

Bulk electroconvection in electrolyte

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Bulk electroconvection pertains to flow induced by the action of the mean electric field upon the residual space charge in the macroscopic regions of a locally quasielectroneutral strong electrolyte. There existed a long time controversy in the literature as to whether quiescent electric conduction from such an electrolyte into a uniform charge selective solid, such as a metal electrode or an ion exchange membrane, is stable with respect to bulk electroconvection and whether bulk electroconvection at a nonuniform solid of this type may develop into a fully fledged flow. Numerical results reported in this paper confirm previous conclusions of a linear stability analysis concerning the nonexistence of bulk electroconvective instability, while we suggest that bulk electroconvection at a nonuniform charge selective solid results in a fully fledged flow on the length scale of nonuniformity of the surface.

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I. INTRODUCTION

The term electroconvection is used in at least four different contexts. One often refers to the electric-field-induced flow of nematic liquid crystals [1–3]. One also refers to the flow of liquid dielectrics caused by the action of the electric field on the space charge of ions of the appropriate sign injected in a low quantity into the fluid [4–6]. This term is also applied to the effects of an electric field acting on the surface charge accumulated at the interface between two weakly conducting fluids. Namely this has been studied by Taylor who, in the mid 1960s, introduced the leaky dielectric model to explain the behavior of droplets deformed by a steady field. This model, later extensively used by Melcher [7], formed an important step in the construction of a unified treatment of electrohydrodynamics of liquid dielectrics [8].

As opposed to the aforementioned systems, from here on, by the term electroconvection we refer to the flow of strong electrolytes at moderate concentration, that is, to liquids abundant with charge carriers of both signs. This type of electroconvection has been invoked, in particular, as a mechanism crucial for “overlimiting” conductance through cation-exchange electrodialysis membranes [9,10] and is important for ramified electrodeposition [11–13] and layering of colloid crystals on electrode surfaces [14,15].

The following two modes of electroconvection in strong electrolytes may be distinguished. The first is the relatively recently invoked “bulk” electroconvection due to the volume electric forces acting on a macroscopic scale in a locally quasielectroneutral electrolyte [16–20]. The second is the common electroosmosis, either of the classical “first” kind or of the “second” kind, according to the terminology of Dukhin [21]. Electroosmosis of the first kind relates to the electrolyte slip resulting from the action of the tangential electric field upon the space charge of a quasiequilibrium diffuse electric double layer. Electroosmosis of the second kind invoked by Dukhin [21–23] pertains to the similar action of a tangential electric field upon the extended space charge of the nonequilibrium double layer [24]. Both types of electroconvection could arise either in a thresholdless manner, due to inhomogeneity of the solid/liquid interface

(mechanical, such as roughness, or electric), or with a threshold via instability of quiescent electric conduction through a solution layer near a uniform flat charge-selective (permselective) solid, such as an electrode or ion exchange membrane. Passage of a dc current through such a layer causes the formation of electrolyte concentration gradients—concentration polarization in electrochemical terminology.

There was a long term controversy as to the existence of bulk electroconvective instability [16–19,25,26]. Bulk electroconvective instability was reported by Grigin [16]. In his paper, Grigin used the lowest order Galerkin approximation to study the critical perturbation mode for unrealistic boundary conditions as he did in subsequent publications on this subject [16–18]. Grigin’s papers were followed by an independent study by Bruinsma and Alexander in which they investigated the bulk electroconvective instability in a very thin polarization cell of finite width, for galvanostatic condition [19]. In terms of concentration polarization in a flat layer this setup amounted to the consideration of a short wave perturbation mode. The authors concluded that bulk electroconvective instability did exist, but, based on heuristic energy balance arguments, argued that it could hardly develop into a major mixing mechanism on a macroscopic scale. The linear stability analysis of Bruinsma and Alexander employed fewer boundary conditions (four) than was the order of the basic equation of the model (sixth), which led the authors to fix arbitrarily certain integration constants in the solution of the relevant spectral problem. This rendered questionable their conclusion concerning the occurrence of instability.

Following Ref. [16], a numerical study of linear bulk electroconvective instability in an electrolyte layer flanked by cation-selective surfaces has been carried out for galvanostatic and potentiostatic conditions in Refs. [25–27]. The conclusion of these studies was that instability did exist. Thus, both the numerical and analytical studies, including the “thin cell” linear stability analysis of Ref. [19] predicted the existence of bulk electroconvective instability.

On the other hand, in the numerical study by Buchanan and Saville [28] no evidence of this instability was found. The conclusion, hopefully final, of our recent analysis was

that bulk electroconvective instability of steady state quiescent concentration polarization did not exist [29]. (This conclusion of linear stability analysis is supported by the numerical results of Sec. III for the full nonlinear problem.) Thus, all reports regarding the existence of instability resulted from either analytical inaccuracies, such as an insufficient number of boundary conditions [19], their unphysical nature [16–18], or numerical artifacts. The latter likely rooted in the stiffness of the ordinary differential equations of the spectral problem [27], slow convergence of the Galerkin expansions, besides the unphysical Dirichlet boundary conditions for the electric potential [16–18], or too coarse finite difference grids employed [24–26].

Still, it remained unclear whether and at what scale bulk electroconvection due to conductive or mechanical nonuniformities of the charge selective surface may develop into a major mixing mechanism (it was argued in Ref. [19] that it may not). Answering this question is our main purpose in this paper. We are about to study the bulk electroconvective flow near an electrically homogeneous membrane with a specified periodic mechanical nonflatness of the membrane's surface. Recent experiments with membranes of this type with surface shape tailored based on heuristic electroconvective considerations showed a virtual elimination of saturation of the current-voltage curves [30].

Our paper is organized as follows. In Section II we present the basic equations of bulk electroconvection and formulate the model problem to be studied.

In Sec. III we present and discuss the results of a numerical solution of this problem. The main conclusion of this study is that bulk electroconvective instability at a flat charge selective surface, indeed, does not exist, whereas at a “wavy” surface bulk electroconvection represents an efficient mixing mechanism on the typical roughness length scale.

II. EQUATIONS OF BULK ELECTROCONVECTION: MODEL PROBLEM

Consider a univalent electrolyte layer flanked by two ideal cation exchange membranes (electrodes) placed at an average distance $2L$ from each other, with a dc electric current passed from the right (anode) to the left (cathode) membrane. With a natural scaling, the complete set of equations of convective electrodiffusion of ions in the electrolyte reads [29]

$$c_t^+ + \text{Pe}(\mathbf{v} \cdot \nabla)c^+ = \nabla \cdot (\nabla c^+ + c^+ \nabla \varphi), \quad (1)$$

$$c_t^- + \text{Pe}(\mathbf{v} \cdot \nabla)c^- = D \nabla \cdot (\nabla c^- - c^- \nabla \varphi), \quad (2)$$

$$\varepsilon^2 \Delta \varphi = c^- - c^+, \quad (3)$$

$$-\nabla p + \Delta \varphi \nabla \varphi + \Delta \mathbf{v} = 0, \quad (4)$$

$$\nabla \cdot \mathbf{v} = 0. \quad (5)$$

Here,

$$c^+ = \frac{\tilde{c}^+}{c_0}, \quad (6)$$

$$c^- = \frac{\tilde{c}^-}{c_0}, \quad (7)$$

$$\varphi = \frac{F\tilde{\varphi}}{RT} \quad (8)$$

are the dimensionless concentrations of cations and anions and the electric potential (dimensional variables are marked with tildes) and c_0 , typical electrolyte concentration (e.g., the average concentration in the layer); F , Faraday constant; R , universal gas constant; and T , absolute temperature. Furthermore,

$$\mathbf{v} = \frac{\tilde{\mathbf{v}}}{v_0} = v_x \mathbf{i} + v_y \mathbf{j} \quad (9)$$

$$p = \frac{\tilde{p}}{p_0} \quad (10)$$

are the dimensionless velocity vector (bold notations indicate vectors) and the pressure, respectively, with the typical velocity v_0 and pressure p_0 determined from the force balance in the dimensional version of the momentum equation (4) as

$$v_0 = \frac{d(RT/F)^2}{4\pi\eta L}, \quad (11)$$

$$p_0 = \frac{\eta v_0}{L}, \quad (12)$$

where d is the dielectric constant and η the dynamic viscosity of the solution.

Finally,

$$t = \tilde{t} \frac{D_+}{L^2} \quad (13)$$

is the dimensionless time and D_+ , cation diffusivity. The dimensionless spatial coordinates in (1)–(5) are normalized by L .

Equations (1) and (2) are those of convective electrodiffusion of cations and anions, respectively. Equation (3) is the Poisson equation for the electric potential, with $c^- - c^+$ in the right-hand side—the space charge due to the lack of local balance of ionic concentrations. The Stokes equation (4) is obtained from the full momentum equations by omitting the inertia terms. Finally, (5) is the continuity equation for an incompressible solution.

The dimensionless parameters in the system (1)–(5) are as follows.

(1) The dimensionless Debye length ε , defined as

$$\varepsilon = \left(\frac{r_d}{L} \right). \quad (14)$$

Here

$$r_d = \left(\frac{dRT}{4\pi C_0 F^2} \right)^{1/2} \quad (15)$$

is the dimensional Debye length.

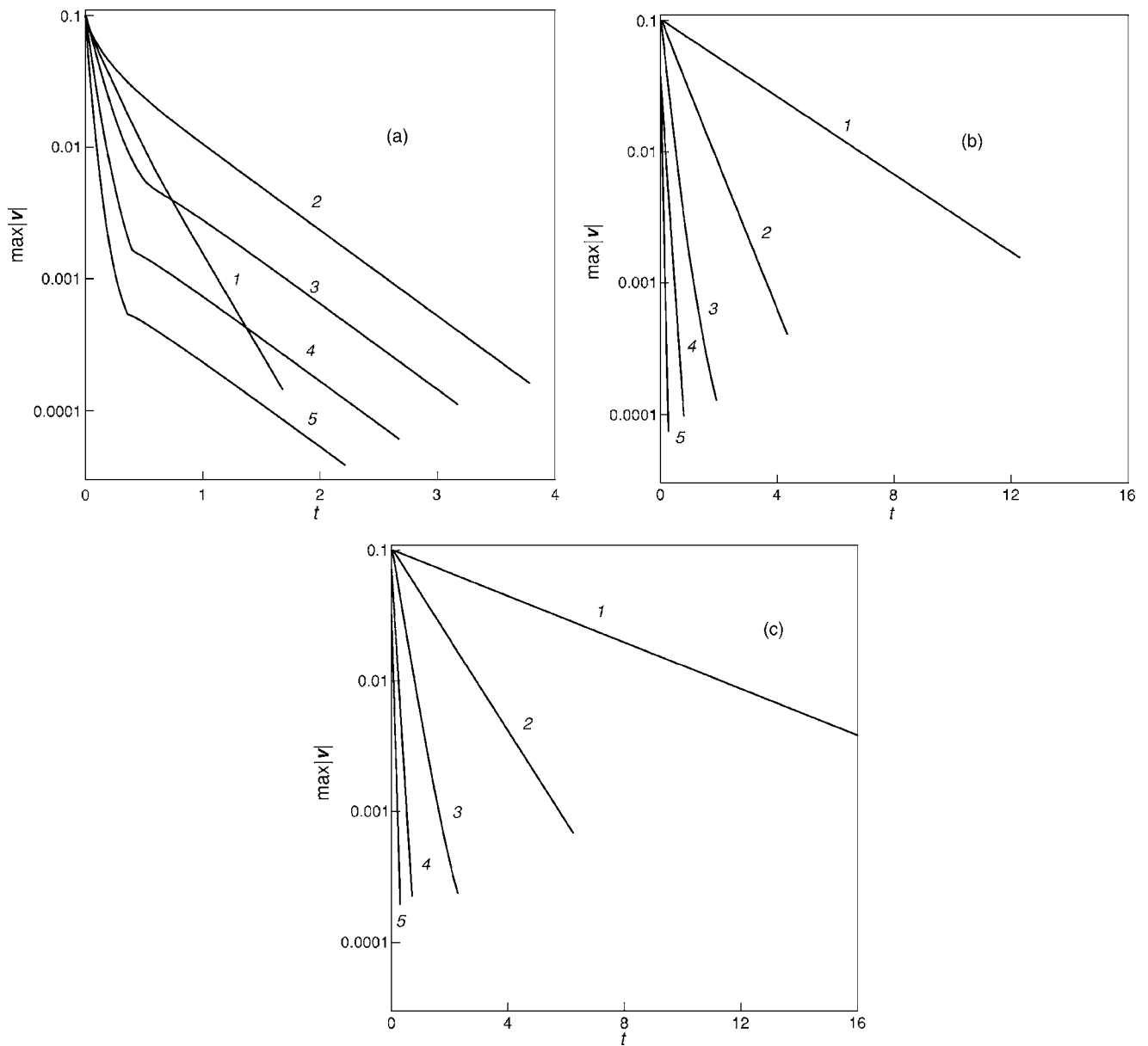


FIG. 1. Time dependence of maximal velocity for $A=0.1$ and five values of the wave number k (1, $k=0.5$; 2, $k=1$; 3, $k=2$; 4, $k=4$; 5, $k=8$): (a) $D^*=0.1$, (b) $D^*=1$, (c) $D^*=10$.

For a realistic macroscopic electrolyte system ($10^{-4} < L(\text{cm}) < 10^{-1}$), ($10^{-5} < c_0(\text{mol cm}^{-3}) < 10^{-3}$) ϵ^2 is a very small number in the range

$$0.2 \times 10^{-12} < \epsilon^2 < 2 \times 10^{-5}. \tag{16}$$

(2) The Peclet number is defined as

$$\text{Pe} = \frac{v_0 L}{D_+}, \tag{17}$$

or, using (11),

$$\text{Pe} = \left(\frac{RT}{F}\right)^2 \frac{d}{4\pi\eta D_+}. \tag{18}$$

According to (18), Pe does not depend on c_0 , L and for a typical aqueous low molecular electrolyte is of order unity, more precisely

$$\text{Pe} \approx 0.5. \tag{19}$$

(3) Finally, the relative anionic diffusivity is defined as

$$D = \frac{D_-}{D_+} \tag{20}$$

where D_+ and D_- are the dimensional cationic and anionic diffusivities, respectively. For realistic aqueous electrolyte solutions D may vary by two orders of magnitude in the range

$$0.1 < D < 10. \tag{21}$$

The extreme smallness of ϵ^2 motivates the commonly employed approximation of local “stoichiometric” electroneutrality, which amounts to setting $\epsilon=0$ in (3) yielding

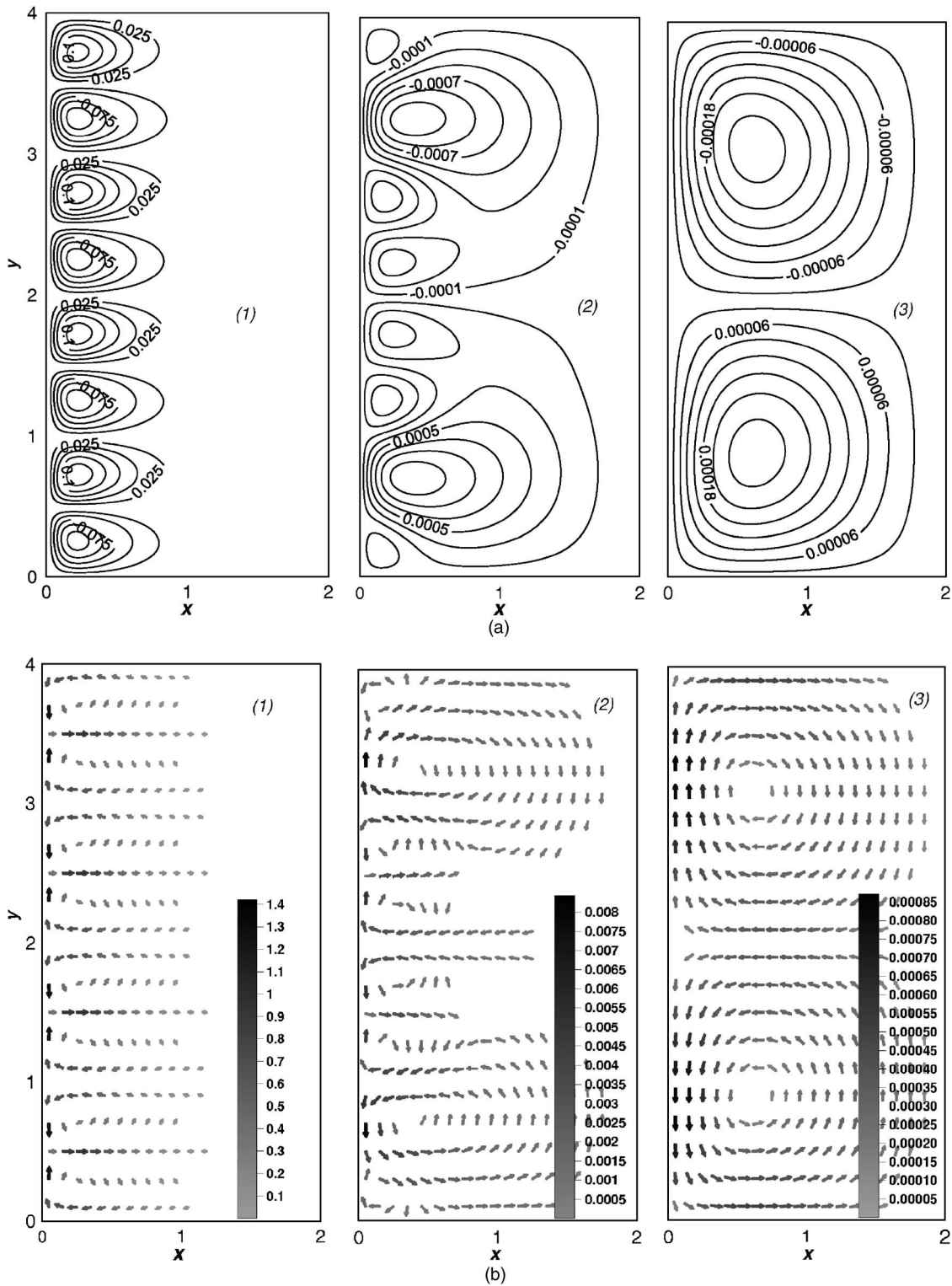


FIG. 2. (a) Plots of streamlines for $D^*=0.1$, $A=0.1$ and three consecutive moments of time: (1) $t=0.001$, (2) $t=0.2$, (3) $t=0.6$. (b) Plots of velocity field for $D^*=0.1$, $A=0.1$ and three consecutive moments of time: (1) $t=0.001$, (2) $t=0.2$, (3) $t=0.6$.

$$c^+ = c^- = c \quad (22)$$

everywhere in the bulk of the electrolyte, except for the boundary (electric double) layers of thickness ε . Note that although the space charge is very small (order ε^2) in the

Poisson equation (3), it is sufficient to generate an electroconvective flow with a Peclet number of order unity through the force term in the Stokes equation (4).

By adding (1) and (2), divided by D , and using (22) we arrive at the equation

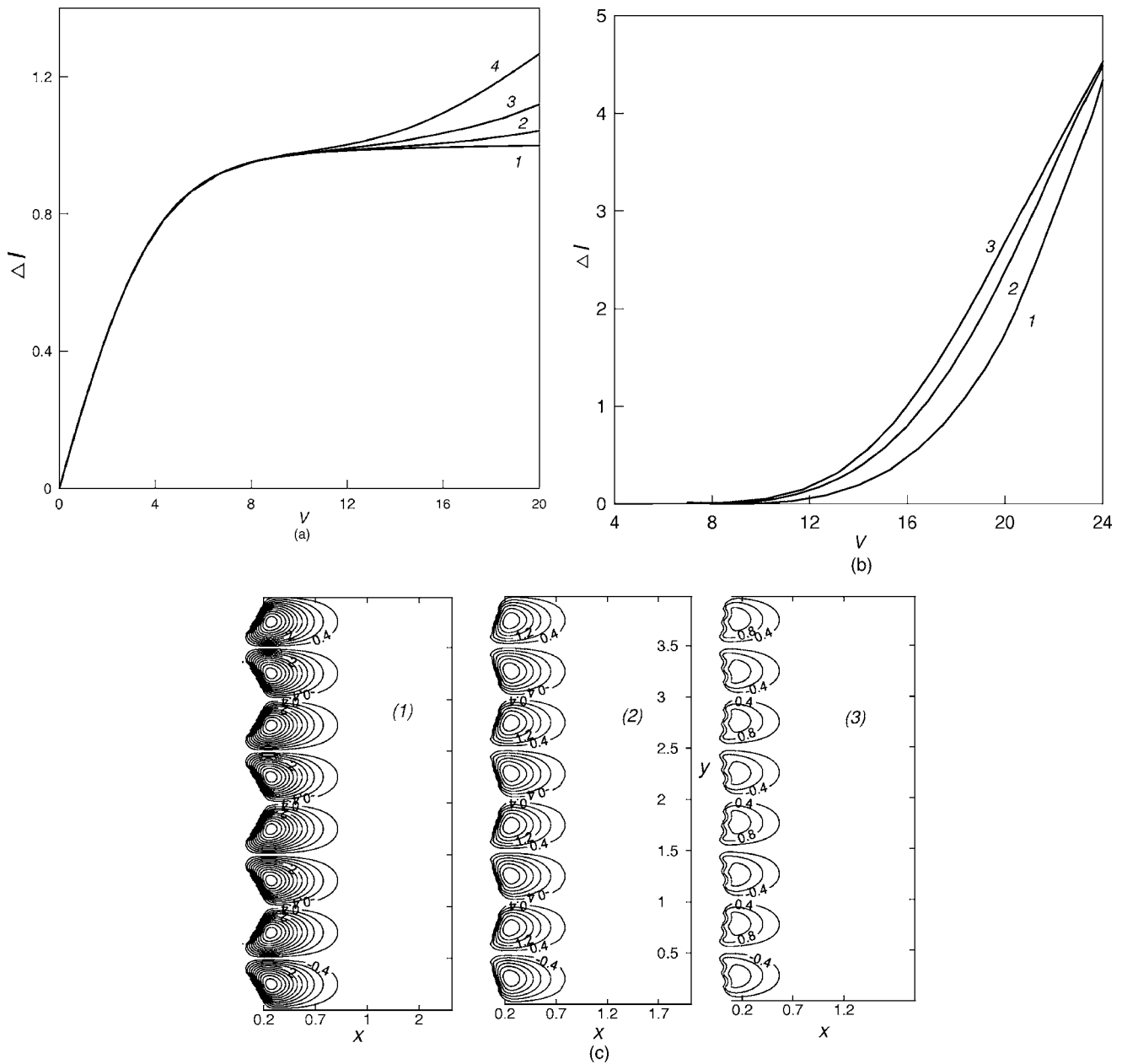


FIG. 3. (a) Relative current vs voltage plots for $D^* = 1$ and three cathode surface perturbation amplitudes with the same spacial period corresponding to $k = 4$ (1, unperturbed surface $A = 0$; 2, $A = 0.025$; 3, $A = 0.05$; 4, $A = 0.1$). (b) Plots of the increments of the relative current above the unity limiting value, normalized by perturbation amplitude, $\Delta I = (I - 1)/A$ as a function of voltage V for $D^* = 1$, $k = 4$, and three cathode surface perturbation amplitudes (1, $A = 0.025$; 2, $A = 0.05$; 3, $A = 0.1$). (c) Plots of streamlines for $D^* = 1$, $V = 20$, $k = 4$ and three cathode surface perturbation amplitudes (1, $A = 0.1$; 2, $A = 0.05$; 3, $A = 0.025$).

$$\text{Pe}(\mathbf{v} \cdot \nabla)c = D^* \Delta c. \quad (23)$$

Here,

$$D^* = \frac{2D}{1 + D}. \quad (24)$$

Similarly, by subtracting (2) from (1) we obtain, using (22)

$$(1 - D)\Delta c + (1 + D)\nabla \cdot (c \nabla \varphi) = 0. \quad (25)$$

Equations (23) and (25) together with Eqs. (4) and (5) form the set of equations of macroscopic bulk electroconvection.

In order to specify the boundary conditions, let us define a Cartesian coordinate system with the \hat{x} axis directed from the left membrane (cathode) to the right one (anode). Thus, the electrolyte layer occupies the domain

$$\Sigma = \{x_0(y) < x < 2, -\infty < y < \infty\}.$$

Here $x_0(y) = A \cos 2\pi k(y/Y)$ is a perturbation, of the membrane surface, k is the wave number of the perturbation, and A is its amplitude.

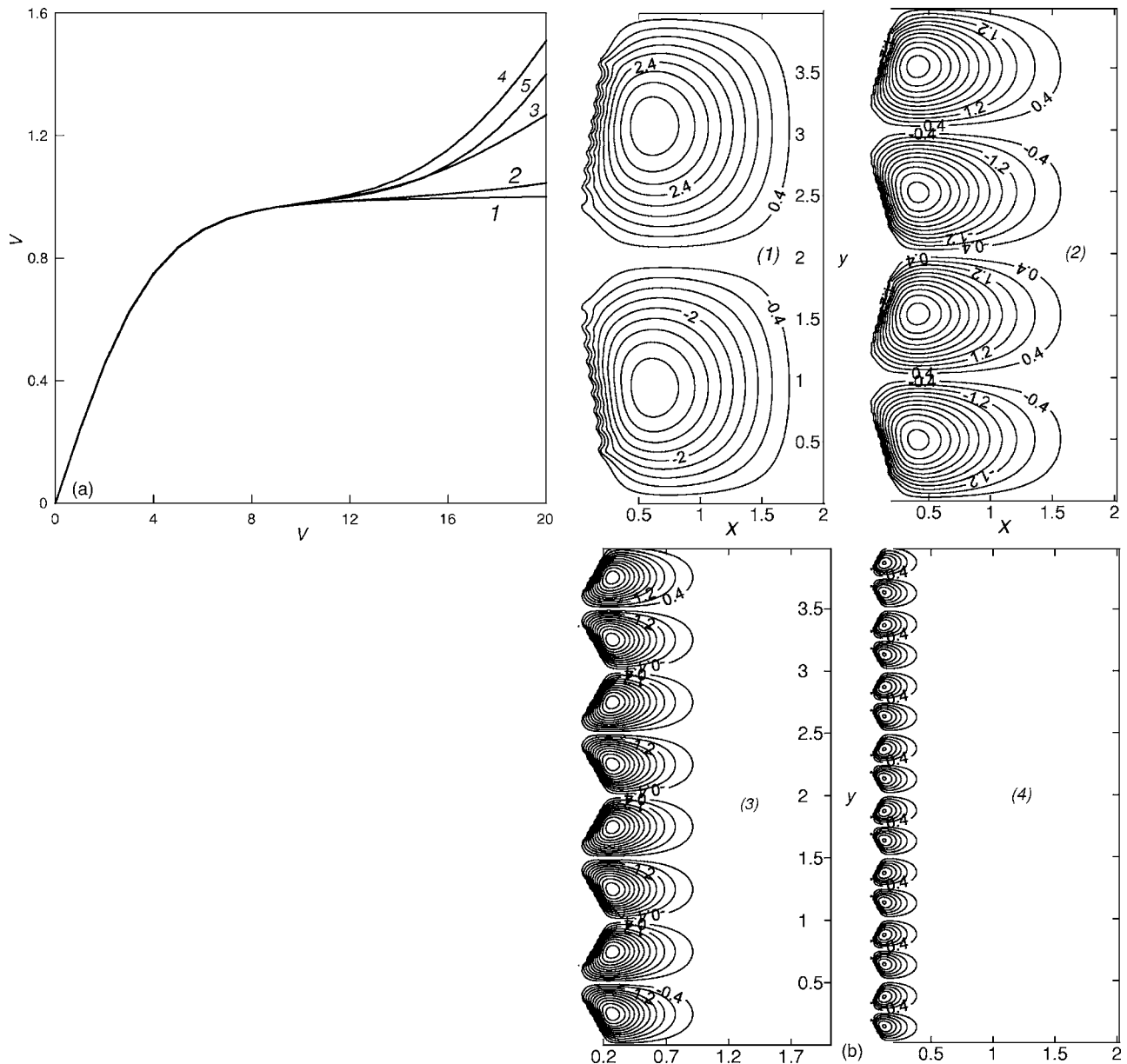


FIG. 4. (a) Relative current vs voltage plots for $D^*=1$, $A=0.1$ and four cathode surface perturbation wave numbers (1, unperturbed surface $k=0$; 2, $k=1$; 3, $k=2$; 4, $k=4$; 5, $k=8$). (b) Plots of streamlines for $D^*=1$, $V=20$, $A=0.1$ and four cathode surface perturbation wave numbers (1, $k=1$; 2, $k=2$; 3, $k=4$; 4, $k=8$).

The simplest version of potentiostatic nonslip boundary conditions reads

$$v_{x|x=x_0(y)} = v_{y|x=x_0(y)} = 0, \tag{26}$$

$$(\ln c + \varphi)|_{x=x_0(y)} = \ln(p_1) - V, \tag{28}$$

$$(\ln c + \varphi)|_{x=2} = \ln(p_1), \tag{29}$$

$$(c_x - c\varphi_x)|_{x=2} = (c_x - c\varphi_x)|_{x=0} = 0, \tag{30}$$

$$\int_{\Sigma} (c - 1) dx dy = 0. \tag{31}$$

Here p_1 is the fixed charges concentration inside the membrane and V (voltage) is the potential drop between the membranes (control parameter in our treatment). Equation (31) specifies at unity the average concentration of anions in the system. To complete the formulation we also assume periodicity of the solution in y with period $Y=4$.

III. RESULTS AND DISCUSSION

The boundary value problem (4), (5), (23), and (25)–(31) was solved numerically for given values of parameters D , Pe ,

and V using an iterative explicit finite difference scheme with a second-order accuracy approximation in the equations and boundary equations. Stability and convergence of the numerical code were tested by varying the grid spacing.

First, we employ the developed numerical code in order to verify the linear stability analysis of Refs. [29,31] of the one-dimensional quiescent conduction (concentration polarization) solution for the flat membrane ($x_0 \equiv 0$). This solution reads [31]

$$\bar{c}(x) = \frac{I}{2}x + 1 - \frac{I}{2}, \quad (32)$$

$$\bar{\varphi}(x) = \ln\left(\frac{I}{2}x + 1 - \frac{I}{2}\right) + \ln\frac{P_1}{\left(1 + \frac{I}{2}\right)^2}, \quad (33)$$

where

$$I \stackrel{def}{=} (\bar{c}_x + \bar{c}\varphi_x) \quad (34)$$

is the electric current density given by the expression

$$I = 2 \frac{1 - e^{-V/2}}{1 + e^{-V/2}}. \quad (35)$$

We study the evolution of a periodic perturbation of the quiescent state (32) and (33) by solving the time-dependent version of the boundary value problem (4), (5), (23), and (25)–(31) for the flat membrane ($x_0 \equiv 0$) subject to the initial conditions

$$c(x, y, 0) = \bar{c}(x) + A \cos 2\pi k \frac{y}{Y}, \quad (36)$$

$$\varphi(x, y, 0) = \bar{\varphi}(x), \quad (37)$$

where k is the wave number of the perturbation and A is its amplitude. Thus, in Figs. 1(a)–1(c) we present the plots of time dependence of maximal velocity for D^* equal 0.1, 1, 10, respectively, for various k . It is observed that for the cationic diffusivity higher than the anionic one ($D^* < 1$; equal to 0.1 in our example) bulk electroconvection selects by the slowest decay the mode with a finite nonvanishing wavelength of the order of the diffusion layer thickness. (This is particularly clearly seen in Figs. 2(a) and 2(b) where we present the flow fields for three consecutive moments of time starting from a short-scale vortical initial state—large vortices picked by the selection “die last.”) This stands in accord with the linear

stability analysis of the nonequilibrium electroosmotic instability for which bulk electroconvection provides a wave number selection for the same conditions [31]. On the other hand, for $D^* \geq 1$, the decay rate increases monotonically with the wave number of perturbation.

We next investigate the flow dependence on the boundary perturbation amplitude for a given spatial period of the former. It is observed, as illustrated in Figs. 3(a)–3(c), that a detectable flow appears at a definite stage of concentration polarization which is largely independent of amplitude, whereas the vigor of the flow tends to become proportional to the amplitude with the development of concentration polarization. As a natural measure of contribution of convection to the ionic transport, we employ the ratio of the actual electric current in the system to the unity limiting quiescent conduction current in a plane-parallel cell I^{lim} , corresponding to a vanishing concentration at the solution/cathode interface (this is the Nusselt number for our system). In Fig. 3(a) we present this relative current vs voltage plots for three cathode surface perturbation amplitudes with the same spacial period corresponding to $k=4$. It is observed that all three overlimiting voltage-current curves take off at roughly the same voltage. Furthermore, in Fig. 3(b) we present the plots of the increments of the relative current above the unity limiting value, normalized by perturbation amplitude, as a function of voltage. It is observed that upon the increase of the voltage all three plots tend to a single asymptotic curve. In Fig. 3(c) we illustrate the arising flow pattern by the plots of streamlines for the same three boundary perturbation amplitudes as in Figs. 3(a) and 3(b).

Finally, our tests of the effect of variation of the spacial period of surface perturbation upon the mass transfer show that the latter increases with the increase of period as long as this is smaller than the cell thickness. For an illustration we present in Fig. 4(a) the plots of relative current versus voltage for four surface perturbation periods. The streamline plots of the respective flow pattern are presented in Fig. 4(b).

IV. CONCLUSIONS

Bulk electroconvection, while universally stabilizing in quiescent concentration polarization in a system with plane-parallel geometry [29,31], provides an efficient mixing mechanism in a system with nonplanar periodic distortion of the cathode surface. The mixing is due to a vortex pattern which develops on the length scale of the spatial period of surface perturbation.

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