Electroconvective instability in concentration polarization and nonequilibrium electro-osmotic slip

Isaak Rubinstein and Boris Zaltzman

DSEEP, Blaustein Institute for Desert Research, Ben-Gurion University of the Negev, Sede Boqer Campus 84990, Israel

Irina Lerman

Department of Mathematics, Ben-Gurion University of the Negev, Beer-Sheva, Israel

This paper concerns the comparison of electroconvective instability in concentration polarization at an ion-selective membrane with previously reported nonequilibrium electro-osmotic instability. Electro-osmotic formulation represents an asymptotic limit case of the electroconvective one. An improved nonequilibrium electro-osmotic slip formula is derived. Linear stability analysis for various nonequilibrium electro-osmotic formulations is carried out, including the analytic studies of the short- and long-wave limits. The obtained results are compared with those for a full electroconvective formulation. It is observed that the shortwave singularity typical for the nonequilibrium electro-osmotic instability is removed in the full electroconvective formulation. The effect of ionic diffusivities ratio on stability is discussed.

I. INTRODUCTION

The term electroconvection is being used in at least four different contexts. Thus, by this term one often refers to the electric field induced flow of nematic liquid crystals [1–3]. Besides, the same term relates to the flow of liquid dielectrics caused by the action of 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 being 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, hereon we refer by term electroconvection 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 [16–23]. The second is the common electro-osmosis, either of the classical "first" kind or of the "second" kind, according to terminology of Dukhin [24]. Electro-osmosis 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 electric double layer [24–29]. Electro-osmosis of the "second" kind

invoked by Dukhin [24–27] pertains to the similar action of a tangential electric field upon the extended space charge of the nonequilibrium double layer [42]. In our previous studies we developed a theory of nonequilibrium electro-osmotic slip of this kind.

We showed that this slip causes instability of quiescent passage of a dc electric current from an electrolyte solution into a charge selective solid, such as an electrode or ion-exchange electrodialysis membrane [9–33]. This instability was of a singular shortwave type: marginal stability curve in the control parameter (voltage) versus wave number plane did not have a minimum whereas the linear growth rate increased indefinitely upon the increase of the wave number. This suggested a need to look for a regularized formulation and a wave number selection criterion. (Numerical computations in the full nonlinear problem showed selection of convective vortices on the length scale of the liquid layer thickness, likely due to shortwave cutoff by the finite difference grid.) Inclusion of higher order terms into the limiting formulation did provide the necessary regularization [33], although it is worth remembering in this connection that electro-osmotic slip as such is just a limiting expression of electroconvection in the boundary (electric double) layer whose thickness is negligible compared to the macroscopic length scale in the system. Thus it seems natural in discussing an adequate regularization of the shortwave catastrophe to compare linear stability results for the limiting electro-osmotic formulations with those for the full electroconvective one. Such a comparison is the central goal of the present study.

Concentration polarization (CP) is the electrochemical term for a complex of 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. Expression of CP is a current/voltage (*CV*) curve of a characteristic shape: current saturation at the "limiting" value, corresponding to the van-

ishing interface concentration is followed by inflexion and transition to the "overlimiting" conductance regime, accompanied by the appearance of the low frequency excess electric noise. The search for a mechanism of "overlimiting" conductance and the related noise phenomena was the main motivation for our study of electroconvection.

Our presentation is organized as follows. In Sec. II we recapitulate the formulation for electroconvection in a solution layer flanked by two solid cation-selective walls. (In our previous studies we dealt with a less physical case of a diffusion layer at such a wall.) Furthermore, we outline the theory of quiescent CP in such a layer and summarize the main features of nonequilibrium electric double layer. This is followed by a review of two types of electroconvection in our system: bulk electroconvection, due to the action of the self-consistent electric field upon the residual space charge of stoichiometrically locally electroneutral bulk; and electroosmotic slip due to the electric forces acting in the diffuse part of the electric double layer. Furthermore, we derive the full expression for the limiting nonequilibrium electroosmotic slip, taking into account contributions disregarded in our previous leading order derivation [31]. Next, in Sec. III we employ this, and the previously derived leading order slip formula to study the linear hydrodynamic stability of quiescent concentration polarization, while taking into account bulk electroconvection, which universally has a stabilizing effect. Finally, in Sec. IV we compare these linear stability results for the limiting slip formulations with the corresponding results for the full electroconvective formulation. It is shown that the shortwave blow up present in all limiting formulations is removed in the full formulation, providing for a linear wave number selection criterion. Except for this feature, the improved slip formula derived in Sec. II yields a neutral stability curve extremely close to that in full formulation. Finally, it is observed that the "two solid walls" formulation, as opposed to that for "diffusion layer" yields a linear growth rate of the Nikolayewsky type [48] in which a shortwave instability is accompanied by a slow decay of the long wave mode. This may provide for a spatiotemporal chaos in the system—possibly a source of the excess electric noise in the overlimiting conductance.

II. TWO TYPES OF ELECTROCONVECTION IN CONCENTRATION POLARIZATION, NONEQUILIBRIUM ELECTRIC DOUBLE LAYER, AND NONEQUILIBRIUM ELECTRO-OSMOTIC SLIP

The prototypical two-dimensional model problem for concentration polarization in a layer of a univalent electrolyte flanked by two ideally permselective cation-exchange membranes under the passage of a normal electric current in the dimensionless form reads [10,31,34], (tilded notations are used below for the dimensional variables, as opposed to their untilded dimensionless counterparts):

Equations $\{-\infty < x < \infty, \quad 0 < y < 2\}$:

$$c_t^+ + \text{Pe}(\mathbf{v} \cdot \boldsymbol{\nabla})c^+ = \frac{D+1}{2} \boldsymbol{\nabla}(\boldsymbol{\nabla}c^+ + c^+\boldsymbol{\nabla}\varphi), \quad (1)$$

$$c_t^- + \text{Pe}(\mathbf{v} \cdot \boldsymbol{\nabla})c^- = \frac{D+1}{2D} \boldsymbol{\nabla}(\boldsymbol{\nabla}c^- - c^-\boldsymbol{\nabla}\varphi), \quad (2)$$

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

$$\frac{1}{\text{Sc}}\mathbf{v}_t = -\boldsymbol{\nabla}p + \Delta\varphi\boldsymbol{\nabla}\varphi + \Delta\mathbf{v}, \quad (4)$$

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

The Nernst-Planck equations (1) and (2) describe convective electrodiffusion of cations and anions, respectively. Equation (3) 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 (4) is obtained from the full momentum equation by omitting the nonlinear inertia terms. Finally, Eq. (5) is the continuity equation for an incompressible solution. Spatial variables in Eqs. (1)–(5) have been nondimensionalized with the half layer thickness L whereas

$$t = \frac{\tilde{t}D_0}{L^2}, \quad (6)$$

$$c^+ = \frac{\tilde{c}^+}{c^0}, \quad (7)$$

$$c^- = \frac{\tilde{c}^-}{c^0}, \quad (8)$$

$$\varphi = \frac{F\tilde{\varphi}}{RT} \quad (9)$$

are, respectively, the dimensionless time, concentrations of cations and anions and the electric potential, with c_0 the typical concentration, e.g., average anion concentration in the layer, F is the Faraday constant, R is the universal gas constant, T is the absolute temperature, and the "salt" diffusivity D_0 is defined as

$$D_0 = \frac{2D_+D_-}{D_+ + D_-}, \quad (10)$$

where D_+ and D_- are the cationic and anionic diffusivities, respectively. Furthermore, $\mathbf{v}$ and p in Eqs. (4) and (5) are the dimensionless velocity vector and pressure, defined as

$$\mathbf{v} = \frac{\tilde{\mathbf{v}}}{v_0} = u\hat{\mathbf{i}} + w\hat{\mathbf{j}}, \quad (11)$$

$$p = \frac{\tilde{p}}{p_0}, \quad (12)$$

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

$$v_0 = \frac{d(RT/F)^2}{4\pi\eta L}, \quad (13)$$

$$p_0 = \frac{\eta v_0}{L}, \qquad (14)$$

where d is the dielectric constant of the solution and η is the dynamic viscosity of the fluid. Below we list and discuss the dimensionless parameters in the system (1)–(5).

(1) The dimensionless Debye length ε is defined as

$$\varepsilon = \frac{(dRT)^{1/2}}{2F(\pi c_0)^{1/2}}. \qquad (15)$$

ε^2 lies in the range $0.2 \times 10^{-12} < \varepsilon^2 < 2 \times 10^{-5}$, for a realistic macroscopic system with $10^{-4} < L(\text{cm}) < 10^{-1}$, $10^{-4} < c_0(\text{mol}) < 1$.

(2) The Peclet number Pe is defined as

$$\text{Pe} = \left(\frac{v_0 L}{D_0}\right), \qquad (16)$$

or, using Eq. (13),

$$\text{Pe} = \left(\frac{RT}{F}\right)^2 \frac{d}{4\pi\eta D_0}. \qquad (17)$$

As indicated previously [35], Pe does not depend on c_0, L and for a typical aqueous low molecular electrolyte is of order unity (more precisely, $\text{Pe} \simeq 0.5$).

(3) Sc is the Schmidt number defined as

$$\text{Sc} = \frac{\nu}{D_0}. \qquad (18)$$

Here ν is the kinematic viscosity of the fluid.

(4) Finally, the relative cationic diffusivity D is defined as

$$D = \frac{D_+}{D_-}. \qquad (19)$$

Boundary conditions:
$y=0$ *(cathode membrane's surface)*

$$(c_y^- - c^-\varphi_y)|_{y=0} = 0. \qquad (20)$$

Condition (20) states impermeability for anions of an ideally permselective cation exchange membrane.

$$c^+|_{y=0} = p_1. \qquad (21)$$

This condition, prescribing interface concentration equal to that of the fixed charges inside the membrane (p_1), is asymptotically valid for $p_1 \gg 1$ and amounts to disregarding the coion invasion of an ideally permselective membrane and the presence of an $O(\varepsilon/\sqrt{p_1})$ thick boundary layer on the membrane side of the interface

$$\varphi|_{y=0} = -V. \qquad (22)$$

This condition, valid for the so-called potentiostatic operation, specifies at value V (voltage) a potential drop between the membranes; V is the control parameter in our treatment.

$$\mathbf{v}|_{y=0} = \mathbf{0}. \qquad (23)$$

This is the common nonslip condition.

$y=2$ *(anode membrane's surface)*:

$$(c_y^- - c^-\varphi_y)|_{y=2} = 0, \qquad (24)$$

$$c^+|_{y=2} = p_1, \qquad (25)$$

$$\varphi|_{y=2} = 0, \qquad (26)$$

$$\mathbf{v}|_{y=2} = \mathbf{0}. \qquad (27)$$

Conditions (24)–(26) are analogous to Eqs. (20)–(23).

Conditions (20)–(27) are complemented by

$$\lim_{l\to\infty} \frac{1}{2l} \int_{-l}^{l} \int_0^2 c^-(x,y)dydx = 2, \qquad (28)$$

specifying the number of anions in the system.

When time dependent situations are addressed, the boundary value problem, Eqs. (1)–(5) and (20)–(28), is supplemented by a suitable set of initial conditions.

The boundary value problem, Eqs. (1)–(5) and (20)–(28), possesses a one-dimensional quiescent conduction solution with $\mathbf{v}=\mathbf{0}$, and c^+, c^-, and φ satisfying the relations

$$(c_y^+ + c^+\varphi_y)_y = 0, \qquad (29)$$

$$(c_y^- - c^-\varphi_y)_y = 0, \qquad (30)$$

$$\varepsilon^2\varphi_{yy} = c^- - c^+, \qquad (31)$$

$$(c_y^- - c^-\varphi_y)|_{y=0,2} = 0, \qquad (32)$$

$$c^+|_{y=0,2} = p_1 \qquad (33)$$

$$\int_0^2 c^-(x,y)dy = 2, \qquad (34)$$

$$\varphi|_{y=2} = 0, \qquad (35)$$

$$\varphi|_{y=0} = -V, \qquad (36)$$

and

$$p(y) = \frac{1}{2}\varphi_y^2 + p_c, \qquad (37)$$

where p_c is an arbitrary integration constant.

For quasiequilibrium conditions the solution of the boundary value problem, Eqs. (29)–(36), splits into the "outer" locally electroneutral solution, valid in the "bulk" of the segment $0 < y < 2$, and the "inner" or electric double layer solutions, valid in the ε vicinity of the interfaces at $y=0,2$ [10,31,34]. The inner and outer solutions are connected through the standard procedures of matched asymptotic expansions. The outer leading order solution is that to the quasielectroneutral boundary value problem:

$$(\bar{c}_y + \bar{c}\bar{\varphi}_y)_y = 0, \quad 0 < y < 2, \qquad (38)$$

$$(\bar{c}_y - \bar{c}\bar{\varphi}_y)_y = 0, \quad 0 < y < 2, \qquad (39)$$

$$(\bar{c}_y - \bar{c}\bar{\varphi}_y)|_{y=0,2} = 0, \tag{40}$$

$$(\ln \bar{c} + \bar{\varphi})|_{y=0} = \ln p_1 - V, \tag{41}$$

$$(\ln \bar{c} + \bar{\varphi})|_{y=2} = \ln p_1, \tag{42}$$

$$\int_0^2 \bar{c}(y)dy = 2. \tag{43}$$

Here

$$\bar{c} \stackrel{\text{def}}{=} c^+ = c^-, \tag{44}$$

and Eq. (41) expresses the continuity of the electrochemical potential of cations (capable of penetrating the interfaces at $y=0,2$) across the discontinuities of the electric potential and ionic concentration, modeling the electric double layer in the outer problem. The outer (quiescent concentration polarization) solution is obtained by a straightforward integration of the boundary value problem, Eqs. (38)–(43), in the form

$$\bar{c}(y) = \frac{I}{2}y + 1 - \frac{I}{2}, \tag{45}$$

$$\bar{\varphi}(y) = \ln\left(\frac{I}{2}y + 1 - \frac{I}{2}\right) + \ln\frac{p_1}{\left(1 + \frac{I}{2}\right)^2}, \tag{46}$$

where

$$I \stackrel{\text{def}}{=} (\bar{c}_y + \bar{c}\varphi_y) \tag{47}$$

is the electric current density in the system. Expression (47) yields the current-voltage relation

$$I = 2\frac{1 - e^{-V/2}}{1 + e^{-V/2}}. \tag{48}$$

From Eq. (48), when $V \to \infty$, $I \to I^{\text{lim}} = 2$ and, simultaneously, by Eq. (45), $\bar{c}(0) \to 0$. 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, currents much greater than the limiting one are readily passed through virtually ideally permselective cation-exchange membranes (overlimiting conductance mentioned in Sec. I). The 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 in general [9,10,31,35–37] and the present study, in particular.

In order to investigate the stability of the quiescent concentration polarization solution, Eqs. (45)–(48), one has to allow for lateral motions. In this case too the problem splits into those 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 read [35]:

$$\bar{c}_t + \text{Pe}(\bar{\mathbf{v}} \cdot \nabla)\bar{c} = \frac{D+1}{2}\nabla(\nabla\bar{c} + \bar{c}\nabla\bar{\varphi}), \tag{49}$$

$$\bar{c}_t + \text{Pe}(\bar{\mathbf{v}} \cdot \nabla)\bar{c} = \frac{D+1}{2D}\nabla(\nabla\bar{c} - \bar{c}\nabla\bar{\varphi}), \tag{50}$$

$$\frac{1}{\text{Sc}}\bar{\mathbf{v}}_t = -\nabla\bar{p} + \Delta\bar{\varphi}\nabla\bar{\varphi} + \Delta\bar{\mathbf{v}}, \tag{51}$$

$$\nabla \cdot \bar{\mathbf{v}} = 0, \tag{52}$$

whereas the boundary layer analysis provides, in addition to boundary conditions, Eqs. (41) and (42), an expression for electro-osmotic slip that is the tangential fluid velocity at the outer edge of the electric double layer. Disregarding this, and assuming nonslip at the solid wall instead, yields the bulk electroconvection formulation, for which a long time controversy existed with regard to stability of one-dimensional quiescent concentration polarization solution, Eqs. (45)–(48). Recently, it has been finally shown that for bulk electroconvection this solution is stable. Moreover, it will be shown below that the electric force term in Eq. (51) always has a stabilizing effect on the instability due to nonequilibrium electro-osmosis.

For electro-osmotic 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, quasiequilibrium electro-osmosis, or electro-osmosis of the first kind, following terminology of Dukhin [24], pertains to currents below the limiting value. For such currents the diffuse part of the electric double layer (EDL) preserves its common quasiequilibrium structure essentially identical with that for zero current. Theory of quasiequilibrium electro-osmosis at a permselective interface was developed by Dukhin [25]. An essential part of this theory is accounting for polarization of the EDL 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

$$-\frac{1}{2}[(\varphi_z)^2]_x + \varphi_x\varphi_{zz} + u_{zz} = 0, \tag{53}$$

where $z = y/\varepsilon$ is the cathodic boundary layer coordinate (correspondingly, $z = 2 - y/\varepsilon$ for the anodic boundary layer). For a quasiequilibrium boundary layer, potential $\varphi(x,z)$ in Eq. (53) is substituted from the solution of the Poisson-Boltzmann equation

$$\varphi_{zz} = \bar{c}(x,0)(e^{\varphi - \bar{\varphi}(x,0)} - e^{-\varphi + \bar{\varphi}(x,0)}) \tag{54}$$

of the form

$$\varphi(x,z) = \bar{\varphi}(x,0) + 2\ln\frac{e^{s/2} + 1 + (e^{s/2} - 1)e^{-\sqrt{2\bar{c}(x,0)}}}{e^{s/2} + 1 - (e^{s/2} - 1)e^{-\sqrt{2\bar{c}(x,0)}}}. \tag{55}$$

Here $\bar{c}(x,0)$, $\bar{\varphi}(x,0)$ are, respectively, the electrolyte concentration and the electric potential at the outer edge of the electric double layer and

$$\varsigma(x) = \varphi(x,0) - \bar{\varphi}(x,0) \qquad (56)$$

is the dimensionless ς potential.

Integration of Eq. (53) with Eq. (55) yields for the electro-osmotic slip velocity, instead of the common Helmholtz-Smoluchowsky formula,

$$u_s = \varsigma\bar{\varphi}_x \qquad (57)$$

valid for an impermeable interface, the expression

$$u_s = \varsigma\left(\bar{\varphi}_x + \frac{\bar{c}_x}{\bar{c}}\right) - 4\frac{\bar{c}_x}{\bar{c}}\ln\frac{1+e^{\varsigma/2}}{2}. \qquad (58)$$

A peculiarity of Eq. (58) is that for an ideally permselective cation exchange membrane maintained at a constant potential $\ln\bar{c}+\bar{\varphi}=$const, that is, $\bar{c}_x/\bar{c}=-\bar{\varphi}_x$ and for $\varsigma\to-\infty$, Eq. (58) yields

$$u_s = -(4\ln 2)\bar{\varphi}_x. \qquad (59)$$

That is, the factor at $-\bar{\varphi}_x$ (electro-osmotic factor) tends to a maximal upper value upon the increase of ς (negative). This stands in contrast with the respective prediction of Helmholtz-Smoluchowsky formula, Eq. (57), and is a direct consequence of polarization of the EDL at a permselective interface.

Hydrodynamic stability of the quiescent concentration polarization with a limiting quasiequilibrium electro-osmotic slip, Eq. (59), was studied in [28]. 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, EDL remains at quasiequilibrium. Namely this ceases being the case at the cathodic membrane ($y=0$) when the current approaches the limiting value. We already saw that in this case $\bar{c}\to 0$ and $\bar{\varphi}\to-\infty$, which makes Eq. (54) formally unsuitable for calculation of φ in EDL and, thus, through Eq. (53), for calculation of electro-osmotic velocity u_s. This reflects a fundamental structural change which occurs in the system as it moves away from quasiequilibrium upon $I\to I^{\lim}$.

Generally, quasiequilibrium is typified by the division of the system into a locally quasielectroneutral bulk and a quasiequilibrium boundary layer (diffuse EDL). This picture breaks down upon $I\to I^{\lim}$, as reflected, in particular, in the inconsistency of the local electroneutrality approximation which appears in the basic concentration polarization solution Eqs. (45)–(48) in this limit. Indeed, according to Eq. (46)

$$\varphi_{yy}(0) = \frac{I^2}{4}\frac{1}{\left(1-\frac{I}{2}\right)^2} \to \infty, \quad \text{when } I\to I^{\lim}=2. \quad (60)$$

This implies that for any finite ε, however small, setting the left-hand side of the Poisson equation (3) equal to zero, becomes inconsistent. This breakdown, first notified by Levich [38], has motivated several studies [39–45,31] of the space
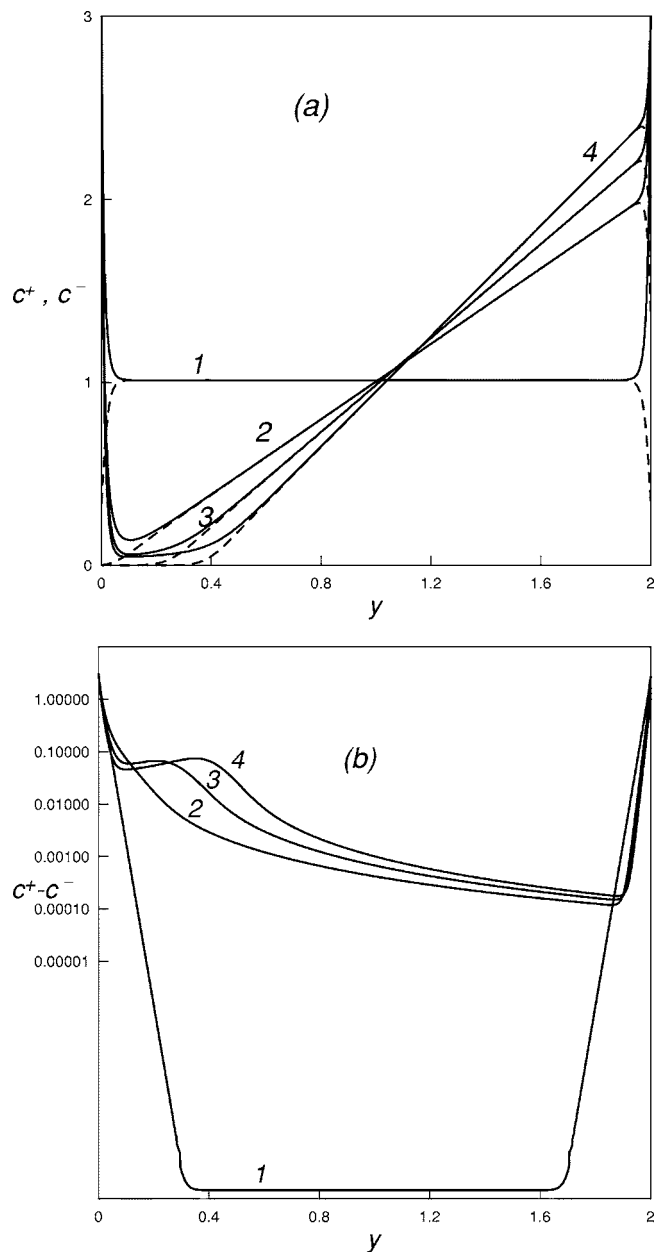

FIG. 1. (a) Ionic concentration profiles (c^+: continuous lines, c^-: dashed lines) for $\varepsilon=0.01$ and four values of voltage ($1-V=0$, $2-V=7$, $3-V=15$, and $4-V=25$). (b) Space charge density (c^+-c^-) profile for $\varepsilon=10^{-2}$ and four values of voltage ($1-V=0$, $2-V=7$, $3-V=15$, and $4-V=25$).

charge of the nonequilibrium electric double layer (also [46] and references therein). The picture of it that emerged from a numerical solution of the one-dimensional problem (29)–(37) [42], subsequently confirmed and elaborated by several numerical and analytic studies [43–45,31,46], may be summarized as follows [see Figs. 1(a), 1(b), and 2].

For $0 < V = O(1)$ ($I < I^{\lim}$), 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 the respective electroneutral region a linear ionic concentration profile holds in accordance with Eq. (45). The maximal slope of the concentration profile in these conditions is 1 (which corre-
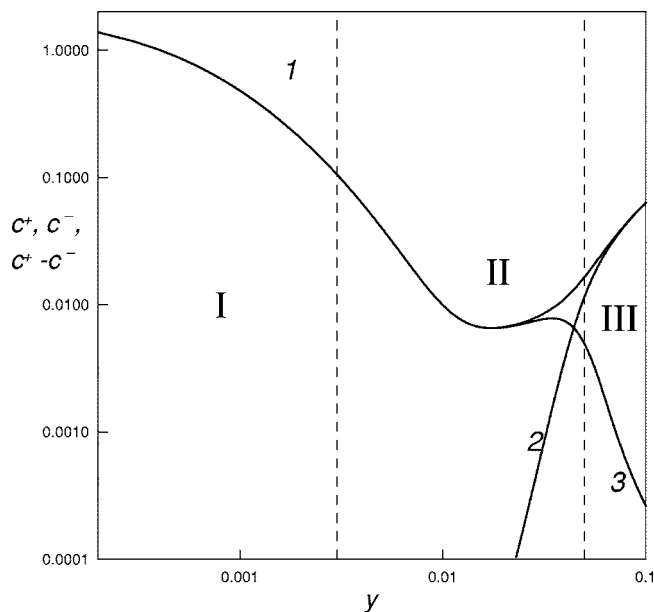
FIG. 2. Structure of the nonequilibrium boundary layer. I: quasiequilibrium boundary layer, II: extended space charge region, and III: transition layer to electroneutral bulk. 1: cation concentration, 2: anion concentration, and 3: space charge density ($c^+ - c^-$). $\varepsilon = 10^{-3}$, $V = 20$.

sponds to $I = I^{lim} = 2$. This picture remains essentially valid up to $V = O(|\ln \varepsilon|)$ ($I \leqslant I^{lim}$). For $O(|\ln \varepsilon|) < V < O(\varepsilon^{-1})$ ($I \approx I^{lim}$), the following three regions may be distinguished (from right to left). The quasielectroneutral "bulk" region with a linear concentration profile with the approximately unity slope. 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 quasiequilibrium, $O(\varepsilon)$ thick, boundary layer at the left edge. Upon a further increase of voltage up to $O(\varepsilon^{-1})$ the extended space charge region reaches a finite size $O(1)$ and so does the current increment over the limiting value $[0 < I - I^{lim} = O(1)]$.

This observation of development in the course of concentration polarization of a nonequilibrium electric double layer with the extended space charge region lead Dukhin and his colleagues [24–27] (see also references in [24]) to conjecture the existence of nonequilibrium electrokinetic phenomena which they termed electrokinetic phenomena of the second kind.

Accurate analysis of nonequilibrium electro-osmotic slip at a flat permselective membrane with an applied voltage V $[V > O(|\ln \varepsilon|)]$, was carried out in [31], resulting in the expression

$$u_s = -\frac{1}{8} V^2 \left. \frac{\frac{\partial^2 c}{\partial x \partial y}}{\frac{\partial c}{\partial y}} \right|_{y=0}. \tag{61}$$

Derivation of Eq. (61) employed the asymptotic theory of the nonequilibrium double electric layer, previously developed by Listovnichy [44], and amounted to carrying out an

analysis similar to that outlined above for quasiequilibrium electro-osmosis. An account for polarization proved to be more necessary here, since a large potential drop between the membrane surface and the bulk was concerned, that is, namely those conditions for which saturation of the electro-osmotic factor occurred for a quasiequilibrium electro-osmotic slip. For obtaining a better physical insight into expression (61), it is worth noting that $c_y|_{y=0}$ is one-half the local current density through the membrane which is the main local characteristic controlling the thickness of the non-equilibrium EDL and thus the electric potential in it.

Expression (61) is valid to the leading quadratic order in V, for $V > O(|\ln \varepsilon|)$. Below we rederive this expression while keeping the next order term linear in V. As shown in the next section, this term is crucially important with regard to its effect on linear stability for voltage in the physically relevant range. In our derivation we shall follow that of Ref. [31]. The leading order inner problem for the depleted (cathodic) boundary layer near $y = 0$, written in the original variables, reads

Equations:

$$(c_y^+ + c^+ \varphi_y)_y = 0, \tag{62}$$

$$(c_y^- - c^- \varphi_y)_y = 0, \tag{63}$$

$$\varepsilon^2 \varphi_{yy} = c^- - c^+, \tag{64}$$

$$-\frac{1}{2}[(\varphi_y)^2]_x + \varphi_x \varphi_{yy} + u_{yy} = 0, \tag{65}$$

$$w = 0. \tag{66}$$

[Equation (53) has been reproduced here as Eq. (65) for convenience of presentation.]

Boundary conditions:

$$\varphi(x,0) = -V, \tag{67}$$

$$c^+(x,0) = p_1, \tag{68}$$

$$(c_y^- - c^- \varphi_y)|_{y=0} = 0, \tag{69}$$

$$u(x,0) = 0. \tag{70}$$

Solutions c^+, c^-, φ, u, w are to be matched with those of the electroneutral outer (bulk) problem $\overline{c^+} = \overline{c}$, $\overline{c^-} = \overline{c}$, $\overline{\varphi}$, $\overline{u}$, $\overline{w}$, respectively.

Equations (62)–(66) may be rewritten as

$$\varepsilon(c^+ - c^-)_y = E(c^+ + c^-) + \varepsilon I, \quad 0 < y < 2, \tag{71}$$

$$\varepsilon c_y^+ = Ec^+ + \varepsilon I, \quad 0 < y < 2, \tag{72}$$

$$\varepsilon E_y = c^+ - c^-, \quad 0 < y < 2, \tag{73}$$

where

$$E = -\varepsilon \varphi_y \tag{74}$$

and constant I, defined by Eq. (47), is the current density at the outer edge of the boundary layer.

We are concerned with the solution in the extended space charge region, developing near the cathodic membrane. By substituting Eqs. (72)–(74) into Eq. (71) and integrating the resulting equation, we obtain

$$c^+ = \frac{\varepsilon}{2}E_y + \frac{1}{4}E^2 + \frac{I}{2}(y - y_0). \tag{75}$$

Integration constant y_0, corresponding to the value of y at the outer edge of the extended space charge region, will be determined in due course. By substituting Eq. (75) into Eq. (72) we obtain the following equation for E:

$$\varepsilon^2 E_{yy} = \frac{1}{2}E^3 + \frac{I}{2}(y - y_0)E + \varepsilon I. \tag{76}$$

Seeking an outer asymptotic solution of Eq. (76) as a power expansion in ε, we find that

$$E = \begin{cases} -\dfrac{\varepsilon}{y - y_0} - \dfrac{3\varepsilon^2}{2I}\dfrac{1}{(y - y_0)^4} + \cdots & \text{for } y - y_0 \gg \varepsilon^{2/3}, \\[4mm] -\sqrt{2I(y - y_0)} - \dfrac{\varepsilon}{2(y - y_0)} + \dfrac{5\varepsilon^2}{8\sqrt{2I}}\dfrac{1}{(y - y_0)^{5/2}} + \cdots & \text{for } y - y_0 \ll -\varepsilon^{2/3}. \end{cases} \tag{77}$$

This outer solution is valid for $O(|y - y_0|) > \varepsilon^{2/3}$, with the range $y - y_0 \gg \varepsilon^{2/3}$ corresponding to the quasielectroneutral bulk, where $|c^+ - c^-| = O(\varepsilon^{2/3})$ and $|\varphi_y| \leq O(\varepsilon^{-2/3})$.

On the other hand, the range $y - y_0 \ll -\varepsilon^{2/3}$ corresponds to the extended space charge zone with $O(|\varphi_y|) > \varepsilon^{-2/3}$. Furthermore, the range $|y - y_0| \leq O(\varepsilon^{2/3})$ corresponds to the transition layer between the two aforementioned regions. To analyze the solution of Eq. (72) in this layer, we define the respective layer variables F and z through the equalities

$$E = I^{1/3}\varepsilon^{1/3}F, \tag{78}$$

$$y - y_0 = \frac{\varepsilon^{2/3}}{I^{1/3}}z. \tag{79}$$

In terms of F and z, Eq. (72) is transformed into the inhomogeneous Painleve equation of the second kind of the form

$$F_{zz} = \frac{1}{2}F^3 + zF + 1, \tag{80}$$

with z in the range $-\infty < z < \infty$, for $\varepsilon \to 0$. Details of solution of Eq. (80) for finite z are of no importance for us in the current context. It is sufficient only to point out that, by assuming that the left-hand side of Eq. (75) vanishes for $z \to \pm\infty$, we obtain an asymptotic representation of $F(z)$ in the form

$$F = \begin{cases} -\dfrac{1}{z} - \dfrac{3}{2}\dfrac{1}{z^4} + o\!\left(\dfrac{1}{z^4}\right), & z > 0, \\[4mm] -\sqrt{-2z} - \dfrac{1}{2z} - \dfrac{5}{8\sqrt{2}}\dfrac{1}{(-z)^{5/2}} + \left(\dfrac{1}{|z|^{5/2}}\right), & z < 0, \end{cases} \tag{81}$$

in accordance with Eq. (77). Moreover, function $F(z)$, as defined by Eq. (80) with asymptotics (81), is independent of

ε, I, y_0, and fully describes the transition from the locally quasielectroneutral bulk to the extended space charge zone. Finally, the region $0 < y < O(\varepsilon)$ corresponds to the quasiequilibrium boundary layer at the membrane/solution interface in which the following equalities hold to the leading order in ε [47]:

$$c^+ = \text{const} \times e^{-\varphi}, \quad 0 < y < O(\varepsilon), \tag{82}$$

$$\varepsilon^2\varphi_{yy} = -c^+, \quad 0 < y < O(\varepsilon). \tag{83}$$

A unique solution of Eqs. (82) and (83) is found using boundary conditions (33) and (36) and the condition of matching of φ_y with E in the extended space charge region for $y/\varepsilon \to \infty$.

Thus, referring to the sketch in Fig. 2, the nonequilibrium double layer at the cathode $y = 0$ has the following structure:

1. quasiequilibrium sublayer of width $O(\varepsilon)$: $0 < y < O(\varepsilon)$;

2. extended space charge zone of width of the order larger than $\varepsilon^{2/3}$:

$$O(\varepsilon) < y < y_0 - O(\varepsilon^{2/3}), \quad O(y_0) > \varepsilon^{2/3}; \text{ and}$$

3. transition layer around y_0 of width of the order of $\varepsilon^{2/3}$, separating between the extended space charge zone and quasielectroneutral bulk

$$|y - y_0| \leq O(\varepsilon^{2/3}).$$

It has been shown in Ref. [31] that whenever the extended space charge is present $[V > O(|\ln \varepsilon|)]$, it gives the major contribution to the electro-osmotic slip. We note that for the very notion of slip to be applicable, the width of the nonequilibrium double layer has to shrink to zero upon $\varepsilon \to 0$. This sets an upper bound on the voltage concerned. On the other hand, this voltage has to be sufficiently high for the extended space charge zone to form, that is for electro-

osmosis to switch from the first to the second kind. As shown in [31], the voltage range resulting from these two limitations is

$$|\ln \varepsilon| \leqslant O(V) < \frac{1}{\varepsilon}. \qquad (84)$$

We precede next to calculation of the slip velocity. For this purpose we evaluate the electric force terms in Eq. (65). We have in accordance with Eqs. (74), (78), and (79)

$$\varphi_y^2 = I^{2/3} \varepsilon^{-4/3} F^2(z), \quad z = \frac{y - y_0}{\varepsilon^{2/3}} I^{1/3}, \qquad (85)$$

which yields

$$\frac{1}{2}\frac{\partial}{\partial x}(\varphi_y)^2 = \frac{1}{3} I_x I^{-1/3} \varepsilon^{-4/3} F^2(z) + I^{2/3} \varepsilon^{-4/3} F(z) F'(z) z_x. \qquad (86)$$

Next, in the spirit of analysis in Ref. [31], let us define "the cathodic" edge of the quasielectroneutral bulk y^* (or z^*) by the equality

$$c^+(y^*) - c^-(y^*) = O(\varepsilon). \qquad (87)$$

By Eqs. (73) and (78) this implies

$$I^{2/3} \varepsilon^{-1/3} F'(z^*) = O(1)$$

or

$$F'(z^*) = \varepsilon^{1/3} I^{-2/3}, \qquad (88)$$

which yields, taking into account Eqs. (79) and (81)

$$z^* = I^{1/3} O(\varepsilon^{-1/6}), \qquad (89)$$

$$y^* = O(\varepsilon^{1/2}) + y_0. \qquad (90)$$

Furthermore, for the electric potential in the boundary layer we have, in accordance with Eqs. (74), (78), and (79),

$$\varphi(x,z) = \int_z^{z^*} F(s)ds + \Phi(x), \qquad (91)$$

where

$$\overset{\text{def}}{\Phi(x)} = \varphi(x,y^*). \qquad (92)$$

Equation (91) yields

$$\varphi_x(x,z) = -F(z)z_x + \Phi'(x). \qquad (93)$$

On the other hand, we have, taking into account Eqs. (78) and (79),

$$\varphi_{yy} = -I^{2/3} \varepsilon^{-4/3} F'(z). \qquad (94)$$

Equations (93) and (94) imply

$$\varphi_x \varphi_{yy} = -[\Phi'(x) - F(z)z_x] I^{2/3} \varepsilon^{-4/3} F'(z). \qquad (95)$$

Substitution of Eqs. (86) and (95) into Eq. (65) yields

$$u_{yy} = -\Phi'(x)\varphi_{yy} + \frac{1}{3} I^{-1/3} I_x \varepsilon^{-4/3} F^2. \qquad (96)$$

Integration of Eq. (96) with boundary condition (70) and condition at the infinity $u_y|_{y=y^*(z=z^*)} = 0$ yields

$$u|_{y=y^*} = -\mathsf{s}_x[\mathsf{s} + \varphi_y(y^*)y^*] - \frac{I_x y_0^3}{9\varepsilon^2}. \qquad (97)$$

Here

$$\overset{\text{def}}{\mathsf{s}} = -V - \Phi(x). \qquad (98)$$

Note that

$$O(V) > O(|\ln[\varepsilon]|), \ O(|\Phi(x)|) \leqslant O(|\ln[\varepsilon]|). \qquad (99)$$

Let us evaluate next the second term in parenthesis in Eq. (97). $\varphi_y(y^*)$ is evaluated using the equality

$$(c_y - c\varphi_y)|_{y=y^*} = 0. \qquad (100)$$

By Eq. (100), taking into account Eqs. (74), (87), and (78)

$$c(y^*) = c^-(y^*) = c^+(y^*) = \frac{1}{4}E^2 + \frac{I}{2}(y^* - y_0)$$

$$= \frac{1}{4}\frac{I^{2/3}\varepsilon^{2/3}}{(z^*)^2} + \frac{I}{2}O(\varepsilon^{1/2}) = \frac{I}{2}O(\varepsilon^{1/2}) = c_y(y^*)O(\varepsilon^{1/2}).$$

This, together with Eq. (100), implies

$$\varphi_y|_{y=y^*} = O(\varepsilon^{-1/2}). \qquad (101)$$

Combined with Eq. (91), this in turn implies that the second term in parenthesis in the right-hand side of Eq. (97) is negligible compared to the first one. On the other hand, by the analysis in Ref. [31]

$$y_0 = \left[\frac{3\varepsilon V}{4\sqrt{c_y|_{y=0}}}\right]^{2/3}. \qquad (102)$$

Thus, finally, from Eq. (97), using Eq. (102), for $O(V) > O(|\ln \varepsilon|)$ we have for the slip velocity

$$u|_{y=y^*} = -V\Phi_x - \frac{1}{8}V^2\frac{c_{xy}}{c_y}. \qquad (103)$$

This expression for the slip velocity is different from Eq. (61) by the presence of the first Helmoltz-Smoluchovsky type term. In spite of the fact that this term, linear in $\mathsf{s} = O(V)$, is smaller by the order of magnitude compared to the second quadratic term, it might be quite important for a realistic finite V. In the next section this will be illustrated upon the linear stability analysis of quiescent concentration polarization. We also point out the form of this term, typical for quasiequilibrium conditions of electro-osmosis at a solid impermeable for ions, as opposed to the saturating expression (58). This is intuitively understandable, since development of the extended space charge amounts essentially to "detachment" of quasielectroneutral bulk solution from the solid with the local chemical equilibrium (continuity of the electrochemical potential) holding only across the thin quasiequilibrium part of the electric double layer, but not across

the bulk nonequilibrium part of it, including the extended space charge region.

To conclude this section we recapitulate the formulation of the limiting problem.

Equations $\{-\infty < x < \infty, \quad 0 < y < 2\}$:

$$c_t + \text{Pe}(\mathbf{v} \cdot \boldsymbol{\nabla})c = \Delta c, \tag{104}$$

$$\frac{D-1}{D+1}\Delta c + \boldsymbol{\nabla}(c \boldsymbol{\nabla} \varphi) = 0, \tag{105}$$

$$\frac{1}{\text{Sc}}\mathbf{v}_t = -\boldsymbol{\nabla}p + \mathbf{B}_{ec} + \Delta\mathbf{v}, \tag{106}$$

$$\boldsymbol{\nabla} \cdot \mathbf{v} = 0. \tag{107}$$

Here

$$\mathbf{B}_{ec} = \boldsymbol{\nabla}\varphi\Delta\varphi. \tag{108}$$

Boundary conditions:

$y = 2$ *(anodic membrane's surface)*:

For this "enriched" membrane/solution interface we assume besides impermeability for anions, Eq. (40), local equilibrium Eq. (42) and, correspondingly, a limiting quasiequilibrium electro-osmotic slip of Dukhin's type [Eq. (59)].

$y = 0$ *(cathodic membrane's surface)*:

At the depleted cathodic membrane for voltage in the range $O(|\ln \varepsilon|) < V < O(1/\varepsilon)$ corresponding to electro-osmosis of the second kind, we have, besides the anion impermeability condition (40), vanishing of concentration

$$c|_{y=0} = 0, \tag{109}$$

and the slip condition which we rewrite in the form:

$$w|_{y=0} = 0, \tag{110}$$

$$u|_{y=0} = H_S + E_{O2}. \tag{111}$$

Here

$$H_S = -V\varphi_x, \tag{112}$$

$$E_{O2} = -\frac{1}{8}V^2\frac{c_{xy}}{c_y}. \tag{113}$$

Notations (108), (112), and (113) have been introduced for convenience to ease the formulation of a sequence of limiting problems (e.g., electro-osmotic slip of the second kind without bulk electroconvection: $E_{O2} \neq 0$, $H_S = 0$, $\mathbf{B}_{ec} = \mathbf{0}$; full slip formula without bulk electroconvection: $E_{O2} \neq 0$, $H_S \neq 0$, $\mathbf{B}_{ec} = \mathbf{0}$; electro-osmotic slip of the second kind with bulk electroconvection: $E_{O2} \neq 0$, $H_S = 0$, $\mathbf{B}_{ec} \neq \mathbf{0}$ and, finally, full slip formula with bulk electroconvection: $E_{O2} \neq 0$, $H_S \neq 0$, $\mathbf{B}_{ec} \neq \mathbf{0}$.) In Sec. III, stability of quiescent concentration polarization in these problems will be studied. In Sec. IV results of this study will be compared with those for the full electroconvective problem, Eqs. (1)–(5) and (20)–(28).

III. LINEAR STABILITY OF QUIESCENT CONCENTRATION POLARIZATION IN THE LIMITING ELECTRO-OSMOTIC FORMULATIONS

In this section we deal with linear stability analysis of the limiting current quiescent concentration polarization solution [Eqs. (45) and (46) with $I = I^{\text{lim}} = 2$]

$$c_0(y) = y, \tag{114}$$

$$\varphi_0(y) = \ln y, \tag{115}$$

$$\mathbf{v}_0 = u_0\hat{\mathbf{i}} + w_0\hat{\mathbf{j}} = 0, \tag{116}$$

in the limiting electro-osmotic formulations (104)–(108), (40), (42), (59), and (109)–(113). Because of singularity of potential $\varphi_0(y)$ at $y = 0$ it is preferable to rewrite this boundary value problem in terms of anionic electrochemical potential $\mu^- \overset{\text{def}}{=} \ln c - \varphi$ and concentration c as unknowns in the form:

Equations $\{-\infty < x < \infty, \quad 0 < y < 2\}$:

$$c_t + \text{Pe}(\mathbf{v} \cdot \boldsymbol{\nabla})c = \Delta c, \tag{117}$$

$$c_t + \text{Pe}(\mathbf{v} \cdot \boldsymbol{\nabla})c = \frac{D+1}{2D}\boldsymbol{\nabla} \cdot (c \boldsymbol{\nabla} \mu^-), \tag{118}$$

$$\frac{1}{\text{Sc}}\mathbf{v}_t = -\boldsymbol{\nabla}p + \mathbf{B}_{ec} + \Delta\mathbf{v}, \tag{119}$$

$$\mathbf{B}_{ec} = \boldsymbol{\nabla}(\ln c - \mu^-)\Delta(\ln c - \mu^-), \tag{120}$$

$$\boldsymbol{\nabla} \cdot \mathbf{v} = 0. \tag{121}$$

Boundary conditions:

$y = 0$:

$$c|_{y=0} = 0, \tag{122}$$

$$\mu^-_y|_{y=0} = 0, \tag{123}$$

$$w|_{y=0} = 0, \tag{124}$$

$$u|_{y=0} = H_S + E_{O2}. \tag{125}$$

Let us note that boundary condition (122) yields

$$c(x,y) = c_y(0,y)y + O(y^2) \tag{126}$$

and therefore

$$\mu^-_x(x,0) = \frac{c_{xy}(x,0)}{c_y(x,0)} - \varphi_x(x,0). \tag{127}$$

Thus the linear in ς term in the electro-osmotic slip condition (125) assumes the form

$$H_S = V\left(\mu^-_x|_{y=0} - \frac{c_{xy}}{c_y}\bigg|_{y=0}\right). \tag{128}$$

$y = 2$:

$$2 \ln c - \mu^-|_{y=2} = \ln p_1, \tag{129}$$

$$\mu_y^-|_{y=2} = 0, \tag{130}$$

$$w|_{y=2} = 0, \tag{131}$$

$$u|_{y=2} = (2 \ln 2)\mu_x^-. \tag{132}$$

In terms of μ^- and c concentration polarization solution (114)–(116) reads $c_0(y)=y$, $\mu_0^-(y)=0$, $\hat{\mathbf{v}}_0=u_0\hat{\mathbf{i}}+w_0\hat{\mathbf{j}}=\mathbf{0}$. The linearized problem for the perturbations $c_1(x,y,t)$, μ_1^-, and $\mathbf{v}_1=u_1\hat{\mathbf{i}}+w_1\hat{\mathbf{j}}$ of this solution reads

$$c_{1t} + \text{Pe } w_1 = \Delta c_1, \tag{133}$$

$$c_{1t} + \text{Pe } w_1 = \frac{D+1}{2D} \nabla (c_0 \nabla \mu_1^-), \tag{134}$$

$$\frac{1}{\text{Sc}} \Delta w_{1t} = \Delta^2 w_1 + B_{ec}, \tag{135}$$

$$c_1|_{y=0} = 0, \tag{136}$$

$$\mu_{1y}^-|_{y=0} = 0, \tag{137}$$

$$w_1|_{y=0} = 0, \tag{138}$$

$$w_{1y}|_{y=0} = H_S^{\text{lin}} + E_{O2}^{\text{lin}}, \tag{139}$$

$$c_1 - \mu^-|_{y=2} = 0, \tag{140}$$

$$\mu_{1y}^-|_{y=2} = 0, \tag{141}$$

$$w_1|_{y=2} = 0, \tag{142}$$

$$w_{1y}|_{y=2} = - (2 \ln 2)\mu_{xx}^-. \tag{143}$$

Here

$$B_{ec} = \Delta \left(\frac{c^1}{y} - \mu_1^- \right)_{xx} \frac{1}{y} - \frac{2}{y^3} \left(\frac{c^1}{y} - \mu_1^- \right)_{xx}, \tag{144}$$

$$H_S^{\text{lin}} = V(c_{1yxx}|_{y=0} - \mu_{xx}^-|_{y=0}), \tag{145}$$

$$E_{O2}^{\text{lin}} = \frac{1}{8}V^2 c_{1yxx}|_{y=0}. \tag{146}$$

Equations (133)–(143) yield the spectral (eigenvalue) problem in the form

$$\lambda \xi + \text{Pe } w = \xi'' - k^2 \xi, \quad 0 < y < 2, \tag{147}$$

$$\frac{\lambda \xi + \text{Pe } w}{y} = \frac{D+1}{2D} \left(\mu'' + \frac{\mu'}{y} - k^2 \mu \right), \quad 0 < y < 2, \tag{148}$$

$$w^{(4)} - \left(2k^2 + \frac{\lambda}{\text{Sc}} \right)w'' + \left(k^4 + \frac{\lambda k^2}{\text{Sc}} \right)w = -\widetilde{B_{ec}}, \quad 0 < y < 2, \tag{149}$$

$$\xi(0) = 0, \tag{150}$$

$$\mu'(0) = 0, \tag{151}$$

$$w(0) = 0, \tag{152}$$

$$w'(0) = \widetilde{H_S} + \widetilde{E_{O2}}, \tag{153}$$

$$\xi(2) - \mu(2) = 0, \tag{154}$$

$$\mu'(2) = 0, \tag{155}$$

$$w(2) = 0, \tag{156}$$

$$w'(2) = 2 \ln 2k^2\mu(2). \tag{157}$$

Here

$$\widetilde{B_{ec}} = k^2 \left(\frac{D-1}{(1+D)y^2}[\lambda \xi + \text{Pe } w] + 2\frac{\xi' - \mu}{y^3} - \frac{\mu'}{y^2} \right), \tag{158}$$

$$\widetilde{H_S} = Vk^2[\mu(0) - \xi'(0)], \tag{159}$$

$$\widetilde{E_{O2}} = - \frac{V^2}{8}k^2\xi'(0), \tag{160}$$

and ξ, μ, and w are the Fourier transforms

$$\xi(y) = \int_{-\infty}^{\infty} e^{ikx}\overline{c}_1(x,y)dx, \tag{161}$$

$$\mu(y) = \int_{-\infty}^{\infty} e^{ikx}\overline{\mu_1^-}(x,y)dx, \tag{162}$$

$$w(y) = \int_{-\infty}^{\infty} e^{ikx}\overline{w}_1(x,y)dx, \tag{163}$$

of the spatial factors $\overline{c}_1$, $\overline{w}_1$, $\overline{\mu_1^-}$ in the representation

$$c_1(x,y,t) = \overline{c}_1(x,y)e^{\lambda t}, \tag{164}$$

$$\mu_1^-(x,y,t) = \overline{\mu_1^-}(x,y)e^{\lambda t}, \tag{165}$$

$$w_1(x,y,t) = \overline{w}_1(x,y)e^{\lambda t}, \tag{166}$$

where k is the wave number and λ is the spectral parameter–linear growth rate [Re $\lambda > 0$ implies instability of solution Eqs. (114)–(116). Since $\widetilde{B_{ec}}$ in the right-hand side of Eq. (149) is singular at $y=0$, we employ the approach of Ref. [33] and regularize the unperturbed solution by including in it the higher order terms in ε. Specifically, we assume that at
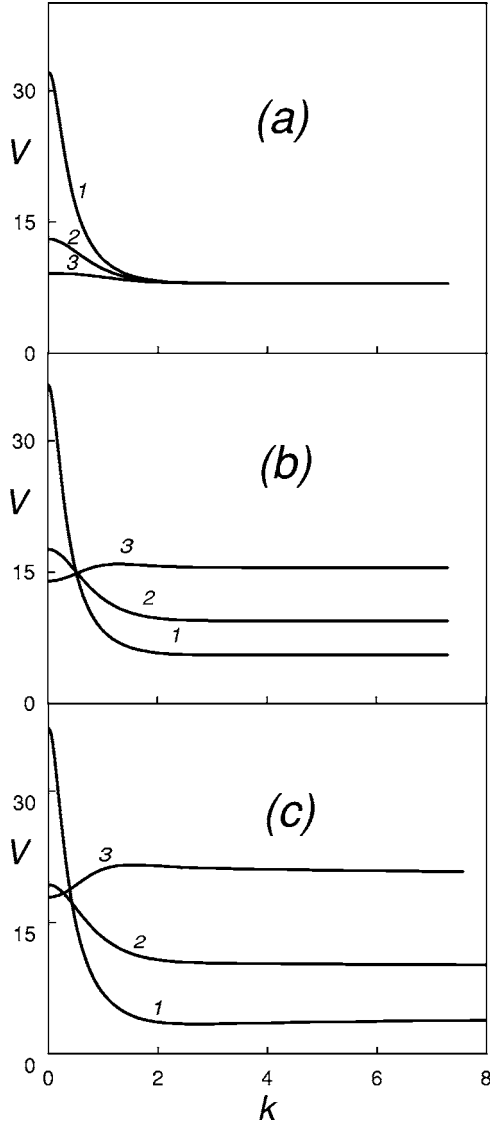
FIG. 3. Marginal stability curves (voltage V vs wave number k) for various limiting electro-osmotic formulations for Pe=0.5 and three values of relative diffusivity $D=0.1$ (line 1), $D=1$ (line 2), and $D=10$ (line 3). (a) Electro-osmotic slip of the second kind without bulk electroconvection ($E_{O2} \neq 0$, $H_S = 0$, $\mathbf{B}_{ec} = \mathbf{0}$). (b) Full slip formulation without bulk electroconvection ($E_{O2} \neq 0$, $H_S \neq 0$, $\mathbf{B}_{ec} = \mathbf{0}$). (c) Full limiting problem with bulk electroconvection ($E_{O2} \neq 0$, $H_S \neq 0$, $\mathbf{B}_{ec} \neq \mathbf{0}$).

the outer edge of the nonequilibrium boundary layer $y = y_0$ the outer solution is matched with the inner one [see Eq. (102)]:

$$\bar{c}(0) = c^+(y_0) = \frac{\varepsilon^{2/3}}{4} [F(0)^2 + 2F'(0)] \approx \alpha = 0.646\varepsilon^{2/3} > 0, \tag{167}$$

and substitute $\varphi_0(y) = \ln(y + \alpha)$ instead of $\varphi_0(y) = \ln y$ into Eqs. (144) and (158). This yields

$$\widetilde{B}_{ec} = k^2 \left(\frac{D-1}{(1+D)(y+\alpha)^2} [\lambda\xi + \mathrm{Pe}\, w] \right.$$
$$\left. + 2\frac{\xi' - \mu}{(y+\alpha)^3} - \frac{\mu'}{(y+\alpha)^2} \right). \tag{168}$$

Let us begin with analyzing electro-osmotic slip of the second kind without bulk electroconvection: $E_{O2} \neq 0$, $H_S = 0$, $B_{ec} = 0$. The spectral problem in this case becomes

$$\lambda\xi + \mathrm{Pe}\, w = \xi'' - k^2\xi, \quad 0 < y < 2, \tag{169}$$

$$\lambda\xi + \mathrm{Pe}\, w = \frac{D+1}{2D}(y\mu'' + \mu' - k^2 y\mu), \quad 0 < y < 2, \tag{170}$$

$$w^{(4)} - \left(2k^2 + \frac{\lambda}{\mathrm{Sc}}\right)w'' + \left(k^4 + \frac{\lambda k^2}{\mathrm{Sc}}\right)w = 0, \quad 0 < y < 2, \tag{171}$$

$$\xi(0) = 0, \tag{172}$$

$$\mu'(0) = 0, \tag{173}$$

$$w(0) = 0, \tag{174}$$

$$w'(0) = -\frac{V^2}{8}k^2\xi'(0), \tag{175}$$

$$\xi(2) - \mu(2) = 0, \tag{176}$$

$$\mu'(2) = 0, \tag{177}$$

$$w(2) = 0, \tag{178}$$

$$w'(2) = 2\ln 2k^2\mu(2). \tag{179}$$

We begin with consideration of marginal stability while assuming exchange of stabilities $\{\lambda = 0\}$. Substituting $\lambda = 0$, integrating Eqs. (169) and (171) analytically with boundary conditions (172), (174), and (178), and solving the inhomogeneous Bessel equation (170) numerically with boundary conditions (173) and (177) we find using boundary conditions (175), (176), and (179) the dependence of voltage V on the wave number k. In Fig. 3(a) we present the resulting marginal stability curve in the V/k plane for Pe=0.5 and $D = 0.1$, 1, and 10. We point out the monotonic decrease of $V(k)$ with increasing k towards the "critical" shortwave threshold value $\bar{V} = 8$, the same as was found analytically in "diffusion layer" formulation [30,32]. To recover analytically this shortwave threshold in the current case too, let us consider a shortwave perturbation with $k \gg 1$. Let us define a small parameter $\omega = k^{-1}$. For $\omega \ll 1$ and $\lambda = 0$, Eqs. (169)–(171) are singularly perturbed with two boundary layers at $y = 0, 2$. In order to construct a boundary layer solution valid near $y = 0$, we define the inner variable

$$s = \frac{y}{\omega} = ky. \tag{180}$$

The solution of the respective inner problem bounded at $s \to \infty$ and satisfying conditions (172)–(174) reads

$$\bar{\xi} = -\frac{Pe}{4}(s+1)se^{-s}, \tag{181}$$

$$\frac{\bar{w}}{k^2} = se^{-s}. \tag{182}$$

Substituting Eqs. (181) and (182), into boundary condition (175) yields the desired result

$$\bar{V} = \lim_{k \to \infty} V(k) = 4\sqrt{\frac{2}{Pe}}. \tag{183}$$

Similarly, for $\lambda \neq 0$ the solution of the respective inner problem reads

$$\bar{\xi} = Pe \frac{-\left(2 - \frac{1}{Sc}\right)e^{-\sqrt{1+\tilde{\lambda}}s} - \left(\frac{1}{Sc} - 1\right)e^{-s} + e^{-(1+\tilde{\lambda}/Sc)s}}{\tilde{\lambda}\left(\frac{1}{Sc} - 1\right)}, \tag{184}$$

$$\frac{\bar{w}}{k^2} = (e^{-s} - e^{-[1+\tilde{\lambda}/Sc]s}), \tag{185}$$

where

$$\tilde{\lambda} = \frac{\lambda}{k^2}. \tag{186}$$

Substitution of Eqs. (184) and (185) into Eq. (175) yields the following algebraic equation for $\tilde{\lambda}$:

$$\frac{\tilde{\lambda}}{Pe\,Sc} = \frac{V^2}{8}\frac{1}{1-Sc}[-\tilde{\lambda} + (1 - 2\,Sc)(\sqrt{1+\tilde{\lambda}} - 1)]. \tag{187}$$

For realistic values of the Schmidt number $Sc = O(10^3)$, Eq. (187) yields for the largest eigenvalue the shortwave asymptotic relation

$$\lambda_0 \approx \left(Pe\frac{V^2 - \bar{V}^2}{8}Sc\right)^{2/3} k^2. \tag{188}$$

The respective solution of the outer problem and right-edge inner boundary layer problem is identical to zero.

Asymptotic expressions for smaller eigenvalues λ are all of diffusion type:

$$\lambda_n = -k^2 + \pi^2 n^2 + O\left(\frac{1}{k^2}\right), \quad n = 1, 2, \ldots. \tag{189}$$

Let us note that a nontrivial inner boundary layer solution corresponding to the unstable shortwave mode and leading to the "short-wave" catastrophe appears because of the very

particular character of the nonequilibrium slip condition at $y = 0$ with tangent velocity proportional to the tangent derivative of the electric current, yielding the normal velocity of the order $O(k^2)$.

Finally, let us show that the "two solid walls" formulation, as opposed to that for "diffusion layer" yields a characteristic linear growth rate dependence on k [48] with a shortwave instability accompanied by a slow decay of the long wave mode. Let us expand ξ, μ, and w in even powers of k for $k \ll 1$ as

$$\xi = \xi_0 + O(k^2), \tag{190}$$

$$\mu = \mu_0 + k^2\mu_1 + O(k^4), \tag{191}$$

$$w = k^2 w_1 + O(k^4), \tag{192}$$

$$\lambda = \lambda_0 + \lambda_1 k^2 + O(k^4). \tag{193}$$

Substitution of Eqs. (190)–(193) into Eq. (170) yields upon integration with respect to y over the interval $(0,2)$, using conditions (173) and (177),

$$\lambda_0 = 0. \tag{194}$$

Then, by substituting Eqs. (190)–(193) into Eqs. (169)–(179) we find that

$$\xi_0 = \frac{y}{2}, \tag{195}$$

$$\mu_0 = 1, \tag{196}$$

$$w_1 = \left(\frac{V^2}{16} + \left[\frac{\ln 2}{2} - \frac{V^2}{32}\right]y\right)(y-2)y. \tag{197}$$

Integrating the next-order equation for μ_1

$$Pe\,w_1 + \lambda_1\xi_0 = \frac{D+1}{2D}[(y\mu_1')' - \mu_0 y], \tag{198}$$

with respect to y we find, using Eq. (177),

$$Pe\int_0^2 w_1\,dy = -\frac{D+1}{D} - \lambda_1, \tag{199}$$

or, substituting Eq. (197),

$$\lambda_1 = Pe\frac{32\ln(2) + V^2}{48} - \frac{D+1}{D}. \tag{200}$$

By defining

$$\underline{V} = \lim_{k \to 0} V(k) = 4\sqrt{\frac{3(D+1)}{Pe\,D} - 2\ln 2} \tag{201}$$

and referring to Eqs. (193) and (194) we finally conclude that for $k \ll 1$

$$\lambda = k^2 Pe\frac{V^2 - \underline{V}^2}{48} + O(k^4). \tag{202}$$

Next, we analyze the full slip formula without bulk electroconvection: $E_{O2} \neq 0$, $H_S \neq 0$, $B_{ec} = 0$. Here, the only differ-

ence in the spectral problem compared to the previous case [Eqs. (169)–(179)] resides in the inclusion of the linear V term in the boundary condition (175):

$$w'(0) = -\left(\frac{V^2}{8} + V\right)k^2\xi'(0) + Vk^2\mu(0). \qquad (203)$$

This inclusion, as seen from comparison of data in Fig. 3(b) with those in Fig. 3(a) may have a considerable effect on stability characteristics. (In particular, for $D=10$ the long wave threshold $\underline{V}$ is lower than the shortwave on $\bar{V}$.) To assess this effect analytically we reproduce below the short- ($k \gg 1$) and long-wave ($k \ll 1$) asymptotic analysis which led to expressions (183) and (201) and find expressions for short- ($\bar{V}$) and long-wave ($\underline{V}$) thresholds in this case. Bounded solution of the relevant short wave ($k \gg 1$) inner problem for $\lambda=0$ reads:

$$\bar{\xi} = -\frac{Pe}{4}(s+1)se^{-s}, \qquad (204)$$

$$\frac{\bar{w}}{k^2} = se^{-s}, \qquad (205)$$

$$\frac{\bar{\mu}}{k} = -\frac{2D\,Pe}{3(D+1)}(s+1)e^{-s}, \qquad (206)$$

where s is defined by Eq. (180). Substitution of Eqs. (204)–(206) into the boundary condition (203) yields

$$\bar{V} = \lim_{k \to \infty} V(k)$$
$$= 4\left(-1 + \frac{8D}{3(D+1)} + \sqrt{\left(1 - \frac{8D}{3(D+1)}\right)^2 + \frac{2}{Pe}}\right). \qquad (207)$$

There is no analytical solution to the inner boundary problems for $\lambda \neq 0$, thus these problems had to be solved numerically yielding results similar to the previous one: the largest eigenvalue yields the "shortwave catastrophe" for $V > \bar{V}$ is determined from solution of the suitable inner problem [as it was done previously in Eq. (188)] whereas all smaller eigenvalues are negative corresponding to stable, decaying modes behaving in a diffusionlike fashion Eq. (189).

To complete comparison between the two slip formulations (A) and (B), let us consider the long-wave asymptotics $k \ll 1$. Similarly to Eqs. (195)–(197), we find that for $k \ll 1$

$$\xi = \frac{y}{2} + O(k^2), \qquad (208)$$

$$\mu_0 = 1 + O(k^2), \qquad (209)$$

$$w_1 = \frac{y(y-2)}{64}(2y[32\ln 2 - V^2 + 8V] + 2V^2 - 16V). \qquad (210)$$

Furthermore, similarly to Eqs. (200) and (201), we find that

$$\underline{V} = \lim_{k \to 0} V(k) = 4\left(1 + \sqrt{1 - 2\ln 2 + \frac{3(D+1)}{D\,Pe}}\right) \qquad (211)$$

and

$$\lambda = k^2\,Pe\frac{(V-\underline{V})\left(V - 4\left[1 - \sqrt{1 - 2\ln 2 + \frac{3(D+1)}{D\,Pe}}\right]\right)}{48}$$
$$+ O(k^4). \qquad (212)$$

We note, in particular, that for D sufficiently large the long-wave threshold is lower than the shortwave one.

We conclude this section with analysis of the full slip formulation with bulk electroconvection: $E_{O2} \neq 0$, $H_S \neq 0$, $B_{ec} \neq 0$. The relevant spectral boundary value problem reads:

$$\lambda\xi + Pe\,w = \xi'' - k^2\xi, \quad 0 < y < 2, \qquad (213)$$

$$\lambda\xi + Pe\,w = \frac{D+1}{2D}(y\mu'' + \mu' - k^2 y\mu), \quad 0 < y < 2, \qquad (214)$$

$$w^{(4)} - \left(2k^2 + \frac{\lambda}{Sc}\right)w'' + \left(k^4 + \frac{\lambda k^2}{Sc}\right)w$$
$$= -k^2\left(\frac{D-1}{(1+D)(y+\alpha)^2}[\lambda\xi + Pe\,w] + 2\frac{\xi'-\mu}{(y+\alpha)^3}\right.$$
$$\left. - \frac{\mu'}{(y+\alpha)^2}\right), \quad 0 < y < 2, \qquad (215)$$

$$\xi(0) = 0, \qquad (216)$$

$$\mu'(0) = 0, \qquad (217)$$

$$w(0) = 0, \qquad (218)$$

$$w'(0) = -\left(\frac{V^2}{8} + V\right)k^2\xi'(0) + Vk^2\mu(0), \qquad (219)$$

$$\xi(2) - \mu(2) = 0, \qquad (220)$$

$$\mu'(2) = 0, \qquad (221)$$

$$w(2) = 0, \qquad (222)$$

$$w'(2) = 2\ln 2 k^2\mu(2). \qquad (223)$$

Once again, we begin with consideration of marginal stability while assuming exchange of stabilities $\{\lambda=0\}$. Substituting $\lambda=0$, and integrating Eqs. (213)–(215) numerically we find the dependence of the critical voltage V on the wave number k. In Fig. 3(c) we present the marginal stability curve for $Pe=0.5$ and three values of diffusivity $D=0.1$, 1, and 10. Comparing this curve with those found in Figs. 3(a) and 3(b) we conclude that bulk electroconvection has a stabilizing effect. This conclusion is supported by the following calcu-

lation of the long-wave threshold $\underline{V}$, similar to those leading to Eqs. (201) and (211). Thus, solving Eqs. (213)–(223), we find that for $k \ll 1$

$$\xi = \frac{y}{2} + O(k^2), \tag{224}$$

$$\mu_0 = 1 + O(k^2), \tag{225}$$

$$\frac{w_1}{k^2} = \frac{1}{2}\Bigg((y+\alpha)\ln(y+\alpha) - \alpha\ln\alpha + \left[-1 - \ln\alpha + V - \frac{V^2}{8}\right]y$$

$$+ \left[\frac{3}{2} - V + \frac{V^2}{8} - \left(\frac{3}{4}\alpha + 1\right)\ln\frac{2+\alpha}{\alpha} - 2\ln 2\right]y^2$$

$$+ \left[-\frac{1}{2} + \ln 2 + \frac{V}{4} - \frac{V^2}{32} + \frac{1+\alpha}{4}\ln\frac{2+\alpha}{\alpha}\right]y^3\Bigg) + O(k^2), \tag{226}$$

and

$$\underline{V} = \lim_{k\to 0} V(k) = 4(1 + \sqrt{d}), \tag{227}$$

where

$$d = -\frac{1}{2} + \left(\frac{1}{2} + \frac{3}{2}\alpha + \frac{3}{4}\alpha^2\right)\ln\frac{2+\alpha}{\alpha} - 2\ln 2 - \frac{3}{2}\alpha$$

$$+ \frac{3(D+1)}{D\,\mathrm{Pe}},$$

and

$$\lambda = k^2\,\mathrm{Pe}\,\frac{(V-\underline{V})[V - 4(1-\sqrt{d})]}{48} + O(k^4). \tag{228}$$

Comparing Eqs. (227) and (211) we conclude that taking into account bulk electroconvection results in increasing the threshold V. Let us note that the employed regularization (167) and (68) leaves a trace of slight $[O(\sqrt{|\ln\varepsilon|})]$ dependence on ε in the threshold value. Since the bulk force term in Eq. (215) does not affect the leading order in k^{-2} the inner left boundary layer problem (near $y=0$), the short-wave threshold $\bar{V}$ is the same as in the previous case [see Eq. (207)], with the "short wave" catastrophe occurring for $V > \bar{V}$. Thus we conclude that the stabilizing effect of bulk electroconvection decreases with the increasing wave number k.

IV. LINEAR STABILITY OF QUIESCENT CONCENTRATION POLARIZATION IN THE FULL ELECTROCONVECTIVE FORMULATION

In order to simplify the full formulation Eqs. (1)–(5) and (20)–(28), and to avoid the detailed study of the double electric layer at the "enriched" anodic membrane's surface ($y=2$) we assume there local electroneutrality with local equilibrium and limiting electro-osmotic slip of the kind Eq. (59) which yields boundary conditions of the form:

$$\mu^+\big|_{y=2} = \ln p_1, \tag{229}$$

$$\mu_y^-\big|_{y=0} = 0, \tag{230}$$

$$\varphi\big|_{y=2} = \left.\frac{\mu^+ + \mu^-}{2}\right|_{y=2}, \tag{231}$$

$$u\big|_{y=2} = 2\ln 2\,\mu_x^-\big|_{y=2}, \tag{232}$$

$$w\big|_{y=0} = 0. \tag{233}$$

Here μ^+ and μ^- are cationic and anionic electrochemical potentials. Conditions (229) and (230) imply local equilibrium for cations at the membrane-solution interface and its impermeability for anions whereas Eqs. (231) and (232) imply, respectively, the local electroneutrality and the limiting quasiequilibrium electro-osmotic slip.

The quiescent steady state concentration polarization solution $\mu_0^\pm$, φ_0, $\mathbf{v}_0$, p_0 whose stability we are about to study is found numerically as a solution of the following one-dimensional boundary value problem:

$$(e^{\mu_0^+ - \varphi_0}\mu_{0y}^+)_y = 0, \quad 0 < y < 2, \tag{234}$$

$$\varepsilon^2\varphi_{0yy} = e^{\mu_0^- + \varphi_0} - e^{\mu_0^+ - \varphi_0}, \quad 0 < y < 2, \tag{235}$$

$$\mu_0^+\big|_{y=0} = \ln p_1 - V, \tag{236}$$

$$\varphi_0\big|_{y=0} = -V, \tag{237}$$

$$\mu_0^+\big|_{y=2} = \ln p_1, \tag{238}$$

$$\varphi_0\big|_{y=2} = \frac{1}{2}\ln\left(p_1\int_0^2 e^{\varphi_0}dy\right), \tag{239}$$

$$\mu_0^- = (\mu_0^+ - 2\varphi_0)\big|_{y=2}, \quad 0 < y < 2, \tag{240}$$

$$\mathbf{v}_0 = 0, \quad 0 < y < 2, \quad 0 < y < 2, \tag{241}$$

$$p_0 = \frac{1}{2}\varphi_{0y}^2 + \mathrm{const}, \quad 0 < y < 2. \tag{242}$$

Profiles in Figs. 1(a), 1(b), and 2 depict solutions of this problem computed for different values of ε and V, for $p_1 = 1$. The linearized problem for perturbations $\mu_1^\pm$, φ_1, $\underline{\mathbf{v}}_1 = u_1\hat{\mathbf{i}} + w_1\hat{\mathbf{j}}$ reads

$$(\mu_1^+ - \varphi_1)_t + \mathrm{Pe}\,w_1(\mu_0^+ - \varphi_0)_y$$

$$= \frac{D+1}{2}\{\Delta\mu_1^+ + (\mu_1^+ - \varphi_1)\mu_{0yy}^+[(\mu_1^+ - \varphi_1)_y$$

$$+ (\mu_0^+ - \varphi_0)_y(\mu_1^+ - \varphi_1)]\mu_{0y}^+ + (\mu_0^+ - \varphi_0)_y\mu_{1y}^+\}, \tag{243}$$

$$(\mu_1^- + \varphi_1)_t + \mathrm{Pe}\,w_1\varphi_{0y} = \frac{D+1}{2D}[\Delta\mu_1^- + \varphi_{0y}\mu_{1y}^-], \tag{244}$$

$$\varepsilon^2\varphi_{1yy} = e^{\mu_0^- + \varphi_0}(\mu_1^- + \varphi_1) - e^{\mu_0^+ - \varphi_0}(\mu_1^+ - \varphi_1), \tag{245}$$

$$\frac{1}{Sc}\Delta w_{1t} = \Delta^2 w_1 + \Delta\varphi_{1xx}\varphi_{0y} - \varphi_{0yyy}\varphi_{1xx}, \qquad (246)$$

$$\mu_1^+|_{y=0,2} = 0, \qquad (247)$$

$$\mu_{1y}^-|_{y=0,2} = 0, \qquad (248)$$

$$\varphi_1|_{y=0} = 0, \qquad (249)$$

$$(2\varphi_1 + \mu_1^-)|_{y=2} = 0, \qquad (250)$$

$$w_1|_{y=0,2} = 0, \qquad (251)$$

$$w_{1y}|_{y=0,2} = 0, \qquad (252)$$

$$w_{1y}|_{y=2} = -2\ln 2\,\mu_{1xx}^-|_{y=2}. \qquad (253)$$

Equations (243)–(253) yield a spectral problem in the form

$$Pe\,W(\mu_0^{+\prime} - \varphi_0') = \frac{D+1}{2}\left[M^{+\prime\prime} - k^2 M^+ + \mu_0^{+\prime}(M^+ - \Phi)'\right.$$

$$+ (\mu_0^+ - \varphi_0)' M^{+\prime} - \left(\lambda\frac{D+1}{2D}\right.$$

$$\left.\left. - \mu_0^{+\prime}(\mu_0^+ - \varphi_0)' - \mu_0^{+\prime\prime}\right)(M^+ - \Phi)\right], \qquad (254)$$

$$Pe\,W\varphi_0' = \frac{D+1}{2D}[M^{-\prime\prime} - k^2 M^- + \varphi_0' M^{-\prime} - \lambda(M^- + \Phi)], \qquad (255)$$

$$\varepsilon^2(\Phi'' - k^2\Phi) = e^{\mu_0^- + \varphi_0}(M^- + \Phi) - e^{\mu_0^+ - \varphi_0}(M^+ - \Phi), \qquad (256)$$

$$W^{(4)} - \left(2k^2 + \frac{\lambda}{Sc}\right)W'' + \left(k^4 + \frac{\lambda k^2}{Sc}\right)W$$

$$= -k^2\varphi_0'''\Phi + k^2(\Phi'' - k^2\Phi)\varphi_0', \qquad (257)$$

$$M^+|_{y=0,2} = 0, \qquad (258)$$

$$M^{-\prime}|_{y=0,2} = 0, \qquad (259)$$

$$\Phi|_{y=0} = 0, \qquad (260)$$

$$2\Phi(2) + M^-(2) = 0, \qquad (261)$$

$$W|_{y=0,2} = 0, \qquad (262)$$

$$W'(0) = 0, \qquad (263)$$

$$W'(2) - 2\ln 2 k^2 M^-(2) = 0. \qquad (264)$$

Here $\Phi(y,k)$, $M^\pm(y,k)$, and $W(y,k)$ are the Fourier transforms of spatial factors of perturbations of the electric poten-

tial, ionic electrochemical potentials and normal velocity with k and λ being the wave number and linear growth rate, respectively, equivalent to those in Eqs. (161)–(166).

We start with the analysis of the shortwave asymptotic behavior ($k \gg 1/\varepsilon$) of λ in the problems (254)–(264) by considering asymptotic expansions of the form:

$$M^\pm = M_0^\pm(y) + O\left(\frac{1}{k^2}\right), \qquad (265)$$

$$\Phi = \Phi_0(y) + \frac{\Phi_1(y)}{k^2} + O\left(\frac{1}{k^4}\right), \qquad (266)$$

$$W = W_0(y) + O\left(\frac{1}{k^2}\right), \qquad (267)$$

$$\lambda = \lambda_0 k^2 + \lambda_1 \frac{D+1}{2D} + O\left(\frac{1}{k^2}\right). \qquad (268)$$

By substituting these expansions into the spectral problems (254)–(264) we find that a nontrivial solution to the leading order problem exists only if

$$\lambda_0 = -\frac{2}{D+1}. \qquad (269)$$

The corresponding leading order solution is

$$M_0^-(y) = 0, \qquad (270)$$

$$\Phi_0(y) = 0, \qquad (271)$$

$$W_0(y) = 0, \qquad (272)$$

$$\Phi_1(y) = -\frac{e^{\mu_0^- + \varphi_0}}{\varepsilon^2}M_0^+, \qquad (273)$$

whereas λ_1 and $M_0^+(y)$ are obtained from solution of the following eigenvalue problem:

$$M_0^{+\prime\prime} + (2\mu_0^+ - \varphi_0)'M_0^{+\prime}$$

$$+ \left[\mu_0^{+\prime}(\mu_0^+ - \varphi_0)' + \frac{e^{\mu_0^- + \varphi_0}}{\varepsilon^2} - \lambda_1\right]M_0^+ = 0, \quad (274)$$

$$M_0^+|_{y=0,2} = 0. \qquad (275)$$

Thus for very large wave numbers $k \gg 1/\varepsilon$ the quiescent concentration polarization solution is stable with perturbations decaying in a diffusionlike fashion. This implies in turn that the "shortwave catastrophe" does not occur in the full formulation.

Next we study the long-wave asymptotics $k \ll 1$ in the spectral problems (254)–(264) by considering the following expansions of $M^\pm$, Φ, W, and λ in even powers of k

$$M^\pm = M_0^\pm + k^2 M_1^\pm + O(k^4), \qquad (276)$$

$$\Phi = \Phi_0 + O(k^2), \qquad (277)$$
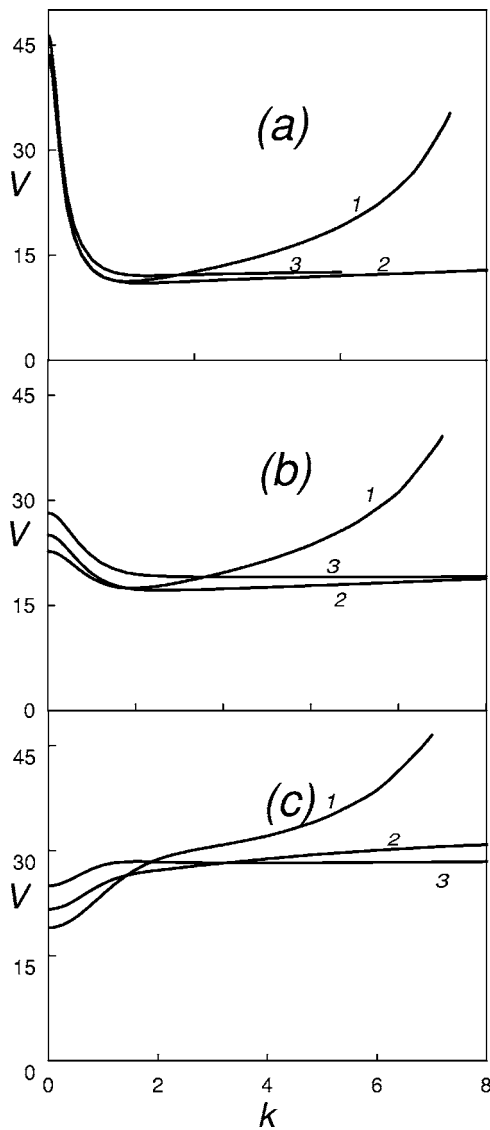
$$W = k^2 W_1 + O(k^4), \qquad (278)$$

FIG. 4. Marginal stability curves (voltage V vs wave number k) for full electroconvective problem with three values of ε ($1-\varepsilon=10^{-2}$, $2-\varepsilon=10^{-3}$, $3-\varepsilon=3\times10^{-5}$) and Pe=0.5 for various relative diffusivities [(a) $D=0.1$, (b) $D=1$, and (c) $D=10$].
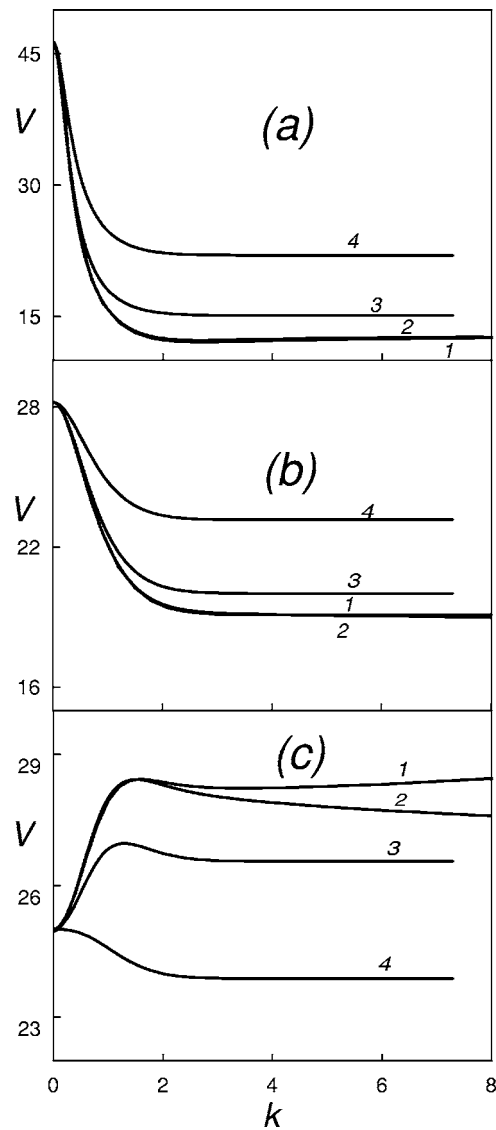
FIG. 5. Comparison of marginal stability curves for different formulations (1: full electroconvective problem, $\varepsilon=3\times10^{-5}$, 2: full limiting problem, $E_{O2}\neq0$, $H_S\neq0$, $\mathbf{B}_{ec}\neq\mathbf{0}$, 3: full slip formulation without bulk electroconvection, $E_{O2}\neq0$, $H_S\neq0$, $\mathbf{B}_{ec}=\mathbf{0}$, 4: electroosmotic slip of the second kind without bulk electroconvection, $E_{O2}\neq0$, $H_S=0$, $\mathbf{B}_{ec}=\mathbf{0}$) with Pe=0.5 for various relative diffusivities [(a) $D=0.1$, (b) $D=1$, and (c) $D=10$]. Limiting curves (2–4) have been shifted upwards to match at a common value at $k=0$.

$$\lambda = \lambda_0 + \lambda_1 k^2 + O(k^4). \tag{279}$$

Substitution of Eqs. (276)–(279) into Eq. (255), followed by multiplication by $\exp(\mu_0^- + \varphi_0)$ and integration with respect to y over the interval (0, 2), using condition (259) and normalization condition for the perturbation of anion concentration in the form

$$\int_0^2 e^{\varphi_0}(M_0^- + \Phi_0)dy = 1 \tag{280}$$

yields

$$\lambda_0 = 0. \tag{281}$$

This yields the leading order problem of the form

$$M_0^{+\prime\prime} + (\mu_0^+ - \varphi_0)'M_0^{+\prime} + \mu_0^{+\prime}(M_0^+ - \Phi_0)' $$
$$+ \mu_0^{+\prime}(\mu_0^+ - \varphi_0)'(M_0^+ - \Phi_0) = 0, \tag{282}$$

$$M_0^{-\prime\prime} + \varphi_0'M_0^{-\prime} = 0, \tag{283}$$

$$\varepsilon^2\Phi_0'' - e^{\mu_0^- + \varphi_0}(M_0^- + \Phi_0) + e^{\mu_0^+ - \varphi_0}(M_0^+ - \Phi_0) = 0, \tag{284}$$

$$W_1^{(4)} + \varphi_0'''\Phi_0 - \varphi_0'\Phi_0'' = 0, \tag{285}$$

$$M_0^+|_{y=0,2} = 0, \tag{286}$$
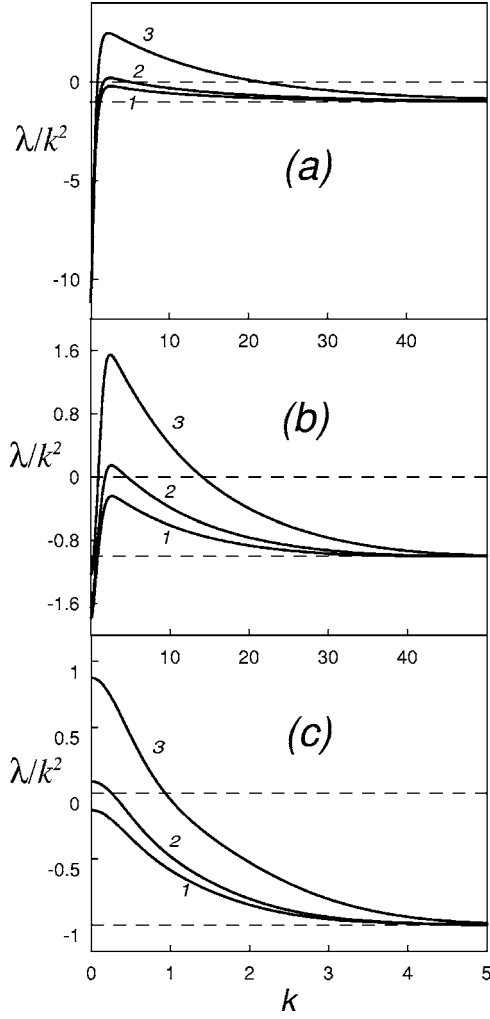
FIG. 6. Normalized linear growth rate (λ/k^2) dependence on k for $\varepsilon=10^{-3}$, Pe=0.5 and three values of voltage for various relative diffusivities [(a) $D=0.1$; 1: $V=10.5$, 2: $V=11.5$, 3: $V=15$, (b) $D=1$; 1: $V=16.5$, 2: $V=17.5$, 3: $V=20$, (c) $D=10$; 1: $V=21$, 2: $V=22$, 3: $V=25$].

$$M_0^{-\prime}|_{y=0,2} = 0, \tag{287}$$

$$\Phi_0|_{y=0} = 0, \tag{288}$$

$$2\Phi_0(2) + M_0^-(2) = 0, \tag{289}$$

$$W_1|_{y=0,2} = 0, \tag{290}$$

$$W_1'(0) = 0, \tag{291}$$

$$W_1'(2) + 2\ln 2 M_0^-(2) = 0. \tag{292}$$

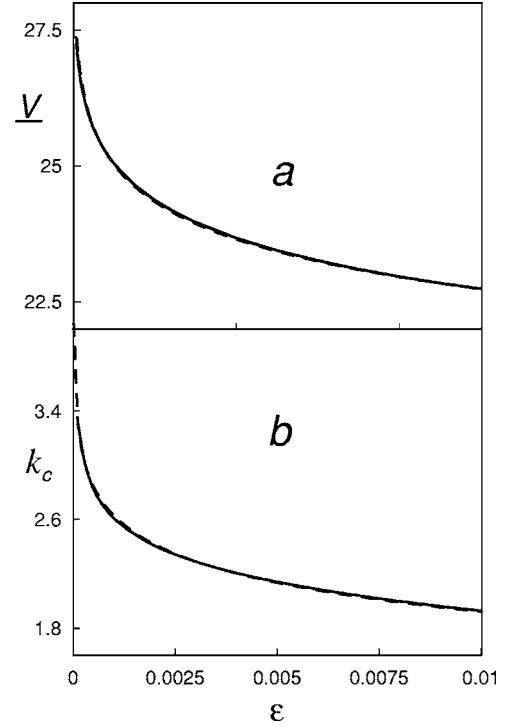Integrating Eq. (283) and using conditions (280) and (287), we find

FIG. 7. ε-dependence of the (a) long-wave threshold $\underline{V}$ (continuous line: exact value, dashed line: empirical formula $\underline{V}=-\ln\varepsilon+18.14$), (b) critical wave number k_c (continuous line: exact value, dashed line: empirical formula $k_c=-1/3.27\ln\varepsilon+10.51$), for $D=1$, Pe=0.5.

$$M_0^- = \frac{1 - \int_0^2 e^{\varphi_0}\Phi_0 dy}{\int_0^2 e^{\varphi_0}dy}, \tag{293}$$

with the rest of the solution calculated numerically. In order to find λ_1 we use the next order equation for M_1^-, which reads

$$\text{Pe } W_1\varphi_0' = \frac{D+1}{2D}(M_1^{-\prime\prime} + \varphi_0'M_1^{-\prime} - 1) - \lambda_1. \tag{294}$$

Integration of this equation in combination with conditions

$$M_1^{-\prime}|_{y=0,2} = 0 \tag{295}$$

yields

$$\lambda_1 = -\frac{D+1}{2D}\int_0^2 e^{\varphi_0}dy + \text{Pe}\int_0^2 W_1'e^{\varphi_0}dy. \tag{296}$$

Substituting $\lambda_1=0$ into Eq. (296) we obtain the equation for the long-wave threshold potential $\underline{V}$:

$$\frac{\int_0^2 W_1'e^{\varphi_0}dy}{\int_0^2 e^{\varphi_0}dy} = \frac{D+1}{2D\text{ Pe}}. \tag{297}$$

This concludes our study of the short- and long-wave asymptotics in the full electroneutral formulation. Below we present the results of numerical solution of the spectral problems (254)–(264) for intermediate wave-number range and the same three values of the ionic diffusivities ratios D =0.1, 1, and 10 as in the previous section dealing with limiting slip formulations. Thus in Fig. 4(a) we present the marginal stability curves in the V/k plane for $D=0.1$ and three values of $\varepsilon=10^{-2}$, 10^{-3}, and 3×10^{-5}. It is observed that the minimum in V versus k curve is the more pronounced, the larger is ε. In Fig. 5(a) we compare the marginal V/k curve from Fig. 4(a) with $\varepsilon=3\times10^{-5}$ with the respective marginal stability curves obtained in various limiting formulations. We point out the extremely close agreement between the marginal stability curve in the full formulation and that for the full nonequilibrium slip formula (203) (with the important exception that for the latter there is no wave number selection and shortwave singularity occurs). Furthermore, in Fig. 6(a) we present the normalized linear growth rate λ/k^2 dependence on k for $\varepsilon=10^{-3}$ and three values of voltage, one below and two above the instability threshold. We point out that in the unstable case these are dispersion relations of Nikolaewsky type with a finite wave number instability accompanied by a slow decay of the long-wave mode (λ vanishing as k^2 with a negative coefficient). The latter feature is due to additional symmetry related to anion conservation in the two charge-selective wall formulations considered herein. Results for $D=1$ [Figs. 4(b), 5(b), and 6(b)] are qualitatively similar to those in Figs. 4(a), 5(a), and 6(a). This is not the case for $D=10$ [Figs. 4(c), 5(c), and 6(c)] characterized by long-wave instability and a slower convergence with ε. In Fig. 7(a) we present the ε-dependence of the long-wave threshold V for $D=1$. (This threshold is useful for fixing the unknown order $O(|\ln \varepsilon|)$ shifts of potential in the asymptotic

limiting slip calculations.) Finally, in Fig. 7(b) we present the ε-dependence of the critical wave number $k_c(\varepsilon)$ for $D=1$. The found dependence closely approximated by the empirical formula

$$k_c = -\frac{1}{3.27} \ln \varepsilon + 0.51 \qquad (298)$$

is remarkably close to the leading order value $k_c=-\frac{1}{3}\ln \varepsilon$ obtained in Ref. [33] for regularized nonequilibrium electro-osmotic slip.

V. CONCLUDING REMARKS

Thus, summarizing the short-wave singularity of electro-osmotic instability typical for the nonregularized limiting nonequilibrium electro-osmotic formulations with equal ionic formulations is removed by considering the full electroconvective formulation. (Shortwave singularity also disappears in certain limiting electro-osmotic formulations with differing ionic diffusivities.) Additional symmetry related to conservation of coions in a system flanked by charge selective membranes yields slow decay of long-wave perturbation modes which, combined with shortwave instability is likely to result in spatiotemporal chaos at the nonlinear stage. We reiterate the peculiarity of the obtained linear stability results for large cation diffusivity ($D\gg1$). Comparison of these results with those of numerical solution of the full non-linear problem will be the topic of our forthcoming study [49].

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