POlarographic maxima of the third kind. III*

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In 1959 Doss and Venkatesan1 were the first to observe the tangential motions and current maxima on the polarographic I, φ curves of the copper ions reduction at the adsorption–desorption potentials of sodium dioctylsulfosuccinate. We suggested to call these current maxima, which are due to the tangential motions caused by the adsorption process itself, polarographic maxima of the third kind2.

It has been shown by us3–5.11 that the polarographic maxima of the third kind arise over the whole range of potentials of organic substances adsorption if the surface coverage (θ) is not too large (0.2–0.5). The connection between the maxima of the third kind and the adsorption–desorption potentials, established in earlier work6, is accounted for by the fact that in the vicinity of these potentials the surface coverage varies abruptly from unity to zero2. This paper reports some new data obtained by the authors on the conditions of appearance of the polarographic maxima of the third kind.

In spite of the diversity of the organic compounds whose adsorption is attended by the appearance of these maxima, they have a common property, viz. under equilibrium conditions they form two-dimensional condensed layers at the mercury/solution interface, which can be described by means of the so-called Frumkin isotherm with the attraction constant values7–9 a > 2. In this case, no pronounced adsorption–desorption peaks appear on the C, φ curves, but they show an abrupt transition from θ = 1 to θ = 0 and under equilibrium conditions, in a wide concentration range the minimum capacity value does not depend markedly on the organic substance concentration in solution. Figure 1 (curves 4–7) shows the C, φ curves for camphor, borneol, adamantanol-1, adamantonic acid, whose adsorption is attended by the appearance of the polarographic maxima of the third kind**. Similar C, φ curves and current maxima on the I, φ curves have been obtained by us for aminoadamantanone hydrochloride, adamantanone, acetoaminoadamantanone, guanine, 5-methylcytosine, tribenzylmethylammonium sulfate.

All these compounds are sparingly soluble in water and strongly surface active. But if a substance of similar structure does not form two-dimensional condensed layers under equilibrium conditions, no polarographic maxima of the third kind appear during its adsorption. As an example, Fig. 1 (curves 2, 3) shows

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* Dedicated to Prof. K. S. G. Doss on the occasion of his reaching his 70th year.
** All potentials are referred to the NCE.
Fig. 1. Dependence of differential capacity on potential in 1 M Na$_2$SO$_4$ (1); with additions of (2) 0.1 M urotropin; (3) $2 \times 10^{-3}$ M adamantane diol; (4) $6 \times 10^{-4}$ M bornol; (5) $2.8 \times 10^{-4}$ M adamantyl acid; (6) $3 \times 10^{-4}$ M adamantanol-1; (7) $7 \times 10^{-4}$ M camphor.

the $C, \varphi$ curves obtained in the presence of urotropin and adamantane diol, which unlike other substances with diamond-like structure, do not cause tangential motions of the mercury surface. As is clear from the figure, the adsorption behavior of these substances is similar to that of other organic substances with $a < 2$.

It was of interest to study the appearance of the polarographic maxima during the adsorption of organic substances with a simple structure. For this purpose, we have chosen 2-oxo adamantane, a compound of diamond-like structure which has no substituents in the side chain and a saturated normal fatty acid: C$_8$H$_{17}$COOH (pelargic acid).

Figure 2 shows the $I, \varphi$ curves obtained for $10^{-3}$ M AgNO$_3$ + 1 M Na$_2$SO$_4$ solution with additions of varying amounts of 2-oxo adamantane (OxAd). When $4.1 \times 10^{-5}$ M OxAd is introduced into the solution (Fig. 2, curve 2), in the region of the potential of zero charge a current increase is observed over its diffusion controlled limiting value in the absence of OxAd (Fig. 2, curve 1). With rising
OxAd concentration, the maximum current increases and the region of the potentials of the polarographic maximum of the third kind widens (Fig. 2, curves 3–6). Further increase of the OxAd concentration leads to the splitting up of the maximum and to a current decrease in the region of the potential of zero charge (Fig. 2, curves 7–13). Two maxima appear on the $I, \varphi$ curves at positive and negative charges of mercury surface, which with increasing OxAd concentration shift in the direction of higher surface charges. At the highest OxAd concentrations the current maxima are observed only at the desorption potentials (Fig. 2, curve 13).

We measured also the dependence of the differential capacity on potential (Fig. 3). It follows from the comparison of the $I, \varphi$ and $C, \varphi$ curves that the polarographic maxima of the third kind appear in the range of potentials of the organic substance adsorption at small concentrations of the addition (Fig. 2, curves 2–6) when the mean surface coverage is relatively small. Figure 4 shows the dependence of the maximum current in the presence of OxAd on the surface coverage, calculated from the $C, \varphi$ curves. As it follows from these data, the development of the motions during the adsorption of OxAd is maximum at the measured surface coverages 0.2–0.5. Inasmuch as the maxima of the third kind
Fig. 3. Dependence of differential capacity on potential in 1 M Na₂SO₄ with additions of 2-oxo-adamantane in the concentrations: (1) 0, (2) 4.5 x 10⁻⁵, (3) 5.5 x 10⁻⁵, (4) 5.6 x 10⁻⁵, (5) 5.75 x 10⁻⁵, (6) 6.0 x 10⁻⁵, (7) 7.0 x 10⁻⁵, (8) 8.0 x 10⁻⁵, (9) 9.0 x 10⁻⁵, (10) 1.1 x 10⁻⁴, (11) 1.5 x 10⁻⁴, (12) 3.3 x 10⁻⁴, (13) 5.0 x 10⁻⁴ M.

arise during the adsorption of the organic substances which form two-dimensional condensed layers at the mercury/solution interface under equilibrium conditions, we can assume that at relatively low mean coverages the interaction between molecules still remains strong. In this case there exists perhaps on the surface of the mercury drop at a definite mean coverage a most favorable ratio between the areas in which the surface tension is strongly reduced and those with higher values of the surface tension. However this question should be studied further.

As has been shown in ref. 11, the dependence of the rate of tangential motions of the drop surface on potential is similar to the potential dependence of the quantity (\(\frac{\partial \Gamma}{\partial c}\)). From the \(C, \phi\) curves of Fig. 3 we have calculated the values of (\(\frac{\partial \Gamma}{\partial c}\)) during the adsorption of 2-oxoadamantane (Fig. 5). As can be seen from Fig. 5, the dependence of the function (\(\frac{\partial \Gamma}{\partial c}\)) on potential in solutions with different OxAd concentrations is similar to the dependence on potential of the current value (Fig. 2). A more detailed comparison of the \(I, \phi\) and (\(\frac{\partial \Gamma}{\partial c}\)) curves (Fig. 6) shows that the potentials of the maxima of the third kind coincide with those of the maximum slope of the experimentally determined adsorption isotherm, as was earlier observed for borneol and adamantanol¹¹. It should,
Fig. 4. Dependence of the current value of the maximum in the presence of 2-oxoadamantane on the surface coverage at different potentials: (1) \( \varphi = -0.45 \) V, (2) \( \varphi = -0.80 \) V, (3) \( \varphi = -0.60 \) V.

Fig. 5. Dependence of \( (\partial I/\partial c)_S \) on potential in 1 \( M \) Na\(_2\)SO\(_4\) in the presence of 2-oxoadamantane in the concentrations: (1) \( 5.5 \times 10^{-5} \), (2) \( 5.6 \times 10^{-5} \), (3) \( 5.75 \times 10^{-5} \), (4) \( 6.0 \times 10^{-5} \), (5) \( 7.0 \times 10^{-5} \), (6) \( 8.0 \times 10^{-5} \), (7) \( 9.0 \times 10^{-5} \), (8) \( 1.1 \times 10^{-4} \), (9) \( 1.5 \times 10^{-4} \), (10) \( 3.3 \times 10^{-4} \) M.

however, be kept in mind that the values obtained from differential capacity measurements are averaged over the drop surface, the adsorbed layer being certainly inhomogeneous.

The surface coverage with organic substance depends on its activity in the solution bulk\(^8\). The activity of an organic substance at its constant bulk concentration can be varied by changing the supporting electrolyte concentration. The increase in the activity with increasing supporting electrolyte concentration \( c_0 \), that is the salting out effect, is described quantitatively by Sechenov's semi-empirical formula

\[
S''/S = \frac{f^o}{f} = 10^{Kc},
\]

where \( f^o \) and \( f \) are the activities of the organic substance, \( S^o \) and \( S \) its solubilities in water and in the supporting electrolyte solution, respectively and \( K \) the salting out constant\(^{10}\).

We have studied the influence of the supporting electrolyte Na\(_2\)SO\(_4\)...
Fig. 6. Comparison of the $I, \varphi (1, 2)$ and $(\partial I/\partial \varphi)_{0}, \varphi (1', 2')$ curves at 2-oxoadamantane concentrations $5.5 \times 10^{-5}$ M (1, 1') and $1.1 \times 10^{-4}$ M (2, 2').

concentration on the appearance of the maxima of the third kind in solutions of camphor and borneol. Fig. 7 shows the polarization curves of reduction of the silver cation in the presence of $10^{-4}$ M borneol in $\text{Na}_2\text{SO}_4$ solutions of varying concentration. As is clear from the figure, in 1 M $\text{Na}_2\text{SO}_4$ two current maxima are observed in the region of positive and negative surface charges in the neighborhood of the adsorption–desorption potentials of borneol. When passing from 1 M to 0.3 M $\text{Na}_2\text{SO}_4$ solution, the polarographic maxima shift into the region of smaller surface charges. As the $\text{Na}_2\text{SO}_4$ concentration decreases further, only one polarographic maximum is observed in the region of the potential of zero charge. Similar data have been obtained for camphor.

In accordance with the above conclusions concerning the relationship between the value of the current maximum of the third kind and the surface coverage with organic substance, it follows from Fig. 7 that the range of potentials of the organic substance adsorption widens and the coverage at a given potential increases with increasing supporting electrolyte concentration. In this connection,
Fig. 7. Dependence of current on potential during the reduction of Ag\(^+\) in 10\(^{-3}\) M AgNO\(_3\) + 10\(^{-4}\) M borneol + Na\(_2\)SO\(_4\) solutions of different concentrations: (1) 0.1, (2) 0.3, (3) 0.5, (4) 1 M.

We have investigated the adsorption of these organic surfactants as well as of adamantanol\(^{12,13}\) at constant organic substance concentration and different concentrations of Na\(_2\)SO\(_4\) by measuring the dependence of differential capacity on potential. The data obtained support the conclusion made earlier from the polarization measurements. For instance, the negative potentials of desorption of borneol (10\(^{-4}\) M) and camphor (9 × 10\(^{-5}\) M) shift in the direction of more negative values by 180 mV and those of adamantanol by 130 mV when the Na\(_2\)SO\(_4\) concentration is increased from 0.1 M to 1 M. From the C, \(\varphi\) curves we have calculated the mean surface coverages for camphor and borneol in the potential range of maximum adsorption for various Na\(_2\)SO\(_4\) concentrations. We have found that when the Na\(_2\)SO\(_4\) concentration varies from 0.1 M to 1 M, \(\vartheta\) varies from 0.4 to 0.9. Since the optimum mean surface coverages for the development of the maxima of the third kind are 0.2 - 0.5, this increase of \(\vartheta\) leads to a gradual damping of the motions in the maximum adsorption region and to the shifting of the maxima in the direction of larger surface charges. Such significant changes of the coverages due to salting out apparently have not been described in electrochemical literature so far.

The investigation of the arising of motions during the adsorption of pelargic acid is of special interest, since the adsorption behavior of saturated fatty acids is described quite well by Frumkin's adsorption equation, the attraction interaction increasing with the number of carbon atoms in the chain\(^{14}\).
As is clear from Fig. 8 (curve 1), in $0.75 \times 10^{-3} \text{ M} \text{CdSO}_4 + 2.0 \text{ M} \text{MgSO}_4$ with addition of $10^{-4} \text{ M} \text{C}_8\text{H}_{17}\text{COOH}$ a current maximum is observed in the region of high negative surface charges. This maximum is however lower (and the potential range in which it is observed is wider) than the negative maxima of the third kind in sufficiently concentrated solutions of camphor, borneol, adamantanol-1 or 2-oxoadamantane (Fig. 2).

Just as in the case of camphor, borneol, adamantanol-1 and 2-oxoadamantane, the decrease in the concentration of pelargic acid leads to the shift of the maximum into the region of less negative potentials and the height of the maximum goes down. However, unlike organic substances whose adsorption is attended by formation of two-dimensional condensed layers under equilibrium conditions (Fig. 1, curves 4–7), the dilution of pelargic acid does not lead to the appearance of the maximum of the third kind in the potential range of maximum adsorption. Possibly, this phenomenon is associated with the fact that according to ref. 14, at the potential of maximum adsorption of pelargic acid the attraction constant $a_0 \approx 1.5$. For the adsorption–desorption potentials the values of $a$ are not known because the authors of ref. 14 did not succeed in determining the whole $a, \varphi$ curve for pelargic acid. However, for fatty acids with the number of carbon atoms from four to six the $a, \varphi$ curves are of a parabolic shape, the values of $a$ increasing and the dependence of $a$ on $\varphi$ being more pronounced for greater chain length. Thus, we can suppose that for pelargic acid as well, the attraction constant increases markedly with rising negative potentials, reaching at the desorption potential the values necessary for the formation on the mercury electrode.
POLAROGRAPHIC MAXIMA OF THE THIRD KIND. III

1.4C ~-- 5

1.3C ~-- 4

1.2C ~-- 3

1.1C ~-- 2

0.9 ~-- 1

-0.8 -1.0 -1.2 -1.4

Fig. 9. Dependence of current on potential in solutions of $0.75 \times 10^{-3} \text{ M CdSO}_4 + 2 \times 10^{-4} \text{ M C}_8\text{H}_{17}\text{COOH} + \text{MgSO}_4$ of different concentrations: (1) 0.25, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0 M.

The intensification of the motions of the third kind which were relatively slightly pronounced in 1 M Na$_2$SO$_4$, observed in MgSO$_4$ solutions (Fig. 8), could be explained by the salting out action of MgSO$_4$.

In fact, as it follows from Fig. 9, which gives the data obtained in solutions with a constant concentration of pelargic acid and different MgSO$_4$ concentrations, the increase in the MgSO$_4$ concentration leads to an intensification of the motions of the third kind and to the shift of the potential of the maximum in the direction of more negative values.

Measurements of the $C, \varphi$ curves in MgSO$_4$ solutions with pelargic acid additions, carried out by us, and their comparison with the corresponding $I, \varphi$ curves show that the tangential motions of the third kind are observed in the region of the adsorption–desorption potentials and that with increasing MgSO$_4$ concentration, the surface activity of pelargic acid rises, as shown by the widening of the adsorption region on the $C, \varphi$ curves.

SUMMARY

The polarographic maxima of the third kind in solutions of 2-oxoadamantanone and of pelargic acid (C$_8$H$_{17}$COOH) were investigated. The behavior of 2-
oxo adamantane is similar to that of other adamantane and camphor derivatives. The surface activity of pelargic acid is markedly enhanced in 2 \textit{M} \text{MgSO}_4 solutions, however a polarographic maximum of the third kind is observed in the neighborhood of the cathodic desorption potential only. The appearance of the polarographic maxima of the third kind seems to be related to the faculty of the surfactant to form under equilibrium conditions two-dimensional condensed layers on the mercury drop surface.

REFERENCES