Ionic currents in the presence of supporting electrolytes

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Abstract

We analyze one-dimensional charge conduction within an ionic solution in the presence of supporting electrolytes that do not discharge on the electrodes. For thin Debye layers, numerical simulations predict current abatement, in agreement with existing experimental observations; in addition, they reveal unconventional features absent from classical analyses of binary solutions, such as high cation concentration near the electrodes. We derive a companion asymptotic description of the problem in the singular thin-Debye-layer limit, reproducing these attributes. The asymptotic analysis reveals a nested boundary-layer structure about the reactive electrodes and furnishes a universal current–voltage relation.

Introduction.— The analysis of ionic currents driven by reactive electrodes is a classical problem in electrochemistry [1]. When analyzed using a continuum description [2], the electrodes are conceptually represented as ion-selective membranes that generate and consume only one ionic species. Classical analyses of the one-dimensional transport process have typically considered the simplest case of a dilute *binary* solution bounded by cation-exchange membranes. At steady-state the solution is approximately electro-neutral, except for two narrow Debye layer adjacent to the membranes. At the electro-neutral region, the (identical) concentrations of the two ionic species are nonuniform, decreasing toward the cathode; the associated diffusive flux guarantees zero anionic current. This generic picture also applies to transport through other ion-selective obstacles, such as porous granules [3] and nano-channel arrays [4]; it leads a universal current–voltage (j–V) relation at the thin-Debye-layer limit, which agrees well with numerical simulations.

In most realistic scenarios, however, the dissolved salt ions do not discharge on the electrodes and act as *supporting* electrolytes; charge is then carried by an additional *reactive* ionic species. The transport in these ternary solutions is significantly different from that in their binary counterparts. Indeed, it is well known that the presence of supporting electrolytes significantly reduces the electric field and reactive ions concentration, resulting in weak currents [2]. Since the active species is generated and consumed at the electrodes, its concentration cannot be “prescribed” in any manner; it is therefore *a priori* unclear what would render its concentration “small” — what does this small concentration scale with?

In the early electro-neutral models of transport in the presence of supporting electrolytes [1, 2], small reactive-species concentration was assumed at the outset, allowing for straightforward linearization. Employing a more realistic Poissonn–Nernst–Planck model, the transport problem was recently analyzed using singular perturbations in the thin-Debye-layer limit [5], with integral “memory” conditions on the ionic concentrations (cf. [6]). By assigning different weights to the initial concentrations, the authors obtain a generalization of the binary-solution description [7] to ternary systems. Since this generalization is naturally associated with comparable concentrations of active and inert species, it cannot explain the underlying cause of concentration disparity. Our goal here is to present a systematic model which undertakes this task.

Problem formulation.—Consider a prototypical electrochemical cell comprising an electrolyte solution (permittivity ϵ_*) flanked between two cation exchange membranes spaced a distance L_* apart. The salt in the solution is dissolved into two univalent ionic species (of identical global concentration c_*); these "inert" species do not interact with the electrodes. Charge flow occurs through transport of a third (positive) univalent ionic species which can discharge on the electrodes — the "reactive" species.

At time zero, the cell is exposed to an externally imposed voltage, applied to the two electrodes. Our interest lies in steady-state transport in the system. We employ a dimensionless notation wherein the coordinate x and electric potential φ are respectively normalized by the cell width L_* and the thermal voltage k_*T_*/e_* (k_*T_* being the Boltzmann factor and e_* the elementary charge). The inert species concentrations $c^{\pm}$ and the reactive species concentration r are normalized by c_*. The cathode ($x = 0$) is maintained at a negative electric potential, $-V$, relative to the anode ($x = 1$).

Due to the one-dimensional geometry, steady-state ionic conservation implies uniform fluxes for all ionic species. Since the two inert species do not discharge at the membranes, their respective fluxes must vanish. The active cations, on the other hand, experience a uniform flux, say j (normalized with D_*c_*/L_*, D_* being their diffusivity) directed towards the cathode. Thus, the Nernst–Planck equations possess the following integrals:

$$\mp\frac{dc^{\pm}}{dx} + c^{\pm}e = 0, \qquad -\frac{dr}{dx} + re = -j. \tag{1}$$

The electric field $e = -d\varphi/dx$, in turn, is governed by the Poisson equation

$$c^{+} - c^{-} + r = 2\delta^{2}\frac{de}{dx}. \tag{2}$$

Here, $\delta = \lambda_*/L_*$ is the dimensionless Debye thickness, in which λ_* is the Debye width, $\lambda_*^2 = \epsilon_*k_*T_*/2e_*^2c_*$.

In addition to the differential equations (1)–(2), the pertinent fields are also governed by kinetic boundary conditions, representing cation exchange. Following [3, 7], we adopt the simplest model of ideal cationic selectivity, whereby the reactive-species concentration is specified at the electrodes:

$$r = p \quad \text{at} \qquad x = 0, 1. \tag{3}$$

Supplementing the preceding equations are three integral conditions. The first reflects the imposed voltage:

$$\int_0^1 e\,dx = -V. \tag{4}$$

The other two represent "memory conditions" [5, 6], specifying the invariance of the total amount of inert cations and anions,

$$\int_0^1 (c^{\pm} - 1)\, dx = 0. \tag{5}$$

This invariance reflects membrane impermeability to the dissolved salt ions.

When employing the alternative variables, $c = c^+ + c^- + r$ and $q = c^+ - c^- + r$, the Nersnt–Planck equations become $dc/dx - qe = dq/dx - ce = j$. Following [7], these equations (in conjunction with (2)) are integrated to yield $c = jx + \delta^2 e^2 + D$ as well as an independent differential equation for the electric field

$$2\delta^2 \frac{d^2 e}{dx^2} - e\left(jx + \delta^2 e^2 + D\right) = j. \tag{6}$$

The integration constant D is found from the normalization conditions (5) in conjunction with (2):

$$D = 2 - \frac{j}{2} + \delta^2 \left[2e(x = 1) - 2e(x = 0) - \int_0^1 e^2\, dx\right]. \tag{7}$$

The potentio-static problem (1)–(5) determines j (together with the pertinent field variables) as a function of V, δ, and p. Note that j constitutes the electric current towards the membrane (normalized with $e_* D_* c_* / L_*$). No closed-form solution is available for this problem; note however that (1) implies the Boltzmann distributions $c^{\pm} \propto e^{\mp\varphi}$, whereby $c^+ c^- = \text{const}$.

The thin-Debye-layer limit.—We focus upon the limit $\delta \ll 1$ at moderate voltages, $V = O(1)$. Poisson's equation (2) then suggests approximate electro-neutrality, just as in the comparable case of binary solutions. While in that case one expects $j = O(1)$, the situation here is more delicate. Indeed, electro-neutrality implies $r \approx c^- - c^+$; but then the integral constraints (5) and the positivity of r indicate that it must be asymptotically small:

$$r \sim \mu(\delta) r_0 + \cdots, \tag{8}$$

where $\mu(\delta) \ll 1$ is a (yet unknown) pre-factor. This minute concentration results in comparably small currents (see (10)), in agreement with the experimental observations.

The smallness of r is supported by numerical solution of the problem (1)–(5), which can be reduced to a boundary-value problem. In all numerical simulations we use $p = 2$ (cf. [3, 7]). Figure 1 presents the numerically evaluated concentration profiles for $V = 1$ and $\delta = 0.01$; it indicates that r is indeed small (and that $c^{\pm}$ constitute small perturbations

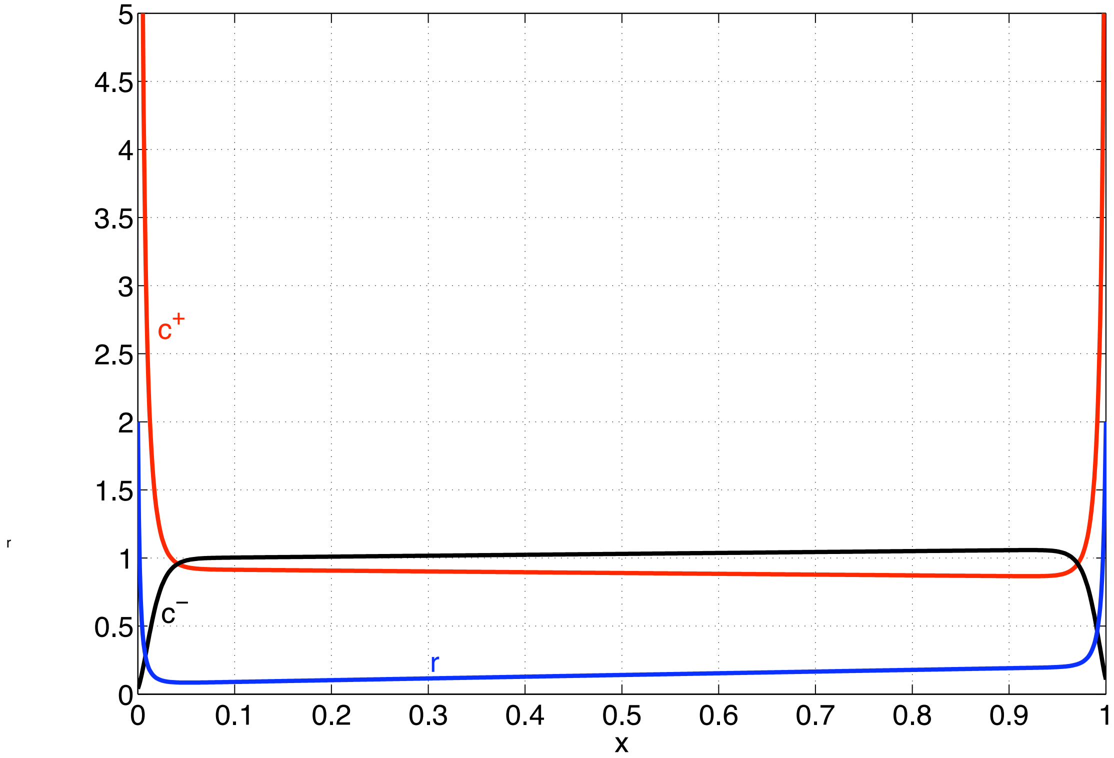

FIG. 1. Numerically evaluated c^+, c^- and r ($V = 1$, $\delta = 0.01$).

to the unity equilibrium value). The numerical results clearly show the emergence of two boundary ("Debye") layer, familiar from the comparable binary case. Surprisingly, Fig. 1 indicates large cation concentration at these layers; this feature is unfamiliar from the binary case, where ionic concentrations are $O(1)$ in the Debye layer [7]. Moreover, the numerically-evaluated electric field in the layers reach extremely high values, much larger than the familiar $O(1/\delta)$ scaling of the binary case.

Another departure from the binary case is revealed in Fig. 2 which depicts the current–voltage correlation, evaluated numerically for several δ-values. While this correlation approaches a universal limit in the binary case, it fails to do so in the present problem; rather, the figure indicates diminishing currents as $\delta \to 0$.

In what follows we devise an analytic approximation that explains the non-conventional features of the problem; *inter alia*, it provides the scaling factor $\mu(\delta)$ and the j–V correlation.

Asymptotic approximations.—In view of (8), we postulate the following expansions for

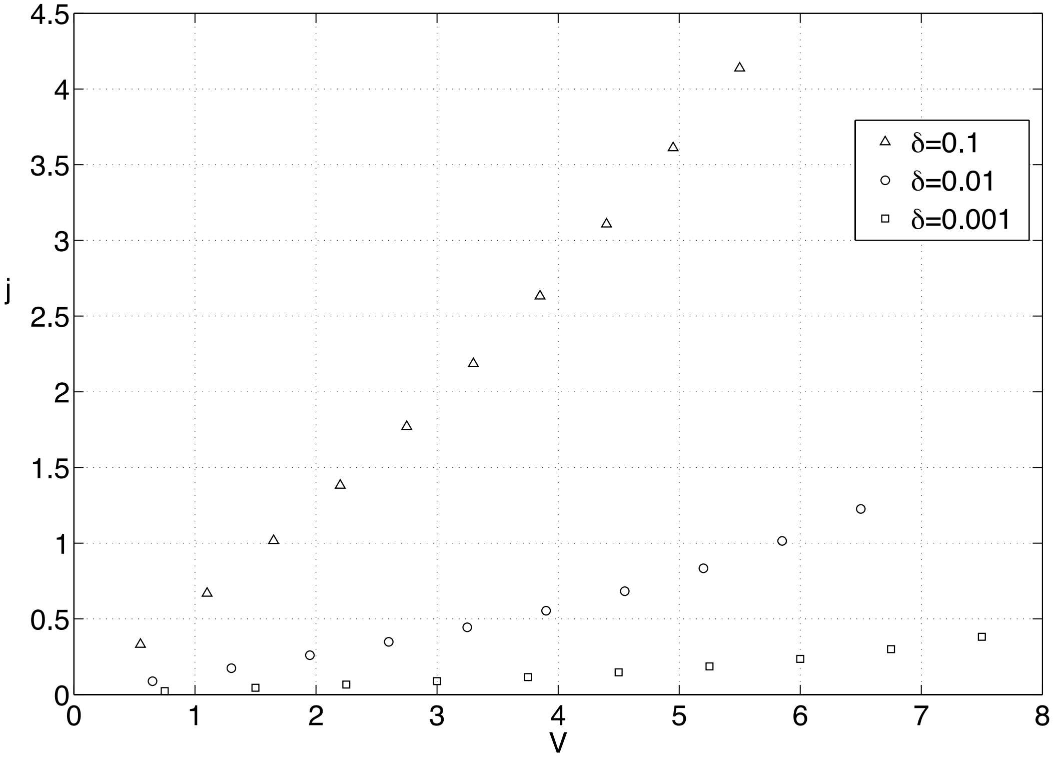

FIG. 2. Numerically evaluated j as a function of V for the indicated δ values.

the two inert species and the electric field,

$$c^{\pm} \sim 1 + \mu(\delta) c_0^{\pm} + \cdots, \quad e \sim \mu(\delta) e_0 + \cdots; \tag{9}$$

in view of (1), these Poincaré series approximation suggest the parametric expansion

$$j \sim \mu(\delta) j_0 + \cdots. \tag{10}$$

The solution of the transport problem readily gives the linealry-varying concentrations (cf. Fig. 1):

$$c_0^{\pm} = \mp \frac{1}{2} j_0 (x - x_{\pm}), \quad r_0 = \frac{1}{2} j_0 \left(2x - x_+ - x_-\right) \tag{11}$$

(where $x_{\pm}$ are integration constants) and the uniform electric field

$$e_0 = -\frac{1}{2} j_0. \tag{12}$$

The preceding approximations cannot satisfy the boundary conditions (3); this non-uniformity originates at the singular nature of the limit $\delta \to 0$ reflected in the Poisson equation (2). Indeed, this equation suggests the existence of two $O(\delta)$-thick boundary layers about $x = 0$ and $x = 1$, where the preceding electro-neutral approximations constitute an "outer" solution outside them. The "left" layer about $x = 0$ is descried by the inner variable $X = x/\delta$. Following the well known Debye-layer structure in the binary case [7], the concentrations $c^{\pm}$ are assumed $O(1)$ and the electric field $O(1/\delta)$:

$$c^{\pm} \sim C_0^{\pm}(X;\delta) + \cdots , \quad e \sim \delta^{-1} E_0(X;\delta) + \cdots . \tag{13}$$

The scaling of the reactive concentration r, on the other hand, must be compatible with (8):

$$r \sim \mu(\delta) R_0(X;\delta) + \cdots . \tag{14}$$

We tacitly assume, subject to *a posteriori* verification, that $D \sim 2$ (see (7)). Substitution into (6) then yields

$$2\frac{d^2 E_0}{dX^2} - E_0^3 - 2E_0 = 0. \tag{15}$$

Two successive integrations, in conjunction with the decay of E_0 at large X (necessitated by the required matching with the outer solution) yield

$$E_0 = -\frac{2}{\sinh(X + X_0)}, \tag{16}$$

where X_0 is a constant of integration.

With the electric field known, the leading-order Nernst–Planck equations (1) readily yield

$$C_0^{+} = \tanh^{-2}\frac{X + X_0}{2}, \quad C_0^{-} = \tanh^{2}\frac{X + X_0}{2}, \tag{17}$$

wherein matching with the outer solution is already accounted for. In addition, since R_0 satisfies the same differential equation as C_0^{+}, it has a similar solution

$$R_0 = \Gamma_0 \tanh^{-2}\frac{X + X_0}{2}, \tag{18}$$

wherein matching with the "left" end of the outer solution (11) yields $\Gamma_0 = -j_0(x_+ + x_-)/2$.

A similar boundary layer exists about $x = 1$, where the electric field is positive. Defining now $X = (1 - x)/\delta$, and using expansions comparable to (13)–(14) we readily obtain the electric field $\bar{E}_0 = 2/\sinh(X + \bar{X}_0)$ (cf. (16)). The concentrations $\bar{C}_0^{\pm}$ and $\bar{R}_0$ in that layer are provided by (17) (with X_0 and Γ_0 respectively replaced by $\bar{X}_0$ and $\bar{\Gamma}_0$), wherein matching with the "right" end of the outer solution yields $\bar{\Gamma}_0 = j_0[1 - (x_+ + x_-)/2]$.

Direct application of condition (3) to (18) yields

$$\tanh\frac{X_0}{2}=\mu^{1/2}\left(\frac{\Gamma_0}{p}\right)^{1/2}, \tag{19}$$

with a similar expression for $\bar{X}_0$.

Scaling and j–V relation.—Consider now the integral condition (5). Assuming (subject to *a posteriori* verification) $\mu \gg \delta$ we readily find that the leading-order contribution to the integral appearing in the constraint on c^- is $O(\mu)$ and is provided only by the outer region. Equation (11) then yields $x^- = 1/2$.

Since (19) implies $c^+ \sim O(\mu^{-1}) \gg 1$ near $x = 0$, the situation is different when considering the constraint (5) on c^+. Here, one needs to consider both the outer leading-order contribution

$$\mu\int_0^1 c_0^+(x)\,dx, \tag{20}$$

and the combined leading-order contributions from the boundary layers,

$$\delta\int_0^\infty \left\{C_0(X;\delta)+\bar{C}_0(X;\delta)-2\right\}\,dX. \tag{21}$$

Using (19), the latter are readily evaluated as $O(\delta\mu^{-1/2})$. The dominant balance then implies

$$\mu(\delta)=\delta^{2/3}, \tag{22}$$

which indeed satisfies $\mu \gg \delta$. (Note that the scaling of the outer and Debye-layer fields immediately implies $D \sim 2$, thereby confirming our *a priori* assumption.) Evaluation of (20)–(21) with the aid of (11), (17), and (19) yields

$$\frac{1}{2}j_0\left(x_+-\frac{1}{2}\right)+2p^{1/2}\left(\Gamma_0^{-1/2}+\bar{\Gamma}_0^{-1/2}\right)=0. \tag{23}$$

Consider now the leading-order balance of the voltage condition (4):

$$\int_0^\infty \left\{E_0(X;\delta)+\bar{E}_0(X;\delta)\right\}\,dX \to -V \quad \text{as} \quad \delta\to 0.$$

Performing the integration in conjunction with (19) yields $\bar{\Gamma}_0/\Gamma_0 = e^V$. Using (23) we then obtain the desired relation between j_0 and V:

$$j_0^{3/2}=4p^{1/2}(e^V-1)^{1/2}\left(e^{-V/2}+1\right)\tanh\frac{V}{2}. \tag{24}$$

Results and discussion.—The combination of electro-neutrality and memory conditions (5) with equal amounts of cations and anions is naturally translated to a small current whose scaling is *a priori* unknown. This was entirely missed in previous analyses of the problem [5, 6], where a greater weight is assigned to c^- in their counterparts of the integral conditions (5). This imposed asymmetry leads to a straightforward extension of the binary-solution scheme. It is therefore hardly surprising that these analyses have overlooked the highly singular nature of the present problem which leads to low concentrations of the reactive ions away from the boundaries and, consequently, to an asymptotically small $O(\delta^{2/3})$ current.

The weak current scaling, as well as the additional unconventional features of the present problem, are all related to (19) which implies a transition to an $O(\delta^{4/3})$-thick *sub-layer* wherein $e \sim O(\delta^{-4/3})$ and $c^+ \sim O(\delta^{-2/3})$; this is consistent with the numerically-observed exceptional values attained by c^+ and e near $x = 0, 1$. The sub-layer adjacent to $x = 0$ is described by the inner variable $x = \delta^{4/3}\xi$. At that sub-layer, the electric field is

$$e \sim -\frac{\delta^{-4/3}}{\frac{1}{2}\xi + (\Gamma_0/p)^{1/2}}. \tag{25}$$

The emergence of the sub-layer originates from the similarity in the transport of the two positive species, see (1). To leading order, c^+ and r satisfy the same first-order equation in the Debye layer (where the effect of the net current opon r is relegated to higher orders) and are therefore proportional. At the electro-neutral outer edge of the layer, where $r \sim O(\delta^{2/3})$, c^+ is $O(1)$; the kinetic condition (3) then necessities $O(\delta^{-2/3})$ large c^+-values near $x = 0$. The diffusive flux on the short $O(\delta^{4/3})$ scale is subsequently countered by strong electro-migration.

The asymptotic results agree favorably with numerical solutions of the potentiostatic problem (1)–(5) for $V = 1$. In Fig. 3 we show the electric field near $x = 0$; because of its intense values (see (25)) we use logarithmic scales. For $x \lesssim \delta^{4/3}$ the exact solution agrees with the sub-layer approximation (25). The Debye-layer approximation (16) is in good agreement with the numerical simulation up to the edge of electro-neutral region, at about $x \approx 10\delta$, whereupon the outer approximation (12) becomes useful.

The lumped description of the transport process is provided by the j–V relation. The electric-current scaling (10) with $\delta^{2/3}$ clearly explains the spurious scatter in the numerically evaluated data in Fig. 2. In Fig. 4 we re-plot the same data with j normalized by $\delta^{2/3}$, where they collapse on a single curve. This curve agrees with the universal relation (24).

Conclusions.—Numerical simulation of one-dimensional ionic currents in the presence of supporting electrolytes predicts small currents, as in experimental data. In addition, it also

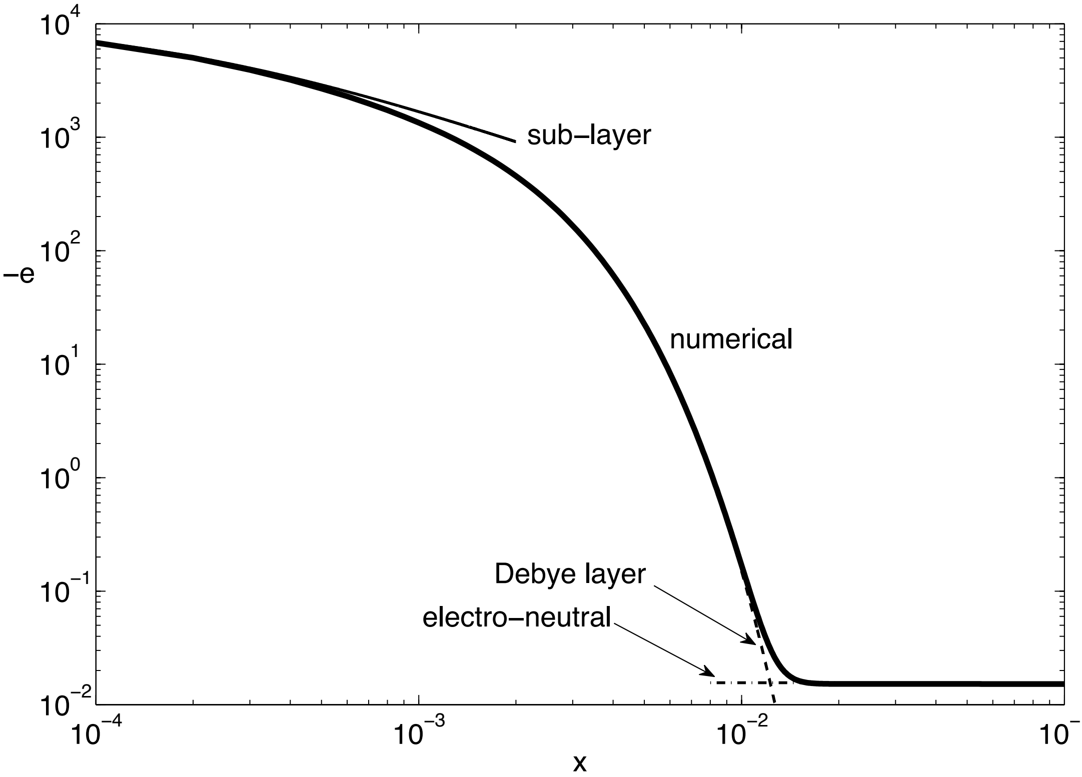

FIG. 3. Electric field in the left boundary layer for $V = 1$ and $\delta = 0.001$: numerical solution (solid), Debye-layer approximations (dashed), electro-neutral approximations (dashed-dotted), sub-layer approximation (thin).

reveals a number of features unfamiliar from conventional analysis of binary solutions, the most remarkable being high cation concentration near the electrode. Asymptotic analysis of the problem reveals a highly singular behavior, wherein internal sub-layers emerge within the Debye layers. This nested structure results in electric current that scales as the 2/3-power of the Debye width. The analytic and numerical results agree favorably.

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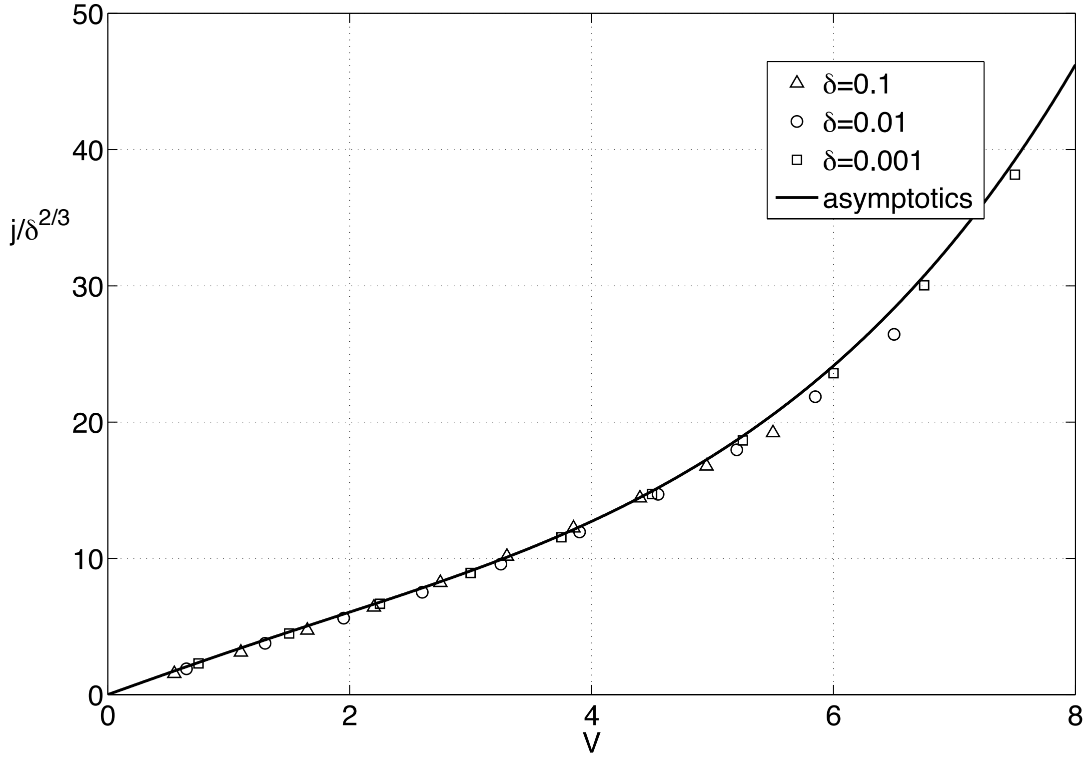

FIG. 4. j, scaled by $\delta^{2/3}$, as a function of V. The data is that of Fig. 2. The solid line is (24).

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