SOME NEW FORMS OF POLAROGRAPHIC MAXIMA

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At the present time descriptions are found in the literature of current maxima in the $I-\varphi$ curves for reduction reactions on a mercury drop electrode, which are neither maxima of the first kind nor of the second kind, although the current strength at these maxima even exceeds the normal value of the limiting diffusion current. Doss [1] has observed current maxima at the potential where organic substances are desorbed from the electrode surface. According to Doss, the maxima occur as a result of tangential motions of the mercury drop surface when organic substances are desorbed. Doss has proposed the name "Electrocapallarophoresis" for these motions, and has advanced the idea that the motions are the cause of the well-known sharp maxima (desorption peaks) in the curves giving the differential capacity as a function of potential. Veronskii has described a maximum at o-xylene desorption potentials in a copper reduction wave [2]. Attention may also be called to the unusual maxima in the Co^{2+} reduction wave in the presence of dimethylglyoxime [3], and in the presence of 8-hydroxyquinoline [4], and the maxima on the tellurite reduction wave [5]. There is no unity of opinion among the authors as to the nature of these maxima.

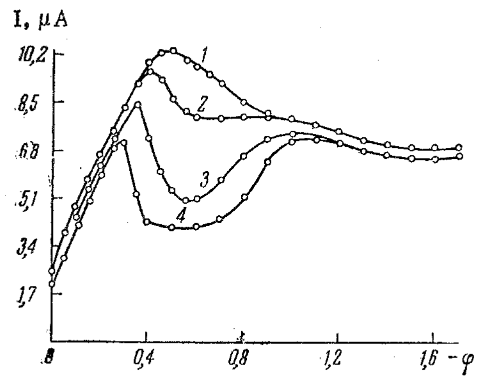

Fig. 1. Polarization curves for the reduction of Hg^{2+} on a mercury drop electrode: 1) $0.68 \cdot 10^{-4}$ M $HgCl_2$ + 0.1 M $BaCl_2$; 2) the same + 0.013 M C_4H_9OH; 3) the same + 0.026 M C_4H_9OH; 4) the same + 0.052 M C_4H_9OH.

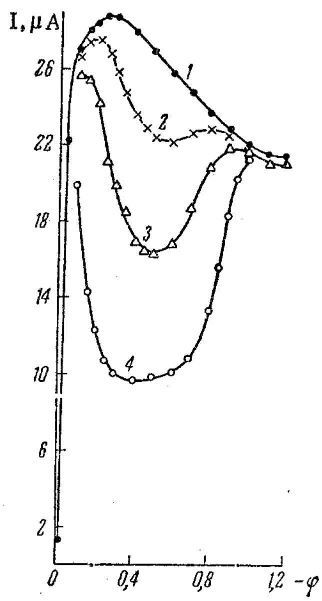

Fig. 2. Polarization curves for the reduction of Cu^{2+} on a mercury drop electrode: 1) 10^{-3} M $CuSO_4$ + 0.25 M H_2SO_4; 2) the same + $2.2 \cdot 10^{-5}$ M o-xylene; 3) the same + $6.4 \cdot 10^{-5}$ M o-xylene; 4) the same + $5.0 \cdot 10^{-4}$ M o-xylene.

The purpose of the present paper was to investigate the possibility of maxima occurring in the $I-\varphi$ curves when organic substances are desorbed. The first thing to do is to try to find out whether or not the maxima observed at the desorption potential have anything to do with the tangential motions of the mercury surface produced when it flows out of the capillary. It is well known that if the mercury flows out at high enough velocities so-called maxima of the second kind [6] appear in the I−φ curves as a result of tangential motions of the mercury electrode surface. If adsorbed organic substances and charge are present on the surface of the mercury drop, the hindrance to motions of the second kind is given by the sum of the adsorptive (γ_a) and electric (γ_ε) terms, and in particular the rate of the tangential motion, v, with the hindrance present is related to the unhindered motion, v_0, as

$$\frac{v}{v_0} = \frac{2\mu + 3\mu'}{2\mu + 3\mu' + \gamma_\varepsilon + \gamma_a} \tag{1}$$

where μ and μ' are the kinematic viscosities of water and mercury. Further

$$\gamma_\varepsilon = \frac{\varepsilon^2}{\varkappa} \tag{2}$$

where ε is the charge density on the mercury surface, and $\varkappa$ is the specific electrical conductivity of the solution and

$$\gamma_a \sim \frac{2RT\Gamma^2\delta}{Dac} \tag{3}$$

under the assumption that the surface active substance is quite easily soluble, and that its adsorption rate is determined solely by the rate of diffusion from the volume of the solution [6, 7]. Here c is the concentration of surface active substance, D is the diffusion coefficient, Γ is the amount of material adsorbed per cm^2, δ is the thickness of the diffusion layer, and a is the radius of the drop.

If adsorption is present, it may be assumed approximately that

$$\varepsilon = C\left(1 - \frac{\Gamma}{\Gamma_\infty}\right)\varphi + C'\frac{\Gamma}{\Gamma_\infty}\varphi \tag{4}$$

where C is the capacity of the double layer in the absence of adsorbed material, C' is the capacity when the surface is filled, Γ_∞ is the limiting value of Γ, and φ is the electrode potential referred to the zero charge point. It is easily shown that the expression $\gamma_\varepsilon + \gamma_a$ can go through a minimum in the desorption region. If we make the simplifying assumptions $C' \ll C$ and $\left|\varphi \frac{\partial \Gamma}{\partial \varphi}\right| \gg \Gamma_\infty$ (the latter inequality will always be true if the desorption is sharply enough defined), it follows from Eqs. (2-4) that the minimum in $\gamma_\varepsilon + \gamma_a$ lies at

$$\frac{\Gamma}{\Gamma_\infty} = \frac{(\gamma_\varepsilon)_{\Gamma=0}}{(\gamma_a)_{\Gamma=\Gamma_\infty} + (\gamma_\varepsilon)_{\Gamma=0}} \tag{5}$$

where $(\gamma_\varepsilon)_{\Gamma=0} = \frac{C^2}{\varkappa}\varphi^2$, i.e., the value of γ_ε in the absence of adsorption, and $(\gamma_a)_{\Gamma=\Gamma_\infty} = \frac{2RT\Gamma_\infty^2\delta}{Dac}$, i.e., the value of γ_a at $\Gamma = \Gamma_\infty$. It may be seen from Eq. (5) that the minimum in $\gamma_\varepsilon + \gamma_a$, and, accordingly, the maximum in v/v_0 and the maximum current in the I−φ curve in the desorption region will be observed in those cases where the value of Γ/Γ_∞, in the adsorption region is greater than the value given by Eq. (5). If $(\gamma_\varepsilon)_{\Gamma=0} \ll (\gamma_a)_{\Gamma=\Gamma_\infty}$, this latter value will be small, in other words, the maximum will lie at very small values of filling of the surface by the adsorbed material, where the current is only slightly different from the value which it reaches after complete desorption. Thus, a clearly defined maximum in the I−φ curves will be observed in those cases where the adsorptive hindrance is not too great in comparison with the hindrance coming from electric charges. Such maxima in the I−φ curves in the cathode desorption potential region are visible in Figs. 1 and 2, and particularly in the curves given in [8]*. However the value of I at the maximum in the I−φ curve in the desorption re-

* It follows from an analysis of the form of the I−φ curves given in [8] that the hindering effect of butyl alcohol on the reduction of H^{2+} ions in the presence of Cl^- ions is limited to hindrance of the tangential motions and does not affect the kinetics of the process itself, which is justified from an application of the considerations given in the text.

gion in the cases investigated lies below the value on the curve found in the absence of surface active material, in other words, adding surface active material and solution lowers the value of the current in all cases. For the opposite condition to occur would require at some value of the potential satisfying the inequality

$$\gamma_\varepsilon + \gamma_a < (\gamma_\varepsilon)_{\Gamma=0} \tag{6}$$

Substituting for γ_ε the expression from (2), it is easily shown that satisfying the inequality (6) means satisfying the inequality

$$\gamma_a < (\gamma_\varepsilon)_{\Gamma=0} \frac{\Gamma}{\Gamma_\infty} \tag{6a}$$

Since the inequality (6a) cannot be satisfied at a small value of Γ/Γ_∞, the condition which it expresses is not very different from the condition

$$(\gamma_a)_{\Gamma=\Gamma_m} < (\gamma_\varepsilon)_{\Gamma=0} \tag{6b}$$

Where $(\gamma_a)_{\Gamma=\Gamma_m}$ is the adsorptive hindrance corresponding with maximum surface filling at the concentration in question in the adsorption region. In other words, acceleration of the tangential motions from the effect of adsorbing an organic substance would be expected in those cases where the hindrance from charges in the absence of adsorption is greater than the adsorptive hindrance when the surface is to a considerable extent filled.

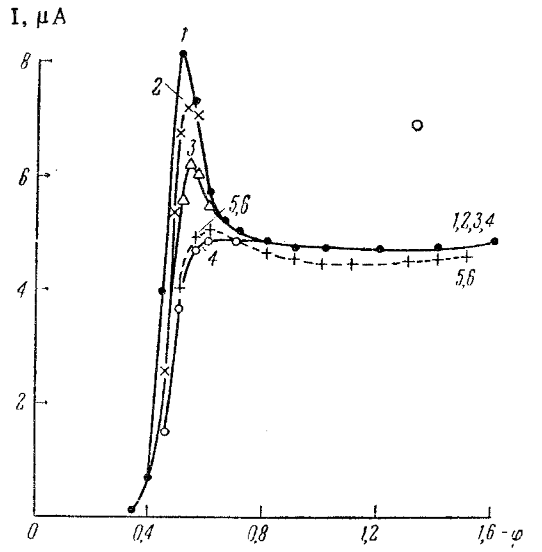

Fig. 3. Polarization curves for the reduction of Tl^+ on a mercury drop electrode: 1) $9.3 \cdot 10^{-4}$ M TlCl+ + 0.02 M $BaCl_2$; 2) the same + 0.016 M C_4H_9OH; 3) the same + 0.032 M C_4H_9OH; 4) the same + 0.064 M C_4H_9OH; 5) the same +0.113 M C_4H_9OH; 6) the same + 0.43 M C_4H_9OH.

In the investigations made previously on hindrances to motions of the second kind, the conditions were chosen in such a way that γ_ε was as small as possible, and the principal effect was that of the hindrance caused by adsorption of dissolved molecules. In this case, in the range of potentials in which adsorption occurs, a reduction is observed in the rate of motion which disappears at the desorption potential. However, the relations between the hindrance to motion coming from adsorption and the hindrance to motion coming from charges could be changed if conditions were set up favorable to a large value of γ_ε in the absence of adsorption and a relatively small value of γ_a when the surface is filled with an adsorbed substance that sharply reduces γ_ε as a result of the reduction in $|\varepsilon|$. It follows from Eqs. (2) and (3) that this result would be expected if the value of γ_ε were large with $\varkappa$ small, i.e., at small electrolyte concentration [especially in the case of multiply charged cations, for example in $La_2(SO_4)_3$ solution], and with a concentration of surface active substance such as to insure sufficiently high surface fillings*.

* The considerations given assume that the surface concentrations are leveled out as a result of convective diffusion in the volume of the solution. If the leveling out occurs as a result of surface diffusion [8], the adsorptive hindrance is expressed by the quantity

$$\frac{2a\Gamma}{D_s}\left(\frac{\partial\sigma}{\partial\Gamma}\right).$$

In the case the sum $\gamma_a + \gamma_\varepsilon$ could also go to a minimum at the desorption potential, since at this potential the adsorption isotherms take on a pronounced S-shape [9], which corresponds with small values of $\partial\sigma/\partial\Gamma$ over a wide range of values of Γ.

EXPERIMENTAL

In order to check these conclusions we made measurements of the polarization curves of a number of systems under conditions favorable to the appearance of maxima of the second kind, the compositions of the systems being taken such as to satisfy the inequality (4), i.e., the solution had small electrical conductivity in the presence of large concentrations of not very surface active substances. Thus, for example, a study was made of hindrance to motions of the second kind by butyl alcohol in the reduction of Hg^{2+} and of Tl^{+} on a background of KCl, $BaCl_2$, and $La_2(SO_4)_3$ (Figs. 1, 3, 4). Further, a study was made of hindrance to motion of the second kind by o-xylene, n-butyl and secondary octyl alcohols in Cu^{2+} reduction, and of the hindrance to the motions of propyl alcohol in Hg^{2+} reduction. The measurements were made on a mercury drop electrode with the capillary constants: M = 6.18 mg/sec, τ = 1.63 sec, in 0.1 N KCl in an open circuit. The salts KCl, $BaCl_2$, $La_2(SO_4)_3$, and $CuSO_4$ were twice recrystallized from double distilled water, and the organic materials were redistilled. All the solutions were prepared from double distilled water. The mercury was given a chemical purification and was twice distilled. All the potentials in the paper are given against a normal calomel electrode.

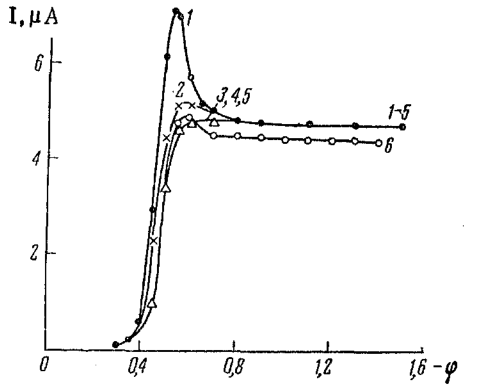

Fig. 4. Polarization curves for the reduction of Tl^{+} on a mercury drop electrode: 1) $9.3 \cdot 10^{-4}$ M TlCl + 0.02 M $La_2(SO_4)_3$; 2) the same + 0.016 M C_4H_9OH; 3) the same + 0.032 M C_4H_9OH; 4) the same + 0.064 M C_4H_9OH; 5) the same + 0.113 M C_4H_9OH; 6) the same + 0.43 M C_4H_9OH.

As may be seen from Figs. 1, 3, 4, we were not able to observe an increase in current above the value which it has in solutions without additives during desorption of an organic substance from the electrode surface as a result of acceleration of motion of the second kind. Apparently in making our experiments we were not able to achieve the condition

$$\left|\frac{\partial \gamma_\varepsilon}{\partial \Gamma}\right| \ll \left|\frac{\partial \gamma_a}{\partial \Gamma}\right|$$

with $|\gamma_\varepsilon|_{\Gamma=0} \gg |\gamma_a|_{\Gamma=\Gamma_m}$. Further investigations in this direction are desirable.

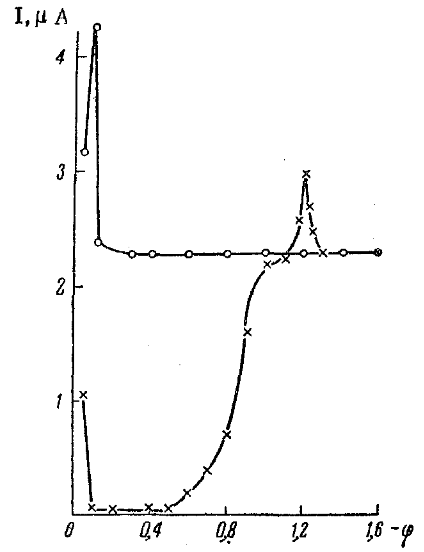

Fig. 5. Polarization curves for the reduction of Cu^{2+} on a mercury drop electrode: 1) $5.7 \cdot 10^{-4}$ M $CuSO_4$ + 0.5 M Na_2SO_4; 2) the same + saturated solution of secondary octyl alcohol.

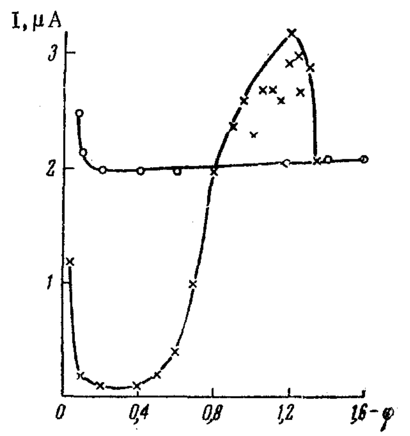

Fig. 6. Polarization curves for the reduction of Cu^{2+} on a mercury drop electrode: 1) $5.7 \cdot 10^{-4}$ M $CuSO_4$ + 1 M Na_2SO_4; 2) the same + saturated solution of C_4H_9OH.

Another reason for the motions in the mercury surface could be inhomogeneity in the adsorption of the surface active substance, which can occur as a result of a concentration gradient existing in the adsorbed substance in the volume of the solution adjacent to the drop. A concentration gradient can occur as a result of the adsorption process itself. Actually, if the drop grows in a solution with a small concentration of surface active substance, i.e., under conditions such that during the growth of the drop the equilibrium value Γ is not reached for the adsorption per cm^2, the values of the boundary tension σ in different parts of the drop will be different. An approximate theory of these phenomena may be given starting with the results of calculations made for the motion of a drop in an electric field [8]. Let the x axis be in the direction of growth in the concentration c. The difference in the boundary tension σ between the "poles" of a drop with radius a is in order of magnitude

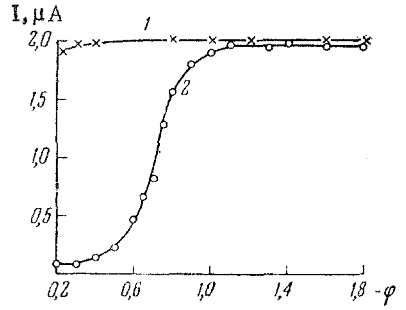

Fig. 7. Polarization curves for the reduction of Cu^{2+} on a mercury drop electrode: 1) $5.7 \cdot 10^{-4}$ M $CuSO_4$ + 1 M Na_2SO_4; 2) the same + saturated solution of C_4H_9OH (without droplets).

$$\left|\frac{\partial\sigma}{\partial c}\frac{\partial c}{\partial x}a\right| = \left|\frac{RT\Gamma_a a}{\bar{c}}\frac{\partial c}{\partial x}\right|$$

where Γ_a and $\bar{c}$ are some mean values of Γ and c. This quantity is completely analogous to the quantity $\left|\frac{\partial\sigma}{\partial\varphi}\frac{\partial\varphi}{\partial x}a\right| = \varepsilon E a$ for a drop in an electric field of intensity E. Accordingly, for a rate of motion v of the drop in the presence of a concentration gradient, we can write

$$v \sim \frac{\frac{RT\Gamma_a a}{\bar{c}}\frac{\partial c}{\partial x}}{2\mu + 3\mu' + \gamma_a + \gamma_\varepsilon} \tag{7}$$

The motion of the drop as a whole is in the direction of increasing c, while the motion of the surface is in the direction of decreasing c.

The quantity $\frac{\partial c}{\partial x}$ is proportional to Γ_a, depends on how the drop flows out, and on geometric factors, and for small deviations of c from the mean value of $\bar{c}$ is independent of c. Assuming that γ_ε may be neglected in comparison with γ_a, and that the rate of leveling out of concentration in different points of the volume of the solution is accomplished by diffusion, we obtain from (7)

$$v \sim \frac{A\Gamma_a^2/\bar{c}}{2\mu + 3\mu' + B\frac{\Gamma_a^2}{\bar{c}}} \tag{8}$$

where A is a coefficient which is a constant for fixed conditions under which the drop flows out, and $B \sim \frac{2RT\sigma}{Da}$. If Γ_a changes from its maximum value Γ_m to 0, the quantity v goes through a maximum at $\Gamma_a = (\bar{c})^{1/2}(2\mu + 3\mu')^{1/2}B^{-1/2}$, if the condition satisfied is

$$\frac{B\Gamma_m^2}{\bar{c}} > 2\mu + 3\mu' \tag{9}$$

i.e., if the adsorptive hindrance is great enough. The maximum value of v is equal to

$$v_m \sim \frac{A}{2B} \tag{10}$$

It thus follows from Eq. (8) that it is possible to have a maximum in the region of desorption potentials*

We set up some experiments to investigate the limiting diffusion current as a function of potential in this range of of potentials with the usual dropping conditions. A measurement was made on a drop electrode with the capillary constants: m = 1.05 ml/sec, τ = 4.6 sec in 0.1 N KCl solution with an open circuit. As may be seen from Figs. 5, 6, we were able to observe an increase in current above its normal limiting value, but the maxima in the $I-\varphi$ curves were not easily reproducible, and occurred only in those cases were the polarization curve was taken in saturated solutions of a surface active substance containing an excess of the substance, emulsified by stirring up in the form of drops. It was only necessary to let the drops peel off, to get $I-\varphi$ curves without maxima in the same solution (Fig. 7). It is possible that having drops present, which on touching the mercury surface cause a reduction in boundary tension in a very short interval of time**, makes it possible for large gradients in φ to arise along the surface, but this question requires further study.

Although in this way we come to the conclusion that under some conditions which still need to be precisely defined, additional agitation of the solution is actually observed in the range of potentials where desorption of the surface active substances occurs, it is impossible to agree with Doss's [1] opinion as to the relation between these motions and the occurrence of maxima in the curves giving the capacity as a function of the potentials. The quantitative theory of these maxima, which shows that they are completely determined by the equilibrium and kinetics of the adsorption process on the surface at rest, is quite well worked out, and in good agreement with the experimental data [11, 12]. In addition, the experiments made in our laboratory by B. B. Damaskim have shown that a moderable amount of agitation of the solution, not causing deformation of the mercury surface, has no effect on the electrode capacity as measured with alternating current.

SUMMARY

1. It is shown that it is, in principal, possible to choose the composition of the solution in such a way that hindrance from charges on the mercury surface exceeds hindrance by the surface active substance. It has, however, so far not been possible to confirm this conclusion by experimental data.

2. Approximate expressions are given for the motion of a mercury drop if a gradient is present in the concentration of surface active substance, resulting from the adsorption process.

3. Maxima have been observed in the desorption potential range on the curves giving the limiting current as a function of potential in solutions containing an excess of surface active material, emulsified in the form of droplets.

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* There is interest in the case where the surface active material arises from a less surface active material as a result of a reaction taking place at the drop electrode, which is, for example, possible in reduction with subsequent dimerization, and the inhomogeneity in the adsorption is no longer determined simply by the adsorption process itself, but by the inhomogeneous current distribution as well. As long as the current strength i, and, accordingly, v are small, a rough approximation is given by

$$\bar{c} \sim k'i, \quad \frac{\partial c}{\partial x} \sim k''i\Gamma_a$$

$$v \sim \frac{A\Gamma_a^2}{2\mu + 3\mu' + \frac{B\Gamma_a^2}{k'i}} \qquad (11)$$

** The conditions under which droplets of organic substances adhere to mercury are discussed in [10]

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.