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Abstract

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EFFECTS OF CHARGE DISCRETENESS AND PROPERTIES OF THE DOUBLE LAYER AT THE METAL-SOLUTION INTERFACE

(ALLOWING FOR THE DISCRETE STRUCTURE OF THE CHARGE OF SPECIFICALLY ADSORBED IONIC LAYERS)

The possibility of a substantial influence of charge-discreteness effects on the properties of the double layer was noted already quite some time ago by A. N. Frumkin ([1]). Recently the necessity of taking these effects into account in the theory of the double layer has also been emphasized by a number of other authors ([2,3,6]). This question acquired special interest in connection with experimental studies ([2–4]), and subsequently also those of other authors ([13]). As a result of these studies it was shown that the experimental data on the influence of surface-active electrolytes on the potential of zero charge cannot be explained by the Stern theory, which is based on a one-dimensional model of the layer and operates with averaged values of characteristic quantities (potential, field, etc.).

The circumstances indicated above testify to the inadequacy of the model of a double layer with uniformly "smeared-out"charge and to the need for a consistent allowance for the discrete structure of the charge of specifically adsorbed ionic layers.

Attempts at a theoretical consideration of charge-discreteness effects in the double layer on the basis of various layer models were undertaken earlier in the works ([2,5,6]). A thermodynamic analysis of the influence of adsorption of surface-active substances on the properties of the double layer was given in ([7]). However, the results obtained in ([2,5,6]) are qualitative in character and leave open questions connected with the calculation of the discrete structure of the double layer in the presence of specific adsorption of ions.

The present work is devoted to a quantitative consideration of charge-discreteness effects in the electric double layer at the metal-solution interface.

On the basis of the theory developed in the work, charged phase boundaries are also considered and an adsorption isotherm for anions on a metal is derived.

Let us consider the interphase boundary between a metal and an electrolyte solution. The latter occupies the half-space $x > 0$, where x is the coordinate characterizing the distance from the boundary surface ($x = 0$). In view of the small radius of action of the specific adsorption forces, it may be assumed that the centers of gravity of all adsorbed charges lie in one and the same plane, located at a distance $x = \beta$ from the boundary surface.

When the discrete character of the charge distribution in the ion-adsorbed layer is taken into account, the equations for determining the potential in the inner ($0 \le x \le \beta+\gamma$) and outer (diffuse) regions of the double layer take, respectively, the form

$$\Delta\psi(\mathbf{r}) = -\frac{4\pi}{D}\sum_i e_0 z_i \delta(\mathbf{r}-\mathbf{r}_i); \tag{1}$$

$$\Delta\varphi(\mathbf{r}) = -\frac{4\pi}{D_0}\sum_{1\le a\le M} e_0 z_a n_a \exp\left\{-\frac{e_0 z_a \varphi(\mathbf{r})}{kT}\right\}, \tag{2}$$

where D and D_0 are the dielectric constants of the indicated regions; z_a is the valence and n_a the average density of ions of the given kind in the bulk of the solution; $\delta(\mathbf{r})$ is the three-dimensional δ-function. The summation in (1) is carried out over all charges of the layer in the plane $x = \beta$.

In the case of a metal-solution boundary, the solution of equations (1) and (2) must satisfy the boundary conditions

$$\psi(0,y,z) = \psi_0; \qquad \varphi(\infty,y,z) = 0;$$

$$\psi(\beta+\gamma,y,z) = \varphi(\beta+\gamma,y,z); \qquad D\,\partial\psi/\partial x = D_0\,\partial\varphi/\partial x \quad (x = \beta+\gamma), \tag{3}$$

which express the continuity of the potential and of the normal component of the electric induction vector at the boundary between the inner and diffusion regions of the double layer ($\psi_0 = \text{const}$ denotes the total potential drop between the metal and the depth of the solution).

As applied to the calculation of average values of characteristic quantities (in particular, the potential drop, etc.), the work derives the relation

$$\overline{\Phi} = \overline{\Phi}(x) = \lim_{\substack{N\to\infty\\ S\to\infty}}\left\{\frac{1}{S}\iint_S \Phi(x,y,z)\,dy\,dz\right\} = \frac{2\pi\sigma}{e}\,\eta(0,x); \tag{4}$$

$$\Phi(x,y,z) = \sum_n \sum_n \int_0^\infty \eta(\lambda,x)\, J_0\Big(\lambda\sqrt{(y-y_m)^2+(z-z_n)^2}\Big)\,\lambda\,d\lambda,$$

where σ is the average charge density of the surface adsorbed layer; $J_0(\lambda)$ is the Bessel function of the first kind of zeroth order.

In view of the brevity of the present communication, we give here the main results obtained in the work. Starting from the solutions of the corresponding boundary-value problems found by the Green' s-function method, the work calculates the potential drop in the inner and outer (diffusion) regions of the double layer and the layer micropotential ψ^A (the potential at the point where a fixed ion is adsorbed) as functions of the degree of filling of the surface adsorbed layer, the dielectric permittivities of the phases, the magnitude of the electronic charge component q on the metal, and other characteristics. It is shown in the work that, for an arbitrary character of the charge distribution in the adsorbed layer, the potential drop $\delta\psi_a$, created by a layer of specifically adsorbed anions, at the electrocapillary maximum (e.c.m.) is equal to

$$\delta\psi_a = \psi_0 = -\frac{4\pi\sigma}{D}\,\gamma, \tag{5}$$

where σ is the average charge density in the adsorbed layer; D is the dielectric constant of the inner region; β and $\beta+\gamma$ are the distances of closest approach to the metal of the anion and cation, respectively.

This and the subsequent results refer to the case of preferential specific adsorption at the boundary of ions of one sign—anions.

If the phases at whose contact boundary the double layer arises are not, as a whole, electrically neutral (a charged interface), then, along with the potential drop caused by the ionic component of the charge $\delta\psi_a$, there also arises a potential component $\delta\psi_q$, due to the presence of the electronic charge q on the metal (referred to unit surface). In this case the total potential drop $\delta\psi$ in the inner region of the double layer turns out to be equal to

$$\delta\psi = \psi_0 = \delta\psi_a + \delta\psi_q; \qquad \delta\psi_q = -\frac{4\pi q}{D}(\beta+\gamma). \tag{6}$$

The layer micropotential ψ^A for a system of point charges localized at the nodes of a plane hexagonal lattice with parameter r_0, at arbitrary degrees of filling θ, is given by the expression

$$\psi^A = \frac{\gamma}{\beta+\gamma}(\delta\psi_a + \delta\psi_q) + \psi \;\; + a\delta\psi_a, \tag{7}$$

where ψ_{im} is a function independent of r_0 (representing, figuratively speaking, a system of "images" of a point charge from two equipotential plane surfaces):

$$\psi_{\rm im} = \frac{e}{D}\int_0^\infty \{e^{-\lambda\gamma}\,{\rm sh}\,\lambda\beta + e^{-\lambda\beta}\,{\rm sh}\,\lambda\gamma\}\,{\rm sh}^{-1}\,\lambda(\beta+\gamma)\,d\lambda \simeq \frac{e}{D\gamma}\ln 2, \quad (8)$$

and the coefficient α at $\delta\psi_a$ in the last term is equal to

$$\alpha = \alpha(\beta,\gamma,r_0) = 1.656\,\frac{r_0^2}{\gamma(\beta+\gamma)}\left\{\sum_{m=1}^{\infty}\sum_{p=1}^{\infty}\sin^2\left(\frac{\beta}{r_0}\xi p\right)\cdot K_0(mp\xi) + \right.$$

$$\left. + \sum_{m=2}^{\infty}\sum_{n=1}^{m-1}\sum_{p=1}^{\infty}\sin^2\left(\frac{p}{r_0}\xi p\right)\cdot K_0\left(\xi p\sqrt{m^2+n^2-mn}\right)\right\}. \quad (9)$$

Here $K_0(\lambda)$ is the Macdonald function (a cylindrical function of an imaginary argument of zero order); $-e$ is the charge of the anion and $\xi = \pi r_0/(\beta+\gamma)$. The micropotential of the layer at the point of a zero charge is determined by the preceding formula with $q = 0$.

Investigation of series (9) shows that, for realistic degrees of filling of the surface adsorbed layer, not exceeding according to electrocapillary measurements [(4)] 25–30%, the last term in the right-hand side of (7) is practically insignificant ($\alpha \ll 1$) and, consequently, in the indicated range of values of θ

$$\psi^A = \psi_{\rm im} + \frac{\gamma}{\beta+\gamma}(\delta\psi_a + \delta\psi_q). \quad (10)$$

The potential $\psi(r)$ in the inner region of the double layer then changes mainly according to a linear law.

The results obtained confirm, in the indicated range of degrees of filling, the qualitative considerations on the structure of the discrete double layer put forward in the works of D. Grahame [(2)].

A substantial deviation from (10) occurs at considerably larger degrees of filling, corresponding to values of the parameter $(\beta+\gamma)/2r_0$ approximately equal to 0.3–0.4, which corresponds to values of θ close to unity. Strictly speaking, these results are valid under the assumption that the outer Helmholtz plane (the limit of the approximation of the cation to the metal) is equipotential and that the adsorbed ions are rigidly fixed in fixed positions.*

It is shown in the work that, when the thermal motion of ions in solution is taken into account and the restriction associated with the assumption of equipotentiality of the outer Helmholtz plane is abandoned, the results obtained above practically remain valid at sufficiently large bulk concentrations of the solution and a significant difference between the dielectric constants of the inner and outer regions of the double layer. Thus, for example, the potential jump $\delta\psi_a$ in the inner region of the double layer at the electrocapillary maximum proves to be equal to

$$\delta\psi_a = -\frac{4\pi\delta}{D}\gamma - \frac{4\pi}{D}\sigma\,\frac{D}{D_0\varkappa}\left(\frac{D/D_0 + \varkappa\gamma}{D/D_0 + \varkappa(\beta+\gamma)}\right) \tag{11}$$

instead of (6), where $\varkappa$ is the inverse Debye length, depending on the temperature and concentration of the solution. The corrections to the micropotential of the layer and to other characteristic quantities have an analogous character.

On the basis of the calculated values of the micropotential of the layer ψ^A, one can determine the dependence of the potential jump $\delta\psi_a$ on concentration (activ-

* As an approximate calculation shows, allowance for the thermal motion of ions in the adsorbed layer does not substantially affect the preceding results.

···of $a_\pm$ anions in the solution, or, equivalently, to calculate the quantity $\partial(\delta\psi_a)/\partial\ln a_\pm$ as a function of $\delta\psi_a$:

$$\frac{\partial(\delta\psi_a)}{\partial\ln a_\pm} = \left(\frac{RT}{F\delta\psi_a} - \frac{\partial\psi^A}{\partial(\delta\psi_a)}\right)^{-1}\frac{RT}{F}. \tag{12}$$

Relation (12) was derived on the assumption that the dependence $\sigma = \sigma(a_\pm, \psi^A)$ is determined with respect to ψ^A mainly by the Boltzmann factor

$$\sigma = ka_\pm \exp\left\{-\frac{\psi^A F}{RT}\right\}, \tag{13}$$

and the potential drop in the diffuse region of the double layer may be neglected.

If the potential drop in the diffuse region of the double layer is also taken into account, then according to [(2)] $\partial(\delta\psi_a)/\partial\ln a_\pm$ is determined through the values of ψ^A by the relation

$$\frac{\partial(\delta\psi_a)}{\partial\ln a_\pm} = \left[\frac{RT}{F\delta\psi_a} - \frac{\partial\psi^A}{\partial(\delta\psi_a)} - \frac{\partial(\varphi_{\beta+\gamma} - \varphi^*)}{\partial(\delta\psi_a)}\right]^{-1}\left(1 + \frac{\partial\ln(\gamma/D)}{\partial\ln a_\pm^2}\right)\frac{RT}{F}, \tag{14}$$

where φ^* is the statistical mean of the values of $\varphi(r)$ in the diffuse region of the double layer.

An approximate estimate of the quantities β and γ from data on ionic radii and calculation of $\partial(\delta\psi_a)/\partial\ln a_\pm$ by formula (12) indicate a fairly close agreement of the theoretical results with the known experimental data relating to the mercury–solution interface [(13)]. A separate communication will be devoted to consideration of charge-discreteness effects at the dielectric–solution interface.

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