Wave number selection in a nonequilibrium electro-osmotic instability

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Nonequilibrium electro-osmotic slip causes instability of quiescent ionic conductance through a diffusion layer of a strong electrolyte at a charge selective solid such as ion-exchange membrane or electrode. This instability, as inferred from the outer asymptotic limit of the full singularly perturbed ionic transport problem, is of the short-wave type. This latter is a serious shortcoming of the limiting model. In this Brief Report we show that inclusion in the model of the first asymptotic corrections yields a reasonable finite wavelength selection.

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In Refs. [1,2] we reported a nonequilibrium electro-osmotic instability of quiescent ionic conductance through a diffusion layer of a strong electrolyte at a charge selective solid (ion-exchange electrodialysis membrane, electrode). The short wavelength character of this instability represented a serious shortcoming of the model. Indeed, the numerical solution showed that the nonlinearity selected the wavelength (the average convective vortex size) on the length scale of the diffusion layer thickness. Nevertheless, the related oscillations and noise may well have been due to the ill-posedness of the model owing to the "short-wave catastrophe." This model was the leading order outer limit of the full singularly perturbed ionic transport problem. In this Brief Report we show that consideration of the next order corrections removes the short-wave catastrophe and yields a reasonable finite wavelength selection.

Concentration polarization (CP) is the electrochemical term for a set of complex effects related to the formation of concentration gradients in electrolyte solution adjacent to a permselective (charge selective) solid/liquid interface upon the passage of a direct electric current. The expression for CP is a voltage/current (VC) curve with a typical nonlinearity: initial Ohmic low polarization region followed by current saturation at the "limiting" current, corresponding to the vanishing interface concentration followed, in turn, by inflexion of the VC curve and transition to the "overlimiting" conductance regime, accompanied by the appearance of the low frequency excess electric noise.

As shown in Refs. [1,2], 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 is described, in terms of natural dimensionless variables, by the following free boundary problem (outer problem in terms of the boundary layer analysis of the full singularly perturbed problem described in Refs. [1,2]).

$y_0(x,t)<y<1$, $t>0$.

$$c_t+\mathrm{Pe}\underline{v}\,\nabla c=\Delta c,\quad \underline{v}=u\underline{i}+w\underline{j}, \tag{1}$$

$$\frac{1}{\mathrm{Sc}}\underline{v}_t=-\nabla p+\Delta\underline{v}, \tag{2}$$

$$\nabla\underline{v}=0. \tag{3}$$

$y=y_0(x,t)$.

$$c|_{y=y_0}=c_0,\quad c_0=a(\varepsilon c_y|_{y=y_0})^{2/3}, \tag{4}$$

$$u|_{y=y_0}=-\frac{1}{8}V^2\left(\frac{c_{xy}}{c_y}\right)\bigg|_{y=y_0}, \tag{5}$$

$$w|_{y=y_0}=0. \tag{6}$$

$y=1$.

$$c|_{y=1}=1, \tag{7}$$

$$u|_{y=1}=0, \tag{8}$$

$$w|_{y=1}=0. \tag{9}$$

Here, x and y are, respectively, the coordinates tangential and normal to the membrane ($y=0$ is membrane/solution interface and $y=1$ is the outer edge of the diffusion layer), u and w are the respective components of the fluid velocity $\underline{v}$, and $c(x,y,t)$ is the electrolyte concentration. Furthermore,

$$\mathrm{Pe}=\left(\frac{RT}{F}\right)^2\frac{d}{4\pi\eta D} \tag{10}$$

is the electroconvective Peclet number and

$$\mathrm{Sc}=\frac{\nu}{D} \tag{11}$$

is the Schmidt number. Here, R is the universal gas constant; T is the absolute temperature; F is the Faraday number; d is the dielectric permittivity of the solution; η is the dynamic viscosity; D is ionic diffusivity, assumed equal, for simplicity, for both ions; and ν is kinematic viscosity. V is the voltage applied to the diffusion layer, a control parameter in the problem, and

$$\varepsilon=\frac{(dRT)^{1/2}}{2F(\pi c_0)^{1/2}\delta} \tag{12}$$

is the dimensionless Debye length (c_0 is the bulk electrolyte concentration and δ is the diffusion layer thickness). For a realistic system ε is a small parameter in the range $10^{-4}<\varepsilon<10^{-6}$.

Finally, the free boundary

$$y_0(x,t)=\left(\frac{3}{4}\varepsilon V\right)^{2/3}[(c_y|_{y=y_0})^{-1/3}-1] \tag{13}$$

is the outer edge of the nonequilibrium extended space charge region [2] and a is a positive constant of order one provided by the boundary layer analysis [2] as

$$a = 2^{-1/3}\sqrt{\frac{[F(0)]^4}{4} - [F'(0)]^2}. \tag{14}$$

Here, F is a solution of the inhomogeneous Painleve equation of the second kind of the form

$$F_{zz} = \frac{1}{2}F^3 - zF + 1, \tag{15}$$

satisfying the matching conditions

$$F(z) = \begin{cases} O\left(\frac{1}{z}\right), & z \to \infty \\ O(\sqrt{-z}), & z \to -\infty. \end{cases} \tag{16}$$

To the leading order in ε, the free boundary problem (1)–(9), Eq. (13) is reduced to the fixed boundary value problem for Eqs. (1)–(3) with boundary conditions (7)–(9), $y_0 = 0$, and boundary conditions (4)–(6) assuming the form

$$c|_{y=0} = 0, \tag{17}$$

$$u|_{y=0} = -\frac{1}{8}V^2\left(\frac{c_{xy}}{c_y}\right)\Bigg|_{y=0}, \tag{18}$$

$$w|_{y=0.} \tag{19}$$

This leading order boundary value problem (bvp), studied in Refs. [1,2], is singular in the sense that it yields a short-wave instability of the conduction state. Namely, the bvp (1)–(3), (7)–(9), (17)–(19) possesses a trivial "limiting" steady state quiescent concentration polarization solution

$$c_0(y) = y, \tag{20}$$

$$\underline{v}_0 = u_0\underline{i} + w_0\underline{j} \equiv 0. \tag{21}$$

Linear stability analysis of this solution yields monotonic instability for voltages above the threshold value provided by the marginal stability relation [1,2]:

$$\frac{1}{8}V^2\mathrm{Pe} = 4\frac{\sinh k \cosh k - k}{\sinh k \cosh k + k - 2k^2 \coth k}, \tag{22}$$

with k being the the perturbation wave number. A characteristic feature of the respective marginal stability curve (line 4 in Fig. 1) 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 of Ref. [2], the linear growth rate of the perturbation λ also increases with wave number as $\lambda = \mathrm{Pe}^{1/3}V^{-2/3}k^{5/3} + O(k^{4/3})$.] Numerical solution of the full nonlinear limiting problem (1)–(3), (7)–(9), (17)–(19) [2] 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. These chaotic oscillations were interpreted in Ref. [2] as the mechanism of the low frequency access electric noise in overlimiting region in electrodialysis [1]. Our recent numerical experiments indicate that periodic and chaotic oscillations thresholds (but not the spatial period of the vortex sequence) are space discretization dependent. Thus, they are, at least in part, numerical artifacts, stemming from the possible mathematical ill-posedness of the bvp (1)–(3), (7)–(9), (17)–(19). This ill-posedness might well be one of the mathematical expressions of the short-wave instability of the quiescent steady state.

It is our purpose to show in this Brief Report that retaining the "small" terms y_0 and c_0 in Eqs. (4)–(6) removes this short-wave "catastrophe" and yields a reasonable linear wavelength selection. Seeking a solution of the free boundary problem (1)–(9), Eqs. (13) as a perturbation of the quiescent state (20), Eq. (21) of the form

$$c = c_0 + \alpha e^{\lambda t}e^{ikx}c_1(y), \tag{23}$$

$$\underline{v} = \underline{v}_0 + \alpha e^{\lambda t}e^{ikx}\underline{v}_1(y), \underline{v}_1 = u_1\underline{i} + v_1\underline{j}, \tag{24}$$

$$y_0 = 0 + \alpha e^{\lambda t}e^{ikx}y_1, \tag{25}$$

where $\alpha \ll 1$ is a perturbation parameter, yields, upon linearization with respect to α, the spectral problem

$$\lambda c_1 + \mathrm{Pe}w_1 = c_1'' - k^2c_1, \quad 0 < y < 1, \tag{26}$$

$$w_1^{(4)} - \left(2k^2 + \frac{\lambda}{\mathrm{Sc}}\right)w_1'' + \left(k^4 + \frac{\lambda}{\mathrm{Sc}}\right)w_1 = 0, \tag{27}$$

$$c_1(0) = \frac{\varepsilon^{2/3}}{3}\left[2a + \left(\frac{3}{4}V\right)^{2/3}\right]c_1'(0), \tag{28}$$

$$c_1(1) = 0, \tag{29}$$

$$w_1|_{y=0,1} = 0, \tag{30}$$

$$w_1''(1) = 0, \tag{31}$$

$$w_1'(0) = -\frac{V^2}{8}k^2c_1'(0). \tag{32}$$

Solution of Eqs. (23)–(32) yields for $\lambda = 0$ the implicit marginal stability relation between the threshold value of the control parameter V and the wave number k of the form

$$4\frac{\sinh k \cosh k - k + \frac{\varepsilon^{2/3}}{3}\left[2a + \left(\frac{3}{4}V\right)^{2/3}\right]k(\cosh^2 k - k\coth k)}{\sinh k \cosh k + k - 2k^2\coth k} = \mathrm{Pe}\frac{V^2}{8}. \tag{33}$$

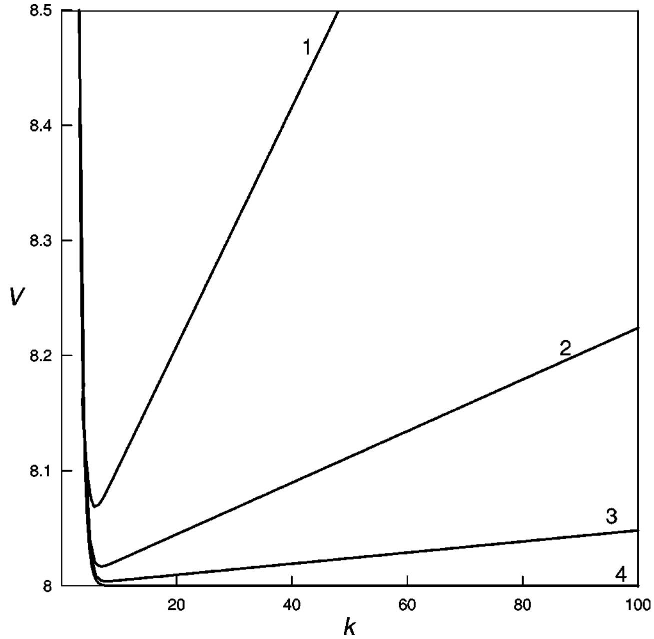

FIG. 1. Marginal stability curves in the V-k plane (V is the dimensionless voltage and k is the dimensionless wave number) for different values of the dimensionless Debye length ε: $1-\varepsilon=10^{-4}$, $2-\varepsilon=10^{-5}$, $3-\varepsilon=10^{-6}$, and $4-\varepsilon=0$.

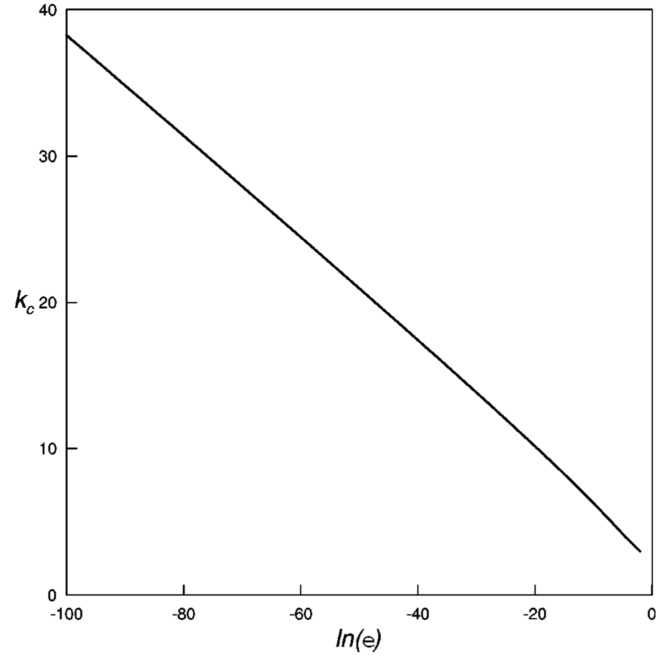

FIG. 2. Dependence of the dimensionless critical wave number k_c on the dimensionless Debye length ε.

In Fig. 1 we present the respective marginal stability curve for Pe$=0.5$ and three realistic values of ε, $\varepsilon=10^{-4}$, 10^{-5}, and 10^{-6}, as well as $\varepsilon=0$, corresponding to the short-wave instability. It is observed that for $\varepsilon>0$ all marginal stability curves 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 $0.7<2\pi/k_c<1.2$, in qualitative agreement with the nonlinear numerical results of Refs. [1,2]. The only weak variation of k_c for ε varying by orders of magnitude is easily inferred from Eq. (33). Indeed, taking the limit $\varepsilon\to 0$ in the equation for k_c we find

$$k_c \simeq \frac{1}{3}|\ln\varepsilon| + O(|\ln|\ln(\varepsilon)||) \quad \text{for} \quad \varepsilon \ll 1. \tag{34}$$

The full dependence of k_c on $|\ln(\varepsilon)|$ is presented in Fig. 2. The critical value V_c of the control parameter V at the minimum of the marginal stability curve is very close to the limiting value $4\sqrt{2/\text{Pe}}$.

Note that the short-wave instability and the related flattening of the marginal stability curve for large k both imply the presence of length scales in the outer problem comparable to those of the boundary layer. This explains why keeping the small boundary layer contributions produced the first significant term in the equation for k_c and, thus, resulted in removing the short-wave catastrophe, an effect whose significance likely transcends the limits of the particular phenomenon addressed herein. This is similar to the effect of surface tension in morphological instability in solidification and Saffman-Taylor instability [3–5], except that in our case the regularization comes from the boundary layer. This is in a way reminiscent of the viscous drag resolution of the D'Alembert paradox in the high Reynolds number potential flow around a symmetric body.

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