DETERMINATION OF THE ATTRACTION CONSTANT OF ORGANIC COMPOUNDS FORMING TWO-DIMENSIONAL CONDENSED LAYERS ON MERCURY

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A number of organic compounds which form two-dimensional condensed layers on the mercury—solution interface are already known [1-5]. An instantaneous transition from a state corresponding to a completely filled surface ($\theta = 1$) to a state with $\theta = 0$ has been observed in solutions of these compounds, and the plots of the differential capacitance as a function of the potential (C vs E curves) can be described by the Frumkin—Damaskin theory [6] under the assumption that the attraction constant a is greater than 2. At the present time the literature does not offer a unified opinion regarding the value of the attraction constant for compounds which form two-dimensional condensed layers owing to the lack of reliable methods for its determination [3, 11, 12] (for example, the values that have been presented for the attraction constant of camphor range from 1.95 to 3.5). At the same time, polarographic maxima of the third kind appear only when these compounds are adsorbed [5, 7-9], and the theoretical interpretation of these phenomena requires knowledge of the attraction constant of the organic compound [10].

The purpose of the present work was to determine the attraction constant of adamantanol (AdOH) by comparing theoretically calculated C vs E curves for various values of the attraction constant and the experimental C vs E curve in a solution of $3\cdot10^{-4}$ M AdOH + 0.1 M NaF. The study made in [4] of the adsorption behavior of adamantanol with the aid of electrocapillary and capacitance measurements led to the establishment of the following absorption parameters: $\Gamma_\infty = 4.1\cdot10^{-10}$ mole/cm^2, $C = 3.5$ μF/cm^2, $A = RT\Gamma_\infty = 1.04$ μJ/cm^2, $\varphi_N = +0.46$ V, and $\ln B_0 + a_0 = 10.07$ (B is the adsorption equilibrium constant, and the subscript 0 indicates that B and a refer to $\varphi = E - E_{q=0}^{\theta=0} = 0$).

To calculate the C vs E curves in the presence of AdOH we used the following equation, which follows from a model of two parallel capacitors [6]:

$$C=C_0(1-\theta)+C'\theta+\frac{[q_0+C'(\varphi_N-\varphi)]^2}{A}\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (1)$$

The values of θ appearing in this equation were determined in the following manner. Various values of the attraction constant were assigned (2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5) under the assumption that they are independent of the potential ($a = a_0$). The corresponding value of the parameter $B_0 = 10.07 - a$ was found for each value of a. Then the equation [6]

$$B=B_0\exp\left[-\int_0^{\varphi}\int_0^{\varphi} C\,dE-C'\varphi\left(\varphi_N-\frac{\varphi}{2}\right)\Big/A\right] \quad (2)$$

was used to calculate the value of B at various potentials, and the equation of the Frumkin isotherm

$$Bc=\frac{\theta}{1-\theta}e^{-2a\theta} \quad (3)$$

was used to find the value of θ for each of the assigned values of a. The calculation was carried out for 45 values of E ranging from −1.3 V to +0.2 V, the calculations being performed at 10-mV intervals in the region of adsorption—desorption potentials. Then Eq. (1) was used to determine the value of C for each potential. The calculations employing Eqs. (1) and (3) were carried out with the aid of an Élektronika TZ-16 computer.

The results of the calculation are presented in Fig. 1. As we see, an increase in the attraction constant is accompanied by a decrease in the values of the differential capaci-

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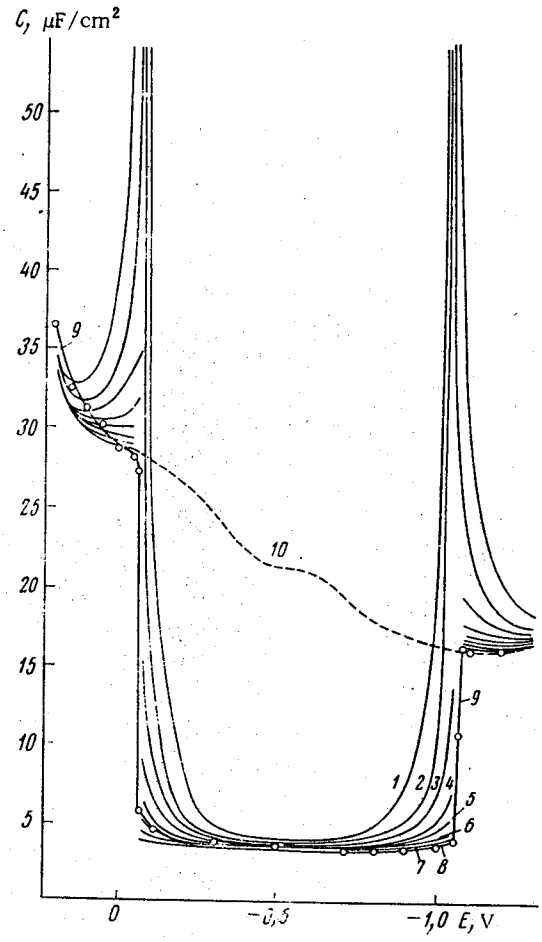

Fig. 1. Comparison of an experimental C vs E curve in a solution of 0.1 M NaF + $3 \cdot 10^{-4}$ M AdOH (9) with C vs E curves calculated with various values of α: 1) 2; 2) 2.5; 3) 3; 4) 3.5; 5) 4; 6) 4.5; 7) 5; 8) 5.5. The dashed line is the C vs E curve in an 0.1 M NaF solution (10).

tance in the region of the adsorption—desorption peaks until they completely disappear at values of $\alpha \geqslant 4.5$ and the appearance of an increasingly sharper jump in the differential capacitance in this potential range at $\alpha \geqslant 3.5$, as has already been pointed out in [2]. According to the data in that report, at values of α not exceeding 2.5 the C vs E curves resemble ordinary plots of the differential capacitance for adsorption processes that are not accompanied by two-dimensional phase transformations. The comparison presented in this figure of an experimental C vs E curve in the presence of adamantanol and C vs E curves calculated with different values of the attraction constant indicates that there is a practically complete fit between the experimental curve and the theoretically calculated curve for $\alpha = 5.5$. Thus, the value $\alpha = 5.5$ may be taken as the value of the attraction constant of adamantanol.

Additional support for this conclusion comes from the measurements we made in a study of the adsorption behavior of camphor and adamantanol in the presence of ethanol. The investigation was carried out according to the method described in [3] in the presence of various concentrations of camphor and adamantanol on a background of 1 M Na_2SO_4 with an addition of 15 vol.% ethanol in the experiments with camphor and 10 vol.% ethanol in the experiments with adamantanol. It was found that the presence of ethanol appreciably alters the shape of the $\Delta\sigma$ vs log c curves: While in the absence of ethanol this dependence is linear and, thus, corresponds to the same value of Γ, which is equal to Γ_∞, for all concentrations (see Fig. 2 in [4]), when ethanol is added to the solutions, there is a gradual change in

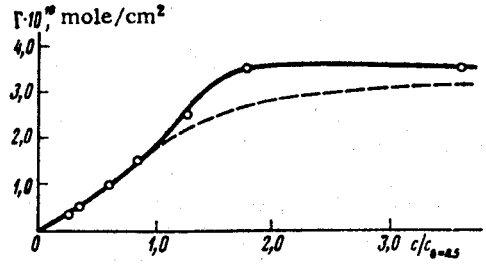

Fig. 2

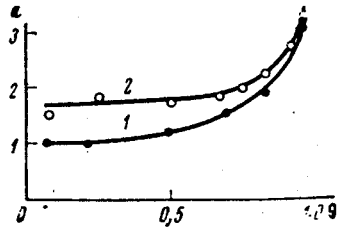

Fig. 3

Fig. 2. Adsorption isotherm of camphor on an uncharged mercury surface in a system of 1 M Na_2SO_4 + 15 vol.% C_2H_5OH + camphor. The solid line corresponds to the experimental data, and the points were calculated from Eq. (3) with consideration of the dependence of a on φ. The dashed line was calculated from Eq. (3) under the condition $a = 1$.

Fig. 3. Dependence of the attraction constant on the degree of filling following the adsorption on an uncharged mercury surface of: 1) Camphor in a system of 1 M Na_2SO_4 + 15 vol.% C_2H_5OH + camphor; 2) adamantanol in a system of 1 M Na_2SO_4 + 10 vol.% C_2H_5OH + AdOH.

the slope of the $\Delta\sigma$ vs log c plot as the camphor or adamantanol concentration is increased. This makes it possible to construct adsorption isotherms of camphor and adamantanol in the presence of C_2H_5OH.

An adsorption isotherm of camphor on an uncharged mercury surface in the presence of 15 vol.% C_2H_5OH is presented in Fig. 2. A comparison of this isotherm with the results of the calculation based on Eq. (3) reveals that the attraction constant a increases monotonically with increasing θ, a good fit between the experimental and calculated adsorption isotherms being observed only in that case (curve 1 in Fig. 3). A similar result was also obtained for the system of 1 M Na_2SO_4 + 10% C_2H_5OH + AdOH (see curve 2 in Fig. 3). The observed law may be attributed to the fact that the combined adsorption of ethanol results in drastic weakening of the attraction interaction between the molecules of camphor or adamantanol. As the concentration of these compounds is increased, the degree of filling of the surface with ethanol decreases, and the value of a increases. However, in the solutions containing ethanol the maximum values of a were still slightly lower than in the solutions in which there was no addition of ethanol. Apparently, even at very high degrees of filling of the surface with camphor or adamantanol the surface layer still contains ethanol molecules, which weaken the attraction interaction between the molecules in the two-dimensional condensed layer. This conclusion is supported by the fact that an addition of ethanol caused a decrease in the limiting adsorption from $\Gamma_\infty = 4.2 \cdot 10^{-10}$ to $3.6 \cdot 10^{-10}$ mole/cm² in the case of camphor and from $\Gamma_\infty = 4.1 \cdot 10^{-10}$ to $2.95 \cdot 10^{-10}$ mole/cm² in the case of adamantanol.

According to the data obtained, at the large values of the attraction constant which we obtained for adamantanol and camphor, the adsorption–desorption peaks on the C vs E curves should be completely absent. The experimental C vs E curves with very narrow and high peaks in the presence of camphor which were obtained in [11, 12] can probably be attributed to the nature of the adsorption layer at the low ac frequencies used in those studies. As has been shown theoretically in [13], in the case of two-dimensional condensation, when a variable voltage in the range of the adsorption–desorption potential is applied to the electrode, relatively smooth changes in θ with the potential, whose form depends on the ratio between the rate of diffusion and of the adsorption–desorption of the organic compound, rather than instantaneous changes in the degree of filling from $\theta = 0$ to $\theta = 1$, should occur owing to the finite rate of diffusion. Thus, in a low-frequency ac field, at the adsorption–desorption potentials the two-dimensional condensed layer is, so to speak, partially eroded, and the attraction constant is lower than its equilibrium value for a two-dimensional condensed layer.

This study, whose findings were discussed in detail with A. N. Frumkin, was the last of the studies he reviewed on polarographic maxima of the third kind, which were part of a

series of investigations that were undertaken under his initiative and carried out under his direct supervision.

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INTERACTION OF THE OXYGEN RADICAL ANION $O_2^{\cdot-}$ WITH Fe(III) PORPHYRINS. A NEW OXYGENATED HEME COMPLEX

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It was established long ago that the natural complexes hemoglobin (Hb) and myoglobin (Mb) form the oxygenated complexes HbO_2 and MbO_2, which are oxygen carriers in living cells, at room temperature, while the simpler Fe(II) complexes react with oxygen in an irreversible manner to form Fe(III)—O—Fe(III) dimers. It has also been shown that HbO_2 is capable of dissociating into Hb and $O_2^{\cdot-}$ either spontaneously [1] or in ligand-substitution reactions [2]. The reverse reaction, i.e., the reduction of Fe(III) porphyrins by the oxygen radical anion has been studied to a considerably lesser extent. It has been shown that O_2 reduces methemoglobin [which contains Fe(III)] to oxyhemoglobin [3] and ferricytochrome c to ferrocytochrome [4], the latter reaction occurring without the intermediate formation of an oxygenated complex, i.e.,

$$O_2^{\cdot-} + \text{met Hb} \rightleftharpoons [\text{met HbO}_2^{\cdot-}] \rightleftharpoons \text{HbO}_2, \quad (1)$$

$$O_2^{\cdot-} + \text{cyt. c (Fe(III))} \rightleftharpoons \text{cyt. c (Fe(II))} + O_2. \quad (2)$$

According to the data in [5], the radical anion of O_2 forms an oxygenated Fe(II)O_2 complex with the dimethyl ester of Fe(III) protoporphyrin IX at −50°C in dimethylformamide.

In the present work we investigated the interaction of $O_2^{\cdot-}$, which was obtained by the electrochemical reduction of oxygen, with the following Fe(III) porphyrins: Fe(III) protoporphyrin IX [Fe(III)PP], hemin c, the dimethyl ester of Fe(III) protoporphyrin IX [Fe(III) DMPP], Fe(III) deuteroporphyrin [Fe(III)DP], and Fe(III) coproporphyrin [Fe(III)CP]. In a number of experiments the complex with dibenzo-18-crown-6 (crown·O_2) served as the source of O_2. The reactions were carried out in an inert gas atmosphere at room temperature in dimethylformamide (DMF) and, in some cases, in dimethyl sulfoxide (DMSO) and acetonitrile (CH_3CN). After preliminary scavenging by argon, the solutions of the reagents were transferred to hermetically sealed spectrophotometer cuvettes. The absorption spectra were recorded on a Specord UV-VIS spectrophotometer. The spectral characteristics of the original complexes and the reaction products are presented in Table 1.

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