Electroanalytical Chemistry and Interfacial Electrochemistry, 50 (1974) 103–111
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

POLAROGRAPHIC MAXIMA OF THE THIRD KIND

A. N. FRUMKIN, N. V. FEDOROVICH, B. B. DAMASKIN, E. V. STENINA and V. S. KRYLOV
Moscow State University, Institute of Electrochemistry of the Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

(Received 2nd October 1973)

The polarographic maxima of the third kind arise during adsorption of some organic substances on the surface of a mercury drop. They were first described by Doss and Venkatesan[1]. The possibility of the appearance of polarographic maxima in the presence of a concentration gradient of a surfactant was considered in refs. 2 and 3. Sathyanarayana[4,5] showed that well-defined maxima of the third kind are observed in camphor solutions. The authors of refs. 1, 4 and 5 believed that the potentials of the maxima of the third kind must coincide with the potentials of the desorption peaks of the organic substance on the C–φ curve (C = differential capacity, φ = electrode potential). In refs. 6–9 it was shown, by correlation of the results of measurements of the differential capacity and of the current I on a drop, that the maxima can be observed at any potential within the adsorption range of the organic substance if the coverage $\theta \simeq 0.3$–0.5. It was also established that the appearance of these maxima is not associated with the presence of an electric field gradient.

So far typical maxima of the third kind have been observed during adsorption of some organic substances belonging to different classes: camphor, borneol, adamantanol (AdOH)[6–9], guanine*. All these substances are sparingly soluble in water, show a large surface activity and, at sufficient concentration, form two-dimensional condensed layers on a mercury surface[5,10,11].

The tangential motions of the drop surface accompanying the appearance of the maxima of the third kind could be revealed by the motion of carbon particles suspended in solution, which was observed with the help of a cathetometer[12,13]. The carbon particles were first cleansed by the technique described in ref. 14. In order to avoid a change in the organic substance concentration upon introduction of carbon into solution, the carbon had previously been brought into equilibrium with the solution, *e.g.* 0.01 g of the carbon was kept in 5 ml of 1 M $Na_2SO_4 + 10^{-3}$ M AdOH solution for a day. The observation of the suspended carbon particles showed that over the whole potential range of the appearance of the polarographic maxima of the third kind the solution at the drop surface was in motion. However, when the streaming of the solution for maxima of the third and that of the second kind

* Ill-defined maxima of the third kind are observed at the desorption potentials of nonyl alcohol and tribenzylmethylammonium sulfate. We leave open the question whether various anomalies of the I–φ curves at a DME occurring in the presence of surfactants and described in the polarographic literature should be identified with typical maxima of the third kind.

are compared at the same current strength of the respective maximum, the particles' velocity proves to be much less in the former case, with the exception of the region directly adjoining the drop surface. Near and on the drop surface the motions are intensive and irregular. The motions of the surface seem to be of turbulent nature, just as those described for the case of the catalytic maxima[15].

An attempt has been made to elucidate the mechanism of the appearance of the maxima of the third kind on the basis of the theory developed in refs. 2 and 3. According to this theory, the velocity of the drop surface v is approximately equal to

$$v \sim \frac{(\partial\sigma/\partial c)(\partial c/\partial x)a}{2\mu+3\mu'+\gamma_\varepsilon+\gamma_a} \tag{1}$$

where $\partial\sigma/\partial x=(\partial\sigma/\partial c)(\partial c/\partial x)$ is the surface tension gradient along the drop surface, a is a quantity with dimension of length, c is the bulk concentration of the substance being adsorbed, μ' and μ are the viscosities of mercury and solution, respectively, γ_ε and γ_a are the hindrance of the streaming caused by the double layer charges and the adsorbed layer, respectively.

If it is assumed that the leveling of surface concentrations occurs by the surface diffusion mechanism (see ref. 2, footnote on p. 1980) and the inequality $\gamma_a \gg 2\mu+3\mu'+\gamma_\varepsilon$ are valid, then to a certain approximation[16] we can obtain

$$v \sim K' D_s \, \partial\Gamma/\partial c \tag{2}$$

where D_s is the surface diffusion coefficient. It follows from eqn. (2) that the dependence of the velocity of streaming of the drop surface on potential should be similar to the potential dependence of $\partial\Gamma/\partial c$.

To check this conclusion, we calculated the $\partial\Gamma/\partial c$–$\varphi$ dependences for AdOH (and borneol) adsorption from experimental C–φ curves and compared the data obtained with the corresponding I–φ curves. When the current is flowing on the drop, the effects associated with the radial expansion of the drop and with mixing caused by the surface streaming are summed up. Since there is no quantitative theory for this summation[17] and considering the approximate treatment of the problem in the present paper, we shall confine ourselves to the correlation of I with the value of v expressed by eqn. (2).

The measurements of the C–φ and I–φ curves were carried out by the technique described in refs. 6–9. The C–φ curves for 1 M Na_2SO_4 with additions of AdOH of different concentrations were measured for a dropping mercury electrode and the results are given in Fig. 2 of ref. 7. The measurements of the capacity and of the current flowing on the drop were performed at the end of the drop-life and refer to the same life-time.

Figure 1 shows the I–φ curves in 10^{-3} M $AgNO_3+1$ M Na_2SO_4 solution with additions of varying amounts of adamantanol. When 1.5×10^{-5} M AdOH (Fig. 1, curve 1) is introduced into the solution, the current near the zero charge potential exceeds the limiting diffusion current in the absence of AdOH (curve 10). With increasing AdOH concentration, the current maximum rises and the potential range of its appearance widens (Fig. 1, curves 2 and 3). Further increase in the AdOH concentration leads to splitting of the current maximum and decrease of the current in the region of the zero charge potential (Fig. 1, curves 4–7). Simultaneously, two current maxima appear on the I–φ curves on both sides of the

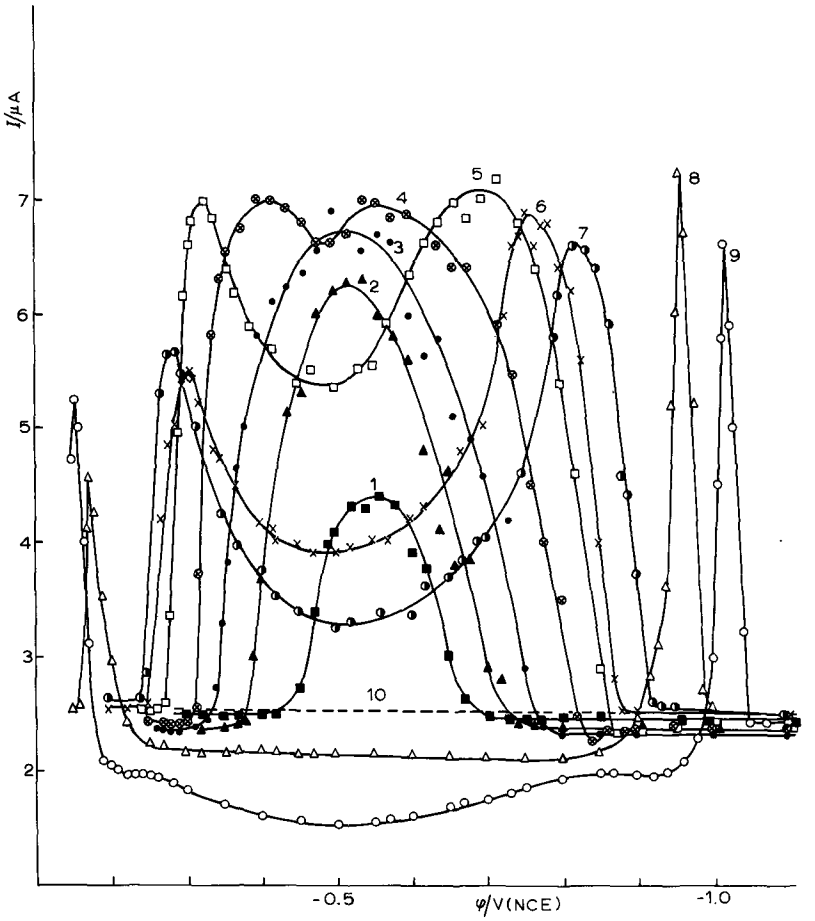

Fig. 1. I–φ curves in 10^{-3} M $AgNO_3 + 1$ M Na_2SO_4 solution with 1-AdOH additions in concentrations: (1) 1.5×10^{-5}, (2) 1.7×10^{-5}, (3) 2×10^{-5}, (4) 2.5×10^{-5}, (5) 3×10^{-5}, (6) 3.5×10^{-5}, (7) 4×10^{-5}, (8) 8×10^{-5}, (9) 10^{-4} M (from ref. 7).

p.z.c., whose potentials move away from the p.z.c. as the AdOH concentration increases. At the highest AdOH concentrations the current maxima are observed only at the desorption potentials of AdOH (Fig. 1, curves 8 and 9). In this case the current strength in the intermediate potential range is less than the limiting diffusion current in the absence of AdOH, which is due to the inhibition of the electrochemical process of the Ag^+ ion discharge.

Figure 2 shows the dependences of $\partial\Gamma/\partial c$ on φ for a 1 M Na_2SO_4 solution with AdOH additions. Since $\Gamma = \Gamma_m\theta$, where Γ_m is the limiting adsorption and θ the surface coverage, it is necessary to know θ to calculate $\partial\Gamma/\partial c$. The values of θ were found from eqn. (3)

$$C = C_0(1-\theta) + C'\theta \tag{3}$$

where C_0 and C' are the capacity values at $\theta = 0$ and $\theta = 1$, respectively. The values of Γ_m were calculated from the dependence of the desorption potential on

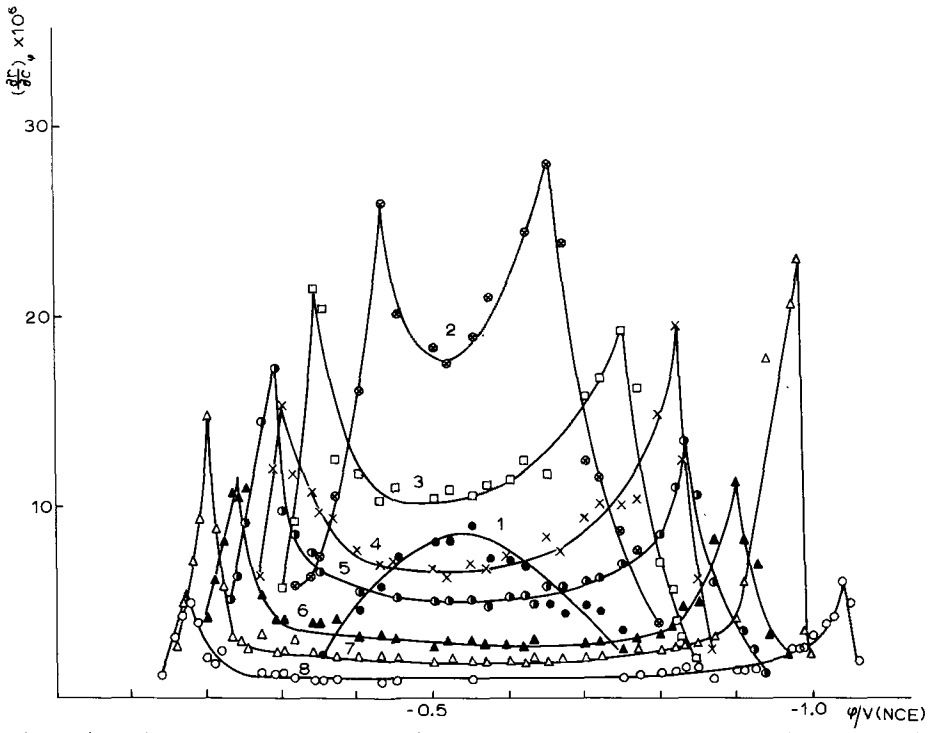

Fig. 2. $(\partial\Gamma/\partial c)_\varphi$–$\varphi$ curves in 1 *M* Na_2SO_4 solution with 1-AdOH additions in concentrations: (1) 2×10^{-5}, (2) 2.5×10^{-5}, (3) 3×10^{-5}, (4) 3.5×10^{-5}, (5) 4×10^{-5}, (6) 6×10^{-5}, (7) 8×10^{-5}, (8) 10^{-4} *M*.

the AdOH concentration by the method described in ref. 11. The values of $(\partial\Gamma/\partial c)_\varphi$ were determined by graphical differentiation of the adsorption isotherm. We calculated θ by means of eqn. (3) without taking the additional capacity into account, because it follows from the theory of the non-equilibrium differential capacity curves in the presence of organic substances[18,19] that the additional capacity value decreases with increase of the attractive interaction between adsorbed molecules. If the value of the attraction constant in the Frumkin isotherm is greater than 2, as is the case in the adsorption of camphor and adamantanol, then in the frequency range 400–1000 Hz it is possible to the first approximation to equate the capacity being measured with the true double layer capacity expressed by eqn. (3). By means of eqn. (3) we calculated the dependence of the surface coverage on the electrode potential at different adamantanol and camphor concentrations. At large camphor concentrations the θ–φ curves found by means of eqn. (3) were compared with similar curves calculated by means of the formula

$$\varepsilon = \varepsilon_0(1-\theta)+\varepsilon'\theta \tag{4}$$

where ε_0 and ε' are the surface charge values at $\theta=0$ and $\theta=1$, respectively. The ε–φ curves in the presence of camphor were obtained by the method of integration of the non-equilibrium C–φ curves described in ref. 20. The agreement between the two calculation methods indicates that it is possible to use eqn. (3)

for the determination of the surface coverage during camphor and adamantanol adsorption.

Comparison of Figs. 1 and 2 shows that the value $\partial\Gamma/\partial c$ reaches its maximum approximately at the same potentials as I at the corresponding AdOH concentrations. With increase of the AdOH concentration, the dependence $\partial\Gamma/\partial c$–$\varphi$ follows the I–φ curves measured in solutions with the same AdOH concentrations.

A more detailed comparison of the I–φ and $\partial\Gamma/\partial c$–$\varphi$ curves is made in Figs. 3–5. At the values of $[\text{AdOH}] \leqslant 2\times10^{-5}$ M, both the I–φ and the $\partial\Gamma/\partial c$–$\varphi$ curves pass through a maximum near the p.z.c. (Fig. 3). With increasing concentration, the maximum on both curves splits up, the potentials of the maxima of $\partial\Gamma/\partial c$ and I remaining practically coincident (Fig. 4). With further increase of concentration, the potentials of the maxima on both curves approach the desorption peak potentials (Fig. 5) and in the limit coincide with them. However, there is a certain quantitative difference between the relative height of the maxima in both series

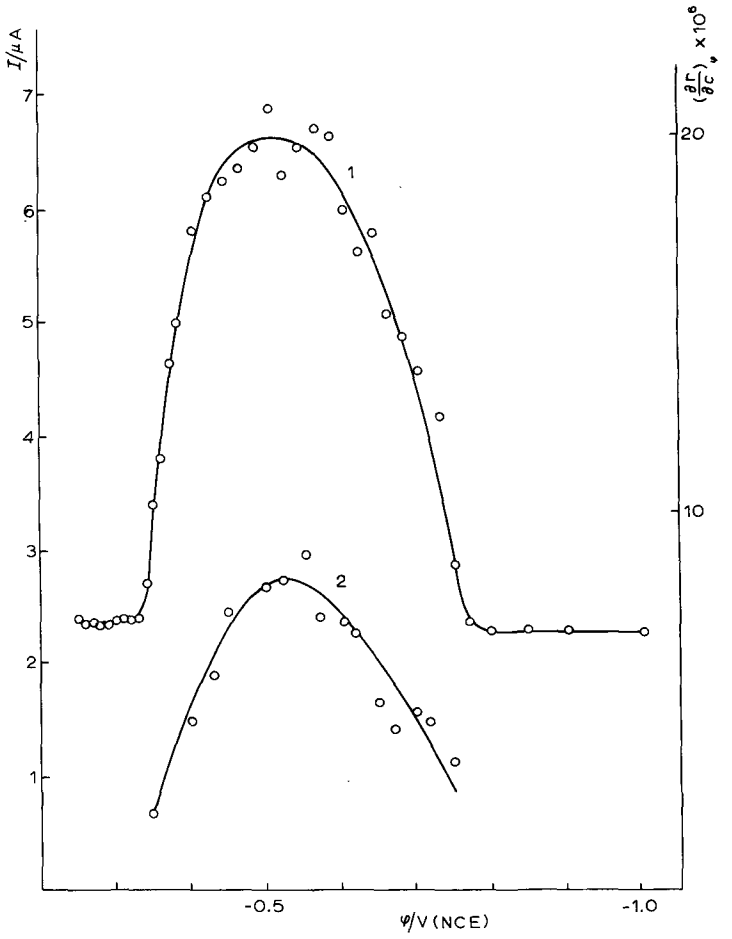

Fig. 3. Comparison of the I–φ dependence in 1 M $Na_2SO_4+10^{-3}$ M $AgNO_3+2\times10^{-5}$ M 1-AdOH solution (1) and the $(\partial\Gamma/\partial c)_\varphi$–$\varphi$ dependence in 1 M $Na_2SO_4+2\times10^{-5}$ M 1-AdOH solution (2).

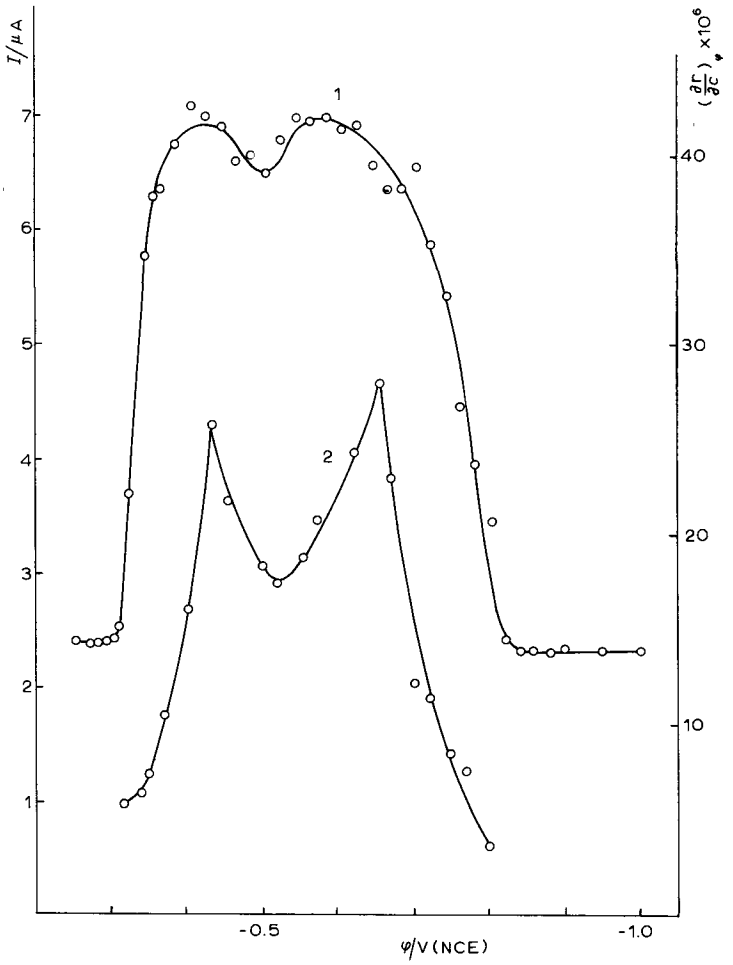

Fig. 4. Comparison of the I–φ dependence in 1 M $Na_2SO_4 + 10^{-3}$ M $AgNO_3 + 2.5 \times 10^{-5}$ M 1-AdOH solution (1) and the $(\partial\Gamma/\partial c)_\varphi$–$\varphi$ dependence in 1 M $Na_2SO_4 + 2.5 \times 10^{-5}$ M 1-AdOH solution (2).

of the curves: in the lowest concentration range $\partial\Gamma/\partial c$ increases with c slower than I does (Fig. 3). On the contrary, when the solution is near to saturation with AdOH, the maxima of $\partial\Gamma/\partial c$ decrease more sharply than those of I. In spite of these discrepancies, there is no doubt about the existence of a correlation between the appearance of the maxima of the third kind and the potential of the maximum steepness of the Γ–C dependence in the case of camphor, adamantanol and their derivatives.

The limitation of the above treatment is that in the deduction of eqn. (2) the assumption is used that the leveling of the surface concentration of adsorbed substance follows the surface diffusion mechanism (*cf.* refs. 24–26). A somewhat different approach to the establishment of the relationship between the potential of the maximum of the third kind and the steepness of the adsorption isotherm is also possible. The latter factor can be considered not only as determining the mini-

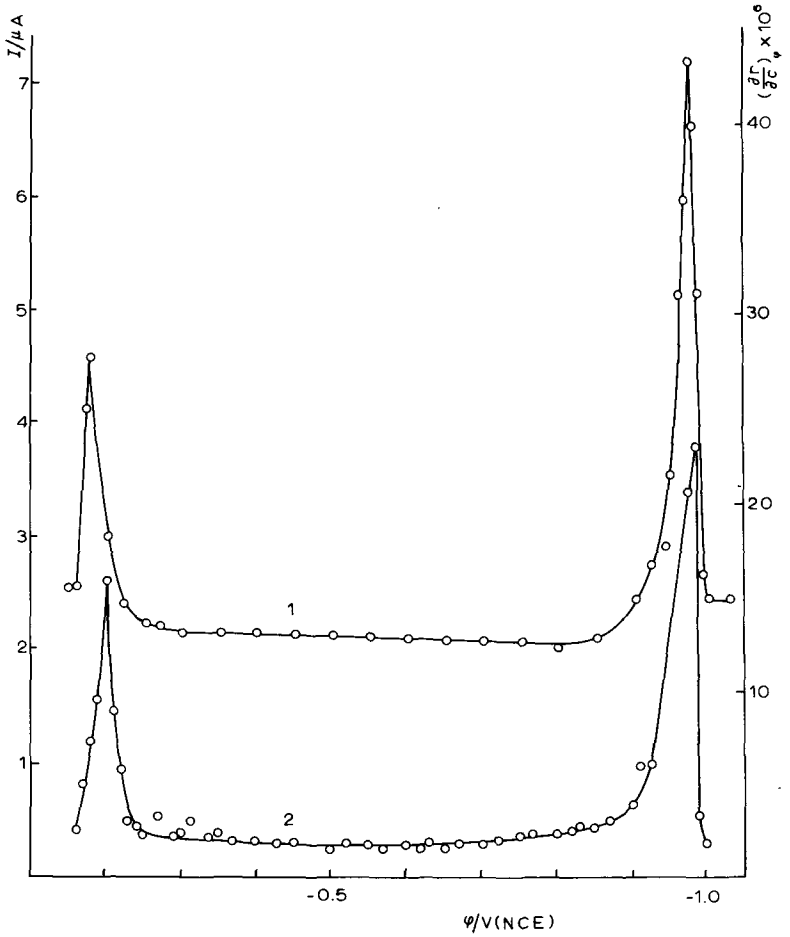

Fig. 5. Comparison of the I–φ dependence in 1 M $Na_2SO_4+10^{-3}$ M $AgNO_3+8\times10^{-5}$ M 1-AdOH solution (1) and the $(\partial\Gamma/\partial c)_\varphi$–$\varphi$ dependence in 1 M $Na_2SO_4+8\times10^{-5}$ M 1-AdOH solution (2).

mal hindrance, but also as being the cause of the appearance of surface streaming. The possibility of such an approach is mentioned in a number of papers concerned with the theoretical investigation of the influence of adsorption and diffusion processes on the hydrodynamic stability of mobile interfacial boundaries[21–26]. It was established in those papers, in particular in ref. 21, that instability due to local changes in the interfacial surface tension during mass transfer can arise in the case of a quite definite type of dependence of the surface tension σ on the Gibbs adsorption Γ. In the case of adsorption at the liquid/gas interface when the rate of surfactant supply to the interface is limited by convective diffusion in the liquid phase, quantitative relations have been obtained which describe the influence of the Gibbs' adsorption on the stability of the interface against small perturbations induced by the inhomogeneity of the concentration field of adsorbed substance[24–26]. According to the results obtained, the surface convection in the liquid–gas systems produces a much stronger leveling effect on the concentration field of adsorbed substance than the

surface diffusion. An important conclusion, which is in qualitative agreement with our results, was drawn in ref. 23, where a critical value of $\partial \ln c/\partial \ln \Gamma$ was found to exist, which separates the regions of stable and unstable hydrodynamic flows. According to the results of ref. 23, the interface is hydrodynamically stable, if at the adsorption equilibrium under given unperturbed flow conditions, $\partial \ln c/\partial \ln \Gamma$ exceeds a certain value. In the case of an S-shaped adsorption isotherm, the plot of $(\partial \ln c/\partial \ln \Gamma)$ *vs.* Γ is in the form of a curve with a minimum. The interfacial boundary is stable at $\Gamma < \Gamma_1$ and $\Gamma > \Gamma_2$ and unstable in the range $\Gamma_1 \leqslant \Gamma \leqslant \Gamma_2$, where Γ_1 and Γ_2 are the points of intersection of the $(\partial \ln c/\partial \ln \Gamma)$–$\Gamma$ curve with the straight line $(\partial \ln c/\partial \ln \Gamma) = (\partial \ln c/\partial \ln \Gamma)_{\text{crit}}$.

At present no analysis of the influence of the kind of the adsorption isotherm on the hydrodynamics of interfacial boundaries in liquid–liquid systems is available in the literature. Apparently, such an analysis would help to explain the phenomena discussed above*.

So far no light has been thrown on the question why well-defined motions of the third kind arise during adsorption of surfactants with a compact molecule structure, such as adamantanol or camphor, and do not manifest themselves (or at least do so much more weakly) in the case of adsorption of substances with a long chain.

SUMMARY

The conditions of the appearance of the maxima of the third kind have been investigated. It is shown that these maxima are due to turbulent motions of the mercury drop surface, arising during adsorption of sparingly-soluble surfactants (camphor, adamantanol and their derivatives), forming condensed adsorption layers when their concentration in the solution bulk is not too small. The potentials of the maxima of the third kind are close to the potentials corresponding to the maximum values of $\partial\Gamma/\partial c$ and to values of the coverage, θ, in the $\theta = 0.3$–0.5 range.

REFERENCES

1 K. Doss and D. Venkatesan, *Proc. Indian Acad. Sci.*, 49 (1959) 129.
2 A. Frumkin, S. Sathyanarayana and N. Nikolaeva-Fedorovich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1962) 1977.
3 V. Levich and A. Kusnezov, *Dokl. Akad. Nauk SSSR*, 146 (1962) 145.
4 S. Sathyanarayana, *J. Electroanal. Chem.*, 10 (1965) 56.
5 S. Sathyanarayana and K. Baikerikar, *J. Electroanal. Chem.*, 21 (1969) 449.
6 A. Frumkin, E. Stenina and N. Fedorovich, *Elektrokhimiya*, 6 (1970) 1572.
7 A. Frumkin, E. Stenina, N. Fedorovich, G. Petukhova, V. Yusupova and E. Shokova, *Dokl. Akad. Nauk SSSR*, 201 (1971) 1406.
8 N. Nikolaeva-Fedorovich, E. Stenina, G. Petukhova, V. Yusupova and E. Shokova, *Elektrokhimiya*, 8 (1972) 157.

* The theoretical investigation of the stability of the liquid/gas interface in the presence of insoluble films of surfactants carried out in ref. 27 has proved the possibility of the existence of a periodic pattern of circulation flows at the interface. This treatment applies to the liquid/liquid interface as well.

9 A. Frumkin, E. Stenina, N. Nikolaeva-Fedorovich, G. Petukhova and V. Yusupova, *Rev. Roum. Chim.*, 17 (1972) 155.
10 B. Damaskin, O. Petrii and V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York, 1971.
11 K. Baikerikar and S. Sathyanarayana, *J. Electroanal. Chem.*, 24 (1970) 333.
12 N. Beresina and N. Nikolaeva-Fedorovich, *Elektrokhimiya*, 3 (1967) 3.
13 T. Kryukova and B. Kabanov, *Zh. Fiz. Khim.*, 13 (1939) 1454.
14 T. Kryukova, *Zh. Fiz. Khim.*, 21 (1947) 365.
15 M. Stackelberg and H. Fassbender, *Z. Elektrochem.*, 62 (1958) 834.
16 A. Frumkin, N. Fedorovich, B. Damaskin, E. Stenina and V. Krylov, *Elektrokhimiya*, 10(6) (1974).
17 T. Kryukova and A. Frumkin, *Zh. Fiz. Khim.*, 23 (1949) 1477.
18 G. Tedoradse and Ya. Zolotovitzkii, *Elektrokhimiya*, 1 (1965) 201.
19 B. Damaskin, *Elektrokhimiya*, 1 (1965) 255.
20 B. Damaskin and S. Dyatkina, *Elektrokhimiya*, 7 (1971) 260.
21 C. V. Sternling and L. E. Scriven, *AIChEJ*, 5 (1959) 514.
22 S. Whitaker, *Ind. Eng. Chem. Fundam.*, 3 (1964) 132.
23 J. Berg and A. Acrivos, *Chem. Eng. Sci.*, 20 (1965) 737.
24 P. Brian, *AIChEJ*, 17 (1971) 765.
25 P. Brian and K. Smith, *AIChEJ*, 18 (1972) 231.
26 P. Brian and J. Ross, *AIChEJ*, 18 (1972) 582.
27 H. Linde and P. Schwartz, *Teor. Osn. Khim. Tekhnol.*, 5 (1971) 401.