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Asymmetry of cross kinetic coefficients in the cell model of a charged membrane

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Highlights:

- Asymmetry of conjugated kinetic coefficients in a cell model of a charged membrane is shown.
- Asymmetry is confirmed by the transport characteristics of some cation exchange membranes.
- The revealed asymmetry violates Onsager’s well-known principle of reciprocity.
- The mismatch of the conjugated coefficients should be considered in water and ions transfer.

Abstract: Theoretical study was performed earlier for the cell model of a charged porous membrane based on Onsager’s approach and the result was calculation of all electrokinetic coefficients. Experimental dependences of electroosmotic permeability, conductivity, and diffusion permeability of some perfluorinated membranes on electrolyte concentration were simultaneously and quantitatively described using exact analytical formulae based on the same set of physicochemical and geometrical parameters. It is shown here that for the developed cell model of the ion–exchange membrane, the Onsager principle of reciprocity is violated—the coupled cross kinetic coefficients are not equal. The violation is associated with the fact that the reciprocity principle takes place only for systems for which generalized fluxes are zero at thermodynamic forces other than zero within the framework of linear thermodynamics of irreversible processes.

Keywords: kinetic coefficients; Onsager matrix; asymmetry; cell model; charged membrane

1. Introduction

The cell method proposed by J. Happel and H. Brenner in the middle of the last century is widely and effectively used to study concentrated dispersed systems, including membranes [1]. The cell model of an ion exchange membrane assumes the replacement of a real system of randomly arranged ionite grains with a periodic lattice, in particular, identical porous charged balls enclosed in concentric spherical shells filled with electrolyte and forming a porous layer. The impact of neighboring particles in the cell method is considered by setting special boundary conditions on the surface of the liquid shell. It is assumed that the gradients of the external forces acting on the porous layer coincide with the local gradients on the unit cell. The advantage of the described approach is that all the quantities included in the equations of electrolyte transfer through a porous layer: thermodynamic fluxes and forces, can be directly measured in experiments.

Earlier in 2018, a new cell model of an ion exchange membrane was proposed by A. N. Filippov, the problem of finding the kinetic coefficients L_{ij} was posed and solved in general, and accurate algebraic formulas for the hydrodynamic permeability L_{11}, the electroosmotic permeability L_{12} and the specific electrical conductivity L_{22} of the cation exchange membrane were derived for the first time. In the subsequent works in 2019–2022, based on the cell model developed, the diffusion permeability L_{33} and the electrodiffusion coefficient L_{23} were found. At the same time, the cell model was successfully verified by A.N. Filippov and S.A. Shkirskaya on the base of experimental data obtained for a cast perfluorinated MF-4SK membrane and its modifications using halloysite nanotubes functionalized with platinum and iron nanoparticles in aqueous HCl solutions, as well as an MF-4SK extrusion membrane in aqueous solutions of 1:1 electrolyte (HCl, NaCl, KCl, LiCl, CsCl). Later (2023), the same model was successfully applied to the description of the diffusion permeability and electrical conductivity of heterogeneous cation exchange MK-40 and anion exchange MA-41 membranes, as well as to the calculation of the hydrodynamic permeability of macroporous membranes made of sodium borosilicate glass (2024). To determine the physicochemical and geometric parameters of the model, a special algorithm and program were created in the Mathematica® computing environment to simultaneously optimize the specific electrical conductivity and electroosmotic or diffusion permeability according to their experimental dependencies. In reference [2], the capillary osmotic L_{13} and reverse osmotic L_{31} coefficients were calculated, and their mismatch was shown, which violates the Onsager reciprocity principle (symmetry of cross coefficients) [3]. Therefore, the motivation of this work is to check whether the remaining two pairs L_{12} and L_{21}, L_{23} and L_{32} of the cross kinetic coefficients have asymmetry.

2. Methods

When calculating the kinetic coefficients L_{ij} of the Onsager matrix, as independent thermodynamic forces that are set during the experiment of transferring an electrolyte solution through a thin infinitely extended charged porous layer, we select gradients of pressure $dp/dx \approx (p_{20} - p_{10})/h$, electrical $d\varphi/dx \approx (\varphi_{20} - \varphi_{10})/h$ and chemical $d\mu/dx \approx RT(C_{20} - C_{10})/(C_0 h)$, $\mu(C) = \mu_0 + RT\ln(C/C_0)$ potentials perpendicular to the surface of this layer. Here, C_0 is the equivalent concentration of an electrolyte solution in equilibrium with the membrane, μ_0 is the standard chemical potential, h is the membrane thickness, x is the coordinate perpendicular to the membrane surface and measured from its receiving surface, R is the universal gas constant, T is the absolute temperature, and the indices “1” and “2” indicate the left and right sides of the membrane, located in a measuring cell filled with a binary electrolyte solution (Figure 1).

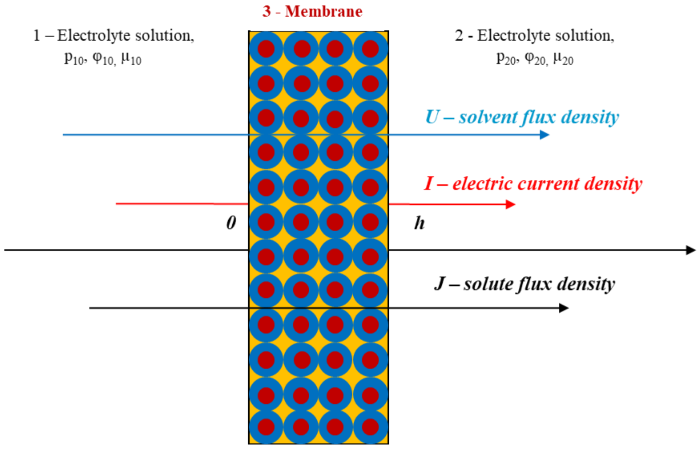


Figure 1. Membrane cell for the study of nonequilibrium processes: 1 and 2— receiving and giving chambers, 3—membrane as an assembly of porous charged particles.

As dependent thermodynamic parameters determined in the experiment, we take the flux densities: *U*—solvent (for example, water), *I*—mobile charges (electric current density), *J*—solute (density of the diffusion flux of the electrolyte).

Then the phenomenological transport equations in the case of isothermal processes can be written as the following system of linear equations:

$$\begin{cases} U=-\left(L_{11}\dfrac{dp}{dx}+L_{12}\dfrac{d\varphi}{dx}+L_{13}\dfrac{d\mu}{dx}\right), \\ I=-\left(L_{21}\dfrac{dp}{dx}+L_{22}\dfrac{d\varphi}{dx}+L_{23}\dfrac{d\mu}{dx}\right), \\ J=-\left(L_{31}\dfrac{dp}{dx}+L_{32}\dfrac{d\varphi}{dx}+L_{33}\dfrac{d\mu}{dx}\right). \end{cases} \tag{1}$$

The capillary osmotic L_{13} and reverse osmotic L_{31} coefficients were calculated in reference [2], and their inequality was found, that violates the Onsager reciprocity hypothesis—symmetry of cross coefficients [3]. The violation is since the principle of reciprocity in the framework of linear thermodynamics of irreversible processes works only for dispersed systems for which generalized fluxes are zero with thermodynamic forces other than zero [4]. In this paper, in addition to L_{13} and L_{31}, we compare pairs of cross coefficients L_{12} and L_{21}, as well as L_{23} and L_{32}, to confirm their asymmetry. At the same time, as will be shown below, the smallest difference is observed for the pair L_{12} and L_{21}, and the largest, apparently, for the pair L_{13} and L_{31}. The results of comparisons of coupled cross coefficients of the Onsager matrix are discussed in the next section.

3. Results and discussion

We will model a charged membrane by a periodic lattice of porous charged spherical particles of the same radius a enclosed in liquid spherical shells of a radius b chosen so that the ratio of particle volume to cell volume is equal to the volume fraction of particles in a dispersed system:

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

where m_0—macroscopic porosity, depending on the method of packing porous particles in a charged layer (membrane).

The mathematical formulation of the boundary value problem for the system of Stokes-Nernst-Planck-Poisson equations for a unit cell (Figure 2) is given, for example, in reference [2] and is not repeated here for the sake of brevity. We only note that the solution of the boundary value problem is obtained in a linear field approximation, that is, small deviations of the desired values (velocity, concentration and density of ion fluxes, electrical potential) from their equilibrium values are considered. The limits of applicability of the linear field approximation depend on the specificity boundary value problem and the comparison of theoretical predictions with experimental results. In general, it can be argued that this method provides a consistently good approximation in the case of equilibrium electrolyte concentrations of less than 0.2–0.3 mol/dm^3 and sometimes up to 1 mol/dm^3. The designations of variables and parameters used in this work completely coincide with those in the article [2]. The motion of an incompressible fluid (electrolyte) in the external region $\left(a < r < b\right)$ is described by the vector differential equation of Stokes at low Reynolds numbers ("creeping flow"), supplemented by a spatial electric force. The motion of the fluid in the inner region $\left(0 \le r < a\right)$ obeys the Brinkman vector differential equation, complicated by the same spatial electric force. Traditionally, the "Brinkman fluid" is assumed to be incompressible. The electrical potential satisfies the Poisson equation inside and outside porous particles, and the Nernst–Planck representation is used for the density of ion fluxes. At the same time, there are no sources and drains of charges in the system, and the problem itself is considered in a stationary formulation. The influence of neighboring particles is considered by the special boundary conditions on the surface of the liquid shell. There are 4 known variants of these conditions in the literature: the Happel (absence of viscous forces on the cell surface), Kuwabara (flow potentiality—absence of vorticity on the cell surface), Kvashnin (symmetry of cells) and Mehta–Morse/Cunningham (uniformity of flow) models. It was shown earlier in our article in *Adv. Colloid Interface Sci.* (2011) that for hydrodynamic permeability the models of Happel, Kvashnin, and Kuwabara, in contrast to the more "rigid" Cunningham model, give qualitatively identical, but slightly different quantitative results. These conditions are equal in the physical sense, however, in reference [5] it was argued that the Kuwabara model is more suitable for the study of electrokinetic phenomena. Therefore, we will focus here on the Kuwabara model. At the interface of the porous particle-electrolyte layer, conditions are set for the continuity of velocities, stresses, the radial component of ion fluxes, the electrical potential and its derivative along the radius (the dielectric permittivities of the electrolyte-saturated porous ionite grain and the electrolyte solution itself are assumed to be equal). Using a special procedure of the cell method proposed by J. Hapell and H. Brenner, local velocity fields and ion flux densities are recalculated into linear filtration rate U, electric current density I, and salt flux density J through a porous layer.

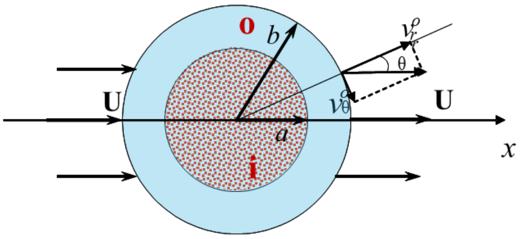


Figure 2. Single cell of the membrane: i—charged porous spherical particle; o—spherical layer of electrolyte solution; *U*—filtration rate; *x*—flow direction.

So, in order to correctly measure the above pairs of electrokinetic coefficients in an experiment or calculate them in a model, it is necessary to strictly observe a number of conditions. For example, the capillary osmotic L_{13} and reverse osmotic L_{31} coefficients of the ion exchange membrane can be found using the formulas following from (1):

$$L_{13} = -U \Big/ \left.\frac{d\mu}{dx}\right|_{\frac{dp}{dx}=0,\frac{d\varphi}{dx}=0} \tag{2}$$

$$L_{31} = -J \Big/ \left.\frac{dp}{dx}\right|_{\frac{d\mu}{dx}=0,\frac{d\varphi}{dx}=0} \tag{3}$$

Relations (2)–(3) mean that the correct measurement of the coefficient L_{13} is possible only in the absence of pressure and electrical potential differences and a given constant chemical potential difference $\mu_{20} - \mu_{10} \approx h\, d\mu / dx = \text{const}$ on the membrane, and the coefficient L_{31}—in the absence of chemical and electrical potential differences and a given constant pressure difference $p_{20} - p_{10} \approx h\, dp/dx = \text{const}$. Similar formulas are written for the remaining two pairs of cross coefficients. In general, formulas for cross coefficients have a very cumbersome form and can be found in reference [2] or based on our previous works. In the special case of an ideally selective cationite membrane for baromembrane processes, when the equilibrium distribution coefficient γ for the cation-anion pair is infinitely large, the formulas for kinetic coefficients L_{13} and L_{31} are significantly simplified [2]:

$$L_{13} = \frac{3k_{\mathrm{D}}}{2\mu^{\mathrm{o}}} \frac{\bar{\rho} C_0}{m_0 \bar{\rho}\left(\frac{D_{\mathrm{m}+}}{D_+} + \frac{\bar{\rho}}{\bar{\rho}_0}\right) + \left(3 - m_0\left(1 + \frac{\bar{\rho}}{\bar{\rho}_0}\right)\right) C_0} \tag{4}$$

$$L_{31} = \frac{k_{\mathrm{D}} C_0}{\mu^{\mathrm{o}}} \left(\begin{array}{l} \dfrac{m s^2 f\left(\sqrt[3]{1-m_0}; s_0\right)}{3(1-m_0)} + \dfrac{m_0 \dfrac{D_{\mathrm{m}+}}{D_+} + (3-m_0)\dfrac{C_0}{\bar{\rho}}}{m_0\left(\dfrac{D_{\mathrm{m}+}}{D_+} + \dfrac{\bar{\rho}}{\bar{\rho}_0}\right) + \left(3 - m_0\left(1 + \dfrac{\bar{\rho}}{\bar{\rho}_0}\right)\right)\dfrac{C_0}{\bar{\rho}}} \times \\ \left(\dfrac{1}{1-m_0} + \dfrac{3}{2}\left(\dfrac{\left(1 - \dfrac{C_0}{\bar{\rho}}\right)}{m_0 \dfrac{D_{\mathrm{m}+}}{D_+} + (3-m_0)\dfrac{C_0}{\bar{\rho}}} - \dfrac{1}{(3-m_0)} \right)\right) \end{array} \right) \tag{5}$$

where the auxiliary function is introduced,

$$f\left(\sqrt[3]{1-m_0}; s_0\right) = 1 - \frac{6\sqrt[3]{1-m_0}}{5} + \frac{(1-m_0)^2}{5} - 2\left(\frac{1}{s_0^2} + \frac{1}{6} + \frac{1}{3}\frac{\operatorname{th} s_0}{\operatorname{th} s_0 - s_0}\right) m_0^2 \tag{6}$$

and $\bar{\rho} > 0$—exchange capacity of cationite grain (mol/dm^3), k_{D}—specific hydrodynamic permeability of this grain (m^2), $\bar{\rho}_0 = \mu^{\mathrm{o}} D_+ / k_{\mathrm{D}} RT$—the characteristic scale of the exchange capacity (mol/dm^3), $D_{\mathrm{m}\pm}$ and $D_\pm$ (m^2/s)—diffusion coefficients of ions in a grain of cationite and in a surrounding liquid shell, $s_0 = a\big/\sqrt{k_{\mathrm{D}}}$—a dimensionless parameter responsible for the relative thickness of the flow penetration area into the near-surface layer of the ionite grain (the larger s_0, the thinner this area).

Figure 3 shows a comparison of the behavior of a pair of normalized coefficients $\bar{L}_{13}$ and $\bar{L}_{31}$, depending on the concentration of the NaCl electrolyte at the values of physicochemical parameters that are characteristic of the perfluorinated cast membrane MF-4SK in a NaCl solution studied in one of our previous work (2018): $D_{\mathrm{m}+} = D_{\mathrm{m}-} = 23.7$ μm^2/s, $\bar{\rho} = 1.08$ mol/dm^3, $\bar{\rho}_0 = 2.18$ mol/dm^3, $m_0 = 0.2$.

Curves *1* and *3* are built for $\bar{L}_{31}$ and $\bar{L}_{13}$ according to exact formulas, and curves *2* and *4* are drawn according to formulas for an ideally selective membrane with equal viscosities of pure liquid μ^{o} and liquid in a porous Brinkman medium μ^{i} with an infinitesimal ionite grain size, a=0. It can be seen that at C_0=0.15 mol/dm^3, an extremum is observed on the exact curve *1*. This means a decrease in the osmotic permeability of the system at electrolyte concentrations exceeding that indicated, which may be due to a significant (one and a half times) excess of the mobility of the chlorine anion over that of the sodium cation. At the same time, if there were an ideally selective membrane with the same properties, then there would be no drop of $\bar{L}_{13}$ at all and this coefficient would reach a noticeable positive value (curve *2*). This can be explained by the fact that there is no flow of co-ions through the ideally selective membrane.

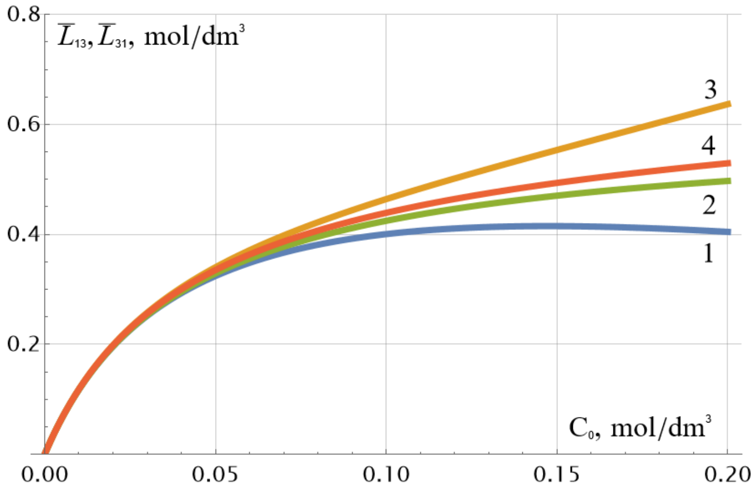


Figure 3. Calculated dependences of the normalized capillary osmotic $\bar{L}_{13}=\left(\mu^{\mathrm{o}}/k_{\mathrm{D}}\right)L_{13}$—*1,2* and reverse osmotic $\bar{L}_{31}=\left(\mu^{\mathrm{o}}/k_{\mathrm{D}}\right)L_{31}$—*3,4* coefficients for the cast perfluorinated MF-4SK membrane on the concentration C_0 of an aqueous NaCl solution at $\gamma=0.527$—*1,3*; $\gamma=+\infty$—*2,4* (ideally selective cation exchange membrane).

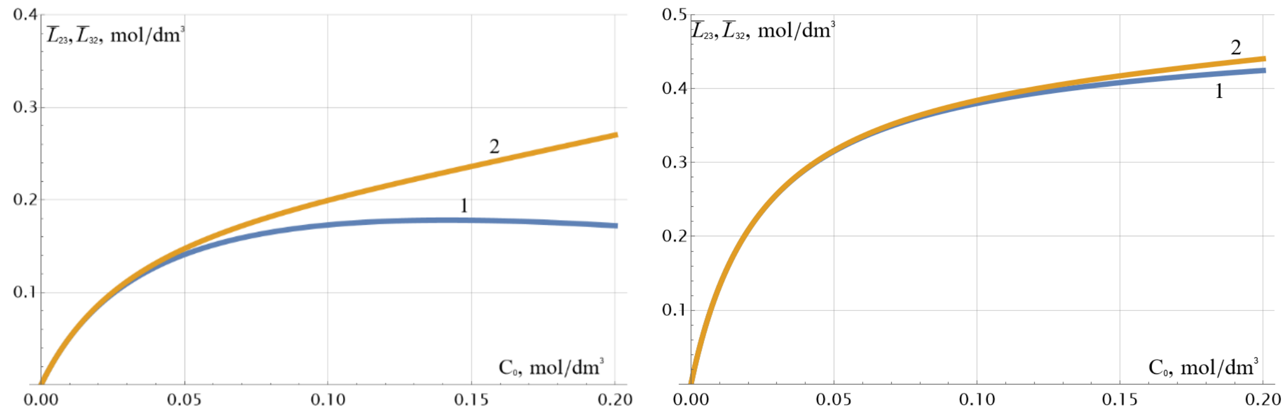
It can be seen from Figure 3 that the cross coefficients differ little only at small concentrations of electrolyte (up to 0.1 M). At high concentrations, there is a significant quantitative and qualitative discrepancy between L_{13} and L_{31}: the reverse osmotic coefficient (curve *3*) increases with increasing electrolyte concentration, and the capillary osmotic coefficient (curve *1*) decreases. At the same time, there is not such a significant difference between these coefficients calculated for ideally selective membranes (curves *2* and *4*).

As for the electrodiffusion coefficients L_{23} (determines the diffusive current) and L_{32} (determines the transfer of salt under the action of an electric potential drop), they have the following forms for the case of an ideally selective membrane for baromembrane processes:

$$L_{23}=\frac{FD_{+}C_{0}}{RT\left(3-m_{0}\right)}\left(m_{0}\left(1-\frac{D_{-}}{D_{+}}\right)+\frac{\frac{9}{2}\left(1-m_{0}\right)\left(\frac{D_{\mathrm{m}+}}{D_{+}}+\frac{\bar{\rho}}{\rho_{0}}\right)}{m_{0}\left(\frac{D_{\mathrm{m}+}}{D_{+}}+\frac{\bar{\rho}}{\rho_{0}}\right)+\left(3-m_{0}\left(1+\frac{\bar{\rho}}{\rho_{0}}\right)\right)\frac{C_{0}}{\bar{\rho}}}\right), \qquad (7)$$

$$L_{32}=\frac{FD_{+}C_{0}}{RT\left(3-m_{0}\right)}\times$$
$$\left[\begin{array}{l}\left(m_{0}\frac{\bar{\rho}}{\bar{\rho}_{0}}-\frac{3\left(1-m_{0}\right)}{2}\right)\dfrac{\left(3-m_{0}\right)\left(1+\dfrac{\bar{\rho}}{\bar{\rho}_{0}}\dfrac{D_{+}}{D_{-}}\right)\dfrac{C_{0}}{\bar{\rho}}-3\left(\left(\dfrac{\bar{\rho}}{\bar{\rho}_{0}}+\dfrac{D_{\mathrm{m+}}}{D_{+}}\right)-\dfrac{C_{0}}{\bar{\rho}_{0}}\right)}{m_{0}\left(\dfrac{D_{\mathrm{m+}}}{D_{+}}+\dfrac{\bar{\rho}}{\bar{\rho}_{0}}\right)+\left(3-m_{0}\left(1+\dfrac{\bar{\rho}}{\bar{\rho}_{0}}\right)\right)\dfrac{C_{0}}{\bar{\rho}}}+\\ \dfrac{3\left(1-m_{0}\right)}{2}\dfrac{D_{-}}{D_{+}}\dfrac{\left(3-m_{0}\left(1+\dfrac{\bar{\rho}}{\bar{\rho}_{0}}\dfrac{D_{+}}{D_{-}}\right)\right)\dfrac{C_{0}}{\bar{\rho}}}{m_{0}\left(\dfrac{D_{\mathrm{m+}}}{D_{+}}+\dfrac{\bar{\rho}}{\bar{\rho}_{0}}\right)+\left(3-m_{0}\left(1+\dfrac{\bar{\rho}}{\bar{\rho}_{0}}\right)\right)\dfrac{C_{0}}{\bar{\rho}}}+\left(3-m_{0}\right)\left(\dfrac{\bar{\rho}}{\bar{\rho}_{0}}+\dfrac{1}{2}\left(1-\dfrac{D_{-}}{D_{+}}\right)\right)\end{array}\right], \tag{8}$$

where F—the Faraday constant. Despite the external structural similarity of formulas (7) and (8), they differ significantly. This allows us to talk about the asymmetry of the electrodiffusion coefficients in the cell model of a charged porous layer. Figure 4 shows a comparison of the behavior of a pair of normalized coefficients $\bar{L}_{23}$ (curves *1*) and $\bar{L}_{32}$ (curves *2*) depending on the concentration of the NaCl electrolyte in the case of a cast perfluorinated MF-4SK membrane (a), mentioned earlier (Figure 3) and an extrusion perfluorinated MF-4SK membrane (b), investigated in our previous work (2022): $D_{\mathrm{m+}}=915$, $D_{\mathrm{m-}}=80$ μm^2/s, $\bar{\rho}$=1.11 mol/dm^3, $\bar{\rho}_0=5.23$ mol/dm^3, $m_0=0.077$, $\gamma=0.95$.



(a) (b)

Figure 4. Exact calculated dependences of normalized electrodiffusion coefficients $\bar{L}_{23}=L_{23}RT/\left(FD_{+}\right)$—curves 1 and $\bar{L}_{32}=L_{32}RT/\left(FD_{+}\right)$—curves 2 for cast perfluorinated MF-4SK membrane depending on concentration C_0 of an aqueous solution of NaCl (a) and the MF-4SK extrusion membrane (b).

The curves in Figure 4 are drawn for coefficients $\bar{L}_{23}$ and $\bar{L}_{32}$ using exact formulas. For an extrusion membrane, these coefficients practically do not differ up to a NaCl concentration of 0.2 M. In the case of a cast membrane, there is a slight difference up to a concentration of 0.05 M. That is, at low concentrations of the electrolyte, small differences in the cross electrodiffusion kinetic coefficients can also be detected.

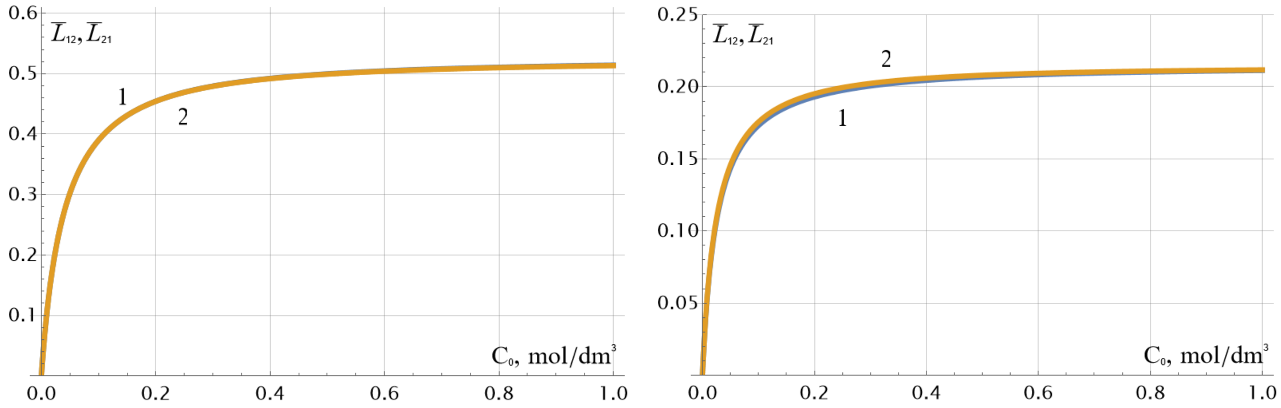
However, not all pairs of coupled cross coefficients at high concentrations of electrolyte differ as radically as L_{13} and L_{31}. In the case of coefficients L_{12} (electroosmotic permeability) and L_{21} (kinetic coefficient responsible for the streaming current), the difference is practically negligible. Indeed, in the case of an ideally selective cation exchange membrane and a symmetrical 1:1 electrolyte, we have the formulas:

$$L_{12}=3\frac{FD_+}{RT}\frac{\dfrac{C_0}{\bar{\rho}}}{m_0\left(\dfrac{D_{m+}}{D_+}\dfrac{\bar{\rho}_0}{\bar{\rho}}+1\right)+\left(\left(3-m_0\right)\dfrac{\bar{\rho}_0}{\bar{\rho}}-m_0\right)\dfrac{C_0}{\bar{\rho}}}, \qquad (9)$$

$$L_{21}=3\frac{FD_+}{RT}\frac{\left(1+\dfrac{m_0}{3-m_0}\dfrac{D_{m+}}{D_+}\right)\dfrac{C_0}{\bar{\rho}}}{m_0\left(\dfrac{D_{m+}}{D_+}\dfrac{\bar{\rho}_0}{\bar{\rho}}+1\right)+\left(\left(3-m_0\right)\dfrac{\bar{\rho}_0}{\bar{\rho}}-m_0\right)\dfrac{C_0}{\bar{\rho}}}. \qquad (10)$$

Comparing (9) and (10), we conclude that $L_{12}\neq L_{21}$. However, we note that the difference between these coefficients is very insignificant and is determined by the multiplier $1+\left(m_0/\left(3-m_0\right)\right)\left(D_{m+}/D_+\right)$, which is slightly more than one, since the following restrictions are met in real conditions: $0<m_0/\left(3-m_0\right)<1/2$ and $D_{m+}/D_+<<1$.

Figure 5 shows the behavior of dimensionless coefficients L_{12} and L_{21} as a function of NaCl concentration, calculated using exact formulas for a cast perfluorinated MF-4SK membrane (a) and for an extrusion perfluorinated MF-4SK membrane (b). As can be seen, in the case of both membranes, the cross kinetic coefficients L_{12} and L_{21} practically coincide up to high values of the electrolyte concentration. Note that in the known literature, the pairs of coefficients L_{13} and L_{31} or L_{23} and L_{32} have not been compared when defining some model of a porous medium carrying a fixed charge. As for the pair of cross coefficients L_{12} and L_{21}, there are works that prove their symmetry [6]. At the same time the Onsager reciprocity relation is not satisfied under concentration polarization conditions [7]. Note that in Peusner's thermodynamics, the reciprocity theorem is not assumed to be true [8–10]. Moreover, the cross coefficients themselves may depend non-linearly on thermodynamic forces [11], which implies their asymmetry.



(a) (b)

Figure 5. Exact calculated dependences of the dimensionless electroosmotic coefficient $\bar{L}_{12}=L_{12}RT/\left(FD_+\right)$ —curves 1 and the coefficient determining the streaming current $\bar{L}_{21}=L_{21}RT/\left(FD_+\right)$ —curves 2 for MF-4SK cast perfluorinated membrane depending on concentration C_0 of aqueous NaCl solution (a) and the MF-4SK extrusion membrane (b).

4. Conclusion

Thus, the developed cell model within the framework of linear thermodynamics of irreversible processes [2] can be applied to any membranes carrying a volume charge (in particular, to ion exchange, reverse osmotic, nano-, ultra- and microfiltration membranes). At the same time, the possibility of calculating, for example, the electroosmotic flux of water or water transference numbers using the obtained finite algebraic formulas with parameters that have a clear physical meaning is important not only in electromembrane processes (*i.e.* in fuel cells, sensors, electrolyzers, *etc.*), but also in calculations of electroosmotic pumps in microfluidics, in determining the water content in food products during their long-term storage, and in analyzing the reduction of liquid transfer through concrete, since excessive humidity leads to corrosion of metal reinforcement and premature destruction of concrete.

We have shown here that in the case of the cell membrane model, the Onsager reciprocity principle is violated—the matrix of kinetic coefficients is not symmetric. Onsager himself, in his famous work of 1931 [3], did not provide a phenomenological proof of the validity of his hypothesis and referred to the fact that experimental data could be a measure of the validity of the principle of reciprocity. At the same time, Mamedov published such proof in 2003 [4]. In this regard, it is necessary to be careful about determining the transport characteristics of membranes, which depend on the cross kinetic coefficients due to the asymmetry of the latter. In present paper, it is shown that the coupled cross coefficients can differ not only quantitatively, but also qualitatively. Mamedov showed [4] that the Onsager reciprocity principle strictly holds only for systems with zero generalized fluxes under action of nonzero generalized forces, *i.e.*, in fact in an equilibrium state, which significantly reduces its applicability and contributes to errors in the calculation of cross kinetic coefficients. On the other hand, it can be assumed that the principle of reciprocity will be approximately fulfilled at low values of the densities of these fluxes in the case of a slight deviation of the dispersed system from equilibrium. It remains only to determine what the "low" values of the flux densities of solvent, solute, and electric current are. In the case of solvent flow, such deviation can be observed at Reynolds numbers much lower than unity. Such flows are typical for actual practical problems of fluid transfer through porous collectors, electrolyte solutions through charged membranes, extended channels with porous walls, *etc.*

In this work, using the example of two types of perfluorinated membranes, it is shown that the coupled cross coefficients in the cell model of a charged membrane practically coincide at low concentrations of electrolyte (up to 0.1 mol/dm^3). The asymmetry of these coefficients at high concentrations of the electrolyte may also be a consequence of the linearization of the boundary value problem of the transfer of substances through a porous charged layer.

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Conflicts of interests

The author declares no conflict of interest.

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