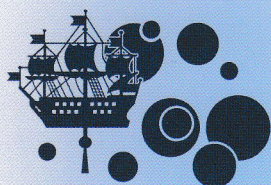




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MODELING ELECTROCONDUCTIVITY AND ELECTROOSMOTIC PERMEABILITY OF ION-EXCHANGE MEMBRANE

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Electroosmotic permeability of ion-exchange membranes is an important factor that significantly limits their use, for example, in fuel cells (FCs). Excessive water loss by such membranes leads to their overheating and possible destruction of the fuel cell itself. Therefore, for efficient operation of ion-exchange membranes in the FCs, it is necessary to know how their electroosmotic permeability will change when the moisture content and the background electrolyte concentration as well as the geometric and physicochemical characteristics of the ionite grains are varied. The existing theories for calculations of electroosmotic permeability do not fully answer the abovementioned questions. So, we decided to develop a closed cell model of an ion-exchange membrane, taking into account the transfer of water or another solvent in the hydrated/solvate ion shells. Basing on the thermodynamics of non-equilibrium processes (the Onsager approach), we have set up and solved here the boundary value problem (BVP) for the Stokes, Brinkman, Nernst-Planck-Poisson system of equations governing the flow of a binary non-symmetric electrolyte through a liquid cell in the center of which there is a porous spherical particle, having a certain constant density of a fixed space charge (exchange capacity). At the boundary of the liquid shell, we used Kuwabara's (absence of vorticity) most adequate for electrokinetic phenomena condition, and at the interface between the porous particle and the electrolyte solution, we used conditions for the continuity of the velocity and the total stress tensor. Utilizing the cell approach developed by Happel and Brenner, the results of the BVP solution were applied to calculate the electroosmotic permeability of a charged membrane as a function of the fraction of the solid conducting phase (or moisture content), geometric and physicochemical characteristics of an ion-exchange grain and concentration of electrolyte. The currently available formulas for calculating the electrical conductivity do not fully describe experimental results. In this connection, a cell approach was also applied to calculate the membrane specific electrical conductivity.

Let us choose the following thermodynamic forces as independent variables to be given during experimental observation: pressure gradient $\Phi_1 = \nabla p = (p_{20} - p_{10})/h$, electric potential gradient $\Phi_2 = \nabla \varphi = (\varphi_{20} - \varphi_{10})/h$ and concentration gradient $\Phi_3 = \nabla C = (C_{20} - C_{10})/h$ be arisen on a porous charged film (membrane) with the thickness h immersed in a measuring device which is filled by binary electrolyte solution. As dependent experimentally determined variables we can take densities of thermodynamic fluxes: I_1 – fluid flux; I_2 – charge flux (electric current); I_3 – diffusion flux. Then the phenomenological transport equations may be written in the following way:

$$I_i = -\sum_{k=1}^3 L_{ik} \Phi_k, \quad i = 1, 2, 3, \quad (1)$$

where kinetic coefficients L_{ik} will be determined using the cell model. Due to Onsager's theorem, the matrix of kinetic coefficients is symmetrical one, i.e. $L_{ik} = L_{ki}$. The main point is to calculate electroosmotic permeability $L_{12} = -I_2/\Phi_1|_{\Phi_2=0, \Phi_3=0}$ and specific electrical conductivity $L_{22} = -I_2/\Phi_2|_{\Phi_1=0, \Phi_3=0}$ of the membrane. The fluid motion in an outer region ($a < r < b$) is described by Stokes' equations ("creeping flow") with additional electro-massive force. The fluid motion in an inner region ($0 \leq r < a$) is governed by the modified Brinkman equations taken with volumetric electrical force. The process is considered to be steady-state, the Nernst representation is used for ion fluxes, and the electrical potential satisfies the Poisson equation. So, the problem reduces to solving

two boundary value problems for the unit cell by linearization with respect to small deviations of the required velocity fields, the electric potential, and the concentration of ions from their equilibrium values. Exact analytical expressions are obtained for the electroosmotic permeability and conductivity of the cation-exchange membrane with respect to arbitrary binary electrolyte solution. We applied developed theory to characterization of cation-exchange MF-4SC membrane, modified by halloysite nanotubes (HNT) functionalized with Pt nanoparticles, and immersed in electrolyte (HCl) solution. The quantitative characteristic of electroosmosis is the electroosmotic permeability (D_1), which is equal to the volume of liquid (I_1) transferred per unit area (S) per unit time (τ) at a current density (I_2) equal to unity $D_1 = I_1 / (SI_2\tau)$. According to the Onsager theory from (1) we have a simple relation $D_1 = L_{12} / L_{22}$. The electroosmotic permeability of the membrane under constant current was determined by the volumetric method in a two-chamber cell with polarizing silver chloride electrodes. The specific electrical conductivity of the membrane was calculated on the basis of the measurement of its active resistance. The results of comparison between theoretical (curves) and experimental (symbols) data are shown in Fig. 1 and 2. There is a good agreement between the cell model of ion-exchange membrane and experimental observations. Using fitting procedure we have found such physicochemical parameters of the hybrid nanocomposite MF-4SC+HNT+Pt as proton diffusivity $D_{m+} = 150 \mu\text{m}^2/\text{s}$ inside membrane matrix, coefficient of equilibrium distribution $\gamma_m = 0.335$ of the HCl molecules, specific hydrodynamic permeability of the cationite grains – $k_D = 25 \text{ \AA}^2$ and macroscopic porosity 10.2% which is in agreement with porosity 12% independently found by method of standard contact porosimetry. Membrane exchange capacity was equal to $\rho_v = 1.22 \text{ mole/dm}^3$. Obtained results are important in the study of ion-exchange membranes modified by inorganic nanotubes/nanoparticles, since in a number of practical importance cases there is an extreme dependence of the transport, mechanical, structural properties of hybrid membranes on the content of dopant. Therefore, a systemic study of the electroosmotic permeability of a membrane coupled with its specific electric conductivity fulfilled in our research will make it possible to apply the cell approach to the characterization of membrane materials, and hence to the possibility of their correct choice and modification.

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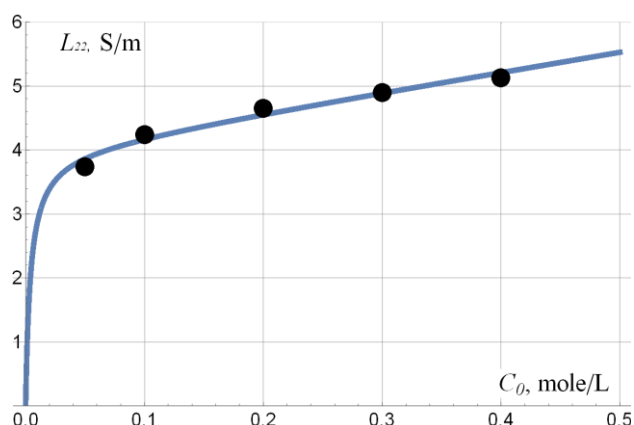


Figure 1. Dependence of electrical conductivity L_{22} of MF-4SC modified by HNT with Pt on HCl concentration C_0 .

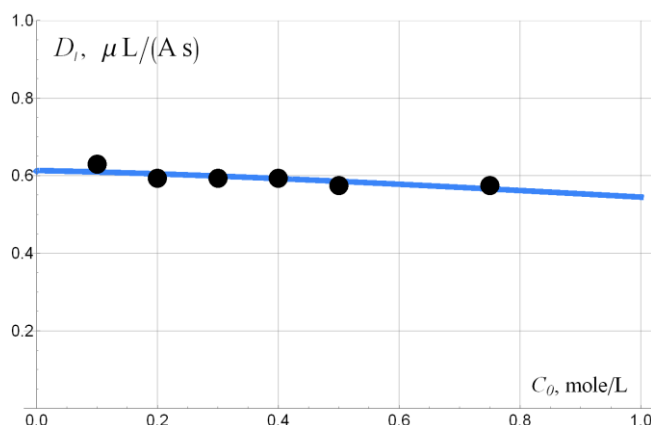


Figure 2. Dependence of electroosmotic permeability $D_1 = L_{12} / L_{22}$ of MF-4SC modified by HNT with Pt on HCl concentration C_0 .