Self-Similar Solutions in Ion-Exchange Membranes and Their Stability

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Time-dependent processes in the electrolyte solution between ion exchange membranes are considered for the case of a small ratio of the thickness of the double ion layer to the thickness of the diffusion layer, \( \varepsilon \rightarrow 0 \). It is numerically shown that these processes are determined by the time-dependent self-similar expansion of space-charge region and the diffusion layer inside the electroneutral region and electrohydrodynamic instability of a self-similar solution leading to the electroconvection mode. The obtained theoretical results are qualitatively confirmed by recent experiments.

1. Micro- and nanoflows in semipermeable membranes are presently attracting the attention of researchers due to their application in micropumps, micro- and nanochannels, and fuel cells, as well as in modern medicine (artificial cells, new methods of delivery of drugs, etc.).

It is known [1] that the current–voltage curve of the process has three clearly pronounced regions by the potential difference, according to which we can distinguish the under-limiting modes, when the current is proportional to the potential difference; limiting modes, when an increase in the potential difference almost does not exert an effect on an increase in the current [2]; and over-limiting modes, when the average current is proportional to the applied voltage again. This phenomenon is explained by electrohydrodynamic instability [3], which is confirmed experimentally [4–6].

It was originally assumed in [7] that the time-dependent, one-dimensional solution has a self-similar character. It was shown that at a sufficiently large potential difference, this solution loses stability. The spectral problem of stability of this solution is presented in [7].

In this work, the self-similar character of the one-dimensional time-dependent solution of the problem in the complete statement is originally shown by the numerical solution of the Nernst–Plank–Poisson–Stokes system. On the self-similar portion of the development, this solution loses stability, which leads to the electroconvection mode. This agrees qualitatively with the experimental results [6].

2. The behavior of a simple binary electrolyte in the space between two electric membranes \( y = 0 \) and \( y = 1 \) is described by the following set of Nernst–Plank–Poisson–Stokes equations:

\[
\frac{\partial c^\pm}{\partial t} + \mathbf{U} \cdot \nabla c^\pm = \pm \nabla \cdot (c^\pm \nabla \Phi) + \nabla^2 c^\pm,
\]

\[
\varepsilon^2 \nabla^2 \Phi = c^- - c^+,
\]

\[
- \nabla P + \nabla^2 \mathbf{U} + \frac{K}{\varepsilon^2} (c^- - c^+) \nabla \Phi = 0,
\]

\[
\nabla \cdot \mathbf{U} = 0,
\]

with edge conditions

\[
y = 0: \quad c^+ = p, \quad -c^- \frac{\partial \Phi}{\partial y} + \frac{\partial c^-}{\partial y} = 0, \quad \Phi = 0, \quad \mathbf{U} = 0,
\]

\[
y = 1: \quad c^+ = p, \quad -c^- \frac{\partial \Phi}{\partial y} + \frac{\partial c^-}{\partial y} = 0, \quad \Phi = \Delta V, \quad \mathbf{U} = 0.
\]

At the initial point in time \( t = 0 \), a certain equilibrium distribution of concentrations of positive and negative ions \( c^\pm = 1 \) is specified.

Set (1), (2) is written in a dimensionless form. As the characteristic quantities, we accepted thermodynamic potential \( \Phi_0 = RT/F \), distance between mem-
branes, $L$, time $t$, dynamic viscosity of the liquid $\mu$, and ion concentration $c_0$ at $t = 0$.

Here, $D$ is the diffusivity of ions, $F$ is the Faraday number, $R$ is the universal gas constant, $p$ is the concentration of positive ions on a membrane ($p = e^+ / e^0 \gg 1$, in this work $p = 5$), $d$ is the absolute permittivity of the medium, and parameter $\kappa = d\Phi_0 / \mu D$.

A problem is described by three dimensionless parameters $\varepsilon$, $\Delta \Phi$, and $\kappa$; the latter weakly depends on the physical properties of the medium. In these calculations, we took $\kappa = 0.239$ (the aqueous NaCl solution) excluding the special calculation of comparison with [8], where $\kappa = 0.077$. At fixed $\kappa$, the number of parameters reduces to two ($\varepsilon$, $\Delta \Phi$).

A one-dimensional variant of problem (1), (2),

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial z} = 0, U = 0,$$ has the form

$$\frac{\partial c^+}{\partial t} = \pm \left( \frac{\partial}{\partial y} \left( \frac{\partial \Phi}{\partial y} + \frac{\partial c^+}{\partial y} \right) + \varepsilon^2 \frac{\partial^2 \Phi}{\partial y^2} \right),$$

$$\varepsilon^2 \frac{\partial^2 \Phi}{\partial y^2} = c^- - c^+,$$

$$y = 0: c^+ = p, \quad -c^- \frac{\partial \Phi}{\partial y} + \frac{\partial c^-}{\partial y} = 0, \quad \Phi = 0; \quad (3)$$

$$y = 1: c^+ = p, \quad -c^- \frac{\partial \Phi}{\partial y} + \frac{\partial c^-}{\partial y} = 0, \quad \Phi = \Delta V,$$

$$t = 0: c^+ = c^- = 1.$$

The current across a membrane at $y = 0$ is determined as

$$j = c^+ \frac{\partial \Phi}{\partial y} + \frac{\partial c^+}{\partial y}, \quad y = 0.$$

Problem (3) was solved numerically. When solving the problem, certain difficulties appear since it contains a small parameter as the higher order derivative. To overcome these difficulties, the numerical method used in [7] was generalized for the solution of set (3).

Calculations showed that, at $t \to \infty$, the solution tends to the steady-state solution, $\frac{\partial}{\partial t} = 0$. In our calculations performed in the region of superlimiting modes, $\varepsilon$ and $\Delta V$ varied in the ranges $\varepsilon = 0.0001-0.01$ and $\Delta V = 50-200$. At these parameters, the process is virtually established at $t_e = 0.1-0.2$.

3. We are interesting in certain intermediate times. Let us note that, at $t \ll t_e$, the influence of the upper membrane is negligibly small, and the process is far from established. On the other hand, at $t \gg \varepsilon^2$, the double ion layer already does not substantially affect the process. In this intermediate range of times, $\varepsilon^2 \ll r \ll t_e$, neither the Debye thickness $\lambda_D$ nor $L$ could not be a characteristic spatial scale, and solution of set (3) should behave as self-similar.

In new variables

$$\tau = t, \quad \eta = \frac{\sqrt{\epsilon} \Delta \Phi}{2\sqrt{\epsilon}},$$

set (3) is reduced to the form

$$4\tau \frac{\partial c^+}{\partial \tau} = 2\eta \frac{\partial c^+}{\partial \eta} + \frac{\partial}{\partial \eta} \left( \pm c^+ \frac{\partial \Phi}{\partial \eta} + \frac{\partial c^+}{\partial \eta} \right),$$

$$\varepsilon^2 \frac{\partial^2 \Phi}{\partial \eta^2} = c^- - c^+, \tag{4}$$

$$\eta = 0: c^+ = p, \quad c^- \frac{\partial \Phi}{\partial \eta} - \frac{\partial c^-}{\partial \eta} = 0,$$

$$\eta = \infty: c^+ = c^- = 1,$$

$$\lim_{\eta \to \infty} \left( \Phi - \frac{\eta}{2} \right) = \Delta \Phi.$$

The last condition also used in [7] means that the ohmic part $J/2$ is subtracted from the entire potential difference $\Delta V$. In this case, parameter $\Delta \Phi$ physically means the potential drop in the space-charge region and can be used as a new control parameter instead of $\Delta V$. Usually, $\Delta V \approx \Delta \Phi$. It is also convenient to redetermine the notion of the current at $\eta = 0$:

$$J = c^+ \frac{\partial \Phi}{\partial \eta} + \frac{\partial c^+}{\partial \eta}. \tag{5}$$

The relation between the old and new self-similar variables is given by the relations

$$\nu = \frac{\epsilon \Phi}{2\sqrt{\epsilon} \tau}, \quad J = 2j \sqrt{\tau}, \quad \Delta V = \Delta \Phi + \frac{t}{2}. \tag{6}$$

It is convenient to pass to variable $\nu$ from time $\tau$ in equations of ion transfer (4) using the first of relations (6). In this case, Eqs. (4) transform into

$$-2\nu \frac{\partial c^+}{\partial \nu} = 2\eta \frac{\partial c^+}{\partial \eta} + \frac{\partial}{\partial \eta} \left( \pm c^+ \frac{\partial \Phi}{\partial \eta} + \frac{\partial c^+}{\partial \eta} \right).$$

It is correct to integrated the obtained set numerically towards smaller $\nu$. During such integration, the left side becomes negligibly small almost immediately, and time-dependent terms can be omitted. In this case, the set indeed becomes self-similar:

$$2\eta \frac{\partial c^+}{\partial \eta} + \frac{\partial}{\partial \eta} \left( \pm c^+ \frac{\partial \Phi}{\partial \eta} + \frac{\partial c^+}{\partial \eta} \right) = 0,$$

$$\nu^2 \frac{\partial^2 \Phi}{\partial \eta^2} = c^- - c^+, \tag{6}$$