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POLAROGRAPHIC MAXIMA OF THE THIRD KIND. VII.

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The development of polarographic maxima of the third kind has been studied during the adsorption of 2-oxatwistane on the dropping mercury electrode, and these maxima were compared with the polarographic maxima arising in the adsorption of the stereoisomer, 2-oxadamantane. It is shown that by going to the more compact structure one alters the character of the two-dimensional condensed layer and the intensity of motions of the third kind.

It can be regarded as established by now that polarographic maxima of the third kind will only arise during the adsorption of organic materials forming two-dimensional condensed layers at the mercury/solution interface [1-5]. However, one can see when comparing the differential capacity vs potential (C vs φ) curves for different compounds (Fig. 1) that there may be highly significant differences in the adsorption-desorption potentials while the adsorption behavior exhibits a number of common traits such as are typical for two-dimensional condensation, viz., practical absence of capacity peaks from C vs φ curves and independence of the differential capacity on potential in the region of maximum adsorption. One can see from Fig. 1 that the C vs φ curves for camphor, borneol, adamantanol, and oxadamantane at the adsorption-desorption potentials exhibit a sharp transition within about 20 mV from a surface which is completely covered by organic material to one that is free of adsorbed organic material, while in the presence of fenchone, pelargonic acid, tribenzylmethylammonium sulfate, and some other organic cations this transition is much smoother (e.g., during the desorption of fenchone it occurs over a range of 100 mV, and during the desorption of tribenzylmethylammonium sulfate it occurs over a range of 200 mV).

These differences probably are due to the fact that the two-dimensional phase transitions observed with these groups of materials are substantially different in character, which can be explained in terms of intensity differences in the attractive interaction of the molecules in the adsorbed layer. So remarkable a difference in adsorption behavior often is caused by very small changes in molecular structure (e.g., in the camphor molecule, the two methyl groups are located in the bridge, while in the fenchone molecule they are at the carbon atom which belongs to the cyclohexane ring). There are data in the literature indicating that borneol and isoborneol, which only differ in the orientation of the OH group relative to the six-membered ring, i.e., in the compactness of the molecule, will form adsorbed layers which are substantially different in their effect on cation discharge kinetics.

It is of interest in this connection to examine molecules which are very similar in their structure, so that one will be able to recognize the effect of small changes in molecular structure on the adsorption properties of the material and on the tangential motions produced during its adsorption. To this end we selected 2-oxatwistane for an examination; it is the stereoisomer of 2-oxadamantane which has been investigated previously [5], and its structure is less compact. The polarographic maxima of the third kind were investigated by recording

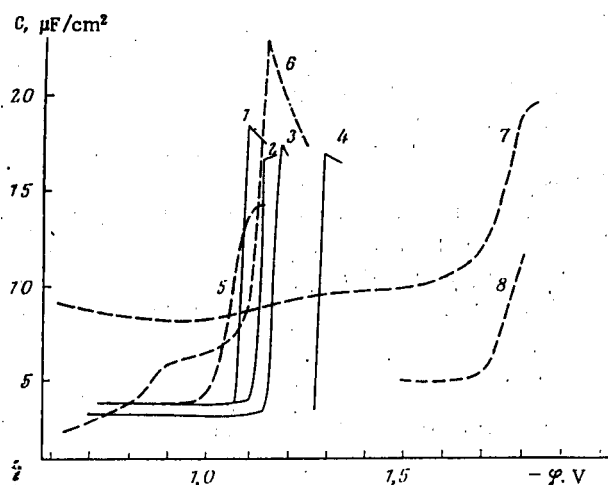


Fig. 1. The C vs ϕ curves in solutions with additives: 1) $1 \text{ M Na}_2\text{SO}_4 + 6 \cdot 10^{-4} \text{ M borneol}$ [3]; 2) $1 \text{ M Na}_2\text{SO}_4 + 5 \cdot 10^{-4} \text{ M 2-oxaadmantane}$ [5]; 3) $1 \text{ M Na}_2\text{SO}_4 + 3 \cdot 10^{-4} \text{ M adamantanol}$ [4]; 4) $0.1 \text{ N NaF} + 2 \cdot 10^{-3} \text{ M camphor}$ [8]; 5) $0.5 \text{ M Na}_2\text{SO}_4$ solution saturated with fenchone [9]; 6) $1 \text{ N Na}_2\text{SO}_4$ solution saturated with pelargonic acid; 7) $0.1 \text{ M Na}_2\text{SO}_4 + 3 \cdot 10^{-5} \text{ N tribenzylmethylammonium sulfate}$; 8) $1 \text{ N Na}_2\text{SO}_4 + 10^{-4} \text{ M decamethylene-bis (N-dimethyl,N-adamantyl)ammonium chloride}$.

polarization curves at the dropping mercury electrode, and C vs ϕ curves were recorded to examine the adsorption behavior [5]. The careful purification of water and chemicals used in the work was supplemented by a purification of the working solutions using a suspension of purified activated carbon which had been presaturated with the organic material to be examined [6].

The I vs ϕ curves measured in $10^{-3} \text{ N AgNO}_3 + 1 \text{ M Na}_2\text{SO}_4$ solution containing different concentrations of 2-oxatwistane are presented in Fig. 2. One can see from the figure that at low concentrations of the additive there is one current maximum in the region of the point of zero charge, which becomes higher with increasing concentration of the organic material. A further increase of the 2-oxatwistane concentration leads to gradual inhibition of the motions of third kind in the potential range of zero charge, and to the appearance, first of two rounded, and then of two sharp current maxima on the polarization curves; one of these maxima is located at positive, the other at negative charges of the mercury surface.

An investigation of the adsorption of 2-oxatwistane using C vs ϕ curves yielded confirmation for the conclusion drawn previously for other organic materials which during adsorption give rise to tangential motions of the third kind, viz., that the potential regions of adsorption and of the tangential motions coincide at low concentrations of the organic material, while the sharp current maxima observed at high concentrations of the organic additive coincide with its adsorption-desorption potentials from the mercury electrode surface.

Using experimental data for the differential capacity as function of potential we calculated the degrees of surface coverage (θ) of the mercury by 2-oxatwistane. In Fig. 3 the calculated θ values are compared at different potentials with the current increments (ΔI) found in the region where the tangential motions arise. One can see from this figure that the law is the same for all potentials: Optimum conditions for the development of motions of the third kind are present in the interval of degrees of coverage from 0.1 to 0.3; at lower and higher degrees of coverage the tangential motions die away, and one must note that already at $\theta = 0.05$, ΔI has decreased to one-half of its maximum value.

The approximate expression

$$v = \frac{D_s}{2\Gamma} \cdot \frac{\partial C}{\partial x} \cdot \frac{\partial \Gamma}{\partial C} \quad (1)$$

has been suggested in [7] as a link between the shape of the adsorption isotherm and the rate, v , of the tangen-

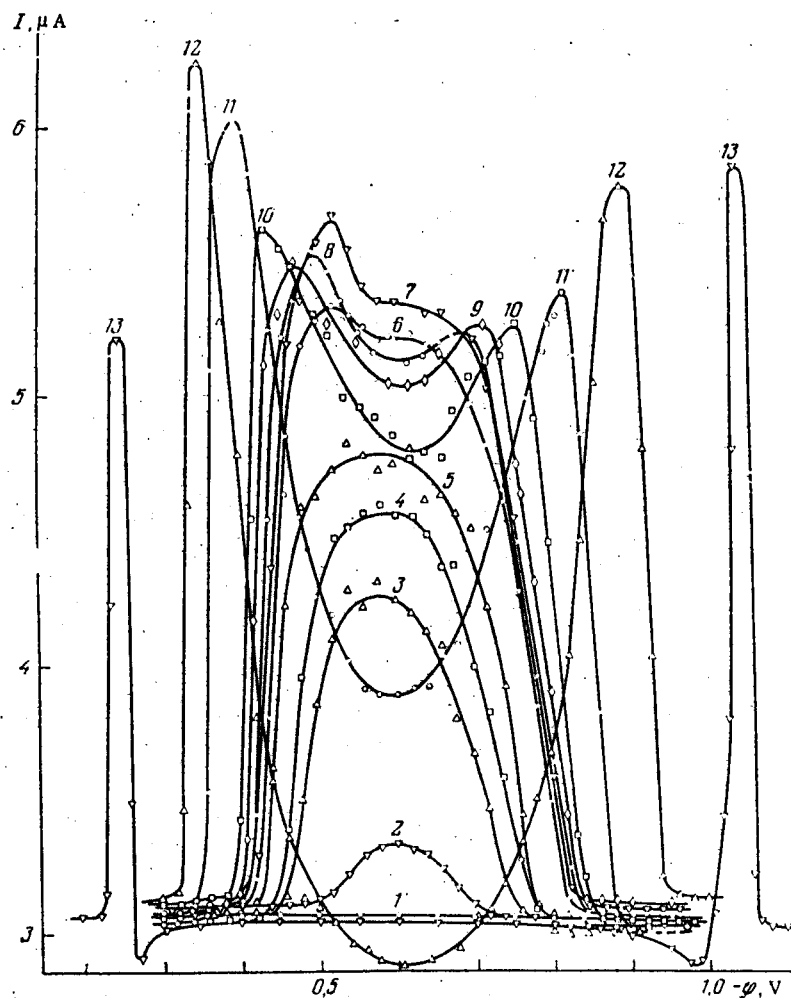


Fig. 2. The current as function of potential during the reduction of 10^{-3} N AgNO_3 + 1 M Na_2SO_4 in the presence of 2-oxatwistane in the following concentrations: 1) 0, 2) $5 \cdot 10^{-5}$, 3) $8 \cdot 10^{-5}$, 4) $8.2 \cdot 10^{-5}$, 5) $8.35 \cdot 10^{-5}$, 6) $8.5 \cdot 10^{-5}$, 7) $9.0 \cdot 10^{-5}$, 8) $9.5 \cdot 10^{-5}$, 9) 10^{-4} , 10) $1.1 \cdot 10^{-4}$, 11) $1.3 \cdot 10^{-4}$, 12) $1.5 \cdot 10^{-4}$, and 13) $3.3 \cdot 10^{-4}$ M.

tial motions, which are caused by nonuniformity of the adsorption of organic material. In Eq. (1), D_s is the surface diffusion of the organic molecules, c is the concentration of organic material in the solution, and Γ is the adsorption of organic material.

The existence of said connection has been confirmed in a number of papers [5, 7] during the adsorption of adamantanol, borneol, and x-oxadamantane. Relation (1) was tested in the present work in the case of 2-oxatwistane adsorption. The necessary values for the derivative $\partial\Gamma/\partial c$ were found by us from the slope of the adsorption isotherms at different potentials, quantities θ were calculated from the experimental C vs φ curves, and the value of $\Gamma_\infty = \Gamma/\theta$ for 2-oxatwistane was assumed to be the same as Γ_∞ for adamantanol i.e., $4.1 \cdot 10^{-10}$ mole/cm².

One can see from Fig. 4, where values of the derivative $\partial\Gamma/\partial c$ are plotted against φ , that these curves are similar in shape to the I vs φ curves: The maxima on the I vs φ curves practically coincides with those of the $(\partial\Gamma/\partial c)_\varphi$ vs φ curves, i.e., the motions of the third kind are most intense under the same conditions under which the adsorption isotherm has maximum steepness. Thus, the law reflected by relation (1) is valid in the case of 2-oxatwistane. The above connection between the value of current and the value of the derivative $\partial\Gamma/\partial c$ in all likelihood is a general phenomenon for materials forming two-dimensional condensed layers on mercury, even though the dependence of the intensity of motion of a liquid electrode on the steepness of the adsorption isotherm probably can also be interpreted somewhat differently, as shown in [7].

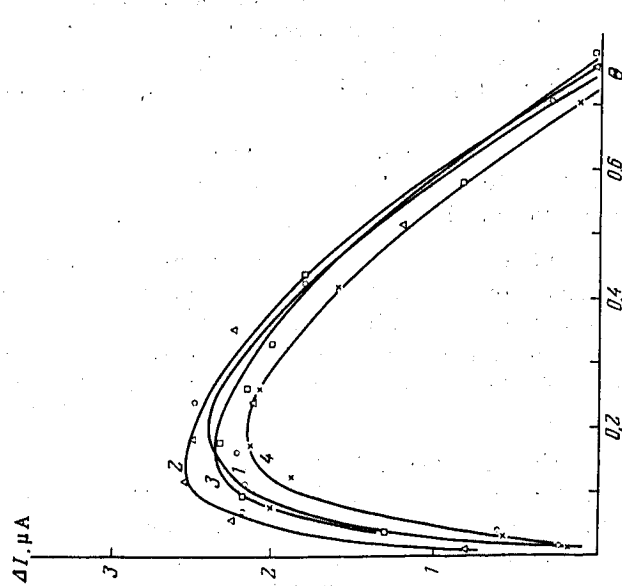


Fig. 3. The currents of the polarographic maxima of the third kind during 2-oxatwistane adsorption as functions of coverage at potentials of -0.46 (1), -0.5 (2), -0.6 (3), and -0.74 V (4).

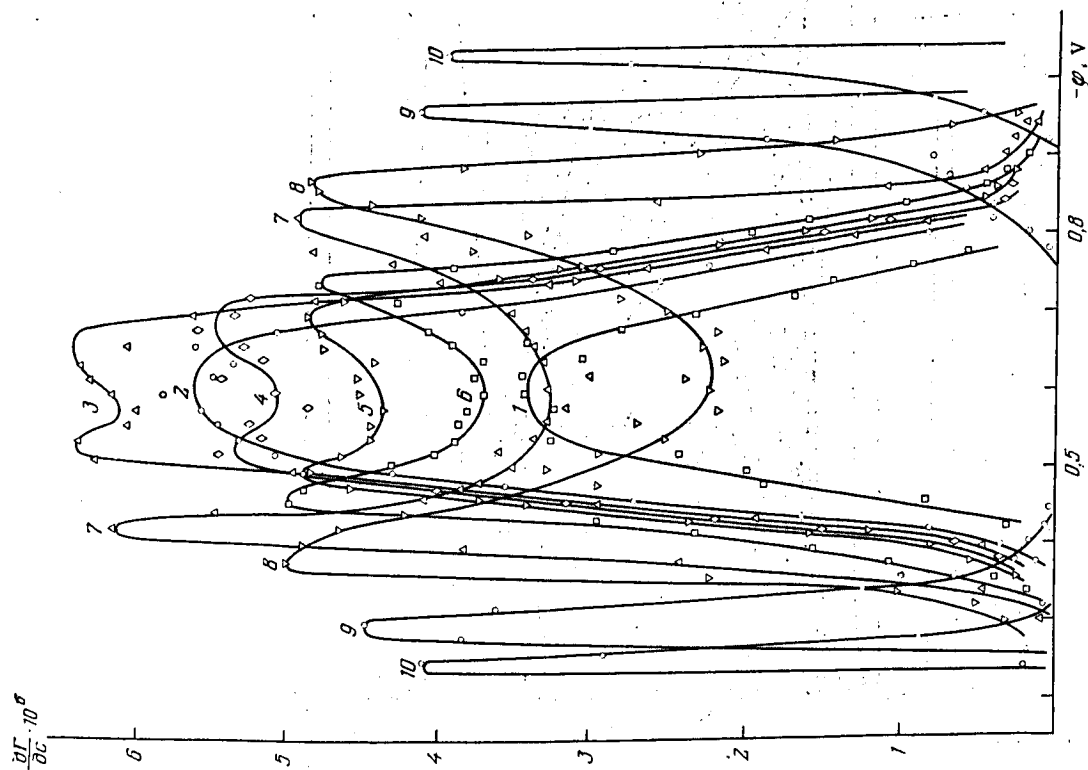


Fig. 4. The $(\partial I / \partial c)_{\phi}$ values as function of potential in 1 M Na_2SO_4 containing 2-oxatwistane in different concentrations: 1) $8 \cdot 10^{-5}$, 2) $8.5 \cdot 10^{-5}$, 3) $9.0 \cdot 10^{-5}$, 4) $9.5 \cdot 10^{-5}$, 5) 10^{-4} , 6) $1.1 \cdot 10^{-4}$, 7) $1.3 \cdot 10^{-4}$, 8) $1.5 \cdot 10^{-4}$, 9) $2.4 \cdot 10^{-4}$, and 10) $3.3 \cdot 10^{-4}$ M.

One can see by comparing the adsorption behavior of 2-oxatwistane with that of 2-oxadamantane that the adsorption properties of these materials are similar, although in the case of 2-oxatwistane one finds a more appreciable potential dependence of differential capacity in this region of maximum adsorption, which can be attributed to the less compact molecular structure of 2-oxatwistane. In accordance with the practically identical adsorption behavior of these materials one finds almost the same intensities of the tangential motions during their adsorption. Whereas, in going from 2-oxadamantane to dihydroxyoxadamantane, which differs from oxadamantane by the presence of two hydroxyl groups, one finds that the maximum of the third kind disappears, just as seen previously when going from adamantanol to adamantanediol.

The positional change of the methyl groups which occurs as one goes from the camphor to the fenchone molecule (Fig. 1) leads to a very appreciable broadening of the region of two-dimensional phase transition, probably because of the weaker interaction between the molecules in the two-dimensional condensed layer of fenchone. An investigation carried out by us has shown that the polarographic maxima of the third kind have become practically extinct in fenchone adsorption.

An examination of different derivatives of oxadamantane and bicyclooxanonane (diacetoxyoxadamantane, diacetoxybicyclooxanonane, bicyclo [3.3.1]nonadiene, and bicyclononanol), and also of dimethylglyoxime and the tetramethyl ester of cyclobutanetetracarboxylic acid has shown that polarographic maxima of the third kind disappear as one goes to a less compact structure or to molecules with functional groups in the side chain.

It follows from the data obtained by us that both the adsorption and the development of tangential motions often depend on small changes in the structure of the organic molecule, and on the position and composition of functional groups.

In conclusion we express our sincere gratitude to N.K. Sadova and N. V. Averina for giving us samples of 2-oxatwistane, 2-oxadamantane, and the derivatives of 2-oxadamantane and bicyclooxanonane.

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