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John Newman

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ABSTRACT

A singular-perturbation expansion of the electric field and the concentrations provides a rigorous justification for dividing an electrolytic solution into the diffuse part of the double layer at an interface and a diffusion layer on the solution side of the interface. At the same time this expansion provides a means for calculating corrections to the equilibrium electric field within the diffuse part of the double layer.

INTRODUCTION

Electroneutrality prevails in the bulk of an electrolytic solution, but near an interface with an electrode or with an insulator there is a region about 10 to 100 angstroms thick in which there is considerable departure from electroneutrality. The whole interface is referred to as the electric double layer and includes, possibly, a charge layer in the metal phase, if any, a charge layer of "specifically adsorbed" ions at the interface, and a diffuse part of the double layer which extends a short distance into the electrolytic solution. The double layer as a whole is electrically neutral, but each part of the double layer may have a net charge.

It is natural to try to treat separately processes in the electrically neutral solution "outside" the double layer and processes inside the diffuse part of the double layer even though both regions are in the electrolytic solution and there is no sharp boundary dividing them. Thus, for mass transfer studies it is the practice to include the effects of the diffuse part of the double layer in the boundary conditions describing the behavior of the interface. Conversely, it is desirable that the behavior of the diffuse part of the double layer be characterized by the concentration at the "edge" of the double layer and by the current passing through it, but should not depend directly on events far away from the interface in the liquid phase.

We have achieved here a rigorous justification of this separation of the electrolytic solution into two regions by means of singular-perturbation expansions of the electric field and the concentrations. A singular perturbation consists of two perturbation expansions valid respectively in the region far from the interface and close to the interface. Since these are two expansions of the same function, they must "match" in an intermediate region. (A more precise statement is that the outer limit of the inner expansion coincides with the inner limit of the outer expansion.)

The reason for constructing two such perturbation expansions is that different approximations are valid in the two regions. In the outer region (in the bulk of the solution), one can neglect deviations from electro-neutrality as a first approximation. In the inner region (near the interface) it is permissible to neglect convection. Furthermore, the electric field can be quite large in the double layer even in the absence of current, and the disturbance due to the passage of current can be treated as a perturbation.

STATEMENT OF THE PROBLEM

We illustrate these principles for the case of a symmetric, binary electrolyte. If dilute-solution theory is applicable, then the concentrations and the electric field are to be determined from the equations

$$\frac{d}{dy} \left(z \frac{D_+ F}{RT} c_+ \mathcal{E} - D_+ \frac{dc_+}{dy} \right) + v_y \frac{dc_+}{dy} = 0, \quad (1)$$

$$\frac{d}{dy} \left(-z \frac{D_- F}{RT} c_- \mathcal{E} - D_- \frac{dc_-}{dy} \right) + v_y \frac{dc_-}{dy} = 0, \quad (2)$$

$$\frac{d\mathcal{E}}{dy} = \frac{F}{\epsilon} z(c_+ - c_-). \quad (3)$$

The first two equations express conservation of cations and anions respectively, while the last is Poisson's equation. It is assumed that the Nernst-Einstein relationship between diffusion coefficients and mobilities is valid, that a steady state prevails, and that the concentrations and potential vary only in the y-direction.

These equations are to be solved subject to the following four boundary conditions:

1. The average concentration is c_∞ far from the surface.
2. The cation flux N_+^0 is specified at the interface.
3. The anion flux N_-^0 is specified at the interface.
4. The total electric charge in the diffuse part of the double layer (and in the diffusion layer) is σ .

A realistic velocity profile, which we shall use for the convective velocity, is

$$v_y = -Ay^2. \quad (4)$$

This could correspond, for example, to a rotating disk at high Schmidt numbers, in which case A is given by^{1,2}

$$A = 0.51023 \Omega^{3/2} \nu^{-1/2}.$$

It will become apparent later that the first several terms of the expansions describing the diffuse part of the double layer will remain valid for other hydrodynamic conditions.

It is convenient to use dimensionless variables.

Therefore, we define

- a) dimensionless concentrations and charge density

$$C = \frac{c_+ + c_-}{2c_*}, \quad C_\infty = \frac{c_\infty}{c_*}, \quad \rho = \frac{c_+ - c_-}{2c_*}, \quad (5)$$

- b) dimensionless electric field and position coordinate

$$E = \frac{zF}{RT} \lambda \mathcal{E}, \quad x = y/\lambda, \quad (6)$$

- c) dimensionless fluxes

$$a = \frac{1}{2c_*} \left(\frac{3D}{A} \right)^{1/3} \left(\frac{N_+}{D_+} + \frac{N_-}{D_-} \right), \quad b = \frac{1}{2c_*} \left(\frac{3D}{A} \right)^{1/3} \left(\frac{N_+}{D_+} - \frac{N_-}{D_-} \right), \quad (7)$$

- d) dimensionless parameters

$$r = \frac{D_+ - D_-}{D_+ + D_-}, \quad \delta = \left(\frac{A}{3D} \right)^{1/3} \lambda, \quad (8)$$

where

$D = \frac{2D_+ D_-}{D_+ + D_-}$ is the diffusion coefficient of the

binary salt.

$\lambda = \sqrt{\frac{\epsilon RT}{2z^2 F^2 c_*}}$ is the Debye length.

c_* is the concentration just "outside the double layer", which will be defined presently.

In terms of these dimensionless quantities, the differential equations become

$$C'' + 3\delta^3 x^2 C' = 3r\delta^3 x^2 \rho' + (\rho E)', \quad (9)$$

$$\rho'' + 3\delta^3 x^2 \rho' = 3r\delta^3 x^2 C' + (CE)', \quad (10)$$

$$\rho = E', \quad (11)$$

where primes denote differentiation with respect to x .

These are to be solved subject to the following four boundary conditions:

1. $C \rightarrow C_\infty$ as $x \rightarrow \infty$.

2. $\delta a = \rho E - C'$ at $x = 0$.

3. $\delta b = CE - \rho'$ at $x = 0$.

4. $E(x=\infty) - E(x=0) = \int_0^\infty \rho \, dx = \frac{-4K}{1-K^2} = \frac{\sigma}{2zFc_*\lambda}$,

where K is defined by the last boundary condition.

The perturbation parameter is δ , which represents a ratio of the Debye length (characteristic of the diffuse double layer) to a length characteristic of the thickness of the diffusion layer. Since δ is of the order of 10^{-5} for most aqueous electrolytic solutions, the prospect of a useful perturbation expansion is promising.

Different independent variables are used in the inner and outer expansions. The inner variable is

$$\bar{x} = x = y/\lambda,$$

which serves to stretch the coördinate so that \bar{x} is of order unity in the diffuse double layer. The outer variable is

$$\tilde{x} = \delta x = \left(\frac{A}{3D}\right)^{1/3} y.$$

SUMMARY OF THE PRINCIPAL RESULTS

The electric field and the average concentration can be expressed as

$$E = \bar{E}_0(\bar{x}) + \delta \tilde{E}_0(\tilde{x}) + \delta \bar{E}_1(\bar{x}) - \delta b + \bigcirc(\delta^2). \quad (12)$$

$$C = \bar{C}_0(\bar{x}) + \tilde{C}_0(\tilde{x}) + \delta \bar{C}_1(\bar{x}) - (1 - \delta a \bar{x}) + \bigcirc(\delta^2). \quad (13)$$

These expressions are uniformly valid up to order δ^2 over the entire domain of x , both inside the diffuse double layer and in the region outside the double layer. The terms \bar{E}_0 and \bar{C}_0 describe the electric field and average concentration in a diffuse double layer at equilibrium. The terms \tilde{E}_0 and \tilde{C}_0 are the first approximation to the electric field and the concentration in the region outside the double layer as calculated by the standard techniques of diffusion theory. The terms \bar{E}_1 and \bar{C}_1 represent the corrections to the equilibrium situation in the diffuse double layer to account for the passage of current. The terms δb and $(1 - \delta a \bar{x})$ serve to cancel overlapping terms already included twice.

The various terms are given as follows:

$$\bar{E}_0(\bar{x}) = \frac{4K e^{-\bar{x}}}{1 - K^2 e^{-2\bar{x}}} \quad (14)$$

$$\bar{C}_0(\bar{x}) = 1 + \frac{1}{2} \bar{E}_0^2. \quad (15)$$

$$\tilde{C}_0(\tilde{x}) = 1 - a \int_0^{\tilde{x}} e^{-x^3} dx. \quad (16)$$

$$\tilde{E}_0(\tilde{x}) = \frac{1}{\tilde{C}_0} [b - ra(e^{-x^3} - 1)]. \quad (17)$$

$$\bar{C}_1(\bar{x}) = \bar{E}_0 \bar{E}_1 - a\bar{x}. \quad (18)$$

$\bar{E}_1(\bar{x})$ satisfies the linear, nonhomogeneous differential equation

$$\bar{E}_1' - (1 + \frac{3}{2} \bar{E}_0^2) \bar{E}_1 = -b - a\bar{x}\bar{E}_0 \quad (19)$$

with the boundary conditions

$$\bar{E}_1 = (b + ra)/C_\infty \text{ at } \bar{x} = 0. \quad (20)$$

$$\bar{E}_1 \rightarrow b \text{ as } \bar{x} \rightarrow \infty. \quad (21)$$

This gives a clearly defined, linear problem for the perturbation of the electric field in the diffuse part of the double layer. We choose to leave this problem to a more erudite mathematician and instead adopt the approximation

$$\bar{E}_0 \approx 4Ke^{-\bar{x}} \ll 1,$$

so that the solution for \bar{E}_1 is

$$\bar{E}_1 \approx e^{-\bar{x}}(b + ra)/C_\infty + aK(\bar{x} + \bar{x}^2) e^{-\bar{x}} + b(1 - e^{-\bar{x}}). \quad (22)$$

Even when \bar{E}_0 is not small compared to unity, this solution is qualitatively correct in the sense that it satisfies the correct boundary condition at $\bar{x} = 0$ and behaves correctly as $\bar{x} \rightarrow \infty$.

The concentration c_* is

$$c_* = c_\infty + \frac{1}{2} \Gamma(1\frac{1}{3}) \left(\frac{3D}{A}\right)^{1/3} \left(\frac{N_+}{D_+} + \frac{N_-}{D_-}\right). \quad (23)$$

This concentration just "outside the double layer" is just what would be calculated by diffusion theory when the effects of the diffuse double layer are ignored and electroneutrality is assumed (compare, for example, Randles³, p.124).

If we define the ζ -potential as that part of the potential drop across the diffuse double layer which is not accounted for by an extrapolation of the outer expansion of the electric field, then the dimensionless ζ -potential is

$$\zeta = \zeta_0 + \delta \zeta_1 + O(\delta^2), \quad (24)$$

where

$$\zeta_0 = \int_0^\infty \bar{E}_0(\bar{x}) d\bar{x} = 2 \ln \frac{1+K}{1-K}. \quad (25)$$

$$\zeta_1 = \int_0^\infty [\bar{E}_1(\bar{x}) - b] d\bar{x} \approx \frac{b+ra}{C_\infty} - b + 3aK. \quad (26)$$

EXAMPLE

Let us illustrate these results with a specific example, dissolution at an anode under the following conditions

$$\begin{aligned} i &= 0.1 \text{ A/cm}^2. & N_-^0 &= 0. & c_\infty &= 0.05M = 5 \times 10^{-5} \frac{\text{mole}}{\text{cm}^3}. \\ \sigma &= 10^{-5} \text{ coul/cm}^2. & z &= 1. & \Omega &= 900 \text{ rpm} = 94.2 \text{ rad/sec.} \\ v &= 10^{-2} \text{ cm}^2/\text{sec.} & D_+ &= 10^{-5} \text{ cm}^2/\text{sec.} & D_- &= 1.2 \times 10^{-5} \text{ cm}^2/\text{sec.} \\ \text{relative dielectric constant} &= 80. & T &= 293^\circ \text{K.} \end{aligned}$$

From these, we calculate values for the following parameters:

$$D = 1.09 \times 10^{-5} \text{ cm}^2/\text{sec.} \left(\frac{3D}{A} \right)^{1/3} = 1.91 \times 10^{-3} \text{ cm.}$$

$$N_+^0 = 1.036 \times 10^{-6} \text{ mole/cm}^2\text{-sec.} \quad c_* = 1.385 \times 10^{-4} \text{ mole/cm}^3.$$

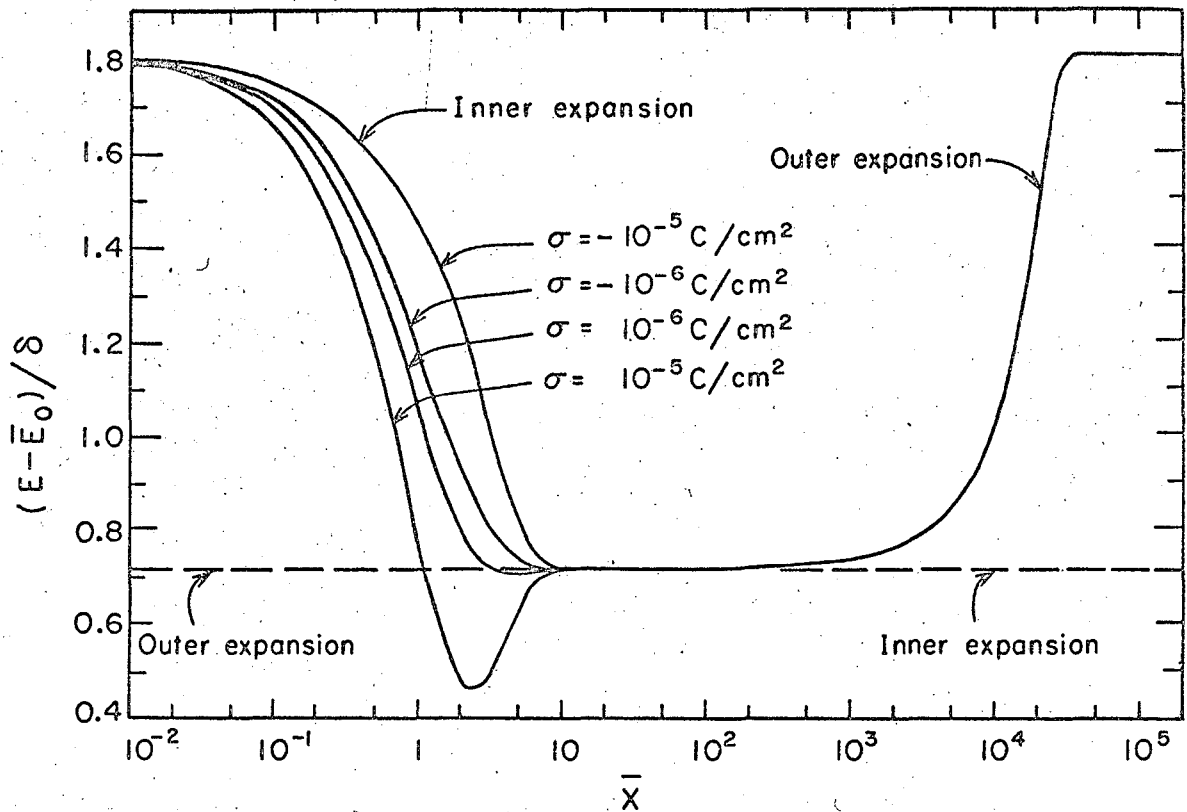
$$\lambda = 0.817 \times 10^{-7} \text{ cm.} \quad \delta = 4.27 \times 10^{-5}. \quad r = -0.091.$$

$$a = b = 0.7156 \quad K = -0.654. \quad C_\infty = 0.361.$$

It should be noted that the dimensionless fluxes a and b are of order unity as assumed and that δ is quite small. The magnitude of K is so large that the maximum value of \bar{E}_0^2 is 21, and consequently values of \bar{E}_1 calculated according to equation (22) are only qualitatively correct.

Figure 1 shows $E - \bar{E}_0$ as a function of position for this value of σ and also for $\sigma = 10^{-6}$, $\sigma = -10^{-6}$ and $\sigma = -10^{-5}$ coul/cm². The quantity $E - \bar{E}_0$ can be regarded as the correction to the equilibrium electric field \bar{E}_0 as a result of the passage of current. The inner and outer expansions are also shown. The composite expansion (12) provides a smooth transition between the inner and outer expansions, but in this case δ is so small that there is an obvious region of overlap of the inner and outer expansions. Note that there is no tendency for the electric field to become an oscillating function of position for $\tilde{x} > 8.07$ (compare Bass⁴, pp.1659-1660).

Further calculations for $\sigma = 10^{-5}$ coul/cm² show that ζ_0 corresponds to a ζ -potential of -79.0 mV while $\delta\zeta_1$ corresponds to a correction of only -0.34 μ V. A desire to improve upon such a small correction would not, we think, justify solving for \bar{E}_1 (from equations (19), (20), and (21)) without approximation.



Electric field in excess of "equilibrium" electric field.
The diffuse part of the double layer extends to about $\bar{x} = 10$.
The diffusion layer lies between $\bar{x} = 10^2$ and $\bar{x} = 3 \times 10^4$.

Figure 1.

THE BOUNDARY CONDITIONS

The first three boundary conditions (requiring specification of the average concentration far from the surface and the cation and anion fluxes at the interface) are straightforward and are easily satisfied in careful experimental work. However, it is impossible to determine the surface charge in the diffuse part of the double layer without resorting to some model of the double layer. Possible experimental aids include electrocapillary curves, double-layer capacitances, and electrophoretic mobilities. Nevertheless, the assignment of charge to the various parts of the double layer is still not certain. The reassignment of this charge in the presence of current requires a model of the inner parts of the double layer, and this model cannot be separated from the model used to describe the kinetics of the electrode process. Thus, it is clear from this analysis that the specification of this surface charge is necessary in order to describe the diffuse double layer and that factors outside the diffuse double layer determine the magnitude of the surface charge.

On the other hand, it is also clear that these four boundary conditions are sufficient. Bass⁴ also states the value of the derivative of the electric field $E'(0)$ at the interface as a boundary condition. This is not necessary.

SUMMARY AND CONCLUSIONS

We have developed a singular-perturbation solution of the problem of the polarized, diffuse double layer. This procedure provides a rigorous justification of the use of an equilibrium potential distribution in the diffuse double layer and of the usual practice in diffusion theory of assuming electroneutrality and relegating the diffuse double layer to a boundary condition. In addition, the method shows how to calculate corrections to the electric field within the diffuse double layer, and, in particular, how to match these corrections to the electric field outside the diffuse double layer. In other words, the question of boundary conditions at infinity is clarified.

Even if an exact solution, rather than a perturbation solution, were available, we should prefer the latter because it would be simpler and because it illuminates the classical electrochemical literature instead of obscuring it. It allows us to estimate the error of the classical methods instead of trying to replace them.

The perturbation solution has an obvious advantage over the solution of Bass⁴ since it is not necessary to linearize the problem in order to find \bar{E}_0 . The problem defined by equations (19), (20), and (21) for the perturbation \bar{E}_1 involves only quantities characteristic of the double layer and not of the external hydrodynamic and diffusion problem. The separation of the problem of the

electrically neutral solution "outside" the double layer from the double-layer problem is thus effected.

Acknowledgment

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APPENDIX: MATHEMATICAL DETAILS

Inner Expansion

Let the inner expansions of the electric field, the average concentration, and the charge density be

$$\bar{E} = E = \bar{E}_0 + \delta \bar{E}_1 + \delta^2 \bar{E}_2 + \mathcal{O}(\delta^3).$$

$$\bar{C} = C = \bar{C}_0 + \delta \bar{C}_1 + \delta^2 \bar{C}_2 + \mathcal{O}(\delta^3).$$

$$\bar{\rho} = \rho = \bar{\rho}_0 + \delta \bar{\rho}_1 + \delta^2 \bar{\rho}_2 + \mathcal{O}(\delta^3).$$

In terms of the inner variables, the differential equations are the same as equations (9), (10), and (11). The inner expansions of E , C , and ρ are substituted into these equations, and the coefficients of like powers of δ are equated to zero. This then gives a series of differential equations for the various terms in the perturbation series.

For the first term the conservation equations can be integrated to give

$$\bar{C}'_0 - \bar{\rho}_0 \bar{E}_0 = \text{const} = 0,$$

$$\bar{\rho}'_0 - \bar{C}_0 \bar{E}_0 = \text{const} = 0,$$

where the second and third boundary conditions have been used to evaluate the constants of integration. Since the inner solution must match the outer solution, $\bar{\rho}_0 \rightarrow 0$ as $\bar{x} \rightarrow \infty$, which implies, from the second flux equation, that \bar{E}_0 also vanishes.

Since the integration constants are zero in these flux equations, the solution for \bar{E}_0 , \bar{C}_0 , and $\bar{\rho}_0$ is no different from the classical problem of the equilibrium

double layer and is given by equations (14) and (15). Note that $\bar{\rho}_0 = \bar{E}'_0$ and that we have required \bar{C}_0 to approach unity as $\bar{x} \rightarrow \infty$, thereby specifying the concentration c_* used to make the problem dimensionless.

For the higher order terms of the inner expansion, the conservation equations can be integrated to give

$$\begin{aligned}\bar{C}'_n - \bar{\rho}_0 \bar{E}_n - \bar{E}_0 \bar{\rho}_n &= f_n(\bar{x}), \\ \bar{\rho}'_n - \bar{C}_0 \bar{E}_n - \bar{E}_0 \bar{C}_n &= g_n(\bar{x}),\end{aligned}$$

where the second and third boundary conditions have again been used to evaluate the constants of integration. The functions f_n and g_n can be considered to be known; for example, $f_1(\bar{x}) = -a$ and $f_2(\bar{x}) = \bar{\rho}_1 \bar{E}_1$. By substituting Poisson's equation $\bar{\rho}_n = \bar{E}'_n$ into the first flux equation and integrating we obtain

$$\bar{C}_n = \bar{E}_0 \bar{E}_n + J_n + \int_0^{\bar{x}} f_n(\bar{x}) d\bar{x},$$

where J_n is an integration constant. Substitution into the second flux equation gives a second order, linear differential equation for \bar{E}_n :

$$\bar{E}''_n - (1 + \frac{3}{2} \bar{E}_0^2) \bar{E}_n = \bar{E}_0 J_n + g_n(\bar{x}) + \bar{E}_0 \int_0^{\bar{x}} f_n(\bar{x}) d\bar{x}.$$

Even though the solution of this equation is not evident, we can find how \bar{E}_n behaves for large \bar{x} , without actually solving it. If

$$g_n(\bar{x}) \rightarrow G_0 + G_1 \bar{x} + G_2 \bar{x}^2 + G_3 \bar{x}^3 \text{ as } \bar{x} \rightarrow \infty,$$

then

$$\bar{E}_n(\bar{x}) \rightarrow -G_0 - G_1 \bar{x} - G_2(\bar{x}^2 + 2) - G_3(\bar{x}^3 + 6\bar{x}) \text{ as } \bar{x} \rightarrow \infty.$$

The solution for the various terms of the inner expansion has been outlined above. An explicit solution has not been obtained, but it has been shown that the several terms of the inner expansion of the electric field obey linear differential equations which differ only in the non-homogeneous part. (An approximate solution could be obtained by assuming that $\bar{E}_0^2 \ll 1$.) The higher terms of the inner expansion still have two undetermined integration constants, J_n and $\bar{E}_n(0)$. The second will eventually be determined from the fourth boundary condition, and J_n will be obtained by matching with the outer expansion.

Outer Expansion

Let the outer variable be $\tilde{x} = \delta x$ and let the outer expansions be

$$\tilde{E} = E/\delta = \tilde{E}_0 + \delta \tilde{E}_1 + \delta^2 \tilde{E}_2 + \mathcal{O}(\delta^3).$$

$$\tilde{C} = C = \tilde{C}_0 + \delta \tilde{C}_1 + \delta^2 \tilde{C}_2 + \mathcal{O}(\delta^3).$$

$$\tilde{\rho} = \rho = \delta^2 \tilde{\rho}_2 + \mathcal{O}(\delta^3).$$

In terms of the outer variables the differential equations become

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

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

$$\tilde{\rho} = \delta^2 \tilde{E}'.$$

The first term of the outer expansion satisfies the equation

$$\tilde{C}_0'' + 3\tilde{x}^2 \tilde{C}_0' = 0$$

whose general solution is

$$\tilde{C}_0 = C_\infty + P_0 \int_\infty^{\tilde{x}} e^{-x^3} dx.$$

Since then $\tilde{C}'_0 = P_0 e^{-\tilde{x}^3}$, the electric field is determined from

$$(\tilde{C}_0 \tilde{E}_0)' = -3r\tilde{x}^2 P_0 e^{-\tilde{x}^3}$$

with the solution

$$\tilde{C}_0 \tilde{E}_0 = I_0 + rP_0 e^{-\tilde{x}^3}.$$

The higher order terms of the outer expansion are obtained in a straightforward manner. The average concentration is determined from the equation

$$\tilde{C}_n'' + 3\tilde{x}^2 \tilde{C}_n' = F_n(\tilde{x})$$

whose general solution satisfying the boundary condition at infinity is

$$\tilde{C}_n = P_n \int_\infty^{\tilde{x}} e^{-x^3} dx + \int_\infty^{\tilde{x}} e^{-x^3} \int_0^x e^{t^3} F_n(t) dt dx.$$

The function F_n is known; for example, $F_1(\tilde{x}) = 0$ and

$$F_2 = 3r\tilde{x}^2 \tilde{E}_0'' + (\tilde{E}'_0 \tilde{E}_0)'$$

There is then no problem in determining the electric field from the equation

$$(\tilde{C}_0 \tilde{E}_n)' = G_n(\tilde{x})$$

with the solution

$$\tilde{E}_n(\tilde{x}) = \frac{1}{\tilde{C}_0} \left[I_n + \int_0^{\tilde{x}} G_n(x) dx \right].$$

For the outer expansion, the charge density can always be determined from Poisson's equation. Each term

of the outer expansion contains two undetermined integration constants, P_n and I_n , which are eventually determined by matching with the inner solution.

Matching

The inner and outer expansions of the average concentration are really two different expansions of the same function. For example, we can say

$$\bar{C}_0(\bar{x}) = \lim_{\delta \rightarrow 0} C(\bar{x}) \text{ at constant } \bar{x}.$$

$$\tilde{C}_0(\tilde{x}) = \lim_{\delta \rightarrow 0} C(\tilde{x}) \text{ at constant } \tilde{x} = \delta \bar{x}.$$

These are two different limit processes performed on the same function. Consequently, the two expansions are related. This matching requirement is that the inner limit of the outer expansion should be the same as the outer limit of the inner expansion. This is best understood by means of a specific example.

In the inner limit, as $\tilde{x} \rightarrow 0$,

$$\begin{aligned} \tilde{C}_0 &= C_\infty - P_0 \Gamma(1\frac{1}{3}) + P_0 \int_0^{\tilde{x}} e^{-x^3} dx \\ &= C_\infty - P_0 \Gamma(1\frac{1}{3}) + P_0 \tilde{x} + \mathcal{O}(\tilde{x}^4) \end{aligned}$$

and similarly

$$\tilde{C}_1 = -P_1 \Gamma(1\frac{1}{3}) + P_1 \tilde{x} + \mathcal{O}(\tilde{x}^4),$$

$$\tilde{C}_2 = \tilde{C}_2(0) + \mathcal{O}(\tilde{x}).$$

Thus the inner limit of the outer expansion for the concentration is

$$\tilde{C} = C_\infty - P_0 \Gamma(1\frac{1}{3}) + \delta [-P_1 \Gamma(1\frac{1}{3}) + P_0 \bar{x}] + \delta^2 [\tilde{C}_2(0) + P_1 \bar{x}] + \mathcal{O}(\delta^3).$$

This has been expressed in terms of the inner variable $\bar{x} = \tilde{x}/\delta$ in order to facilitate the comparison with the outer limit of the inner expansion.

On the other hand, in the outer limit as $\bar{x} \rightarrow \infty$, we have

$$\bar{c}_0 \rightarrow 1$$

$$\bar{c}_1 \rightarrow J_1 - a\bar{x}$$

$$\bar{c}_2 \rightarrow J_2 + \frac{1}{2} \bar{E}_1^2 - \frac{1}{2} \bar{E}_1^2(0) = J_2 + \frac{1}{2} b^2 - \frac{1}{2} \bar{E}_1^2(0),$$

and so the outer limit of the inner expansion is

$$\bar{c} = 1 + \delta(J_1 - a\bar{x}) + \delta^2(J_2 + \frac{1}{2} b^2 - \frac{1}{2} \bar{E}_1^2(0)) + \mathcal{O}(\delta^3).$$

Since this must be the same as the inner limit of the outer expansion, the comparison gives

$$C_\infty - P_0 \Gamma(1\frac{1}{3}) = 1.$$

$$P_0 = -a.$$

$$J_1 = -P_1 \Gamma(1\frac{1}{3}).$$

$$P_1 = 0.$$

$$\tilde{c}_2(0) = J_2 + \frac{1}{2} b^2 - \frac{1}{2} \bar{E}_1^2(0).$$

It is necessary for the two expansions of the electric field to match in a similar fashion. Comparison of the inner limit of the outer expansion with the outer limit of the inner expansion yields, for example,

$$I_1 - ra = b.$$

$$I_2 = -J_1 b = 0.$$

From the matching one therefore finds that $\tilde{c}_1 = 0$ and $\tilde{E}_1 = 0$. Other results are given in equations (14) through (18).

The matching requirements, of course, also apply to higher order terms. We have carried this out for terms through $\mathcal{O}(\delta^4)$ and have found no inconsistencies. The

inner expansion satisfies the boundary conditions at $x = 0$, and the outer expansion satisfies the boundary conditions at $x = \infty$. Other integration constants arising out of the solution of the differential equations are determined by the matching requirement.

The Composite Expansion

The inner expansion applies near $x = 0$, and the outer expansion applies near $x = \infty$, but in the intermediate region there may be some uncertainty as to which value to use. To meet this need, the composite expansion is formed by adding the inner and outer expansions and subtracting the terms common to the two expansions. Here "common terms" refer to the outer limit of the inner expansion, which is the same as the inner limit of the outer expansion. For this problem the composite expansions of the electric field and the average concentration are given by equations (12) and (13). It is easily shown that the composite expansion is a uniformly-valid (for all x) expansion of the function, C or E .

NOMENCLATURE

- D_+, D_- - diffusion coefficients of cations and anions (cm²/sec).
- \mathcal{E} - component of the electric field in the y-direction (volt/cm).
- N_+^0, N_-^0 - cation and anion fluxes at the interface (mole/cm²-sec).
- v_y - component of the velocity in the y-direction (cm/sec).
- y - distance from the interface (cm).
- $\Gamma(4/3) = 0.89298.$
- ϵ - dielectric constant (farad/cm).
- ν - kinematic viscosity of the fluid (cm²/sec).
- σ - total electric charge in the diffuse part of the double layer and in the diffusion layer (coulomb/cm²).
- Ω - rotation rate for a rotating disk (radians/sec).

REFERENCES

1. Veniamin G. Levich. Physicochemical Hydrodynamics. Englewood Cliffs: Prentice-Hall, Inc., 1962. Pages 63-64.
2. Hermann Schlichting. Boundary Layer Theory. New York: McGraw-Hill Book Company, Inc., 1960. Pages 85-87.
3. John E. B. Randles. "Concentration Polarization and the Study of Electrode Reaction Kinetics." P. Zuman, ed. Progress in Polarography. New York: Interscience Publishers, 1962. Pages 123-144.
4. L. Bass. "Electrical Structures of Interfaces in Steady Electrolysis." Transactions of the Faraday Society, 60, 1656-1663 (1964).

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