POLAROGRAPHIC MAXIMA OF THE THIRD KIND. III

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The conditions were investigated under which polarographic maxima of the third kind will arise. It is shown that these maxima are caused by turbulent motions of the mercury drop's surface. These motions arise during the adsorption of poorly soluble, surface-active substances (camphor, adamantanol, and their derivatives) which form condensed adsorption layers when their concentration in the bulk of the solution is not too small. The potentials of the maxima of the third kind are close to the potentials which correspond to the maximum values of the function $\partial\Gamma/\partial c$.

Polarographic maxima of the third kind arise during the adsorption of certain organic substances at the surface of the mercury drop. They were first described by Doss and Venkatesan [1]. The possibility that polarographic maxima arise in the presence of a concentration gradient of the surface-active substance was considered in [2, 3]. Sathyanarayana showed that well-developed maxima of the third kind can be observed in camphor solutions [4]. Doss, Venkatesan, and Sathyanarayana [1, 4] thought that the potential at which maxima of the third kind arise should coincide with the potentials of the desorption peaks of organic material on the differential capacitance (C)—electrode potential (φ) curve. By comparison of experimental data on the differential capacitance and the current at the drop, it was shown in [5, 6] that the maxima can be observed at any potential within the adsorption range of the organic material, provided that the coverage $\Theta \simeq 0.3$ to 0.5. These authors also established that the appearance of these maxima is not linked to the presence of an electric-field gradient.

Presently maxima of the third kind have been obtained during the adsorption of organic substances belonging to different classes, such as, e.g., camphor, borneol, adamantanol (AdOH) [5, 6], and guanine.* All these compounds are poorly soluble in water, are highly surface active, and form two-dimensional condensed layers on the mercury surface when the concentration is high enough [7, 8]. The tangential motions of the drop surface which accompany the appearance of maxima of the third kind were ascertained by us with the aid of a KM-6 cathetometer by following the rate of motion of carbon particles which had been purified by the technique described in [9] and were suspended in the solution [10].

A weighed portion of 0.01 g of the carbon was first kept for a day in 5 ml of a 1 M $Na_2SO_4 + 10^{-3}$ M AdOH solution so that, when introduced into the solution, it would not lead to a change in the concentration of the organic material. It was found that motion of the solution at the drop surface can be seen over the entire range of potentials where polarographic maxima of the third kind arise in the solution. However, when one compares the motion of the solution for maxima of the third and the second kind at the same value of current (that which corresponds to the maximum current), then the rate of motion of the carbon particles in the solution is appreciably lower in the first case (excepting the region directly adjoining the drop surface) than in the second. Near the drop surface, the rate of motion of the particles increases drastically,

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*Rather more weakly developed maxima of the third kind are observed at the desorption potential in solutions of nonyl alcohol and methyltribenzylammonium sulfate. It is not clear as yet whether the ideas developed here can be extended to these maxima.

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and both near the drop surface and right at it the motion is very intense and irregular. In the presence of the substances studied, the motion of the drop surface appears to be eddy in character, similar to the motions described for the case of catalytic maxima [11].

The following expression for the rate of motion of the drop surface follows from the approximate theory developed in [2, 3]:

$$v \sim \frac{a\,\partial\sigma/\partial\varkappa}{2\mu+3\mu'+\gamma_\varepsilon+\gamma_a}, \tag{1}$$

where $\partial\sigma/\partial\varkappa$ is the surface-tension gradient along the drop surface, a is a quantity having the dimension of length, μ and μ' are the viscosities of the mercury and the solution, respectively, and γ_ε and γ_a are the retardations of the motion caused, respectively, by the electric-double-layer charges and by the adsorbed layer. The numerator of the right-hand side of Eq. (1) can be expressed as follows:

$$\frac{\partial\sigma}{\partial x}a = \frac{\partial\sigma}{\partial c}\cdot\frac{\partial c}{\partial x}a, \tag{2}$$

where c is the bulk concentration of the adsorbate. This relation presupposes that at least approximate equilibrium between the bulk and surface concentration of the adsorbate is established.

In the denominator of the right-hand side of Eq. (1), which constitutes the sum of all retarding effects, one can neglect the term γ_ε containing charge density, just as was done in [12], because our experiments were carried out at appreciable base-electrolyte concentration. We have also assumed that the forces of viscous braking are small relative to the retardation by adsorption.* Thus, if the inequality

$$\gamma_a \gg 2\mu+3\mu'+\gamma_\varepsilon$$

is fulfilled and we assume that the surface concentrations are leveled out via surface diffusion (cf. [2], the footnote to p. 1980), then we obtain for the retardation by adsorption, according to [13, 14],

$$\gamma_a = -\frac{2a\Gamma}{D_s}\left(\frac{\partial\sigma}{\partial\Gamma}\right), \tag{3}$$

where D_s is the surface diffusion coefficient and Γ is the amount adsorbed per cm^2. Then

$$v \infty \frac{\partial\sigma/\partial c\cdot\partial c/\partial x\cdot a}{2a\Gamma/D_s\cdot(\partial\sigma/\partial\Gamma)} = \frac{D_s}{2\Gamma}\frac{\partial\Gamma}{\partial c}\cdot\frac{\partial c}{\partial x}. \tag{4}$$

Important in the derivation of Eqs. (3) and (4) is the assumption that the surface concentrations are leveled out by a surface diffusion mechanism. By comparison of the different leveling mechanisms, Frumkin and Levich [13, 14] came to the conclusion that in the case of such typical, soluble surface-active substances as, e.g., n-$C_5H_{11}OH$, the leveling efficiency of bulk diffusion was many orders of magnitude larger than that of surface diffusion. However, the relations derived in [2] which were based on the assumption that leveling occurs via bulk diffusion provide no explanation for the effects observed in the presence of such substances as camphor and adamantol. Factors which will favor transition to the other leveling mechanism are the significantly higher value of the ratio Γ/c, the smaller values of the constant a when the motion is turbulent (the calculations in [13, 14] were carried out under the assumption that a is a quantity of the order of drop size), and possibly a larger value of D_s. The last assumption, however, is purely hypothetical so far.

If it is assumed that the change in concentration of the organic substance occurs as a result of impoverishment of the solution as caused by the adsorption process itself, then one can accept that

$$\frac{\partial c}{\partial x} \simeq k\Gamma,$$

and then

$$v \simeq k'D_s\cdot\frac{\partial\Gamma}{\partial c}, \tag{5}$$

where k and k' are certain constants.

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*This assumption has been made to simplify the calculations. One can readily verify that it is not reflected in the basic results of the present work. It will be easy to lift it in the future.

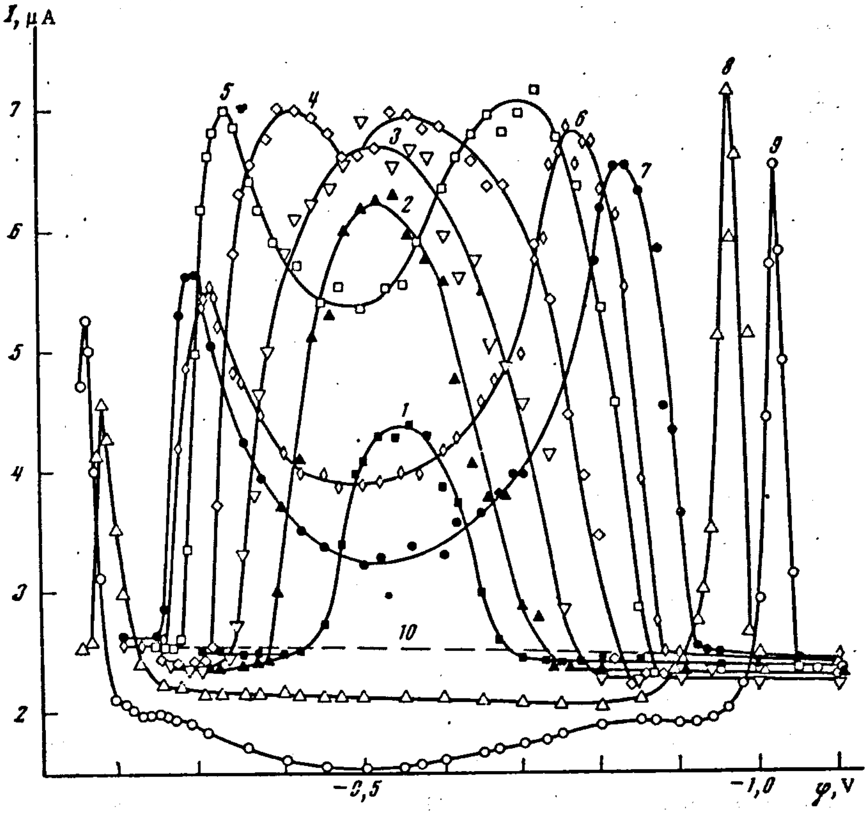

Fig. 1. The current as function of potential (against s. c. e.) during the reduction of 10^{-3} N $AgNO_3$ + 1 M Na_2SO_4 in the presence of adamantan-1-ol: 1) [AdOH] = 1.5×10^{-5} M; 2) 1.7×10^{-5}; 3) 2×10^{-5}; 4) 2.5×10^{-5}; 5) 3×10^{-5}; 6) 3.5×10^{-5}; 7) 4×10^{-5}; 8) 8×10^{-5}; 9) 1×10^{-4}; 10) 0.0. τ = 9 sec, m = 0.591 mg/sec.

Thus, the potential dependence of the rate of the tangential motions of the drop surface should be similar to that of the quantity $\partial\Gamma/\partial c$.

With the aim of verifying this result we have calculated the $\partial\Gamma/\partial c-\varphi$ dependence for the adsorption of adamantan-1-ol and borneol from the experimental $C-\varphi$ curves, and compared the data obtained with the corresponding $I-\varphi$ curves. When a current I arises which flows to the drop, there occurs a summation of effects due to radial drop growth and due to the stirring which is caused by the tangential surface motions. We shall designate the currents which would arise if each of these effects were present separately by I_r and I_t, respectively. There is no quantitative theory linking I with I_r and I_t. It was shown in [12] that the approximate relation

$$I \simeq (I_r^2 + I_t^2)^{1/2} \tag{6}$$

is practically applicable. On the other hand, according to [14],

$$I_t \sim k'' v^{1/2}. \tag{7}$$

Equation (7) was derived under the assumption of laminar liquid flow. The transition to turbulent conditions must cause an increase in the exponent of v [14]. Thus,

$$I \sim (I_r^2 + k''' v^n)^{1/2}, \tag{8}$$

where $1 < n < 2$. In the present communication we shall limit our comparison of I to the v value expressed by Eq. (5), since we are primarily interested in the case where $I_t \gg I_r$, and also since the entire analysis of the problem is grossly approximate in character.

The $C-\varphi$ and $I-\varphi$ curves were measured according to the technique described in [5, 6]. The $C-\varphi$ curves for 1 M Na_2SO_4 containing various concentrations of AdOH have been measured at a dropping mercury electrode using the R-568 bridge, and are reported in Fig. 2 of [15]. The capacitance and the current flowing to the drop were measured at the end of drop-life, and refer to drops of the same age.

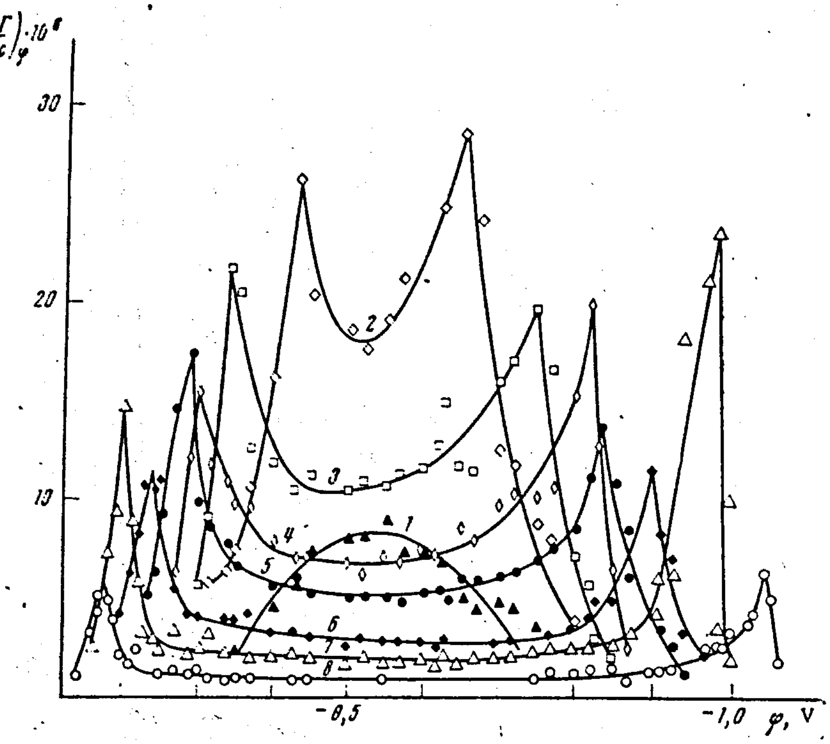

Fig. 2. The potential dependence of $\partial\Gamma/\partial c$ in 1 M Na_2SO_4 in the presence of adamantan-1-ol: 1) 2×10^{-5} M; 2) 2.5×10^{-5}; 3) 3×10^{-5}; 4) 3.5×10^{-5}; 5) 4×10^{-5}; 6) 6×10^{-5}; 7) 8×10^{-5}; 8) 1×10^{-4} M.

The I–φ curves in 10^{-3} N $AgNO_3$+1 M Na_2SO_4 solution containing different amounts of adamantanol are presented in Fig. 1. Upon introduction of 1.5×10^{-5} M AdOH into the solution (Fig. 1, curve 1), one observes an increase in current near the potential of zero charge (pzc) above the limiting diffusion current in the absence of AdOH (curve 10). The current maximum increases, and the range of potentials where it arises becomes broader, as the AdOH concentration is made larger (Fig. 1, and curves 2 and 3). A further increase in AdOH concentration causes the current maximum to split up, and the current to decrease in the region of the pzc. (Fig. 1, curves 4-7). At the same time two current maxima appear on the I–φ curves to both sides of the pzc; the potentials of these maxima move further and further away from the pzc as the AdOH concentration is increased. At the highest AdOH concentrations attainable, the current maxima are only observed at the AdOH desorption potentials (Fig. 1, curves 8 and 9). In the intermediate potential range the current falls to values which are below the limiting diffusion current in the absence of AdOH. This demonstrates that AdOH adsorption inhibits not only the tangential surface motions but also the electrochemical process itself, viz., the discharge of the Ag^+ ion.* The $\partial\Gamma/\partial c$ relations for 1 M Na_2SO_4 solution containing AdOH are presented in Fig. 2.

The Θ values required to calculate the function $\partial\Gamma/\partial c$ from the relation $\Gamma=\Gamma_m\Theta$ were found from the equation

$$C=C_0(1-\theta)+C'\theta, \tag{9}$$

where C_0 and C' are the values of capacitance at the degrees of coverage Θ=0 and Θ=1, respectively.

The Γ_m values were calculated from the dependence of the desorption potential on AdOH concentration according to the method described in [7]. The values of $(\partial\Gamma/\partial c)\varphi$ were determined from the slope of the adsorption isotherm. We calculated Θ from Eq. (9) without taking into account any additional capacitance, since it follows from the theory of nonequilibrium differential–capacitance curves in the presence of organic substances [16, 17] that the magnitude of the additional capacitance turns out to be smaller the higher the attractive interaction between the adsorbed organic molecules. If the attraction constant contained in

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*There is no systematic connection between these two effects, however. Thus, when $AgNO_3$ is reduced in the presence of borneol [6], the general picture of the phenomenon is similar to that observed in AdOH solutions. However, even at the highest borneol concentrations attainable, the current does not fall below the limiting diffusion currents observed in the absence of the adsorbate.

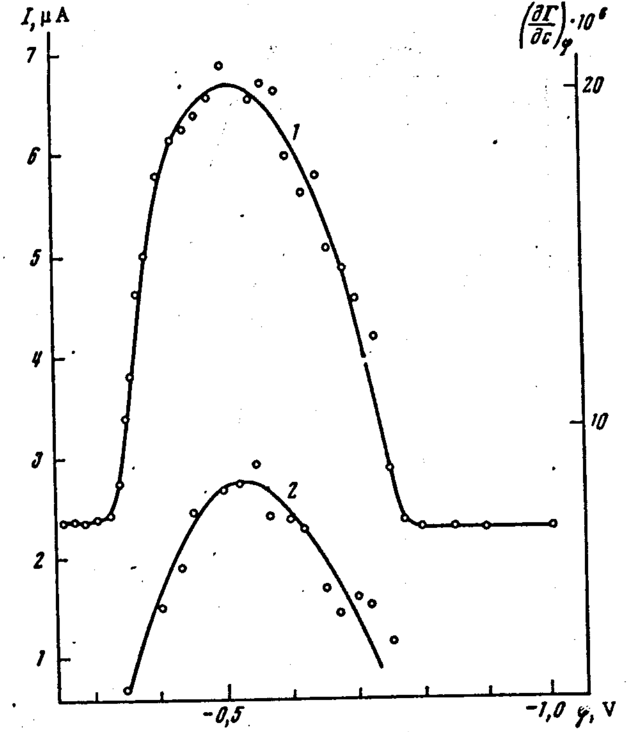

Fig. 3. Comparison between $\partial\Gamma/\partial c$-$\varphi$ and I-φ curves at an adamantan-1-ol concentration of 2×10^{-5} M. 1) The I$-\varphi$ curve in 10^{-3} N $AgNO_3$+1 M Na_2SO_4+adamantan-1-ol solution; 2) the $\partial\Gamma/\partial c$$-\varphi$ curve in 1 M Na_2SO_4+adamantan-1-ol solution.

the Frumkin isotherm is larger than 2, as is true for the adsorption of camphor and adamantanol molecules, then in the frequency range of 400 to 1000 Hz one can equate the measured capacitance, to a first approximation, to the true double-layer capacitance which is conveyed by Eq. (9). With Eq. (9), it is possible to calculate the dependence of the degree of coverage on electrode potential at different adamantanol and camphor concentrations.*

By comparing Figs. 1 and 2 for corresponding AdOH concentrations, one can see that the quantity $\partial\Gamma/\partial c$ has maximum values at the same potentials as I. As the AdOH concentration is increased, the $\partial\Gamma/\partial c$$-\varphi$ dependence repeats the shape of the I$-\varphi$ curves recorded in solutions having the same AdOH concentrations. A more detailed comparison between I$-\varphi$ and $\partial\Gamma/\partial c$$-\varphi$ curves in solutions of matching composition is provided in Figs. 3-5. At values [AdOH] $\leq 2 \times 10^{-5}$ M, both the I$-\varphi$ and the $\partial\Gamma/\partial c$$-\varphi$ curve go through a maximum near the pzc (Fig. 3). When the concentration is increased, the maximum splits apart on both curves, but the potentials of the maxima of $\partial\Gamma/\partial c$ and I remain practically coincident (Fig. 4). When the concentration is further increased, the potentials of the maxima on both curves begin to approach those of the desorption peaks (Fig. 5) and in the limit, coincide with them.

However, there is also some quantitative difference between the relative heights of the maxima in the two series of curves. To wit, at the lowest concentrations $\partial\Gamma/\partial c$ increases slower with c than does I (Fig. 3). To the contrary, as saturation of the AdOH solution is approached, one finds that the drop of the maxima of $\partial\Gamma/\partial c$ is more sharply developed than that of the maximum I values. Despite these differences, there can be no doubt about the existence of a relation between the appearance of maxima of the third kind

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*At large camphor concentrations we compared the $\Theta-\varphi$ curves found with Eq. (9) with similar curves calculated from the equation

$$\varepsilon=\varepsilon_0(1-\theta)+\varepsilon'\theta, \tag{10}$$

where ε_0 and ε' are the values of surface charge density at $\Theta=0$ and $\Theta=1$, respectively. The charge density curves in the presence of camphor were obtained by the method of integration of nonequilibrium C$-\varphi$ curves described in [18]. The agreement between the two methods of calculation shows that it is possible to use Eq. (9) for calculating the degree of surface coverage during the adsorption of camphor and adamantanol.

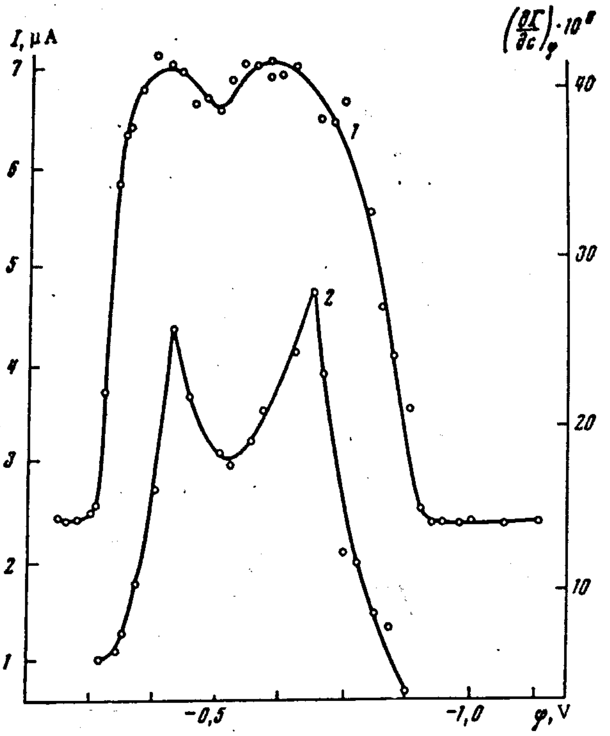

Fig. 4. Comparison between $\partial\Gamma/\partial c-\varphi$ and $I-\varphi$ curves at an adamantan-1-ol concentration of 2.5×10^{-5} M. 1) the $I-\varphi$ curve in 10^{-3} N $AgNO_3$+M Na_2SO_4+adamantan-1-ol solution; 2) the $\partial\Gamma/\partial c-\varphi$ curve in 1 M Na_2SO_4+adamantan-1-ol solution.

and the potentials of maximum steepness of the $\Gamma-c$ relation for the derivatives of camphor and adamantanol.*

The explanation proposed for the mechanism by which polarographic maxima of the third kind arise is based on the idea that at certain degrees of coverage corresponding to maximum values of the function $\partial\Gamma/\partial c$, the retarding effect of the liquid at the interface is weakened by the surface-active substance. We made the assumption, moreover, that the contributions of surface diffusion and surface convection are commensurate in the total mass balance of material adsorbed. In a more rigorous approach to analyzing how polarographic maxima of the third kind are produced, one must start from the complete system of equations and boundary conditions which describe the simultaneous transfer of mass and momentum near the interface of the two immiscible liquids while accounting for the adsorption of the surface-active substance and for the concentration dependence of interfacial tension.

There are a number of papers in the literature which theoretically investigate the influence of adsorption and diffusion processes upon the hydrodynamic stability of mobile interfaces [19-24]. It has been established in these papers, especially in [19], that an instability caused by local variations in the interfacial tension during mass exchange can only arise when the dependence of surface tension σ on Gibbs adsorption Γ is completely definite in character. For the case of adsorption at the liquid–gas interface occurring under conditions where the rate of transport of the surface-active material to the interface is limited by convective diffusion from the liquid phase, quantitative relations have been obtained which describe the influence of Gibbs adsorption upon the stability of the interface relative to small perturbations induced by inhomogeneity of the adsorbate concentration field [22-24]. According to the results obtained in [22-24], surface convection in liquid–gas systems has an appreciably stronger leveling effect upon the adsorbate concentration field than does surface diffusion. A very important conclusion with which our results

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*The question remains open at this time whether this conclusion can be extended to all cases where maxima of the third kind arise. Thus, certain preliminary results obtained in nonyl alcohol solutions appear not to fit the picture described here. In this case one has to do, however, with weakly developed maxima of the third kind which cannot at all be compared to the effects observed, e.g., in AdOH solutions.

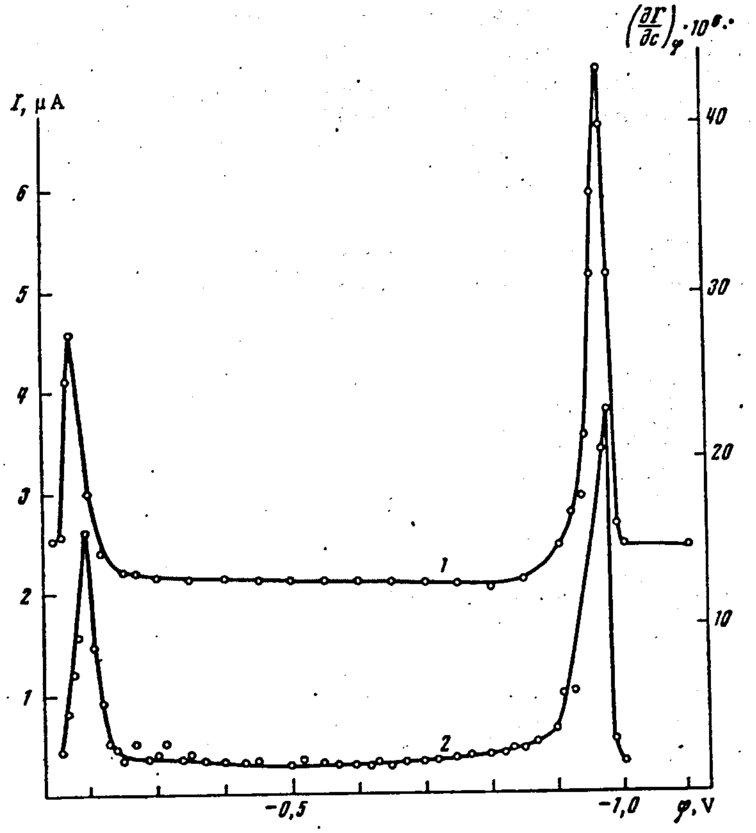

Fig. 5. Comparison between $\partial\Gamma/\partial c-\varphi$ and $I-\varphi$ curves at an adamantan-1-ol concentration of 8×10^{-4} M. 1) The $I-\varphi$ curve in 10^{-3} N $AgNO_3+1$ M Na_2SO_4+adamantan-1-ol solution; 2) the $\partial\Gamma/\partial c-\varphi$ curve in 1 M Na_2SO_4+adamantan-1-ol solution.

are in qualitative agreement has been drawn in [20]. It is shown there that a critical value of the quantity $(\partial \ln c/\partial \ln \Gamma)$ exists which delimits the regions of stable and unstable hydrodynamic surface flows. According to the results of [20], an interface will be hydrodynamically stable when under conditions of adsorption equilibrium and a given regime of unperturbed flow, the quantity $(\partial \ln c/\partial \ln \Gamma)$ exceeds a certain value. In the case of an S-shaped adsorption isotherm, the plot of $(\partial \ln c/\partial \ln \Gamma)$ against Γ is a curve with minimum. Therefore the interface should be stable when $\Gamma<\Gamma_1$ and when $\Gamma>\Gamma_2$, and unstable in the interval $\Gamma_1\leq\Gamma\leq\Gamma_2$, where Γ_1 and Γ_2 are the points where the $(\partial \ln c/\partial \ln \Gamma)-\Gamma$ curve intersects with the straight line $(\partial \ln c/\partial \ln \Gamma)=(\partial \ln c/\partial \ln \Gamma)_{\mathrm{crit}}$.

However, the literature so far contains no analysis of how the shape of the adsorption isotherm will influence the hydrodynamics of interfaces in liquid–liquid systems. Such an analysis evidently could provide a quantitative explanation for the behavior discussed above.

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