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Abstract

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Properties of the Double Layer and the Character of Electrostatic Adsorption of Ions

It has already been noted earlier that, although the Gouy–Chapman–Stern theory of the double layer is widely used in electrochemistry and colloid chemistry, its statistical foundations and limits of applicability cannot be regarded as clarified. In previous works ([1]) the problem of the equilibrium double layer was considered directly on the basis of Gibbs statistics (the method of correlation functions). This method makes it possible to take into account the spatial localization of layer charges and the effects of spatial correlation between ions. In subsequent works ([2,3]) questions of the theory of the discrete double layer in the presence of specific adsorption of ions were also considered. The present work is devoted to further detailing the picture of the structure of the double electric layer.

The properties and structure of the solvent in the immediate vicinity of the interface differ from its properties and structure in the bulk (homogeneous) phase. The orienting action of the boundary on the solvent molecules is most strongly expressed with respect to the layer of molecules in direct contact with the external phase. From a macroscopic point of view, this circumstance manifests itself as a change in the effective dielectric permittivity of the Helmholtz (or compact) layer as compared with its value in the homogeneous phase of the solution. In the case of a charged interface the dielectric permittivity of the compact layer depends on the field strength, and in the presence of adsorption of dipolar capillary-active substances, also on the magnitude of the adsorption of these substances. As a definite approximation it is expedient to adopt for the compact layer a continuum model.* The existence of such a "dielectric interlayer" must substantially affect the character of the interaction of ions located in the diffuse layer, since in this case an additional interaction of these ions with the polarization of the interlayer is included. In the present work the influence of the "dielectric interlayer" on the electrostatic adsorption of ions and on the surface tension of the interface will be investigated.

We shall assume that the solution occupies the half-space $x > 0$, while the external phase occupies the half-space $x < -d$, and let the dielectric permittivities of the external phase, the compact layer, and the bulk of the solution be equal, respectively, to D_ϕ, D, and D_0. As the initial system we shall consider an ensemble $N = \sum_{(a)} N_a$ of ions interacting with one another by means of a binary potential $U_{ab}(\mathbf{q})$. The total energy of the system $U_N(\mathbf{q}_1, \dots, \mathbf{q}_N)$, where $\mathbf{q}_i = (x_i, y_i, z_i)$ are the coordinates of the particles, is equal to

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

* Although such a quasi-macroscopic approach is not entirely consistent, it nevertheless appears probable that it does make it possible to reveal the basic regularities of the real picture of the interaction of ions with the interface.

Here $\Psi_N(\mathbf{q}_1, \dots, \mathbf{q}_N)$ is the energy of interaction of the ions with the external phase in the presence of a dielectric interlayer, while $\widetilde{U}_{ab}$ differs from U_{ab} owing to the interaction of ion a with the image of ion b.

The analysis of the equilibrium properties of this system can be carried out, as before, on the basis of the method of correlation functions ([2],[3]). It is first necessary to solve the problem of the interaction of a point charge e_0, located in phase III ($x > 0$), with the external phase I ($x < -d$) in the presence of a dielectric interlayer. It can be shown that the field potential in phase III is determined by the expression

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

where $J_0(x)$ is the Bessel function of zero order,

$$\rho_{q\mathbf{q}_0} = [(y - y_0)^2 + (z - z_0)^2]^{1/2},$$

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

$$\lambda = \left[e^{2kd}\left(\frac{D + D_\phi}{D - D_\phi}\right)^5 + 1\right]\left[e^{2kd}\left(\frac{D + D_\phi}{D - D_\phi}\right) - 1\right]^{-1}. \tag{4}$$

For a metal $\lambda = \lambda_M = \operatorname{th} kd$. Analysis of formulas (2)–(4) shows that, for $D \ll D_0$, the energy of interaction of the charge with the metal, as a function of the distance of the charge from the metal, changes sign at distances of the order of $10d$ from the interface. At small distances, repulsive forces arise, increasing as the distance decreases according to a logarithmic law, and only at relatively large distances from the metal does the interaction of the charge with the metallic phase have the character of attraction.

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

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

where $g_{ab}(\mathbf{q},\mathbf{q}')$ is the binary distribution function, related to distribution functions of higher orders, and $\Psi_a(x)$ and $\widetilde{U}_{ab}(\mathbf{q},\mathbf{q}')$ are determined by the expressions:

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

$$\widetilde{U}_{ab}(\mathbf{q},\mathbf{q}') = \frac{e_{ae}b}{D_0|\mathbf{q}-\mathbf{q}'|} - \frac{e_{ae}b}{D_0}\int_0^\infty J_0(k\rho_{q\mathbf{q}'})e^{-k(x+x')}\xi(D_0, D, D_\phi, d, k)\, dk. \quad (7)$$

Here ξ is defined by formula (3), e_a is the charge of an ion of species a, and $c_a = N_a/V$ is the density.

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

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

In the general case, i.e., over the entire range of distances,

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

where $G_a(x)$ also contains the screening form factor, while at small distances $G_a(x) \to \Psi_a(x)$.

At small electrolyte concentrations the asymptotic behavior of $G_a(x)$ can be established approximately by introducing expansions in the parameter $\varkappa^3 V/N$.

For this purpose, let us represent g_{ab} in the form $g_a g_b \psi_{ab}$ and introduce the expansions

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

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

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

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

The solution of equation (12), found by the method of Fourier transformations, has the form:

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

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 determined by the former expressio (13)

Solving next equation (11), we find

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

where $Y(x)$ is defined by the formulas

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

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

Thus, for $g_a(x)$ over the entire range of distances we have

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

In the case of an uncharged interphase boundary, the adsorption magnitude is given by the expression

Fig. 1. Surface tension of the metal–solution interface

Figure 1: Fig. 1. Surface tension of the metal–solution interface

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

The study of this expression for the case $d = \infty$ was carried out in works ([4],[5]). In the present work the case of the metal–solution boundary ($D_\phi = \infty$) is investigated in detail. Although in this case formula (18) cannot be reduced to finite combinations of elementary functions, for certain relations among the parameters entering it substantial simplifications prove possible, and the adsorption magnitude can be calculated with sufficient accuracy. In particular, such simplifications are possible when the conditions $\varkappa d \ll (D/D_0) \ll 1$ are satisfied. For this case, with accuracy up to terms of first order···

terms of smallness in the parameters $\varkappa d D_0/D^*$ and $(D/D_0)\ln(D_0/D)$, the values of ion adsorption were calculated as functions of the mean electrolyte concentration c and the parameter $b = (D_0 - D)/(D_0 + D)$ at a fixed thickness of the interlayer $d = 3.3$ Å. In addition, adsorption values were calculated for the case $D = D_0$ ($b = 0$). The results of the calculation, relating to 1–1-valent electrolytes at room temperature, are given in Table 1.

Analysis of the formulas obtained and of the results of the numerical calculation shows that adsorption on a metal may be either positive or negative, depending on the relation between the dielectric permittivities of the dense layer and of the bulk solution, on the thickness of the dense layer, and on the electrolyte concentration. This conclusion is also confirmed by the behavior of the curves of the interfacial surface tension. The curves were constructed from the data on electrostatic adsorption with the aid of the Gibbs adsorption formula and are shown in Fig. 1, where $\Delta\gamma$ denotes the change in the surface tension of the solution as compared with the surface tension of the pure solvent.

Fig. 1. Surface tension of the metal–solution interface

Quantitative calculations were carried out over a fairly narrow range of variation of the parameters b and c. A more general investigation of the dependences obtained in the present work shows, however, that the effect of negative electrostatic adsorption of ions is the more significant, the higher the electrolyte concentration. These conclusions are in qualitative agreement with the results of electrocapillary measurements obtained in concentrated solutions of inorganic acids ([6],[7]).

Table 1

$$\Gamma_a \cdot 10^{16} \text{ mol/cm}^2$$

c (mol/l)	$b = 0.9$	$b = 0.8$	$b = 0.7$	$b = 0$	c (mol/l)	$b = 0.9$	$b = 0.8$	$b = 0.7$	$b = 0$
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					

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REFERENCES

1. V. G. Levich, V. A. Kir' yanov, DAN, **131**, 1134 (1960).

2. V. G. Levich, V. A. Kir' yanov, V. S. Krylov, DAN, **135**, 1425 (1960); V. G. Levich, V. S. Krylov, DAN, **142**, 123 (1962); V. S. Krylov, DAN, **144**, 155 (1962).

3. V. S. Krylov, V. G. Levich, ZhFKh, **37**, No. 1 (1963); **37**, No. 10 (1963).

4. L. Onsager, N. T. Samaras, J. Chem. Phys., **2**, 528 (1934).

5. V. E. Bravina, ZhETF, **33**, 1065 (1957); Vestn. Moscow Univ., Ser. Math., No. 2, 85 (1958); DAN, **120**, 815 (1958).

6. S. Iofa, A. Frumkin, Acta phisic. chim., **10**, 473 (1939).

7. Z. Iofa, B. Kustinskii, F. Eiman, ZhFKh, **13**, 934 (1939).