EQUILIBRIUM DOUBLE-LAYER CAPACITANCE
AT THE METAL–BINARY ELECTROLYTE INTERFACE

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The calculation of the capacitance of an ideally polarized electrode, existing in a solution of a binary electrolyte, does not encounter any special difficulties.* The corresponding mathematical problem is exactly solved. The situation is sharply complicated when it is necessary to calculate the capacitance of the equilibrium electrode at an exchange current not equal to zero. In this case, the problem of the distribution of the field and concentrations in the nonequilibrium double layer must be preliminarily solved. As was shown in [1], this problem has no exact solution in elementary functions. Below is presented a method permitting a reduction of the calculation of the capacitance of the equilibrium electrode in the general case to the solution of the problem of the distribution of the field and concentrations in the equilibrium double layer (this nonlinear boundary value problem can be solved exactly) and to the solution of some linear boundary value problem.

We shall consider that electrolysis is conducted in a capillary with length L, at the open end of which a constant concentration of NO ions is maintained [2]. For the sake of definition, let us assume that the electrode exists in a solution of intrinsic ions and that the anions do not take part in the electrode reaction. Let us assume also that the kinetics of the electrode reaction \( M^+ + e^{-} \rightarrow M \) is determined by the equation

\[
I_+ = k'_2 e^{-\frac{\varphi(N_+(0)) - U}{kT}} - k'_1 N_+(0) e^{-\frac{\varphi(N_+(0)) - U}{kT}}
\]

where \( U \) is the electrode potential; \( \varphi(N_+(0)), N_+(0) \) are the potential and concentration of positive ions in the plane of greatest approximation; \( e \) is the charge of the electrode (\( e > 0 \)); \( K \) is Boltzmann's constant; \( T \) is the absolute temperature; \( I_+ \) is the reaction rate; \( k'_2, k'_1 \) are the reaction rate constants; \( \alpha, \beta > 0 \) are some numbers (\( \alpha + \beta = 1 \)).

Then the stationary distribution of the field and concentrations in the system may be found by solving the following boundary value problem, which is conveniently formulated in dimensionless form

\[
\frac{dn_+}{ds} = E n_+ - j_+,
\frac{dn_-}{ds} = -E n_-, \quad e^2 \frac{dE}{ds} = n_+ - n_-, \quad (0 < s < 1)
\]

\[
j_+ = k'_2 e^{-\beta \varphi(N_+(0)) - v_1} - k'_2 N_+(0) e^{\varphi(N_+(0)) - v_1},
V - \varphi(0) = \lambda E(0), \quad n_+(1) = n_-(1) = 1.
\]

The relationship of the dimensionless variables to the dimensional variables is accomplished by means of the formulas

\[
n_+ = \frac{N_+}{N_0}, \quad n_- = \frac{N_-}{N_0}; \quad E = e \varphi L / kT; \quad j_+ = I_+ L / D_+ N_0^2; \quad V = eU / kT; \quad s = X / L; \quad \varphi = \varphi_0 / kT; \quad k_2 = k'_2 L / D_+ N_0; \quad k_1 = k'_1 L / D_-
\]

where \( N_+, N_- \) are the concentrations of positive and negative ions; \( \varphi \) is the electrical field intensity; \( X \) is the coordinate (the point \( X = 0 \) corresponds to the plane of greatest approach of the ions); \( I_+ \) is the flux density of positive ions; \( U, \varphi(X) \) are the electrode potential and potential of the solution, respectively.

*We have in mind the phenomenological theory, based on the coordinated system of transport equations and Poisson equation.

counted from the point \( X = L \); \( D_+ \) is the diffusion coefficient of positive ions; \( \varepsilon = L^{-1}\sqrt{\varepsilon_0 kT/4\pi e^2 N_0} \); \( \varepsilon_0 \) is the dielectric constant of the solution.

The boundary condition \( V - \psi (0) = \lambda E(0) \) corresponds to the concept of the structure of the dense portion of the double layer at the metal-electrolyte interface, generally used in electrochemistry, and is the condition of continuity of induction. In such an interpretation

\[
i = \frac{\varepsilon_0 d_+^2}{\varepsilon_0 L}
\]

where \( \varepsilon_0 \) is the dielectric permeability, while \( d_+ \) is the thickness of the dense portion of the double layer.

Let us determine the differential capacitance of the electrode by the formula

\[
G = -\frac{\partial q}{\partial V}
\]

where

\[
q = \int_0^1 [n_+(s) - n_-(s)] ds
\]

From (2) it follows that

\[
G = \varepsilon^2 \left\{ \left( \frac{\partial E}{\partial j_+} \right)_{s=0} - \left( \frac{\partial E}{\partial j_+} \right)_{s=1} \right\} \frac{dj_+}{dV}
\]

The quantity \( \sigma = \frac{dj_+}{dV} \) is naturally called the electrochemical conductivity of the electrode–solution system. Thus, a calculation of the capacitance of the equilibrium electrode reduces to a calculation of the derivatives \( \frac{\partial E}{\partial j_+} \) and \( \frac{dj_+}{dV} \) at \( j_+ = 0 \).

Let us compile a system in variations of [3], corresponding to (2)-(3):

\[
\begin{align*}
\frac{\partial}{\partial s} \left( \frac{\partial n_+}{\partial j_+} \right) &= E(s) \left( \frac{\partial n_+}{\partial j_+} \right) + n_+(s) \left( \frac{\partial E}{\partial j_+} \right)_{s=0} - 1 \\
\frac{a}{\partial s} \left( \frac{\partial n_-}{\partial j_+} \right) &= -E(s) \left( \frac{\partial n_-}{\partial j_+} \right) - n_-(s) \left( \frac{\partial E}{\partial j_+} \right)_{s=1} \\
\varepsilon^2 \frac{\partial}{\partial s} \left( \frac{\partial E}{\partial j_+} \right) &= \left( \frac{\partial n_+}{\partial j_+} \right)_{s=1} - \left( \frac{\partial n_-}{\partial j_+} \right)_{s=0}
\end{align*}
\]

\[
k_2 \lambda \exp \left[ \mu \lambda E(0) \right] \left( \frac{\partial n_+}{\partial j_+} \right)_{s=0} - k_1 \exp \left[ -\omega \lambda E(0) \right] \left( \frac{\partial n_-}{\partial j_+} \right)_{s=1} = 1
\]

\[
\left( \frac{\partial n_+}{\partial j_+} \right)_{s=1} = \left( \frac{\partial n_-}{\partial j_+} \right)_{s=0} = 0
\]

Here all the derivatives with respect to \( j_+ \) are taken at the point \( j_+ = 0 \), while the functions \( n_-(s), \bar{E}(s) \) are the solutions of the corresponding boundary value problem

\[
\begin{align*}
\frac{dn_+}{ds} &= \bar{E} n_1, \\
\frac{dn_-}{ds} &= -\bar{E} n_1, \\
\varepsilon^2 \frac{dE}{ds} &= n_+ - n_-
\end{align*}
\]

\[
\bar{n}_+(1) = \bar{n}_-(1) = 1, \quad \bar{n}_+(0) = \frac{k_2}{k_1} \exp [\lambda E(0)]
\]

The latter, as is easily shown, has an exact solution in elliptical functions. Thus, by solving the linear boundary value problem (8)-(9) and then determining \( \frac{dj_+}{dV} \) from (3), we can obtain an expression for the capacitance \( G \).

Let us consider first one particular case, namely, let us assume in (11) that \( k_1 = k_2 \). In this case, the problem (10)-(11) has an especially simple solution.