Physical Chemistry

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Abstract

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ALTERNATING CURRENT IN A BINARY ELECTROLYTE

It is of fundamental interest to investigate the pattern of distribution of the field and of matter in the simplest electrochemical system—a cell with a binary electrolyte in the presence of a reversible electrode reaction. Below we consider the impedance of such a system.

The distribution of the field and concentrations in the cell is given by the well-known equations

$$j_+ = D_+ \left(-\partial n_+/\partial x + z_+ E n_+ e/kT\right); \tag{1}$$

$$j_- = D_- \left(-\partial n_-/\partial x - z_- E n_- e/kT\right); \tag{2}$$

$$\partial E/\partial x = 4\pi e \left(z_+ n_+ - z_- n_-\right)/\varepsilon; \tag{3}$$

$$\partial j_+/\partial x + \partial n_+/\partial t = 0, \qquad \partial j_-/\partial x + \partial n_-/\partial t = 0, \tag{4}$$

where j_+, j_-; n_+, n_-; z_+, z_- are, respectively, the fluxes, concentrations, and valences of the ions; E is the electric field.

We shall examine the polarization of the cell by a weak sinusoidal current, using the notion of a sharp transition between the region of the diffuse layer and the diffusion region. In order to exclude the influence of natural convection, we shall assume that electrolysis is carried out in a capillary of length L, at the open end of which the initial ion concentrations n_+^0 and n_-^0 are maintained ([1]). Any quantity may be represented as the sum of an equilibrium value (we shall denote it by a straight overbar) and an alternating increment (we shall denote it by a wavy overbar). In the diffusion region $x^{(d)} \ll x \leq L$, taking into account the electroneutrality condition, from (1), (2), and (4) one may obtain

$$z_- \tilde{n}_- = z_+ \tilde{n}_+ = z_+ \tilde{n}_+^{(d)} e^{-k_\omega (x - x^{(d)})}, \tag{5}$$

$$z_+\tilde{n}_+^{(d)} = \frac{\tilde{j}_+^{(d)} D_+^{-1} + \tilde{j}_-^{(d)} D_-^{-1}}{k_\omega (z_+^{-1} + z_-^{-1})}; \qquad k_\omega = \left[i\omega \frac{(D_+ z_+)^{-1} + (D_- z_-)^{-1}}{z_+^{-1} + z_-^{-1}} \right]^{1/2}, \tag{6}$$

where ω is the frequency of the sinusoidal current $I = I_0 \exp(i\omega t)$. In writing (5) and (6) it was assumed that $|k_\omega^{-1}| \ll L$, and therefore the solution was sought in an unbounded region. Quantities with the index (d) refer to the boundary of the diffuse and diffusion layers. From (1) and (2), taking into account that $\overline{E} = 0$, $\overline{n}_+ = n_+^0$, $\overline{n}_- = n_-^0$, for the potential drop in the diffusion region one can obtain

$$\widetilde{\varphi}^{(d)} - \widetilde{\varphi}^{(L)} = \left(z_+ \tilde{j}_+^{(d)} - z_- \tilde{j}_-^{(d)} \right) \lambda^{-1} L + (D_- - D_+)\, \lambda^{-1} e z_+ \tilde{n}_+^{(d)}, \tag{7}$$

where λ is the conductivity of the solution. The first term in (7) represents ohmic losses in a solution of constant concentration. We shall not take this term into account further, meaning that the ohmic losses are included in a certain ohmic resistance connected in series with the cell. The second term in (7) is associated with concentration changes.

in the diffusion region

$$\left(\widetilde{\varphi}^{(d)} - \widetilde{\varphi}^{(L)} \right)_{\text{conc}} = e\,(D_- - D_+)\, \lambda^{-1} \tilde{n}_+^{(d)} z_+. \tag{8}$$

Let us now turn to consideration of the region of the diffuse part of the double layer $0 \leqslant x \leqslant x^{(d)}$. We shall assume that positive ions take part in the electrochemical reaction, while the electric charge in the diffuse layer is determined by negative ions. Poisson’ s equation (3) may be rewritten in the form

$$\frac{\partial \mathcal{E}}{\partial x} = -\frac{4\pi e^2 z_-}{\varepsilon\theta}\, n_- \qquad \left(\mathcal{E} = \frac{eE}{\theta};\ \theta = kT \right). \tag{9}$$

The concentration of negative ions increases toward the electrode. The passage of electric current will practically not change their distribution according to Boltzmann’ s law

$$n_- = n_-^{(d)} e^{z_-(\psi - \psi^{(d)})} \qquad \left(\mathcal{E} = -\frac{\partial \psi}{\partial x} \right). \tag{10}$$

In order to obtain (10) formally, the term with the current must be omitted in (2). If the frequency of the alternating current ω is much smaller than the charge-relaxation frequency in the double layer ω_0, then, as estimates show, this may be done. The order of ω_0 is $D_- \varkappa^2$, where $\varkappa^2 = 4\pi e^2 n_-^0/(\varepsilon\theta)$. We shall assume that the inequality $\omega \ll \omega_0$ is well satisfied.

Using (10), one can obtain the solution of (9) in the form

$$\frac{1}{2}\mathcal{E}^2 = \frac{4\pi e^2}{\varepsilon\theta}\, n_-^{(d)} \left(e^{z_-(\psi-\psi^{(d)})} - 1\right) + \frac{1}{2}\left(\mathcal{E}^{(d)}\right)^2 .$$

The integration constant is determined from the matching condition with the diffusion region. Taking into account the smallness of the electric field in the diffusion region and the rapid change of the exponential function, one may write that for the greater part of the diffuse layer, in any case when $\psi - \psi^{(d)} \gg 1$, the relation

$$\frac{1}{2}\mathcal{E}^2 = \varkappa_-^2 \frac{n_-}{n_-^0} = \varkappa_-^2 \frac{n_-^{(d)}}{n_-^0} e^{z_-(\psi-\psi^{(d)})} \tag{11}$$

is fulfilled.

The displacement current in the Helmholtz part of the double layer is due to oscillations of the density of negative ions in the diffuse part of the double layer. As one moves away from the electrode, the displacement current will pass into the electric current of the negative ions. Therefore the current of negative ions at the boundary with the diffusion layer will be equal to the displacement current in the plane of closest approach. Quantities referring to this plane will be marked with an asterisk,

$$\tilde{j}_-^{(d)} = -\frac{\varepsilon\theta}{4\pi e^2 z_-}\, i\omega\, \tilde{\mathcal{E}}^* . \tag{12}$$

Since positive ions do not participate in the formation of the charge of the double layer and the displacement current is not created by oscillations of their density, the current of positive ions will not change with distance within the limits of the double layer,

$$\tilde{j}_+^{(d)} = \tilde{j}_+^* . \tag{13}$$

Using (11) and (13), the solution of equation (2) may be written in the form

$$n_+ = n_+^{(d)} e^{-z_+(\psi-\psi^{(d)})} + \tilde{j}_+^{(d)} e^{-\frac{z_-}{2}(\psi-\psi^{(d)})} \left[\varkappa_- D_+ \left(z_+ - \frac{z_-}{2}\right)\sqrt{2\,\frac{n_-^{(d)}}{n_-^0}}\right]^{-1} . \tag{14}$$

Here it was assumed that $z_+ > z_-/2$, and the large value of $\psi - \psi^{(d)}$ was used (we leave aside the case $z_+ < z_-/2$). The relations connecting the small variable quantities may be found from (10), (11), (14) by direct differentiation. Thus, we have

$$\tilde{\psi}^* - \tilde{\psi}^{(d)} = \frac{1}{z_-}\frac{\tilde{n}_-^*}{n_-^0} e^{-z_-\bar{\psi}^*} - \frac{1}{z_-}\frac{\tilde{n}_-^{(d)}}{n_-^0};$$

$$\tilde{\mathcal{E}}^*\tilde{\mathcal{E}}^* = \frac{\chi^2\tilde{n}_-^*}{n_-^0}; \tag{15}$$

$$\tilde{n}_+^* = \left(z_+^{-1} + z_-^{-1}\right) z_+ n_+^{(d)} e^{-z_+\bar{\psi}^*} - \frac{z_+}{z_-}\bar{n}_+^* e^{-z_-\bar{\psi}^*}\frac{\tilde{n}_-^*}{n_-^0} + \frac{\tilde{j}_+^{(d)} e^{-\frac{z_-}{2}\bar{\psi}^*}}{D_+\chi_-(z_+ - z_-/2)\sqrt{2}}. \tag{16}$$

In the case of a reversible reaction, for the concentration of the discharging ions one may write

$$n_+^* = \bar{n}_+^* e^{z_+\Delta\psi}; \qquad \Delta\psi = \varepsilon\delta_\mathrm{r}(\mathcal{E}^* - \bar{\mathcal{E}})/\varepsilon_\mathrm{r},$$

where δ_r and ε_r are the thickness and dielectric constant of the Helmholtz layer. Hence, for the alternating quantities we find

$$\tilde{n}_+^* = \bar{n}_+^* z_+ \Delta\tilde{\psi}; \qquad \Delta\tilde{\psi} = \varepsilon\delta_\mathrm{r}\tilde{\mathcal{E}}^*/\varepsilon_\mathrm{r}. \tag{17}$$

Using (6), (12), (13), (15), (16), (17), one can obtain for the complex conductivity of the cell the expression

$$\sigma = \frac{i\omega C \ + \dfrac{\left[z_+\bar{n}_+^* + k_\omega^{-1} D_-^{-1} e^{-z_+\bar{\psi}^*}\theta i\omega C \ \left(e^2 z_-\right)^{-1}\right] z_+ e^{2\theta-1}}{k_\omega^{-1} D_+^{-1} e^{-z_+\bar{\psi}^*} + e^{-z_-\bar{\psi}^*/2}\left[D_+\chi_-\sqrt{2}(z_+ - z_-/2)\right]^{-1}}}{1 - \dfrac{D_+ k_\omega^{-1}}{n_+^0(z_+D_+ + z_-D_-)}\,\dfrac{z_+\bar{n}_+^* - i\omega C \ e^{-z_-\bar{\psi}^*/2}\left[e^2 z_- D_-\chi_-\sqrt{2}(z_+ - z_-/2)\right]^{-1}}{k_\omega^{-1} e^{-z_-\bar{\psi}^*/2}\left[\chi_-\sqrt{2}(z_+ - z_-/2)\right]^{-1}}}, \tag{18}$$

where $C \ = \varepsilon_\mathrm{r}/(4\pi\delta_\mathrm{r})$.

In writing (18), the quantity $\varepsilon_\mathrm{r}(\varepsilon\delta_\mathrm{r}\mathcal{E}^*)^{-1}$ was omitted as small compared with unity. In the case of a sufficiently small value of ω, when the condition

$$L_\omega = |k_\omega^{-1}| \gg L \ = \chi_-^{-1}\left[\sqrt{2}(z_+ - z_-/2)\right]^{-1} e^{(z_+ - z_-/2)\bar{\psi}^*}, \tag{19}$$

is fulfilled, from (18) one can obtain

$$\sigma = \left(\frac{z_+D_+ + z\_D\_}{z\_D\_}\right)^2 i\omega C \; + \frac{z_+D_+ + z\_D\_}{z\_D\_}\frac{z_+^2 e^2}{\theta} n_+^0 k_\omega . \tag{20}$$

In deriving (20) it was assumed that the quantity $\left|\varepsilon_\mathrm{r} k_\omega^2 L \; [\varepsilon \delta_\mathrm{r} \chi^2]^{-1}\right|$ is small compared with unity. If the inequality opposite to (19) is satisfied, but the frequency is still not very large, so that $\left|k_\omega^2 L \; \chi^{-1}\right| \ll 1$, then from (18) we obtain

$$\sigma = i\omega C \; - \frac{z\_D\_}{z_+D_+ + z\_D\_}\frac{e^2 z_+^2 n_+^0 D_+}{\theta L \; k_\omega L} + \frac{e^2 z_+^2 n_+^0 D_+}{\theta L}. \tag{21}$$

Finally, in the case of still higher frequencies, when, in addition to the inequality opposite to (19), the inequality $\left|k_\omega^2 L \; \chi^{-1}\right| \gg 1$ is satisfied, we obtain from (18)

$$\sigma = i\omega C \; + e^2 z_+^2 n_+^0 D_+ \theta^{-1} L^{-1}. \tag{22}$$

Let us note that the expression for L in (19), obtained by us for the case of alternating current, coincides with the expression for the effective length of diffusions in the double layer under direct current, obtained in work (^{2}). Oscillations of negative ions, associated with the presence of a displacement current, in the diffusion region, owing to the electroneutrality of the solution, lead to oscillations of the discharging (positive) ions. When (19) is satisfied, these oscillations can easily reach the electrode and cause a current whose order of magnitude coincides with that of the displacement current. The first term in (20) corresponds to this current and to the displacement current. If the value of the quantity $[(z_+D_+ + z\_D\_)/z\_D\_]^2$ is large in comparison with unity, then the capacitance, independent of frequency, is anomalously large. When (19) is fulfilled, the density oscillations of the positive ions satisfying condition (17) easily penetrate through the double-layer region into the diffusion region, causing there oscillations that lead to the appearance in (20) of a second term, whose form coincides with that of the ordinary Faradaic impedance, the properties of which are well known (^{3}).

If the inequality opposite to (19) is fulfilled, then the connection between the oscillations of the positive ions in the Helmholtz plane and the oscillations in the diffusion region is disrupted. In this case, as (22) shows, the capacitance of the cell is determined by the charge capacitance, while the resistance does not depend on frequency and is determined by the oscillations of the positive ions within the limits of the double layer.

In conclusion, we note that the theory set forth above is naturally carried over to the case in which the charge in the double layer is determined by positive ions, while negative ions are discharged.

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Note: Figure translations are in progress. See original paper for figures.