THE ADSORPTION ISOTHERM ON THE DISCRETE ELECTRIC DOUBLE LAYER MODEL

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Let the plane $x = 0$ separate the medium ($x \leq 0$), characterized either by the dielectric constant D_1 (dielectric), or by the potential Ψ_0 (metal), from the solution of electrolyte ($x \geq 0$), which is so concentrated that the potential drop within it need be considered only in a narrow region $0 \leq x \leq \delta$, several angstroms wide, which we shall call the internal double layer region (for aqueous solutions of 1−1-valent electrolytes, this assumption is justified for concentrations exceeding 1 mole/liter). The potential jump in this region we shall designate as Ψ_0. In the plane $x = \beta$ ($0 < \beta < \delta$) let there be located centers of specifically adsorbed ions having the same charge z, which, in this plane, produce the mean surface density of charge σ.

At realizable degrees of filling of the adsorbed layer, which are substantially less than unity, the density σ is given by Boltzmann's formula

$$\sigma = k_0 \exp\left\{\frac{\mu_z - \Phi_z - ez\psi_M}{kT}\right\}, \tag{1}$$

where k_0 is a dimensional constant, μ_z is the chemical potential of the adsorbed ions, Φ_z is the energy of the ions in the field of the short-range specific adsorption forces, and Ψ_M is the electrostatic potential at the point where the ion is adsorbed (the so-called micropotential).

If the boundary $x = 0$ does not contain free electric charges, and D_2 is the dielectric constant of the internal double layer region, then, as was shown in [1], the relation that is found is

$$\psi_0 = \frac{4\pi(\delta - \beta)\sigma}{D_2}. \tag{2}$$

After substituting Eq. (1) in Eq. (2), and making simple transformations, a relation $\partial\psi_0/\partial \ln a_z = f(\psi_0)$, is obtained, which is called the adsorption isotherm:

$$\frac{\partial\psi_0}{\partial \ln a_z} = \left[\frac{RT}{F\psi_0}\left(1 - \psi_0 \frac{\partial \ln \frac{\gamma}{\gamma_0 D_2}}{\partial\psi_0}\right) + z\frac{\partial\psi_M}{\partial\psi_0}\right]^{-1}\frac{RT}{F}, \tag{3}$$

where $\gamma = \delta - \beta$, γ_0 is an arbitrary constant with the dimension of length, and $a_z = \exp(\mu_z/kT)$ is the activity of the ion z. For $\gamma/D_2 = \text{const}$, and $z = -1$, Eq. (3) goes over into the well known formula of B. V. Ershler [2].

To get a clear picture of the function $\partial\psi_M/\partial\psi_0$, 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. In this case, $\sigma = 2ez/\sqrt{3}\,r_0^2$, and Eq. (2) takes on the form

$$\psi_0 = \frac{8\pi ez\gamma}{\sqrt{3}\,D_2 r_0^2}. \tag{4}$$

The exact analytical expression for the micropotential on this model is found in [1, 3, 4] and has the form

$$\psi_{\text{м}} = \frac{\gamma\psi_0}{\beta+\gamma}\delta_{1\omega} + \frac{ez}{D_2(\beta+\gamma)}\left\{-G_1(\omega, \beta, \gamma) + \sum_{mn} G_2^{(mn)}(\omega, \beta, \gamma, r_0)\right\}, \tag{5}$$

where

$$\omega = \frac{D_1 - D_2}{D_1 + D_2}; \qquad \delta_{1\omega} = \begin{cases} 1, & \omega = 1, \\ 0, & \omega \neq 1, \end{cases}$$

$$G_1(\omega, \beta, \gamma) = (\beta+\gamma)\int_0^\infty \frac{\omega e^{-2\lambda\beta}(1-e^{-2\lambda\gamma}) + e^{-2\lambda\gamma}}{1-\omega e^{-2\lambda(\beta+\gamma)}} d\lambda;$$

$$G_2^{(mn)}(\omega, \beta, \gamma, r_0) = (\beta+\gamma)\int_0^\infty \frac{(1-e^{-2\lambda\gamma})(1-\omega e^{-2\lambda\beta})}{1-\omega e^{-2\lambda(\beta+\gamma)}} J_0(\lambda r_0 a_{mn})\, d\lambda.$$

The method of summing all the functions $f(a_{mn})$ over (m, n) is given by the expression

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

Assuming from now on for simplicity that $\beta = \gamma$, and evaluating the intergrals G_1 and $G_2^{(mn)}$, we obtain

$$\psi_{\text{м}} = \begin{cases} \frac{1}{2}\psi_0\left\{1 - \frac{\sqrt{3}\ln 2}{\pi\xi^2}\left[1 - \frac{2}{\ln 2}\sum_{mn}\sum_{k=1}^{\infty} K_0\left(\frac{(2k-1)\pi a_{mn}}{\xi}\right)\right]\right\} & (\omega = 1), \\ -\frac{\sqrt{3}\ln 2}{4\pi\xi^2}\psi_0\left[1 - \frac{2}{\ln 2}\sum_{mn}\sum_{k=1}^{\infty} K_0\left(\frac{(2k-1)\pi a_{mn}}{2\xi}\right)\right] & (\omega = -1), \\ \frac{\sqrt{3}}{4\pi\xi^2}\psi_0\left\{-G_1(\omega) + \xi\sum_{mn}\left[\frac{1}{a_{mn}} - \frac{1}{\sqrt{a^2_{mn}+\xi^2}} + \right.\right. & \\ + \sum_{k=1}^{\infty}\omega^k\left(\frac{2}{\sqrt{a_{mn}+\xi^2(2k)^2}} - \frac{1}{\sqrt{a^2_{mn}+\xi^2(2k+1)^2}} - \right. & \\ \left.\left. - \frac{1}{\sqrt{a^2_{mn}+\xi^2(2k-1)^2}}\right)\right]\right\} & (\omega \neq \pm 1), \end{cases} \tag{6}$$

where $\xi = 2\gamma/r_0$; $K_l(x)$ is the Bessel function of the second kind of imaginary argument (Macdonald's functions) of l-th order (l = 0, 1, ...), and

$$G_1(\omega) = \begin{cases} \ln(1-\omega) - \frac{1+\omega}{2\sqrt{\omega}}\ln\frac{1-\sqrt{\omega}}{1+\sqrt{\omega}} & (0 < \omega < 1), \\ \ln(1-\omega) + \frac{1+\omega}{\sqrt{-\omega}}\operatorname{arc\,tg}\sqrt{-\omega} & (-1 < \omega < 0). \end{cases} \tag{7}$$

It is easily shown that all the series entering into Eq. (6) converge absolutely and uniformly. Differentiating (6), we obtain:

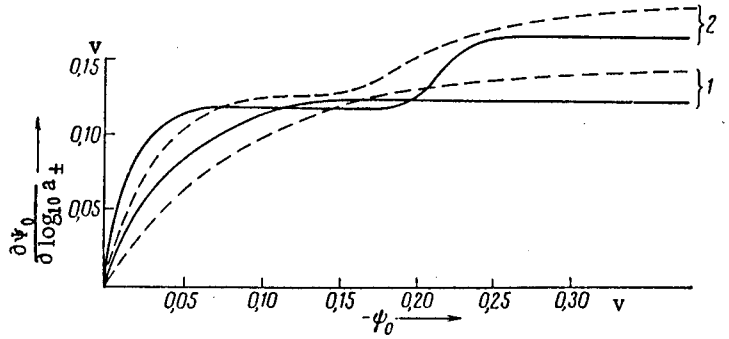
$$\frac{\partial\psi_{\text{м}}}{\partial\psi_0} = \begin{cases} 0{,}5 + \frac{0{,}866}{\xi^3}S_1(\xi)\left\{1 + \left(\frac{2\psi_0}{\xi}\frac{\partial\xi}{\partial\psi_0} - 1\right)\left[1 + \frac{0{,}221\,\xi(1-2{,}886S_0(\xi))}{S_1(\xi)}\right]\right\} & (\omega = 1), \quad (8a) \\ \frac{0{,}217}{\xi^3}S_1(2\xi)\left\{1 + \left(\frac{2\psi_0}{\xi}\frac{\partial\xi}{\partial\psi_0} - 1\right)\left[1 + \frac{0{,}442\,\xi(1-2{,}886\,S_0(2\xi))}{S_1(2\xi)}\right]\right\} & (\omega = -1), \quad (8b) \end{cases}$$

where

$$S_0(x) = \sum_{mn} \sum_{k=1}^{\infty} K_0\left(\frac{(2k-1)\,\pi a_{mn}}{x}\right);$$

$$S_1(x) = \sum_{mn} \sum_{k=1}^{\infty} (2k-1)\, a_{mn} K_1\left(\frac{(2k-1)\,\pi a_{mn}}{x}\right).$$

The corresponding analytic expression for $d\Psi_M/d\Psi_0$, with arbitrary $\omega \neq \pm 1$, contains series which converge very slowly, and admit of only very rough numerical evaluation. Since, experimentally, it is usual to investigate the metal–solution boundary ($\omega \to 1$), and the air–solution boundary ($\omega \to 1$), it is precisely the limiting formulas (8a) and (8b) which are of practical interest. It follows from Eqs. (3), (4), (8) that, to find the theoretical adsorption isotherm unambiguously, a knowledge is required of any pair of the three quantities γ, D_2, and r_0 as a function of Ψ_0.



1)HCl–mercury boundary; 2) HCl–air boundary. Solid lines are experimental, broken lines are theoretical.

In experiments with mercury–solution boundaries, A. C. Grahame [5] found that at comparatively small concentrations, the field of the adsorbed anions has practically no effect on γ or D_2, while in highly concentrated solutions, this effect may become substantial. Therefore, it is a matter of interest to compare the theory with the experimental data of Z. A. Iofa and A. N. Frumkin [6], and B. S. Gurenkov [7], which were taken under conditions in which Eq. (3) are applicable. Since, for a mercury–solution boundary, the results of [6, 7] are quite close, we shall use the more recent data of B S. Gurenkov, and shall consider a solution of HCl. The characteristic features of Gurenkov's results consist, first, in that the isotherms for the solution–air boundary and for the solution–mercury boundary have comparatively close absolute magnitudes, and, second, in that the isotherm for the solution–air boundary has a peculiar step form (see figure).

TABLE. The Parameters γ and D_2 as a function Ψ_0

	$-\Psi_0$, in volts												
	0,062	0,112	0,125	0,162	0,187	0,225	0,238	0,266	0,290	0,313	0,325	0,362	0,375
HCl – mercury boundary													
D_2	14,11	13,92	13,86	13,71	13,61	13,48	13,44	13,40	13,28	13,20	13,17	13,04	13,00
γ (Å)	0,847	0,835	0,832	0,823	0,817	0,809	0,806	0,804	0,797	0,792	0,790	0,782	0,780
HCl – air boundary													
D_2	28,16	28,05	27,98	27,87	27,48	26,96	26,78	26,42	25,93	25,57	25,44	24,96	24,80
γ (Å)	2,112	2,104	2,099	2,090	2,061	2,022	2,008	1,982	1,945	1,918	1,908	1,872	1,860

It turns out that if we study the behavior of the theoretical adsorption isotherms as a function of the parameters $\gamma(\Psi_0)$, and $D_2(\Psi_0)$, we can obtain curves which are not far from the experimental ones. Here, γ and D_2 vary within reasonable limits, and decrease with increasing $|\Psi_0|$. The variation is more pronounced in the case of the boundary

with air, than in the case of the boundary with mercury. The parametric relations, $\gamma(\Psi_0)$ and $D_2(\Psi_0)$, for which the theory agrees with experiment, are given in the table.

The theoretical and experimental isotherms are shown in figure (the experimental isotherms were obtained by differentiating the curves $\Psi_0 = f(\log_{10} a_{\pm})$, given in [7]).

We note that rather good agreement with experiment is found for the solution–mercury boundary even with constant γ and D_2.

From the point of view of elucidating the theory, the similarity in the isotherms for boundaries with completely different media is to be explained not by the fact that these media behave in the same way with respect to the specific adsorption of anions, as had been assumed, but by the fact that the field of the adsorbed anions has in each case a different effect on the properties of the internal double layer region, which, in individual cases, leads to pretty much the same results in the end.

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LITERATURE CITED

1. V. G. Levich, V. A. Kir'yanov, V. S. Krylov, DAN, 136, No. 6 (1960).
2. B. V. Ershler, ZhFKh, 20, 679 (1946).
3. V. G. Levich, V. A. Kir'yanov, V. S. Krylov, ZhFKh, 36, (1962) (in press).
4. V. G. Levich, V. A. Kir'yanov, ZhFKh, 36 (1962) (in press).
5. A. C. Grahame, J. Am. Chem. Soc., 80, 4201 (1958).
6. Z. A. Iofa, A. N. Frumkin, ZhFKh, 18, 268 (1944).
7. B. S. Gurenkov, ZhFKh, 30, 1830 (1956).
