

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

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A general method for the quantitative treatment of the discrete structure of specifically adsorbed ionic layers on different interphase boundaries has been given in [1-3]. The adsorption isotherms for the metal-solution and air-solution [4] boundaries calculated by this method have turned out to be very nearly the same as the experimental isotherms for concentrated solutions [5,6]. Recently, Watts-Tobin [7] attempted to give a theoretical explanation of the experimental data obtained from measuring the differential capacity of the dense part of the double layer at a metal-solution boundary [8]. In [7] the electric field in the dense layer is assumed to be homogeneous. It was shown in [9] that this assumption is only correct for points which are far enough removed from adsorbed ions, and does not take account of any oscillations of the field in planes parallel to the electrode. The field distribution also depends strongly on the nature of the phase adjacent to the solution. There is therefore no doubt of the importance to be attached to a rigorous quantitative calculation of the potential and field intensity in the dense layer, which is what the present paper deals with.

If the solutions are sufficiently concentrated, we can neglect the potential drop in the diffuse region of the double layer. If it is here assumed that the centers of the specifically adsorbed ions with charge z_0 occupy fixed positions in the plane $x = 0$ ($x = -\beta$ is the interface, $x = \gamma$ is the boundary between the dense and the diffuse region), defined by the indices m, n , it was shown in [2,3] that the potential distribution in the dense part of the double layer has the form

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

where $\delta = \beta + \gamma$; $\omega = \frac{D_1 - D_2}{D_1 + D_2}$; D_1 and D_2 are the dielectric permeabilities respectively of the phase bounding the solution, and of the dense part of the double layer, $J_0(\lambda R_{mn})$ is the 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 $x = \gamma$, and $\delta_{1\omega}$ is Kronecker's symbol.

For purposes of numerical calculation it is convenient to set $\beta = \gamma$ and express $\psi(r)$ in the form of a sum

$$\psi(r) = \psi_1(r) + \psi_2(r),$$

where

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

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

(m_0, n_0 , is the position of some adsorbed ion), with

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

Due to the accuracy of terms of order $(x/\delta)^4$

$$Q(x) = \begin{cases} 2 \left[\ln 2 + 0,90 \left(\frac{x}{\delta} \right)^2 + 0,97 \left(\frac{x}{\delta} \right)^4 \right], & \omega = 1, \\ \frac{\delta}{\delta - x}, & \omega = 0; \\ 2 \left[\frac{1}{2} \ln 2 + 0,92 \frac{x}{\delta} + 0,11 \left(\frac{x}{\delta} \right)^2 + 0,99 \left(\frac{x}{\delta} \right)^3 + 0,03 \left(\frac{x}{\delta} \right)^4 \right], & \omega = -1, \end{cases}$$

The integral term in the expression for $\Psi_1(r)$ may be evaluated for the cases $\omega = \pm 1$ from the theory of differences. We obtain as a result:

$$\Psi_1(r) = \begin{cases} \left(\frac{1}{2} - \frac{x}{\delta} \right) \psi_0 + \frac{4ez_0}{D_2\delta} \sum_{mn} \sum_{k=1}^{\infty} \cos \frac{\pi x(2k-1)}{\delta} K_0 \left(\frac{\pi(2k-1)R_{mn}}{\delta} \right), & \omega = 1, R_{mn} > 0; \\ \frac{ez_0}{D_2} \sum_{mn} \left(\frac{1}{\sqrt{R_{mn}^2 + x^2}} - \frac{1}{\sqrt{R_{mn}^2 + (\delta-x)^2}} \right), & \omega = 0, R_{mn} > 0; \\ \frac{2ez_0}{D_2\delta} \sum_{mn} \sum_{k=1}^{\infty} \left\{ \cos \frac{\pi x(2k-1)}{2\delta} + (-1)^k \sin \frac{\pi x(2k-1)}{2\delta} \right\} K_0 \left(\frac{\pi(2k-1)R_{mn}}{2\delta} \right), & \omega = -1, R_{mn} > 0, \end{cases}$$

where K_0 is MacDonald's function.

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

$$\psi_0 = 4\pi ez_0 \delta / \sqrt{3} D_2 r_0^2.$$

We shall introduce the following dimensionless quantities into the discussion:

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

It follows from the preceding formulas that:

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

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

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

The dimensionless component of the field intensity along the x axis, which we shall designate as

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

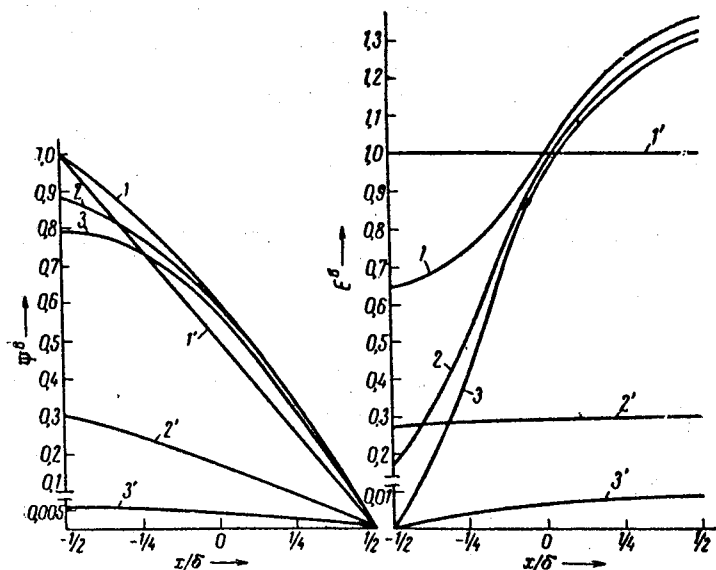
is equal to

$$E(r) = E_1(r) + E_2(r),$$

where

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

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



Distribution of potential Ψ^B and electric field intensity E^B in the dense part of the electric double 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') $\omega = -1$.

We shall find the potential and the field intensity at points lying on two straight lines parallel with the x axis, one of which goes through some adsorbed ion (Case A), while the other is equally distant from the three nearest ad-

Potential ψ^A and Field Intensity E^A as a Function of the x Coordinate and the Parameter ξ

$\frac{x}{\delta}$	$\xi = 0,1$						$\xi = 0,5$					
	ψ^A			E^A			ψ^A			E^A		
	$\omega=1$	$\omega=0$	$\omega=-1$	$\omega=1$	$\omega=0$	$\omega=-1$	$\omega=1$	$\omega=0$	$\omega=-1$	$\omega=1$	$\omega=0$	$\omega=-1$
$-1/2$	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

sorbed ions (Case B). It is clear from the symmetry of the problem that in both cases the electric field intensity is directed along the x axis. The properties of a regular hexagonal network make it possible to formulate the following convenient summing rules:

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

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

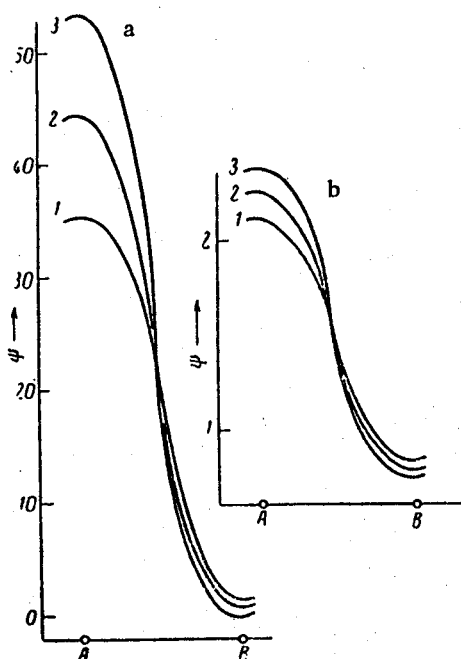


Fig. 2. Distribution of potential ψ in the plane $x = -1/4\delta$. The point A is located at the adsorbed ion, the point B is equidistant from the three nearest adsorbed ions. a) $\xi = 0.1$; b) $\xi = 0.5$; 1) $\omega = 1$; 2) $\omega = 0$; 3) $\omega = -1$.

For $\omega = \pm 1$, the series converge so rapidly that a quite accurate calculation of the quantities ψ^A , ψ^B , E^A and E^B may be made for any physically realizable degree of filling. The case $\omega = 0$ can be calculated only for rather small values of ξ . The present paper gives the numerical calculation of the x -dependence 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, the table).

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

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