Revue Roumaine de Chimie, **17**, *1*, *2*, 155–160 (1972)

Dedicated to Professor I. G. MURGULESCU on his 70th birthday

POLAROGRAPHIC MAXIMA OF THE THIRD KIND. II

BORNEOL

A.N. FRUMKIN, E.V. STENINA, N.V. NIKOLAEVA-FEDOROVICH, G.N. PETUKHOVA, V.A. YUSUPOVA

Moscow State University, USSR

Received September 24, 1971

It was shown that in the presence of borneol well defined maxima of the third kind appear on the current-voltage curve of the 10^{-3} M $AgNO_3$ + M Na_2SO_4 solution. The maxima can be obtained at any potential but only as long as the coverage of the mercury surface by the surfactant does not exceed a certain limit.

INTRODUCTION

In [1] the polarographic maxima, which are due to tangential motions caused by the adsorption process itself, were called polarographic maxima of the third kind. For the first time current maxima on the current-potential (I, φ) curves and tangential motions of the mercury drop surface were observed at the desorption potentials of a surfactant by Doss. [2] Current maxima at the desorption potentials were observed in solutions in which butyl and octyl alcohols were emulgated. [3] In [3] it was suggested that the appearance of the current maxima at the adsorption-desorption potentials is related to the presence of a concentration gradient of surfactants, which results from the adsorption process itself. Sathyanarayana [4] for the first time obtained well-defined and reproducible current maxima in the case of reduction of Cu^{2+} and Cd^{2+} in the presence of camphor additions. Comparing the I, φ—and the differential capacity-potential (C, φ) curves he showed that the largest maximum corresponds to the desorption potential of camphor. In, [1] at the desorption potentials of

[1] A.N. FRUMKIN, E.V. STENINA and N.V. FEDOROVICH, *Elektrokhimiya*, **6**, 1572 (1970).

[2] K. Doss and D. VENKATESAN, *Proc. Indian Acad. Sci*, **49**, 129 (1959).

[3] A.N. FRUMKIN, S. SATHYANARAYANA and N.V. NIKOLAEVA-FEDOROVICH, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, **1962**, 1977.

[4] S. SATHYANARAYANA, *J. Electroanalyt. Chem.*, **10**, 56 (1965).

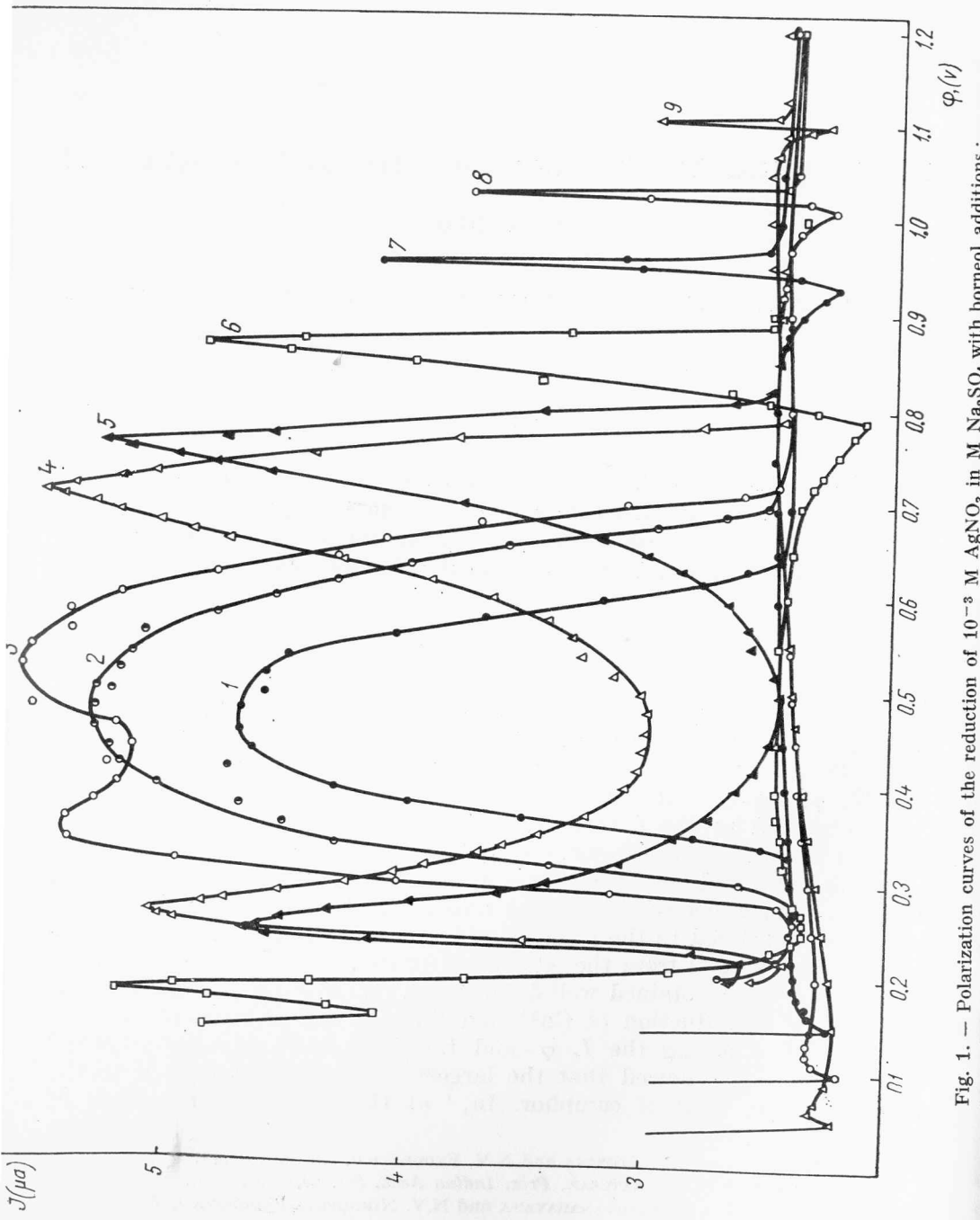

Fig. 1. — Polarization curves of the reduction of 10^{-3} M $AgNO_3$ in M Na_2SO_4 with borneol additions: *1*, 3×10^{-5} M; *2*, 3.5×10^{-5} M; *3*, 4×10^{-5} M; *4*, 5×10^{-5} M; *5*, 6×10^{-5} M; *6*, 1×10^{-4} M; *7*, 1.8×10^{-4} M; *8*, 3×10^{-4} M; *9*, 6×10^{-4} M.

camphor, positive and negative current maxima were obtained for the reduction reaction of Cu^{2+}, Ag^{+} and Tl^{+}, but at small camphor concentrations the current increase was observed over the whole range of adsorption potentials.

Thus, so far well defined polarographic maxima of the third kind have been obtained only in the case of camphor adsorption. For further investigation of these maxima we studied their appearance in the case of adsorption of other substances whose structure is similar to that of camphor, such as borneol, for example. In this investigation we used the experimental technique described in. [1]

DISCUSSION

Figure 1 shows the I, φ-curves for 10^{-3} M $AgNO_3$ + M Na_2SO_4 with different borneol additions. The most positive part of the I, φ-curves where a polarographic maximum of the first kind appears is not reproduced in the figure. Introduction of 3×10^{-5} M borneol leads to a current increase in the region of the potential of zero charge (pzc) (Fig. 1, curve 1). With rising borneol concentration, the current at the maximum increases and the potential range in which the polarographic maximum is observed widens. Further increase of borneol concentration leads first to a splitting of the maximum and then to a decrease in the current at the maximum and even to a complete disappearance of the maximum in the pzc range (Fig. 1, curves 3—5). At borneol concentrations in excess of a certain limit, maxima appear only at relatively large positive and negative charges of mercury surface.

We have also measured the dependence of the current on the drop growth time (I, t-curves). In the range of potentials of the maxima of the third kind we found considerable distortions of the I, t-curves in the form of irregular oscillations, which suggests that the current maxima observed are associated with irregular mercury surface motions. [5]

To establish the relation between the appearance of the maxima and the surface coverage we measured the C, φ-curves in M Na_2SO_4 in the presence of borneol (Fig. 2). The shape of the C, φ-curves in these solutions is similar to that of the C, φ-curves in solutions with camphor additions. [6] There are no pronounced capacity peaks on the C, φ-curves at the adsorption-desorption potentials, which is characteristic of adsorp-

[5] A.B. Ershler, D.I. Dzhaparidze and G.A. Tedoradze, *Zhur. fiz. Khim.*, **37**, 666 (1963).
[6] S. Sathyanarayana and K. Baikerikar, *J. Electroanalyt. Chem.*, **21**, 449 (1969).

tion processes which follow the Frumkin isotherm with a value of the attraction constant $a \geqslant 2$.[7] If we compare the I, φ and the, C, φ-curves, we see that at small borneol concentrations the potential range in which

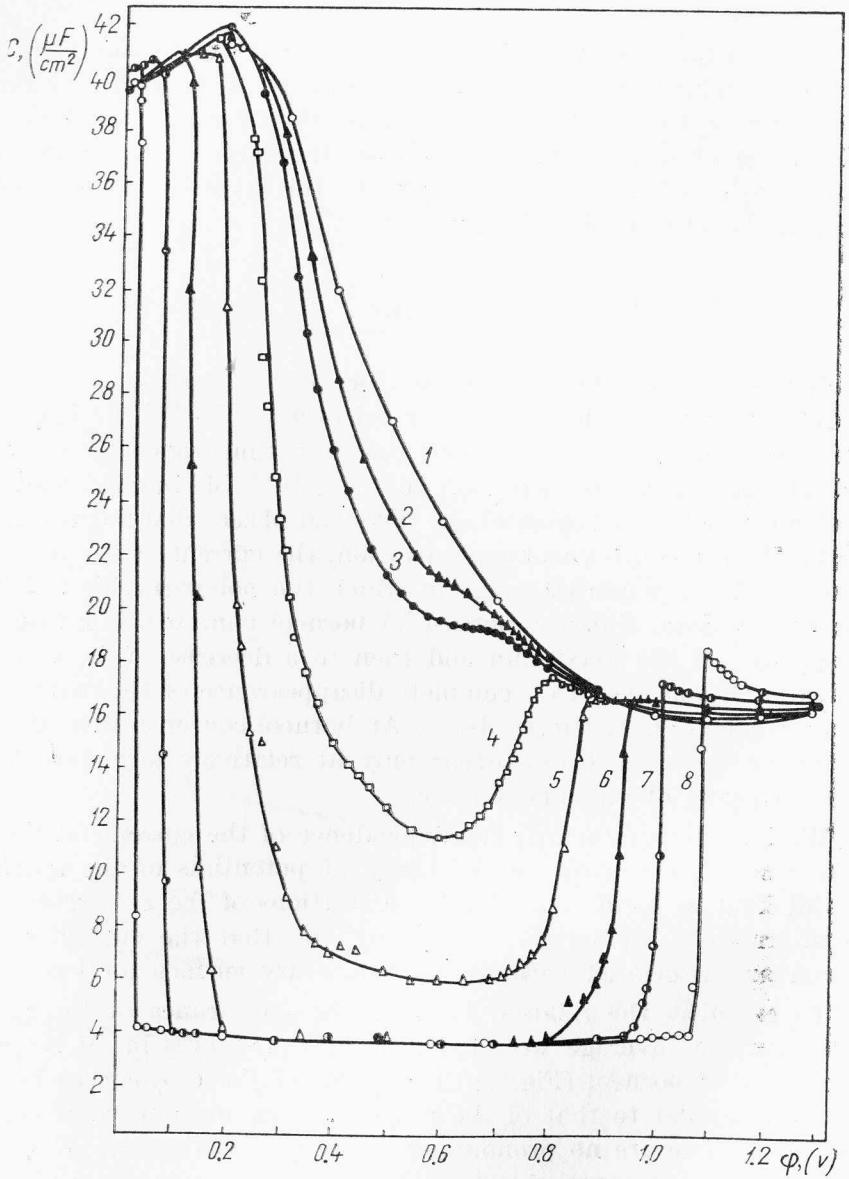

Fig. 2. — Differential capacity -potential curves in M Na_2SO_4 solutions (1) with borneol additions :
2, 3×10^{-5} M; *3*, 4×10^{-5} M; *4*, 6×10^{-5} M; *5*, 10^{-4} M; *6*, 1.8×10^{-4} M; *7*, 3×10^{-4} M; *8*, 6×10^{-4} M.

[7] A.N. Frumkin and B.B. Damaskin, "Sovremenniye aspekti elektrokhimii", J.O.'M. Bockris ed. 1967, Moscow, "Mir", p. 170.

the current increases in excess of the diffusion current coincides with the potential range in which borneol is adsorbed (Fig. 3), the highest current maximum corresponding to the greatest adsorption of borneol. At these

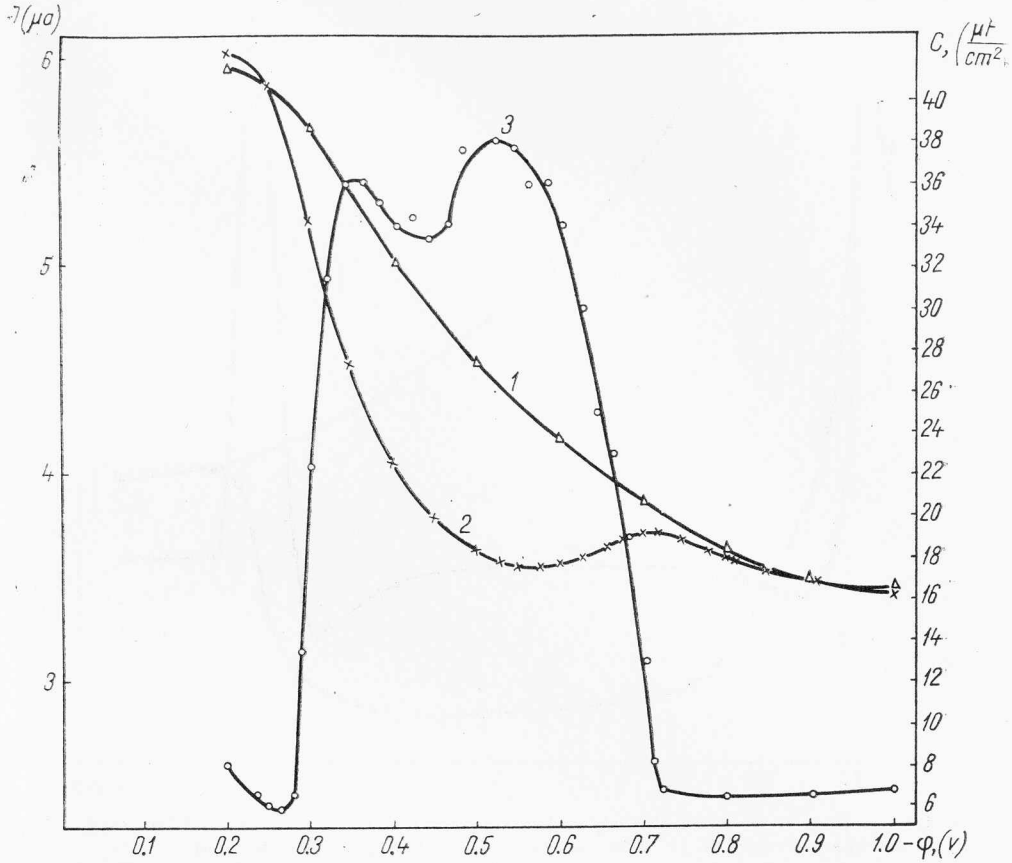

Fig. 3. — *1*, C, φ-curve in MNa_2SO_4 and *2*, same with borneol addition in the concentration 4×10^{-5} M; *3*, I, φ-curve in the solution 10^{-3} M $AgNO_3$ + M Na_2SO_4 + 4×10^{-5} M borneol.

borneol concentrations the surface coverage θ is much less than unit at all potentials. With increasing borneol concentrations, when the surface coverage in the pzc region increases, the tangential motions of mercury surface caused by nonuniform borneol adsorption diminish and when a certain surface coverage value is reached, the maxima of the third kind disappear. At these, and higher, borneol concentrations the maxima are observed only at the desorption potential (Fig. 4), as was the case with camphor.

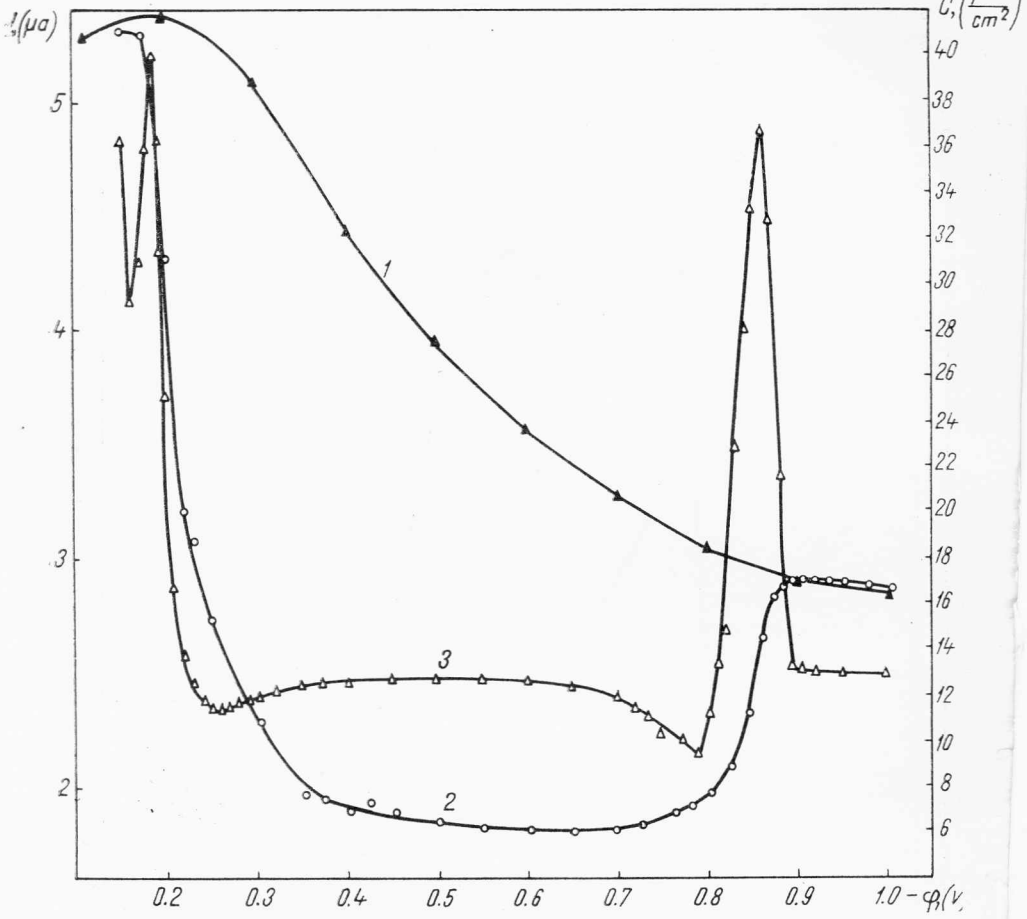

Fig. 4. — *1*, *C*, φ-curve in M Na_2SO_4 and *2*, same with addition of 10^{-4} M borneol; *3*, *I*, φ -curve in the solution of 10^{-3} M $AgNO_3$ + M Na_2SO_4 + 10^{-4} M borneol.

CONCLUSIONS

From the above it results that the appearance of the sharp polarographic maxima of the third kind at the adsorption-desorption potentials is associated only with the fact that at these potentials the surface coverage can assume any value from zero to unit in a narrow potential range.

As will be shown in a subsequent paper the disappearance of the maxima at higher surfactant concentration is caused by the inhibition of the tangential motions under the action of the adsorbed layer.