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DEVELOPMENT OF POLAROGRAPHIC MAXIMA OF THE THIRD KIND DURING THE GROWTH OF THE SURFACE OF A DROPPING MERCURY ELECTRODE

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The adsorption of certain organic surfactants, which form two-dimensional condensed layers on the boundary of two liquid phases of mercury and a solution results in the appearance of tangential motions of the mercury surface and an increase in the rate of electrochemical reactions which are limited by the diffusion step. The current maxima which are observed in this case on the polarization curves have been termed polarographic maxima of the third kind [1]. These maxima appear as a result of the nonuniform adsorption of the organic surfactants over the surface of the dropping electrode, the formation of large associates from the organic molecules [2, 3] resulting in the appearance of regions with sharply different values of the surface tension σ on the surface of the drop. The phenomena associated with the hydrodynamic instability of the phase boundary, which is due to the σ gradient on that boundary, are known as the Marangoni—Gibbs effect [4]. Thus, polarographic maxima of the third kind may be treated as a special case of this effect [5].

In [6-8] it was established that the highest values of the maximum currents are achieved at a given potential E at degrees of filling (θ) of the surface by the organic compound ranging from 0.1 to 0.5, the changes in θ being achieved by changing the volume concentration (c) of the organic surfactant. The value of θ can also be varied at c = const by varying the concentration of the supporting electrolyte owing to the salting-out effect [9]. Investigations of polarographic maxima of the third kind have been carried out on the dropping mercury electrode, the polarization curves, I(E), and the plots of the differential capacitance C(E) having been recorded with the use of practically identical capillary tubes, and the values of I and C having been determined at the end of the life of the mercury drop.

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M. V. Lomonosov Moscow State University. Translated from Doklady Akademii Nauk SSSR, Vol. 236, No. 1, pp. 161-164, September, 1977. Original article submitted March 30, 1977.

0012-5016/77/0009-0869$07.50

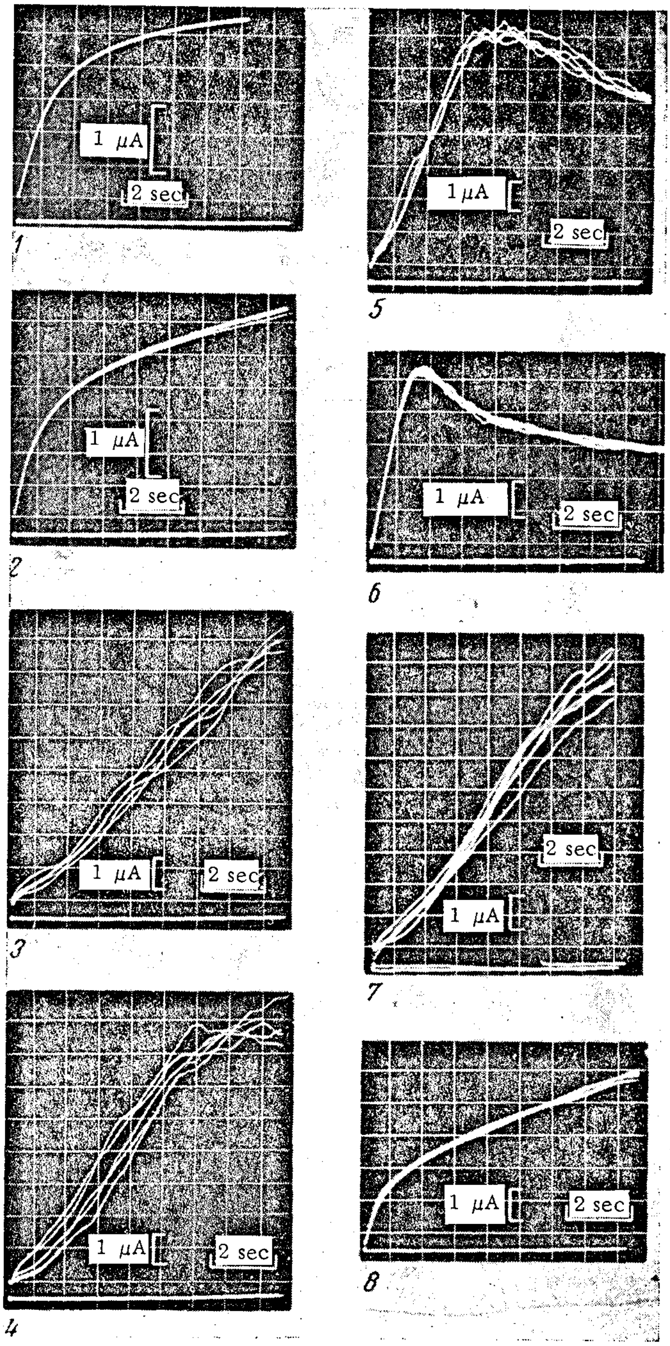

Fig. 1. Dependence of the current flowing in a dropping mercury electrode on the time in a solution of $7 \cdot 10^{-4}$ M $CuSO_4$ + 1 M Na_2SO_4 with additions of AdOH in a concentration of $6 \cdot 10^{-5}$ M (1–6) at various values of the potential (V): 1) E = −1.402; 2) E = −0.905; 3) E = −0.92; 4) E = −0.901; 5) E = −0.85; 6) E = −0.52; and with an addition of AdOH in a concentration of $1.8 \cdot 10^{-4}$ M at E = −1.036 (7) and $2 \cdot 10^{-5}$ M at E = −0.497 V (8).

Such a procedure did not make it possible to investigate the development of the tangential motions and the formation of the adsorption layer during the growth of the drop, which information is important for devising a theory for the phenomena studied.

In the present work we carried out an investigation of the appearance and development of polarographic maxima of the third kind on the dropping mercury electrode on the basis of

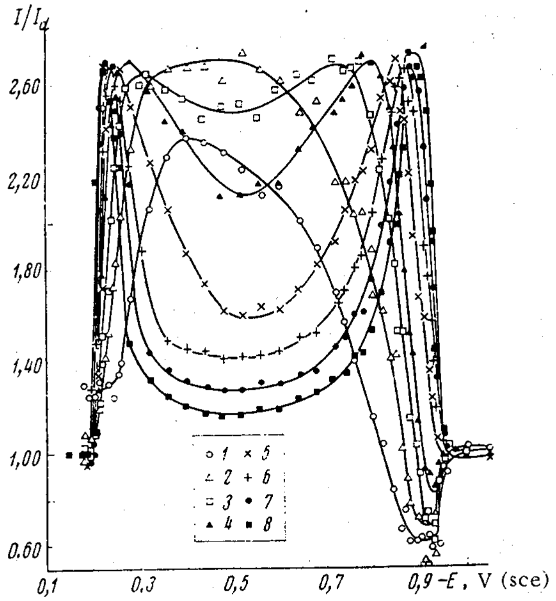

Fig. 2. Polarization curves in a solution of $7 \cdot 10^{-4}$ M $CuSO_4$ + 1 M Na_2SO_4 + $6 \cdot 10^{-5}$ M AdOH constructed from I(t) plots for various values of the time (sec) from the beginning of the growth of the drop: 1) 0.5; 2) 1.0; 3) 1.5; 4) 2.0; 5) 3.0; 6) 4.0; 7) 5.0; 8) 6.0.

measurements of the dependence of the current flowing in the mercury on the time t at E = const. The recording of the I(t) plots was carried out with the aid of a model OZ TsLA oscillographic polarograph. Figure 1 (curves 1-6) presents photographs of several I(t) curves for various values of E in a solution of $7 \cdot 10^{-4}$ M $CuSO_4$ + 1 M Na_2SO_4 + $6 \cdot 10^{-5}$ M adamantanol (AdOH). These data were used to construct plots of I(E) for different values of t (Fig. 2). As we see, for the small values of the time (0.1-0.5 sec) and $c = 6 \cdot 10^{-5}$ M, the I(E) curve shows one maximum. As the time for the growth of the drop is increased to t = 1.5 sec, the current in the vicinity of the potential of the electrocapillary maximum decreases, and the maximum gradually bifurcates (t = 2-6 sec).

Along with the recording to the I(t) plots, we carried out the recording of C(E) plots on an apparatus which permits the measurement of the capacitance of the double layer at different moments in the life of a drop, beginning with 10^{-1} sec (Fig. 3). As t increases, the differential capacitance decreases. The data presented were used to calculate the values of θ for the same moments in the life of the drop for which the I(E) plots were constructed (Fig. 2). These data show that θ increases with increasing t.

Let us consider the nature of the dependence of the current on the time for various potentials. At E = –1.402 V (Fig. 1, curve 1), which corresponds to $\theta \approx 0$ and the absence of tangential motions on the surface of the mercury drop, the current is proportional to $t^{1/6}$, which is characteristic of electrochemical reactions whose rates are determined by diffusion under the condition that the surface of the dropping mercury electrode moves only in the radial direction. At E = –0.905 V (Fig. 1, curve 2), at which AdOH begins to be adsorbed on the mercury–solution interface, an increase in the current associated with the tangential motions is observed only at the end of the life of the drop ($t \geqslant 5$ sec). At E = –0.920 V (Fig. 1, curve 3), at which the degree of filling which is optimal for the development of the motions is achieved at the end of the life of the drop, the dependence of the current on the time is practically linear over the course of the entire life of the drop, this being significantly different from the conditions for diffusion to a radially expanding drop. The presence of tangential motions is also manifested in the irregular nature of the I(t) curves (Fig. 1, curves 3-8) and some difference between the I(t) curves recorded on different drops due to the nonequilibrium nature of the phenomenon under study. The values of the currents in Fig. 2 were determined by averaging 5 to 10 instantaneous current values.

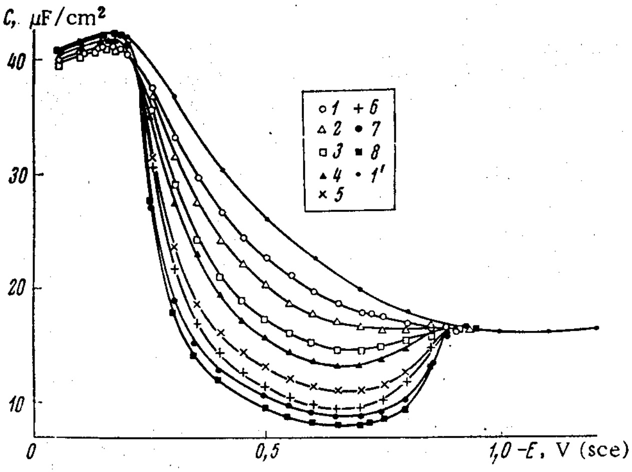

Fig. 3. Dependence of the differential capacitance on the potential in a solution of 1 M Na_2SO_4 + $6 \cdot 10^{-5}$ M AdOH for various values of the time from the beginning of the growth of the drop: 1-8) Same as in Fig. 2; 1') plot of C(E) in 1 M Na_2SO_4.

The rate of adsorption increases as the potential of the maximum adsorption E_{max} is approached ($E_{max} = -0.560$ V for adamantanol), causing a shift of the range of optimum degrees of filling to smaller values of the time and an increase in θ at the end of the life of the drop. The general shape of the I(t) curves also changes as a result: Upon the transition from $E = -0.920$ to $E = 0.901$ V (Fig 1, curve 4) the current ceases to increase at the end of the life of the drop. At $E = -0.850$ V (Fig. 1, curve 5) the slowing of the tangential motions at the end of the life of the drop is already appreciable, and the maximum development of the motions occurs in the middle of the life of the drop. At a potential of -0.520 V, which is close to E_{max}, the degrees of filling which are optimal for the development of motion are achieved approximately 1 sec after the breaking away of the previous drop, and the maximum values of the currents under these conditions are thus observed at the same time (Fig. 1, curve 6). Similar laws are also observed for the maximum with positive charges on the surface.

The measurements of the I(t) curves were also carried out in solutions of adamantanol with $c = 2 \cdot 10^{-5}$ M and $c = 1.8 \cdot 10^{-5}$ M, and the main laws in these solutions are similar to those described above (Fig. 1, curves 7 and 8).

Our comparison of the I(E), C(E), and θ(E) under the conditions $c = 6 \cdot 10^{-5}$ M and $t = 1$ sec shows that the appearance of the polarographic maxima of the third kind is due to the adsorption of organic surfactants, in agreement with the previously established laws.

The comparison of the dependence of I on θ for several potentials in the vicinity of the maximum adsorption shows that the most intense motions of the mercury surface are observed at θ values ranging from 0.1 to 0.5. This is consistent with the results obtained by other methods [6-8].

The analysis of the C(t) curves we obtained shows that, unlike most organic surfactants, in the case of the adsorption of AdOH, the slowness of the adsorption step itself, along with the slowness of the diffusion step, has a significant effect on the adsorption kinetics.

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PHYSICOCHEMICAL ANALYSIS OF EXTRACTION SYSTEMS WITH NEUTRAL REAGENTS

UDC 542.621

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Physicochemical analysis, whose principles were developed by N. S. Kurnakov et al. [1, 2], has been widely used for the determination of the composition and type of compounds forming in liquid and solid solutions from composition—property diagrams. The use of the methods employing isomolar series, displacement of the equilibrium, saturation, and so forth for the determination of the solvate numbers q_i, as well as the construction of partition-coefficient—composition diagrams in the analysis of the partition of inorganic compounds in heterogeneous liquid—liquid systems, usually does not lead to unambiguous results [3, 4].

The extraction of acids and salts of metals by neutral organic reagents is accompanied by the formation of hydrated solvates [5]. In the case of the partition of a one-to-one electrolyte upon the formation in the system of hydrated solvates which are undissociated in the organic phase, we can write

$$\sum p_i \mathrm{MX} + \sum q_i \bar{\mathrm{S}} + \sum h_i \mathrm{H_2O} \rightleftharpoons \sum \overline{(\mathrm{MX})_{p_i} \mathrm{S}_{q_i} \mathrm{H_2O}_{h_i}},$$

where M and X are the cation and anion of the substance being extracted, S is the extractant, h_i is the extent of hydration, and the bar above the letters signifies here and in the following that the component or its property belongs to the organic phase.

With consideration of the equations of material balance and the definition of the activity of a solute in an organic solvent in the presence of water [6], the expression for the calculation of the thermodynamic partition (P^t) and extraction (K^t) constants becomes

$$P = \bar{m}/a = \sum p_i P_i^{t} \bar{\gamma}_i^{*} \exp\{h_{0,i} Y\} \tag{1}$$

and

$$P = \sum p_i K_i^{t} (\bar{m}_{\mathrm{s}}^{\mathrm{in}} - \sum q_i \bar{m}_i)^{q_i} \bar{\gamma}_{\mathrm{s},i}^{q_i} / \bar{\gamma}_i^{*} \exp\{h_{0,i} Y\}, \tag{2}$$

where a is the activity of the partitioned substance in the equilibrium aqueous solution, $Y = (a_W - 1)(1 - \ln a_W)$, a_W is the equilibrium activity of water in the system, $\bar{m}$ and $\bar{m}_i$ are the molar concentrations of the partitioned substance and the corresponding complexes in the organic phase, $\bar{m}_S^{in}$ is the initial concentration of the extractant, γ_i^* is the activity coefficient of the partitioned substance in the dry extractant, $\bar{\gamma}_{S,i}$ is the activity coefficient of the "free" extractant, and P is the effective partition constant. As before [6], it is assumed that the extent of hydration h_i is linearly dependent on the activity of the water $h_{0,i}$ and $h_{q,i}$, i.e., the extent of hydration of the complexes in the organic phase when $a_W = 1$. The activity of the complexes in the organic phase is defined relative to hypothetical solutions of unit molarity with the properties of infinitely dilute solutions in the extractant saturated with water when $a_W = 1$.

The values of P and Y are easily found from the experimental data. From Eqs. (1) and (2) it follows that the plots of the dependence of ln P on Y in the case of the formation

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D. I. Mendeleev Moscow Chemical-Engineering Institute. Translated from Doklady Akademii Nauk SSSR, Vol. 236, No. 1, pp. 165-167, September, 1977. Original article submitted May 30, 1977.

0012-5016/77/0009-0873$07.50