}{5} \right) s_0^2 - 2 \left(1 + \frac{s_0^2}{6} + \frac{1}{3} \frac{s_0^2 \tanh s_0}{\tanh s_0 - s_0} \right) m_0^2}{3(1-m_0)} + \frac{2m_0 + 3(1-m_0) \left(\frac{D_+}{D_{m+}} + \frac{D_-}{D_{m-}} \right)}{m_0(1-m_0) \left(2 + \left(\frac{D_+}{D_{m+}} - \frac{D_-}{D_{m-}} \right) \frac{\bar{\rho}}{\rho_0} \right)} \right) \quad (50)$$

It follows from Eq. (50) that the reverse-osmosis coefficient of an ideal cation-exchange membrane is directly proportional to electrolyte concentration. Figure 3 shows variations in normalized reverse-osmosis coefficient $\bar{L}_{13} \equiv (\mu^0/k_D) L_{13}$ of a cation-exchange membrane with a rise in the electrolyte concentration for the same of membrane–electrolyte system parameters, for which curves 1 and 2 were plotted. Curve 3 has been plotted for \bar{L}_{13} by exact equation (47), while curve 4 has been plotted by Eq. (48) for an ideally selective membrane at $m = 1$ (equal viscosities) and $s_0 = 0$ (infinitely small size of ion exchanger grains). Figures 3a and 3b differ from each other by the ranges of variations in electrolyte concentration. As is seen in Fig. 3b, the cross coefficients do not differ significantly only at low electrolyte concentrations (below 0.1 M). At higher concentrations, marked quantitative and qualitative differences are observed between L_{13} and L_{31} : the reverse-osmosis coefficient (curve 3) increases, while the capillary-osmosis coefficient (curve 1) decreases with a rise in electrolyte

concentration. At the same time, no such substantial difference is observed between these coefficients calculated for ideally selective membranes (curves 2, 4).

Figure 4 illustrates the behavior of normalized reverse-osmosis coefficient $\bar{L}_{31} \equiv (\mu^0/k_D) L_{31}$ with a rise in electrolyte concentration C_0 at different viscosity ratios between the liquids inside of the porous layer and inside of the liquid shell: $m = 1$ (Fig. 4a) and 5 (Fig. 4b). The value $m = 5$ corresponds to 20% porosity of the ion exchanger grain and coincides with macroporosity value $m_0 = 0.2$ chosen to construct the presented plots. In both figures, curves 1, 2, 3, and 4 correspond to the values of parameter $s_0 \equiv a/\sqrt{k_D} = 0.1, 1, 10, \text{ and } 50$, respectively. The comparison between Figs. 4a and 4b indicates that an increase in the apparent viscosity of a Brinkman medium leads to a reduction in coefficient L_{31} , other conditions being equal. This reduction becomes stronger with an increase in parameter s_0 (a rise in the ion exchanger grain size). Therewith, the growth of the grain size leads to an increase in the reverse-osmosis

permeability of the medium. Specific permeability k_D of the porous ion exchanger grain in Figs. 3 and 4 cannot be changed, because both coefficients L_{13} and L_{31} are normalized with respect to it. Curves 1 and 2 in Fig. 4 almost coincide with one another, while curve 3 is located close to them; hence, coefficient L_{31} weakly depends on parameter s_0 within a range of its values from 0 to 10 and at electrolyte concentrations lower than 1 M. A further increase in this parameter by a half of an order of magnitude already leads to a marked growth of the reverse-osmosis permeability, which also grows with electrolyte concentration in all cases.

Figure 5 shows the behavior of reverse-osmosis coefficient \bar{L}_{31} with a rise in electrolyte concentration C_0 at different viscosity ratios between the liquids inside of the porous layer and inside of the liquid shell: $m = 1$ (Fig. 5a) and 5 (Fig. 5b) for a virtual MF-4SC membrane, as if it had an equilibrium distribution coefficient typical of reverse-osmosis membranes, $\gamma = 100$. It is clearly seen that the reverse-osmosis permeability of such a membrane is lower (other conditions being equal), and a twofold difference is reached at a NaCl concentration of 1 M. This effect is related to different signs of ion adsorption inside of the membrane matrix. In the first case (Fig. 4), the positive adsorption takes place; i.e., the ion concentration in the pores is higher than the equilibrium one. In the second case (Fig. 5) the sorption of the ions is negative; i.e., their concentration in the pores is decreased. This is quite natural, because reverse-osmosis membranes must retain a dissolved salt to a maximal extent. It is also worth noting that the difference between curves 1–3 in Fig. 5 is more substantial than that in Fig. 4.

Note that, as in previous works, at very low electrolyte concentrations, when the thicknesses of the outer and inner EDLs at the interfaces become comparable with the ion exchanger grain radius, the equations derived in this and previous works for the kinetic coefficients may lead to incorrect results. Here, we have ignored the EDL thicknesses to analytically solve the boundary value problem for an individual cell. This approach is quite justified for an ion-exchange membrane that operates in underlimiting regimes, when the electrolyte concentration near the interface is not extremely low. If electrodialysis is implemented in overlimiting regimes, when regions of spatial charges arise inside of diffusion layers and it is necessary to take into account the concomitant effects of electroconvection and dissociation of water molecules, the exactly formulated problem can be solved only numerically. Such models are known and have been published in, e.g., [7, 8]. It should be noted that there are other models of an ion-exchange membrane, e.g., microheterogeneous one [9, 10], which is actively developed by the researchers of the Kuban scientific school of membrane electrochemistry. The author intends to compare the microheterogeneous and cell models of an ion-exchange membrane in subsequent works.

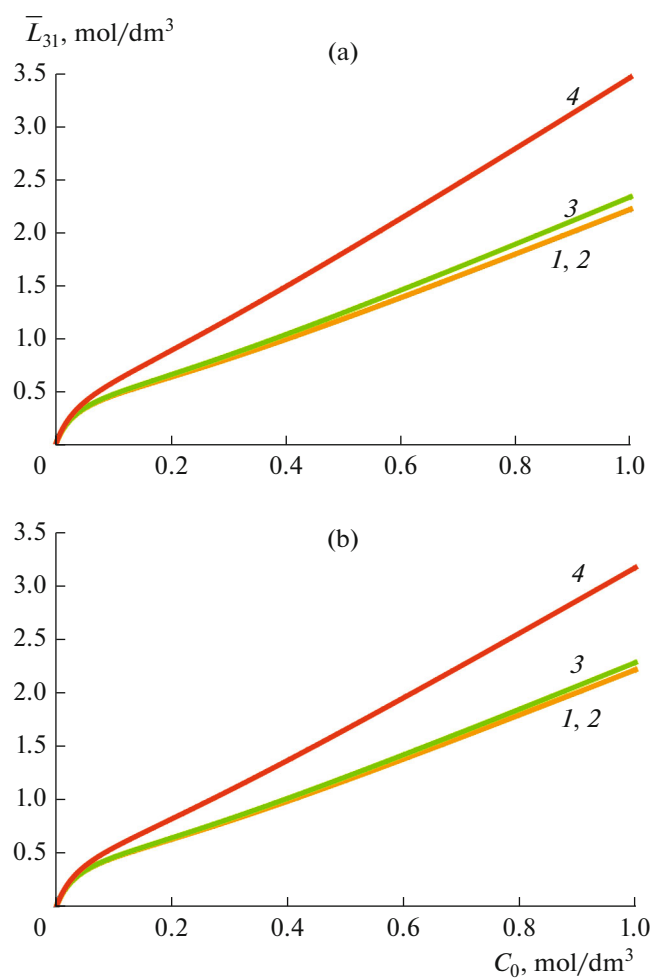


Fig. 4. Calculated dependences of normalized reverse-osmosis coefficient $\bar{L}_{31} = (\mu^0/k_D)L_{31}$ (mol/dm³) on aqueous NaCl solution concentration C_0 (mol/dm³) for a cast perfluorinated MF-4SC membrane at $\gamma = 0.527$; $s_0 =$ (1) 0.1, (2) 1, (3) 10, and (4) 50; and $m =$ (a) 1 and (b) 5. See text for other parameters.

It should also be noted that, to derive equations for the capillary-osmosis and reverse-osmosis coefficients of an anion-exchange membrane, it is necessary reverse the sign of σ (or $\bar{\rho}$) in the equations obtained for these parameters.

CONCLUSIONS

In this work, the capillary-osmosis and reverse-osmosis coefficients of an ion-exchange membrane have been calculated in terms of thermodynamics of irreversible processes on the basis of the cell model that we developed previously for such membranes. The membrane is considered as an ordered array of porous charged spherical particles placed into spherical shells filled with a binary electrolyte solution. The consideration has been carried out within the frame-

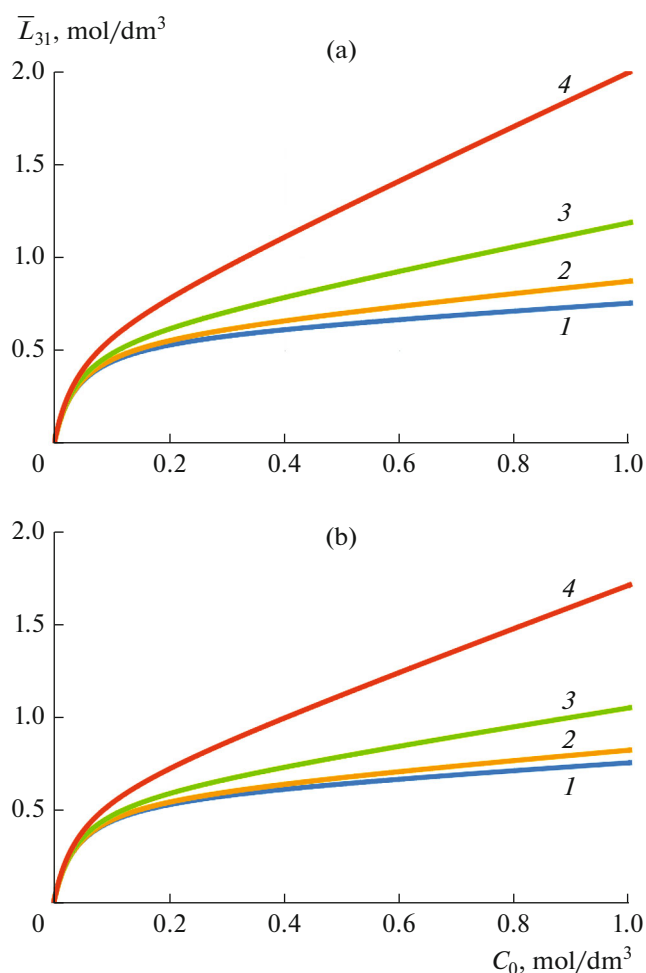


Fig. 5. Calculated dependences of normalized reverse-osmosis coefficient $\bar{L}_{31} = (\mu^0/k_D)L_{31}$ (mol/dm³) on aqueous NaCl solution concentration C_0 (mol/dm³) for a virtual MF-4SC membrane at $\gamma = 100$; $s_0 = (1)$ 0.1, (2) 1, (3) 10, and (4) 50; and $m = (a)$ 1 and (b) 5. See text for other parameters.

work of a small deviation of membrane system parameters from their equilibrium values in the presence of an external concentration field and a field of pressure. The Kuwabara boundary condition (the absence of liquid vorticity) has been imposed on the surfaces of liquid cells. The flows inside and outside of a porous particle have been described by the Brinkman equation and the Stokes equation of the “creeping flow,” respectively, taking into account the spatial electric force. Different limiting cases have been considered, in particular the cases of a symmetric 1:1 electrolyte and an ideally selective cation-exchange membrane. It has been shown that, for the considered cell model of an ion-exchange membrane, the Onsager reciprocity theorem is violated; i.e., the found kinetic cross coefficients are unequal to each other. This violation is explained by the fact that the reciprocity theorem is

applicable only to nonequilibrium systems within the framework of linear thermodynamics of irreversible processes, for which the generalized fluxes are equal to zero at nonzero thermodynamic forces. The results of this study may be used not only for electrodialysis and electrofiltration through charged membranes, but also for the account of water transport in fuel cells, with this transport governing the lifetime of these devices. The developed model is applicable to any membranes carrying charges (in particular, to reverse-osmosis and nano-, ultra-, and microfiltration membranes).

FUNDING

This work was supported by the Russian Foundation for Basic Research (project no. 20-0-00661).

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

REFERENCES

1. Happel, J. and Brenner, H., *Low Reynolds Number Hydrodynamics*, Hoboken: Prentice-Hall, 1965.
2. Filippov, A.N., *Colloid J.*, 2018, vol. 80, p. 728.
3. Filippov, A.N., *Colloid J.*, 2021, vol. 83, p. 387.
4. Brinkman, H.C., *Appl. Sci. Res., Sect. A*, 1947, p. 27.
5. Saffman, P.G., *Stud. Appl. Math.*, 1971, vol. 50, p. 93.
6. Mamedov, M.M., *Pis'ma Zh. Tekh. Fiz.*, 2003, vol. 29, no. 16, p. 39.
7. Uzdenova, A., Kovalenko, A., Urtenov, M., and Nikonenko, V., *Membranes*, 2018, vol. 8, no. 3, p. 84.
8. Nikonenko, V., Urtenov, M., Mareev, S., and Pourcelly, G., *Membranes*, 2020, vol. 10, no. 2, p. 22.
9. Nichka, V.S., Mareev, S.A., Porozhnyi, M.V., Shkirs-kaya, S.A., Safronova, E.Yu., Pis'menskaya, N.D., and Nikonenko, V.V., *Membr. Membr. Tekhnol.*, 2019, vol. 9, p. 222.
10. Davidov, D.V., Nosova, E.N., Loza, S.A., Achoh, A.R., Korzhov, A.N., and Melnikov, S.S., *Chim. Techno Acta*, 2021, vol. 8, Article No. 20218205.

Translated by A. Kirilin