# POLAROGRAPHIC MAXIMA OF THE THIRD KIND. VI

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UDC 543.253

It had been established previously in [1-4] that polarographic maxima of the third kind are found during the adsorption of organic substances which at the mercury/solution interface form two-dimensional condensed layers for which it is characteristic that the differential capacity of the electric double layer under equilibrium conditions is practically independent of electrode potential and concentration of the organic material over a wide range of variation of these parameters. The materials studied so far were distinguished by compact structure of the molecules.

It was of interest to determine the conditions under which polarographic maxima of the third kind will arise during the adsorption of simpler organic substances of linear structure, e.g., of aliphatic acids; their adsorption behavior on mercury has been studied thoroughly [5, 6]. For the investigation we selected n-pelargonic acid (normal nonanoic acid, n-$C_8H_{17}COOH$). Its adsorption had been studied in [5, 6], and according to the authors, the potential dependence of double-layer differential capacity (the $C-\varphi$ curves) on mercury in solutions of this acid is similar in character to the $C-\varphi$ curves for organic substances forming two-dimensional condensed layers. The experimental technique has been described in detail in [4].

The $I-\varphi$ curves relative to the normal calomel electrode in $1.5 \cdot 10^{-3}$ N $CdSO_4$ + 2.0 M $MgSO_4$ solutions containing different concentrations of n-pelargonic acid are presented in Fig. 1. The ratio of the current in the maximum to the diffusion current is plotted on the ordinate axis. As the base electrolyte we chose magnesium sulfate which has a stronger salting-out effect than sodium sulfate; in sodium-sulfate solutions we found

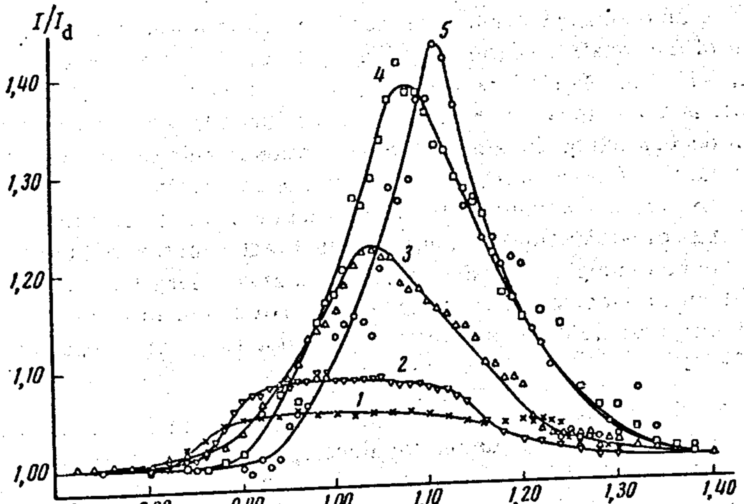

Fig. 1. Potential dependence of the current in $1.5 \cdot 10^{-3}$ N $CdSO_4$ + 2.0 M $MgSO_4$ solutions with different concentrations of n-pelargonic acid: 1) $2 \cdot 10^{-5}$ M, 2) $5 \cdot 10^{-5}$ M, 3) $1.0 \cdot 10^{-4}$ M, 4) $1.5 \cdot 10^{-4}$ M, and 5) $2.0 \cdot 10^{-4}$ M.

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M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 12, No. 7, pp. 1149-1152, July, 1976. Original article submitted July 15, 1975.

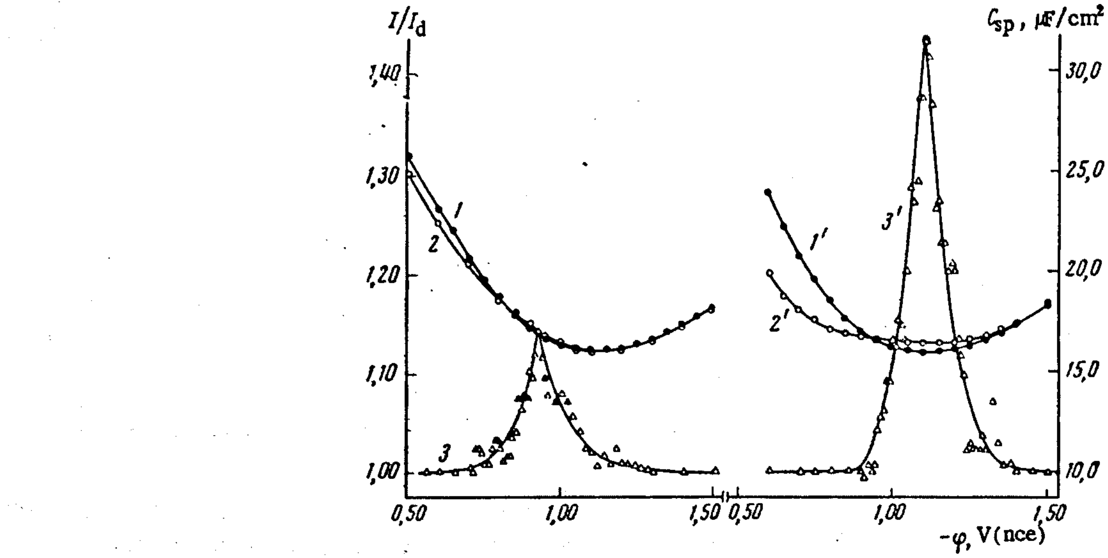

Fig. 2. Comparison of the $I_d-\varphi$ (3, 3') and $C-\varphi$ curves (1, 1', 2, 2') in the following solutions: 1) 0.5 M $MgSO_4$; 2) 0.5 M $MgSO_4$ + $2.0 \cdot 10^{-4}$ M n-$C_8H_{17}COOH$; 3) the same as (2), plus $1.5 \cdot 10^{-3}$ N $CdSO_4$; 1') 2.0 M $MgSO_4$; 2') 2.0 M $MgSO_4$ + $2.0 \cdot 10^{-4}$ M n-$C_8H_{17}COOH$; 3') the same as (2'), plus $1.5 \cdot 10^{-3}$ N $CdSO_4$.

only very weak motions of the third kind during the adsorption of n-pelargonic acid. It was assumed that an increase in the activity of the organic substance will be favorable for the development of these motions. The solutions were not acidified since at such a high $MgSC_4$ concentration the dissociation of the pelargonic acid will practically be suppressed even without acidification.

It can be seen from Fig. 1 that in n-$C_8H_{17}COOH$ solutions there are current maxima at negative surface charges. With decreasing acid concentration the range of potentials where they appear shifts to less negative values, while the height of the maxima becomes gradually less. The maxima disappear at n-polargonic-acid concentrations below $2.0 \cdot 10^{-5}$ M. When $I-\varphi$ and $C-\varphi$ curves recorded in 2.0 M $MgSO_4$ solutions at corresponding acid concentrations are compared (Fig. 2), then it is seen that the current maxima develop primarily in the potential range of desorption of the acid, while no motions arise on the mercury during adsorption of n-$C_8H_{17}COOH$ at the potentials of zero charge, whereas in the adsorption of the organic substances studied previously [1-4], the polarographic maxima of the third kind over a certain range of concentrations are observed over the full potential range of adsorption. It must be noted that a distinguishing feature of the maxima in the presence of pelargonic acid as compared to the negative maxima during the adsorption of, e.g., borneol [3] and oxaadamantane [4] is the much wider potential range of the motions of third kind. Apparently this is due to the fact that desorption of pelargonic acid takes place over a wider range of potentials than the desorption of the substances studied in [1-4].

Since the adsorption of organic substances and their adsorption parameters depend in a substantial way on base-electrolyte concentration [7], we studied the development of the maxima in solutions of constant n-$C_8H_{17} \cdot$ COOH concentration but different $MgSO_4$ concentrations (Fig. 3). The decrease in magnesium-sulfate concentration causes the maxima to shift to less negative potentials and to become lower. It follows from a comparison of the $I-\varphi$ and $C-\varphi$ curves that in these systems, too, the polarographic maxima are observed only in the potential range of desorption of the pelargonic acid but not in that of maximum adsorption.

The absence of motions of the mercury surface at the potentials of maximum adsorption of the pelargonic acid and the presence of current maxima at the adsorption–desorption potentials probably are due to a somewhat different structure of the adsorption layer, which may change with electrode potential. The attraction constant, $a$, for pelargonic acid at the potential of zero charge is 1.5 [6], which is typical for uncondensed layers. Damaskin et al. [6] had been unable to calculate an $a-\varphi$ curve for n-$C_8H_{17}COOH$, but it had been shown by them that for the saturated aliphatic acids with a number of carbon atoms between four and six this curve is parabolic in shape, that the $a$ values are increasing with charge, and that this increase is more pronounced the longer the chain. One therefore can assume that the appearance of polarographic maxima of the third kind in n-$C_8H_{17}COOH$ solutions only at the potentials of desorption is due to the fact that only near these potentials does the value of

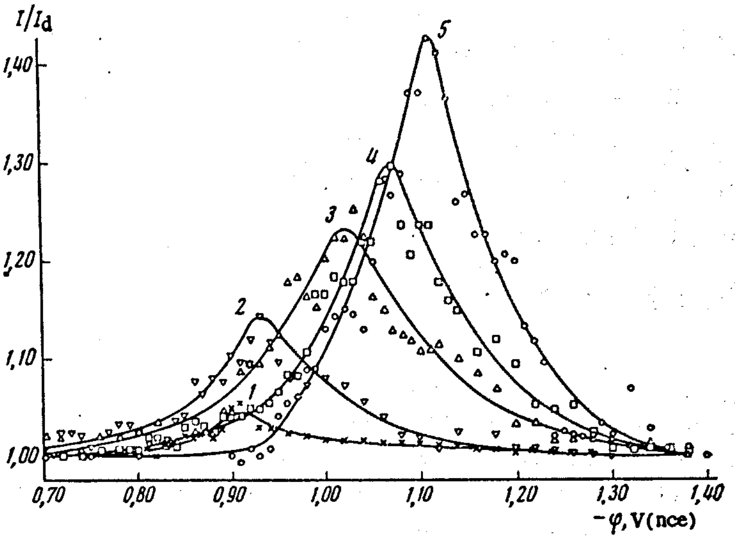

Fig. 3. Potential dependence of the current in $1.5 \cdot 10^{-3}$ N $CdSO_4$ + $2.0 \cdot 10^{-4}$ M n-$C_8H_{17}COOH$ solutions with $MgSO_4$ in different concentrations: 1) 0.25 M, 2) 0.5 M, 3) 1.0 M, 4) 1.5 M, and 5) 2.0 M.

*a* increase drastically, and the adsorption layer of pelargonic acid acquires the properties of a two-dimensional condensed layer.

Small polarographic maxima observable near the adsorption–desorption potential were obtained by us also in tribenzylmethylammonium sulfate solutions (Fig. 4). The potential dependence of the differential capacity during the adsorption of this compound has the shape which is typical for substances forming two-dimensional condensed layers, but the transition from an electrode surface which is completely occupied by organic material to a surface which is free from organic material is seen to occur over a wider range of potentials than for camphor, borneol, adamantanol, and oxaadamantane. This probably is an indication for weaker interaction between the adsorbed particles, which can be attributed to the presence of charge on these particles. However, further work will be required to elucidate the question whether the potential dependence of constant *a* in the equation of state will suffice for the complete explanation of the difference between the polarographic maxima of the third kind described in the present communication and the maxima caused by camphor or adamantanol.

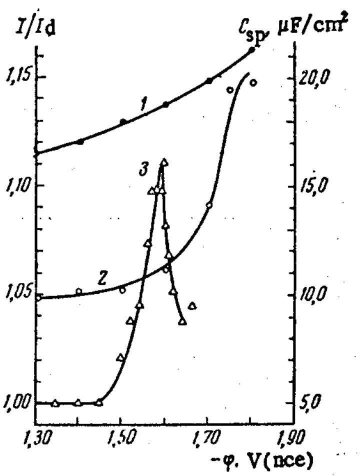

Fig. 4. Comparison of the $I/I_d$–$\varphi$ (3) and $C$–$\varphi$ curves (1, 2) in the following solutions: 1) 1.0 M $Na_2SO_4$, 2) 1.0 M $Na_2SO_4$ + $1.5 \cdot 10^{-5}$ M $(TBMA)_2SO_4$; 3) $7 \cdot 10^{-4}$ M $CuSO_4$ + 1.0 M $Na_2SO_4$ + $1.5 \cdot 10^{-5}$ M $(TBMA)_2SO_4$.

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