EFFECT OF THE DISCRETENESS OF THE ADSORBED CHARGE ON THE INTERPHASE SURFACE TENSION

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An experimental study of the capillary phenomena occurring at metal–solution and gas–solution boundaries shows that these phenomena depend to a considerable extent on the adsorbability of the ions in the solution. As early as 1924, A. N. Frumkin [1] found that the increase in surface tension (as compared with the pure solvent) observed in aqueous solutions of inorganic salts [2-4] at the boundary with air decreases on going to more surface active anions. The strong adsorbability of the salts of some organic acids may even lead to a reduction in the surface tension. A similar reduction also occurs in the case of solutions of inorganic acids. A very substantial influence exerted by adsorption effects is observed at a mercury–solution boundary [5]. As a result of a detailed analysis of the electrocapillary data obtained from the boundaries between concentrated solutions of inorganic acids and mercury [6, 7], the following fact in particular has been found: As the concentration of electrolyte is increased, the amounts adsorbed of both anion and cation change from positive to negative sign at the electrocapillary maximum point. A similar phenomenon was observed recently in solutions of inorganic salts [8]. A tendency to change the sign of the adsorption as the concentration is increased is also observed at the boundary between solutions of inorganic acids and air [9]. As has already been pointed out repeatedly in the literature, there are many cases in which appreciable parallelism occurs between the measured relations associated with the specific adsorption of ions on interphase boundaries of completely different nature, such as mercury–solution and gas–solution. A parallelism of this sort has been observed, in particular, in measuring the relation between the adsorption potential jump and the activity of the electrolyte [9], and has been accounted for in terms of the effect exerted by the discreteness of the adsorbed charge [10]. It will be shown in the present paper that for a given (and not very high) degree of filling of the specifically adsorbed charged layer, the electrostatic interaction between the discrete charges forming the layer results in approximately the same increase in the interphase surface tension in the case of either a metal–solution boundary or a gas–solution boundary.

Assume that on the plane interface between an electrolyte and some other medium, there is a specifically adsorbed monolayer, consisting of N identical ions with the charges ez. The change in surface density of the free energy in the double layer, due to electrostatic interaction between the adsorbed ions, may be written, following Guntelberg's method, in the form:

$$\Delta F_S^{(\mathrm{in})} = \int_0^{\sigma} d\sigma' \int_0^1 \varphi^{(\mathrm{in})}(\sigma'\lambda, ez\lambda)\, d\lambda, \qquad (1)$$

where $\sigma = ezN/A$ is the mean density of the adsorbed charge, A is the surface area of the adsorbed layer, $\varphi^{\mathrm{in}}(\sigma, ez) = \psi_M(\sigma, ez) - \psi(\sigma)$ – is the difference between the true value of potential ψ_M at the point where the center of the adsorbed ion is located and the mean potential ψ, which the adsorption plane would have if the adsorbed charge were continuously distributed over it. Thus, the right hand side of Eq. (1) represents the difference between the work of reversible charging of all the ions in the monolayer, performed at constant temperature T, volume V, and surface area A, and the work done in charging the plane A with the continuous surface charge σ. Using Eq. (1), it is possible to find the change in surface tension of the interphase boundary, due to the discreteness of the adsorbed charge. This change is equal to:

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

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

To find the explicit form of the function $\varphi^{(in)}(\sigma, ez)$, we have to solve the problem of the potential distribution in the double layer. In [11], to find the value of $\Delta\gamma^{(in)}$, an approximate expression was used for the micropotential ψ_M, obtained by means of a simplified model for the adsorbed charge [12], and applying to the case of highly dilute solutions. It was shown that for air–solution and oil–solution boundaries, the value of $\Delta\gamma^{(in)}$ is positive, while the theoretical relation between this quantity and the mean density of the adsorbed particles turned out to be in qualitative agreement with the experimental data. A more exact solution of the problem of the potential distribution may be found for the case of extremely high electrolyte concentrations, where the effective thickness of the diffuse layer is negligibly small in comparison with the thickness of the dense layer. In this case, for definite assumption as to the way in which the adsorbed charges are distributed in the plane of adsorption, it is possible to get an exact expression for the micropotential. Two such expressions are known at the present time, based on two different models for the distribution of the adsorbed charges: the hexagonal lattice model [13-15], and the cut-out disk model [12]. These expressions make possible a detailed analysis of the relation (2).

Thus, we shall assume the thickness of the diffuse layer to be negligibly small, and let δ and D be respectively the thickness and the dielectric constant of the dense layer, and the distance between the interface and the plane of adsorption is set equal to $\delta/2$ for simplicity. Under these conditions, as shown in [12, 15, 16], the function $\varphi^{(in)}(\sigma, ez)$ is to the form:

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

where:

$$\alpha_1^{(c.d.)}(\tau) = 0{,}67\,\tau\sum_{k=1}^{\infty} K_1(1{,}648\,(2k-1)\,\tau)/(2k-1); \tag{4a}$$

$$\alpha_2^{(c.d.)}(\tau) = 0{,}67\,\tau\sum_{k=1}^{\infty} K_1(0{,}824\,(2k-1)\tau)/(2k-1); \tag{4b}$$

$$\alpha_1^{(h.l.)}(\tau) = 3{,}31\,\tau^2\sum_{k=1}^{\infty}\sum_{(m,n)} K_0(\pi\,(2k-1)\,a_{mn}\tau); \tag{4c}$$

$$\alpha_2^{(h.l.)}(\tau) = 1{,}65\tau^2\sum_{k=1}^{\infty}\sum_{(m,n)} K_0(\pi\,(2k-1)\,a_{mn}\tau/2). \tag{4d}$$

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

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

In the hexagonal lattice model, the values of σ and τ are related by the equation $\sigma = 2ez/\sqrt{3}\delta^2\tau^2$. Substituting this relation in (2), and integrating with respect to λ, we obtain:

$$\frac{3D\delta^3}{16\pi(ez)^2}\Delta\gamma^{(in)} = \begin{cases} 0{,}125\,\tau^{-4} - g_1(\tau)\,\tau^{-6} + 2\int_{\tau}^{\infty} g_1(t)\,t^{-7}\,dt & \text{metal—solution} \\ 0{,}250\,\tau^{-4} - g_2(\tau)\,\tau^{-6} + 2\int_{\tau}^{\infty} g_2(t)\,t^{-7}\,dt & \text{gas—solution} \end{cases} \quad (6)$$

$$g_1^{(c.d.)}(t) = 0{,}303 - 0{,}407t^2 \sum_{k=1}^{\infty} K_2(1{,}648\,(2k-1)\,t)/(2k-1)^2; \quad (7^a)$$

$$g_2^{(c.d.)}(t) = 2{,}425 - 0{,}813\,t^2 \sum_{k=1}^{\infty} K_2(0{,}824\,(2k-1)\,t)/(2k-1)^2; \quad (7^b)$$

$$g_1^{(h.l.)}(t) = 0{,}178 - 3{,}31t^3 \sum_{k=1}^{\infty} \sum_{(m,n)} K_1(\pi\,(2k-1)\,a_{mn}t)/(2k-1)a_{mn}\pi - 6{,}62t^2 \sum_{k=1}^{\infty} \sum_{(m,n)} K_2(\pi\,(2k-1)a_{mn}t)/(2k-1)^2 a_{mn}^2\pi^2; \quad (7^c)$$

$$g_2^{(h.l.)}(t) = 1{,}423 - 3{,}31t^3 \sum_{k=1}^{\infty} \sum_{(m,n)} K_1(\pi\,(2k-1)\,a_{mn}t/2)/(2k-1)\,a_{mn}\pi - 13{,}24t^2 \sum_{k=1}^{\infty} \sum_{(m,n)} K_2(\pi\,(2k-1)\,a_{mn}t/2)/(2k-1)^2 a_{mn}^2\pi^2. \quad (7^d)$$

The integration in Eqs. (6) leads to very unwieldy expressions, which we shall not write out here. The resulting expressions contain series of exponential functions, Macdonald functions, and additional error probability integrals. These series converge quite rapidly for all physically realizable values of the parameter τ (inversely proportional to the square root of the degree of filling of the adsorbed layer). For some 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 calculations are shown graphically in Fig. 1. In calculating the parameters of the dense layer, the values assumed were: z = 1, δ = 3.5 A, D = 10.

The results obtained show that in the case of concentrated solutions, interaction between the adsorbed charges results in an increase in surface tension, independently of what phase (gas or metal) bounds the solution. More than that, for quite small fillings of the adsorbed layer, the values of $\Delta\gamma^{(in)}$, calculated for each of the boundaries, turn out to be very nearly the same. This is due to the following causes. It follows from Eq. (3) that the value of $\Delta\gamma^{(in)}$ is made up of two parts: One due to distortion of the mean field at the adsorbed ion resulting from the discreteness of the charge on the ion itself, and the other due to the change in the micropotential brought about by the effect of the additional electric field induced by the discrete charges of all the adsorbed ions in both the external phase and the diffuse region of the double layer. This latter field may be designated symbolically as the field of the electrostatic "images" of the adsorbed charges in the planes bounding the dense layer. It is perfectly obvious that the first of the parts mentioned depend in an essential way on the nature of the external phase, and are thus different depending on whether the boundary is metal—solution or gas—solution. However, the second parts, which are related to the polarizabilities of the external phases and the fillings of the adsorbed layers, are also different. A calculation shows that if we neglect the differences in the degrees of filling and assume them to be quite small, the total effect exerted on the surface tension of metal—solution and gas—solution boundaries by the discreteness of the adsorbed charge is of the same sign and the same order of magnitude in both cases. It must also be pointed out that for comparatively small fillings, both models for the distribution of the adsorbed charge lead to very nearly the same numerical results. The reason for this agreement is provided by the following obvious fact: the contribution made to $\Delta\gamma^{(in)}$ by the set of images of the adsorbed charges (and the above models differ mainly in the magnitude of this contribution) is smaller, the smaller the degree of filling.

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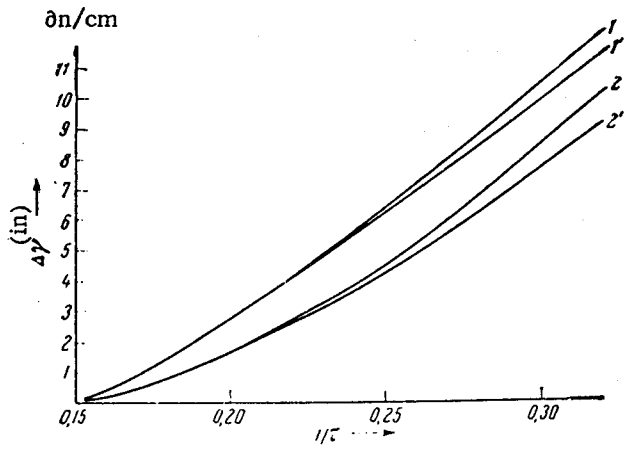

$\Delta\gamma^{(in)}$ as a function of the parameter $1/\tau$. The curves 1 and 1' correspond to a gas–solution boundary (1–on the hexagonal lattice model, 1'–on the cut-out disc model), while curves 2 and 2' correspond to a metal–solution boundary (2–on the hexagonal lattice model, 2' on the cut-out disc model).

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