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Abstract

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ADSORPTION ISOTHERM IN A MODEL OF A DISCRETE ELECTRICAL DOUBLE LAYER

Let the plane $x = 0$ separate a medium ($x \leq 0$), characterized either by the dielectric constant D_1 (dielectric) or by the potential ψ_0 (metal), and an electrolyte solution ($x \geq 0$) so concentrated that the potential drop within it may be taken into account only in the narrow region $0 \leq x \leq \delta$, a few angstroms wide, which we shall call the inner region of the double layer (for aqueous solutions of 1–1-valent electrolytes such an assumption is justified at concentrations exceeding 1 mole/liter). We shall denote the potential jump in this region by ψ_0. Let the centers of specifically adsorbed ions of identical charge z, which create in this plane an average surface charge density σ, be located in the plane $x = \beta$ $(0 < \beta < \delta)$.

At actual degrees of filling of the adsorbed layer that are substantially less than unity, the density σ is determined by the Boltzmann formula

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

where k_0 is a dimensional constant; μ_z is the chemical potential of the adsorbed ions; Φ_z is their energy in the field of the short-range forces of specific adsorption; ψ_{M} is the electrostatic potential at the point where the ion is adsorbed (the so-called micropotential).

If the boundary $x = 0$ contains no free electric charges and D_2 is the dielectric constant of the inner region of the double layer, then, as shown in ([1]), the relation holds

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

After substituting expression (1) into (2) and performing simple transformations, one obtains the dependence $\partial\psi_0/\partial \ln a_z = f(\psi_0)$, which is called the adsorption isotherm:

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

where $\gamma = \delta - \beta$; γ_0 is an arbitrary constant with the dimension of length; $a_z = \exp(\mu_z/kT)$ is the activity of ions z. For $\gamma/D_2 = \text{const}$ and $z = -1$, expression (3) reduces to the well-known formula of B. V. Ershler (^{2}).

To determine the explicit form of the function $\partial\psi_\text{M}/\partial\psi_0$, let us assume that the centers of the adsorbed ions are located at the nodes of a regular hexagonal lattice with parameter r_0. In this case $\sigma = 2ez/\sqrt{3}\,r_0^2$, and relation (2) takes the form:

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

An exact analytical expression for the micropotential in such a model was obtained in works (^{1,3,4}) and has the form

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

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

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

Assuming hereafter, for simplicity, that $\beta = \gamma$, and evaluating the integrals G_1 and $G_2^{(mn)}$, we obtain

$$\psi_{\mathrm{M}} = \begin{cases} \dfrac{1}{2}\psi_0 \left\{ 1 - \dfrac{\sqrt{3}\ln 2}{\pi\xi^2} \left[1 - \dfrac{2}{\ln 2} \sum_{mn} \sum_{k=1}^{\infty} K_0\left(\dfrac{(2k-1)\pi a_{mn}}{\xi} \right) \right] \right\}, \\ -\dfrac{\sqrt{3}\ln 2}{4\pi\xi^2}\psi_0 \left[1 - \dfrac{2}{\ln 2} \sum_{mn} \sum_{k=1}^{\infty} K_0\left(\dfrac{(2k-1)\pi a_{mn}}{2\xi} \right) \right], \\ \dfrac{\sqrt{3}}{4\pi\xi^2}\psi_0 \left\{ -G_1(\omega) + \xi \sum_{mn} \left[\dfrac{1}{a_{mn}} - \dfrac{1}{\sqrt{a_{mn}^2 + \xi^2}} + \sum_{k=1}^{\infty} \omega^k \left(\dfrac{2}{\sqrt{a_{mn}^2 + \xi^2 (2k)^2}} - \dfrac{1}{\sqrt{a_{mn}^2 + \xi^2 (2k+1)^2}} - \right. \right. \right. \end{cases} \tag{6}$$

where $\xi = 2\gamma/r_0$; $K_l(x)$ are Bessel functions of the second kind of imaginary argument (Macdonald functions) of order l ($l = 0, 1, \ldots$);

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

It is easy to show that all the series entering into (6) converge absolutely and uniformly. Differentiating (6), we obtain:

$$\frac{\partial\psi_{\mathrm{M}}}{\partial\psi_0} = \begin{cases} 0.5 + \dfrac{0.866}{\xi^3} S_1(\xi) \left\{ 1 + \left(\dfrac{2\psi_0}{\xi} \dfrac{\partial\xi}{\partial\psi_0} - 1 \right) \left[1 + \dfrac{0.221\,\xi\,(1 - 2.886 S_0(\xi))}{S_1(\xi)} \right] \right\}, & (\omega = 1), \quad \text{(8a)} \\ \dfrac{0.217}{\xi^3} S_1(2\xi) \left\{ 1 + \left(\dfrac{2\psi_0}{\xi} \dfrac{\partial\xi}{\partial\psi_0} - 1 \right) \left[1 + \dfrac{0.442\,\xi\,(1 - 2.886 S_0(2\xi))}{S_1(2\xi)} \right] \right\}, & (\omega = -1), \quad \text{(8b).} \end{cases}$$

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 analytical expression for $d\psi_M/d\psi_0$ at arbitrary $\omega \neq \pm 1$ contains series that converge very slowly and are amenable only to very crude numerical estimates. Since experiments usually investigate the metal-solution ($\omega \to 1$) and air-solution

(Figure: Fig. 1. 1 –HCl-mercury interface; 2 –HCl-air interface. Solid lines –experiment; dashed lines –theory)

Fig. 1. 1 –HCl-mercury interface; 2 –HCl-air interface. Solid lines –experiment; dashed lines –theory

($\omega \to -1$) interfaces, it is precisely the limiting formulas (8a) and (8b) that are of practical interest. From formulas (3), (4), and (8) it follows that, for an unambiguous determination of the theoretical adsorption isotherm, it is necessary to know the dependence on ψ_0 of any pair of the three quantities: γ, D_2, r_0.

In experiments with the mercury-solution interface, D. C. Grahame (^{5}) established that at comparatively low concentrations the field of the adsorbed anions has practically no effect on γ and D_2; however, in strongly concentrated solutions this effect may become appreciable. It is therefore of interest to compare the theory with the experimental data of Z. A. Iofa and A. N. Frumkin (^{6}) and B. S. Gurenkov (^{7}), obtained under conditions where expression (3) is applicable. Since the results of works (^{6},^{7}) for the mercury-solution interface are close to one another, we shall use the later data of B. S. Gurenkov and consider an HCl solution. The characteristic features of Gurenkov' s results are, first, that the isotherms for the solution-air and solution-mercury interfaces have comparatively close absolute values and, second, that the isotherm for the solution-air interface has a distinctive step-like form (see Fig. 1).

It turns out that, by studying the behavior of the theoretical adsorption isotherms as functions of the parameters $\gamma(\psi_0)$ and $D_2(\psi_0)$, one can obtain curves close to the experimental ones. In doing so, γ and D_2 vary within reasonable intervals, decreasing as $|\psi_0|$ increases. In the case of the interface with air, this change is expressed more sharply than in the case of the interface with mercury. The parametric dependences $\gamma(\psi_0)$ and $D_2(\psi_0)$ for which the theory agrees with experiment are presented in Table 1.

The theoretical and experimental isotherms are shown in Fig. 1 (the experimental isotherms were obtained by differentiating the curves $\psi_0 = f(\lg a_\pm)$ presented in work (^{7})).

We note that for the solution-mercury interface a sufficiently good agreement with experiment is obtained even with constant γ and D_2.

From the standpoint of the theory set forth, the closeness of the isotherms for interfaces with completely different media is explained not by the fact that these media behave identically with respect to the specific adsorption of anions, as is commonly assumed, but by the fact that the fields of the adsorbed anions in each case affect the properties of the inner region of the double layer in different ways, leading in individual cases to similar resultant effects.

Table 1

Dependence of the parameters γ and D_2 on 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 interface													
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 interface													
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

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