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DOUBLE LAYER STRUCTURE AT THE LIMITING CURRENT

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Abstract

Apparent anomalies in charge and field distributions in the diffusion layer and the diffuse double layer at the limiting current are resolved by means of two matching expansions valid in the two regions. The region of appreciable deviation from electroneutrality is thicker, and in this region the electric field is expected to be smaller, than at currents below the limiting current. Modified zeta potentials are calculated for a cation-discharge reaction.

Introduction

In the diffuse part of the double layer at equilibrium, the concentration c_i of an ion obeys a Boltzmann distribution as a function of the electrical potential Φ (cf. Grahame[1]):

$$c_i = c_i^o \exp(-z_i F\Phi/RT) , \tag{1}$$

where c_i^o is the concentration of i in the bulk, $z_i F$ is the charge on species i, and RT has its usual meaning. The concentration and potential distribution in the double layer during the passage of current is of interest, for example, in electrode kinetics. Levich[2,3] has found that for small currents the concentration of non-discharging ions obeys a Boltzmann-type dependence on the electrical potential in the double layer. It was also found that the discharging ions follow very closely a Boltzmann-type distribution.

More recent work[4,5,6] has been directed toward obtaining the concentration and potential distribution not only in the double layer, but also in the diffusion layer outside the double layer, again for small currents. For many years it has been believed that an electrolytic solution, even during passage of current, can be treated as two regions: (1) the diffuse part of the double layer, where deviations from electroneutrality are significant but convection can be neglected and the concentrations and potential are distributed approximately as in a double layer at equilibrium, and (2) the diffusion layer where convection must be taken into account but electroneutrality is a good approximation. Bass[7] has criticized the assumption of electroneutrality in the diffusion layer but failed to appreciate the nature of this approximation, i.e., the charge density is small compared to the concentration of the electrolyte. For a binary, symmetric electrolyte in solution, this approximation is expressed by

$$|c_+ - c_-| \ll c_+ + c_- . \tag{2}$$

The concept of two distinct regions of the solution was given a firm mathematical basis in the previous paper[8], and in addition it was demonstrated how one may make the corrections to the "equilibrium" distributions to account for the passage of current. Again, the analysis was for currents smaller than the limiting current.

The intent of the present paper is to elucidate the structure of the double layer at limiting current. The classical treatment of the diffusion layer at limiting current shows the concentration approaching zero at the electrode surface. As a consequence, the electric field approaches infinity, and this raises a question about the validity of the electroneutrality assumption, at least in the inner part of the diffusion layer. An infinite electric field implies an infinite charge density, but one would expect the surface charge density actually to be smaller at limiting current. It is also found that within the diffuse part of the double layer the electric field associated with the passage of current must be accounted for in the first approximation.

The analysis is carried out for a symmetric electrolyte of valence z. The governing differential equations, the conservation equations for anions and cations and Poisson's equation, are taken to be the same as before[8], and are subject to the same restrictions and boundary conditions. The convective velocity is taken to be that for a rotating disk, $v_y = -A\,y^2$, but this is appropriate for other hydrodynamic situations as well. The dimensionless formulation is also very similar, but the bulk concentration c_∞ is used in forming dimensionless variables and parameters instead of the concentration just outside the diffuse double layer. Thus we use

i) concentration and charge density,

$$C = (c_+ + c_-)/2c_\infty\,, \qquad \rho = (c_+ - c_-)/2c_\infty\,, \tag{3}$$

ii) electric field and independent variable appropriate for the diffusion layer,

$$\tilde{E} = zF\xi(3D/A)^{1/3}/RT\,, \qquad \tilde{x} = y/(3D/A)^{1/3}\,, \tag{4}$$

iii) fluxes at the interface,

$$a = \frac{(3D/A)^{1/3}}{2c_\infty}\left(\frac{N_+^o}{D_+} + \frac{N_-^o}{D_-}\right), \qquad b = \frac{(3D/A)^{1/3}}{2c_\infty}\left(\frac{N_+^o}{D_+} - \frac{N_-^o}{D_-}\right), \tag{5}$$

iv) parameters,

$$r = (D_+ - D_-)/(D_+ + D_-), \qquad \delta = \lambda/(3D/A)^{1/3}, \tag{6}$$

where $\lambda = \sqrt{\epsilon RT/2c_\infty z^2F^2}$, $D = 2D_+D_-/(D_+ + D_-)$.

In terms of these quantities, the differential equations become

$$C'' + 3\tilde{x}^2C' = 3r\tilde{x}^2\rho' + (\rho\tilde{E})', \tag{7}$$

$$\rho'' + 3\tilde{x}^2\rho' = 3r\tilde{x}^2C' + (C\tilde{E})', \tag{8}$$

$$\rho = \delta^2\tilde{E}', \tag{9}$$

where the primes denote differentiation with respect to $\tilde{x}$.

The First Approximations

In the diffusion layer, equation (9) indicates that the charge density is small and of order δ^2. Let the first approximations to the concentration and the electric field in the diffusion layer be denoted by $\tilde{C}_o(\tilde{x})$ and $\tilde{E}_o(\tilde{x})$, with the anticipation that higher order terms can be obtained later. Since ρ is small, $\tilde{C}_o$ satisfies the equation

$$\tilde{C}_o'' + 3\tilde{x}^2\tilde{C}_o' = 0 \tag{10}$$

with the solution

$$\tilde{C}_o = 1 + P_o\int_\infty^{\tilde{x}} e^{-x^3}\,dx, \tag{11}$$

which satisfies the boundary condition $\tilde{C}_o \to 1$ as $\tilde{x} \to \infty$. To correspond to the classical limiting current, $\tilde{C}_o \to 0$ as $\tilde{x} \to 0$, and the integration constant is $P_o = 1/\Gamma(4/3)$. Equation (11) becomes

$$\tilde{C}_o = \frac{1}{\Gamma(4/3)}\int_0^{\tilde{x}} e^{-x^3}\,dx. \tag{12}$$

This function is tabulated in reference 9. The first approximation to the electric field is obtained from equation (8)

$$(\tilde{C}_o\tilde{E}_o)' = -3r\tilde{x}^2\tilde{C}_o' = \frac{-3r\tilde{x}^2e^{-\tilde{x}^3}}{\Gamma(4/3)} , \tag{13}$$

with the solution

$$\tilde{E}_o = \frac{I_o+re^{-\tilde{x}^3}}{\tilde{C}_o\Gamma(4/3)} . \tag{14}$$

The first approximation to the charge density is related to the derivative of the electric field by equation (9). For small values of $\tilde{x}$ this becomes infinite in the following manner:

$$\rho \approx \delta^2\tilde{E}_o' \rightarrow -\delta^2(I_o+r)/\tilde{x}^2 \text{ as } \tilde{x} \rightarrow 0 . \tag{15}$$

This becomes of the same order of magnitude as the concentration $\tilde{C}_o \approx \tilde{x}/\Gamma(4/3)$, and the electroneutrality approximation breaks down, for values of $\tilde{x}$ on the order of $\delta^{2/3}$. This indicates that the outer edge of the diffuse double layer extends to the region where $\tilde{x} = O(\delta^{2/3})$, and an appropriate inner variable for the double-layer region is

$$\bar{x} = \tilde{x}/\delta^{2/3} . \tag{16}$$

The double-layer region is still thin compared to the diffusion layer but is considerably thicker than the double-layer region at currents much below the limiting current, where the thickness, in terms of $\tilde{x}$, is of order δ. This result is in agreement with that of Grafov and Chernenko[4] and Chernenko[6], who touch briefly on the structure of the double layer at limiting current.

In terms of the inner variable $\bar{x}$, the differential equations are

$$C'' + 3\bar{x}^2\delta^2C' = 3r\bar{x}^2\delta^2\rho' + (\rho E)'/\delta^{1/3} , \tag{17}$$

$$\rho'' + 3\bar{x}^2\delta^2\rho' = 3r\bar{x}^2\delta^2C' + (CE)'/\delta^{1/3} , \tag{18}$$

$$\rho = \delta^{1/3}E' , \tag{19}$$

where $E = \delta\tilde{E} = zF\lambda\xi/RT$ and where the primes now denote differentiation with respect to $\bar{x}$.

For $\tilde{x} = O(\delta^{2/3})$, the concentration and the charge density are of order $\delta^{2/3}$, while the electric field $\tilde{E}$ is of order $\delta^{-2/3}$ or $E = O(\delta^{1/3})$. Hence, the first approximations to the concentration, the charge density, and the electric field in the diffuse part of the double layer are

$$C = \delta^{2/3}\overline{C}_o(\overline{x}), \quad \rho = \delta^{2/3}\overline{\rho}_o(\overline{x}), \quad E = \delta^{1/3}\overline{E}_o(x) \ . \tag{20}$$

When equations (20) are substituted into equations (17), (18), and (19) and higher order terms in δ are neglected, the following differential equations are obtained for determining the first approximations in the diffuse part of the double layer:

$$\overline{C}_o'' - (\overline{\rho}_o\overline{E}_o)' = 0, \quad \overline{\rho}_o'' - (\overline{C}_o\overline{E}_o)' = 0 \ , \tag{21}$$

$$\overline{\rho}_o = \overline{E}_o' \ . \tag{22}$$

Equations (21) can be integrated to yield

$$\overline{C}_o' = \overline{\rho}_o\overline{E}_o - a \ , \tag{23}$$

$$\overline{\rho}_o' = \overline{C}_o\overline{E}_o - b \ , \tag{24}$$

where the integration constants have been evaluated from the boundary conditions for the fluxes at the interface:

$$a\delta^{2/3} = E\rho/\delta^{1/3} - C' \quad \text{at } \overline{x} = 0 \ . \tag{25}$$

$$b\delta^{2/3} = EC/\delta^{1/3} - \rho' \quad \text{at } \overline{x} = 0 \ . \tag{26}$$

Substitution of equation (22) into equation (23) and integration yields

$$\overline{C}_o = \frac{1}{2}\overline{E}_o^2 - a\overline{x} + J_o \ . \tag{27}$$

Substitution of equations (22) and (27) into equation (24) yields a differential equation for the determination of $\overline{E}_o$:

$$\overline{E}_o'' + b = \overline{E}_o(\frac{1}{2}\overline{E}_o^2 - a\overline{x} + J_o) \ . \tag{28}$$

Since the electric field must become small outside the diffuse double layer, one of the boundary conditions for equation (28) is

$$\overline{E}_o \to 0 \quad \text{as} \quad \overline{x} \to \infty \ . \tag{29}$$

The other boundary condition is related to the specified surface charge density σ in the diffuse part of the double layer and the diffusion layer. This takes the form

$$E(\infty) - E(0) = \delta^{-1/3} \int_0^\infty \rho \, d\bar{x} = -K\delta^{1/3} = \sigma/2zFc_\infty\lambda \ . \tag{30}$$

To express $\sigma/2zFc_\infty\lambda$ as $-K\delta^{1/3}$ reflects the fact that the surface charge density is smaller at the limiting current than at lower currents and also reflects the order of magnitude found for ρ within the diffuse part of the double layer. On this basis, the other boundary condition for equation (28) is

$$\bar{E}_o = K \quad \text{at } \bar{x} = 0, \tag{31}$$

since E is of higher order at $\tilde{x} = \infty$.

The outer solution for $\tilde{C}_o$ and $\tilde{E}_o$ contains one, as yet, undetermined integration constant, I_o in equation (14). The inner solution contains J_o, which also has not yet been evaluated. In addition the flux parameter a must be selected so as to correspond to the limiting current condition. These constants can be evaluated by the condition that the inner and outer solutions must match. The inner limit of the outer solution for the concentration is

$$C \approx \tilde{C}_o \rightarrow \tilde{x}/\Gamma(4/3) = \delta^{2/3}\bar{x}/\Gamma(4/3) \text{ as } \tilde{x} \rightarrow 0 \ . \tag{32}$$

Since $\bar{E}_o \rightarrow 0$ as $\bar{x} \rightarrow \infty$, the outer limit of the inner solution for the concentration is

$$C \approx \delta^{2/3}\bar{C}_o \rightarrow -\delta^{2/3}a\bar{x} + J_o\delta^{2/3} \text{ as } \bar{x} \rightarrow \infty \ . \tag{33}$$

In order for these to match, a must take the value

$$a = -1/\Gamma(4/3) \ . \tag{34}$$

The constant J_o would need to match with a term of the outer solution of order $\delta^{2/3}$ and will later be shown to be equal to zero.

From equation (14), the inner limit of the outer solution for the electric field is

$$E = \delta\tilde{E} \approx \delta\tilde{E}_o \rightarrow \delta(I_o+r)/\tilde{x} = \delta^{1/3}(I_o+r)/\bar{x} \text{ as } \tilde{x} \rightarrow 0 \ . \tag{35}$$

The outer limit of the inner solution for the electric field can be obtained directly from equation (28) without solving the differential equation. The result is

$$E \approx \delta^{1/3}\bar{E}_o \rightarrow -\delta^{1/3}b/a\bar{x} \ . \tag{36}$$

These two limits match if

$$I_o = -r - b/a \ . \tag{37}$$

It is not very easy to obtain an analytic solution for $\bar{E}_o$ from equation (28). However, there are only two parameters, b and K, involved, since $J_o = 0$. Furthermore $b = a = -1/\Gamma(4/3)$ for a cation-discharge process, and it is feasible to solve equation (28) numerically for various values of the parameter K. For this case the results are shown in figure 1.

In the course of the numerical calculations it was found that, for the case $b = a$, values of K greater than about -0.741 have no physical meaning since for such values the cation concentration becomes negative near the electrode surface. Near the limiting current anions are driven away from the interface by the electric field, while cations are driven toward the interface and react there. The net charge in the diffuse double layer and the diffusion layer cannot drop below the value corresponding to $K \approx -0.741$ without the cation concentration decreasing to zero at the interface.

It might be noted that convection is negligible in the first approximation within the diffuse part of the double layer and that, in contrast to the situation at currents below the limiting current[8], the electric field within the diffuse double layer does not have an "equilibrium" distribution but instead involves the flux parameters a and b.

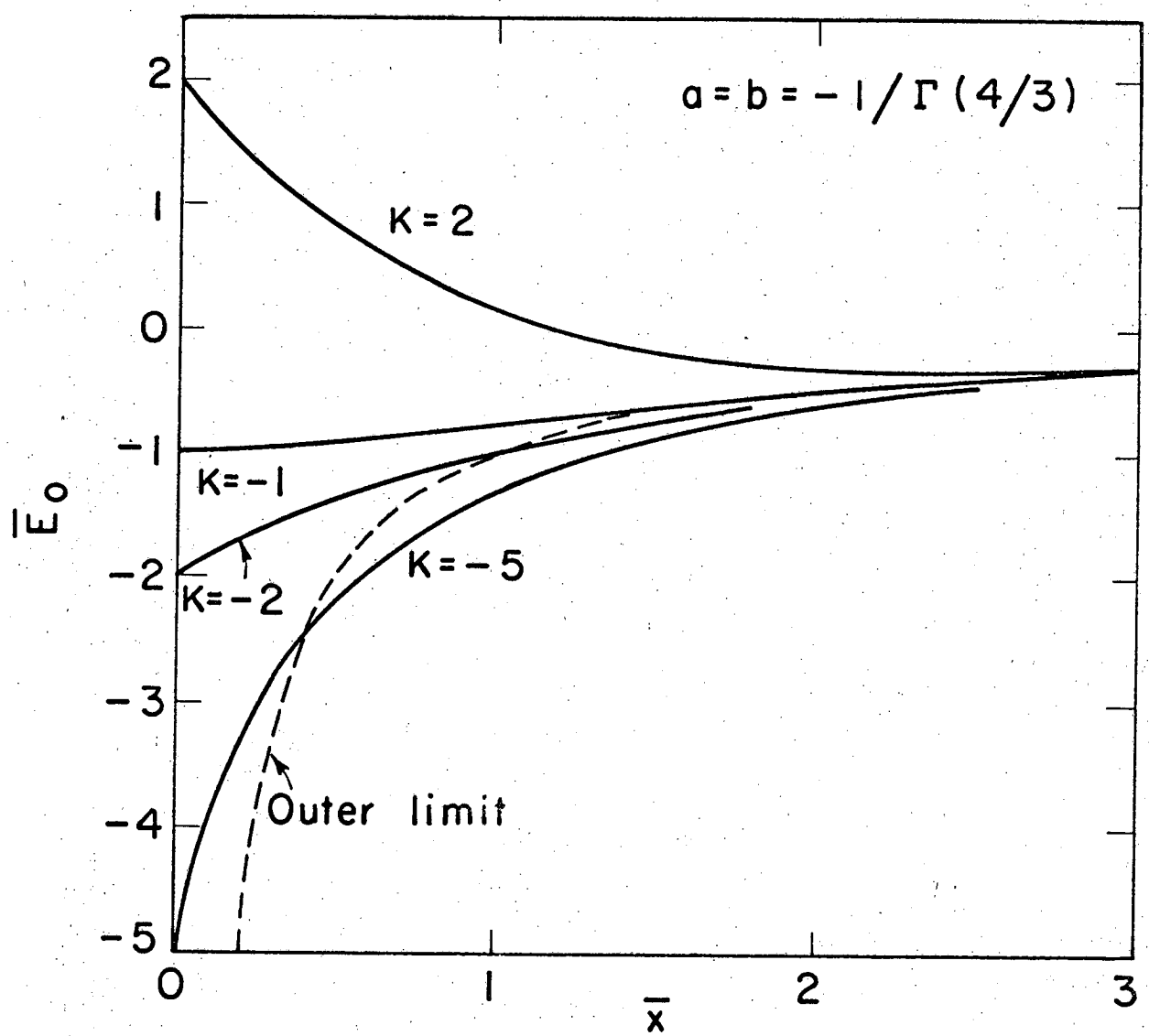

Figure 1. First approximation to the electric field within the diffuse part of the double layer, corresponding to the classical limiting current for a cation discharge reaction from a solution of a symmetric binary electrolyte. The parameter K corresponds to the total surface charge density in the diffuse double layer and in the diffusion layer. For $K > -0.741$, the true limiting current has already been exceeded, and the cation concentration at the interface is negative.

Higher Order Terms

The purpose of this section is to show how to calculate higher order terms, both within the diffuse double layer and in the diffusion layer, in order to account for the terms neglected in the first approximations. The necessity for these higher order terms may be due to terms neglected in the differential equations themselves or in the boundary conditions, or they may be required by the fact that the inner and outer expansions must match.

Inner Expansions

The next terms in the inner expansion arise from the boundary condition (30) since $E(\infty)/\delta \approx \tilde{E}_o(\infty) = I_o/\Gamma(4/3) = b + r\,a$. The inner expansions are found to take the form

$$\left.\begin{aligned} C &= \delta^{2/3}\bar{C}_o(\bar{x}) + \delta^{4/3}\bar{C}_1(\bar{x}) + \delta^{2}\bar{C}_2(\bar{x}) + O(\delta^{8/3}). \\ E &= \delta^{1/3}\bar{E}_o(\bar{x}) + \delta\,\bar{E}_1(\bar{x}) + \delta^{5/3}\bar{E}_2(\bar{x}) + O(\delta^{7/3}). \\ \rho &= \delta^{2/3}\bar{\rho}_o(\bar{x}) + \delta^{4/3}\bar{\rho}_1(\bar{x}) + \delta^{2}\bar{\rho}_2(\bar{x}) + O(\delta^{8/3}). \end{aligned}\right\} \tag{38}$$

If these expansions are substituted into equations (17), (18), and (19) and terms in equal powers of δ are equated, one obtains equations (21) and (22) and

$$\bar{C}_1'' = (\bar{\rho}_o\bar{E}_1)' + (\bar{\rho}_1\bar{E}_o)', \qquad \bar{C}_2'' = (\bar{\rho}_2\bar{E}_o + \bar{\rho}_1\bar{E}_1 + \bar{\rho}_o\bar{E}_2)', \tag{39}$$

$$\bar{\rho}_1'' = (\bar{C}_o\bar{E}_1)' + (\bar{C}_1\bar{E}_o)', \qquad \bar{\rho}_2'' = (\bar{C}_2\bar{E}_o + \bar{C}_1\bar{E}_1 + \bar{C}_o\bar{E}_2)', \tag{40}$$

$$\bar{\rho}_1 = \bar{E}_1', \qquad \bar{\rho}_2 = \bar{E}_2'. \tag{41}$$

Equations (39) and (40) can be integrated to yield

$$\bar{C}_1' = \bar{\rho}_o\bar{E}_1 + \bar{\rho}_1\bar{E}_o, \qquad \bar{C}_2' = \bar{\rho}_2\bar{E}_o + \bar{\rho}_1\bar{E}_1 + \bar{\rho}_o\bar{E}_2, \tag{42}$$

$$\bar{\rho}_1' = \bar{C}_o\bar{E}_1 + \bar{C}_1\bar{E}_o, \qquad \bar{\rho}_2' = \bar{C}_2\bar{E}_o + \bar{C}_1\bar{E}_1 + \bar{C}_o\bar{E}_2, \tag{43}$$

where the integration constants have been evaluated from the boundary conditions (25) and (26) for the fluxes at the interface. Substitution of equations (41)

into equations (42) and integration yields

$$\bar{C}_1 = \bar{E}_o\bar{E}_1 + J_1 \ . \tag{44}$$

$$\bar{C}_2 = \bar{E}_o\bar{E}_2 + \frac{1}{2}\bar{E}_1^2 + J_2 \ . \tag{45}$$

Substitution of equations (41), (44), and (45) into equations (43) yields differential equations for the determination of $\bar{E}_1$ and $\bar{E}_2$:

$$\bar{E}_1'' = \bar{E}_1(-a\bar{x} + \frac{3}{2}\bar{E}_o^2 + J_o) + J_1\bar{E}_o. \tag{46}$$

$$\bar{E}_2'' = \bar{E}_2(-a\bar{x} + \frac{3}{2}\bar{E}_o^2 + J_o) + J_2\bar{E}_o + J_1\bar{E}_1 + \frac{3}{2}\bar{E}_o\bar{E}_1^2 \ . \tag{47}$$

The constants J_o, J_1, and J_2 still need to be evaluated.

Outer Expansions

In the diffusion layer the first neglected terms in equations (7) and (8) are of order δ^2. However, it is not immediately apparent that terms for C and $\tilde{E}$ of order $\delta^{2/3}$ and $\delta^{4/3}$ might not be necessary in order to match with terms of the inner expansion. Thus, for the outer expansions we adopt the form

$$\left.\begin{aligned} C &= \tilde{C}_o(\tilde{x}) + \delta^{2/3}\tilde{C}_1(\tilde{x}) + \delta^{4/3}\tilde{C}_2(\tilde{x}) + O(\delta^2) \ . \\ \tilde{E} &= \tilde{E}_o(\tilde{x}) + \delta^{2/3}\tilde{E}_1(\tilde{x}) + \delta^{4/3}\tilde{E}_2(\tilde{x}) + O(\delta^2) \ . \\ \rho &= \delta^2\tilde{\rho}_3(\tilde{x}) + O(\delta^{8/3}). \end{aligned}\right\} \tag{48}$$

We shall show that $\tilde{C}_1$, $\tilde{C}_2$, $\tilde{E}_1$, and $\tilde{E}_2$ are, in fact, identically zero.

Substitution of these expansions into equation (7) shows that $\tilde{C}_1$ and $\tilde{C}_2$ satisfy the differential equation

$$\tilde{C}_n'' + 3\tilde{x}^2\tilde{C}_n' = 0 \ , \qquad n = 1,2 \ , \tag{49}$$

with the solution

$$\tilde{C}_n = P_n \int_{\infty}^{\tilde{x}} e^{-x^3}\, dx \ , \qquad n = 1,2 \ , \tag{50}$$

where the other integration constants, besides P_1 and P_2 have been evaluated so that $C \to 1$ as $\tilde{x} \to \infty$.

The terms for the electric field satisfy the equations, obtained from equation (8),

$$\left.\begin{aligned}(\tilde{C}_1\tilde{E}_o)' + (\tilde{C}_o\tilde{E}_1)' &= -3r\tilde{x}^2\tilde{C}_1' = -3r\tilde{x}^2P_1e^{-\tilde{x}^3}\,,\\ (\tilde{C}_2\tilde{E}_o + \tilde{C}_1\tilde{E}_1 + \tilde{C}_o\tilde{E}_2)' &= -3r\tilde{x}^2\tilde{C}_2' = -3r\tilde{x}^2P_2e^{-\tilde{x}^3}\,,\end{aligned}\right\} \quad (51)$$

which can be integrated to yield

$$\left.\begin{aligned}\tilde{E}_1 &= (I_1 + rP_1e^{-\tilde{x}^3} - \tilde{C}_1\tilde{E}_o)/\tilde{C}_o\,,\\ \tilde{E}_2 &= (I_2 + rP_2e^{-\tilde{x}^3} - \tilde{C}_2\tilde{E}_o - \tilde{C}_1\tilde{E}_1)/\tilde{C}_o.\end{aligned}\right\} \quad (52)$$

Matching

The integration constants J_o, J_1, J_2, P_1, P_2, I_1, and I_2 must be determined by matching the inner and outer expansions for the concentration and the electric field.

The inner limit of the outer expansion for the concentration is

$$\left.\begin{aligned}C(\tilde{x}\to 0) &= \lim_{\tilde{x}\to 0}\,(\tilde{C}_o + \delta^{2/3}\tilde{C}_1 + \delta^{4/3}\tilde{C}_2 + O(\delta^2))\\ &= (\tilde{x}+O(\tilde{x}^4))/\Gamma(4/3) + \delta^{2/3}P_1[-\Gamma(4/3) + \tilde{x} + O(\tilde{x}^4)]\\ &\quad + \delta^{4/3}P_2[-\Gamma(4/3) + \tilde{x} + O(\tilde{x}^4)] + O(\delta^2)\,.\end{aligned}\right\} \quad (53)$$

The outer limit of the inner expansion for the concentration is

$$\left.\begin{aligned}C(\bar{x}\to\infty) &= \lim_{\bar{x}\to\infty}\,(\delta^{2/3}\bar{C}_o + \delta^{4/3}\bar{C}_1 + O(\delta^2))\\ &= \delta^{2/3}[J_o - a\bar{x} + O(\bar{x}^{-2})] + \delta^{4/3}[J_1 + O(J_1\bar{x}^{-3})] + O(\delta^2)\\ &= -a\tilde{x} + \delta^{2/3}J_o + \delta^{4/3}J_1 + O(\delta^2)\,,\end{aligned}\right\} \quad (54)$$

where equations (27), (44), and (45) have been used. These two expansions must match term by term, with the result

$$a = -1/\Gamma(4/3),\quad J_o = -P_1\Gamma(4/3),\quad P_1 = 0,\quad J_1 = -P_2\Gamma(4/3),\quad P_2 = 0. \quad (55)$$

The inner limit of the outer expansion for the electric field is, since $P_1 = P_2 = 0$,

$$\left.\begin{aligned} E = \delta\tilde{E}(\tilde{x}\to 0) &= \lim_{\tilde{x}\to 0} [\delta\tilde{E}_o + \delta^{5/3}\tilde{E}_1 + \delta^{7/3}\tilde{E}_2 + O(\delta^3)] \\ &= \delta[(I_o + r)/\tilde{x} + O(\tilde{x}^2)] + \delta^{5/3}[I_1\Gamma(4/3)/\tilde{x} + O(\tilde{x}^2)] \\ &\quad + \delta^{7/3}[I_2\Gamma(4/3)/\tilde{x} + O(\tilde{x}^2)] + O(\delta^3) \end{aligned}\right\} \tag{56}$$

$$= \delta^{1/3}(I_o + r)/\bar{x} + \delta I_1\Gamma(4/3)/\bar{x} + \delta^{5/3}I_2\Gamma(4/3)/\bar{x} + O(\delta^{7/3}).$$

The outer limit of the inner expansion of the electric field is, since $J_o = J_1 = 0$,

$$\begin{aligned} E(\bar{x}\to\infty) &= \lim_{\bar{x}\to\infty} [\delta^{1/3}\bar{E}_o + \delta\bar{E}_1 + \delta^{5/3}\bar{E}_2 + O(\delta^{7/3})] \\ &= \delta^{1/3}[-b/a\bar{x} + O(\bar{x}^{-4})] + \delta^{5/3}[-J_2 b/a^2\bar{x}^2 + O(\bar{x}^{-5})] + O(\delta^{7/3}). \end{aligned} \tag{57}$$

The matching condition thus requires that

$$I_o = -r - b/a, \qquad I_1 = I_2 = 0 .$$

The evaluation of J_2 requires the determination of higher order terms which have been neglected.

Composite Expansions

The principal result can be expressed in the form of uniformly-valid, composite expansions, valid for all values of $\tilde{x}$, both in the diffusion layer and in the diffuse part of the double layer. These are formed by adding the inner and outer expansions and subtracting the common terms. The common terms comprise the inner limit of the outer expansion, which is the same as the outer limit of the inner expansion. The composite expansions are

$$C = \tilde{C}_o(\tilde{x}) + \delta^{2/3}\bar{C}_o(\bar{x}) - \tilde{x}/\Gamma(4/3) + \delta^{4/3}\bar{C}_1(\bar{x}) + O(\delta^2) . \tag{58}$$

$$E = \delta^{1/3}\bar{E}_o(\bar{x}) + \delta\bar{E}_1(\bar{x}) + \delta\tilde{E}_o(\tilde{x}) + \delta b/a\tilde{x} + O(\delta^{5/3}). \tag{59}$$

The terms $\overline{E}_o(\overline{x})$ and $\overline{E}_1(\overline{x})$ are to be obtained by solving the differential equations

$$\overline{E}_o'' + b = \overline{E}_o(\tfrac{1}{2}\overline{E}_o^2 - a\overline{x}) , \tag{60}$$

$$\overline{E}_1'' = \overline{E}_1(\tfrac{3}{2}\overline{E}_o^2 - a\overline{x}) , \tag{61}$$

subject to the boundary conditions

$$\overline{E}_o = K, \quad \overline{E}_1 = b + a\,r \quad \text{at } \overline{x} = 0 , \tag{62}$$

$$\overline{E}_o \to 0, \quad \overline{E}_1 \to 0 \quad \text{as } \overline{x} \to \infty . \tag{63}$$

Solutions for $\overline{E}_o$ are plotted in figure 1 for the case $a = b = -1/\Gamma(4/3)$ and for several values of K. The other terms of the composite expansions are

$$\left.\begin{aligned} &\tilde{C}_o = \frac{1}{\Gamma(4/3)}\int_0^{\tilde{x}} e^{-x^3}\,dx, \quad \tilde{E}_o = -(r+b/a-re^{-\tilde{x}^3})\Big/\int_0^{\tilde{x}} e^{-x^3}\,dx, \\ &\overline{C}_o = \tfrac{1}{2}\overline{E}_o^2 - a\overline{x}, \quad \overline{C}_1 = \overline{E}_o\overline{E}_1 . \end{aligned}\right\} \tag{64}$$

Figure 2 shows the electric field for $\delta = 10^{-5}$, $r = 0$, $a = b$, and several values of K. The long region of overlap of the inner and outer expansions is clearly displayed here.

Discussion

The structure of the diffuse part of the double layer described here is also applicable to other hydrodynamic situations at the limiting current since convection is negligible in the double layer. What is important, as far as the double layer is concerned, is the value of the fluxes and the value of the concentration gradient at the interface as predicted by classical diffusion theory. A particularly simple result is found for a stagnant electrolytic solution in a capillary of length L, sealed at one end with an electrode and open to a reservoir of solution at the other. Although the double layer is restricted to a region very close to the electrode interface, the "inner" expansions for the concentration and the electric field are

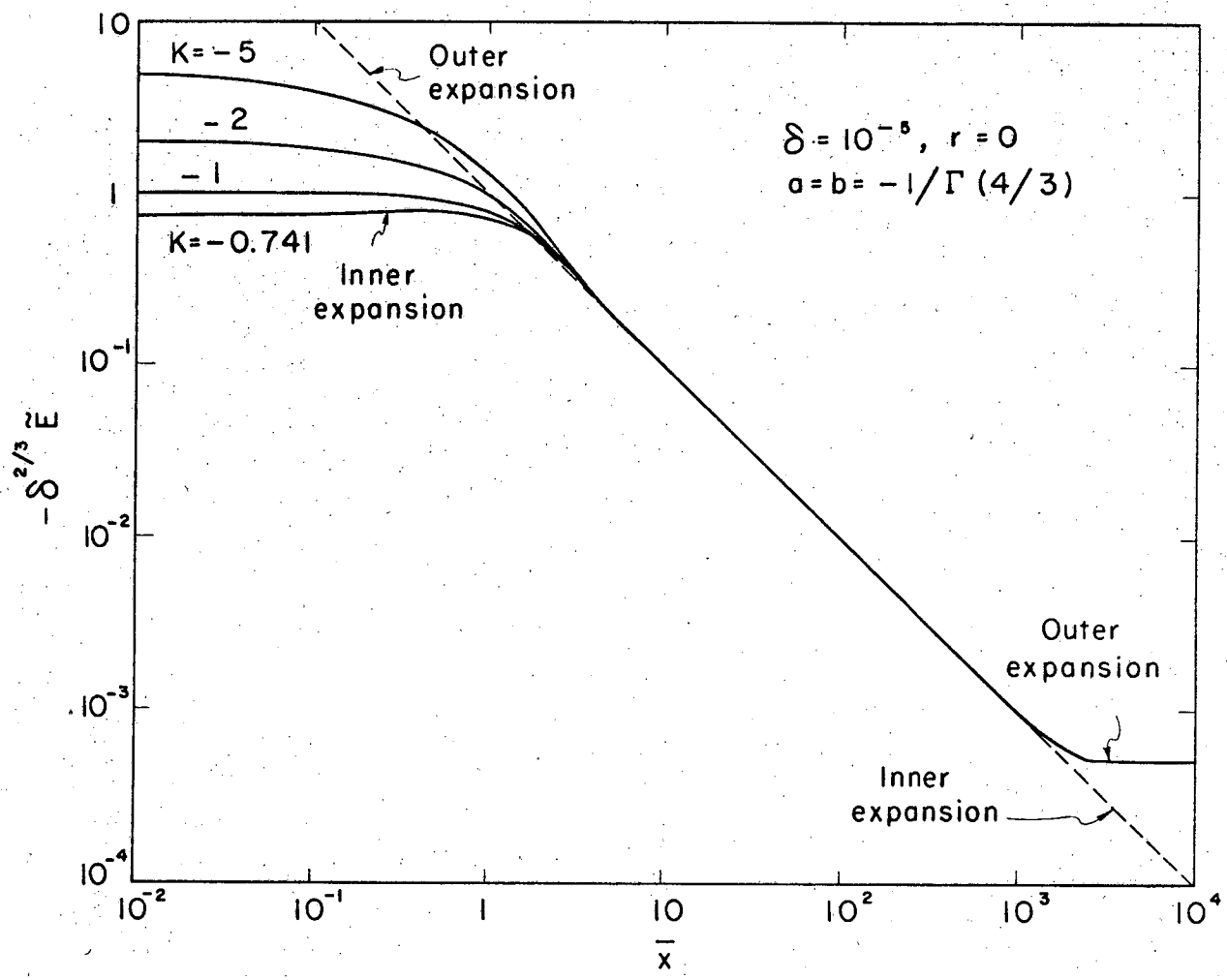

Figure 2. Electric field in the diffuse part of the double layer and in the diffusion layer at the classical limiting current.

uniformly valid throughout the capillary. The value for a may be somewhat different, say $a = -1$ for the capillary if the length L is used instead of $(3D/A)^{1/3}$ in forming the dimensionless variables and parameters.

The results obtained here indicate that, even at the classical limiting current, the potential at the interface or the outer Helmholtz plane relative to a point just outside the diffusion layer is still finite. The current can be varied by a small amount about the classical limiting current before a true limiting current is obtained (zero concentration of the reacting ions at the interface), although for a cation-discharge reaction ($a = b$) and $K \approx -0.741$ the classical limiting current and the true limiting current coincide. The true limiting current and other small variations around the classical limiting current could be investigated by letting

$$a = a_o - \delta^{2/3} a_1 = -1/\Gamma(4/3) - a_1 \delta^{2/3} ,$$

$$b = b_o - b_1 \delta^{2/3} ,$$

instead of $a = -1/\Gamma(4/3)$. The first approximations within the diffuse double layer still follow equations (27) and (28), with a and b replaced by a_o and b_o, but now the constant J_o has the value $J_o = -a_1 \Gamma(4/3)$. The outer solution would also be modified since now $\tilde{C}_1$ and $\tilde{E}_1$ are no longer zero, but $P_1 = a_1$.

The magnitude of the potential ζ in the outer Helmholtz plane relative to the outside of the diffusion layer can be obtained by subtracting the ohmic drop in the solution, extrapolated to the interface with the bulk conductivity.

$$zF\zeta/RT = \int_0^\infty [\tilde{E} - \tilde{E}(\infty)\, d\tilde{x} . \tag{65}$$

By taking proper account of the singular nature of some of the terms for the expansions of the electric field, one can express this as

$$\zeta = (2b/3a)(RT/zF)\, ln\, \delta + \zeta_o + \zeta_1 + \delta^{2/3}\zeta_2 + O(\delta^{4/3}) , \tag{66}$$

where

$$\frac{zF\zeta_o}{RT} = \int_o^1 \left[\tilde{E}_o(\tilde{x}) + \frac{b}{a\tilde{x}}\right] d\tilde{x} + \int_1^\infty [\tilde{E}_o(\tilde{x}) - \tilde{E}_o(\infty)]\, d\tilde{x} - \tilde{E}_o(\infty) , \tag{67}$$

$$\frac{zF\zeta_1}{RT} = \int_o^1 \bar{E}_o(\bar{x})\, d\bar{x} + \int_1^\infty \left[\bar{E}_o(\bar{x}) + \frac{b}{a\bar{x}}\right] d\bar{x} , \tag{68}$$

$$\frac{zF\zeta_2}{RT} = \int_o^\infty \bar{E}_1(\bar{x})\, d\bar{x} . \tag{69}$$

Some calculated values of ζ are given in table 1.

Table 1. Zeta potentials at the classical limiting current. For $\delta = 10^{-5}$, $r = 0$, $a = b = -1/\Gamma(4/3)$, $z = 1$, $T = 298.15°K$.

K	- 5	- 2	- 1	- 0.741
$(2b/3a)\ ln\ \delta$	- 7.675	- 7.675	- 7.675	- 7.675
$zF\zeta_o/RT$	1.017	1.017	1.017	1.017
$zF\zeta_1/RT$	- 2.777	- 1.522	- 0.899	- 0.713
$zF\zeta_2/RT$	- 0.357	- 0.622	- 0.780	- 0.825
$zF\zeta/RT$	- 9.435	- 8.180	- 7.557	- 7.371
ζ, mV	-242.4	-210.2	-194.2	-189.4

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Nomenclature

A - constant in expression for the velocity (cm^{-1}-sec^{-1}).

D_+, D_- - diffusion coefficients of cations and anions (cm^2/sec).

ξ - component of the electric field in the y-direction (V/cm).

N_+^o, N_-^o - cation and anion fluxes at the interface ($mole/cm^2$-sec).

y - distance from the interface (cm).

$\Gamma(4/3) = 0.89298$.

ϵ - dielectric constant (farad/cm).

σ - total electric charge in the diffuse part of the double layer and in the diffusion layer ($coulomb/cm^2$).

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