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POLAROGRAPHIC MAXIMA OF THE THIRD KIND, AND TWO-DIMENSIONAL
CONDENSATION OF ORGANIC SUBSTANCES IN THE ADSORPTION LAYER

E. V. Stenina, N. V. Fedorovich,
I. V. Osipov, and V. A. Yusupova

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It is established at the present time that polarographic maxima of the third kind only arise in the adsorption of organic surface-active substances (surfactants) forming two-dimensional condensed layers at the mercury/solution interface [1-3]; the most favorable conditions for development of the motions are found at degrees of coverage (θ) between 0.1 and 0.5 [4-6]. A number of characteristic signs for the two-dimensional condensed layers of organic substances have been reported in [7]. It follows from [8] that two-dimensional condensation should occur at high values of the attraction constant α contained in the Frumkin isotherm ($\alpha \geq 2$).

The difference in the intensities of motions of the third kind in the presence of various organic surfactants and in the form of the phase change at the adsorption-desorption potentials indicate that there are significant differences in the character of the two-dimensional condensed layers [9, 10]; this is due to changes in the intensity of attractive interactions. The usual methods [11] cannot be used to determine α for these substances since adsorption-desorption peaks on the differential capacity-potential (C vs E) curves are lacking, or do not correspond to equilibrium [12]. A method in which α is determined by comparison of experimental C vs E curves with curves calculated theoretically for different values of the attraction constant was suggested in [13]. The α value found by this method for adamantanol is 5.5. The most intense motions of the third kind are observed in the adsorption of adamantanol and of a number of organic surfactants which, like adamantanol, probably have high α values, since the C vs E curves of these substances, like those of adamantanol, are characterized by a sharp phase change from $\theta = 1$ to $\theta = 0$ [4]. Adsorption of, for example, pelargonic acid for which α at the zero-charge potential is 1.5 gives rise to small polarographic maxima of the third kind only at the adsorption-desorption potentials [3]. Differences in the α values are evidence for different capacities of the organic surfactant molecules for aggregation. The pronounced ability for aggregation found in a number of substances can lead to the formation of large aggregates or clusters of organic surfactant molecules at the mercury/electrolyte interface even at low degrees of coverage. This is one of the reasons why on the surface of the mercury electrode, appreciable surface-tension gradients appear which are sufficient to set the mercury surface in motion in a tangential direction. A mechanism explaining the development of polarographic maxima of the third kind from these ideas had been suggested by us in [3].

Aggregate formation at the gas/liquid interface had been suggested in the work of Frumkin [14], and is not doubted now in the adsorption of insoluble organic surfactants [15]. In a number of cases the existence of such aggregates at the liquid/gas interface has been ascertained experimentally [16, 17]. In the case of the mercury/electrolyte interface, the possibility that organic surfactant molecules form aggregates had been pointed out in [18-23]. Heterogeneity of the adsorption layers was predicted theoretically in [24] for the case where two-dimensional condensed layers are forming at the mercury/solution interface.

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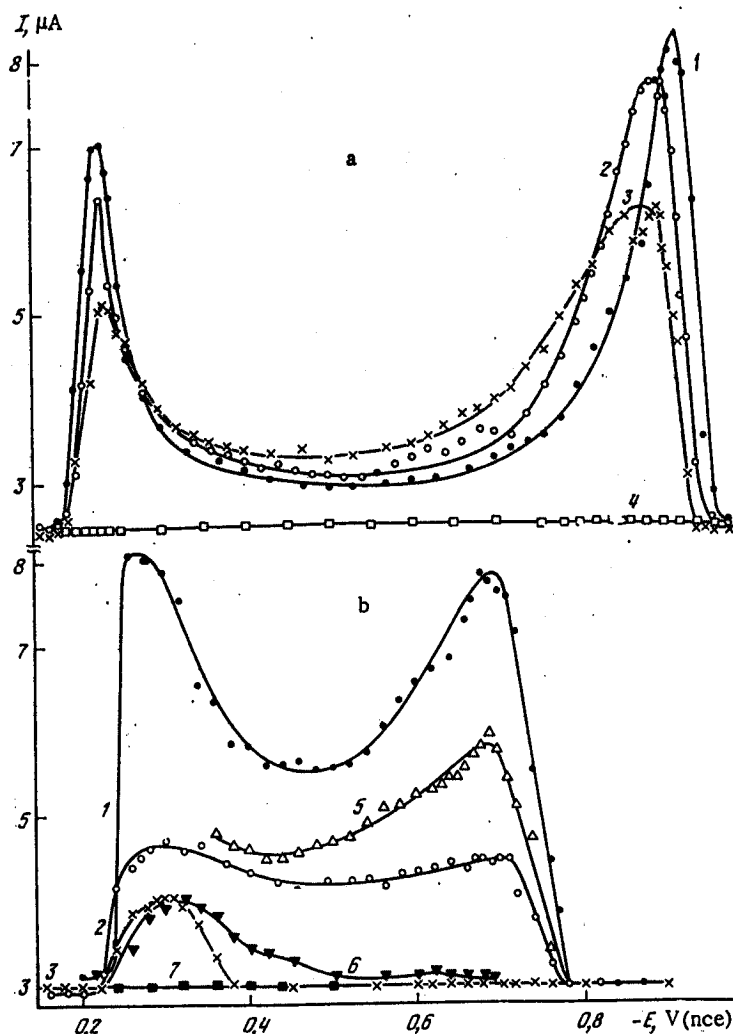


Fig. 1. Polarization curves recorded in the presence of different concentrations of ethyl alcohol in $7 \cdot 10^{-4}$ M CuSO_4 + 1.0 M Na_2SO_4 solution with $6.0 \cdot 10^{-5}$ M AdOH (a) and $6 \cdot 10^{-5}$ M borneol (b). The alcohol concentrations: 1) 0, 2) 0.065, 3) 0.17, 4) 0.86, 5) 0.034, 6) 0.099, and 7) 0.34 M.

Sections of two types should exist on the surface in this case: those with θ close to zero, and those with θ close to unity. Under certain conditions this can cause the diffuse part of the double layer to split up in accordance with the two types of section existing on the surface, i.e., lead to nonequipotentiality of the outer Helmholtz plane; this conclusion was experimentally confirmed in [25].

Heterogeneity of an adsorption layer of organic surfactants can be upset, and may gradually disappear, under the influence of various factors. Thus, coadsorption of ethyl alcohol leads to destruction of the condensed layers of adamantanol and camphor, as demonstrated by lower values of the attraction constant [13]. At the same time the two-dimensional clusters become diffuse, gradually decrease in size, and as a result the potentials at the outer Helmholtz plane are smoothed out [26]. Experimental data for the effect of ethyl alcohol adsorption on the two-dimensional condensed layers of a number of the organic surfactants examined show that these layers are more difficult to destroy the higher the surface activity of the surfactant [26]. This indicates that the surface activity of these materials is chiefly determined by interaction of the adsorbate-adsorbate type. This interaction type, and hence the aggregation tendency, can be weakened not only by coadsorption of foreign organic surfactants but also when the organic material has π -electron interaction with the mercury surface or is adsorbed in the form of ions, which gives rise to stronger repulsive interaction between the adsorbed particles. We believe that materials of this type should

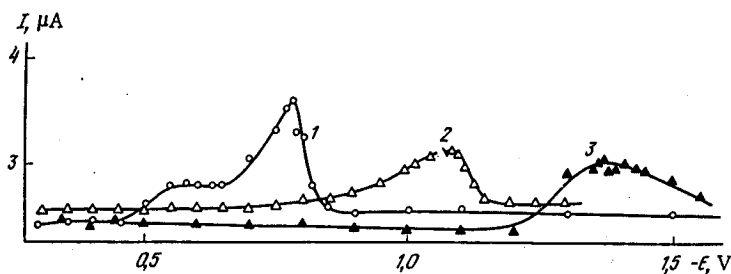


Fig. 2. Polarization curves recorded in $5 \cdot 10^{-4}$ M CuSO_4 + 1.0 M Na_2SO_4 solution with added materials: 1) $5 \cdot 10^{-5}$ M guanine, 2) 10^{-5} M 5-methylcytosine, and 3) $6 \cdot 10^{-5}$ M tribenzylmethylammonium sulfate.

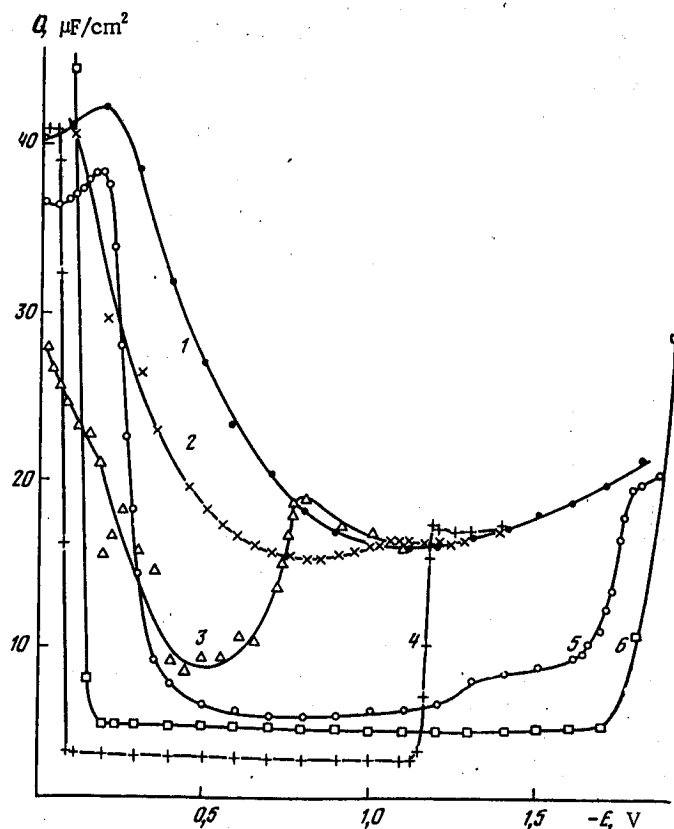


Fig. 3. Potential dependence of the differential capacity in the solutions: 1) 1 M Na_2SO_4 , 2) 0.5 M Na_2SO_4 + 10^{-5} M 5-methylcytosine, 3) 1 M Na_2SO_4 + 10^{-4} M guanine, 4) 1 M Na_2SO_4 + $3 \cdot 10^{-4}$ M adamantanol, 5) 0.1 M Na_2SO_4 + $3 \cdot 10^{-5}$ M tribenzylmethylammonium sulfate, and 6) 0.5 M Na_2SO_4 + 10^{-4} M decamethylene-bis(N-dimethyl-N-adamantanylammonium chloride).

be less surface-active, have a weaker tendency for cluster formation, and hence be less able to give rise to tangential motions of the third kind.

In the present work we examine the effect of ethyl alcohol adsorption on the intensity of the tangential motions of the third kind arising in adamantanol and borneol adsorption. In addition we examine the development of polarographic maxima of the third kind in the adsorption of guanine and 5-methylcytosine, which display π -electron interaction with the mercury, and also in the adsorption of some organic cations. The working procedure has been described in [1-4]. Figure 1 presents the polarization curves recorded in $7 \cdot 10^{-4}$ M CuSO_4 + 1 M Na_2SO_4 solution containing $6 \cdot 10^{-5}$ M AdOH or borneol and different amounts of ethyl alcohol. The heights of the polarographic maxima decrease when ethyl alcohol is added, and they disappear completely when its concentration reaches 0.86 M in the case of adamantanol, and

0.34 M in the case of borneol. It must be noted that coadsorption of ethyl alcohol causes the adsorption regions of borneol and adamantanol on the mercury electrode to become narrower:

Polarization curves for Cu^{2+} ion discharge from 1 M Na_2SO_4 solution recorded in the presence of guanine, 5-methylcytosine, and tribenzylmethylammonium sulfate are presented in Fig. 2. In the adsorption of all these substances, polarographic maxima are observed only at the adsorption-desorption potentials. These maxima are significantly lower, and the potential range over which they develop is wider, than in the presence of, e.g., adamantanol (Fig. 1, curve 1). The capacity peaks at the adsorption-desorption potentials are missing in the C vs E curves recorded for these substances (Fig. 3, curves 2, 3, 5, and 6), but the transition from $\theta = 1$ to $\theta = 0$ is accomplished within a rather wider potential span than, e.g., for adamantanol (Fig. 3, curve 4). According to the data of [13], a wider region of phase changes indicates that the attraction constant is lower. The lower intensity of the tangential motions of the third kind in these systems is due to a lower tendency for aggregation in these systems, which according to the above can have different reasons. Thus, the decrease of the polarographic maxima in the presence of ethyl alcohol (Fig. 1) is due to a coadsorption of the ethyl alcohol with the adamantanol, which drastically lowers the intensity of attractive interaction of the molecules in the condensed layer, and hence causes them to become diffuse. In the adsorption of guanine and 5-methylcytosine, the decrease in the attraction constant can be due to the stronger adsorbate-mercury bond arising from the π -electron interaction. The presence of this interaction is confirmed by the observation that guanine is adsorbed over the entire range of positive surface charge densities that is accessible to the measurements. In the case of the organic cations examined, the attraction constant is lower because of the stronger repulsive interaction arising from the charge that is present on the adsorbed particles.

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ANODIC OXIDATION OF CALCIUM IN THE CaI_2 -DIMETHYLFORMAMIDE SYSTEM

L. I. Stolyarenko, M. I. Strachkov,
and A. G. Demakhin

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The use of calcium as a promising anode material in chemical power sources with organic solvents is mentioned in the patent literature [1-6]. However, many difficulties are encountered in making an actual power source with calcium anodes. One of these difficulties is the selection of a solvent and the assembly of an electrolyte system in this solvent from which one can draw high current densities at low electrode polarization. In the present work we report results obtained when investigating the physicochemical properties of CaI_2 -DMF (dimethylformamide) electrolyte and the anodic dissolution of calcium in solutions of this electrolyte. All experiments and preparative operations were conducted in a dry box (dew point -40°C). Special care was taken in purifying and drying the solvent. Grade "ch." ["pure"] DMF was dried for a day over solid KOH, then distilled under atmospheric pressure, and finally distilled *in vacuo*. The fraction with a boiling point of 153°C and $n_D^{25} = 1.4290$ was selected. The water content determined by Karl Fischer was $10^{-2}\%$.

Appreciable experimental difficulties in making anhydrous calcium iodide forced us instead to use its DMF-containing crystal solvate in determining the solubility and preparing the electrolyte solution. To obtain this the commercial grade "ch." crystal hydrate was subjected to dehydration *in vacuo*. The drying conditions at a residual pressure of 10^{-2} atm (101.3 N/m^2) were: 1 h each at 40 , 60 , and 120°C , and 3 h at 300°C . The sample thus prepared was transferred into dry-box atmosphere, and dissolved in cooled DMF to obtain a saturated solution. The solid phase isolated after a second recrystallization and drying *in vacuo* at 50°C to constant weight had a melting point of 85°C . It was seen by elementary and gravimetric analysis and also by argentometric titration that the composition of the crystal solvate can be written as $\text{CaI}_2 \cdot 7\text{DMF}$, which is in harmony with the data of [7].

To determine the range over which the system is in the homogeneously liquid state we determined the solubilities by isothermal saturation; solution samples were analyzed for iodide ions by precipitation in the form of silver iodide. The results of analysis expressed as nonsolvated CaI_2 are reported below:

t, $^\circ\text{C}$	Solubility (g/100 g solution)	t, $^\circ\text{C}$	Solubility (g/100 g solution)
-20	10.2	10	17.4
-10	12.0	20	19.8
		30	22.3
0	14.4	40	24.7

The data obtained show that the solubility of calcium iodide increases linearly with temperature. A calculation shows that in terms of normality, throughout the temperature range electrolyte solutions with CaI_2 concentrations of no more than 0.9 N can exist. It was determined experimentally that the bottom phase remains unchanged at all temperatures, and has a composition that can be written as $\text{CaI}_2 \cdot 7\text{DMF}$.

The electric conductivity of the calcium iodide solutions was determined at 2000 Hz with an R-568 ac bridge in cells with platinum electrodes. Over the temperature range from 0 to 35°C (in steps of 5°C) the cell constants were determined using 0.1 N potassium chloride solution; at the other temperatures they were calculated by extrapolation of the experimental data.

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