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Two kinds of polarographic current maxima have now been described in the literature. The first kind arises in a dilute electrolytic solution because of the appearance of tangential motion of the surface of the mercury drop, which is caused by the nonequivalence of different parts of the mercury surface with respect to polarization, and by nonuniform supply of the substance being reduced [1, 2]. A semiquantitative theory of maxima of the first kind was given by Frumkin and Levich [3] on the basis of these ideas. The tangential motion which arises as a result of the nonequivalence of different parts of the drop surface with respect to polarization was also treated as the reason for the appearance of maxima of the first kind in studies by Antweiler and Stakelberg [4]. Stakelberg's theory was examined critically by Frumkin [5]. According to de Levie [6], the main reason for the appearance of maxima of the first kind is nonuniform supply of the substance being reduced.

At high solution conductivities and at high mercury flow rates from the capillary, one observed polarographic maxima of the second kind, which were discovered and studied by Kryukova [7]. They appear because of motion of the mercury surface, due to mercury flow from the capillary. Mixed polarographic maxima are also known, caused by the interaction of the first and second kinds of motion; these are the so-called inverted maxima [8].

Having discovered the polarographic maxima, Heyrovsky suggested that currents exceeding the limiting diffusion current to the mercury drop might be due to attraction of the substance being reduced by the nonuniform electric field at the drop surface [9]. The error in this suggestion has been discussed adequately in the literature [1, 2].

Surface-active organic substances suppress polarographic maxima, as was first shown by Heyrovsky [10]. This suppression is due to damping of the tangential motion. A quantitative theory of this damping was derived by Frumkin and Levich [11] and experimentally checked by Kryukova [12].

Evidence has recently appeared that adsorption phenomena may also be able to aid the development of polarographic maxima near the potentials of the reduction halfwave of certain organic substances [13, 14]. According to Barker and Bolzan [15], nonuniform mass transport during the passage of the current may cause concentration gradients of the surface-active depolarizer and thus surface-tension gradients; this nonuniform mass transport accordingly becomes the reason for the tangential motion.

Doss was the first to draw attention to the tangential motion and current maxima on the I, φ curves which arise at the adsorption, desorption potentials of surface-active substances, but he mistakenly suggested that these latter substances caused the peaks on the potential dependences of the differential capacitance [16]. Similar maxima were observed in [17], but their cause was not discussed. Frumkin, Sathyanarayana, and Nikolaeva-Fedorovich [18] found maxima during the desorption of organic substances in solutions containing an excess of butyl or octyl alcohol emulsified in drop form. It was suggested in this study that the concentration gradient of surface-active substances arises because of the adsorption process itself; a quantitative expression was given for the drop velocity when there was a concentration gradient of the adsorbing substance in the solution adjacent to the drop. A theory for the drop motion in the presence of a concentration gradient of a surface-active substance was derived independently by Levich [19].

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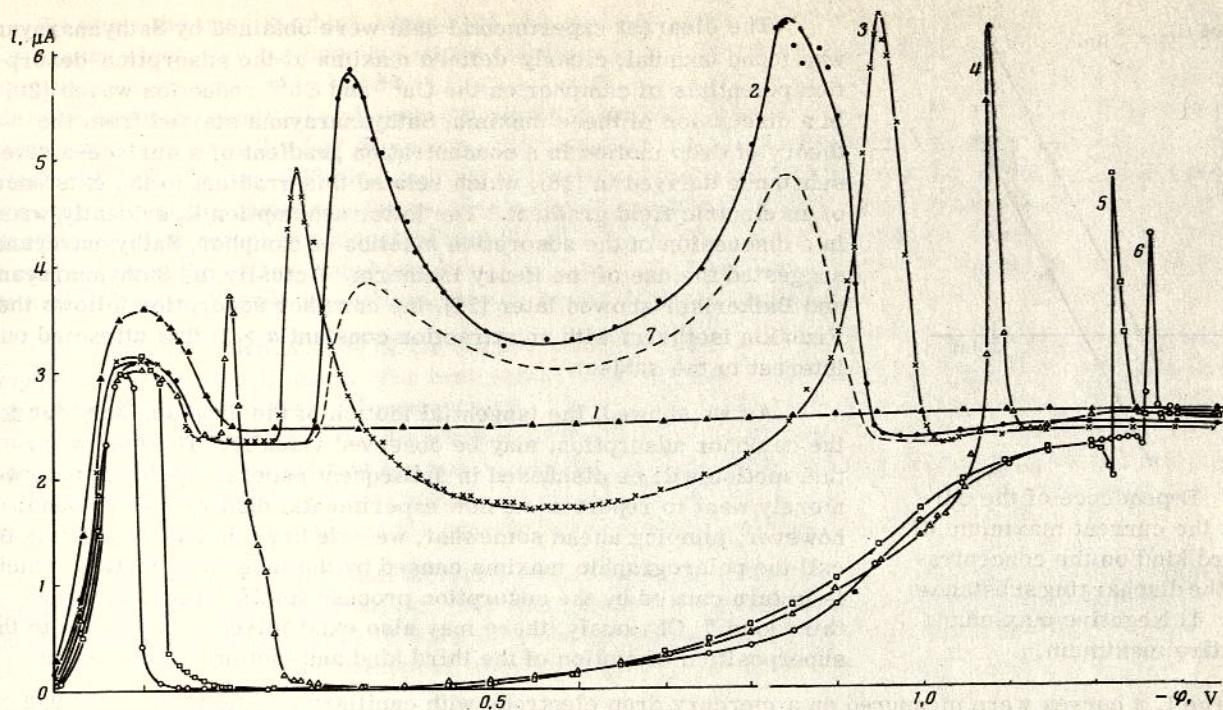


Fig. 1. Polarization curves for Cu^{2+} reduction at a mercury drop electrode in $5 \cdot 10^{-4}$ M CuSO_4 + 1 M Na_2SO_4 with the following camphor admixtures: 1) 0; 2) $6 \cdot 10^{-5}$; 3) $9 \cdot 10^{-5}$; 4) $1.8 \cdot 10^{-4}$; 5) $5 \cdot 10^{-4}$; 6) $7.5 \cdot 10^{-4}$; 7) $6 \cdot 10^{-5}$ M (the solution was prepared from doubly distilled water not purified by activated charcoal).

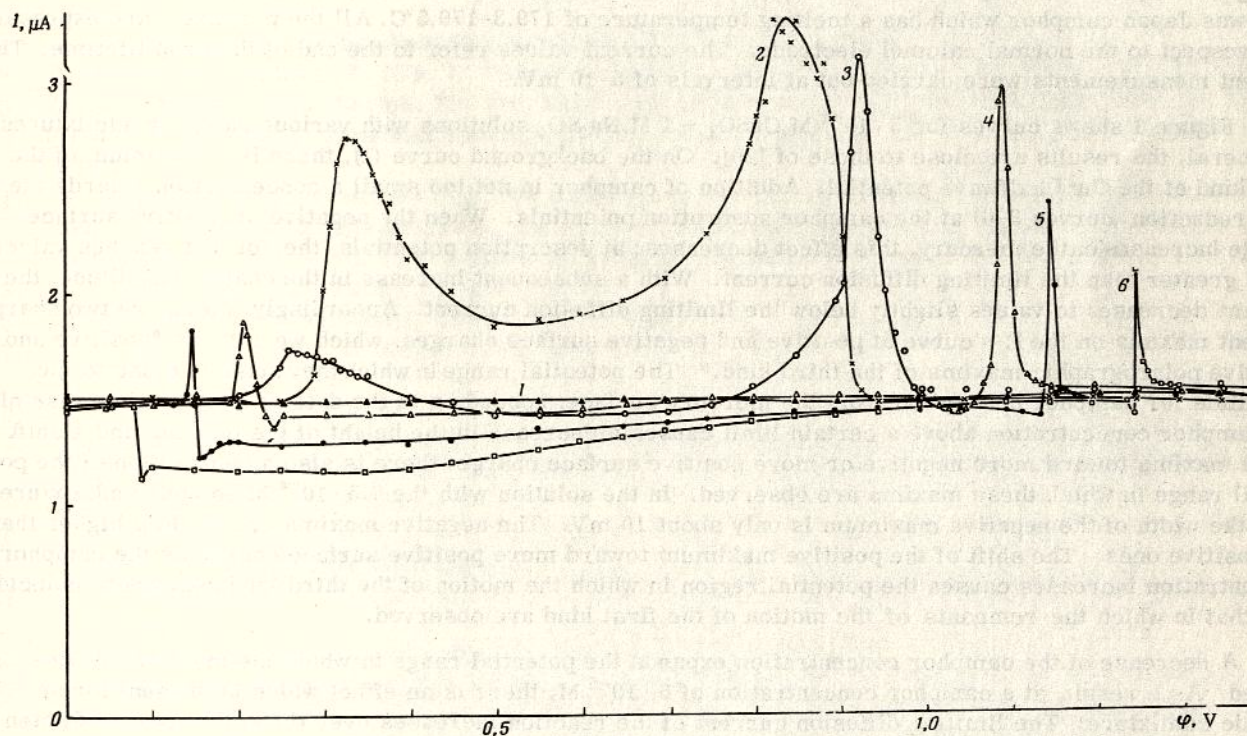


Fig. 2. Polarization curves for Ag^+ reduction in $5 \cdot 10^{-4}$ M AgNO_3 + 1 M Na_2SO_4 with the following camphor admixtures: 1) 0; 2) $6 \cdot 10^{-5}$; 3) $9 \cdot 10^{-5}$; 4) $1.8 \cdot 10^{-4}$; 5) $3 \cdot 10^{-4}$; 6) $7.5 \cdot 10^{-4}$ M.

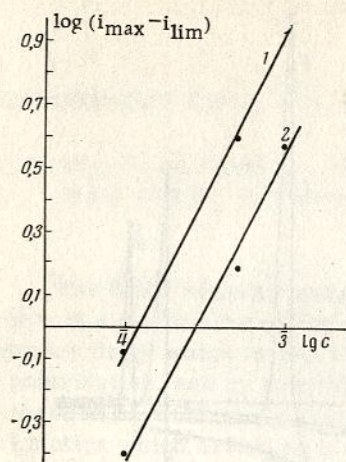


Fig. 3. Dependence of the current at the current maximum of the third kind on the concentration of the discharging substance (Cu^{2+}). 1) Negative maximum; 2) positive maximum.

The I, φ curves were measured on a mercury drop electrode with capillary constants of $m = 0.933$ mg/sec and $\tau = 9$ sec in doubly distilled water under open-circuit conditions. The Na_2SO_4 salt used as the background electrolyte was doubly recrystallized from doubly distilled water and was roasted; the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and TINO_3 salts were synthesized from pure initial substances. All the solutions were prepared from doubly distilled water purified by activated charcoal by the procedure described in [22]. The vessels were treated with concentrated H_2SO_4 and washed successively with "redistilled" and doubly distilled water free of organic impurities. Tap water was not used to wash the cells and vessels. The surface-active substance used was Japan camphor which has a melting temperature of $179.3\text{--}179.5^\circ\text{C}$. All the potentials are expressed with respect to the normal calomel electrode. The current values refer to the end of the drop lifetime. The current measurements were carried out at intervals of 5–10 mV.

Figure 1 shows curves for $5 \cdot 10^{-4}$ M $\text{CuSO}_4 + 1$ M Na_2SO_4 solutions with various camphor admixtures. In general, the results are close to those of [20]. On the background curve (1), there is a maximum of the first kind at the Cu^{2+} halfwave potential. Addition of camphor in not too small a concentration retards the Cu^{2+} reduction (curves 3–6) at the camphor adsorption potentials. When the negative or positive surface charge increases on the mercury, this effect decreases; at desorption potentials, the current reaches values much greater than the limiting diffusion current. With a subsequent increase in the charge magnitude, the current decreases to values slightly below the limiting diffusion current. Accordingly, there are two sharp current maxima on the I, φ curve at positive and negative surface charges, which we call the "positive and negative polarographic maxima of the third kind." The potential range in which they arise is close to the potentials for camphor desorption from the mercury surface, according to the data of [20]. An increase of the camphor concentration above a certain limit causes a decrease in the height of the maxima and a shift of the maxima toward more negative or more positive surface charge; there is also a contraction of the potential range in which these maxima are observed. In the solution with the $7.5 \cdot 10^{-4}$ M camphor admixture, e.g., the width of the negative maximum is only about 10 mV. The negative maxima are slightly higher than the positive ones. The shift of the positive maximum toward more positive surface charge as the camphor concentration increases causes the potential region in which the motion of the third kind appears to coincide with that in which the remnants of the motion of the first kind are observed.

A decrease of the camphor concentration expands the potential range in which the maxima are observed. As a result, at a camphor concentration of $6 \cdot 10^{-5}$ M, there is an effect which is unusual for an organic admixture: The limiting diffusion current of the reaction increases over the entire range of potentials corresponding to the adsorption of this substance (curve 2). This phenomenon has apparently not been described in the literature previously.

The clearest experimental data were obtained by Sathyanarayana, who found unusual, clearly defined maxima at the adsorption-desorption potentials of camphor on the Cu^{2+} and Co^{2+} reduction waves [20]. In a discussion of these maxima, Sathyanarayana started from the theory of drop motion in a concentration gradient of a surface-active substance derived in [18], which related this gradient to the existence of an electric field gradient. The latter assumption is evidently wrong. In a discussion of the adsorption kinetics of camphor, Sathyanarayana suggested the use of the Henry isotherm. Actually, as Sathyanarayana and Baikerikar showed later [21], the camphor adsorption follows the Frumkin isotherm with an attraction constant $a > 2$; this attracted our interest to the subject.

As we showed, the tangential motion of the drop surface, due to the camphor adsorption, may be observed visually. The theory for this motion will be discussed in subsequent papers. In this paper, we merely want to report some new experimental data which we found; however, jumping ahead somewhat, we note here that we would like to call the polarographic maxima caused by the tangential motion, which is in turn caused by the adsorption process itself, "maxima of the third kind." Obviously, there may also exist mixed maxima due to the superposition of motion of the third kind and motion of other kinds.

To study the case in which adsorption of a surface-active substance causes motion at the surface of the mercury electrode, but does not cause a change in the rate of the electrochemical reaction itself, we observed the discharge of Ag^+ and Tl^+ ions in 1 M Na_2SO_4 solution with various camphor additives (Fig. 2). Under the dropping conditions chosen, the camphor caused essentially no decrease in the rate of these reactions. In the case of the Ag^+ discharge, there was only a very slight reduction of the current in comparison with the limiting diffusion current at the highest camphor concentrations. Sharp current maxima were observed at the camphor adsorption-desorption potentials on the polarization curves for Ag^+ and Tl^+ reduction. At low camphor concentrations ($6 \cdot 10^{-5}$ M), as for the Cu^{2+} reduction, there was an increase in the current over the entire camphor adsorption range. For the case of the Tl^+ discharge, whose halfwave potential is -0.504 V, only the cathode maximum is observed naturally.

We studied the dependence of the current at the maximum on the Cu^{2+} concentration at a constant camphor concentration (Fig. 3). For both positive and negative maxima of the third kind, the current is linearly proportional to the Cu^{2+} concentration over an order-of-magnitude change of the latter. This dependence, which differs from the dependence of the maxima of the first kind on the concentration of the substance being reduced, shows that the motion causing the maximum of the third kind is governed only by the adsorption of the surface-active substance on the mercury drop, and does not depend on the flow of current; accordingly, it does not depend on the potential drop along the mercury surface.

The nature of the adsorption isotherm, which depends on the nature of the surface-active substance, affects the appearance of this motion. For example, we found that the current at the maximum in the third kind decreases with an increase in the concentration of organic admixture in the water (Fig. 1, curve 7). The maxima of the third kind disappear when deionized water containing a large organic admixture is used [22].

The relative paucity of information in the literature about the polarographic maxima of the third kind may be due in part to the stiff purity requirements which must be observed in order to study these maxima, and to the narrowness of the potential range in which the motion of the third kind appears at rather high organic admixtures.

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