Modelling of substance interactions in electrochemical membrane processes by basis of the friction theory

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Abstract. An improved mathematical model for calculating the transfer of substances in electrochemical membrane processes based on the Spiegler friction model is developed and presented. This model differs from those presented in the literature in that it takes into account the combined effect of pressure and electric field on the transfer of particles of the solute and solvent and allows calculating the friction coefficients of the interaction of anions, cations, solvent and membrane pore walls among themselves. Calculated friction coefficients can be used in the theoretical calculations and the prediction of change over time of the kinetic parameters of baromembrane, electromembrane and electrobaromembrane separation processes of industrial solutions in various industries.

1. Introduction

Nowadays there are various mathematical models describing the mechanism of mass transfer through membranes [1-5], but they all have their limitations and assumptions. In addition, some models may not always fully reflect the physics of electrobaromembrane processes [6-10].

In this paper an approach based on the friction model or in other words the internal friction model is considered to describe the transport through porous membranes [11]. However, our approach is used for electronaromembrane method as opposed to a separate application for baromembrane and electromembrane processes in the literature [10, 12-16].

The friction model is based on the analogy between the motion of particles (ions, molecules) in a continuous medium and the motion of bodies in a viscous liquid and was first used for membranes by Spiegler [17, 18]. His approaches were further developed by others [19-23]. The theory on which the friction model is based is formally equivalent to nonequilibrium thermodynamics with respect to the resulting transport equations.

The advantages of the friction model include a weaker dependence of the friction kinetic coefficients on the electrolyte concentration, their clear physical meaning and independence from the selected reference system.

According to the friction model [12, 13, 17, 18], all components of the system move relative to each other under the influence of some external forces $F_i$ and experience mutual friction. As a result, the formation of internal frictional forces $F_{ij}$ takes place in the system:
where \( F_{ij} \) is the frictional force between particles \( i \) and \( j \) in a volume unit, \( N \cdot m^{-3} \); \( \bar{c}_i \) is the concentration of particles \( i \) in one volume unit of the system, \( \text{mol} \cdot m^{-3} \); \( f_{ij} \) is the friction coefficient, \( N \cdot s \cdot \text{mol}^{-1} \cdot m^{-1} \); \( v_i \) and \( v_j \) are the absolute velocities of particles \( i \) and \( j \), \( m/s \).

The second aspect of the friction model theory is that the particles always move at a stationary constant speed and in the system there is a balance of the external force applied from the outside and the friction forces that arise due to the frictional interaction of particles \( i \) with all other particles in the volume unit of the system:

\[
\bar{c}_i F_i + \sum F_{ij} = 0, \tag{2}
\]

where \( F_i \) is the driving force (electrochemical potential) to 1 mole of particles \( i \), \( N \cdot \text{mol}^{-1} \).

In the considered case of separation, unlike the one presented in [24], the interaction occurs between anions, cations of the dissolved substance, solvent particles and walls of membrane pores. For designating the types of frictional forces (figure 1) between all particles we use subscripts \(+, -, \omega, m\) for cations, anions, solvent (water) and membrane, respectively.

![Figure 1. Schematic representation of all frictional forces within the membrane pores.](image)

### 2. Calculations

Before describing the mathematical model, we make the following assumptions:

- each particle (of solvent or dissolved substance) experiences the action of the same external forces, and therefore the volume unit should not include elements of different phases.
- the rate of electrode reactions is much higher than the rate of mass transfer;
- fluid flow is stationary;
- regime of fluid flow is laminar (\( \text{Re} < 2300 \));
- the current density is significantly lower than the critical (\( i = 1000 \text{ A/m}^2 \));
- metering pump provides continuous supply of the work solution to the intermembrane channel;
- the friction forces between the cations and anions are negligible and can be neglected.

Taking into account the immobility of the pore walls (\( v_m = 0 \)) and equation (2) we can obtain a system of equations describing the frictional forces:
Further it is necessary to clarify the driving forces included in the electrochemical potential. During electrohyperfiltration process the transfer of solute is the sum of diffusion, electrodiffusion and convection flows. Transfer of the solvent includes convective, electroosmotic and osmotic flows [25-28]. Taking this into account the driving forces can be expressed through the electrochemical potential for the solute and solvent.

For dissolved substance:

\[
\begin{align*}
\bar{c}_+ F_+ + F_{+\omega} + F_{+m} & = 0, \\
\bar{c}_- F_- + F_{-\omega} + F_{-m} & = 0, \\
\bar{c}_\omega F_\omega + F_{\omega+} + F_{\omega-} + F_{\omega m} & = 0, \\
\bar{c}_m F_m + F_{m+} + F_{m-} + F_{m\omega} & = 0.
\end{align*}
\]

where \(c_+\) and \(c_-\) is the concentration of cations and anions in the solution, respectively, mol\(\cdot\)m\(^{-3}\); \(\dot{v}_+\) and \(\dot{v}_-\) is the average velocity of cations and anions in the solution, respectively, m\(\cdot\)s\(^{-1}\); \(K\) is correction factor, N\(\cdot\)m\(^2\)\(\cdot\)s\(\cdot\)mol\(^{-2}\); \(D\) is diffusion coefficient, m\(^2\)\(\cdot\)s\(^{-1}\); \(L\) is the correction factor, N\(\cdot\)m\(\cdot\)s\(\cdot\)mol\(^{-2}\); \(z_+\) and \(z_-\) is the valence of cations and anions, respectively; \(F\) is Faraday constant, C\(\cdot\)mol\(^{-1}\); \(\phi\) is electric potential, V; \(M\) is the correction factor, m\(^{-1}\). Correction factors \(K, L, M\) are numerically equal to one and needed to bring all components of the driving force \(F_i\) to one unit of measurement N\(\cdot\)mol\(^{-1}\).

For solvent:

\[
\begin{align*}
F_\omega = -\frac{d\mu_\omega}{dx} = -c_\omega v_\omega K - z_\omega F \frac{dp}{dx},
\end{align*}
\]

where \(c_\omega\) is the concentration of solvent, mol\(\cdot\)m\(^3\); \(\dot{v}_\omega\) is the average velocity of the particles of the solvent, m\(\cdot\)s\(^{-1}\); \(z_\omega\) is the valence of solvent particles; \(V_\omega\) is the molar volume of solvent, m\(^3\)\(\cdot\)mol\(^{-1}\); \(p\) is pressure, Pa; \(N\) is correction factor, m\(^{-1}\).

Given the assumption that the friction forces between cations and anions are negligible and can be neglected, we introduce an index \(s\) to denote the total friction forces, driving force and concentration for anions and cations. Further, we simplify the equations system (3) to the form:

\[
\begin{align*}
\bar{c}_s F_s + F_{s\omega} + F_{s m} & = 0, \\
\bar{c}_\omega F_\omega + F_{\omega s} + F_{\omega m} & = 0, \\
\bar{c}_m F_m + F_{m s} + F_{m\omega} & = 0.
\end{align*}
\]

Taking into account the equation (1) and the system of equations (7) and stationary state of the membrane (\(\dot{v}_m = 0\)) and as a result \(F_{im} = -f_{im}\dot{v}_i = -f_{im}\dot{J}_i\), we obtain:

\[
\begin{align*}
\bar{c}_s F_s - \bar{c}_s f_{s\omega} (\dot{v}_s - \dot{v}_\omega) - f_{sm} \dot{J}_s & = 0, \\
\bar{c}_\omega F_\omega - \bar{c}_\omega f_{\omega s} (\dot{v}_\omega - \dot{v}_s) - f_{\omega m} \dot{J}_\omega & = 0, \\
\bar{c}_m f_{ms} \dot{v}_s + \bar{c}_m f_{m\omega} \dot{v}_\omega & = 0.
\end{align*}
\]

where \(\dot{J}_s\) and \(\dot{J}_\omega\) are the flux density of the solute and solvent, respectively, mol\(\cdot\)m\(^{-2}\)\(\cdot\)s\(^{-1}\).

Further, we express the friction coefficients of interaction of the systems "solvent – membrane" \(f_{im}\), "dissolved substance – membrane" \(f_{im}\), "dissolved substance – solvent" \(f_{is}\) from the system of equations (8) using equations (4) - (6), the expression \(F_{ij} = F_{ji} = 0\) and derived from it the equality of cross-friction coefficients \(f_{ij} = f_{ji}\).
Water solution of Fe(NO$_3$)$_3$ was chosen in order to show the example of friction coefficient calculation. This solution with concentration $1 \cdot 10^{-5}$ mol·l$^{-1}$ was used in baromembrane experimental plant [29] with application of electric current. Working conditions were following: $p = 4$ MPa, $\varphi = 2$-12 V. After an experiment series the values of flux density of the solute $J_s$ and solvent $J_\omega$ are obtained. These values were also used for further calculation of friction coefficients. Figure 2 (a-c) shows the calculated friction coefficients for selected solution by using the acetate cellulose membrane MGA-95.

\[
\begin{align*}
  f_{\omega m} &= \frac{\varepsilon_\omega (-c_\omega v_\omega K - z_\omega F \frac{d \phi}{dx} M - V_\omega \frac{d \phi}{dx})}{f_\omega}, \\
  f_{s m} &= \frac{\varepsilon_s (-c_s v_s K - D \frac{d c_s}{dx} - z_s F \frac{d \phi}{dx} M)}{f_s}, \\
  f_{s \omega} &= \frac{\varepsilon_s (-c_s v_s K - D \frac{d c_s}{dx} - z_s F \frac{d \phi}{dx} M) \frac{v_\omega v_\omega}{v_\omega v_s} \frac{\frac{d \phi}{dx} M - V_\omega \frac{d \phi}{dx} N}{f_\omega f_s}}{\varepsilon_\omega (v_\omega - v_\omega)}.
\end{align*}
\]

![Figure 2](image-url)

**Figure 2.** The dependence of the friction coefficients $f_{\omega m}$ (a), $f_{s m}$ (b), $f_{s \omega}$ (c) on the electric potential for aqueous solution Fe(NO$_3$)$_3$: 1 – near-anode membrane MGA-95, 2 – near-cathode membrane MGA-95.
The calculated friction coefficients can be used to solve the inverse problem of predicting and finding of the flux values of solvent and solute at the electric potential values outside the initial range.

The value of frictional interactions of cations and anions with a membrane or solvent can be found using the expression:

\[ f_{si} = q_+ f_{si} + q_- f_{si}, \]

where \( q_+ \) and \( q_- \) are coefficients equal to the ratio of the molar mass of the ion to the molar mass of the undissociated molecule of the corresponding substance, i.e. \( q_+ + q_- = 1 \); \( q_+ f_{si} \) is friction coefficient of interaction of cations with substance \( i \), \( N\cdot s\cdot mol^{-1}\cdot m^{-1} \); \( q_- f_{si} \) is friction coefficient of interaction of anions with substance \( i \), \( N\cdot s\cdot mol^{-1}\cdot m^{-1} \).

Thus, the friction coefficients for cations and anions describing their interaction with the membrane walls and the solvent will be as follows:

\[ f_{+m} = q_+ f_{sm}, \]
\[ f_{-m} = q_- f_{sm}, \]
\[ f_{+\omega} = q_+ f_{s\omega}, \]
\[ f_{-\omega} = q_- f_{s\omega}. \]

The following boundary conditions are chosen:

\[
\begin{cases}
\Delta p(0) = p_{in}, \Delta p(L) = p_f, \\
\Delta c(0) = c_{in}, \Delta c(L) = c_f, \\
\Delta \phi(0) = \phi_{in}, \Delta \phi(L) = \phi_f.
\end{cases}
\]

3. Summary

Calculated friction coefficients can be used in the theoretical calculations and the prediction of change over time of the kinetic parameters of baromembrane, electromembrane and electrobaromembrane separation processes of industrial solutions in various industries.

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