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Migration of ion-exchange particles driven by a uniform electric field

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A cation-selective conducting particle is suspended in an electrolyte solution and is exposed to a uniformly applied electric field. The electrokinetic transport processes are described in a closed mathematical model, consisting of differential equations, representing the physical transport in the electrolyte, and boundary conditions, representing the physicochemical conditions on the particle boundary and at large distances away from it. Solving this mathematical problem would in principle provide the electrokinetic flow about the particle and its concomitant velocity relative to the otherwise quiescent fluid.

Using matched asymptotic expansions, this problem is analysed in the thin-Debye-layer limit. A macroscale description is extracted, whereby effective boundary conditions represent appropriate asymptotic matching with the Debye-scale fields. This description significantly differs from that corresponding to a chemically inert particle. Thus, ion selectivity on the particle surface results in a macroscale salt concentration polarization, whereby the electric potential is rendered non-harmonic. Moreover, the uniform Dirichlet condition governing this potential on the particle surface is transformed into a non-uniform Dirichlet condition on the macroscale particle boundary. The Dukhin–Derjaguin slip formula still holds, but with a non-uniform zeta potential that depends, through the cation-exchange kinetics, upon the salt concentration and electric field distributions. For weak fields, an approximate solution is obtained as a perturbation to a reference state. The linearized solution corresponds to a uniform zeta potential; it predicts a particle velocity which is proportional to the applied field. The associated electrokinetic flow is driven by two different agents, electric field and salinity gradients, which are of comparable magnitude. Accordingly, this flow differs significantly from that occurring in electrophoresis of chemically inert particles.

1. Introduction

Volumetric charge in electrolyte solutions is confined to boundary layers of characteristic thickness δ^*, known as the ‘Debye length’. In most practical situations, this thickness is extremely small when compared with the typical scale of interest, say a^*. (Dimensional quantities appear throughout with a star superscript.) Thus, ionic transport is characterized by the parameter

$$\delta = \frac{\delta^*}{a^*} \ll 1. \tag{1.1}$$

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In that asymptotic limit, the vast majority of the fluid remains approximately electroneutral. In symmetric electrolytes, this implies equal anionic and cationic concentrations. The simplest mode of ionic current through such electroneutral bulk is via Ohmic conduction at uniform anionic and cationic concentrations. The electric current is then driven by electromigratory fluxes, proportional to the electric field.

This mode, however, cannot be realized when the current must pass through an adjacent ion-selective medium (Levich 1962; Probstein 1989). Consider for example the ionic transport from an electrolyte to a solid ion exchanger, which is impermeable to anions. In that case, the need for a zero anion flux necessitates the development of anion concentration gradient; electroneutrality then implies a concomitant cation concentration gradient. The simplest situation entails one-dimensional transport in an electrochemical cell of width a^* bounded by ion-exchange membranes. Volumetric charge is limited to the thin Debye layers adjacent to these two membranes. Outside these layers the fluid remains electroneutral. To satisfy zero anionic current, the salt distribution becomes polarized, decreasing towards the cathodic exchanger. Thus, the electroneutral region constitutes a 'diffusion layer' (Rubinstein & Zaltzman 2001).

When the exchanger boundary is curved, as in the case of an ion-exchange particle (e.g. resin or clay), this phenomenon becomes more complicated. While the electric field normal to the boundary again leads to concentration polarization, the tangential field now acts on the Debye layer charge, resulting in a flow field. When the particle is freely suspended, this field leads in general to particle motion relative to the otherwise quiescent electrolyte. The curvilinear geometry affects the diffusion-layer length scale. While in the one-dimensional cell geometry this scale was simply provided by the cell width, in the curvilinear case it is dictated by the characteristic curvature $1/a^*$ of the exchanger boundary (in the case of a particle, a^* is its characteristic size).

Thus, the electrokinetic transport around an ion-exchange particle constitutes a multi-scale physicochemical problem, which is the focus of the present work. Beyond fundamental interest, understanding of this problem constitutes an initial step for modelling of various low-dispersion electro-chromatography protocols. For example, packed beds of spherical ion-exchange particles are used for separation of charged analytes in microfluidic channels (Leinweber & Tallarek 2004).

The aim of this paper is to construct a closed mathematical model which describes the electrokinetic transport under steady-state conditions in the thin-Debye-layer limit. For this purpose, we follow related works (Ben & Chang 2002; Ben, Demekhin & Chang 2004; Kalaĭdin, Demekhin & Korovyakovskiĭ 2009) and consider a simple model of a spherical cation exchanger which is highly conducting, whereby the electric potential at its boundary is uniform. Another assumption appearing in these analyses, analogous to that appearing in prevailing membrane models (Rubinstein & Zaltzman 2001; Zaltzman & Rubinstein 2007), is that of ideal ion selectivity, whereby the cationic concentration at the exchanger boundary is fixed. We here actually allow for a more realistic ion-selectivity model, assuming Butler–Volmer kinetics. As it turns out, the resulting analysis is rather insensitive to the ion-selectivity model. At fast surface kinetics, the Butler–Volmer kinetics degenerate to the ideal-selectivity model.

The coupled chemical and physical transport processes are described in a continuum electrokinetic framework in terms of the two ionic concentrations, the electric potential and the flow field. In addition to the differential equations and boundary conditions which govern these fields the electrokinetic model also comprises the integral constraint of a force-free particle, which serves to uniquely determine the particle velocity with which it translates relative to the quiescent electrolyte.

In the thin-Debye-layer limit the problem is analysed using singular inner–outer perturbations which separately handle the Debye layer and the electroneutral bulk surrounding it. Asymptotic matching between these two regions furnishes a self-contained macroscale model; at leading-order, it comprises of coupled equations governing the electric field, salt concentration and fluid velocity in the electroneutral bulk. These bulk fields also satisfy effective 'boundary conditions', representing the requisite matching with the Debye-layer fields.

An approximate solution is obtained for weak fields, where salt and charge are transported from the anodic part of the particle to its cathodic part. The zeta potential is uniform to leading order, and the particle drifts with a velocity that is linear in the applied electric field. The flow field is driven by both electric field and salinity gradients, and is accordingly different from that in classical electrophoresis of an inert particle. Specifically, Smoluchowski's formula does not apply.

The paper is structured as follows: the governing electrokinetic model is formulated in the next section. The thin-Debye-layer limit is addressed in § 3. In § 4 we obtain the reduced macroscale description, and compare it to the related model of a chemically inert (ideally polarizable) particle. An approximate solution for weak fields, together with an analytic expression for the particle velocity, is outlined in § 5. Another scalar quantity of interest, net particle charge, is evaluated in § 6. The results, and their relations to electro-osmosis of the second kind, are discussed in § 7.

2. Electrokinetic model

We consider an unbounded electrolyte solution (dielectric permittivity ϵ^*, viscosity μ^*, ionic valences $\pm z$). When undisturbed, the cations and anions possess an identical concentration, say c^*. An anion-impermeable spherical particle (radius a^*) is introduced into the solution. The particle is highly conductive, and as such possesses a uniform electric potential. We assume that the cation selectivity of the particle is expressed by the Butler–Volmer kinetics, where the dissolution rate per unit area,

$$k^* \left(1 - \frac{c_+^*}{\gamma c^*}\right), \tag{2.1}$$

is a function of the cationic concentration c_+^* on the surface. The two terms in (2.1) respectively represent cation dissolution and deposition, with k^* acting as an anodic rate constant and γc^* being the fast-kinetics equilibrium concentration.

A uniform electric field E^* is applied at large distances from the particle. After a short transient period (Yossifon, Frankel & Miloh 2009), the electrokinetic transport processes reach a steady state in a particle fixed reference frame. Since the applied field renders the problem asymmetric, it causes the particle to move relative to the quiescent suspending electrolyte. Our goal is to calculate the electrokinetic flow at these steady-state conditions, and, specifically, the associated drift velocity of the freely suspended particle.

2.1. *Dimensionless formulation*

We employ the dimensionless notation of Saville (1977). Thus, the spatial coordinates are normalized by a^*, the concentration $c_\pm$ by c^* and the electric potential φ by the thermal voltage (about 25 mV in a univalent solution)

$$\varphi^* = \frac{R^* T^*}{z F^*}, \tag{2.2}$$

where R^* is the gas constant, T^* the absolute temperature and F^* Faraday's constant. Balancing viscous stresses and Coulomb body forces yields the velocity unit

$$v^* = \frac{\epsilon^* \varphi^{*2}}{\mu^* a^*}, \tag{2.3}$$

for the velocity field $\boldsymbol{v}$. The stress tensors, together with the pressure field p, are normalized by $\mu^* v^*/a^*$. Forces are normalized by $\mu^* v^* a^*$.

2.2. *Governing equations*

The electrokinetic problem is formulated in a reference frame attached to the particle, wherein it is stationary. The differential equations governing the pertinent fields comprise of the following.

(*a*) The Nernst–Planck conservation equations, describing ionic transport by the combined action of diffusion, electromigration and convection (Hunter 2000)

$$\nabla \cdot \boldsymbol{j}_\pm + \alpha\, \boldsymbol{v} \cdot \nabla c_\pm = 0. \tag{2.4}$$

Here

$$\boldsymbol{j}_\pm = -\nabla c_\pm \mp c_\pm \nabla \varphi \tag{2.5}$$

are the ionic fluxes normalized with $D^* c^*/a^*$, wherein D^* is the ionic diffusivity, presumed identical for both ionic species. The dimensionless group $\alpha = a^* v^*/D^*$ constitutes the Péclet number. In view of (2.3),

$$\alpha = \frac{\epsilon^* \varphi^{*2}}{\mu^* D^*}; \tag{2.6}$$

thus, this number is independent of both particle size a^* and ambient salt concentration c^*. For typical ionic diffusivities $\alpha \approx 0.5$ (Saville 1977).
Use of the reduced variables

$$c = \frac{c_+ + c_-}{2} \quad \text{and} \quad q = \frac{c_+ - c_-}{2} \tag{2.7a,b}$$

transforms (2.4) to the salt and charge conservation equations

$$\nabla \cdot (\nabla c + q \nabla \varphi) = \alpha\, \boldsymbol{v} \cdot \nabla c, \tag{2.8}$$

$$\nabla \cdot (\nabla q + c \nabla \varphi) = \alpha\, \boldsymbol{v} \cdot \nabla q. \tag{2.9}$$

These equations can be written in the alternative form

$$\nabla \cdot \boldsymbol{j} + \alpha\, \boldsymbol{v} \cdot \nabla c = 0 \quad \text{and} \quad \nabla \cdot \boldsymbol{i} + \alpha\, \boldsymbol{v} \cdot \nabla q = 0. \tag{2.10a,b}$$

wherein

$$\boldsymbol{j} = -\nabla c - q \nabla \varphi \tag{2.11}$$

is the salt flux, normalized by $2D^* c^*/a^*$, and

$$\boldsymbol{i} = -\nabla q - c \nabla \varphi \tag{2.12}$$

is the current density, normalized by $2zF^* D^* c^*/a^*$. Note that

$$\boldsymbol{j}_+ = \boldsymbol{j} + \boldsymbol{i}, \quad \boldsymbol{j}_- = \boldsymbol{j} - \boldsymbol{i}. \tag{2.13a,b}$$

(*b*) Poisson's equation governing the electric potential φ

$$\delta^2 \nabla^2 \varphi = -q. \tag{2.14}$$

Here, $\delta = \delta^*/a^*$, in which δ^* is the Debye thickness

$$\delta^{*2} = \frac{\epsilon^* \varphi^*}{2zF^* c^*}. \tag{2.15}$$

(*c*) The continuity equation

$$\nabla \cdot \boldsymbol{v} = 0, \tag{2.16}$$

and inhomogeneous Stokes equation

$$\nabla^2 \boldsymbol{v} + \nabla^2 \varphi \nabla \varphi = \nabla p, \tag{2.17}$$

governing $\boldsymbol{v}$ and p. Since the latter represents momentum balance at zero inertia, it can be alternatively written as a statement of a divergence-free stress

$$\nabla \cdot (\boldsymbol{S}_{\mathrm{N}} + \boldsymbol{S}_{\mathrm{M}}) = \boldsymbol{0}. \tag{2.18}$$

Here, $\boldsymbol{S}_{\mathrm{N}}$ and $\boldsymbol{S}_{\mathrm{M}}$ denote the Newtonian and Maxwell stress tensors, respectively

$$\boldsymbol{S}_{\mathrm{N}} = -p\boldsymbol{I} + \nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^{\dagger}, \quad \boldsymbol{S}_{\mathrm{M}} = \nabla \varphi \nabla \varphi - \tfrac{1}{2} \nabla \varphi \cdot \nabla \varphi \boldsymbol{I}, \tag{2.19a, b}$$

$\boldsymbol{I}$ being the unity dyadic and † denoting transposition.

2.3. *Boundary conditions*

The bundary conditions are conveniently presented in a coordinate system whose origin coincides with the particle centre; the x-axis is taken in the direction of the applied field. We also employ spherical coordinates (r, θ, ϖ), r being the radial coordinate, θ the longitudinal angle ($\theta = 0$ in the positive x-direction) and ϖ the azimuthal angle. Thus, the radial ionic fluxes, denoted by $j_{\pm}$, adopt the form

$$j_{\pm} = -\frac{\partial c_{\pm}}{\partial r} \mp c_{\pm} \frac{\partial \varphi}{\partial r}. \tag{2.20}$$

At large distances away from the particle the ionic concentrations approach the ambient unity value,

$$c_{\pm} \rightarrow 1; \tag{2.21}$$

and the electric field approaches the uniform applied field

$$\nabla \varphi \rightarrow -\beta \hat{\boldsymbol{\imath}}. \tag{2.22}$$

Here,

$$\beta = \frac{a^* E^*}{\varphi^*} \tag{2.23}$$

is the dimensionless applied field magnitude, and $\hat{\boldsymbol{\imath}}$ is a unit vector in the x-direction.

In general, a freely suspended particle acquires a non-zero velocity in response to the applied field. Because of axial symmetry, this velocity, say $\mathscr{U}$, is in the x-direction. Thus, at the co-moving reference frame the far-field velocity condition is

$$\boldsymbol{v} \rightarrow -\mathscr{U} \hat{\boldsymbol{\imath}}. \tag{2.24}$$

The value of $\mathscr{U}$ is not specified *a priori*; rather, it is determined using the constraint of a force-free particle

$$\oint_{r=1} (\boldsymbol{S}_{\mathrm{N}} + \boldsymbol{S}_{\mathrm{M}}) \cdot \hat{\boldsymbol{e}}_r \, \mathrm{d}A = \boldsymbol{0}. \tag{2.25}$$

The conditions on the particle boundary $r = 1$ comprise:

(*a*) Anionic impermeability

$$j_- = 0. \tag{2.26}$$

(*b*) Cation selectivity

$$c_+ = \gamma\left(1 - \frac{j_+}{k}\right), \tag{2.27}$$

with $k = k^* a/D^* c^*$. (When transforming from dimensional version (2.1), this equation has been conveniently written as a boundary condition governing c_+.)

(*c*) The requirement of a uniform electric potential, say $\mathscr{V}$,

$$\varphi = \mathscr{V}. \tag{2.28}$$

(*d*) Mass-impermeability and no-slip

$$\boldsymbol{v} = \boldsymbol{0}. \tag{2.29}$$

The dimensionless problem (2.4)–(2.29) is clearly symmetric about the x-axis, whereby all scalar fields must be independent of the azimuthal angle ϖ. This symmetry also implies that the fluid velocity adopts the form $\boldsymbol{v} = \hat{\boldsymbol{e}}_r u + \hat{\boldsymbol{e}}_\theta v$, where both u and v are independent of ϖ.

The present model reflects the physical and chemical processes occurring at steady-state conditions. It expresses the dependence of the dimensionless transport processes upon the five governing parameters α, β, γ, δ and k. (Clearly, these processes cannot depend upon the arbitrary value chosen for the particle potential $\mathscr{V}$.) Solving this model provides the electrokinetic flow, and then the requisite scalar $\mathscr{U}$, as a function of these parameters.

3. The thin-Debye-layer limit

In most realistic scenarios, the Debye thickness is vanishingly small compared with particle size, $\delta \ll 1$. This scale disparity renders any numerical analysis of the model problem (2.4)–(2.29) practically impossible. Fortunately, it is exactly this disparity which allows us to analyse this problem analytically using singular inner–outer expansions, the inner region being the Debye layer of thickness δ around the particle, and the outer region being the remaining fluid bulk surrounding it.

3.1. *Bulk scale analysis*

In the outer region, we employ the macroscale radial coordinate R, which is distinguishable from r in its inability to discern the Debye-layer structure. Specifically, $R = 1$ constitutes the outer edge of the Debye layer – the macroscale particle ‘boundary’ – as opposed to the literal particle boundary $r = 1$.

We postulate the generic expansion

$$f(r, \theta; \delta) \sim F(R, \theta) + \cdots, \tag{3.1}$$

for all the pertinent fields. We only seek the leading-order description F. Substitution into the governing equations readily provides the leading-order outer description. Thus, Poisson’s equation (2.14) implies electroneutrality,

$$Q = 0, \tag{3.2}$$

whereby

$$C_\pm = C. \tag{3.3}$$

Then, the leading-order salt flux and current density become

$$\boldsymbol{J} = -\nabla C \quad \text{and} \quad \boldsymbol{I} = -C\nabla \Phi. \tag{3.4a, b}$$

Matching with the inner region also requires the radial ionic fluxes; use of (2.13) in conjunction with (3.4) readily yields

$$J_+ = -\frac{\partial C}{\partial R} - C\frac{\partial \Phi}{\partial R}, \quad J_- = -\frac{\partial C}{\partial R} + C\frac{\partial \Phi}{\partial R}. \tag{3.5a, b}$$

The leading-order salt and charge conservation equations appear as

$$\nabla \boldsymbol{\cdot} \boldsymbol{J} + \alpha \boldsymbol{V} \boldsymbol{\cdot} \nabla C = 0, \quad \nabla \boldsymbol{\cdot} \boldsymbol{I} = 0, \tag{3.6a, b}$$

Substituting (3.4), we find that the salt concentration C is governed by the diffusion–advection equation

$$\nabla^2 C = \alpha\, \boldsymbol{V} \boldsymbol{\cdot} \nabla C, \tag{3.7}$$

while the electric potential satisfies the elliptic equation

$$\nabla \boldsymbol{\cdot} (C\nabla \Phi) = 0; \tag{3.8}$$

The leading-order flow equations governing $\boldsymbol{V}$ and P retain the following form (similar to (2.16) and (2.17)):

$$\nabla \boldsymbol{\cdot} \boldsymbol{V} = 0, \quad \nabla^2 \boldsymbol{V} + \nabla^2 \Phi \nabla \Phi = \nabla P. \tag{3.9a, b}$$

Note that the Coulomb body force appears in the momentum balance, despite leading-order electroneutrality. This body force reflects $O(\delta^2)$ volumetric charge density, which is non-zero whenever Φ is non-harmonic.

The differential equations are supplemented by far-field conditions,

$$C \to 1, \quad \nabla \Phi \to -\beta \hat{\boldsymbol{\imath}}, \quad \boldsymbol{V} \to -\mathscr{U} \hat{\boldsymbol{\imath}}, \tag{3.10a, b, c}$$

wherein $\mathscr{U}$ is now to be interpreted as the leading-order particle velocity.

The boundary conditions (2.27) and (2.28) and the integral condition (2.25) apply at the literal boundary $r = 1$, and as such are not applicable to the outer region. The conditions on the 'effective' boundary $R = 1$ will be obtained using asymptotic matching with the inner region solutions, describing the Debye-scale transport processes.

3.2. *Debye-scale analysis*

The inner problem is analysed using the stretched radial coordinate

$$\rho = \frac{r - 1}{\delta}. \tag{3.11}$$

Thus, conditions (2.27) and (2.28) apply at $\rho = 0$, as does the integral constraint (2.25). We employ the standard expansions (Rubinstein & Zaltzman 2001)

$$c_\pm \sim c_\pm^{(0)}(\rho, \theta) + \delta c_\pm^{(1)}(\rho, \theta) + \cdots, \quad \varphi \sim \varphi^{(0)}(\rho, \theta) + \delta \varphi^{(1)}(\rho, \theta) + \cdots, \tag{3.12a, b}$$

which imply

$$c \sim c^{(0)}(\rho, \theta) + \delta c^{(1)}(\rho, \theta) + \cdots, \quad q \sim q^{(0)}(\rho, \theta) + \delta q^{(1)}(\rho, \theta) + \cdots. \tag{3.13a, b}$$

The corresponding expansions for the radial fluxes begin at $O(\delta^{-1})$:

$$j_\pm \sim \delta^{-1} j_\pm^{(-1)}(\rho, \theta) + j_\pm^{(0)}(\rho, \theta) + \cdots, \tag{3.14}$$

in which

$$j_{\pm}^{(-1)} = -\frac{\partial c_{\pm}^{(0)}}{\partial \rho} \mp c_{\pm}^{(0)} \frac{\partial \varphi^{(0)}}{\partial \rho}. \tag{3.15}$$

The momentum balance in the radial direction implies $O(\delta^{-2})$ large pressure scaling. The tangential momentum balance then suggests $O(1)$ tangential velocities, whereby the continuity equation, in conjunction with mass impermeability at $\rho = 0$, imposes $O(\delta)$ radial velocities. We therefore postulate the following expansions:

$$p \sim \delta^{-2} p^{(-2)}(\rho, \theta) + \cdots, \tag{3.16a}$$

$$v \sim v^{(0)}(\rho, \theta) + \cdots, \tag{3.16b}$$

$$u \sim \delta u^{(1)}(\rho, \theta) + \cdots. \tag{3.16c}$$

Substitution of (3.12)–(3.16) into the governing equation, in conjunction with the transformation (3.11), yields the Debye-scale differential equations. Thus, the radial components of the Nernst–Planck equations (2.4) now appear as

$$\delta^{-2} \frac{\partial j_{\pm}^{(-1)}}{\partial \rho} + \delta^{-1} \left(\frac{\partial j_{\pm}^{(0)}}{\partial \rho} + 2 j_{\pm}^{(-1)} \right) + O(1) = 0. \tag{3.17}$$

Note that matching to the leading-order outer ionic fluxes requires the evaluation of the correction term $j_{\pm}^{(0)}$ in (3.14), and hence requires solving (3.17) up to $O(\delta^{-1})$. The two terms in that asymptotic order, respectively, represent transverse ionic transport (via both diffusion and electromigration) across the Debye layer and a curvature-driven correction; because of the scale disparity, tangential ionic transport and ion convection are manifested only at the $O(1)$-balance of (3.17).

At leading order, (3.17) yields $\partial j_{\pm}^{(-1)}/\partial \rho = 0$, implying uniform $O(\delta^{-1})$ fluxes. Matching to the $O(1)$ fluxes in outer region is only possible if these fluxes vanish,

$$j_{\pm}^{(-1)} = 0. \tag{3.18}$$

Use of (3.15) then yields the Boltzmann distributions

$$c_{\pm}^{(0)}(\rho, \theta) = C(R = 1, \theta) \exp\left\{ \mp \left[\varphi^{(0)}(\rho, \theta) - \Phi(R = 1, \theta) \right] \right\}, \tag{3.19}$$

wherein matching with the outer solution is accounted for. At $O(\delta^{-1})$ (3.17) yields

$$\frac{\partial j_{\pm}^{(0)}}{\partial \rho} + 2 j_{\pm}^{(-1)} = 0. \tag{3.20}$$

The second term in (3.20) represents the boundary curvature effect; in view of (3.18) this term nullifies here, giving

$$\frac{\partial j_{\pm}^{(0)}}{\partial \rho} = 0. \tag{3.21}$$

Accordingly, these two fluxes are functions of θ only. Result (3.21) allows to connect between the $O(1)$ ionic fluxes at $\rho = 0$ and $\rho \to \infty$

$$j_{\pm}^{(0)}(\rho = 0, \theta) = j_{\pm}^{(0)}(\rho \to \infty, \theta). \tag{3.22}$$

The leading-order electric potential is governed by Poisson equation (cf. (2.14))

$$\frac{\partial^2 \varphi^{(0)}}{\partial \rho^2} = -q^{(0)}, \tag{3.23}$$

Substitution of the Boltzmann distributions (3.19) yields the nonlinear Poisson–Boltzmann equation

$$\frac{\partial^2 \varphi^{(0)}}{\partial \rho^2} = C(R=1,\theta)\sinh\left[\varphi^{(0)}(\rho,\theta) - \Phi(R=1,\theta)\right]. \tag{3.24}$$

A single integration (Prieve *et al.* 1984; Rubinstein & Zaltzman 2001) and application of the matching requirements yield the first-order differential equation

$$\frac{\partial \varphi^{(0)}}{\partial \rho} = -2C(R=1,\theta)\sinh\frac{\varphi^{(0)}(\rho,\theta) - \Phi(R=1,\theta)}{2}. \tag{3.25}$$

Subsequent integration yields the familiar Gouy–Chapman distribution, describing a monotonic approach (with exponential attenuation at large ρ) to the macroscale distribution $\Phi(R=1,\theta)$.

The pressure field is now obtained from the leading-order radial momentum balance (see (2.17))

$$\frac{\partial p^{(-2)}}{\partial \rho} = \frac{\partial^2 \varphi^{(0)}}{\partial \rho^2}\frac{\partial \varphi^{(0)}}{\partial \rho}. \tag{3.26}$$

The need to match the $O(1)$ outer pressure, in conjunction with the exponential attenuation of $\partial\varphi^{(0)}/\partial\rho$ at large ρ, readily yields

$$p^{(-2)} = \frac{1}{2}\left(\frac{\partial \varphi^{(0)}}{\partial \rho}\right)^2. \tag{3.27}$$

This expression can be interpreted as an integral momentum equation, wherein the mechanical pressure is balancing the Maxwell stress.

With the electric and pressure fields evaluated, it is now possible to solve the leading-order tangential momentum balance (see (2.17))

$$\frac{\partial^2 v^{(0)}}{\partial \rho^2} = \frac{\partial^2 p^{(-2)}}{\partial \theta} - \frac{\partial^2 \varphi^{(0)}}{\partial \rho^2}\frac{\partial \varphi^{(0)}}{\partial \theta}. \tag{3.28}$$

Integration of this equation (Prieve *et al.* 1984; Rubinstein & Zaltzman 2001) provides $v^{(0)}(\rho)$. Extracting to $\rho \to \infty$ yields

$$v^{(0)} \to \zeta\frac{\partial \Phi}{\partial \theta} + 2\ln\left(1 - \tanh^2\frac{\zeta}{4}\right)\frac{\partial}{\partial \theta}\ln C, \tag{3.29}$$

in which the right-hand side is evaluated at $R=1$, with

$$\zeta = \varphi^{(0)}(\rho=0,\theta) - \Phi(R=1,\theta) \tag{3.30}$$

being the leading-order Debye-layer voltage (the ‘zeta potential’), in general a function of θ.

4. Macroscale transport

With the Debye-scale fields available, the effective boundary conditions for the outer fields at $R=1$ are readily obtained using asymptotic matching.

(*a*) Matching of the tangential velocity component, together with (3.29), yields the Dukhin–Derjaguin slip formula

$$V = \zeta\frac{\partial \Phi}{\partial \theta} + 2\ln\left(1 - \tanh^2\frac{\zeta}{4}\right)\frac{\partial}{\partial \theta}\ln C \quad \text{at} \quad R=1. \tag{4.1a}$$

Matching of the radial component, in conjunction with the inner scaling (3.16*c*), implies

$$U(R=1,\theta)=0. \tag{4.1b}$$

Equations (4.1) are joined to form the vector condition

$$\boldsymbol{V}=\zeta\nabla_S\Phi+2\ln\left(1-\tanh^2\frac{\zeta}{4}\right)\nabla_S\ln C \quad \text{at} \quad R=1, \tag{4.2}$$

wherein

$$\nabla_S=(\boldsymbol{I}-\hat{\boldsymbol{n}}\hat{\boldsymbol{n}})\boldsymbol{\cdot}\nabla \tag{4.3}$$

is the surface gradient operator, in which $\hat{\boldsymbol{n}}$ is an outward pointing unit vector, normal to the surface $R=1$. The first term in (4.2) reflects electro-osmotic flow due to tangential electric field; the second term, which originates in the pressure-gradient term of (3.28), reflects diffusio-osmotic flow due to tangential salt gradients.

(*b*) The boundary condition governing Φ is provided by combining the uniform Dirichlet condition (2.28) on the literal particle boundary $r=1$ with the zeta potential definition (3.30), to obtain

$$\Phi(R=1,\theta)=\mathscr{V}-\zeta(\theta). \tag{4.4}$$

Thus, the uniform Dirichlet condition at $r=1$ is transformed into a non-uniform Dirichlet condition on the macroscale.

(*c*) The condition of zero anionic flux (2.26) at $r=1$ is transformed using (3.22) to the comparable requirement $J_-(R=1,\theta)=0$. Use of (3.5*b*) furnishes the effective boundary condition.

$$\frac{\partial C}{\partial R}=C\frac{\partial \Phi}{\partial R} \quad \text{at} \quad R=1. \tag{4.5}$$

(*d*) Similarly, kinetic condition (2.27) at $r=1$ is transformed using (3.19) and (3.22) to the equation

$$C(R=1,\theta)\exp\{-\zeta(\theta)\}=\gamma\left\{1-\frac{J_+(R=1,\theta)}{k}\right\}. \tag{4.6}$$

Use of (3.5*a*) furnishes the zeta potential distribution,

$$\zeta=\ln C-\ln\gamma-\ln\left\{1+\frac{1}{k}\left(\frac{\partial C}{\partial R}+C\frac{\partial \Phi}{\partial R}\right)\right\}, \tag{4.7}$$

in which the right-hand side is evaluated at $R=1$.

Lastly, it is necessary to rewrite force-free integral condition (2.25) in terms of the macroscale variables. Since the total stress is divergence free (see (2.18)), Gauss theorem allows us to replace the surface $r=1$ with any other surface that encapsulates it. We therefore choose the outer edge of the Debye layer, $R=1$

$$\oint_{R=1}\left[-P\,\boldsymbol{I}+\nabla\boldsymbol{V}+(\nabla\boldsymbol{V})^{\dagger}+\nabla\Phi\nabla\Phi-\tfrac{1}{2}\nabla\Phi\boldsymbol{\cdot}\nabla\Phi\,\boldsymbol{I}\right]\boldsymbol{\cdot}\hat{\boldsymbol{n}}\,\mathrm{d}A=\boldsymbol{0}. \tag{4.8}$$

System (4.2)–(4.8), together with differential equations (3.7)–(3.9) and boundary conditions (3.10), constitutes a self-contained macroscale model which represents electrokinetic transport on the single length scale a^*. In principle, it can be solved to obtain the electrokinetic flow, and specifically the particle velocity $\mathscr{U}$.

The preceding analysis can be easily extended to particles of arbitrary shape (see Yariv 2010). By redefining ρ as a local coordinate normal to the surface, the entire inner derivation remains valid when $r=1$ and θ are respectively interpreted as the particle boundary and its parameterization. In the macroscale model, the surface $R = 1$ is replaced throughout with the effective particle boundary. If the particle does not possess an axis of symmetry which is aligned with the electric field, the problem is no longer axisymmetric; then far-field condition (3.10*c*) must be modified to account for particle rotation, whereby force-free condition (4.8) must be supplemented by a comparable torque-free condition.

4.1. *Comparison to the macroscale model of a comparable inert particle*

In general, the particle acquires electric charge at steady-state condition (with equal and opposite screening charge in the Debye layer). Accordingly, the present problem is reminiscent of the electrophoresis of an ideally polarizable particle which possesses a net electric charge; that problem, described in detail by Squires & Bazant (2004), was analysed by Yariv (2008) for arbitrary values of electric field strength. It is illuminating to compare the two macroscale models.

In the case of ideally polarizable particle, where the surface is chemically inert, connection formulae (3.21) together with ionic impermeability on the particle surface imply that the bulk ionic fluxes $J_{\pm}$ vanish at the effective boundary (see Yariv 2010). In view of (3.5), both the electric potential and the salt concentration then satisfy a homogeneous Neumann condition on that boundary. Since no salt gradient is externally imposed, the salt distribution is rendered uniform, $C \equiv 1$. This uniformity dramatically simplifies the governing equations, since the nonlinear terms in (3.7) and (3.8) disappear. Then, ionic transport is decoupled from the flow, and is simply described by Laplace's equation governing Φ. Nonlinearity is then limited to the Debye-layer capacitance model, whereby the problem can be solved in closed form (Yariv 2008). In the present case, on the other hand, J_{+} is in general non-zero at $R = 1$ (although its integral vanishes at steady-state conditions). Salt polarization appears, significantly affecting the transport process. The governing equations are inherently nonlinear, and in general do not admit a closed-form solution.

The difference between the present problem and the more familiar case of a chemically inert ideally polarizable particle is also manifested in the effective boundary condition on the electric potential. In both cases, the electric potential is uniform on the literal boundary of the particle. In the present problem, this condition is transformed into an effective non-uniform Dirichlet condition, where the potential distribution is found (see (4.4)) by subtracting the zeta potential distribution – obtained using the cation-selectivity condition (see (4.7)) – from the uniform particle potential. While (4.4) is also valid for the case of an inert particle, it cannot be considered a boundary condition, since the zeta potential distribution is unknown. In that case, the electric potential is calculated using the homogeneous Neumann type condition, and (4.4) then serves for the calculation of the zeta potential. These two distinct mathematical procedures reflect the different underlying physics in the two problems.

In addition, the slip condition in the inert case constitutes a simplified version of (4.2); since Φ and C satisfy homogeneous Neumann conditions on the macroscale boundary $R = 1$, the surface gradient in (4.2) may be replaced with the ordinary gradient operator. Moreover, with $C \equiv 1$ the second term in (4.2), representing diffusio-osmosis, is missing.

5. Weak-field analysis

We here calculate an approximate solution of macroscale model (4.2)–(4.8) for weak applied fields, $\beta \ll 1$. This solution is obtained using linearization about the reference state (corresponding to the absence of an applied field)

$$C = 1, \quad \Phi = 0, \quad \boldsymbol{V} = \boldsymbol{0}, \quad P = 0, \tag{5.1a,b,c,d}$$

in which all ionic fluxes vanish. The uniform zeta potential in that state is provided by (4.7)

$$\zeta = -\ln\gamma, \tag{5.2}$$

and with no loss of generality we choose $\mathscr{V} = -\ln\gamma$.

For weak fields we accordingly write (primed variables denote perturbations relative to the reference state)

$$C(R,\theta;\beta) = 1 + \beta C'(R,\theta) + \cdots, \quad \Phi(R,\theta;\beta) = \beta\Phi'(R,\theta) + \cdots, \tag{5.3a,b}$$

whereby the salt flux $\boldsymbol{J}$ and current density $\boldsymbol{I}$ become

$$\boldsymbol{J} = \beta\boldsymbol{J}' + \cdots, \quad \boldsymbol{I} = \beta\boldsymbol{I}' + \cdots, \tag{5.4}$$

with (see (3.4))

$$\boldsymbol{J}' = -\nabla C', \quad \boldsymbol{I}' = -\nabla\Phi'. \tag{5.5a,b}$$

Similarly, the zeta potential is linearized relative to (5.2)

$$\zeta(\theta;\beta) = -\ln\gamma + \beta\zeta'(\theta) + \cdots. \tag{5.6}$$

The $O(1)$ zeta potential and $O(\beta)$ electric field, in conjunction with the slip formula (4.2), suggest $O(\beta)$ velocity and pressure fields

$$U(R,\theta;\beta) = \beta U'(R,\theta) + \cdots, \tag{5.7a}$$

$$V(R,\theta;\beta) = \beta V'(R,\theta) + \cdots, \tag{5.7b}$$

$$P(R,\theta;\beta) = \beta P'(R,\theta) + \cdots. \tag{5.7c}$$

Similarly,

$$\mathscr{U} = \beta\mathscr{U}' + \cdots. \tag{5.8}$$

Both C' and Φ' satisfy Laplace's equation

$$\nabla^2 C' = 0, \quad \nabla^2\Phi' = 0. \tag{5.9a,b}$$

At large distances, as $R \to \infty$

$$C' \to 0, \quad \Phi' \sim -R\cos\theta. \tag{5.10a,b}$$

On the effective particle boundary C' satisfies the Neumann condition

$$\frac{\partial C'}{\partial R} = \frac{\partial \Phi'}{\partial R} \quad \text{at} \quad R = 1, \tag{5.11}$$

while Φ' satisfies the Dirichlet condition

$$\Phi' = -\zeta'(\theta) \quad \text{at} \quad R = 1, \tag{5.12}$$

wherein the zeta potential perturbation is obtained by linearization of (4.7)

$$\zeta' = C' - \frac{1}{k}\left(\frac{\partial C'}{\partial R} + \frac{\partial \Phi'}{\partial R}\right). \tag{5.13}$$

Note that the linearized equations are semi-coupled: the ionic transport problem is unaffected by the flow.

Since (5.10*b*) constitutes the single inhomogeneity in the transport problem, it is readily verified that the harmonic fields C' and Φ' involve only spherical harmonics of the first degree. The solution of (5.9)–(5.13) is

$$C'(R,\theta) = \frac{3}{4R^2(1+2/k)}\cos\theta, \quad \Phi'(R,\theta) = \left\{\frac{1-4/k}{4R^2(1+2/k)} - R\right\}\cos\theta. \quad (5.14a,b)$$

Thus, the application of an electric field induces a dipole of salt concentration. As expected, this dipole corresponds to salt enhancement (depletion) near the anodic (cathodic) side of the particle, $0 < \theta < \pi/2$ ($\pi/2 < \theta < \pi$). This dipole represents salt flux from the anodic hemisphere to the cathodic hemisphere.

We can now solve the flow problem, consisting of the homogeneous Stokes equations,

$$\nabla \cdot \boldsymbol{V}' = 0, \quad \nabla^2 \boldsymbol{V}' = \nabla P'; \quad (5.15a,b)$$

the slip condition at $R = 1$, obtained by substituting (5.2) into (4.2),

$$\boldsymbol{V}' = -\ln\gamma \nabla_S \Phi' + 4\ln\frac{2}{\gamma^{1/4}+\gamma^{-1/4}}\nabla_S C'; \quad (5.16)$$

the far-field attenuation to a uniform stream

$$\boldsymbol{V}' \to -\mathscr{U}'\hat{\boldsymbol{\imath}}; \quad (5.17)$$

and the force-free constraint

$$\oint_{R=1} \left[-P'\boldsymbol{I} + \nabla\boldsymbol{V}' + (\nabla\boldsymbol{V}')^{\dagger}\right]\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A = \boldsymbol{0}, \quad (5.18)$$

in which only the Newtonian stress appears, since the Maxwell stress is quadratic in β.

Our goal does not lie in the structure of the flow field, but rather in the particle velocity $\mathscr{U}'$. Since the flow is governed by the standard Stokes equations, it is possible to evaluate $\mathscr{U}'$ without the detailed calculation of the velocity field: thus, using the method given by Brenner (1964), the force on the particle which is delivered by the Newtonian stresses is provided by the quadrature

$$-\frac{3}{2}\oint_{R=1} (\boldsymbol{V}' + \mathscr{U}'\hat{\boldsymbol{\imath}})\,\mathrm{d}A. \quad (5.19)$$

It is illuminating to focus upon the limit of fast kinetics, $k \to \infty$. Then, $C' = -\Phi'$ at $R = 1$. Considering slip condition (5.16), it is evident that for $\gamma > 1$, where the reference zeta potential is negative, the electro-osmotic and diffusio-osmotic contributions act in opposite directions, with the electro-osmotic component dominating. For $\gamma < 1$, where the reference zeta potential is positive, the two contributions act together. Thus, the direction in which the particle moves is that predicted by classical electrophoresis; due to diffusio-osmosis, however, the electrophoretic velocity differs from that associated with the reference zeta potential $-\ln\gamma$.

Calculation of $\boldsymbol{V}'$ on $R = 1$ using (5.16) together with (5.14), followed by substitution into (5.19), yields the force

$$12\pi\ln\frac{\gamma^{1/4}+\gamma^{-1/4}}{2\gamma^{1/4}} - 6\pi\mathscr{U}' \quad (5.20)$$

in the x-direction. The second term is the familiar Stokes drag on a no-slip stationary particle under an imposed uniform stream $-\mathscr{U}'\hat{\boldsymbol{\imath}}$.

Since (5.19) (or (5.20)) is equivalent to the left-hand side of (5.18), it must vanish. We therefore obtain

$$\mathscr{U}' = 2\ln\frac{\gamma^{1/4}+\gamma^{-1/4}}{2\gamma^{1/4}}. \tag{5.21}$$

Thus, $\mathscr{U}'$ is positive for $\gamma < 1$ and negative for $\gamma > 1$, as expected. For a highly charged particle, where $\gamma \gg 1$, $\mathscr{U}' \sim -\ln 4$. Note that $\mathscr{U}'$ represents a normalization of the dimensional velocity with the Smoluchowski-type scale $\epsilon^*\varphi^*E^*/\mu^*$.

6. Particle charge

Another quantity of interest is the net charge the particle acquires at steady state. In principle, the particle may exchange charge with its surrounding electrolyte because of its permeability to cations. The sign of this charge depends upon the kinetic constant γ. For $\gamma > 1$, selectivity relation (2.27) suggets positive Debye layer space charge, corresponding to negative zeta potential. We then expect a negative particle charge.

Use of Gauss law yields the following expression for the total particle charge (normalized by $\epsilon^*a^*\varphi^*$)

$$-\oint_{r=1}\frac{\partial\varphi}{\partial r}\,\mathrm{d}A. \tag{6.1}$$

In the thin-Debye-layer limit, this integral is expressed using the inner variable (see (3.11)) as

$$-\delta^{-1}\oint_{\rho=0}\frac{\partial\varphi}{\partial\rho}\,\mathrm{d}A. \tag{6.2}$$

Substitution of (3.25) in conjunction with (3.30) yields the leading-order charge approximation in terms of the zeta potential and bulk concentration at $R = 1$

$$2\delta^{-1}\oint_{R=1} C\sinh\frac{\zeta}{2}\,\mathrm{d}A. \tag{6.3}$$

It is again useful to focus upon the limit $k \to \infty$, where (4.7) yields, for the leading-order zeta potential,

$$\zeta = \ln C - \ln\gamma. \tag{6.4}$$

Then, (6.3) becomes

$$\delta^{-1}\oint_{R=1} C\left[(C/\gamma)^{1/2} - (\gamma/C)^{1/2}\right]\mathrm{d}A. \tag{6.5}$$

For weak fields, where $C \sim 1 + O(\beta)$, this quadrature yields the value

$$\frac{4\pi(1-\gamma)}{\delta\gamma^{1/2}}. \tag{6.6}$$

For $\gamma > 1$, this value is indeed negative, corresponding to a negative value of $\mathscr{U}$ (see (5.21)).

7. Discussion

A closed microscale model of the electrokinetic flow about a conducting cation exchanger was formulated. The dimensionless problem depends upon the following parameters: (i) the Péclet number α, a dimensionless group which is independent of particle size; (ii) the applied field magnitude β (normalized with the thermal scale);

(iii) the two kinetic parameters, γ and k, which describe the cation exchange; and (iv) the Debye thickness δ (normalized with particle size).

In all realistic situations $\delta \rightarrow 0$ whereby practical interest lies in the macroscale transport. Using matched asymptotic expansions, an effective bulk model is extracted on the particle scale. The bulk-scale differential equations comprise a diffusion–advection equation governing the salt concentration, an elliptic equation governing the electric potential and the Stokes equations with an electric body force. These equations are supplemented by far-field conditions, as well as effective boundary conditions which represent asymptotic matching with the Debye-scale field. The governing equations are closed by macroscale version of the force-free integral constraint.

An important element of the macroscale model is the emergence of the zeta potential (the Debye-layer voltage) in the effective boundary condition governing the fluid velocity. This quantity, which in general varies along the macroscale particle boundary, can be determined only once wheras the salt concentration and the electric field both are evaluated in the bulk.

The dependence of the zeta potential distribution upon the applied field is reminiscent of 'induced-charged' electro-osmosis (Squires & Bazant 2004). Prevailing models of induced-charge flows, however, tend to focus upon ideally polarizable surfaces. While highly conducting, these surfaces are chemically inert also. As such, the analysis of ideally polarizable surfaces is relatively simple: the salt concentration is uniform, whereby ionic transport is decoupled from the flow. None of these benefits applies to the present analysis; thus, the extracted macroscale model, valid for $O(1)$ values of the applied fields (comparable with the thermal scale), cannot be solved analytically even for the simplest geometries.

Approximate solutions, however, can be obtained for weak fields, wherein the particle velocity scales linearly with the applied field magnitude. Even that problem is rather complicated because of the inevitable presence of concentration polarization. Thus, while the uniform zeta potential and the linear dependence upon the electric field may superficially resemble classical electrophoresis, particle motion is actually driven by both electro-osmotic and diffusio-osmotic slip. Moreover, the diffusio-osmotic flow mechanism differs from that in a classical diffusio-phoretic problem: here, salt gradients are driven by salt 'injection' at the particle boundary (associated with the need for zero anionic flux there), rather than an externally imposed ambient gradient. Consequently, the diffusio-osmotic flow component is rotational, in contrast to the irrotational flow structure in classical diffusio-phoresis (Prieve *et al.* 1984). The existence of electric-field-driven salt gradients that affect particle velocity clearly implies that Smoluchowski's formula does not hold.

When the applied field is strong ($\beta \gg 1$) it is anticipated that the fluid velocity becomes large, whereby α no longer qualifies as a Péclet number. Diffusion is then dominated by convection except in a narrow layer surrounding the particle. Outside that layer, the fluid is approximately ohmic. This situation somewhat resembles singular convective–diffusive processes (Leal 2007), where the diffusive boundary-layer thickness scales as an inverse power of the Péclet number. The present problem is more subtle because of the active role of both convection and electromigration as competitors to ion diffusion. Moreover, the (presumably large) velocity magnitude (or, equivalently, the effective Péclet number) is not known a priori, and must be found – together with the scaling of the other pertinent variables and the diffusion-layer thickness – throughout the solution procedure. The investigation of this challenging open problem constitutes a desired extension of the present analysis.

There is an additional complication at strongly applied fields, which is best understood in the one-dimensional framework which motivated the present analysis. As the applied voltage increases, the salt gradient in the diffusion layer steepens, eventually leading to vanishing salt concentrations at the cathodic exchanger (Levich 1962). While this phenomenon may appear to suggest a diffusion-limited current, it is actually possible to achieve currents exceeding this limit. As explained by Rubinstein, Zaltzman & Kedem (1997), the diffusion-layer structure breaks down at $O(\ln\delta)$ voltages, wherein a new 'extended space charge' region is formed between the cathodic Debye layer and the diffusion layer (Rubinstein & Shtilman 1979). At $O(1/\delta)$ voltages this space-charge region extends over an $O(1)$ distance, in which the salt concentration is small and the electric field is intense, scaling as $1/\delta$ (Zaltzman & Rubinstein 2007). The required voltages are then dominated by this region, and possess an identical scaling (Ben & Chang 2002; Chu & Bazant 2005; Yariv 2009).

When the boundary is curved and the applied field is sufficiently strong, similar transition may occur over part of the boundary; this renders a more complex electrokinetic flow mechanism, termed as 'electro-osmosis of the second kind' (Dukhin 1991). It was suggested by Dukhin (1991) that the familiar Smoluchowski slip formula can be applied to second-kind electro-osmosis at overlimiting conditions, provided the zeta potential also accounts for the voltage drop on the extended-space-charge layer. Using these heuristic arguments and assuming large Péclet numbers, Dukhin (1991) obtained an electrophoretic velocity that scales as the square of the applied field. This analysis was improved by Mishchuk & Takhistov (1995). Ben & Chang (2002) employed asymptotic methods to derive an approximate current–voltage characteristics for a one-dimensional model problem; using these characteristics to describe transport process on the cathodic hemisphere, the authors obtained a more sophisticated model for the electrophoretic problem. In a later analysis, Ben *et al.* (2004) found a different scaling for the velocity, as the electric-field to the 2/3-power, at the large-Péclet limit. Both of these power-law predictions are in some qualitative agreement with existing experimental data at different regimes (Mishchuk & Takhistov 1995; Barany, Mishchuk & Prieve 1998). A different velocity scaling, with the third power of electric field, was found by Zaltzman & Rubinstein (2007) (see also Kim *et al.* 2007). The singular problem of large Péclet numbers and overlimiting currents was recently analysed by Kalaïdin *et al.* (2009) for a specific distinguished limit, where the applied field scales as $\delta^{-1/2}$.

The transition to overlimiting currents occurs when the electric field becomes large, in some sense. The same is true for the transition to the strong-convection regime (large Péclet numbers), since the velocity scale is set by the applied field magnitude. In general, the strong convection regime is reached when the applied field E^* becomes large compared with the thermal field scale φ^*/a^* (see (2.2)); overlimiting currents, on the other hand, occur at voltages which are greater than $O(\ln\delta)$. Whether and how these two 'strong-field' limits are related is yet unclear. The obvious difficulties in resolving the problem of second-kind electro-osmosis at the overlimiting current regime only emphasize the importance of the present systematic analysis.

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