GENERAL QUESTIONS OF THERMODYNAMICS, STATISTICAL PHYSICS, AND QUANTUM MECHANICS

GENERALIZED EQUATIONS FOR IONIC AND MOLECULAR TRANSPORT IN ELECTROLYTE SOLUTIONS THROUGH MEMBRANE STRUCTURES, TAKING ELECTROMAGNETIC PROCESSES INTO ACCOUNT

E.M. SOVYAK, I.J. KURYLYAK, YU.I. CHERNOMORETS, M.V. TOKARCHUK

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Institute for Condensed Matter Physics, Nat. Acad. Sci. of Ukraine
(1, Sventsitskyi Str., Lviv 79011; Ukraine; e-mail: mtok@icmp.lviv.ua)

Generalized equations, which describe the transport of ions and molecules in an electrolyte solution through a reverse osmotic membrane under the action of the temperature and concentration gradients and the difference between the external and osmotic pressures and which include the dielectric properties of the solution, membrane, and filtrate as parameters, have been obtained. Making use of the Zubarev nonequilibrium statistical operator method, the generalized transport equations for ions and molecules in the system "electrolyte solution–membrane–filtrate" have been derived in the framework of the diffusive and viscous motion models. The electromagnetic transport processes have been taken into account for the system under investigation by averaging the Maxwell's microscopic equations.

1. Introduction

The reverse osmosis, which occurs in the course of electrolyte solution separation at a membrane, is a diffusion process governed by the concentration and temperature gradients, as well as by the difference between the external and osmotic pressures and the differences between the dielectric functions of the initial electrolyte solution, the membrane, and the filtrate. The optimum choice for the regime of separation of the initial solution into its components depends to a great extent on the coordination between all those factors.

In works [1, 2], we proposed to describe the diffusion-governed processes of electrolyte solution particle transport through a reverse-osmotic membrane in a three-phase system "initial electrolyte solution–membrane–filtrate" on the basis of generalized diffusion equations; in work [3], this approach was generalized for the hydrodynamic model. In so doing, the membrane was considered as an inertial diffusive medium. Theoretical researches of porous media filled with an electrolyte testify that different geometries of the medium make its final characteristics also different. Polymeric or vitreous membranes are actually microporous materials possessing selective properties with respect to ionic transport. As a result, a selective ionic electroconductivity is observed [4], giving rise to the emergence of near-surface electric fields and intramembrane electromagnetic fields. The latter generate ionic and dipole fluxes in the membrane medium. This means that the processes of electrolyte solution separation by membrane structures – in particular, the selective ionic electroconductivity – are substantially affected by electromagnetic processes, which themselves are a result of the ion separation of the solution into its components.

A number of works [5–8] is to be noted, in which the coefficients of ionic electroconductivity were studied under conditions that the solution ions penetrate into a porous medium. In particular, in work [7], the electromagnetic fields and their influence on the processes of ionic transport in pores have been made allowance for, and the macroscopic transport equations

consistent with the averaged – in the case of a porous medium – Maxwell's equations for the electromagnetic field have been derived. A similar approach for the macroscopic description of the electrodiffusion in aqueous solutions in porous media making use of the methods of nonequilibrium thermodynamics and representing the considered medium as a continuum has been proposed in work [9].

In this work, we have generalized the diffusion model of membrane separation of electrolyte solutions [1] and considered a viscous model of reverse-osmotic processes, where the influence of the intrinsic electromagnetic field induced by ions at their diffusion through membrane structures is taken into account.

2. Electro-magnetohydrodynamic State of the System "Initial Solution–membrane–filtrate"

While examining the transport processes in the system "initial solution–membrane–filtrate", it is expedient to proceed from the supposition that the system is in the equilibrium state at the initial time moment, being a three-phase system characterized by the volume V. Let the initial solution be a subsystem consisting of ions of kinds a and b, as well as the solvent molecules of kind α with the dipole moment $\mathbf{d}_\alpha$ in the volume V_1 ($z < 0$). We suppose that some electrolyte ions and water molecules are physically and chemically absorbed on the surface of the porous membrane, and that the ionized particles of the membrane are also available. These charged particles form a fixed "Helmholtz internal and external layer", which is so thin (less that 10 Å) that, in the framework of the given approach, it is not considered as a separate phase; its availability is reflected in the form of corresponding boundary conditions at the membrane surface S_w. The charge adsorbed on the surface is compensated by the excess of free ions in the adjacent layer of the electrolyte. This screening surface layer is also referred to as a "diffusion" one. Together with the Helmholtz surface layer, they compose an electric double layer, where the excess charge is spatially distributed, whereas the membrane itself and the electrolyte in the bulk are electrically neutral. Let the membrane substance be an insulator and occupy the volume V_2 ($0 \leq z \leq h$), and let the filtrate occupy the volume V_3 ($z > h$). Hence, the total macroscopic volume of the system amounts to $V = V_1 + V_2 + V_3$.

The equilibrium state of such a system at a constant temperature and provided that the distribution of the average concentrations of the dissolved substance is descendent ($n_1^{a(b)} > n_2^{a(b)} > n_3^{a(b)}$) is determined by the

external pressure exerting on the initial solution, which is compensated by the difference of osmotic pressures on the both sides of the membrane. This state is completely described by the equilibrium distribution function of ions and molecules at a constant external pressure

$$\rho_0(x^N; \Delta P) = \Xi^{-1}(\Delta P) \times \exp\Big\{-\beta(H - \Delta P V_1 -$$

$$- \sum_k \sum_{l=1}^3 \int_{V_l} d\mathbf{r}_l \mu_k(\mathbf{r}_l) \hat{n}^k(\mathbf{r}_l))\Big\}, \qquad (2.1)$$

where

$$\Xi(\Delta p) = \int d\Gamma_N \exp\Big\{-\beta(H - \Delta P V_1 -$$

$$- \sum_k \sum_{l=1}^3 \int_{V_l} d\mathbf{r}_l \mu_k(\mathbf{r}_l) \hat{n}^k(\mathbf{r}_l))\Big\} \qquad (2.2)$$

is a grand partition function at the external pressure ΔP, in which the heterogeneity of the system "initial electrolyte solution–membrane–filtrate" is taken into account by the term $\sum_k \sum_{l=1}^3 \int_{V_l} d\mathbf{r}_l \mu_k(\mathbf{r}_l) \hat{n}^k(\mathbf{r}_l)$ including the local distribution of the chemical potential $\mu_k(\mathbf{r}_l)$ for each component; H is the Hamiltonian of the system [1]; $\hat{n}^k(\mathbf{r}_l) = \sum_{j=1}^{N_k} \delta(\mathbf{r}_l - \mathbf{r}_j)$ is the microscopic density for the number of particles of the k-th kind ($k = a, \alpha$) in the l-th phase ($l = 1, 2, 3$); N_k is the number of particles of the k-th kind; $\beta = (k_B T)^{-1}$; and T is the equilibrium temperature. The condition for the system to be in the equilibrium state – namely, the absence of direct osmosis – looks like

$$\Delta P - \sum_k \left(\prod_3^k - \prod_1^k \right) = 0, \qquad (2.3)$$

where $\prod_l^k$ is the macroscopic osmotic pressure of the k-th component in the l-th phase. Provided that condition (2.3) is violated by applying the external pressure $\Delta P' > \Delta P$,

$$\Delta P' - \lim_{t \to \infty} \sum_k \left(\prod_3^k(t) - \prod_1^k(t) \right) > 0 ,$$

$$\Delta P' + \lim_{t \to \infty} \sum_k \prod_1^k(t) > \lim_{t \to \infty} \sum_k \prod_3^k(t) \qquad (2.4)$$

so that the solvent molecules start to diffuse in the direction that is opposite to that of the process of direct

osmosis (i.e. from the volume V_1 through the membrane into the volume V_3; it is the so-called reverse osmosis), we obtain a process of solvent molecule transport through the membrane into the region with a lower concentration of solutes (ions). In so doing, the densities of ionic and molecular fluxes, their energy densities, and the dielectric properties in each phase change.

Charge separation gives rise to the appearance of ionic currents in the system "aqueous electrolyte solution–membrane–filtrate", which, in their turn, generate electromagnetic fields. According to the Maxwell's equations, these fields enhance the general polarization of the system. As a result of time variations of the ionic charge density and ionic currents, there appear the electromagnetic fields in the corresponding phases, which satisfy the averaged Maxwell's equations for the strengths and inductions of the electric and magnetic fields and, in our case, look like

$$\nabla \cdot \langle \mathbf{B}(\mathbf{r}_l) \rangle^t = 0,$$

$$\nabla \cdot \langle \mathbf{D}(\mathbf{r}_l) \rangle^t = \sum_a z_a e \langle \hat{n}_a(\mathbf{r}_l) \rangle^t + \sum_\alpha \mathbf{d}_\alpha \cdot \nabla \langle \hat{n}_\alpha(\mathbf{r}_l) \rangle^t,$$

$$\nabla \times \langle \mathbf{E}(\mathbf{r}_l) \rangle^t = -\frac{\partial}{\partial t} \langle \mathbf{B}(\mathbf{r}l) \rangle^t,$$

$$\nabla \times \langle \mathbf{H}(\mathbf{r}_l) \rangle^t = \frac{\partial}{\partial t} \langle \mathbf{D}(\mathbf{r}_l) \rangle^t + \sum_a \frac{z_a e}{m_a} \langle \hat{\mathbf{p}}_a(\mathbf{r}_l) \rangle^t +$$

$$+ \sum_\alpha \frac{1}{m_\alpha} \mathbf{d}_\alpha \cdot \nabla \langle \hat{\mathbf{p}}_\alpha(\mathbf{r}_l) \rangle^t. \tag{2.5}$$

At $l = s(1)$, Eqs. (2.5) describe the fields in the "initial electrolyte solution" phase and, at $l = m(2)$, the fields in the "membrane" phase. The boundary conditions at the interface between those two phases ($z_s = z_m = 0$) are

$$\mathbf{n}_1 \cdot (\langle \mathbf{B}(\mathbf{r}_m) \rangle^t - \langle \mathbf{B}(\mathbf{r}_s) \rangle^t) = 0,$$

$$\mathbf{n}_1 \cdot (\langle \mathbf{D}(\mathbf{r}_m) \rangle^t - \langle \mathbf{D}(\mathbf{r}_s) \rangle^t) = Q_1(\mathbf{S}_{w1}; t),$$

$$\mathbf{n}_1 \times (\langle \mathbf{E}(\mathbf{r}_m) \rangle^t - \langle \mathbf{E}(\mathbf{r}_s) \rangle^t) = 0,$$

$$\mathbf{n}_1 \times (\langle \mathbf{H}(\mathbf{r}_m) \rangle^t - \langle \mathbf{H}(\mathbf{r}_s) \rangle^t) =$$

$$= \sum_a Q_a(\mathbf{S}_{w1}; t) \mathbf{v}_a(\mathbf{S}_{w1}; t), \tag{2.6}$$

where the subscripts s and m correspond to the "initial solution" and "membrane" phases, respectively;

$Q_a(\mathbf{S}_{w1}; t)$ is the surface charge created by ions of the a-th kind at the interface between the initial solution and the membrane, and $Q_1(\mathbf{S}_{w1}; t) = \sum_a Q_a(\mathbf{S}_{w1}; t)$ is the total surface charge. From the charge conservation law, it follows that

$$\mathbf{n}_1 \cdot \frac{z_a e}{m_a} \langle \hat{\mathbf{p}}_a(\mathbf{r}_s) \rangle^t = \frac{\partial}{\partial t} Q_a(\mathbf{S}_{w1}; t),$$

where $\mathbf{v}_a(\mathbf{r}; t) = \langle \hat{\mathbf{p}}_a(\mathbf{r}) \rangle^t / (m_a \langle \hat{n}_a(\mathbf{r}) \rangle^t)$ is the average velocity of ions of the a-th kind, $\hat{\mathbf{p}}_a(\mathbf{r}) = \sum_{j=1}^{N_a} \mathbf{p}_j \delta(\mathbf{r} - \mathbf{r}_j)$ is the microscopic density of their momenta, and $\mathbf{n}_1$ is a unit vector directed perpendicularly to the "initial solution–membrane" interface plane. The boundary conditions at the surface S_{w1} are derived by integrating the Maxwell's equations over an infinitesimal volume, which surrounds a small section on S_{w1}.

The averaged Maxwell's equations for the "filtrate" phase are obtained from Eqs. (2.5) by putting $l = h(3)$ there. The boundary conditions at the "membrane–filtrate" interface ($z_h = z_m = -L$) are

$$\mathbf{n}_2 \cdot (\langle \mathbf{B}(\mathbf{r}_h) \rangle^t - \langle \mathbf{B}(\mathbf{r}_m) \rangle^t) = 0,$$

$$\mathbf{n}_2 \cdot (\langle \mathbf{D}(\mathbf{r}_h) \rangle^t - \langle \mathbf{D}(\mathbf{r}_m) \rangle^t) = Q_1(\mathbf{S}_{w2}; t),$$

$$\mathbf{n}_2 \times (\langle \mathbf{E}(\mathbf{r}_h) \rangle^t - \langle \mathbf{E}(\mathbf{r}_m) \rangle^t) = 0,$$

$$\mathbf{n}_2 \times (\langle \mathbf{H}(\mathbf{r}_h) \rangle^t - \langle \mathbf{H}(\mathbf{r}_m) \rangle^t) =$$

$$= \sum_a Q_a(\mathbf{S}_{w2}; t) \mathbf{v}_a(\mathbf{S}_{w2}; t), \tag{2.7}$$

where the subscripts h and m correspond to the "filtrate" and "membrane" phases, respectively; L is the membrane thickness; $Q_a(\mathbf{S}_{w2}; t)$ is the surface charge created by ions of the a-th kind at the filtrate–membrane interface (it is the surface $\mathbf{S}_{w2}$); and $Q_1(\mathbf{S}_{w2}; t) = \sum_a Q_a(\mathbf{S}_{w2}; t)$ is the total surface charge. From the charge conservation law, it follows that

$$\mathbf{n}_2 \cdot \frac{z_a e}{m_a} \langle \hat{\mathbf{p}}_a(\mathbf{r}_h) \rangle^t = \frac{\partial}{\partial t} Q_a(\mathbf{S}_{w2}; t),$$

where $\mathbf{n}_2$ is a unit vector directed perpendicularly to the "membrane–filtrate" interface plane.

In the diffusion membrane model, it is assumed that every component of the initial electrolyte solution undergoes the action of a high pressure $\Delta P = (\tilde{P} - \pi) > 0$ (here, $\tilde{P}$ is the working and π is the osmotic pressure) and, according to the diffusion laws and the specific electro-magnetohydrodynamic properties of

the component, penetrates through the surface into the membrane region, by generating the fluxes of the solvent and solutes. The magnitudes of those fluxes are determined by the driving forces indicated above and the character of all ion-ion, ion-molecule, and molecule-molecule interactions in the interphase region. The last remark means that the microscopic structure of the membrane, its porosity, and its interaction with the solution have to be taken into account.

The averaged quantities, denoted as $\langle \ldots \rangle^t = \int d\Gamma_N \ldots \rho(x^N; t)$, in Eqs. (2.5)–(2.7) are determined by the nonequilibrium distribution function of ions and molecules, $\rho(x^N; t)$, in the system "initial solution–membrane–filtrate". The function $\rho(x^N; t)$ satisfies the Liouville equation

$$\frac{\partial}{\partial t}\rho(x^N; t) + iL_N\rho(x^N; t) = 0 \qquad (2.8)$$

and the normalization condition $\int d\Gamma_N\rho(x^N; t) = 1$, where iL_N is the Liouville operator for the ion-molecular system "initial solution–membrane–filtrate":

$$iL_N = \sum_a \sum_{j=1}^{N_a} \frac{\mathbf{p}_j}{m_a}\frac{\partial}{\partial \mathbf{r}_j} +$$

$$+ \sum_\alpha \sum_{f=1}^{N_\alpha}\left(\frac{\mathbf{p}_f}{m_\alpha}\frac{\partial}{\partial \mathbf{r}_f} + (\mathbf{w}_f \cdot \hat{\mathbf{d}}_f)\frac{\partial}{\partial \hat{\mathbf{d}}_f}\right) -$$

$$- \sum_a \sum_{j=1}^{N_a} \sum_k \sum_{i=1}^{N_k} \frac{\partial}{\partial \mathbf{r}_j}\tilde{\Phi}_{ak}(\mathbf{r}_j, \mathbf{r}_i)\frac{\partial}{\partial \mathbf{p}_j} -$$

$$- \sum_\alpha \sum_{f=1}^{N_\alpha} \sum_k \sum_{i=1}^{N_k}\left(\frac{\partial}{\partial \mathbf{r}_f}\tilde{\Phi}_{\alpha k}(\mathbf{r}_f, \mathbf{r}_i)\frac{\partial}{\partial \mathbf{p}_f} + \right.$$

$$\left. + \left(\hat{\mathbf{d}}_f \frac{\partial}{\partial \mathbf{d}_f}\Phi_{\alpha k}(\mathbf{r}_f, \mathbf{r}_i)\right)\frac{\partial}{\partial J_f w_f}\right). \qquad (2.9)$$

Here, $\mathbf{p}_j$ and $\mathbf{p}_f$ are the momenta of translational motion of ions and molecules, respectively; m_a and m_α are their masses; $\mathbf{w}_f$ and J_f are the angular velocity and the inertia tensor, respectively, of molecules of the α-th kind, the latter being determined with respect to the center of mass of the molecules; $\hat{\mathbf{d}}_f = \mathbf{d}_f/|\mathbf{d}_f|$ is a unit vector which describes spatial orientations of the molecules; $\tilde{\Phi}_{ak}(\mathbf{r}_j, \mathbf{r}_i)$ with $k = (b, \alpha, s)$ are the pair potentials of interaction between the ions of the a-th kind with the ions of other kinds ($k = b$), molecules ($k = \alpha$), or membrane molecules ($k = s$); and $\tilde{\Phi}_{\alpha k}(\mathbf{r}_f, \mathbf{r}_i)$ with $k = (b, \alpha', s)$ are the pair potentials of interaction between molecules (α) and ions ($k = a$), other molecules

($k = \alpha'$), or membrane molecules ($k = s$). The pair interaction potentials $\tilde{\Phi}_{kk'}(\mathbf{r}_j, \mathbf{r}_i)$ consist of long-range, $\Phi_{kk'}(\mathbf{r}_j, \mathbf{r}_i)$, and short-range, $\varphi_{k,k'}(\mathbf{r}_j, \mathbf{r}_i)$, parts. In the case of the ion-dipole solution model, $\Phi_{kk'}(\mathbf{r}_j, \mathbf{r}_i)$ can be written down in the form

$$\Phi_{kk'}(\mathbf{r}_j, \mathbf{r}_i) = \hat{Q}_k(\boldsymbol{\nabla}_j)\hat{Q}_{k'}(\boldsymbol{\nabla}_i)\frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} \ ,$$

where

$$\hat{Q}_k(\boldsymbol{\nabla}_j) = \begin{cases} z_a e, & k = a, b, \\ \mathbf{d}_f\dfrac{\partial}{\partial \mathbf{r}_f}, & k = \alpha, s, \end{cases}$$

z_a is the valency of ions of the a-th kind, and e is the electron charge. The short-range part of the potential energy of interparticle interaction, $\varphi_{k,k'}(\mathbf{r}_j, \mathbf{r}_i)$, can be simulated by the Lennard–Jones potential

$$\varphi_{kk'}(\mathbf{r}_j, \mathbf{r}_i) = \varphi_{kk'}^{(0)}\left\{\left(\frac{\sigma_{kk'}}{|\mathbf{r}_{ji}|}\right)^{12} - \left(\frac{\sigma_{kk'}}{|\mathbf{r}_{ji}|}\right)^{6}\right\},$$

where $\varphi_{kk'}^{(0)}$ and $\sigma_{kk'}$ are the parameters which determine the depth and the position of the potential well.

The averaged quantities in the systems of Maxwell's equations for the three-phase system "aqueous electrolyte solution–membrane–filtrate" are calculated with the help of the nonequilibrium statistical operator $\rho(x^N; \Delta P'; t)$ with a selected set of parameters for a reduced description of nonequilibrium processes, which, as a rule, are the observable quantities. Taking advantage of the Zubarev nonequilibrium statistical operator method [10], the solution of Liouville equation (2.8) can be written down in the general form as follows:

$$\rho(x^N; \Delta P'; t) = \rho_q(x^N; \Delta P'; t) -$$

$$- \int_{-\infty}^{t} e^{\epsilon(t'-t)}T(t, t')(1 - \mathcal{P}_q(t')) \times$$

$$\times iL_N\rho_q(x^N; \Delta P'; t')dt', \qquad (2.10)$$

where

$$T(t, t') = \exp\left\{\int_{t'}^{t}(1 - \mathcal{P}_q(t''))iL_Ndt''\right\} \qquad (2.11)$$

is the operator of time evolution taking the projection operation into account, and $\mathcal{P}_q(t)$ is the generalized Kawasaki–Gunton projection operator. The structure

of the latter is determined by the quasiequilibrium distribution function $\rho_q(x^N; \Delta P'; t)$ at the extremum point of the information entropy, provided that the values of the parameters of the reduced description of nonequilibrium processes $\langle \hat{x}(\mathbf{r}) \rangle^t$ are fixed, and the normalization condition $\int d\Gamma_N \rho_q(x^N; t) = 1$ is obeyed.

Now, consider the influence of electromagnetic interactions on the processes of electrolyte solution transport through membrane structures in the framework of two models used for the description of those processes: a diffusion and a viscous one.

2.1. Diffusion model of electrolyte solution transport through membrane structures

In the diffusion model used for the description of the processes of electrolyte solution transport through membrane structures [1], the parameters of a reduced description are the average values of the ion and the molecule number densities: $\langle \hat{x}(\mathbf{r}) \rangle^t = \{\langle \hat{n}_a(\mathbf{r}) \rangle^t, \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t\}$. In this case, the quasiequilibrium distribution function $\rho_q(x^N; \Delta P'; t)$, which is found from the condition of information entropy extremum at fixed values of the parameters of the reduced description of the nonequilibrium process and provided that the normalization condition $\int d\Gamma_N \rho_q(x^N; t) = 1$ remains valid, looks like

$$\rho_q(x^N; \Delta P'; t) = \exp\{-\Phi(t) - \sum_{l=1}^{3} \int_{V_l} d\mathbf{r}_l \beta(H-$$

$$-V_1 \Delta P' - \sum_a \nu_a(\mathbf{r}_l; t)\hat{n}_a(\mathbf{r}_l)-$$

$$-\sum_\alpha \nu_\alpha(\mathbf{r}_l; t)\hat{n}_\alpha(r_l))\}, \tag{2.12}$$

where $\Phi(t)$ is the Massier–Planck functional

$$\Phi(t) = \ln \int d\Gamma_N \exp\left\{-\sum_{l=1}^{3} \int_{V_l} d\mathbf{r}_l \beta(H - V_1 \Delta P'-\right.$$

$$-\sum_a \nu_a(\mathbf{r}_l; t)\hat{n}_a(\mathbf{r}_l) - \sum_\alpha \nu_\alpha(\mathbf{r}_l; t)\hat{n}_\alpha(\mathbf{r}_l))\right\}. \tag{2.13}$$

The thermodynamic parameters $\nu_a(\mathbf{r}_l; t)$ and $\nu_\alpha(\mathbf{r}_l; t)$ are determined from the conditions of self-consistency

$$\langle \hat{n}_a(\mathbf{r}) \rangle^t = \langle \hat{n}_a(\mathbf{r}) \rangle_q^t, \langle \hat{n}_\alpha(\mathbf{r}) \rangle^t = \langle \hat{n}_\alpha(\mathbf{r}) \rangle_q^t, \tag{2.14}$$

where β is the inverse temperature; $\nu_a(r; t) = \mu_a(r; t) + z_a e\phi_a(r; t)$ is the local electrochemical potential of ions

of the a-th kind; $\phi_a(\mathbf{r}; t)$ is the local electric potential of ions which determines the local electric field of ions, $\langle \mathbf{E}_a(\mathbf{r}_l) \rangle^t = -\nabla \cdot \phi_a(\mathbf{r}_l; t)$, in every phase; $\mu_a(\mathbf{r}; t)$ is the local chemical potential of ions of the a-th kind in the corresponding phase; $\nu_\alpha(\mathbf{r}_l; t) = \mu_\alpha(\mathbf{r}_l; t) - \mathbf{d}_\alpha \cdot \langle \mathbf{E}_\alpha(\mathbf{r}_l) \rangle^t$ is the dipole-chemical potential of molecules of the α-th kind; $\langle \mathbf{E}_\alpha(\mathbf{r}_l) \rangle^t$ is the nonequilibrium electric field created by dipole molecules; and $\mu_\alpha(\mathbf{r}_l; t)$ is the local chemical potential of molecules of the α-th kind in the corresponding phase.

By substituting expression (2.12) for $\rho_q(x^N; \Delta P'; t)$ into Eq. (2.10), we obtain the nonequilibrium statistical operator for the description of diffusion processes:

$$\rho(x^N; \Delta P'; t) = \rho_q(x^N; \Delta P'; t)-$$

$$-\sum_a \sum_{l=1}^{3} \int d\mathbf{r}_l' \int_{-\infty}^{t} e^{\varepsilon(t'-t)} T(t, t') I_n^a(\mathbf{r}_l'; t') \times$$

$$\times \beta \nu_a(\mathbf{r}_l'; t'))\rho_q(x^N; t')dt'-$$

$$-\sum_\alpha \sum_{l=1}^{3} \int d\mathbf{r}_l' \int_{-\infty}^{t} e^{\varepsilon(t'-t)} T(t, t') I_n^\alpha(\mathbf{r}_l'; t') \times$$

$$\times \beta \nu_\alpha(\mathbf{r}_l'; t'))\rho_q(x^N; t')dt', \tag{2.15}$$

where $I_n^a(\mathbf{r}_l'; t')$ and $I_n^\alpha(\mathbf{r}_l'; t')$ are the generalized fluxes of particles of kinds a and α in the l-th phase. They have the following structure:

$$I_n^a(\mathbf{r}_l'; t) = (1 - \mathcal{P}(t))iL_N\hat{n}_a(\mathbf{r}_l),$$

$$I_n^\alpha(\mathbf{r}_l'; t) = (1 - \mathcal{P}(t))iL_N\hat{n}_\alpha(\mathbf{r}_l). \tag{2.16}$$

This structure includes the Mori projection operator, which acts on the dynamic variables,

$$\mathcal{P}(t)\hat{A}(\mathbf{r}) = \langle \hat{A} \rangle_q^t + \sum_k \sum_l \int d\mathbf{r}_l \frac{\delta \langle \hat{A}(\mathbf{r}) \rangle^t}{\delta \langle \hat{n}_k(\mathbf{r}_l) \rangle^t} \times$$

$$\times \left(\hat{n}_k(\mathbf{r}_l) - \langle \hat{n}_k(\mathbf{r}_l) \rangle^t, \right) \tag{2.17}$$

and has the following properties: $\mathcal{P}(t) \cdot \mathcal{P}(t) = \mathcal{P}(t)$, $\mathcal{P}(t)(1 - \mathcal{P}(t)) = 0$, $\mathcal{P}(t) \cdot \hat{x}(\mathbf{r}) = \hat{x}(\mathbf{r})$.

Making use of the nonequilibrium statistical operator (2.15), we obtain the system of equations which describe the electromagnetically governed diffusion transport of

ions and molecules of the electrolyte solution through membrane structures:

$$\frac{d}{dt}\langle \hat{n}_a(\mathbf{r}_l)\rangle^t = -\sum_b \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \times$$

$$\times \nabla \cdot D_{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')(\beta\nabla' \cdot \mu_b(\mathbf{r}_{l'}; t') - z_b e\beta\langle \mathbf{E}_b(\mathbf{r}_{l'})\rangle^{t'}) -$$

$$-\sum_{\alpha'} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \nabla \cdot D_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times \beta\nabla' \cdot \{\mu_{\alpha'}(\mathbf{r}_{l'}; t') - \mathbf{d}_{\alpha'} \cdot \langle \mathbf{E}_{\alpha'}(\mathbf{r}_{l'})\rangle^{t'}\} dt', \qquad (2.18)$$

$$\frac{d}{dt}\langle \hat{n}_\alpha(\mathbf{r}_l)\rangle^t = -\sum_b \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \times$$

$$\times \nabla \cdot D_{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')(\beta\nabla' \cdot \mu_b(\mathbf{r}_{l'}; t') - z_b e\beta\langle \mathbf{E}_b(\mathbf{r}_{l'})\rangle^{t'}) -$$

$$-\sum_{\alpha'} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \nabla \cdot D_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times \beta\nabla' \cdot \{\mu_{\alpha'}(\mathbf{r}_{l'}; t') - \mathbf{d}_{\alpha'} \cdot \langle \mathbf{E}_{\alpha'}(\mathbf{r}_{l'})\rangle^{t'}\} dt', \qquad (2.19)$$

$$\nabla \cdot \langle \mathbf{B}(\mathbf{r}_l)\rangle^t = 0, \qquad (2.20)$$

$$\nabla \cdot \langle \mathbf{D}(\mathbf{r}_l)\rangle^t = \sum_a z_a e\langle \hat{n}_a(\mathbf{r}_l)\rangle_q^t +$$

$$+\sum_\alpha \mathbf{d}_\alpha \cdot \nabla\langle \hat{n}_\alpha(\mathbf{r}_l)\rangle_q^t +$$

$$+\sum_{ab} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} z_a e W_{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times (\beta\nabla' \cdot \mu_b(\mathbf{r}_{l'}; t') - z_b e\beta\langle \mathbf{E}_b(\mathbf{r}_{l'})\rangle^{t'}) +$$

$$+\sum_{a\alpha'} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} z_a e W_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times \beta\nabla' \cdot \{\mu_{\alpha'}(\mathbf{r}_{l'}; t') - \mathbf{d}_{\alpha'} \cdot \langle \mathbf{E}_{\alpha'}(\mathbf{r}_{l'})\rangle^{t'}\} dt' +$$

$$+\sum_{\alpha b} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \mathbf{d}_\alpha \cdot \nabla W_{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times (\beta\nabla' \cdot \mu_b(\mathbf{r}_{l'}; t') - z_b e\beta\langle \mathbf{E}_b(\mathbf{r}_{l'})\rangle^{t'}) +$$

$$+\sum_{\alpha\alpha'} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \mathbf{d}_\alpha \cdot \nabla W_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times \beta\nabla' \cdot \{\mu_{\alpha'}(\mathbf{r}_{l'}; t') - \mathbf{d}_{\alpha'} \cdot \langle \mathbf{E}_{\alpha'}(\mathbf{r}_{l'})\rangle^{t'}\} dt', \qquad (2.21)$$

$$\nabla \times \langle \mathbf{E}(\mathbf{r}_l)\rangle^t = -\frac{\partial}{\partial t}\langle \mathbf{B}(\mathbf{r}_l)\rangle^t, \qquad (2.22)$$

$$\nabla \times \langle \mathbf{H}(\mathbf{r}_l)\rangle^t = \frac{\partial}{\partial t}\langle \mathbf{D}(\mathbf{r}_l)\rangle^t +$$

$$+\sum_{ab} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \times$$

$$\times \{z_a e D_{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\beta\nabla' \cdot \mu_b(\mathbf{r}_{l'}; t') -$$

$$-\sigma_{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\beta\langle \mathbf{E}_b(\mathbf{r}_{l'})\rangle^{t'}\} dt' +$$

$$+\sum_{a\alpha'} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \times$$

$$\times \{z_a e D_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\beta\nabla' \cdot (\mu_{\alpha'}(\mathbf{r}_{l'}; t') -$$

$$-\sigma_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\nabla' \cdot \langle \mathbf{E}_{\alpha'}(\mathbf{r}_{l'})\rangle^{t'}\} dt' +$$

$$+\sum_{\alpha b} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} e^{\varepsilon(t'-t)} \times$$

$$\times \{\mathbf{d}_\alpha \cdot \nabla D_{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\beta\nabla' \cdot \mu_b(\mathbf{r}_{l'}; t') -$$

$$-\sigma_{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\beta\langle \mathbf{E}_b(\mathbf{r}_{l'})\rangle^{t'}\} dt' +$$

$$+\sum_{\alpha\alpha'} \sum_{l'=1}^{3} \int\limits_{V_{l'}} d\mathbf{r}_{l'} \int\limits_{-\infty}^{t} dt' e^{\varepsilon(t'-t)} \times$$

$$\times \{\mathbf{d}_\alpha \cdot \nabla D_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times \beta\nabla'\mu_{\alpha'}(\mathbf{r}_{l'}; t') -$$

$$-\sigma_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\langle \mathbf{E}_{\alpha'}(\mathbf{r}_{l'})\rangle^{t'}\}, \qquad (2.23)$$

where

$$D_{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') = \langle (1 - \mathcal{P}(t))m_a^{-1}\hat{\mathbf{p}}_a(\mathbf{r}_l) \times$$

$$\times T(t,t')(1-\mathcal{P}(t'))m_b^{-1}\hat{\mathbf{p}}_b(\mathbf{r}_{l'})\rangle_q^{t'} \qquad (2.24)$$

are the generalized diffusion coefficients for ions of kinds a and b,

$$D_{a\alpha}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') = \langle(1-\mathcal{P}(t))m_a^{-1}\hat{\mathbf{p}}_a(\mathbf{r}_l)\times$$

$$\times T(t,t')(1-\mathcal{P}(t'))m_\alpha^{-1}\hat{\mathbf{p}}_\alpha(\mathbf{r}_{l'})\rangle_q^{t'} \qquad (2.25)$$

the generalized interdiffusion coefficients for ions of kind a and molecules of kind α,

$$D_{\alpha\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') = \langle(1-\mathcal{P}(t))m_\alpha^{-1}\hat{\mathbf{p}}_\alpha(\mathbf{r}_l)\times$$

$$\times T(t,t')(1-\mathcal{P}(t'))m_{\alpha'}^{-1}\hat{\mathbf{p}}_{\alpha'}(\mathbf{r}_{l'})\rangle_q^{t'} \qquad (2.26)$$

the generalized interdiffusion coefficients for ions of kinds a and a',

$$\sigma_{ab}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') = z_a e D_{ab}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')z_b e \qquad (2.27)$$

the generalized coefficients of electroconductivity for ions of kinds a and b,

$$\sigma_{a\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') = z_a e D_{a\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')\cdot\mathbf{d}_{\alpha'} \qquad (2.28)$$

the generalized coefficients of ion-dipole conductivity for ions of kind a and molecules of kind α', and

$$\sigma_{\alpha\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') = \mathbf{d}_\alpha \cdot D_{\alpha\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')\cdot\mathbf{d}_{\alpha'} \qquad (2.29)$$

the generalized coefficients of dipole-dipole conductivity for dipole molecules of kinds α and α'. The quantities $W_{ab}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')$, $W_{a\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')$, and $W_{\alpha\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')$ are the generalized transport kernels which have the following structure:

$$W_{ab}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') =$$

$$= \langle\hat{n}_a(\mathbf{r}_l)T(t,t')(1-\mathcal{P}(t'))m_b^{-1}\hat{\mathbf{p}}_b(\mathbf{r}_{l'})\rangle_q^{t'}, \qquad (2.30)$$

$$W_{a\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') =$$

$$= \langle\hat{n}_a(\mathbf{r}_l)T(t,t')(1-\mathcal{P}(t'))m_{\alpha'}^{-1}\hat{\mathbf{p}}_{\alpha'}(\mathbf{r}_{l'})\rangle_q^{t'}. \qquad (2.31)$$

$$W_{\alpha\alpha'}(\mathbf{r}_l,\mathbf{r}_{l'};t,t') =$$

$$= \langle\hat{n}_\alpha(\mathbf{r}_l)T(t,t')(1-\mathcal{P}(t'))m_{\alpha'}^{-1}\hat{\mathbf{p}}_{\alpha'}(\mathbf{r}_{l'})\rangle_q^{t'}. \qquad (2.32)$$

The generalized diffusion equations for ions and molecules (2.18) and (2.19) contain the contribution

made by the nonequilibrium electric fields created by ions and dipole molecules in each phase. These fields are generated in accordance with Maxwell's equations (2.20)–(2.23), as well as by the processes of ionic electroconductivity $\sigma_{ab}(\mathbf{r}_l,\mathbf{r}_{l'};t,t')$ and interdiffusion of ions and molecules. The generation of electric and magnetic fields in the phases is a consequence of the non-local, non-Markovian diffusion processes associated with the gradients of the nonequilibrium electrochemical potentials of ions and the nonequilibrium dipole-chemical potentials of molecules.

In the obtained system of transport equations (2.18)–(2.23) for the description of electromagnetically governed diffusion processes, one characteristic feature of electrolyte solutions is not taken into account. This feature is related to the orientational motions of solvent molecules, which are responsible for the rotational diffusion in and the viscosity of the solution. They can substantially influence the transport of ions and molecules in the surface regions "solution–membrane" (e.g., the ordering of dipole molecules can take place) and in the porous medium of the membrane.

2.2. Viscous model of electrolyte solution transport through membrane structures

While considering the viscous model of the reverse osmosis processes, the average values $\langle\hat{n}_k(\mathbf{r}_l)\rangle^t$ of the densities of ion ($k=a$) and molecule ($k=\alpha$) numbers, the corresponding momentum densities $\langle\hat{\mathbf{p}}_a(\mathbf{r})\rangle^t$ and $\langle\hat{\mathbf{p}}_\alpha(\mathbf{r})\rangle^t$, and the angular momentum $\langle\hat{\mathbf{s}}_\alpha(\mathbf{r})\rangle^t$ can be selected as the parameters of the reduced description. Here,

$$\hat{\mathbf{p}}_a(\mathbf{r}) = \sum_{j=1}^{N_a}\mathbf{p}_j\delta(\mathbf{r}-\mathbf{r}_j), \quad \hat{\mathbf{p}}_\alpha(\mathbf{r}) = \sum_{f=1}^{N_\alpha}\mathbf{p}_f\delta(\mathbf{r}-\mathbf{r}_f)$$

$$(2.33)$$

are the momentum densities of ions and molecules, respectively; and

$$\hat{\mathbf{s}}_\alpha(\mathbf{r}) = \sum_{f=1}^{N_\alpha}J_f\mathbf{w}_f\delta(\mathbf{r}-\mathbf{r}_f). \qquad (2.34)$$

is the density of angular momentum of molecules.

Provided that the parameters $\langle\hat{x}(\mathbf{r})\rangle^t = \{\langle\hat{n}_a(\mathbf{r})\rangle^t,$ $\langle\hat{n}_\alpha(\mathbf{r})\rangle^t, \langle\hat{\mathbf{p}}_a(\mathbf{r})\rangle^t, \langle\hat{\mathbf{p}}_\alpha(\mathbf{r})\rangle^t, \langle\hat{\mathbf{s}}_\alpha(\mathbf{r})\rangle^t\}$ of the reduced description of the electro-magnetohydrodynamic state

of the ion-molecular system "initial solution–membrane–filtrate" are given, the quasiequilibrium statistical operator has the following structure:

$$\rho_q(x^N; \Delta P'; t) = \exp\{-\Phi(t) - \sum_{l=1}^{3} \int_{V_l} d\mathbf{r}_l \beta(H - V_1 \Delta P' -$$

$$-\sum_a \mathbf{v}_a(\mathbf{r}_l; t)\hat{\mathbf{p}}_a(\mathbf{r}_l) - \sum_\alpha \mathbf{v}_\alpha(\mathbf{r}_l; t)\hat{\mathbf{p}}_\alpha(\mathbf{r}_l) -$$

$$-\sum_a \nu_a(\mathbf{r}_l; t)\hat{n}_a(\mathbf{r}_l) - \sum_\alpha \nu_\alpha(\mathbf{r}_l; t)\hat{n}_\alpha(\mathbf{r}_l) -$$

$$-\sum_\alpha \mathbf{w}_\alpha(\mathbf{r}_l; t)\hat{\mathbf{s}}_\alpha(\mathbf{r}))\}, \tag{2.35}$$

where

$$\Phi(t) = \ln \int d\Gamma_N \exp\{-\sum_{l=1}^{3} \int_{V_l} d\mathbf{r}_l \beta(H - V_1 \Delta P' -$$

$$-\sum_a \mathbf{v}_a(\mathbf{r}_l; t)\hat{\mathbf{p}}_a(\mathbf{r}_l) - \sum_\alpha \mathbf{v}_\alpha(\mathbf{r}_l; t)\hat{\mathbf{p}}_\alpha(\mathbf{r}_l) -$$

$$-\sum_a \nu_a(\mathbf{r}_l; t)\hat{n}_a(\mathbf{r}_l) - \sum_\alpha \nu_\alpha(\mathbf{r}_l; t)\hat{n}_\alpha(\mathbf{r}_l) -$$

$$-\sum_\alpha \mathbf{w}_\alpha(\mathbf{r}_l; t)\hat{\mathbf{s}}_\alpha(\mathbf{r}))\} \tag{2.36}$$

is the Massier–Planck functional, and $\mathbf{w}_\alpha(\mathbf{r}_l; t)$ is the average angular speed of molecules of kind α. The thermodynamic parameters $\nu_a(\mathbf{r}_l; t)$, $\nu_\alpha(\mathbf{r}_l; t)$, $\mathbf{v}_a(\mathbf{r}; t)$, $\mathbf{v}_\alpha(\mathbf{r}_l; t)$, and $\mathbf{w}_\alpha(\mathbf{r}; t)$ are determined from the self-consistency conditions

$$\langle \hat{n}_a(\mathbf{r})\rangle^t = \langle \hat{n}_a(\mathbf{r})\rangle_q^t, \langle \hat{\mathbf{p}}_a(\mathbf{r})\rangle^t = \langle \hat{\mathbf{p}}(\mathbf{r}_a)\rangle_q^t,$$

$$\langle \hat{n}_\alpha(\mathbf{r})\rangle^t = \langle \hat{n}_\alpha(\mathbf{r})\rangle_q^t, \langle \hat{\mathbf{p}}_\alpha(\mathbf{r})\rangle^t = \langle \hat{\mathbf{p}}(\mathbf{r}_\alpha)\rangle_q^t,$$

$$\langle \hat{\mathbf{s}}_\alpha(\mathbf{r})\rangle^t = \langle \hat{\mathbf{s}}_\alpha(\mathbf{r})\rangle_q^t.$$

By substituting expression (2.35) into expression (2.10) for the nonequilibrium statistical operator, we obtain

$$\rho(x^N; \Delta P'; t) = \rho_q(x^N; \Delta P'; t) -$$

$$-\sum_a \sum_{l=1}^{3} \int d\mathbf{r}'_l \int_{-\infty}^{t} e^{\varepsilon(t'-t)} T(t, t') I_p^a(\mathbf{r}'_l; t') \times$$

$$\times \beta \mathbf{v}_a(\mathbf{r}'_l; t'))\rho_q(x^N; t')dt' -$$

$$-\sum_\alpha \sum_{l=1}^{3} \int d\mathbf{r}'_l \int_{-\infty}^{t} e^{\varepsilon(t'-t)} T(t, t') I_p^\alpha(\mathbf{r}'_l; t') \times$$

$$\times \beta \mathbf{v}_\alpha(\mathbf{r}'_l; t'))\rho_q(x^N; t')dt' - \sum_{l=1}^{3} \sum_\alpha \int d\mathbf{r}'_l \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \times$$

$$\times T(t, t') I_s^\alpha(\mathbf{r}'_l; t')\mathbf{w}_\alpha(\mathbf{r}'_l; t')\beta \rho_q(x^N; t')dt', \tag{2.37}$$

where $I_p^a(\mathbf{r}'_l; t')$ and $I_p^\alpha(\mathbf{r}'_l; t')$ are the generalized momentum fluxes of particles of kinds a and α in the l-th phase, and $I_s^\alpha(\mathbf{r}'_l; t)$ is the generalized flux of angular momentum of molecules of kind α in the l-th phase. These generalized fluxes look like

$$I_p^a(\mathbf{r}'_l; t) = (1 - \mathcal{P}(t))iL_N\hat{\mathbf{p}}_a(\mathbf{r}_l),$$

$$I_p^\alpha(\mathbf{r}'_l; t) = (1 - \mathcal{P}(t))iL_N\hat{\mathbf{p}}_\alpha(\mathbf{r}_l),$$

$$I_s^\alpha(\mathbf{r}'_l; t) = (1 - \mathcal{P}(t))iL_N\hat{\mathbf{s}}_\alpha(\mathbf{r}_l). \tag{2.38}$$

The Mori projection operator acts on the dynamic variables as follows:

$$\mathcal{P}(t)\hat{A}(\mathbf{r}) = \langle \hat{A}\rangle_q^t + \sum_k \sum_l \int d\mathbf{r}_l \frac{\delta \langle \hat{A}(\mathbf{r})\rangle^t}{\delta \langle \hat{\mathbf{p}}_k(\mathbf{r}_l)\rangle^t} \times$$

$$\times \left(\hat{\mathbf{p}}_k(\mathbf{r}_l) - \langle \hat{\mathbf{p}}_k(\mathbf{r}_l)\rangle^t\right) +$$

$$+\sum_k \sum_l \int d\mathbf{r}_l \frac{\delta \langle \hat{A}(\mathbf{r})\rangle^t}{\delta \langle \hat{n}_k(\mathbf{r}_l)\rangle^t} \left(\hat{n}_k(\mathbf{r}_l) - \langle \hat{n}_k(\mathbf{r}_l)\rangle^t\right) +$$

$$+\sum_l \sum_\alpha \int d\mathbf{r}_l \frac{\delta \langle \hat{A}(\mathbf{r})\rangle^t}{\delta \langle \hat{\mathbf{s}}_\alpha(\mathbf{r}_l)\rangle^t} \left(\hat{\mathbf{s}}_\alpha(\mathbf{r}_l) - \langle \hat{\mathbf{s}}_\alpha(\mathbf{r}_l)\rangle^t\right) \tag{2.39}$$

and it has the following properties: $\mathcal{P}(t) \cdot \mathcal{P}(t) = \mathcal{P}(t)$, $\mathcal{P}(t)(1 - \mathcal{P}(t)) = 0$, and $\mathcal{P}(t) \cdot \hat{x}(\mathbf{r}) = \hat{x}(\mathbf{r})$, where $\hat{x}(\mathbf{r}) = \{\hat{\mathbf{p}}_k(\mathbf{r}), \hat{n}_k(\mathbf{r}), \hat{\mathbf{s}}_\alpha(\mathbf{r})\}$ and $k = (a, \alpha)$.

The nonequilibrium statistical operator (2.35) is used to obtain the generalized transport equations for the averaged quantities $\langle \hat{\mathbf{p}}_k(\mathbf{r})\rangle^t$, $\langle \hat{n}_k(\mathbf{r})\rangle^t$, and $\langle \hat{\mathbf{s}}_\alpha(\mathbf{r})\rangle^t$, which – in the matrix form – read

$$\frac{d}{dt}\langle \tilde{x}(\mathbf{r}_l)\rangle^t = \langle \dot{\tilde{x}}(\mathbf{r}_l)\rangle_q^t +$$

$$+\sum_{l'=1}^{3} \int d\mathbf{r}_{l'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)}\varphi(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \times$$

$$\times \langle \tilde{F}(\mathbf{r}_{l'}) \rangle^{t'} dt' = 0, \qquad (2.40)$$

where $\tilde{x}(\mathbf{r}_l)$ stands for the column vector and $\tilde{x}^{(+)}(\mathbf{r}_{l'})$ for the row vector, which are multiplied by the following scalar-product rule:

$$\tilde{x}(\mathbf{r}_l) = \mathrm{col}(\tilde{n}(\mathbf{r}_l), \tilde{\mathbf{p}}(\mathbf{r}_l), \tilde{s}(\mathbf{r}_l)),$$

$$\tilde{x}^{(+)}(\mathbf{r}_{l'}) = (\tilde{n}^{(+)}(\mathbf{r}_{l'}), \tilde{\mathbf{p}}^{(+)}(\mathbf{r}_{l'}), \tilde{s}^{(+)}(\mathbf{r}_{l'})), \qquad (2.41)$$

where $\tilde{n}(\mathbf{r}_l)$, $\tilde{\mathbf{p}}(\mathbf{r}_l)$, and $\tilde{s}(\mathbf{r}_l)$ are column vectors, and $\tilde{n}^{(+)}(\mathbf{r}_{l'})$, $\tilde{\mathbf{p}}^{(+)}(\mathbf{r}_{l'})$, and $\tilde{s}^{(+)}(\mathbf{r}_{l'})$ are row vectors. In the case of a three-component system composed of positively and negatively charged ions and molecules α, $\tilde{n}(\mathbf{r}_l) = \mathrm{col}(\hat{n}^{+}(\mathbf{r}_l), \hat{n}^{-}(\mathbf{r}_l), \hat{n}^{\alpha}(\mathbf{r}_l))$ and $\tilde{s}(\mathbf{r}_l) = \hat{\mathbf{s}}_{\alpha}(\mathbf{r}_l)$. If the number of ionic and molecular components in the electrolyte solution is more than three, this circumstance has to be taken into account in the quantities $\tilde{n}(\mathbf{r}_l)(\tilde{n}^{(+)}(\mathbf{r}_{l'}))$, $\tilde{\mathbf{p}}(\mathbf{r}_l)(\tilde{\mathbf{p}}^{(+)}(\mathbf{r}_{l'}))$, and $\tilde{s}(\mathbf{r}_l)$. $\tilde{F}(\mathbf{r}_{l'}; t') = \mathrm{col}(\beta \tilde{\nu}(\mathbf{r}; t'), \beta \tilde{\nu}(\mathbf{r}_l; t'), \beta \tilde{\mathbf{v}}(\mathbf{r}'_l; t'), \beta \tilde{\mathbf{w}}(\mathbf{r}'_l; t'))$ is the column vector. $\tilde{\varphi}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$ is the transport kernel matrix which describes dissipative processes of interdiffusion, ionic viscosity, and translational and rotational viscosities of electrolyte molecules in the course of reverse osmosis in the system "initial solution–membrane–filtrate" and has the following structure:

$$\tilde{\varphi}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') =$$

$$= \sum_{l''=1}^{3} \int d\mathbf{r}_{l''} \langle \tilde{I}(\mathbf{r}_l; t) T(t, t') \cdot \tilde{I}^{(+)}(\mathbf{r}_{l''}; t') \rangle_q^{t'} =$$

$$= \begin{bmatrix} \tilde{0} & \tilde{0} & \tilde{0} \\ \tilde{0} & \tilde{\varphi}_{I_p I_p} & \tilde{\varphi}_{I_p I_s} \\ \tilde{0} & \tilde{\varphi}_{I_s I_p} & \tilde{\varphi}_{I_s I_s} \end{bmatrix}_{(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')}, \qquad (2.42)$$

where $\tilde{I}(\mathbf{r}_l; t)$ is the column vector and $\tilde{I}^{(+)}(\mathbf{r}_{l'}; t')$ the row vector of the generalized fluxes:

$$\tilde{I}(\mathbf{r}_l; t) = col(\tilde{0}, \tilde{I}_p(\mathbf{r}_l; t), \tilde{I}_s(\mathbf{r}_l; t)),$$

$$\tilde{I}^{(+)}(\mathbf{r}_l; t') = (\tilde{0}^{(+)}, \tilde{I}_p(\mathbf{r}_l; t'), \tilde{I}_s^{(+)}(\mathbf{r}_l; t')). \qquad (2.43)$$

The structures of the column vectors $\tilde{I}_p(\mathbf{r}_l; t)$ and $\tilde{I}_s(\mathbf{r}_l; t)$ and the row vectors $\tilde{I}_p^{(+)}(\mathbf{r}_l; t')$ and $\tilde{I}_s^{(+)}(\mathbf{r}_l; t')$ depend on the number of ion and molecule sorts in the solution. In particular, $\tilde{\varphi}_{I_p I_p}$ is the matrix of transport kernels which determine the coefficients of translational viscosity of ions and molecules, and $\tilde{\varphi}_{I_s I_s}$ is the matrix of transport kernels which determine the coefficients of rotational viscosity of molecules.

Respectively, the transport kernels which are the elements of matrices $\tilde{\varphi}_{I_p I_s}$ and $\tilde{\varphi}_{I_s I_p}$ describe the dissipative correlations between rotational motions of molecules and translational motions of ions and molecules. The system of transport equations (2.40) is supplemented with the system of Maxwell's equations averaged with the help of the nonequilibrium statistical operator (2.35):

$$\nabla \cdot \langle \mathbf{B}(\mathbf{r}_l) \rangle^t = 0, \qquad (2.44)$$

$$\nabla \cdot \langle \mathbf{D}(\mathbf{r}_l) \rangle^t = \sum_a z_a e \langle \hat{n}_a(\mathbf{r}_l) \rangle_q^t + \sum_\alpha \mathbf{d}_\alpha \cdot \nabla \langle \hat{n}_\alpha(\mathbf{r}_l) \rangle_q^t -$$

$$- \sum_{ab\alpha} \sum_{l'=1}^{3} \int_{V_{l'}} d\mathbf{r}_{l'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \{ z_a e \nabla \cdot D_{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') +$$

$$+ \mathbf{d}_\alpha \cdot \nabla\nabla \cdot D_{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \} \cdot \beta \mathbf{v}_b(\mathbf{r}'_l; t') dt' -$$

$$- \sum_{a\alpha\alpha'} \sum_{l'=1}^{3} \int_{V_{l'}} d\mathbf{r}_{l'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \{ z_a e \nabla \cdot D_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') +$$

$$+ \mathbf{d}_\alpha \cdot \nabla\nabla \cdot D_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \} \cdot \beta \mathbf{v}_{\alpha'}(\mathbf{r}'_l; t') dt' +$$

$$+ \sum_{a\alpha\alpha'} \sum_{l'=1}^{3} \int_{V_{l'}} d\mathbf{r}_{l'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \{ z_a e \nabla \cdot M_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') +$$

$$+ \mathbf{d}_\alpha \cdot \nabla\nabla \cdot M_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \} \cdot \beta \mathbf{w}_{\alpha'}(\mathbf{r}'_l; t') dt', \qquad (2.45)$$

$$\nabla \times \langle \mathbf{E}(\mathbf{r}_l) \rangle^t = -\frac{\partial}{\partial t} \langle \mathbf{B}(\mathbf{r}_l) \rangle^t, \qquad (2.46)$$

$$\nabla \times \langle \mathbf{H}(\mathbf{r}_l) \rangle^t = \frac{\partial}{\partial t} \langle \mathbf{D}(\mathbf{r}_l) \rangle^t - \sum_{ab\alpha} \sum_{l'=1}^{3} \int_{V_{l'}} d\mathbf{r}_{l'} \times$$

$$\times \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \{ z_a e D_{pI_p}^{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') +$$

$$+ \mathbf{d}_\alpha \cdot \nabla D_{pI_p}^{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \} \beta \mathbf{v}_b(\mathbf{r}'_l; t') dt' -$$

$$- \sum_{a\alpha\alpha'} \sum_{l'=1}^{3} \int_{V_{l'}} d\mathbf{r}_{l'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \{ z_a e D_{pI_p}^{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') +$$

$$+ \mathbf{d}_\alpha \cdot \nabla D_{pI_p}^{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \} \beta \mathbf{v}_{\alpha'}(\mathbf{r}'_l; t') dt' +$$

$$+ \sum_{a\alpha\alpha'} \sum_{l'=1}^{3} \int_{V_{l'}} d\mathbf{r}_{l'} \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \{ z_a e M_{pI_s}^{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') +$$

$$+\mathbf{d}_\alpha \cdot \nabla M_{pI_s}^{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')\}\beta\mathbf{w}_{\alpha'}(\mathbf{r}_l'; t')dt', \qquad (2.47)$$

where

$$M_{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') =$$

$$= \langle(1 - \mathcal{P}(t))m_a^{-1}\hat{\mathbf{p}}_a(\mathbf{r}_l)T(t, t')(1 - \mathcal{P}(t'))\hat{\mathbf{s}}_\alpha(\mathbf{r}_{l'})\rangle_q^{t'},$$

$$M_{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') =$$

$$= \langle(1 - \mathcal{P}(t))m_\alpha^{-1}\hat{\mathbf{p}}_\alpha(\mathbf{r}_l)T(t, t')(1 - \mathcal{P}(t'))\hat{\mathbf{s}}_\alpha(\mathbf{r}_{l'})\rangle_q^{t'}$$

are the time correlation functions which describe the dissipative correlations between the densities of translational momenta of ions and molecules, on the one hand, and the rotational momenta of solution molecules, on the other hand. The generalized transport kernels $D_{pI_p}^{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$, $D_{pI_p}^{\alpha b}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$, $D_{pI_p}^{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$, and $D_{pI_p}^{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$ are the time cross-correlation functions which give a zero contribution in the spatially homogeneous case, in the limit $t \to \infty$. They describe the dissipative correlations between the momentum densities and the generalized tensors of viscous stresses (e.g., for ions, $I_p^a(\mathbf{r}_l'; t) = -\frac{\partial}{\partial \mathbf{r}_l'}\pi^a(\mathbf{r}_l'; t)$) for ions and solution molecules and have a similar structure, namely,

$$D_{pI_p}^{ab}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') =$$

$$= \langle(1 - \mathcal{P}(t))m_a^{-1}\hat{\mathbf{p}}_a(\mathbf{r}_l)T(t, t')(1 - \mathcal{P}(t'))iL_N\hat{\mathbf{p}}_b(\mathbf{r}_{l'})\rangle_q^{t'}.$$

The generalized transport kernels $M_{pI_s}^{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$ and $M_{pI_s}^{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$ are the time cross-correlation functions, which give a zero contribution in the spatially homogeneous case, in the limit $t \to \infty$. They have a structure that is similar to that of D_{pI_p}:

$$M_{pI_s}^{a\alpha'}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') =$$

$$= \langle(1 - \mathcal{P}(t))m_a^{-1}\hat{\mathbf{p}}_a(\mathbf{r}_l)T(t, t')(1 - \mathcal{P}(t'))iL_N\hat{\mathbf{s}}_{\alpha'}(\mathbf{r}_{l'})\rangle_q^{t'}$$

and describe the dissipative correlations between the momentum densities of ions and molecules, on the other hand, and the generalized rotational momentum of solvent molecules, on the other hand, $I_s^\alpha(\mathbf{r}_l'; t) = -\frac{\partial}{\partial \mathbf{r}_l'}\pi_s^\alpha(\mathbf{r}_l'; t)$.

3. Conclusions

The system of generalized transport equations for ions and molecules in the electrolyte solution has been obtained for the system "initial electrolyte solution–membrane–filtrate", which describes viscous processes in terms of the transport kernels (2.42) and electromagnetically governed diffusion processes in terms of the Maxwell's equations (2.44)–(2.47). As it was in the case of the diffusion model, the system of transport equations in the viscous model is not closed; the equations are strongly inhomogeneous and make allowance for memory effects. In both models, the most important effects associated with the ionic electroconductivity and electromagnetic fields in the system "initial electrolyte solution–membrane–filtrate" have been taken into account. A comparison of the models concerned demonstrates that the viscous model describes electromagnetic processes in more details with respect to the diffusion-viscous dissipative correlations between ionic and molecular fluxes through membrane structures. It is important to note that, in our approach, the dissipative (non-Markovian) contributions to the Maxwell's equations, which are connected with the time correlation functions of ionic and molecular fluxes in the three-phase system, are expressed explicitly. In this work, we have proposed a general approach to the description of the processes of membrane separation of electrolyte solutions, taking the own electromagnetic fields of particles into account. In the authors' opinion, such an approach is of independent physical interest. The consideration of specific examples will be carried out in our further works.

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УЗАГАЛЬНЕНІ РІВНЯННЯ ПРОЦЕСІВ ПЕРЕНОСУ ІОНІВ ТА МОЛЕКУЛ РОЗЧИНІВ ЕЛЕКТРОЛІТІВ КРІЗЬ МЕМБРАННІ СТРУКТУРИ. ВРАХУВАННЯ ЕЛЕКТРОМАГНІТНИХ ПРОЦЕСІВ

Є.М. Сов'як, І.Й. Куриляк, Ю.І. Черноморець, М.В. Токарчук

Р е з ю м е

Одержано узагальнені рівняння переносу іонів та молекул розчину електроліту крізь зворотноосмотичну мембрану, рушійною силою яких є градієнти концентрацій частинок, температури, різниця зовнішнього і осмотичного тисків та діелектричні властивості вихідного розчину, мембрани, фільтрату. Методом нерівноважного статистичного оператора Зубарєва отримано узагальнені рівняння переносу для іонів і молекул системи вихідний розчин електроліту–мембрана–фільтрат для дифузійної та в'язкої моделей. Враховано електромагнітні процеси переносу шляхом усереднення мікроскопічних рівнянь Максвелла для системи вихідний розчин електроліту–мембрана–фільтрат.