Mathematical modelling of transport of single and double charged ions through layered ion exchange membranes

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Abstract. Monovalent selectivity of ion exchange membranes is important for such areas as hardness removal, stabilization of mining waters and fining of foods. The modern approach to the creation of monovalent selective ion exchange membranes is layer-by-layer adsorption of polyelectrolytes onto a membrane surface, which showed significant improvement in comparison with previously used approaches, most notably in comparison with the creation of a single thick layer of polyelectrolyte. Despite the practical importance, the mechanism of improvement in selectivity is unknown. Knowledge of the distribution of ions within the membrane and adjacent layers of solution would answer the question of the mechanism, but such information is unobtainable through the experiment. Hence we develop the 1D mathematical model based on Nernst-Planck-Poisson equations to describe the fluxes and the concentrations of single and double charged ions, as well as potential drop / current density through the ion exchange membrane. In this paper we formulate the problem and list experimentally determined parameters. Results of calculations will be compared with experimentally recorded I-V and V-t curves.

1. Introduction
Electrodialysis with ion-exchange membranes is used in areas requiring fractioning of ions by their charge number. These areas include, among others, stabilization of mining waters, where CaSO₄ containing wastewater should be divided into Ca²⁺ containing stream and SO₄²⁻ containing stream, hardness removal, in which Ca²⁺ and Mg²⁺ should be eliminated, deashing of milk and other dairy products, in which the main reduction of conductivity is achieved through NaCl removal while Ca²⁺ should be preserved for health benefits. The modern approach to the creation of monovalent selective membranes is layer-by-layer adsorption of polyelectrolytes on the membrane surface. In contrast with the method known from the late 20th century, in which the membrane surface is coated with a single, relatively thick (tens of microns, while the membrane thickness usually is 130-550 microns) layer of polyelectrolyte functional groups which are charged oppositely to the groups in the membrane bulk [1], in the novel approach relatively thin (tens of nanometers to single microns) layers of polyelectrolytes with an alternating sign of the charge of functional groups are applied [2]. The results achieved when using these two approaches are very different: the classic method gives an insignificant increase in selectivity (in reported cases not exceeding a twofold increase), growth of electrical resistance and occurrence of side reactions such as generation of H⁺andOH⁻ ions, and the novel method results in K⁺ / Mg²⁺ selectivity exceeding 1000 at preserved electrical resistance. Such
good properties are somewhat unexpected, since for a classic bilayer (asymmetric bipolar), the membrane bipolar boundary is the place of the fastest desalination and location of the generation of H+ and OH- ions [3], and an increasing number of such boundaries should result in growing electric resistance and electrochemical reaction current losses. In our previous studies we initiated the creation of the monovalent selective membrane for electrodialysis basing on the cheap MK-40 membrane (Shchekino Azot, Russia) modified with polyethyleneimine and reported that the application of a single thin layer at least does not worsen its electrochemical properties for a separation process [4], but discovered that the generation of H+ and OH- proceeds, albeit with a low intensity, occurs even for such membrane.

Despite the practical importance of the creation of monovalent selective membranes, simulation of ion transport through such systems presents difficulties due to very large gradients of the potential and concentration at the boundaries. The mechanism of boost of the monovalent selectivity due to the application of polyelectrolyte layers has not been pinpointed yet, which is repeated in studies dedicated to this topic [5]. Published articles give several directions of interest: when modeling the electrochemical impedance spectra of a membrane with a single coating layer in a mixed salt solution, Femmer et al. concluded that the spectra are mostly affected by the charge and by the thickness of the modifying layer due to a change in the absolute transport number of the monovalent ion, while Cheng et al. showed that the monovalent selectivity of multilayered membranes depends on the surface charge of the outermost layer [6]. The reason why the application of multiple thin layers is preferable than the application of a single thick layer is still unclear.

To continue our study, to generalize the obtained results and to explain the differences between the samples produced using different approaches, it is necessary to understand the mechanism of the increase in the monovalent selectivity due to the application of relatively thin layers in comparison with a single thick layer. To this end we will describe the transport of ions in the system using Nernst-Planck-Poisson equations and will calculate the I-V and V-t curves that will be matched against the experimental curves. In this paper we give the described system and model equations.

2. Materials and methods
The modeled system includes the layered ion exchange membrane and two adjacent diffusion boundary layers of the solution. The supporting ion exchange membrane and the layers of polyelectrolytes applied at its surface differ from the external solution in the following parameters. The first of them is the spatial density of fixed charges $C_X$. It should be noted that the model allows introducing $C_X$ as a complicated continuous function which takes into account the distribution of fixed groups in all layers of the composite membrane.
For this function we will use the surface charge densities experimentally determined from the zeta potentials calculated from streaming potential data after the application of each layer of polyelectrolyte. The second and third sets of the parameters are coefficients of diffusion and of activity of ions. Both types of coefficients are relatively constant for each type of the membrane and we will retrieve them from the published data that uses the microheterogeneous model to analyze the diffusion permeability, electrolyte sorption and electrical conductivity of the MK-40 membrane. The activity coefficient will also be introduced as a continuous function depending on the coordinate: within the external solution (at $x<0$ and $x>d$) it is assumed to be equal to 1, since the diluted, about 0.001 M, solutions are used for modeling, and within the membrane it differs from 1 and depends on the Nikolsky constant which we will retrieve from previous experimental reports of our laboratory. Finally, the fourth parameter is the electric permittivity, which in this case depends on the concentration of fixed groups and will also be retrieved from corresponding model calculations.

The transport (diffusion and electromigration) of four ionic species, two single charged (e.g. Na$^+$, Na$^+$ and Cl$^-$) and two double charged (e.g. Ca$^{2+}$ for cation exchange membrane and SO$_4^{2-}$ for anion exchange membrane), is studied. The ionic concentrations, electric potential and space charge density are described by Nernst-Planck-Poisson equations and these values change continuously along the $x$ axis, including points where $x = 0$ and $x = d$ that correspond to boundaries between the composite membrane and the solution.

\[ j_i = -D_i \left( 1 + \frac{d \ln \gamma_i}{d \ln c_i} \right) \frac{dc_i}{dx} + z_i c_i \frac{F}{RT} \frac{d \varphi}{dx} \]

\[ \varepsilon \varepsilon_0 \frac{d^2 \varphi}{dx^2} = -F \left( \sum_i z_i c_i + z_x C_x \right) \]
\[ \frac{\partial c_i}{\partial x} = - \text{div} j_i \]

where \( y_i, c_i, D_i, z_i \) and \( j_i \) are activity coefficient, molar concentration, diffusion coefficient, charge number and flux of ionic species “\( i \)”, respectively; \( z_X \) and \( C_X \) are charge number and concentration of fixed ion in the membrane layer “\( X \)”, respectively; \( \varepsilon_0 \) is electric permittivity; \( \varphi \) is electric potential; \( F \), \( R \) and \( T \) are Faraday constant, gas constant and absolute temperature, respectively.

It is assumed that the equations ruling the ion transport do not change when crossing the membrane/solution boundary. When describing the transport within the membrane it is assumed that the ions pass only within the charged solution of pores in which the electric double layers at the pore walls overlap and the electroneutral solution is absent. Hence we take into account that properties of the solution change at \( x = 0 \) and \( x = d \) since the fixed space charge, \( C_X \), coefficients of diffusion and activity of ions and electric permittivity have different values in external solution and in pore solution.

In this problem we do not take into account the electroosmotic transport of water molecules, the generation of H\(^+\) and OH\(^-\) ions, the presence of gradients of pressure and/or temperature. The flow of the solution along the desalination path is not explicitly taken into account, but the convection in the core of the solution affects through the concentration of ions at the external boundaries of diffusion boundary layers being assumed to be constant and equal to the concentration of the feeding solution and not depending on the current density or time. There is no convective transport through the membrane, and we use the assumption of no convective flow through the modifying layers as well.

In the system two main current modes can be simulated: potentiostatic one and galvanostatic one. For potentiostatic mode we set the potential drop between the external boundaries of diffusion boundary layers and the current density is calculated through the ionic fluxes. For galvanostatic mode we place the boundary condition of the second kind at the potential drop in the entire system at the constant current density. Both modes are used in experimental studies of membrane systems and are necessary for precise interpretation of data concerning the monovalent selectivity.

For calculations we use COMSOL multiphysics simulation software.

3. Results and discussion

The stationary and nonstationary solutions will be obtained for the studied system. The dependence of the potential drop over the system on the scanning current density, obtained for the stationary solution, will be matched against the experimental I-V curve, and the dependences of the potential drop over the system on the time obtained for the nonstationary solution will be matched against the experimental V-t curves. The calculated fluxes will be matched against the experimental fluxes found during electrodialysis desalination of the NaCl+CaCl\(_2\) mixed solution. These comparisons will be used as a measure of adequacy of the model.

Further analysis will be performed as follows.

The modeling of the generation of H\(^+\) and OH\(^-\) ions is very challenging and neither our model nor the model described in [5] take into account this chemical reaction. While article [5] does not venture into the evaluation of the intensity of this process or its effect on monovalent selectivity, we will attempt to evaluate its role through comparison with experimental data. The rate of this reaction is determined when reading the pH difference between the inlet and the outlet of the flow-through electrodialysis cell, and the role of the reaction will be determined when comparing the experimental I-V and V-t curves with theoretical ones. If the calculated potentials in theoretical I-V and V-t curves would be much higher than the experimental ones at the same current densities, then the main role in ion transport is played by the appearance of additional charge carriers – generation of H\(^+\) and OH\(^-\) ions which is not taken into account by the model.

The origin of the effect of monovalent selectivity increasing with a number of applied layers will be determined when comparing the calculated distributions of electrolyte concentrations and of potential drops. If the large deionized zones will appear very quickly around the boundaries between the oppositely charged layers of the composite membrane, then the monovalent selectivity is mostly
affected by desalination within the membrane. If high potential drops and large space charge regions will be found within the membranes, then the monovalent selectivity is affected by the potential barriers for transport of double charged ions as coions through the polyelectrolyte layers.

In both these cases the calculation of the distribution of ions within the membrane will allow testing the hypothesis that the monovalent selectivity is boosted not due to repulsion of double charged ions from the external surface of the membrane, but due to bipolar boundaries between the modifying layers acting as “bottlenecks” for transport of charged species, and the effect of the increased number of the layers is in fact the effect of the increased number of bipolar boundaries. Here our study would differ from the recently published 2D model of transport of the NaCl+CaCl2 mixed solution through a cation exchange membrane coated with a single positively charged polyelectrolyte layer [7]: we plan on focusing on the presence of multiple bipolar boundaries while the cited article considers only one such boundary but has new knowledge regarding the effect of swelling of the coating layer or its defects on the overall monovalent selectivity.

More detailed analysis of the ionic distribution would open the ways for further improvement of the membrane modification. In the case of the desalination or the space charge determining the monovalent selectivity, the polyelectrolytes with higher spatial density of fixed groups become a more preferable form membrane modification since it would result in more efficient exclusion of coions and hence faster desalination, while in the case of space charge densities determining the selectivity, the focus should be placed on the development of roughness of the boundaries between the layers that will allow for higher space charges.

4. Conclusion
The mathematical model is formulated basing on Nernst-Planck-Poisson equations that describes the transport of single and double charged ions through the ion exchange membrane coated with polyelectrolytes with an alternating sign of the charge of fixed groups and two adjacent diffusion boundary layers of the solution. Further studies will be aimed at generation of stationary and nonstationary solutions of the problem and comparison with experimental I-V, V-t curves and electrodialysis desalination of the mixed solution. It is expected that the results of the calculation of distribution of the concentration of ions will allow pinpointing the mechanism of the increase in monovalent selectivity due to the application of a large number of polyelectrolyte layers with an alternating sign of charge of fixed groups in comparison with monovalent selectivity achieved when the single thick layer of polyelectrolyte is applied.

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