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Electro-osmotic convection in concentration polarization

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1. Summary

Nonequilibrium electroosmosis and the related instability of quiescent conduction through a diffusion layer at a charge selective membrane are reviewed as likely mechanisms of transition to overlimiting conductance through such a membrane. The short wave catastrophe in the limiting formulation of electroosmotic instability is discussed along with the possible way of its removal and the related wave length selection principle.

2. Introduction

Concentration polarization (CP) is the electrochemical nickname for a complex of effects related to the formation of concentration gradients in electrolyte solution adjacent to a charge selective solid/liquid interface upon the passage of an electric current. This is, in particular, a basic element of charge transfer across ion exchange electrodialysis membranes. The specific aspect of CP we address here concerns the stationary voltage/current ($V-C$) curves of cation exchange membranes. The following three regions are typically distinguishable in such a curve. The low current ohmic region I is followed by a plateau (region II, the "limiting current") of a much lower slope. Inflection of the $V-C$ curve at the plateau is followed by region III, in which the slope of the $V-C$ curve is somewhat lower than in region I. Inflection of the $V-C$ curve (transition to region III) is accompanied by the appearance of a low-frequency excess electric noise. Noise amplitude increases with the distance above the threshold and may reach up to a few percent of the appropriate mean value. Steady state passage of an electric current higher than the limiting one through an ion exchange membrane is commonly referred to as overlimiting conductance. The mechanisms of it and of the accompanying excess electric noise remained unclear for a long time. Eventually, a fair amount of indications have been accumulated, suggesting that the overlimiting behavior of the ion exchange membranes has to do with some kind of convective mixing that develops spontaneously in the depleted diffusion layer at the advanced stage of concentration polarization. Electroconvection, driven by nonequilibrium electro-osmotic slip at the solution/membrane interface, was suggested as mechanism drawing together the overlimiting phenomena at cation exchange membranes [1].

In our previous publications we developed theory of nonequilibrium electro-osmotic slip at a ion-exchange membrane. It has been shown that this slip

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yields instability of the quiescent concentration polarization at a homogeneous membrane. Electroconvection, developing from this instability , results in destruction of the diffusion layer, causing overlimiting conduction. Not far above the instability threshold, steady state electroconvective vortices start oscillating in a periodic manner. Upon further moving away from that threshold, these oscillations soon become chaotic, resulting in low frequency excess electric noise, typical of the overlimiting conductance. In this paper we recapitulate the basics of electroosmosis and summarize the results pertaining to the nonequilibrium electroosmotic instability.

3. Electro-osmotic slip of the second kind and instability of quiescent concentration polarization

The prototypical two-dimensional model problem for concentration polarization in a diffusion layer of a univalent electrolyte adjacent to a cation-exchange membrane under the passage of a normal electric current in the dimensionless form reads.

$$c_t^+ + \mathrm{Pe}\,(\underline{v}\nabla)\,c^+ = \nabla\left(\nabla c^+ + c^+\nabla\varphi\right), \quad \infty < x < \infty,\ 0 < y < 1 \tag{1}$$

$$c_t^- + \mathrm{Pe}\,(\underline{v}\nabla)\,c^- = \nabla\left(\nabla c^- - c^+\nabla\varphi\right), \tag{2}$$

$$\frac{1}{\mathrm{Sc}}\underline{v}_t = -\nabla p + \Delta\varphi\,\nabla\varphi + \Delta\underline{v}, \tag{3}$$

$$\nabla\,\underline{v} = 0. \tag{4}$$

$$\varepsilon^2\Delta\varphi = c^- - c^+, \tag{5}$$

Here, c^+, c^-, φ are concentrations of cations and anions, and the electric potential; space and time variables are normalized with the diffusion layer thickness L, and diffusional time, respectively; $\underline{v} = u\underline{i} + w\underline{j}$, and p in (3) and (4) are the dimensionless velocity and pressure.

The Nernst-Planck equations (1) and (2) describe convective electrodiffusion of cations and anions, respectively. Equation (5) is the Poisson equation for the electric potential, where $c^+ - c^-$ in the right-hand side is the space charge due to a local imbalance of ionic concentrations. The Stokes equation (3) is obtained from the full momentum equation by omitting the nonlinear inertia terms. Finally, (4) is the continuity equation for an incompressible solution. Ionic diffusivities have been assumed equal for simplicity.

(1) The dimensionless Debye length ε lies in the range $10^{-7} < \varepsilon < 10^{-4}$ for a realistic macroscopic system.

(2) The electroconvective Peclet for a typical aqueous low molecular electrolyte is of order unity and Sc is the Schmidt number typically of the order of 10^2.

Boundary conditions at the membrane/solution interface at $y = 0$ specify impermeability for anions of an ideally charge selective cation-exchange membrane, interface concentration of cations equal to that of the fixed charges inside the membrane (p_1), and the electric potential $-V$ at the interface (V—the potential drop across the diffusion layer).

These boundary conditions are supplemented by the nonslip conditions at the interface and standard conditions for the outer edge of the diffusion layer at $y = 1$, specifying unity ionic concentration, zero potential, zero normal and zero derivative tangent components of the fluid velocity.

When time dependent situations are addressed, the resulting boundary value problem is supplied with a suitable set of initial conditions.

This boundary value problem, possesses a one-dimensional quiescent conduction solution with $\underline{v} = 0$, $p(y) = 1/2\varphi_y^2 + p_c$ (p_c—arbitrary integration constant), and c^+, c^-, and φ satisfying the one-dimensional version of (1), (2), (5).

For quasiequilibrium conditions this solution splits into the "outer" locally electroneutral solution, valid in the "bulk" of the segment $0 < y < 1$, and the "inner" or electric double layer solution, valid in the ε vicinity of the interface at $y = 0$. The inner and outer solutions are connected through the standard procedures of matched asymptotic expansions. The outer leading order quasi-electroneutral solution $\overline{c}(y) = \frac{I}{2}\,y + 1 - \frac{I}{2}$, $\overline{\varphi}(y) = \ln\,\left(\frac{I}{2}y + 1 - \frac{I}{2}\right)$.

Here $\overline{c} \overset{\text{def}}{=} c^+ = c^-$, and $I \overset{\text{def}}{=} (\overline{c}_y + \overline{c}\varphi_y)$ is the electric current density in the system. This yields the current-voltage relation $I = 2\left(1 - e^{(V - \ln\, p_1)}\right)$, such that when $V \to \infty$, $I \to I^{\text{lim}} = 2$ and, simultaneously $\overline{c}(0) \to 0$.

In order to investigate the stability of this quiescent concentration polarization solution, one has to allow for lateral motions. In this case too, the problem splits into that for locally quasielectroneutral bulk and the boundary electric double layer at the membrane/solution interface. Equations describing the ionic transfer and fluid flow in the bulk are (1)–(4) written for $c = c^+ = c^-$, whereas the boundary layer analysis provides an expression for electro-osmotic slip, that is the tangential fluid velocity at the outer edge of the electric double layer.

For electro-osmotic slip at a conductive permselective interface two fundamentally different regimes should be distinguished in accordance with the magnitude of the electric current through the interface.

The first quasiequilibrium electro-osmosis, or electroosmosis of the first kind, following terminology of Dukhin [2], pertains to currents below the limiting value. For such currents the diffuse part of the electric double layer preserves its common quasiequilibrium structure essentially identical with that for zero current. An essential part of the theory of quasiequilibrium electro-osmosis at a charge selective interface is accounting for polarization of the electric double layer by the applied tangential electric field resulting, in particular, in major lateral pressure drops in the double layer due the lateral variation of the Maxwell stresses. This yields for the electroosmotic slip velocity, instead of the common Helmholtz-Smoluchowski formula $u_s = \zeta \overline{\varphi}_x$ valid for an impermeable interface, the expression $u_s = \zeta\left(\overline{\varphi}_x + \frac{\overline{c}_x}{\overline{c}}\right) - 4\frac{\overline{c}_x}{\overline{c}} \ln \frac{1+e^{\zeta/2}}{2}$. Peculiarity of this expression is that, for an ideally permselective cation-exchange membrane maintained at a constant potential ($\ln \overline{c} + \overline{\varphi} = \text{const}$, that is, $\overline{c}_x/\overline{c} = -\overline{\varphi}_x$), and $\zeta \to -\infty$, it yields $u_x = -4 \ln 2)\overline{\varphi}_x$. That is, the factor at $-\varphi_x$ (electro-osmotic factor) tends to a maximal upper value upon the increase of ζ (negative). This stands in contrast with the respective prediction of the Helmholtz-Smoluchowski formula and is a direct consequence of polarization of the electric double layer at a permselective interface.

Hydrodynamic stability of the quiescent concentration polarization with a limiting quasi-equilibrium electro-osmotic slip was studied in the past. It was concluded that electro-osmotic instability of the first kind, although possible in principle near the limiting current, was unfeasible for any realistic low molecular aqueous electrolyte. This conclusion followed from the fact that an electro-osmotic factor at least one order of magnitude higher than the limiting value $4 \ln 2$ is required for this type of instability to occur. This conclusion is valid as long as the system, in particular the electric double layer, remains at quasiequilibrium. This latter is typified by the division of the system into a locally quasielectroneutral bulk and a quasiequilibrium boundary layer (diffuse double electric) layer. This picture breaks down upon $I \to I^{\text{lim}}$. This motivated the study of the space charge of the nonequilibrium electric double layer, which develops in the course of concentration polarization when the interface concentration approaches zero through a numerical solution of the aforementioned one-dimensional steady state version of (1), (2) and (5), [3]. The results of this study may be summarized as follows. For $0 < V = O(1)$ $\left(I < I^{\text{lim}}\right)$, local electroneutrality holds in the entire system except for the boundary layer of the order of thickness ε at the left edge of the region. In this electroneutral region ionic concentration profile is linear in y. The maximal possible slope of the concentration profile in these conditions is 1 (corresponding to $I = I^{\text{lim}}$). This picture remains essentially valid up to $V = O(|\ln \varepsilon|)$ $\left(I \leq I^{\text{lim}}\right)$. For $O(|\ln \varepsilon|) < V < O\left(\varepsilon^{-1}\right)$ $\left(I \sim I^{\text{lim}}\right)$, the following three regions may be distinguished (from right to left).The quasielectroneutral "bulk" region has a linear concentration profile with the slope of approximately 1. This region borders on the left with the extended diffuse space charge region of a width between $O\left(\varepsilon^{2/3}\right)$ and $O(1)$, followed by the quasiequilibrium, $O(\varepsilon)$ thick, boundary layer at the left edge. Upon a further increase of voltage up to $O\left(\varepsilon^{-1}\right))$ the extended space charge region reaches a finite size $O(1)$ and so does the current increment over the limiting value $\left[0 < I - I^{\lim} = O(1)\right]$.

This observation of development in the course of concentration polarization of a nonequilibrium electric double layer with the extended space charge region, guided Dukhin and his colleagues in their discovery of what they termed the electrokinetic phenomena of the second kind [2].

Accurate analysis of nonequilibrium electro-osmotic slip at a flat permselective membrane with an applied voltage V $[V > O(|\ln \varepsilon|)]$ results in the slip condition $u_s = -\frac{1}{8} V^2 \left. \frac{\frac{\partial^2 c}{\partial x \partial y}}{\frac{\partial c}{\partial y}} \right|_{y=y_0}$, where $y_0(x,t) = \left(\frac{3}{4} \varepsilon V\right)^{2/3} \left[\left(c_y|_{y=y_0} \right)^{-1/3} - 1 \right]$ is the outer edge of the nonequilibrium extended space charge region. This condition is the key element of the free boundary problem for the time dependent two-dimensional ion transfer in the locally electroneutral part of a diffusion layer of a univalent electrolyte at a cation-exchange membrane under developed CP conditions. Other conditions at the free boundary $y_0(t)$ specify the electrolyte concentration at the value $c|_{y=y_0} = a \left(\varepsilon c_y|_{y=y_0} \right)^{2/3}$ and zero normal velocity. Here a is a positive order one constant provided by the boundary layer analysis. To the leading order in ε, this free boundary problem is reduced to a fixed boundary value problem with boundary conditions at $y_0 = 0$, and vanishing boundary concentration.

This leading order boundary value problem is singular in the sense that it yields a short-wave instability of the conduction state. Namely, this problem possesses a "limiting" steady state quiescent concentration polarization solution $c_0 = y$, $\underline{u}_0 = u_0 \underline{i} + w_0 \underline{j} \equiv 0$. Linear stability analysis of this solution yields monotonic instability for voltages above the threshold value provided by the marginal stability relation [1]: $\frac{1}{8} V^2 \, \mathrm{Pe} = 4 \frac{\sinh k \ \cosh k - k}{\sinh k \ \cosh k + k - 2k^2 \ \coth k}$, where k is the perturbation wave number. A characteristic feature of the respective marginal stability curve is a monotonic decrease of the threshold voltage towards the limiting value $V_c = 4\sqrt{2/\mathrm{Pe}}$ with the increasing wave number. [According to the linear stability analysis, the linear growth rate of the perturbation λ also increases with wave number as $\lambda = \mathrm{Pe}^{1/3} V^{-2/3} k^{5/3} + O\left(k^{4/3}\right)$.] Numerical solution of the full nonlinear limiting problem has shown that near the threshold, instability of steady state results in the development of a periodic sequence of pairs of symmetric steady state vortices. The spatial period of the sequence, as selected by nonlinearity of the system, was independent of the wavelength of the initial disturbance and roughly matched the thickness of the diffusion layer. This period very slowly, if at all, increased with the increase of voltage. Periodic oscillations of vortices began above a certain voltage threshold, turning chaotic above another, still higher, threshold. Our recent numerical simulations indicate that these thresholds, but not the spatial period of the vortex sequence, are space discretization dependent as a possible evidence of mathematical ill-posedness of the limiting formulation. This might be the mathematical expression of the short-wave instability.

Retaining the "small" terms y_0 and c_0 in the formulation removes this short-wave "catastrophe" and yields a reasonable linear wavelength selection. The resulting implicit marginal stability relation between the threshold value of the control parameter V and the wave number k has the form

$$4\,\frac{\sinh k\ \cosh k - k + \frac{\varepsilon^{2/3}}{3}\left[2a + \left(\frac{3}{4}V\right)^{2/3}\right] k\left(\cosh^2 k - k\ \coth k\right)}{\sinh k\ \cosh k + k - 2k^2\ \coth k} = \mathrm{Pe}\,\frac{V^2}{8},$$

The respective marginal stability curves for $\mathrm{Pe} = 0.5$ in the realistic range $10^{-6} < \varepsilon < 10^{-4}$ possess a minimum at the critical wave number k_c in the range $5 < k_c < 8$. This corresponds to a spatial period $2\pi/k_c$ in the range $0.7 < 22\pi/k_c < 1.2$, in qualitative agreement with numerical results for the nonlinear problem. The only weak variation of k_c for ε varying by orders of magnitude is easily inferred from the above expression. Indeed, taking the limit $\varepsilon \to 0$ in it we find $k_c \approx \frac{1}{3}\,|\ln\varepsilon| + O(|\ln|\ln(\varepsilon)||)$ valid for $\varepsilon \ll 1$. Thus, retaining the leading order small terms in the formulation removes the short wave "catastrophe" and yields a reasonable wave number selection.

Systematic experimental study of electroosmotic instability, including visualization of the flow, remains an open problem.

References

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