EFFECT OF THE HYDROPHILIC CHARACTER OF THE ELECTRODE SURFACE ON THE TEMPERATURE COEFFICIENT OF THE CAPACITANCE OF THE COMPACT PART OF THE ELECTRIC DOUBLE LAYER

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In [1] a model was proposed for the structure of the compact part of the electric double layer in the absence of specific adsorption of ions. Two types of particles adsorbed on the electrode surface were considered: 1) associates of several water molecules freely oriented in the field; 2) chemisorbed water molecules. The c_h, q curve calculated from a model with a reasonable set of parameters for the structure of the double layer was close to the experimental curve for the mercury–aqueous sodium chloride solution boundary [2]. In addition, the dependence of the temperature coefficient of the capacitance of the compact layer on the charge, calculated from the model, was in satisfactory agreement with the analogous relationship obtained by the treatment of Grahame's experimental data [2]. Here it was assumed that, irrespective of the electrode charge, the average number of water molecules in the associate decreases with increase in temperature while the dipole moment for the individual molecule in the associate remains constant. (The dipole moment of the associate as a whole decreases accordingly with increase in temperature.)

In the present work a calculation was made of the capacitance curves for successive increase of the parameter $A_0 = \exp(-U/k \cdot 273)$, which characterizes the energy of specific adsorption of the solvent dipoles U (i.e., the hydrophilic characteristics of the electrode) at T = 273°K. The C_h,q curves calculated from the model for two different temperatures are given in Fig. 1. From the figure it is seen that with constant values of q and T the values for the capacitance of the compact layer increase with increase in the specific interaction between the solvent molecules and the electrode surface. From the physical standpoint this is due to the fact that the number of solvent dipoles chemisorbed on unit surface increases [3].

The dependence of the temperature coefficient of the reciprocal capacitance of the compact layer $\partial(1/C_h)/\partial T$ on the electrode charge q, calculated from the data in Fig. 1, is shown in Fig. 2. As seen from Fig. 2, the specific interaction between the solvent molecules and the electrode surface has a significant effect on the value of $\partial(1/C_h)/\partial T$. With sufficiently large positive values for the surface charge, depending on the parameter A_0, the temperature coefficient can differ not only in value but also in sign. For an arbitrary temperature T the following relationship holds [1]:

$$\ln A = \ln A_0/\theta, \quad (1)$$

where $\theta = T/273$.

Thus, if $A_0 < 1$, the parameter A increases with increase in T (endothermic adsorption). On the other hand, if $A_0 > 1$, the parameter A decreases with increase in T (exothermic adsorption).

The increase in the negative value of $\partial(1/C_h)/\partial T$ when $q > 5$ μC/cm² on metals with weak chemisorption of water is due to the increase in the amount of chemisorbed water molecules on unit surface. Conversely, on metals with high chemisorption, i.e., with sufficiently large coverage of the surface by chemisorbed dipoles, an effect of a different type predominates, i.e., decrease in the amount of specifically adsorbed water molecules with increase in temperature, and it is this which leads to the positive value of $\partial(1/C_h)/\partial T$. The decrease in the negative value of $\partial(1/C_h)/\partial T$ when $q > 11$ μC/cm² on metals with sufficiently small parameters A_0 (Fig. 2) shows that this effect also arises on more hydrophobic electrodes but at higher positive values of q.

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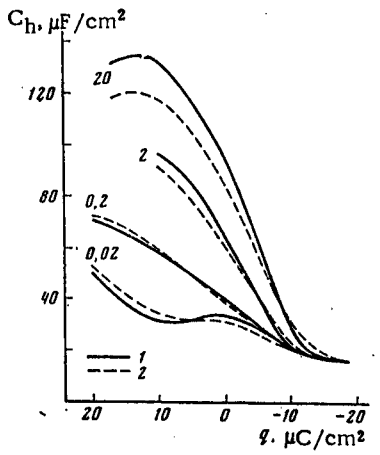

Fig. 1

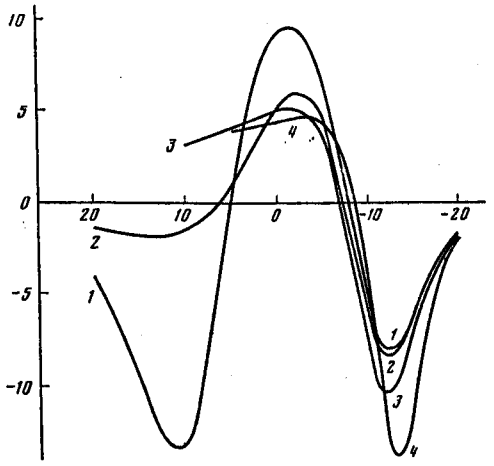

Fig. 2

Fig. 1. Dependence of the capacitance of the compact layer on the charge, calculated by means of Eqs. (16)-(18) [1] for 0°C (1) and 25°C (2) with the following values for the parameters: $\alpha_0 = 0.36$, $n_0 = 3$, $Q_0 = 1.62$, $\varkappa_0 = 23$, $K_0 = 16$. The values of the parameter A_0 are given on the curves.

Fig. 2. Dependence of the mean temperature coefficient $\partial(1/C_h)/\partial T \cdot 10^5$ ($\mu F^{-1} \cdot cm^2 \cdot °K^{-1}$) on the charge q ($\mu C/cm^2$) for the following values of the parameter A_0: 1) 0.02; 2) 0.2; 3) 2.0; 4) 20.0.

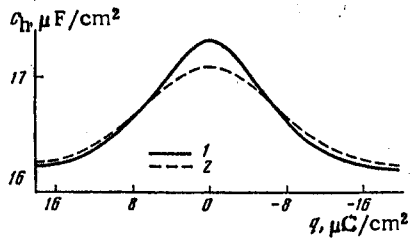

Fig. 3

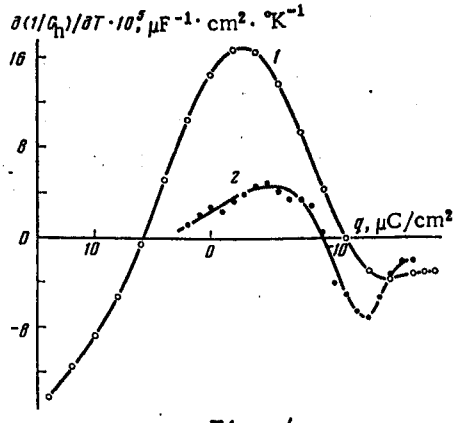

Fig. 4

Fig. 3. Dependence of the capacitance of the double layer on the charge, calculated by means of Eq. (2) for 0°C (1) with the parameters $\gamma_1 = 8$, $K_1 = 200$, $K_0 = 16$ and for 25°C (2) with $\gamma_1 = 9.7$, $K_1 = 242.3$, $K_0 = 16$.

Fig. 4. Dependence of the average temperature coefficient $\partial(1/C_h)/\partial T$ on the charge q for mercury (1) and cadmium (2), calculated from experimental data in [2] and [5] respectively.

Near q = 0 the $\partial(1/C_h)/\partial T$ value is positive and increases with decrease in the hydrophilic character of the electrode. This can be explained by the fact that the decrease in the capacitance of the compact layer with increase in temperature in the present case is due predominantly to partial dissociation of the associates. In order to analyze the effect of temperature on the capacitance of the compact layer, due only to electrostatic adsorption of the associates, we calculated the C_h,q curves for two different temperatures by means of the equation [4]

$$1/C_h = 1/K_0 - 1/K_1 \operatorname{sech}^2 (q/\gamma_1), \qquad (2)$$

where K_0 is the integral capacitance, equal to $\varepsilon_1/4\pi d$ (ε_1 is the dielectric constant, d is the thickness of the compact layer); $K_1 = \varepsilon_1^2 kT/16\pi^2\mu_1^2 N_1$, $\gamma_1 = \varepsilon_1 kT/4\pi\mu_1$ (μ_1 is the dipole moment, N_1 is the total number of associates on unit surface). Here, in contrast to [4],* it was assumed that the dipole moment of the associate decreases with increase in T but at the same time the number of associates on unit surface increases. As in [1], the average dipole moment for one molecule in the associate was considered to be independent of temperature. The results from the calculation are given in Fig. 3. From this figure it is seen that with small negative charges on the electrode $\partial(1/C_h)/\partial T > 0$, and with further increase in the negative value of q the $\partial(1 - C_h)/\partial T$ value changes sign.

In the transition to a more hydrophilic metal, as follows from Fig. 2, the negative value of $\partial(1/C_h)/\partial T$ at the extremum of the curve increases, and this is due to increase in the amount of chemisorbed dipoles.

The dependence of the temperature coefficient of the reciprocal capacitance of the compact layer on the charge of the cadmium electrode [5] is given in Fig. 4.† For comparison the same figure gives the analogous curve calculated from Grahame's data [2]. As we see, the relative arrangement of the $\partial(1/C_h)/\partial T$ curves is consistent with the dependence of the temperature coefficient of the capacitance of the compact layer on the hydrophilic characteristics of the metal electrode emerging from the model [1].

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*In [4] μ_1 and N_1 characterize the individual water molecules.

†The numerical values of the capacitance of the compact layer for the cadmium electrode at various temperatures were kindly provided by K. V. Rybalka.