# CONDITIONS FOR THE APPEARANCE OF POLAROGRAPHIC MAXIMA OF THE THIRD KIND

Academician A.N. Frumkin, E. V. Stenina,
N. V. Nikolaeva-Fedorovich, G. N. Petukhova,
V. A. Yusupova, and É. A. Shokova

UDC 541.13

Polarographic maxima which originate from tangential motions caused by nonuniform adsorption of organic substances at the surface of the mercury drop were named maxima of the third kind, following a suggestion of Frumkin et al. [1]. Doss was the first to detect tangential motions and maxima on $I-\varphi$ curves (I being the current, $\varphi$ the potential); these arose at the adsorption-desorption potentials in the case of sodium dioctylsulfosuccinate [2]. Similar current maxima were observed in [3]. In [4] maxima were obtained during the desorption of octyl and butyl alcohol which had been emulsified in solution in the form of droplets. It has been suggested that maxima of the third kind appear because of tangential motions caused by a concentration gradient of the surface-active substance (SAS) in the solution volume adjoining the drop. But this concentration gradient appears because of the adsorption process itself.

Clearly developed and well reproducible current maxima of the third kind were first obtained in [5] during the reduction of $Cu^{2+}$ and $Co^{2+}$ in 1 M $Na_2SO_4$ in the presence of camphor. In harmony with Doss' original conclusion, it followed from the comparison of $I-\varphi$ with $C-\varphi$ curves (C being the differential capacitance) that the maxima arise at the anodic and cathodic adsorption-desorption potentials of camphor. In explaining the maxima obtained, Sathyanaryana [5] started with the concepts developed in [4] but linked the appearance of the SAS concentration gradient to the presence of an electric-field gradient.

Positive and negative maxima of the third kind were obtained in [1] for the discharge of $Cu^{2+}$, $Ag^+$, and $Tl^+$ over a wide range of camphor concentrations, and it was shown that appearance and intensity of the motions which cause the maxima do not depend on the passage of current. At low camphor concentrations ($6 \cdot 10^{-5}$ M), the increase in the diffusion-limited reaction current was observed over the entire potential range where camphor is adsorbed, but at higher concentrations this increase only remained at the adsorption-desorption potentials. In this connection, and in order to elucidate the conditions under which polarographic maxima of the third kind arise, we have investigated the maxima in the presence of camphor, borneol, and 1-adamantanol, and at the same time measured the potential dependence of the differential capacitance at the drop electrode. The technique used was the same as described in [1]. The drop time in the tests where the $I-\varphi$ and $C-\varphi$ curves were measured was 7 sec in 1 M $Na_2SO_4$ at $\varphi = -0.5$. The potentials are given in volts against the normal calomel electrode.

When camphor, borneol, and 1-adamantanol* were introduced at concentrations of $1.5 \cdot 10^{-5}$ M into $10^{-3}$ N $AgNO_3 + 1$ M $Na_2SO_4$ solution (Fig. 1, curve 1), an increase in current to values appreciably exceeding the limiting diffusion current is observed in the potential range around the point of zero charge. With increasing SAS concentration, the current of the maximum rises, while the potential range over which the polarographic maximum extends broadens (Fig. 1, curves 2 and 3). With the same concentrations of camphor, borneol, and 1-adamantanol in solution, the greatest height of the maximum is observed in the presence of 1-adamantanol.

However, when the SAS concentration increases beyond a certain limit, the current of the maximum stops growing and begins to decrease in the region of the zero-charge potential, and finally disappears altogether in this

---

*Data obtained for adamantanol in [7] were used in the present communication. Analogous data have been obtained for borneol [8].

M. V. Lomonosov Moscow State University. Translated from Doklady Akademii Nauk SSSR, Vol. 201, No. 6, pp. 1406-1409, December, 1971. Original article submitted September 24, 1971.

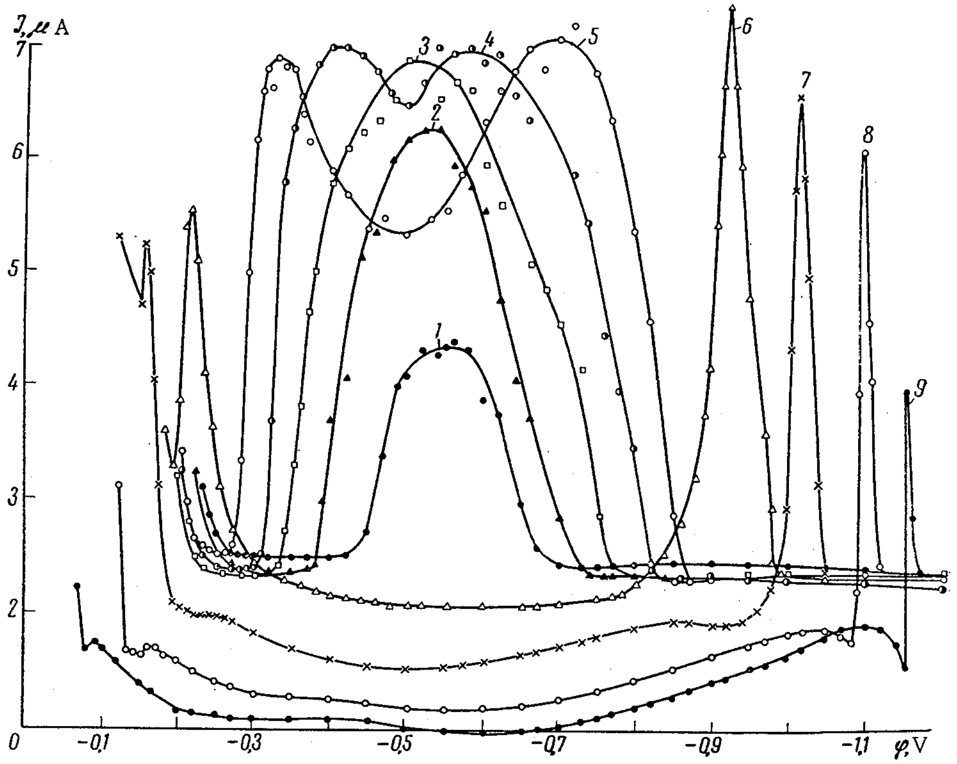

Fig. 1. Potential dependence of the current during the reduction of $10^{-3}$ N $AgNO_3$ + 1 M $Na_2SO_4$ with 1-adamantanol additions: 1) $1.5 \cdot 10^{-5}$ M; 2) $1.7 \cdot 10^{-5}$; 3) $2 \cdot 10^{-5}$; 4) $2.5 \cdot 10^{-5}$; 5) $3 \cdot 10^{-5}$; 6) $6 \cdot 10^{-5}$; 7) $1 \cdot 10^{-4}$; 8) $1.8 \cdot 10^{-4}$; 9) $3 \cdot 10^{-4}$ mole/liter.

potential range (Fig. 1, curves 4-6). At these SAS concentrations there appear on the $I - \varphi$ curves at first two rounded (curves 4 and 5), then two pointed current maxima at positive and negative surface charges (Fig. 1, curves 6-9). As the SAS concentration increases in this range, the height of the maximum decreases, the maxima become narrower and shift toward higher negative or positive surface charges. Besides the inhibition of the motions there begins to appear with increasing SAS adsorption the inhibition of the reaction proper, and over a wide potential range the current drops to values below the limiting diffusion current in the absence of the SAS.

Measurements of the potential dependence of differential capacitance in 1 M $Na_2SO_4$ in the presence of 1-adamantanol (Fig. 2) and borneol have shown that the $C - \varphi$ curves in these solutions are similar in nature to the $C - \varphi$ curves obtained in solutions containing camphor [5, 6]. On the $C - \varphi$ curves recorded in solutions containing borneol and 1-adamantanol (Fig. 2) there are no capacitance peaks, which is typical for adsorption processes following the Frumkin isotherm with a value for the attraction constant $a > 2$. At low SAS concentrations the drop in capacitance grows faster than does the concentration of the substance added (Fig. 2, curves 2-5), which also points to an S-shaped isotherm, although it can also depend in part on autocatalytic features of the adsorption process when there are tangential motions caused by the adsorption which accelerate the attainment of adsorption equilibrium. The minimum value of capacitance becomes constant at sufficiently high SAS concentrations, and when these increase further, only the potential range of adsorption broadens. It follows from a comparison of the $I - \varphi$ and $C - \varphi$ curves at low SAS concentrations that the potential range where the maxima of the third kind appear corresponds to the potential range where these substances are adsorbed (Figs. 1, 2, and 3), with the highest value of the maximum current corresponding to the highest surface coverage at these SAS concentrations.

The maxima in the potential region around the point of zero charge disappear with increasing degree of coverage $\theta$, and one only observes them at the adsorption-desorption potentials around which $\theta$ changes from unity to zero over a narrow potential range (Fig. 4). The data obtained unambiguously show that maxima of the third kind can arise over the entire potential range where the SAS indicated are adsorbed, but only when the degrees of surface coverage are low. The connection established in earlier papers between maxima of the third kind and the adsorption-desorption potentials is apparently determined only by the fact that near these potentials, the degree of coverage changes from unity to zero, so that at certain intermediate $\theta$ values the motions are revived and the inhibition of the reaction is removed.

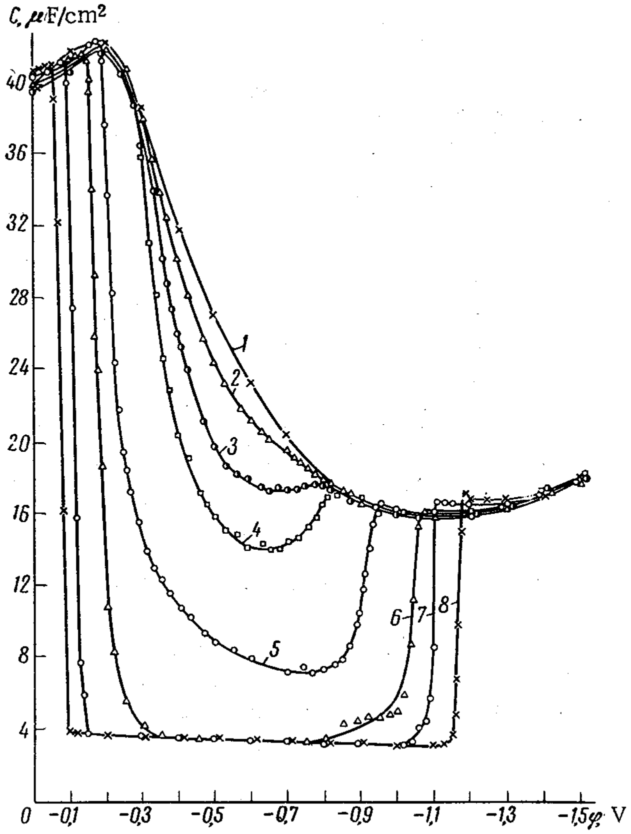

Fig. 2. Potential dependence of the differential capacitance in 1 M $Na_2SO_4$ with additions of 1-adamantanol: 1) 0; 2) $2 \cdot 10^{-5}$ M; 3) $2.5 \cdot 10^{-5}$; 4) $3 \cdot 10^{-5}$; 5) $6 \cdot 10^{-5}$; 6) $1 \cdot 10^{-4}$; 7) $1.8 \cdot 10^{-4}$; 8) $3 \cdot 10^{-4}$ M.

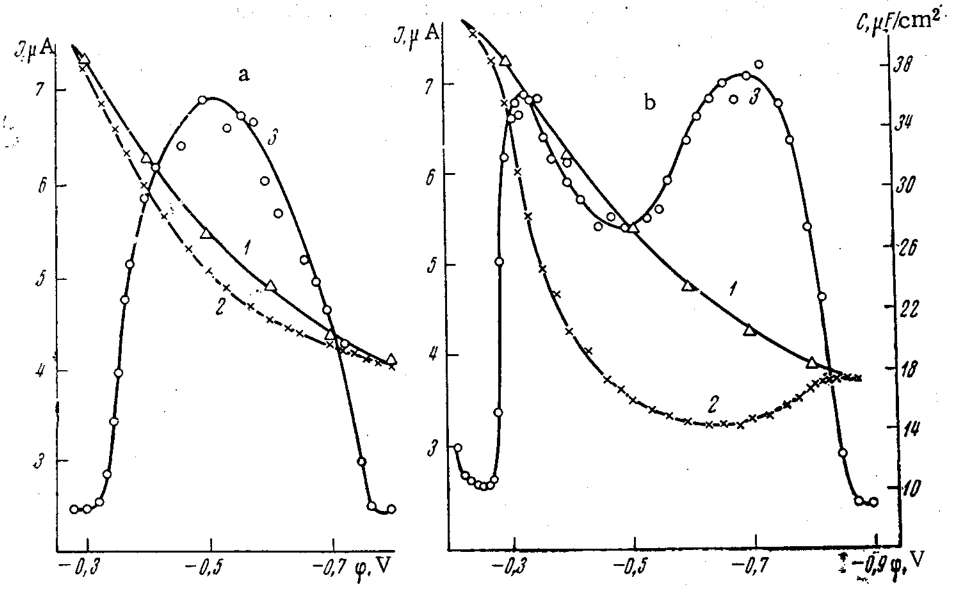

Fig. 3. Comparison of C – φ and I – φ curves at different SAS concentrations (a: $2 \cdot 10^{-5}$, b: $3 \cdot 10^{-5}$ mole/liter 1-adamantanol): 1) C – φ curve in 1 M $Na_2SO_4$; 2) the same in 1 M $Na_2SO_4$ + 1-adamantanol; 3) I – φ curve in 1 M $Na_2SO_4$ + $10^{-3}$ N $AgNO_3$ + 1-adamantanol.

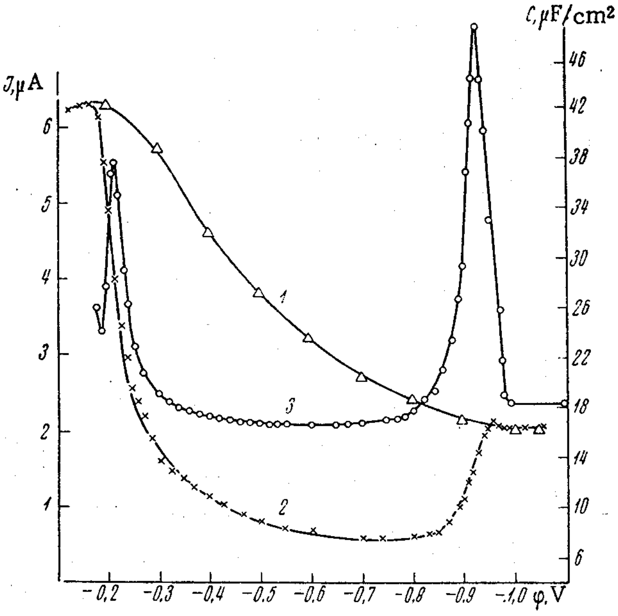

Fig. 4. Comparison of C − $\varphi$ and I − $\varphi$ curves at a 1-adamantanol concentration of $6 \cdot 10^{-5}$ mole/liter: 1) C − $\varphi$ curve in 1 M $Na_2SO_4$; 2) the same in 1 M $Na_2SO_4$ + 1-adamantanol; 3) I − $\varphi$ curve in $10^{-3}$ N $AgNO_3$ + 1 M $Na_2SO_4$ + 1-adamantanol.

## LITERATURE CITED

1. A. N. Frumkin, E. V. Stenina, and N. V. Fedorovich, Élektrokhimiya, 6, 1572 (1970).
2. K. S. G. Doss and D. Venkatesan, Proc. Indian Acad. Sci., 49, 129 (1959).
3. A. P. Martirosyan and T. A. Kryukova, Zh. Fiz. Khim., 27, 851 (1953).
4. A. N. Frumkin, S. Sathyanarayana, and N. V. Nikolaeva-Fedorovich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1962, 1977.
5. S. Sathyanarayana, J. Electroanal. Chem., 10, 56 (1965).
6. S. Sathyanaranaya and K. G. Baikerikar, J. Electroanal. Chem., 21, 449 (1969).
7. N. V. Nikolaeva-Fedorovich, E. V. Stenina, et al., Élektrokhimiya, 8, No. 1 (1972).
8. A. N. Frumkin, E. V. Stenina, et al., Rev. Roum. Chim., 17, No. 1 (1972).