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Abstract

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THE INFLUENCE OF THE DISCRETENESS OF ADSORBED CHARGE ON INTERFACIAL SURFACE TENSION

Experimental study of capillary phenomena at metal-solution and gas-solution interfaces shows that these phenomena depend to a considerable extent on the adsorbability of the ions of the solution. As early as 1924, A. N. Frumkin (ˆ1) established that the increase in surface tension (in comparison with the pure solvent), observed in aqueous solutions of inorganic salts ($^{2-}$4) at the interface with air, decreases on passing to more surface-active anions. Strong adsorbability of salts of certain organic acids may even lead to a decrease in surface tension. An analogous decrease also occurs in the case of solutions of inorganic acids. A very substantial influence of adsorption effects is observed at the mercury-solution interface (ˆ5). As a result of a detailed analysis of electrocapillary data obtained for interfaces of concentrated solutions of inorganic acids with mercury (ˆ6, ˆ7), the following fact was established in particular: with increasing electrolyte concentration, the adsorbed amounts of both the anion and the cation at the point of the electrocapillary maximum change sign from positive to negative. An analogous phenomenon has recently been found in solutions of inorganic salts (ˆ8). A tendency toward a change in the sign of adsorption with increasing concentration is also observed at the interface of solutions of inorganic acids with air (ˆ9). As has already been noted repeatedly in the literature, in many cases there is a noticeable parallelism between measured dependences associated with the specific adsorption of ions at interfacial boundaries of quite different nature: mercury-solution and gas-solution. Such parallelism was observed, in particular, in measuring the dependence of the adsorption jump of potential on electrolyte activity (ˆ9), and was explained by the influence of the effect of discreteness of the adsorbed charge (ˆ10). In the present work it will be shown that, for a given (and not very high) degree of filling of a specifically adsorbed charged layer, the electrostatic interaction between the discrete charges forming this layer leads, both in the case of the metal-solution interface and in the case of the gas-solution interface, to approximately the same increase in interfacial surface tension.

Let us suppose that at a plane interface between an electrolyte and some other medium there is a specifically adsorbed monolayer consisting of N identical ions with charges ez. The change in the surface density of the free energy of the double layer, caused by the electrostatic interaction between the adsorbed ions, may be written, according to the Güntelberg method, in the form:

$$\Delta F_s^{(\ )} = \int_0^\sigma d\sigma' \int_0^1 \varphi^{(\ )}(\sigma'\lambda, ez\lambda)\, d\lambda, \tag{1}$$

where $\sigma = ezN/A$ is the mean density of the adsorbed charge; A is the surface area of the adsorbed layer; $\varphi\ \ (\sigma, ez) = \psi_M(\sigma, ez) - \psi(\sigma)$ is the difference between the true value of the potential ψ_M at the point where the center of the adsorbed ion is located and the mean potential ψ, by which

would have if the adsorbed charge were distributed over it continuously. Thus, the right-hand side of relation (1) is the difference between the work of reversible charging of all ions of the monolayer, performed at constant temperature T, volume V, and surface area A, and the work of charging the plane A with continuous surface charge σ. With the aid of relation (1) one can find the change in the surface tension of the interphase boundary caused by the discreteness of the adsorbed charge. This change is equal to

$$\Delta\gamma^{(\mathrm{vz})} = \left[\frac{\partial}{\partial A}\left(A\Delta F_S^{(\mathrm{vz})}\right)\right]_{T,V,N} = -\sigma \int_0^1 \varphi^{(\mathrm{vz})}(\sigma\lambda, ez\lambda)\, d\lambda + \int_0^\sigma d\sigma' \int_0^1 \varphi^{(\mathrm{vz})}(\sigma'\lambda, ez\lambda)\, d\lambda. \tag{2}$$

Expression (2) is a special case of a more general expression obtained in work ([11]) by considering the dissociation process of an adsorbed monolayer consisting of neutral molecules.

In order to obtain an explicit form of the function $\varphi^{(\mathrm{vz})}(\sigma, ez)$, it is necessary to solve the problem of the potential distribution in the double layer. In work ([11]), to estimate the magnitude of $\Delta\gamma^{(\mathrm{vz})}$, an approximate expression was used for the micropotential ψ_M, found with the aid of a simplified model of the adsorbed charge ([12]) and pertaining to the case of strongly dilute solutions. It was shown that for air—solution and oil—solution interfaces the quantity $\Delta\gamma^{(\mathrm{vz})}$ is positive, and the theoretical dependence of this quantity on the mean density of adsorbed particles proved to be in qualitative agreement with experimental data. A more exact solution of the problem of the potential distribution can be obtained for the case of extremely high electrolyte concentrations, when the effective thickness of the diffuse layer is negligibly small in comparison with the thickness of the compact layer. In this case, under certain assumptions concerning the character of the distribution of adsorbed charges in the adsorption plane, one can obtain an exact expression for the micropotential. At present two such expressions are known, based on two different models of the distribution of the adsorbed charge: the hexagonal-lattice model ([13–15]) and the cut-out disk model ([12]). These expressions make it possible to analyze relation (2) in detail.

Thus, we shall regard the thickness of the diffuse layer as negligibly small and denote by δ and D, respectively, the thickness and dielectric permittivity of the compact layer, while the distance between the phase boundary and the adsorption plane will, for simplicity, be taken equal to $\delta/2$. Under these conditions, as shown in works ([12, 15, 16]), the function $\varphi^{(\mathrm{vz})}(\sigma, ez)$ has the form:

$$\varphi^{(\mathrm{vz})}(\sigma, ez) = \begin{cases} 2\pi\sigma\delta\,[\alpha_1(\tau) - 1/2]/D - 2ez\ln 2/D\delta, & \text{metal—solution;} \\ 2\pi\sigma\delta\,[\alpha_2(\tau) - 1]/D - ez\ln 2/D\delta, & \text{gas—solution,} \end{cases} \tag{3}$$

where

$$\alpha_1^{(c.d.)}(\tau) = 0.67\,\tau\sum_{k=1}^{\infty}\frac{K_1(1.648(2k-1)\tau)}{(2k-1)}; \tag{4 }$$

$$\alpha_2^{(c.d.)}(\tau) = 0.67\,\tau\sum_{k=1}^{\infty}\frac{K_1(0.824(2k-1)\tau)}{(2k-1)}; \tag{4 }$$

$$\alpha_1^{(h.l.)}(\tau) = 3.31\,\tau^2\sum_{k=1}^{\infty}\sum_{(m,n)}K_0(\pi(2k-1)a_{mn}\tau)\,; \tag{4 }$$

$$\alpha_2^{(h.l.)}(\tau) = 1.65\,\tau^2\sum_{k=1}^{\infty}\sum_{(m,n)}K_0(\pi(2k-1)a_{mn}\tau/2)\,. \tag{4 }$$

In formulas (4), K_0 and K_1 are Macdonald functions, $\tau = r_{h.l.}/\delta$, where $r_{h.l.}$ is the distance between the two nearest adsorbed charges in the hexagonal-lattice model, and the summation over (m, n) must be carried out according to the following rule ([17]):

$$\sum_{(m,n)} f(a_{mn}) = \sum_{m=1}^{\infty} f(m) + \sum_{m=2}^{\infty}\sum_{n=1}^{m-1} f\left(\sqrt{m^2+n^2-mn}\right). \tag{5}$$

In the hexagonal-lattice model, the quantities σ and τ are related by $\sigma = 2ez/\sqrt{3\delta^2\tau^2}$. Substituting this relation into (2) and carrying out the integration with respect to λ, we obtain

$$\frac{3D\delta^3}{16\pi(ez)^2}\Delta\gamma^{(\mathrm{vz})} = \begin{cases} 0.125\,\tau^{-4} - g_1(\tau)\tau^{-6} + 2\displaystyle\int_{\tau}^{\infty} g_1(t)t^{-7}\,dt, & \text{metal—solution;} \\ 0.250\,\tau^{-4} - g_2(\tau)\tau^{-6} + 2\displaystyle\int_{\tau}^{\infty} g_2(t)t^{-7}\,dt, & \text{gas—solution.} \end{cases} \tag{6}$$

$$g_1^{(c.d.)}(t) = 0.303 - 0.407t^2 \sum_{k=1}^{\infty} K_2(1.648(2k-1)t)/(2k-1)^2; \tag{7a}$$

$$g_2^{(c.d.)}(t) = 2.425 - 0.813t^2 \sum_{k=1}^{\infty} K_2(0.824(2k-1)t)/(2k-1)^2; \tag{7b}$$

$$\begin{aligned} g_1^{(h.l.)}(t) = 0.178 - 3.31t^3 \sum_{k=1}^{\infty} \sum_{(m,n)} \frac{K_1(\pi(2k-1)a_{mn}t)}{(2k-1)a_{mn}\pi} \\ - 6.62t^2 \sum_{k=1}^{\infty} \sum_{(m,n)} \frac{K_2(\pi(2k-1)a_{mn}t)}{(2k-1)^2 a_{mn}^2 \pi^2}; \end{aligned} \tag{7c}$$

$$\begin{aligned} g_2^{(h.l.)}(t) = 1.423 - 3.31t^3 \sum_{k=1}^{\infty} \sum_{(m,n)} \frac{K_1(\pi(2k-1)a_{mn}t/2)}{(2k-1)a_{mn}\pi} \\ - 13.24t^2 \sum_{k=1}^{\infty} \sum_{(m,n)} \frac{K_2(\pi(2k-1)a_{mn}t/2)}{(2k-1)^2 a_{mn}^2 \pi^2}. \end{aligned} \tag{7d}$$

The integration in formulas (6) leads to very cumbersome expressions, which we shall not write out here. The expressions obtained contain series of exponential functions, Macdonald functions, and complementary probability integrals of errors. These series converge sufficiently rapidly for all physically realistic values of the parameter τ (inversely proportional to the square root of the degree of filling of the adsorbed layer). For several numerical values of the parameter τ, the sums of these series were calculated with an accuracy of the order of 1%. The results of the calculation are shown graphically in Fig. 1. In calculating the parameters of the compact layer, the values adopted were: $z = 1$, $\delta = 3.5$ Å, $D = 10$.

The results obtained show that, in the case of concentrated solutions, the interaction between adsorbed charges leads to an increase in surface tension, regardless of which phase (gas or metal) the solution borders. Moreover, at sufficiently small fillings of the adsorbed layer, the values of $\Delta\gamma^{(\mathrm{vz})}$, calculated for each of the boundaries, turn out to be rather close. This is due to the following reasons. As follows from formulas (3), the quantity $\Delta\gamma^{(\mathrm{vz})}$ consists of two parts: one is associated with the distortion of the mean field near the adsorbed ion as a consequence of the discreteness of the charge of this ion itself, while the other is due to the change in the micropotential under the action of the additional electric field induced by the discrete charges of all the adsorbed ions both in the external phase and in the diffuse region of the double layer. This latter field may symbolically be called

by the field of electrostatic "images" of the adsorbed charges in the planes bounding the dense layer. It is quite obvious that the first of the parts mentioned

Figure 1: Dependence of $\Delta\gamma^{(\mathrm{vz})}$ on the parameter $1/\tau$. Curves 1 and 1′ correspond to the gas—solution interface (1 according to the hexagonal-lattice model, 1′ according to the cut-out disk model); curves 2 and 2′ to the metal—solution interface (2 according to the hexagonal-lattice model, 2′ according to the cut-out disk model).

Figure 1: Figure 1: Dependence of $\Delta\gamma^{(\mathrm{vz})}$ on the parameter $1/\tau$. Curves 1 and 1′ correspond to the gas—solution interface (1 according to the hexagonal-lattice model, 1′ according to the cut-out disk model); curves 2 and 2′ to the metal—solution interface (2 according to the hexagonal-lattice model, 2′ according to the cut-out disk model).

depend substantially on the nature of the external phase and therefore differ for the metal—solution and gas—solution interfaces. However, the second parts as well, associated with the polarizabilities of the external phases and the fillings of the adsorbed layer, are also different. The calculation shows that, if the difference in the degrees of filling is not taken into account and they are assumed to be sufficiently small, then the total effect exerted on the surface tension of the metal—solution and gas—solution interfaces by the discreteness of the adsorbed charge has, in both cases, the same sign and the same order of magnitude. It should also be noted that, at comparatively small fillings, both models of the distribution of the adsorbed charge lead to very close numerical results. The reason for this agreement is the following obvious fact: the contribution made to $\Delta\gamma^{(\mathrm{vz})}$ by the set of images of the adsorbed charges (and the indicated models differ mainly in the magnitude of this contribution) is the smaller, the smaller the degree of filling.

Fig. 1. Dependence of $\Delta\gamma^{(\mathrm{vz})}$ on the parameter $1/\tau$. Curves **1** and **1′** correspond to the gas—solution interface (**1** according to the hexagonal-lattice model, **1′** according to the cut-out disk model); curves **2** and **2′** to the metal—solution interface (**2** according to the hexagonal-lattice model, **2′** according to the cut-out disk model).

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REFERENCES

1. A. N. Frumkin, *Tr. Khim. inst. im. L. Ya. Karpova*, No. 2, 106 (1924).
2. A. Heydweiller, *Phys. Zs.*, **3**, 329 (1902); *Ann. Phys.*, (4) **33**, 154 (1910).
3. P. Debye, E. Hückel, *Phys. Zs.*, **33**, 145 (1910).

4. G. Schwenker, *Ann. Phys.*, **11**, 525 (1921).
5. A. N. Frumkin, *Electrocapillary Phenomena and Electrode Potentials*, Odessa, 1919.
6. S. Iofa, A. Frumkin, *Acta physicochim. URSS*, **10**, 473 (1939).
7. Z. Iofa, B. Ustinskii, F. Eiman, *ZhFKh*, **13**, 934 (1939).
8. A. N. Frumkin, R. V. Ivanova, B. B. Damaskin, *DAN*, **157**, No. 5 (1964).
9. B. S. Gurevich, *ZhFKh*, **30**, 1830 (1956).
10. V. G. Levich, V. S. Krylov, *DAN*, **142**, No. 1 (1962).
11. G. M. Bell, S. Levine, B. A. Pethica, *Trans. Farad. Soc.*, **58**, No. 5 (1962).
12. S. Levine, G. M. Bell, D. Calvert, *Canad. J. Chem.*, **40**, No. 3 (1962).
13. O. A. Esin, V. M. Shikhov, *ZhFKh*, **17**, 236 (1943).
14. B. V. Ershler, *ZhFKh*, **20**, 679 (1946).
15. V. G. Levich, V. A. Kiryanov, V. S. Krylov, *DAN*, **135**, No. 6 (1960).
16. V. S. Krylov, Proceedings of the 14th Meeting of the International Committee on Electrochemistry, Thermodynamics and Kinetics, Moscow, 1963; V. S. Krylov, *Electrochim. Acta*, **9**, 1247 (1964).
17. V. S. Krylov, *DAN*, **144**, No. 1 (1962).

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