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POTENTIALS OF ZERO CHARGE, INTERACTION OF METALS WITH WATER AND ADSORPTION OF ORGANIC SUBSTANCES—III. THE ROLE OF THE WATER DIPOLES IN THE STRUCTURE OF THE DENSE PART OF THE ELECTRIC DOUBLE LAYER

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Summary—Two types of solvent particles resident on the electrode surface have been considered: (1) associates of water molecules freely oriented along the electric field and (2) chemisorbed water dipoles oriented with the oxygen atom towards the metal surface. On the basis of this model, a semi-quantitative interpretation has been given to the dependence of the differential capacity of the dense layer on the electrode charge. It has been shown that a change in this dependence, when passing from mercury to gallium, can be described assuming the energy of interaction of chemisorbed water dipoles with the metal surface to increase.

To-date two significantly different approaches to the interpretation of the adsorption behavior of water dipoles on the electrode surface have been described in literature. The first of these involved two adsorption states of water molecules which differ primarily in the dipole orientation. As regards the specific interaction of water molecules with the electrode surface, this was taken into account in this model only by the value of the electrode charge (or potential) at which the number of water dipoles oriented in one direction is equal to the number of dipoles with opposite orientation. This model was first used in connection with the interpretation of the hump on the differential capacity curves[1–3]. Later various versions of this model were considered by Bockris, Devanathan and Müller[4], Damaskin[5], Levine, Bell and Smith[6]. The second model, assuming chemisorbed water dipoles with a constant orientation turned with their negative end towards the surface, appeared when the properties of the gallium electrode, which differ from mercury, were investigated[7–9]. Some theoretical aspects of this model were developed in[10, 11]. Later the concept of chemisorbed water dipoles was made use of by Trasatti[12] in an analysis of the dependence of the *pzc* on the electron work function.

Evidently, in comparing the adsorption properties of various electrodes, it is necessary to take into account both the chemisorption of water dipoles and the possibility of reorientation of dipoles with changing electrode charge. In this communication we shall consider the simplest phenomenological approach to this problem.

In the absence of specific ions adsorption, the potential difference in the dense part of the electric double layer can be written as

$$\Delta\varphi = \Delta\psi + \Delta\chi \tag{1}$$

Here

$$\Delta\psi = \frac{4\pi d}{D}\epsilon = \frac{\epsilon}{K_0} \tag{2}$$

ie, the potential difference caused by the electrode charge ϵ (D—dielectric constant in the dense layer at constant orientation of water dipoles, d—its thickness and K_0—integral capacity equal to $D/4\pi d$). The $\Delta\chi$ is the potential difference caused by the orientation of adsorbed water dipoles.

It can be assumed that

$$\Delta\chi = \Delta\chi_1 + \Delta\chi_2 \tag{3}$$

where the potential difference $\Delta\chi_1$ is associated with the water dipoles freely oriented along the field and $\Delta\chi_2$—with chemisorbed water dipoles. As it follows from[5], instead of taking account of the pairwise electrostatic interaction of separate water dipoles, as was done in[4], it is possible, and apparently would be more correct,* to assume the non-chemisorbed water

* This is due to the fact that the interaction between the water molecules present on the electrode surface cannot be reduced to the electrostatic dipole–dipole interaction, as the formation of hydrogen bonds seems to be of importance as well[3].

dipoles, present on the electrode surface, to be associated into small groups which only weakly interact with one another. The conclusion about the association of water molecules adsorbed on mercury follows directly from the shape of the adsorption isotherm of a number of organic substances, as was shown in[13, 14]. If we assume in addition that the interaction of these associates of water dipoles with the electrode surface is a purely electrostatic one, then from the BDM theory[4], we obtain for $\Delta\chi_1$ the expression

$$\Delta\chi_1 = -\frac{4\pi\mu_1 N_1}{D}\,\mathrm{th}\left(\frac{4\pi\mu_1\epsilon}{DkT}\right) = -\frac{\gamma_1}{K_1}\,\mathrm{th}\left(\frac{\epsilon}{\gamma_1}\right) \quad (4)$$

Here μ_1 is the normal to the surface component of the effective dipole moment for a water molecules associate; N_1—the total number of such associates per cm^2; k—the Boltzmann constant; T—the absolute temperature; $\gamma_1 = DkT/4\pi\mu_1$ (γ_1 has the dimensionality of unit surface charge) and $K_1 = D^2kT/16\pi^2\mu_1^2 N_1$ (K_1 has the dimensionality of unit surface capacity).*

On the other hand, as a first approximation, for $\Delta\chi_2$ we can write the expression

$$\Delta\chi_2 = -k'N_2 = -k'N_2^0\exp\left(\frac{\epsilon}{\gamma_2}\right) \quad (5)$$

in which it is assumed that $\Delta\chi_2$ is proportional to the number of water dipoles chemisorbed per cm^2 — N_2, and the adsorption energy of these dipoles depends linearly on the electrode charge (by analogy with the interpretation of the specific adsorption of thiourea dipoles in[11]. N_2^0 is the value of N_2 at $\epsilon = 0$ and γ_2 is a parameter characterising the dependence of the adsorption energy on the charge. The larger the value of γ_2, which is inversely proportional to the effective dipole moment of chemisorbed water dipoles, the slower is the increase of the adsorption energy with increasing positive value of ϵ. Equation (5) can be conveniently rewritten as

$$\Delta\chi_2 = -\frac{\gamma_2}{K_2}\exp\left(\frac{\epsilon}{\gamma_2}\right) \quad (5a)$$

where the parameter K_2, which has the dimensionality of a capacity, is equal to $\gamma_2/k'N_2^0$. Since N_2^0 increases exponentially with increasing bonding energy of chemisorbed water dipoles with the electrode surface at $\epsilon = 0$, the larger K_2, the smaller is this energy.

Substituting expressions (4) and (5a) into equation (3), we find

$$\Delta\chi = -\frac{\gamma_1}{K_1}\,\mathrm{th}\left(\frac{\epsilon}{\gamma_1}\right) - \frac{\gamma_2}{K_2}\exp\left(\frac{\epsilon}{\gamma_2}\right) \quad (6)$$

Now taking into account equations (2) and (6), we can write relation (1) as

$$\Delta\phi = \frac{\epsilon}{K_0} - \frac{\gamma_1}{K_1}\,\mathrm{th}\left(\frac{\epsilon}{\gamma_1}\right) - \frac{\gamma_2}{K_2}\exp\left(\frac{\epsilon}{\gamma_2}\right) \quad (7)$$

To avoid additional complications, henceforth we shall assume the quantities K_0, K_1, K_2, γ_1 and γ_2 to be independent of the electrode charge. Under this condition, differentiating equation (7) with respect to ϵ, we obtain an expression for the differential capacity of the dense layer C:

$$\frac{1}{C} = \frac{1}{K_0} - \frac{1}{K_1}\,\mathrm{sech}^2\left(\frac{\epsilon}{\gamma_1}\right) - \frac{1}{K_2}\exp\left(\frac{\epsilon}{\gamma_2}\right) \quad (8)$$

or

$$C = \frac{K_2}{K_2/K_0 - (K_2/K_1)\,\mathrm{sech}^2(\epsilon/\gamma_1) - \exp(\epsilon/\gamma_2)} \quad (8a)$$

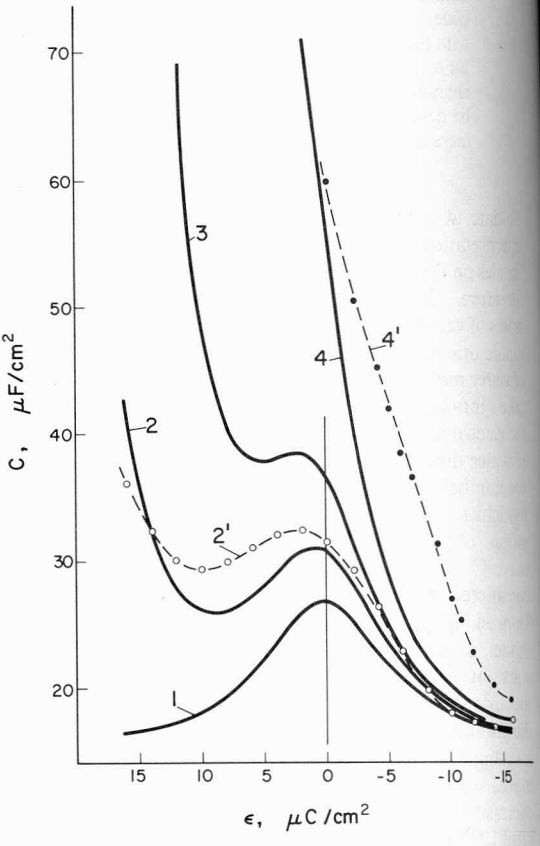

Fig. 1. Dependence of the differential capacity of the dense layer on the electrode charge calculated by means of equation (8a) at $K_0 = 16\ \mu$F/cm^2, $K_1 = 40\ \mu$F/cm^2, $\gamma_1 = \gamma_2 = 8\ \mu$C/cm^2 and K_2 equal to: 1—∞, 2—200, 3—100 and 4—50 μF/cm^2. Dependence of the differential capacity of the dense layer on the electrode charge: 2′—mercury in NaF at 0°C[15], 4′—cadmium in KF at 0°C[17].

* Formula (4) ensues from equation (35)[4] when the coefficient 2π is substituted by the correct value 4π and the energy of interaction of adsorbed particles (in our case, associates of water molecules) is neglected. Unlike the present paper, the quantities μ and N refer to separate water molecules.

The expression for the total integral capacity of the dense layer is as follows:

$$K = \left[\frac{1}{\epsilon}\int_0^{\epsilon}\frac{1}{C}\cdot d\epsilon\right]^{-1} = \frac{\epsilon}{\epsilon/K_0 - (\gamma_1/K_1)\,\mathrm{th}(\epsilon/\gamma_1) - (\gamma_2/K_2)[\exp(\epsilon/\gamma_2) - 1]} \quad (9)$$

Assuming, in order to simplify the calculations, $\gamma_1 = \gamma_2 = \gamma$ and taking as a first approximation $K_0 = 16\,\mu F/cm^2$, we chose the parameters K_1, K_2 and γ approximately corresponding to the experimental C, ϵ curve for the mercury–aqueous NaF solution system at 0°C[15]. Thus we found $K_1 = 40\,\mu F/cm^2$; $K_2 = 200\,\mu F/cm^2$ and $\gamma = 8\,\mu C/cm^2$. The C,ϵ curve, calculated by means of equation (8a) at these values of the parameters, is shown in Fig. 1 as curve 2. Curve 1 in this figure gives the dependence of C on ϵ in the absence of chemisorbed water dipoles ($K_2 = \infty$). It can be readily seen that the appearance of chemisorbed water dipoles, oriented with their negative end towards the electrode surface, leads to an increase in the capacity at positive electrode charges and to a shift of the hump on the C,ϵ curve into the region $\epsilon > 0$. Thus, on one hand, in such interpretation the position of the hump at $\epsilon > 0$ is not inconsistent with the preferred orientation of water dipoles with their negative end towards the uncharged mercury surface. On the other hand, the existence of a capacity increase at large positive charges not associated with specific anions adsorption can be explained.

Since $\gamma_1^2/K_1 = kTN_1 = kT/S_1$, where S_1 is the area per associate of adsorbed water molecules, if we know γ_1 and K_1, we can estimate S_1. This estimate gives a reasonable value of $S_1 \approx 24\,Å^2$, approximately equal the area per adsorbed molecule of simple organic compounds[13, 14]. Then, assuming $d = 3{\cdot}3$ Å[16], we find from the value of $K_0 = D/4\pi d = 16\,\mu F/cm^2$, $D = 6$ in agreement with the BDM theory[4]. Now from the value of $\gamma_1 = DkT/4\pi\mu_1$ we can estimate the effective dipole moment of an associate of water molecules: $\mu_1 \approx 0{\cdot}75$ Debye, which is also a reasonable value.

The increase in the adsorption energy of chemisorbed water dipoles when passing from mercury to gallium[7–9], or cadmium[17], corresponds to a decrease of K_2.* Taking $K_2 = 50\,\mu F/cm^2$ and leaving unchanged all other parameters, we have calculated by means of equation (8a) the relevant C,ϵ curve (curve 4 in Fig. 1). As is clear from the figure, in this case, in agreement with the experimental data for gallium and cadmium electrodes, there is a sharp increase of the capacity in the vicinity of the zero charge and the hump on the C,ϵ curve disappears.

Figure 2 shows the dependence on the charge of the potential difference $\Delta\chi$ due to the combined contribution of water dipoles, which we have calculated by means of equation (6) at the same parameters as the C,ϵ curves in Fig. 1. It can be seen from the figure that the increase in water chemisorption on the electrode surface leads to a shift of *pzc* into the negative direction, if we assume the work function to be constant (see Part II of this contribution). Thus, when passing from curve 2 to curve 3, this effect amounts to ~0·12 V.

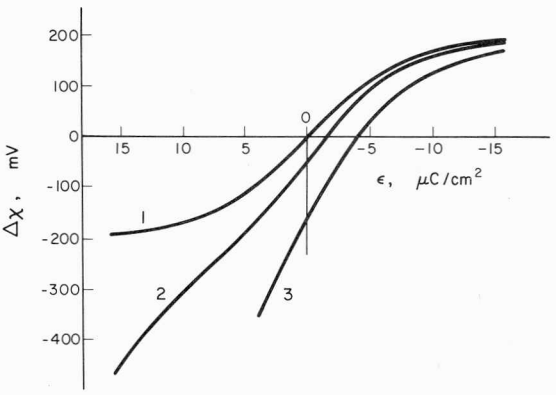

Fig. 2. Dependence of the potential difference due to the combined contribution of water dipoles on the electrode charge, calculated by means of equation (6) at $K_0 = 16\,\mu F/cm^2$ $K_1 = 40\,\mu F/cm^2$, $\gamma_1 = \gamma_2 = 8\,\mu C/cm^2$ and K_2 equal to: 1—∞, 2—200 and 3—50 $\mu F/cm^2$.

Finally, equating the integral capacity of the dense layer K, determined by equation (9), to the capacity of a plane capacitor with a certain effective value of the dielectric constant D_{ef}, $K = D_{ef}/4\pi d$, we can calculate the dependence of D_{ef} on the electrode charge. This dependence is shown in Fig. 3 for the two cases considered earlier: $1 - K_2 = 200$ and $2 - K_2 = 50\,\mu F/cm^2$. The same figure gives the experimental values of D_{ef} for mercury[18] and cadmium[19],

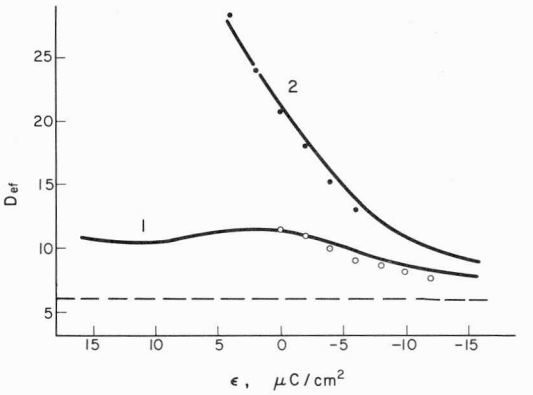

Fig. 3. Dependence of the effective dielectric constant of the dense layer on the electrode charge, calculated by means of equation (9) and the formula for a plane capacitor at $K_0 = 16\,\mu F/cm^2$, $K_1 = 40\,\mu F/cm^2$, $\gamma_1 = \gamma_2 = 8\,\mu C/cm^2$, $d = 3{\cdot}3$ Å and at K_2 equal to: 1—200 and 2—50 $\mu F/cm^2$; dashed line—the dielectric constant of the dense layer $D = 6$. White circles—values of D_{ef} on mercury from the data of[18], black circles—values of D_{ef} on cadmium from the data of[19].

* Simultaneously we should take into account a certain decrease of K_1 due to the decrease of N_1, but as a first approximation, we can ignore this effect.

determined by Parson's method[18] from the adsorption of thiourea on these two electrodes. As is evident from the figure, the theoretical calculation shows clearly the experimentally observed increase of D_{ef} with increasing water dipoles chemisorption.

Thus, the simplified model for the adsorption behavior of water dipoles, considered above, describes qualitatively correctly the peculiarities of the transition from the electrodes of the mercury type to those of the gallium type.

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