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Space charge effect on competitive ion transport through ion-exchange membranes

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Abstract

A mathematical model of the competitive electro-transport of two counter-ions through an ion exchange membrane based on the Nernst-Planck and Poisson equations is developed. A three-layer system is considered: the membrane and two adjacent diffusion layers. Concentration profiles in the three layers, effective transport numbers as functions of the current and current-voltage characteristics are calculated. Deviation from the local electroneutrality in space charge region near the depleted solution/membrane interface is taken into account. It is shown that the space charge region grows with the voltage applied. However the fluxes of the competitive counter-ions at over-limiting currents are determined by their transfer through the electroneutral part of the depleted diffusion layer.

Keywords: Ion-exchange membranes; Concentration polarization; Competitive transport; Space charge region; Mathematical modeling

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1. Introduction

Separation of two ions of the same sign of charge by electrodialysis (ED) with ion-exchange membranes (IEMs) finds many applications in water treatment, hydrometallurgy and others [1]. The ED separation of strong electrolytes in "soft" current modes when the current density *i* does not exceed its "limiting" value i_{lim} is studied in a

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number of papers experimentally as well as theoretically [2–5]. In particular, it was established that the permselectivity at small currents, $i << i_{\lim}$, is essentially determined by the membrane properties, while at high currents, $i \approx i_{\lim}$, this quantity is determined by the transport numbers of competitive ions in the bulk of the depleted solution [4,5]. Application of intensive current modes, when i is above $i_{\lim}$, permits increasing the electrodialysis process rate. It was found [6,7] that the ion transport in this case is coupled with several secondary phenomena caused by the concentration polarization. Firstly, a space charge macroscopic region arises at the membrane/depleted solution interface. Secondly, the interaction of the space charge with the current creates a space electric force acting on the solution volume that gives rise to macroconvective solution flow (electroconvection). Another space force may be caused by the gradient of the solution density due to non-uniform distribution of the concentration and/or temperature (gravitational convection). Thirdly, water "splitting" produces hydrogen and hydroxyl ions, which contribute to the current transfer and interact with the salt ions.

The subject of this theoretical study is the effect of the space charge on the specific permselectivity of ion-exchange membranes.

2. Mathematical problem formulation

The mathematical model presented in this paper is a direct generalization of two other models developed earlier. The first one [4,5] treats the competitive transport at $i \le i_{\lim}$ under the electroneutrality assumption in all three layers. The second one, developed firstly by Rubinstein and Shtilman [8] and later by a number of authors, and, in particular, in our papers [9,10], studies a binary electrolyte transport through an IEM at $i \ge i_{\lim}$ with taking into account deviation from the electroneutrality condition.

A three-layer system is considered: a membrane (for instance, a cation-exchange one) with two adjoining diffusion layers. Let m denote the number of a layer, d the thickness of the membrane and δ that of the diffusion layers. Then in the first depleted diffusion layer the normal coordinate x varies from 0 to δ ($m = 1$), in the membrane $\delta < x < \delta + d, m = 2$, and in the second enriched diffusion layer $\delta + d \le x \le d + 2\delta, m = 3$. Steady-state transport of the ions of two strong electrolytes with the same co-ion (a ternary electrolyte of the $CaCl_2 + NaCl$ type) is described by using the Nernst-Planck equation written in the all three layers and the Poisson equation written only in the first diffusion layer. The electroneutrality condition is supposed valid in the membrane and enriched diffusion layer. Thus we have:

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

$i = 1, 2, 3, m=1, 2, 3$

$$\sum_{i=1}^{3} z_i c_i = -\frac{\tilde{\varepsilon}}{F}\frac{d^2\varphi}{dx^2} \qquad m = 1 \tag{2}$$

$$\sum_{i=1}^{3} z_i c_i = Q \qquad m = 2 \tag{3a}$$

$$\sum_{i=1}^{3} z_i c_i = 0 \qquad m = 3 \tag{3b}$$

where $i = 1$ and 2 for counter-ions and $i = 3$ for the co-ion; j_i, c_i, z_i and D_i are the flux density, the concentration, the charge number and the diffusion coefficient of ion i; φ is the electric potential; $\tilde{\varepsilon}$ is the dielectric permeability of solution; Q is the membrane ion exchange capacity; F, R and T take their usual meanings.

A direct current of density i passing through the system is expressed by the ionic fluxes:

$$\sum_{i=1}^{3} z_i j_i = \frac{i}{F} \tag{4}$$

At the interface between the depleted diffusion layer and the membrane ($x = \delta$) the concentrations c_i and the electric potential φ are assumed to be

given parameters as in the case of binary electrolyte system problem with disturbed electroneutrality [8,9]:
$x = \delta$:

$$c_i \big|_{m=1} = c_i \big|_{m=2} = c_i^m\,,\ \varphi \big|_{m=1} = \varphi \big|_{m=2} = \varphi^m \qquad \text{(5a,b)}$$

$i = 1, 2, 3$

The quantities c_i^m and φ^m are related to the solution, more precisely to the inner boundary of the diffuse part of the double electric layer. As the membrane is assumed electroneutral, these quantities are linked to the corresponding terms ($\bar{c}_i^s$ and $\bar{\varphi}^s$) in the membrane boundary surface layer by the Donnan quasi-equilibrium relations:

$$x = \delta\text{:}\ \frac{\left(\bar{c}_1^s\right)^{1/z_1}}{\left(\bar{c}_j^s\right)^{1/z_j}} \Big|_{m=2} = k_{1j} \frac{\left(c_1^m\right)^{1/z_1}}{\left(c_j^m\right)^{1/z_j}} \Big|_{m=1},\ j = 1, 2 \qquad \text{(6a)}$$

$$\Delta\varphi_D^I = -\frac{RT}{z_1 F} \ln k_{12} \left(\frac{\bar{c}_1^s}{c_1^s} \right) \qquad \text{(6b)}$$

At the other membrane boundary with the enriched diffusion layer where the electroneutrality condition is assumed, the interface concentrations and potentials are linked by Donnan equations as usually accepted [7]:

$x = d + \delta$:

$$\frac{\left(\bar{c}_1^s\right)^{1/z_1}}{\left(\bar{c}_j^s\right)^{1/z_j}} \Big|_{m=2} = k_{1j} \frac{\left(c_1^s\right)^{1/z_1}}{\left(c_j^s\right)^{1/z_j}} \Big|_{m=3}\ ,\quad j = 2, 3 \qquad \text{(7a)}$$

$$\Delta\varphi_D^{II} = \frac{RT}{z_1 F} \ln k_{12} \left(\frac{\bar{c}_1^s}{c_1^s} \right) \qquad \text{(7b)}$$

where subscript *s* denotes that the quantity is taken at the interface in the electroneutral membrane ($m = 2$) or solution ($m = 3$) phases, k_{1j} is the ion exchange coefficient.

At the outer boundaries of the system the concentrations are known, the electric potential is zero at $x = 0$:

$$c_i(0) = c_i^I,\quad c_i(d + 2\delta) = c_i^{II},\quad i = 1, 2, 3 \qquad \text{(8a)}$$

$$\varphi(0) = 0 \qquad \text{(8b)}$$

In the formulated three-layer boundary value problem the electric current density and the concentrations in the bulk of the both solutions as well as the diffusion coefficients and ion exchange constants are supposed known constant parameters. The fluxes j_i constant throughout the system, the concentrations and the potential being functions of the coordinate are to be found.

3. Method of solution

The solution of the problem was found by applying two methods: numerically by the "parallel shouting" method [11], and by an approximation method using the condition of quasi-uniform charge density distribution (QCD) [10]. In a sense, the latter is intermediary between the electroneutrality condition and the Poisson equation; if the current is lower than its limiting value, the application of the QCD condition is equivalent to the electroneutrality one.

To find the distribution of the dimensionless electric field $E = -\dfrac{F\delta}{RT}\dfrac{d\varphi}{dx}$ as a function of the dimensionless coordinate $X = x/\delta$ in the depleted diffusion layer by using the QCD condition, the following Cauchy problem has to be solved [9]:

$$\frac{\mathrm{d}E}{\mathrm{d}X} = \frac{E^2}{G_1} \left[-\frac{\varepsilon}{2} q_3 E^3 + q_3 (G_0 X + \alpha) E - (q_1 G_1 - G_2) \right] \qquad (9)$$

$$E(1) = \frac{\sqrt{2[S_0 + G_0 - \alpha]}}{\sqrt{\varepsilon}}$$

where

$$\varepsilon = \frac{\tilde{\varepsilon}RT}{|z_3|c_3^I F^2 \delta^2},\ q_1 = \sum_{i=1}^{3} z_i,\ q_3 = \prod_{i=1}^{3} z_i,$$

$$G_k = \frac{\delta}{|z_3|c_3^I} \sum_{i=1}^{3} z_i^k \frac{j_i}{D_i},\ \alpha = \sum_{i=1}^{3} \frac{c_i^I}{|z_3|c_3^I},$$

$$S_0 = \sum_{i=1}^{3} \frac{c_i^m}{|z_3|c_3^I}$$

In Eq. (9) the values j_i of fluxes are taken as arbitrary constants to be determined later.

After having found the field, the concentrations $c_i(X)$ are easily calculated from the Nernst-Planck Eq. (1). In the second diffusion layer and the membrane the integration of Eqs. (1–4) is made with the same fluxes j_i as described in [4]. The values j_i are considered as true when the boundary conditions (6) and (7) are satisfied. In practice, the equations are integrated with an arbitrary j_i in the enriched diffusion layer from the right to left boundaries, then Eqs. (7) are used to pass through the interface II and the integration is continued till the interface I where the discrepancy is calculated with Eqs. (6).

To simplify the solution and analysis of the problem, the co-ion flux is assumed negligible ($j_3 = 0$); the influence of this transport on the competition between two counter-ions is not important in dilute solutions [4,5].

4. Concentration profiles

The behaviour of the system is quite different at "under-limiting" ($i < i_{\lim}$) and "over-limiting" ($i \geq i_{\lim}$) currents, where the limiting current is

$$i_{\lim} = \frac{F}{\delta}\left[\sum_{i=1}^{2} D_i\, z_i c_i^I \left(1 + \frac{z_i}{|z_3|}\right)\right] \qquad (10)$$

c_i^I is the concentration of ion i in the bulk of the depleted solution.

At $i < i_{\lim}$ the behavior of the system does not differ from that described earlier under the electroneutrality assumption in all three layers [4].

The solution found in this paper shows that at $i \geq i_{\lim}$ the structure of the depleted diffusion layer becomes complicated. As in the case of binary electrolyte [9], it is possible to distinguish four zones. The first $[0, X_1]$ is an electroneutral zone, the third $[X_2, X_3]$ is a zone with predominant electromigration mechanism of ion transfer where the electroneutrality does not hold, the fourth $[X_3, 1]$ is a quasi-equilibrium part of the solution double electric layer, and the second $[X_1, X_2]$ is an intermediary zone where the space charge density has a maximum. The second, third and fourth zones form a space charge region in the depleted solution.

Fig. 1 shows concentration profiles in the system. In the electroneutral zone of the depleted diffusion layer the profiles for counter-ions and co-ions are linear. In the electro-migration zone the concentration of the co-ion is negligible, while that of the counter-ions decreases slowly and pass

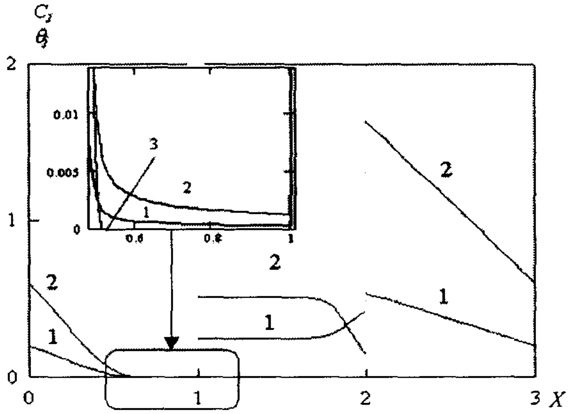

Fig. 1. Distribution of dimensionless molar concentrations in the diffusion layers $\left(C_j = c_j / |z_3| c_3^I\right)$ and in the membrane $\left(\theta_j = \bar{c}_j / Q\right)$ for Ca^{2+} (1) and Na^{2+} (2) at current density $i = 2i_{\lim}$. The model parameters are characteristic for Russian MK-40 cation-exchange membranes in dilute NaCl + CaCl$_2$ solutions ($z_1 = 2, z_2 = 1, z_3 = -1$): the relative membrane resistance $r = \frac{d|z_3|c_3^I}{\delta\, Q}\left(\frac{D_1}{\bar{D}_1} z_1 C_1^I + \frac{D_2}{\bar{D}_2} z_2 C_2^I\right)$ = 5; the small parameter in the dimensionless Poisson equation $\varepsilon = \tilde{\varepsilon}RT / \left(|z_3| c_3^I F^2 \delta^2\right) = 10^{-6}$; D_2/D_1=1.68; D_3/D_1 = 2.55; $\bar{D}_2 / \bar{D}_1 = 3.2$. The concentration of Cl$^-$ ions in the membrane is assumed zero: $k_{13} = 0$

through a minimum at $X = X_3 = 1 - \lambda$ where λ is the thickness of the quasi-equilibrium zone of the space charge region. In the latter zone the concentration and potential gradients are so great that the term of flux in the Nernst-Planck equation becomes negligible compared with the two other terms. As a result, the Donnan relation links the counter-ion concentrations and potential at two boundaries of this zone.

The shape of concentration profiles in the membrane and the enriched diffusion layer do not differ principally from that found earlier in the electroneutral problem [4,7].

At over-limiting currents the main part of the potential difference (pd) across the membrane system falls on the depleted diffusion layer; in diluted (10^{-3}–10^{-2} M) solutions it is about 80% of the total pd. In its turn, the space charge region gives the most essential contribution to the pd over the depleted diffusion layer. The shape of the current-voltage curves is similar to that obtained in the case of binary electrolyte [9].

5. Specific permselectivity

If the concentration profiles in the first electroneutral zone are continued till the intersection with the X-axis at $X = X_1$ where $c_i(X) = 0$, $i = 1,2,3$, the obtained picture is just the same as when consider the problem [4] with electroneutrality in all the layers. The difference is that the electroneutral diffusion layer thickness is now $\delta' = X_1\delta$ instead of δ in the electroneutral problem [4]. Thus, all the relations obtained earlier [4] for the ion fluxes at $i = i_{\lim}$ can be applied for $i > i_{\lim}$ in this problem, only δ' should be substituted for δ. In particular, an important conclusion, true also in the case of electroneutral problem, is that the specific permselectivity at currents equal or higher than the limiting current $i_{\lim}$ does not depend on properties of the membrane and the enriched diffusion layer, but is determined by the transport numbers of the counter-ions in the diluted solution bulk. The following equation is obtained for the effective transport numbers of the counter-ions T_i $(i = 1, 2)$ through the membrane:

$$\left(\frac{T_1}{T_2}\right)_{i \geq i\lim} = \frac{t_1^I}{t_2^I}\left(\frac{z_1 + z_2|z_3|}{z_2 + z_1|z_3|}\right), \quad T_1 + T_2 = 1 \qquad (11)$$

where $t_i^I = z_i^2 D_i c_i^I / \sum_{j=1}^{3} z_j^2 D_j c_j^I$ is the (electro-migration) transport number of ion i in the bulk of the diluted solution; T_i is defined as $T_i = \frac{z_i j_i F}{i}$. As Fig. 2 shows, T_i varies with the current from a value approximately equal to the (electro-migration) transport number of ion i in the membrane at $i = 0$, to a value determined by Eq. (1) at $i \leq i_{\lim}$.

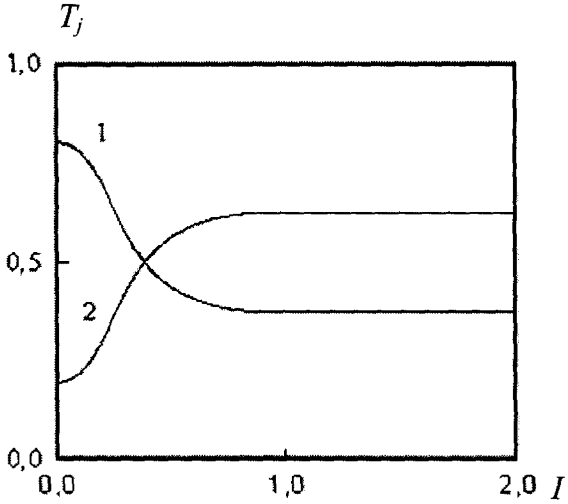

Fig. 2. Effective transport numbers (T_j) of Ca^{2+} (1) and Na^{2+} (2) through a three-layer membrane system as functions of the ratio $I = i/i_{\lim}$. The model parameters used are the same as in Fig. 1.

6. Conclusions

The problem studied may be considered as a generalization of two previously developed problems: the transport of binary electrolyte through a diffusion layer with disturbed electroneutrality adjacent to an ion-exchange membrane, and the competitive transfer of two counter-ions through a three-layer membrane system where the electroneutrality is hold in all the three layers.

The structure of the depleted diffusion layer is similar to that in the case of binary electrolyte: four zones can be distinguished, one of which being electroneutral and three other forming a space charge region.

At $i < i_{\text{lim}}$ the membrane behavior does not differ from that of three-layer electroneutral membrane system. At $i \geq i_{\text{lim}}$ the fluxes are governed exclusively by the ion transfer through the electroneutral zone of the depleted diffusion layer. Hence, the ratio of the counter-ions effective transport numbers through the membrane (T_1/T_2) is proportional to that of the (electro-migration) transport numbers in the bulk of the depleted diffusion layer (t_1^I/t_2^I); T_i does not depend on the membrane and space charge region properties.

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