PHYSICAL CHEMISTRY

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Abstract

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THE RECTIFICATION EFFECT AT AN IDEALLY POLARIZABLE ELECTRODE

It is of fundamental interest to carry out a sufficiently complete quantitative study of the process of current passage through the simplest electrochemical system—a stationary solution of a binary electrolyte. In the present work the mean shift of the potential arising when a sinusoidal current is passed through a cell with an ideally polarizable electrode will be calculated. As will be shown below, the passage of a sinusoidal signal is accompanied by a rectification effect. Measurement of the latter makes it possible, in principle, to find the value of the potential in the plane of closest approach of the ions (the so-called psi-prime potential).

The passage of a sinusoidal current through an ideally polarizable electrode is associated with periodic charging and discharging of the double layer and, in particular, with sinusoidal oscillations of the field strength in the Helmholtz layer. The change in the voltage drop in the Helmholtz layer is proportional to the oscillations of the field strength and therefore has a sinusoidal character. Thus the mean value of the voltage drop in the Helmholtz layer is equal to zero.

We shall assume that the value of the psi-prime potential is sufficiently large, so that the charge in the diffuse layer may actually be regarded as being determined by only one kind of ion. For definiteness we shall take these ions to be negative. Then, in order to calculate the mean value of the voltage drop in the diffuse layer, one may use expression (1)

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

Here and below the notation of work (1) is used. Usually (2), in considering the phenomenon of faradaic rectification, it is assumed that the cell is polarized by a current of sufficiently small amplitude. We shall assume that the condition of small amplitude is satisfied. Then from (1), with accuracy up to terms of second order of smallness, we obtain

$$\tilde{\mathcal{E}}^*\tilde{\mathcal{E}}^* + \frac{1}{2}\tilde{\mathcal{E}}^{*2} = \chi_-^2 e^{z_-\psi^*}\left[\frac{\tilde{n}_-^{(d)}}{n_-^{(0)}} + z_-(\widetilde{\psi}^* - \widetilde{\psi}^{(d)}) + \right.$$

$$+\frac{\tilde{n}_-^{(d)}}{n_-^0} z_-(\widetilde{\psi}^* - \widetilde{\psi}^{(d)}) + \frac{1}{2} z_-^2 (\widetilde{\psi}^* - \widetilde{\psi}^{(d)})^2 \Bigg] . \tag{2}$$

We must calculate the mean value $\langle\widetilde{\psi}^* - \widetilde{\psi}^{(d)}\rangle$

$$\langle\widetilde{\psi}^* - \widetilde{\psi}^{(d)}\rangle = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} [\widetilde{\psi}^* - \widetilde{\psi}^{(d)}] \, dt$$

over the period of the sinusoidal current $2\pi/\omega$. Carrying out the averaging in (2), we obtain

$$z_-\langle\widetilde{\psi}^* - \widetilde{\psi}^{(d)}\rangle = \left\langle \frac{\tilde{n}_-^{(d)}}{n_-^0} z_-(\widetilde{\psi}^* - \widetilde{\psi}^{(d)}) \right\rangle +$$

$$+\frac{1}{2} z_-^2 \langle(\widetilde{\psi}^* - \widetilde{\psi}^{(d)})^2\rangle - \langle\tilde{\mathcal{E}}^{*2}\rangle \chi_-^{-2} e^{-z_- \psi^*} . \tag{3}$$

In calculating the mean values of quantities of second order of smallness of the type $\langle\tilde{n}_-^{(d)}(\tilde{\psi}^* - \tilde{\psi}^{(d)})\rangle$, one may use expressions obtained while retaining only quantities of first order of smallness, i.e., the expressions used in calculating the impedance of the cell [1]. We carry out the averaging of quantities of second order of smallness precisely in this way.

To calculate the mean potential shift in the diffusion region, we use the transport equation

$$j_- = D_- \left(-\frac{\partial n_-}{\partial x} - z_- \mathcal{E} n_- \right) .$$

From this equation, accurate to quantities of second order of smallness, we obtain

$$\langle z_- \tilde{\mathcal{E}}\rangle = \frac{1}{n_-^0} \left\langle \frac{\tilde{n}_-}{n_-^0} \frac{\partial \tilde{n}_-}{\partial x} \right\rangle + \frac{1}{n_-^0 D_-} \langle \tilde{j}_- \tilde{n}_- / n_-^0 \rangle . \tag{4}$$

The value of the mean potential shift in the diffusion region is obtained from (4) by direct integration. If the expression thus obtained is added to (3), then for the mean voltage shift across the entire cell we obtain

$$\begin{aligned} z_-\langle\tilde{V}\rangle &= z_-\langle\widetilde{\psi}^* - \widetilde{\psi}^{(d)}\rangle + z_-\langle\widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)}\rangle \\ &= \frac{1}{4} \left(\frac{D_+ z_+}{D_+ z_+ + D_- z_-} \right)^2 \frac{i_0^2}{z_-^2 e^2 n_-^{02} D_- \omega} - \frac{1}{4} e^{-z_- \bar{\psi}^*} \frac{4\pi i_0^2}{\varepsilon \theta \omega^2 n_-^0} , \end{aligned} \tag{5}$$

where i_0 is the amplitude of the sinusoidal current.

It is interesting to note that the total potential shift is determined by two terms having opposite signs and depending differently on frequency. Therefore, at a certain frequency $\omega = \omega_{\text{crit}}$, the value of the mean potential shift passes through zero. From (5) it follows that

$$\omega_{\text{crit}} = \omega_0 e^{-z_-\bar{\psi}^*}\xi^{-1}, \tag{6}$$

$$\omega_0 = \frac{4\pi e^2 n_-^0 D_-}{\varepsilon\theta} = \chi^2 D_-; \qquad \xi = \frac{1}{z_-^2}\left(\frac{D_+z_+}{D_+z_+ + D_-z_-}\right)^2 .$$

Knowing the value of the frequency at which the rectification effect is absent, one can determine ψ^*, i.e., the psi-prime potential:

$$z_-\bar{\psi}^* = \ln\frac{\omega_0}{\xi\omega_{\text{crit}}}. \tag{7}$$

For $\omega \gg \omega_{\text{crit}}$, rectification is determined by the first term in (5), and therefore the potential shift is inversely proportional to frequency at constant current amplitude. For $\omega \ll \omega_{\text{crit}}$, rectification is determined by the second term in (5), and therefore the potential shift is inversely proportional to the square of the frequency at constant current amplitude.

If the charge in the diffuse layer is determined mainly by positive ions, then expression (5) will again be valid if in it one formally makes the replacement of indices $(+) \to (-)$, $(-) \to (+)$.

In conclusion, we note that the results obtained are valid only under the condition that the frequency ω is much smaller than the relaxation frequency of the double layer. The order of magnitude of the latter coincides with $\omega_0 = \chi^2 D_-$.

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CITED LITERATURE

1. V. G. Levich, B. M. Grafov, DAN, **146**, No. 2 (1962).
2. Yu. A. Vdovin, DAN, **120**, 554 (1958); G. C. Barker, *Trans. Symposium on Electrode Processes*, Philadelphia, 1959.

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