THE PROPERTIES OF A DOUBLE LAYER AND THE ELECTROSTATIC ADSORPTION OF IONS

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It has been noted earlier that although the Gouy-Chapman-Stern theory of the double layer is widely used in electrochemistry and colloid chemistry, its statistical basis and limits of applicability have not been clarified. In a previous paper [1] the double layer equilibrium was discussed directly on the basis of Gibbs statistics (correlation function method). This method makes it possible to take into account the spatial localization of charges in the layer and the effects of spatial correlation between ions. In subsequent papers [2, 3] theories of the discrete double layer in the presence of specific ionic adsorption were discussed. The present paper is devoted to further details of the structure of the electrical double layer.

The properties and structure of a solvent immediately adjacent to an interphase boundary differ from its properties and structure in bulk (homogeneous phase). The orienting effect of the boundary on solvent molecules is strongest at the layer of molecules in direct contact with the external phase. Macroscopically, this appears as a change in the effective dielectric permeability of the Helmholtz (or dense) layer, compared with its value in the homogeneous solution. For a charged interphase boundary the dielectric permeability of the dense layer depends on the field strength and, when dipolar capillary active substances are present, on the amount of adsorption of these substances. As an approximation it is convenient to use a continuum model for the dense layer.* The presence of such a "dielectric layer" must appreciably affect the nature of the ionic interaction in the diffusion layer, since in this case the ions also interact with the polarization of the layer. In the present paper the effect of the "dielectric layer" on the electrostatic adsorption of ions and on the surface tension of the interphase boundary will be discussed.

We shall assume that the solution occupies the semispace $x > 0$ and the external phase the semispace $x < -d$, and let the dielectric premeabilities of the external phase, dense layer and solution volume be D_Φ, D and D_0, respectively. We will consider the initial system of the set of ions $N = \sum_{(a)} N_a$ interacting with one another through the binary potential $U_{ab}(\mathbf{q})$. The total energy of the system $U_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$, where $\mathbf{q}_i = (x_i, y_i, z_i)$ are the coordinates of the particles, is

$$U_N(\mathbf{q}_1, \ldots, \mathbf{q}_N) = \sum_{(a,b)} \tilde{U}_{ab}(\mathbf{q}_i, \mathbf{q}_j) + \Psi_N(\mathbf{q}_1, \ldots, \mathbf{q}_N). \tag{1}$$

Here $\Psi_N(\mathbf{q}_1, \ldots \mathbf{q}_N)$ is the interaction energy of ions with the external phase in the presence of a dielectric layer and $\tilde{U}_{ab}$ differs from U_{ab} owing to reaction of ion a to form ion b.

The equilibrium properties of such a system can be analyzed, as before, using the correlation function method [2, 3]. First of all it is necessary to solve the problem of the interaction of a point charge e_0, in phase III ($x > 0$), with the external phase ($x < -d$) in the presence of the dielectric layer. It can be shown that the field strength in phase III is determined by the expression

$$\varphi_{\text{III}}(\mathbf{q}) = \frac{e_0}{D_0|\mathbf{q}-\mathbf{q}_0|} - \frac{e_0}{D_0}\int_0^\infty J_0(k\rho_{\mathbf{q}\mathbf{q}_0})\, e^{-k(x+x_0)}\xi(D_0, D, D_\Phi, d, k)\, dk, \tag{2}$$

*Although such a quasimacroscopic approach is not completely consistent, nevertheless it seems probable that it enables the basic laws of the actual interaction of ions with the interphase boundary to be developed.

where $J_0(x)$ is a zero order Bessel function, $\rho_{qq_0} = [(y-y_0)^2 + (z-z_0)^2]^{1/2}$,

$$\xi(D_0, D, D_\Phi, d, k) = \left(1 - \frac{D_0}{D}\lambda\right)\left(1 + \frac{D_0}{D}\lambda\right)^{-1}; \tag{3}$$

$$\lambda = \left[e^{2kd}\left(\frac{D+D_\Phi}{D-D_\Phi}\right) + 1\right]\left[e^{2kd}\left(\frac{D+D_\Phi}{D-D_\Phi}\right) - 1\right]^{-1}. \tag{4}$$

For a metal $\lambda = \lambda_M$ = th kd. Analysis of equations (2)-(4) shows that when $D \ll D_0$ the interaction energy of a charge with a metal, as a function of the distance between charge and metal, changes sign at distances about 10 d from the surface of separation. At small distances the repulsion force increases logarithmically with decreasing distance, and only at relatively great distances from the metal does the interaction between charge and metal become attractive.

The equation for the unary distribution function of the a^{th} ionic component of charge g_a in the double layer has the form

$$\frac{\partial g_a(x)}{\partial x} + \frac{1}{\theta}\frac{\partial \Psi_a(x)}{\partial x} g_a(x) + \frac{1}{\theta}\sum_{(b)} c_b \int \frac{\partial \tilde{U}_{ab}(q, q')}{\partial x} g_{ab}(q, q')\, dq' = 0, \tag{5}$$

where $g_{ab}(q, q')$ is a binary distribution function associated with higher order distribution functions while $\Psi_a(x)$ and $\tilde{U}_{ab}(q, q')$ are determined from the expressions

$$\Psi_a(x) = -\frac{e_a^2}{2D_0}\int_0^\infty e^{-2kx}\xi(D_0, D, D_\Phi, d, k)\, dk; \tag{6}$$

$$\tilde{U}_{ab}(q, q') = \frac{e_a e_b}{D_0 |q - q'|} - \frac{e_a e_b}{D_0}\int_0^\infty J_0(k\rho_{qq'})\, e^{-k(x+x')}\xi(D_0, D, D_\Phi, d, k)\, dk. \tag{7}$$

Here ξ is found from equations (3), e_a is the charge on the type a ion and $c_a = N_a/V$ is the density.

The form of the unary distribution function at small distances ($x < \varkappa^{-1}$) can be obtained from (5) by introducing an expansion in the parameter $c = N/V$:

$$g_a(x) = \exp\left\{-\frac{1}{\theta}\Psi_a(x)\right\}. \tag{8}$$

In the general case, i.e., at any distance,

$$g_a(x) = \exp\left\{-\frac{1}{\theta}G_a(x)\right\}, \tag{9}$$

where $G_a(x)$ also contains a screening form-factor and at small distances $G_a(x) \to \Psi_a(x)$.

At small electrolyte concentrations the asymptotic behavior of $G_a(x)$ can be determined approximately by introduction of an expansion in the parameter $\varkappa^3 V/N$.

We put g_{ab} in the form $g_a g_b \psi_{ab}$ introduce the expansions

$$g_a(x) = 1 + g_a^{(1)}(x) + \ldots; \quad \psi_{ab} = \psi_{ab}^{(0)} + \psi_{ab}^{(1)} + \ldots, \tag{10}$$

where $\psi_{ab}(q, q')$ is a binary correlation function. Then for the functions $g_a^{(1)}(x)$ and $\psi_{ab}^{(0)}(q, q')$ we obtain the closed equations:

$$\frac{\partial g_a^{(1)}(x)}{\partial x} + \frac{1}{\theta}\frac{\partial \Psi_a(x)}{\partial x} + \frac{1}{\theta}\sum_{(b)} c_b \int \frac{\partial \tilde{U}_{ab}(q, q')}{\partial x}\left[g_b^{(1)}(x') + \psi_{ab}^{(0)}(q, q')\right] dq' = 0; \tag{11}$$

$$\psi_{ab}^{(0)}(q, q') + \frac{1}{\theta}\sum_{(c)} c_c \int \tilde{U}_{ac}(q, q'')\, \psi_{cb}^{(0)}(q'', q')\, dq'' = -\frac{1}{\theta}\tilde{U}_{ab}(q, q'). \tag{12}$$

TABLE 1. $G_a \cdot 10^{16}$ mole/cm²

c (mole/liter)	$b = 0,9$	$b = 0,8$	$b = 0,7$	$b = 0$	c (mole/liter)	$b = 0,9$	$b = 0,8$	$b = 0,7$	$b = 0$
10^{-3}	—	—	—54,5	+432	10^{-5}	—0,87	+1,13	+2,31	+8,22
$5 \cdot 10^{-4}$	—	—53,3	—15,4	+245	$5 \cdot 10^{-6}$	—0,18	+0,83	+1,42	+4,40
10^{-4}	—22,6	—4,24	+6,03	+62,7	10^{-6}	+0,09	+0,30	+0,42	+1,02
$5 \cdot 10^{-5}$	—9,62	—0,11	+5,38	+34,1					

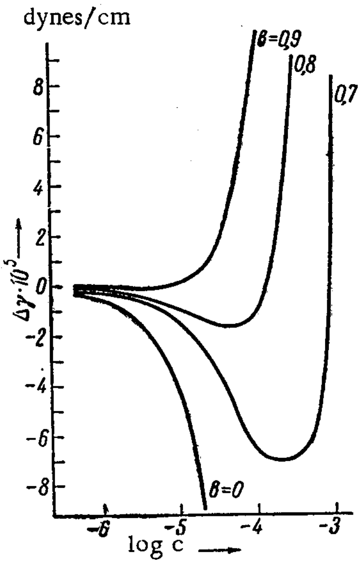

Fig. 1. Surface tension of a metal-solution boundary.

The solution of equation (12), found by a Fourier transformation, has the form:

$$\psi_{ab}^{(0)}(\mathbf{q}, \mathbf{q}') = -\frac{e_a e_b}{D_0 \theta} \int_0^\infty J_0(k\rho_{\mathbf{qq}'}) \frac{k\,dk}{\sqrt{k^2 + \varkappa^2}} \times \left\{ e^{-\sqrt{k^2+\varkappa^2}\,|x-x'|} - \mu(k)\, e^{-\sqrt{k^2+\varkappa^2}\,(x-x')} \right\}; \tag{13}$$

where $\mu(k) = \left(\frac{D}{D_0} - \frac{\sqrt{k^2+\varkappa^2}}{k}\lambda\right)\left(\frac{D}{D_0} + \frac{\sqrt{k^2+\varkappa^2}}{k}\lambda\right)^{-1}$, and λ is found from equation (4).

Solving equation (11) we find

$$g_a^{(1)}(x) = \frac{e_a^2 \varkappa}{2D_0\theta} Y(x), \tag{14}$$

where Y (x) is found from the formulae

$$Y(x) = \int_1^\infty \left\{ \frac{(D/D_0)\sqrt{\tau^2 - 1} - \tau\chi(\tau, D, D_\Phi, d)}{(D/D_0)\sqrt{\tau^2 - 1} + \tau\chi(\tau, D, D_\Phi, d)} \right\} e^{-2\varkappa x\tau}\, d\tau; \tag{15}$$

$$\chi(\tau, D, D_\Phi, d) = \left[\left(\frac{D + D_\Phi}{D - D_\Phi}\right) e^{2\varkappa d\sqrt{\tau^2-1}} + 1\right]\left[\left(\frac{D + D_\Phi}{D - D_\Phi}\right) e^{2\varkappa d\sqrt{\tau^2-1}} - 1\right]^{-1}. \tag{16}$$

Thus for $g_a(x)$ at all distances we have

$$g_a(x) = \exp\left\{\frac{e_a^2 \varkappa}{2D_0\theta} Y(x)\right\}. \tag{17}$$

When there is an uncharged interphase boundary the amount of adsorption is given by

$$\Gamma_a = c_a \int_0^\infty \left\{\exp\left(\frac{e_a^2 \varkappa}{2D_0\theta} Y(x)\right) - 1\right\} dx. \tag{18}$$

An investigation of this expression for the case d = ∞ was carried out in [4, 5]. In the present work we consider in detail the case of a metal-solution boundary ($D_\Phi = \infty$). Although in this case formula (18) cannot be reduced to a final combination of elementary functions, by several correlations between its parameters it appears possible to carry out an effective simplification and to calculate the amount of adsorption with sufficient accuracy. In particular, such a simplification is possible when the condition $\varkappa d \ll (D/D_0) \ll 1$ is fulfilled. In this case the number of ions adsorbed was calculated as a function of the mean electrolyte concentration $\underline{c}$ and the parameter $b = (D_0 - D)/(D_0 + D)$ at a fixed layer thickness d = 3.3 Å, the calculation being correct to terms of first order smallness in the parameters $\varkappa d D_0/D$ and $(D/D_0)\ln(D_0/D)$. In addition the amount of adsorption was calculated for the case $D = D_0$ (b = 0).

The results, which relate to uni-univalent electrolytes at room temperature, are given in Table 1.

Analysis of the formulae obtained, and the results of the numerical calculations, show that adsorption on a metal may be both positive and negative with respect to the relationship between the dielectric permeability of the dense layer and the volume of the solution, and with respect to the thickness of the dense layer and the electrolyte concentration. This conclusion is supported by the interphase surface tension curves. The curves were constructed from data on electrostatic adsorption, using the Gibbs equation for adsorption, and are shown in Fig. 1, where $\Delta\gamma$ is the change in surface tension of the solution in comparison with the surface tension of the pure solvent.

Quantitative calculations have been carried out over a quite narrow range of values of parameters b and c. The more general investigation in the present work shows, however, that the effect of negative electrostatic adsorption of ions is more significant at higher electrolyte concentrations. These results agree qualitatively with electrocapillarity measurements obtained in concentrated solutions of inorganic acids [6, 7].

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
