



Soviet-era science, translated into English

V. S. KRYLOV

1962

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196201.87187>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

V. S. KRYLOV

DISTRIBUTION OF THE POTENTIAL AND ELECTRIC FIELD STRENGTH IN THE DENSE PART OF THE DOUBLE ELECTRIC LAYER

(Presented by Academician A. N. Frumkin, 25 XII 1961)

In works ⁽¹⁻³⁾ a general method was proposed for quantitatively accounting for the discrete structure of specifically adsorbed ionic layers at various phase boundaries. The adsorption isotherms calculated by means of this method for the metal-solution and air-solution interfaces ⁽⁴⁾ proved to be close to the experimental isotherms relating to concentrated solutions ^(5,6). Recently, Watts-Tobin ⁽⁷⁾ made an attempt at a theoretical explanation of experimental data on the measurement of the differential capacitance of the dense part of the double layer at the metal-solution interface ⁽⁸⁾. In ⁽⁷⁾ the electric field in the dense layer is assumed to be uniform. Such an assumption, as shown in ⁽⁹⁾, is valid only for points sufficiently remote from the adsorbed ions, and does not take into account the fluctuations of the field in planes parallel to the electrode. The distribution of the field also depends strongly on the nature of the phase bordering the solution. Therefore a consistent quantitative calculation of the potential and field strength in the dense layer, to which the present work is devoted, is of undoubted importance.

In sufficiently concentrated solutions one may neglect the potential drop in the diffuse region of the double layer. If, moreover, it is assumed that the centers of specifically adsorbed ions possessing charge z_0 occupy fixed positions in the plane $x = 0$ ($x = -\beta$ is the phase boundary, $x = \gamma$ is the boundary between the dense and diffuse regions), specified by the indices m, n , then the distribution of the potential in the dense part of the double layer, as shown in ^(2,3), has the form:

$$\psi(\mathbf{r}) = \frac{\gamma - x}{\delta} \psi_0 \delta_{1\omega} - \frac{ez_0}{D_2} \sum_{mn} \int_0^\infty \frac{(\omega - e^{2\lambda\beta})e^{\lambda x} + \omega(1 - e^{2\lambda\gamma})e^{-\lambda x} - (\omega - e^{2\lambda\delta})e^{-\lambda|x|}}{\omega - e^{2\lambda\delta}} J_0(\lambda R_{mn}) d\lambda,$$

where $\delta = \beta + \gamma$; $\omega = \frac{D_1 - D_2}{D_1 + D_2}$; D_1 and D_2 are the dielectric permittivities, respectively, of the phase bordering the solution and of the dense part of the double layer; $J_0(\lambda R_{mn})$ is a Bessel function of the first kind; $R_{mn}^2 = (y -$

$y_{mn})^2 + (z - z_{mn})^2$; ψ_0 is the mean potential drop between the planes $x = -\beta$ and $x = \gamma$; $\delta_{1\omega}$ is the Kronecker symbol.

For purposes of numerical calculation it is convenient to put $\beta = \gamma$ and represent $\psi(\mathbf{r})$ in the form of sums

$$\psi(\mathbf{r}) = \psi_1(\mathbf{r}) + \psi_2(\mathbf{r}),$$

where

$$\psi_1(\mathbf{r}) = \left(\frac{1}{2} - \frac{x}{\delta}\right) \psi_0 \delta_{1\omega} - \frac{ez_0}{D_2} \sum_{mn} \int_0^\infty \frac{(\omega - e^{\lambda\delta})e^{\lambda x} + \omega(1 - e^{\lambda\delta})e^{-\lambda x} - (\omega - e^{2\lambda\delta})e^{-\lambda|x|}}{\omega - e^{2\lambda\delta}} J_0(\lambda R_{mn}) d\lambda \quad (R_{mn} > 0)$$

$$\psi_2(\mathbf{r}) = \begin{cases} 0, & \text{if } R_{mn} > 0 \text{ for all } m, n; \\ \frac{ez_0}{D_2|x|} - \frac{ez_0}{D_2\delta} Q(x), & \text{if } y = y_{m_0 n_0}, z = z_{m_0 n_0}. \end{cases}$$

(m_0, n_0 —the position of a certain adsorbed ion), where

$$Q(x) = \int_0^1 \frac{\omega(t-1)t^{x/\delta} + (\omega t - 1)t^{-x/\delta}}{\omega t^2 - 1} dt.$$

With accuracy up to terms of order $(\frac{x}{\delta})^4$,

$$Q(x) = \begin{cases} 2 \left[\ln 2 + 0.90 \left(\frac{x}{\delta}\right)^2 + 0.97 \left(\frac{x}{\delta}\right)^4 \right], & \omega = 1, \\ \frac{\delta}{\delta - x}, & \omega = 0, \\ 2 \left[\frac{1}{2} \ln 2 + 0.92 \frac{x}{\delta} + 0.11 \left(\frac{x}{\delta}\right)^2 + 0.99 \left(\frac{x}{\delta}\right)^3 + 0.03 \left(\frac{x}{\delta}\right)^4 \right], & \omega = -1. \end{cases}$$

The integral term in the expression for $\psi_1(\mathbf{r})$ in the cases $\omega = \pm 1$ can be evaluated by means of residue theory. As a result we obtain:

$$\psi_1(\mathbf{r}) = \begin{cases} \left(\frac{1}{2} - \frac{x}{\delta}\right) \psi_0 + \frac{4ez_0}{D_2\delta} \sum_{mn} \sum_{k=1}^\infty \cos \frac{\pi x(2k-1)}{\delta} K_0\left(\frac{\pi(2k-1)R_{mn}}{\delta}\right), & \omega = 1, R_{mn} > 0, \\ \frac{ez_0}{D_2} \sum_{mn} \left(\frac{1}{\sqrt{R_{mn}^2 + x^2}} - \frac{1}{\sqrt{R_{mn}^2 + (\delta - x)^2}} \right), & \omega = 0, R_{mn} > 0, \\ \frac{2ez_0}{D_2\delta} \sum_{mn} \sum_{k=1}^\infty \left\{ \cos \frac{\pi x(2k-1)}{2\delta} + (-1)^k \sin \frac{\pi x(2k-1)}{2\delta} \right\} K_0\left(\frac{\pi(2k-1)R_{mn}}{2\delta}\right), & \omega = -1, R_{mn} > 0, \end{cases}$$

where K_0 is the Macdonald function.

Assume that the centers of the adsorbed ions are located at the nodes of a regular hexagonal lattice with parameter r_0 , and that at the boundary $x = -\beta$ there are no free electric charges (for the metal-solution boundary this corresponds to the point of the electrocapillary maximum). In this case (1-4):

$$\psi_0 = 4\pi e z_0 \delta / \sqrt{3} D_2 r_0^2.$$

Let us introduce the dimensionless quantities:

$$\Psi_1(\mathbf{r}) = \psi_1(\mathbf{r})/\psi_0, \quad \Psi_2(\mathbf{r}) = \psi_2(\mathbf{r})/\psi_0; \quad \Psi(\mathbf{r}) = \Psi_1(\mathbf{r}) + \Psi_2(\mathbf{r}); \quad \xi = \delta/r_0.$$

From the preceding formulas it follows that:

$$\Psi_1(\mathbf{r}) = \begin{cases} \frac{1}{2} - \frac{x}{\delta} + \frac{\sqrt{3}}{\pi \xi^2} \sum_{k=1}^{\infty} \cos \frac{\pi x(2k-1)}{\delta} S_k(\xi), & \omega = 1, R_{mn} > 0, \\ \frac{\sqrt{3}}{4\pi \xi} \sum_{mn} \left(\frac{1}{\sqrt{a_{mn}^2 + \xi^2(x/\delta)^2}} - \frac{1}{\sqrt{a_{mn}^2 + \xi^2(1-x/\delta)^2}} \right), & \omega = 0, R_{mn} > 0, \\ \frac{\sqrt{3}}{2\pi \xi^2} \sum_{k=1}^{\infty} \left\{ \cos \frac{\pi x(2k-1)}{2\delta} + (-1)^k \sin \frac{\pi x(2k-1)}{2\delta} \right\} S_k(2\xi), & \omega = -1, R_{mn} > 0, \end{cases}$$

where

$$a_{mn} = \frac{R_{mn}}{r_0}; \quad S_k(t) = \sum_{mn} K_0 \left(\frac{\pi(2k-1)a_{mn}}{t} \right);$$

$$\Psi_2(\mathbf{r}) = \begin{cases} 0, & \text{if } R_{mn} > 0 \text{ for any } m, n; \\ \frac{\sqrt{3}}{4\pi \xi^2} \left(\frac{\delta}{|x|} - Q(x) \right), & \text{if } y = y_{m_0, n_0}, z = z_{m_0, n_0}. \end{cases}$$

The dimensionless component of the field strength along the x -axis, which we shall denote by

$$E(\mathbf{r}) = -(\partial \Psi(\mathbf{r})/\partial x)\delta,$$

is equal to

$$E(\mathbf{r}) = E_1(\mathbf{r}) + E_2(\mathbf{r}),$$

Fig. 1. Distribution of the potential and electric-field strength in the dense part of the double electric layer.

Figure 1: Fig. 1. Distribution of the potential and electric-field strength in the dense part of the double electric layer.

Fig. 1. Distribution of the potential Ψ^B and the electric-field strength E^B in the dense part of the double electric layer.

1, 2, 3 $-\xi = 0.5$; 1', 2', 3' $-\xi = 0.1$; 1 and 1' $-\omega = 1$;
2 and 2' $-\omega = 0$; 3 and 3' $-\omega = -1$

where

$$E_1(\mathbf{r}) = \begin{cases} 1 + \frac{\sqrt{3}}{\xi^2} \sum_{k=1}^{\infty} (2k-1) \sin \frac{\pi x(2k-1)}{\delta} S_k(\xi), & \omega = 1, R_{mn} > 0; \\ \frac{\sqrt{3}}{4\pi} \xi \sum_{mn} \left\{ \frac{x/\delta}{[a_{mn}^2 + \xi^2(x/\delta)^2]^{3/2}} + \frac{1-x/\delta}{[a_{mn}^2 + \xi^2(1-x/\delta)^2]^{3/2}} \right\}, & \omega = 0, R_{mn} > 0; \\ \frac{\sqrt{3}}{4\xi^2} \sum_{n=1}^{\infty} (2k-1) \left\{ \sin \frac{\pi x(2k-1)}{2\delta} + (-1)^{k+1} \cos \frac{\pi x(2k-1)}{2\delta} \right\} S_k(2\xi), & \omega = -1, R_{mn} > 0; \end{cases}$$

$$E_2(\mathbf{r}) = \begin{cases} 0, & \text{if } R_{mn} > 0 \text{ for all } m, n; \\ \frac{\sqrt{3}}{4\pi\xi^2} \left(\frac{dQ(x)}{dx} \delta + \operatorname{sgn} x \cdot \frac{\delta^2}{x^2} \right), & \text{if } y = y_{m_0 n_0}, z = z_{m_0 n_0}. \end{cases}$$

Let us find the potential and field strength at points belonging to two straight lines parallel to the x -axis, one of which passes through a certain adsorbed ion (case A), while the other is equidistant from the three nearest adsorbed ions (case B). From the symmetry of the problem it is clear that in both cases the electric-field strength is directed along the x -axis. The properties of the regular hexagonal lattice make it possible to formulate the following summation rules, convenient for calculation:

case A:

$$\sum_{nm} f(a_{mn}^A) = 6 \left\{ \sum_{m=1}^{\infty} f(m) + \sum_{m=2}^{\infty} \sum_{n=1}^{m-1} f(\sqrt{m^2 + n^2 - mn}) \right\};$$

case B:

$$\sum_{mn} f(a_{mn}^B) = 3 \left\{ \sum_{m=0}^{\infty} f(\sqrt{3}(m+1/3)) + \sum_{m=1}^{\infty} \sum_{n=1}^{3m} f(\sqrt{(3m+1)(m-n+1/3)+n^2}) \right\}.$$

Figure 2: Distribution of the potential Ψ in the plane $x = -1/4\delta$. Point A is located opposite an adsorbed ion; point B is equidistant from three nearest adsorbed ions. $a-\xi = 0.1$; $b-\xi = 0.5$; $1-\omega = 1$; $2-\omega = 0$; $3-\omega = -1$.

Figure 2: Figure 2: Distribution of the potential Ψ in the plane $x = -1/4\delta$. Point A is located opposite an adsorbed ion; point B is equidistant from three nearest adsorbed ions. $a-\xi = 0.1$; $b-\xi = 0.5$; $1-\omega = 1$; $2-\omega = 0$; $3-\omega = -1$.

Table 1

Dependence of the potential Ψ^A and the field strength E^A on the coordinate x and on the parameter ξ .

x/δ	$\xi = 0.1, \Psi^A, \omega = 1$	$\xi = 0.1, \Psi^A, \omega = 0$	$\xi = 0.1, \Psi^A, \omega = -1$	$\xi = 0.1, E^A, \omega = 1$	$\xi = 0.1, E^A, \omega = 0$	$\xi = 0.1, E^A, \omega = -1$	$\xi = 0.5, \Psi^A, \omega = 1$	$\xi = 0.5, \Psi^A, \omega = 0$	$\xi = 0.5, \Psi^A, \omega = -1$	$\xi = 0.5, E^A, \omega = 1$	$\xi = 0.5, E^A, \omega = 0$	$\xi = 0.5, E^A, \omega = -1$
-1/2	1	18.5	34.4	-99.3	-49.0	0	1	1.36	1.69	-3.05	-1.52	0
-1/4	35.3	44.3	53.5	-234	-212	-191	2.14	2.26	2.38	-8.41	-7.93	-7.44
0	∞	∞	∞	-	-	-	∞	∞	∞	-	-	-
1/4	34.8	36.8	38.6	236	245	253	1.64	1.65	1.66	10.4	10.5	10.6
1/2	0	0	0	101	111	116	0	0	0	5.05	5.11	5.14

Fig. 2. Distribution of the potential Ψ in the plane $x = -1/4\delta$. Point A is located opposite an adsorbed ion; point B is equidistant from three nearest adsorbed ions. $a-\xi = 0.1$; $b-\xi = 0.5$; $1-\omega = 1$; $2-\omega = 0$; $3-\omega = -1$.

For $\omega = \pm 1$, the rapid convergence of the corresponding series makes it possible to calculate, with good accuracy, the quantities Ψ^A , Ψ^B , E^A , and E^B for any physically real degrees of filling. The case $\omega = 0$ is amenable to calculation only for sufficiently small ξ . In the present work a numerical calculation has been carried out of the dependence on x of the quantities Ψ^A , Ψ^B , E^A , and E^B for two values of the parameter ξ : 0.1 and 0.5 (Figs. 1 and 2, Table 1).

It is interesting to note that, as the parameter ξ increases, the values of E^B in the plane $x = 0$ tend to unity for all ω , and in the case $\omega = 1$ for this plane the equality $E^B = 1$ holds for all values of ξ (see Fig. 1). Figures 1 and 2 and Table 1 also demonstrate clearly pronounced periodic oscillations of the potential and field strength in the planes $x = \text{const}$.

The author expresses gratitude to Academician A. N. Frumkin, Corresponding Member of the Academy of Sciences of the USSR, and to V. G. Levich for discussion of the results obtained.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
20 XII 1961

References

1. V. G. Levich, V. A. Kir' yanov, V. S. Krylov, DAN, **135**, No. 6 (1960).
2. V. G. Levich, V. A. Kir' yanov, V. S. Krylov, ZhFKh, **36** (1962) (in press).
3. V. G. Levich, V. A. Kir' yanov, ZhFKh, **36** (1962) (in press).
4. V. G. Levich, V. S. Krylov, DAN, **142**, No. 1 (1962).
5. A. Ioffe, A. N. Frumkin, ZhFKh, **18**, 268 (1944).
6. B. S. Gurenkov, ZhFKh, **30**, 1830 (1956).
7. R. J. Watts-Tobin, Phil. Mag., **6**, No. 61 (1961).
8. D. C. Grahame, J. Am. Chem. Soc., **76**, 4819 (1954); **79**, 2093 (1957);
Zs. Elektrochem., **59**, 740 (1955).
9. B. V. Ershler, ZhFKh, **20**, 679 (1946).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.