Electro-osmotically induced convection at a charge-selective membrane

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**Abstract**

The paper is concerned with convection induced by nonequilibrium electroosmosis at an ion exchange electrodialysis membrane, as a source of overlimiting conductance through the membrane. Derivation of nonequilibrium electroosmotic slip condition is recapitulated along with the results of linear stability analysis of quiescent electrodiffusion through a flat ion exchange membrane. Results of numerical calculation pertaining to nonlinear convection, developing from the respective instability, are reported along with those of recent experiments with modified membranes. These latter rule in favor of surface versus bulk origin of overlimiting conductance through ion exchange membranes.

1 Introduction

The following three regions are typically distinguishable in a stationary voltage-current ($V-C$) curve of a cation-exchange electrodialysis membrane. The low current Ohmic region I is followed by a plateau (region II, the 'limiting current') of a much lower slope. Inflection of the VC curve at the plateau is followed by region III, in which the slope of the VC curve is somewhat lower than in region I. Transition to region III is accompanied by the appearance of a low-frequency excess electric noise [1]. Noise amplitude increases with the distance above the threshold and may reach up to a few percents of the appropriate mean value.

Steady state passage of an electric current higher than the limiting one through an ion exchange membrane and the related appearance of the excess electric noise are commonly referred to as overlimiting conductance. The mechanisms of it remained unclear for a long time. It has been shown
conclusively that no such mechanisms as loss of membrane permselectivity at high voltage or the appearance of additional charge carriers ("water splitting") are responsible for these phenomena at cation-exchange membranes [2], [3] (This is also true for anion exchange membranes, although there the aforementioned overlimiting pattern is obscured by the fact that most anion exchange membranes intensely "split water" in the course of concentration polarization due to a particular catalytic surface reaction).

Eventually, a fair amount of indications has 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 [1], [4]. This has been finally confirmed by a direct experimental observation: if the depleted diffusion layer is immobilized by a gel, a plateau is reached at saturation, and the excess electric noise disappears [5].

Electroconvection driven by nonequilibrium electroosmotic slip at the solution/membrane interface, was suggested as a mechanism drawing together the overlimiting phenomena at cation exchange membranes [6].

In our recent experiments aimed at distinguishing between the bulk and surface driven mechanisms in overlimiting conductance we cast micron to submicron thick layers of non-charged aqueous conductive solid (cross-linked polyvinylalcohol) on the surface of a cation-exchange membrane [7]. Usage of this thus modified membrane in concentration polarization tests in a thin polarization cell [5] showed that immobilization of electrolyte in the vicinity of the depleted solution/membrane interface resulted in elimination of overlimiting conductance. Considering the negligible thickness of the immobilized layer compared to that of the diffusion layer (200 μm in the polarization cell employed), this, as illustrated in Fig.1, rules in favor of a surface (e.g. electro-osmotic slip) driven mechanism of overlimiting conductance versus the bulk electroconvection.

In our previous publications [6], [8] we developed theory of nonequilibrium electroosmotic slip at a permselective membrane (electroosmosis of the second kind, introduced previously by Dukhin and co-workers, see [9] and references therein). It has been shown that this slip 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 conductance. Not far above the instability threshold, steady state electroconvective vortices start oscillating in a periodic manner. Upon a further moving away from that threshold, these oscillations soon become chaotic, resulting in a low frequency excess electric noise, typical of the overlimiting conductance. Below, we briefly review the respective findings.
Figure 1: Current–voltage curves of the modified Ashai Glass membrane for various modification layer thicknesses; degree of cross-linking: 1.12%

2 Concentration polarization

Rewritten in dimensionless variables, a convenient model problem of steady-state concentration polarization in a diffusion layer adjacent to an ideally permselective cation exchange membrane reads

\[
\begin{align*}
(\bar{c}_y + \bar{\varphi}_y)_{y} &= 0, \quad 0 < y < 1 \\
(\bar{c}_y - \bar{\varphi}_y)_{y} &= 0 \\
\bar{c}(1) &= 1 \\
\bar{\varphi}(1) &= 0 \\
(\bar{c}_y - \bar{\varphi}_y)|_{y=0} &= 0 \\
(\ln \bar{c} + \bar{\varphi})|_{y=0} &= \ln p_1 - V
\end{align*}
\]

Here, \(y\) is the dimensionless normal coordinate (scaled by the thickness of the diffusion layer) with the origin at the membrane solution interface, \(\bar{c} = \bar{c}^+ = \bar{c}^-\) are the dimensionless 'bulk' cat- and anion concentrations (scaled by the specified concentration at the outer edge of the diffusion layer) and \(\bar{\varphi}\) is the dimensionless electric potential (scaled by \(RT/F\)). Finally, \(p_1\) and \(V\) in Eq.(6) are, respectively, the dimensionless concentration of fixed charges in the membrane, assumed equal to that of cations and voltage (potential drop on the diffusion and electric double layers).

Eqs.(1), (2) are the Nernst–Planck equations for the cat- and anions, respectively, Eq.(5) states impermeability of the membrane for co-ions (anions), whereas Eq.(6) expresses the continuity of the electrochemical potential of counterions (cations) across the electric double layer. The quiescent
concentration polarization solution is obtained by a straight-forward integration of the boundary value problem \((1)-(6)\) in the form

\[
\overline{c}(y) = \frac{I}{2}y + 1 - \frac{I}{2}
\]

\[
\overline{\varphi}(y) = \ln \left( \frac{I}{2}y + 1 - \frac{I}{2} \right)
\]

where

\[
I \overset{\text{def}}{=} (c_y + \overline{c}\varphi_y)
\]

is the electric current density in the system. Expression \((8)\) yields the current-voltage relation

\[
I = 2(1 - e^{-V/2})
\]

From \((10)\), when \(V \to \infty\), \(I \to I^{\text{lim}} = 2\) and, simultaneously, by \((7)\), \(c(0) \to 0\). This is the key feature in the classical picture of concentration polarization — saturation of the current density towards the limiting value, resulting from the vanishing interface electrolyte concentration at the cathode. In fact, steady state currents much greater than the limiting one are readily passed through virtually ideally permselective cation-exchange membranes (overlimiting conductance mentioned in the Introduction). Search for a mechanism for this, and the related occurrence of the excess electric noise, provided the main motivation for the study of electroconvection in strong electrolytes.

3 Equilibrium and non-equilibrium electric double layer and electro-osmotic slip of two kinds

In order to investigate the stability of the quiescent concentration polarization solution \((7)-(10)\), one has to allow for lateral motions. The problem splits into that for locally quasi-electroneutral bulk and the boundary (electric double) layer at the membrane/solution interface. Boundary layer analysis provides, in addition to boundary conditions \((5)\), \((6)\), an expression for electroosmotic slip, that is the tangential fluid velocity at the outer edge of the electric double layer.

For electroosmotic slip at a conductive permselective interface two fundamentally different regimes are to be distinguished in accordance with the magnitude of the electric current through the interface.

The first (quasi-equilibrium electroosmosis, or electroosmosis of the first kind, following terminology of Dukhin [9]) 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. Theory of quasi-equilibrium electroosmosis at
a permselective interface was developed by Dukhin [10]. An essential part of this theory 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 to the lateral variation of the Maxwell stresses. This results, for the tangential velocity \( u \) in the double layer, in the equation of the form

\[
-\frac{1}{2} \left[ (\varphi_z)^2 \right]_x + \varphi_x \varphi_{zz} + u_{zz} = 0
\]

where \( z \equiv y/\varepsilon \) is the boundary layer coordinate with \( \varepsilon = r_0/\delta \) = dimensionless Debye length and \( x \) = lateral coordinate. For a quasi-equilibrium boundary layer, potential \( \varphi(x, z) \) in (11) is substituted from the solution of the Poisson–Boltzmann equation

\[
\varphi_{zz} = \overline{\varphi}(x, 0) \left( e^{\varphi - \overline{\varphi}(x, 0)} - e^{\varphi + \overline{\varphi}(x, 0)} \right)
\]

Here \( \overline{\varphi}(x, 0), \overline{\varphi}(x, 0) \) are, respectively, the electrolyte concentration and the electric potential at the outer edge of the electric double layer. Subsequent integration of (11) yields for the electroosmotic slip velocity, instead of the common Helmholtz–Smoluchowski formula

\[
u_s = \zeta \varphi_x
\]

valid for an impermeable interface, an expression which yields for \( \zeta \to -\infty \), \( u_s = -(4 \ln 2) \varphi_x \) (\( \zeta(x) = \varphi(x, 0) - \overline{\varphi}(x, 0) \) is the dimensionless \( \zeta \)-potential).

Thus, for a permselective interface, the factor at \( -\varphi_x \) in the expression for the electroosmotic slip velocity (electroosmotic factor) tends to a maximal upper value upon the increase of \( \zeta \) (negative).

Hydrodynamic stability of the quiescent concentration polarization with this limiting quasi-equilibrium electroosmotic slip was studied in [11]. It was concluded that electroosmotic 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 electroosmotic 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, electric double layer remains at quasi-equilibrium. Namely, this ceases being the case when the current approaches the limiting value. We already saw that in this case \( \overline{\varphi} \to 0 \) and \( \overline{\varphi} \to -\infty \), which makes Eq.(12) formally unsuitable for calculation of \( \varphi \) in the double electric layer and, thus, through Eq.(11), for calculation of electroosmotic velocity \( u_s \). This reflects a fundamental structural change which occurs in the system as it moves away from quasi-equilibrium upon \( I \to I^{\text{lim}} \).

Generally, quasi-equilibrium is typified by the division of the system into a locally quasi-electroneutral bulk and a quasi-equilibrium boundary...
layer (diffuse electric double layer). This picture breaks down upon $I \to I^{\text{lim}}$, as reflected, in particular, in the inconsistency of the local electroneutrality approximation which appears in the basic concentration polarization solution Eqs. (7)-(10) in this limit. This was the motivation behind 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 and, accordingly, the local Debye length tends to infinity [12]. This study essentially consisted of a numerical solution of the one-dimensional model problem (1)-(6) with the local electroneutrality condition replaced by the full Poisson equation for electric potential.

In Fig. 2 we present schematically the ionic concentrations profiles obtained in [12] (and in a number of studies that followed [13]-[17]) for a sequence of applied voltages $V$.

The respective results may be summarized as follows. For $0 < V = O(1)$ ($I < I^{\text{lim}}$), local electroneutrality holds in the entire system except for the boundary layer of the order of thickness $\varepsilon$ at the left edge of the region. In the respective electroneutral region a linear ionic concentration profile holds in accordance with Eq. (7). The maximal slope of the concentration profile in these conditions is 1 (which corresponds to $I = I^{\text{lim}} = 2$). This picture remains essentially valid up to $V = O(\ln \varepsilon)$ ($I \leq I^{\text{lim}}$). For $O(\ln \varepsilon) < V < O(\varepsilon^{-1})$ ($I \approx I^{\text{lim}}$), the following three regions may be distinguished (from right to left). The quasi-electroneutral 'bulk' region with a linear concentration profile with the slope approximately 1. This region borders on the left with the extended diffuse space charge region of a width between $O(\varepsilon^{2/3})$ and $O(1)$, followed by the quasi-equilibrium, $O(\varepsilon)$ thick, boundary layer at the left edge. Upon a further increase of voltage up to
does the current increment over the limiting value \(0 < I - I_{\text{lim}} = O(1)\).

Based on this observation of the development in the course of concentration polarization of a nonequilibrium electric double layer with the extended space charge region, Dukhin and his colleagues inferred the so-called electrokinetic phenomena of the second kind (see [9] and references therein).

Accurate analysis of non-equilibrium electroosmotic slip at a flat permselective membrane with an applied voltage \(V\) \((V > O(|\ln \varepsilon|))\), was carried out in [8], resulting in the expression

\[
\begin{align*}
\mathbb{V}_s &= -\frac{1}{8} V^2 \left. \frac{\partial^2 c}{\partial x \partial y} \right|_{y=0} \\
&= O(\varepsilon^{-1})
\end{align*}
\]

Noticeable is the absence of the electric field from Eq. (14), which greatly simplifies the computations of the resulting bulk flow.

### 4 Convection driven by non-equilibrium electro-osmosis

Summarizing the results of previous section, the relevant problem for time dependent ion transfer in the quasi-electroneutral diffusion layer \([-\infty < x < \infty, 0 < y < 1]\) at a permselective solid/liquid interface reads, omitting overbars,

\[
\begin{align*}
\left(1 + \frac{1}{D}\right) (c_t + \text{Pe} \cdot \mathbf{u} \nabla c) &= 2 \Delta c \quad (15) \\
v &= u_x + w_y \\
\frac{1}{Sc} \cdot \mathbf{v} &= -\nabla p + \Delta \mathbf{v} \quad (17) \\
\nabla \cdot \mathbf{v} &= 0
\end{align*}
\]

\(y = 1:\)

\[
\begin{align*}
c|_{y=1} &= 1 \\
|w|_{y=1} &= 0 \\
|w|_{y=1} &= 0
\end{align*}
\]

\(y = 0:\)

\[
\begin{align*}
c|_{y=0} &= 0 \\
|w|_{y=0} &= 0 \\
|w|_{y=0} &= 0
\end{align*}
\]
Figure 3: (a) Marginal stability curve for nonequilibrium electroosmotic instability ($V$ – dimensionless voltage, $k$ – dimensionless wave number); (b) Average dimensionless overlimiting current/voltage curve for an infinite flat membrane; (c) Average dimensionless current density evolution towards the attractor: (i) steady state, $V = V + 1$, (c) periodic oscillations, $V = V + 1.1$, (c) chaotic oscillations, $V = V + 1.2$.

Here $\text{Pe}=6\pi \eta_0 \alpha^2/\alpha$ ($r_0$ – equilibrium Debye length, $\alpha$ – viscous ionic radius, $\alpha$ – average interionic distance) is the electroconvective Peclet number, $Sc = \nu/D_+$ ($\nu$ – kinematic viscosity, $D_+$ – anionic diffusivity) is the Schmidt number and $D = D_+/D_-$ is the relative cationic diffusivity. The boundary value problem (15)-(24) possesses a trivial “limiting” quiescent concentration polarization solution (see Eq. (7) with $I = I_{\text{lim}}$)

$$c_0(y) = y$$
$$\n_0 = u_0 + w_0 = 0$$

The linear stability analysis of this solution yields the marginal stability curve in the $V/k$ ($k$ – the wave number) plane presented in Fig. 3a. No-
noticeable in this curve is the monotonic decrease of the threshold value of $V$ towards the limit $V_\text{th} = 4\sqrt{2D/[(D+1)\text{Pe}]}$.

The fact, that, according to linear stability analysis, the perturbation mode with infinitesimal wavelength is most unstable, suggests the need for a nonlinear wave number selection principle. Information to this regard is provided by the nonlinear convection computations described in Ref. [6].

Nonlinear convection which develops from this instability destroys the diffusion layer, yielding the overlimiting conductance, as illustrated in Fig. 3b, where we present the calculated overlimiting current versus voltage curve. Above a certain secondary threshold, fairly close to the primary instability threshold, the stationary convective vortices, developing at the latter, become oscillatory unstable. Fairly soon, at still higher voltage, these vortex oscillations turn chaotic, becoming the likely source of the excess electric noise in the overlimiting conductance. This sequence of events for three increasing values of voltage is illustrated in Fig. 3c(i-iii).

References


