INFLUENCE OF THE KINETICS OF ADSORPTION OF TETRABUTYLAMMONIUM CATIONS AND NATURE OF METALS REDUCIBLE ON CATALYTIC CURRENT OF HYDROGEN ON A DROPPING MERCURY ELECTRODE

V. F. Khonina, L. M. Roshchupkina,
V. F. Ivanov, and Z. A. Iofa

UDC 541.13

We had earlier [1-2] given an explanation for the mechanism of the formation of catalytic maxima on the I versus φ curves on a dropping mercury electrode in the deposition of metals of the iron group in the presence of tetrabutylammonium salt (TBA).

The purpose of this work was to study the influence of the nature of the metal being reduced and the kinetics of the adsorption of TBA on the investigated catalytic processes.

The investigation indicated that the position of the maxima on the I versus φ curves depends upon the nature of the metal being reduced: for nickel, iron, and cobalt, the maxima lie at –1.47, –1.55, and –1.60 V with respect to the saturated calomel electrode, respectively. These data are confirmed by oscillographic data, taken on a dropping mercury electrode at a TBA concentration of $5 \cdot 10^{-4}$ N with a rate of development v = 0.5 V/sec. It was then shown that the maxima do not appear if the TBA concentration is less than $5 \cdot 10^{-4}$ N (the dropping period of the dropping mercury electrode is equal to 3-4 sec). Increasing the concentration of the background can somewhat compensate for the shortcomings of the volume concentration of TBA on account of an increase in the surface activity of the latter. The absence of a catalytic effect in the presence of low concentrations of TBA may be explained by the fact that during the lifetime of the drop, on account of the slowness of diffusion, the required coverage of the mercury surface is not reached.*

These data indicate a relationship between the kinetics of adsorption and the degree of coverage of the mercury surface by TBA cations, as well as the potential of the catalytic maximum.

To confirm the influence of the kinetics of the adsorption of TBA upon the discharging of hydrogen, it was necessary to obtain a complete picture of the development of the current maxima, i.e., to obtain three-dimensional diagrams of the current versus potential versus time dependence. For this purpose we used a cell permitting work with a stationary hanging drop of mercury as the cathode. The stationary drop permitted the study of the influence of the accumulation of microcrystals, as well as the kinetics of the adsorption and desorption of TBA on the mercury surface. The measurements were performed with an oscillographic polarograph, model TsLA-02.

At the beginning of our work with a hanging drop, we used the same concentrations of TBA (about 10^{-3} N) and one of the cations Ni^{+2}, Fe^{+2}, Co^{+2}, in a concentration of 10^{-3} N, as in work with a dropping mercury electrode. It was found that the catalytic maximum associated with the discharging of water molecules appears in 10 N $CaCl_2$ at $\varphi \cong -1.50$ V only on the first development, rapidly decreasing on the second and third developments and then disappearing entirely.

In the following experiments, the TBA concentration was reduced 100-fold. In this case, a distinct picture first of a gradual (from development to development) decrease in the limiting current of diffusion of metal ions and a simultaneous rapid increase in the height of the catalytic peak of discharging of hydrogen to a maximum could be observed. Then there is a decrease and disappearance of the peak, as a result of further coverage of the mercury surface by TBA cations. This shows that the catalytic discharging of water molecules occurs on microcrystals of the precipitated metals only at a definite degree of coverage of the mercury surface by TBA cations.

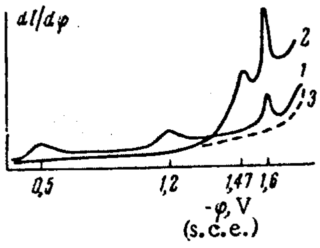
To find the relationship between the potentials of the peaks for different metals to the degree of coverage of the surface by TBA cations, we took oscillograms of the simultaneous reduction of the two metals Ni–Co (or Fe–Ni)

---

*The diffusion coefficient of TBA cations in 10 N $CaCl_2$ is equal to $1.3 \cdot 10^{-6}$ cm²/sec; on account of the increase in viscosity it is smaller than in dilute solutions ($5.1 \cdot 10^{-6}$ cm²/sec).

Tula Polytechnic Institute, M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 2, No. 10, pp. 1212-1214, October, 1966. Original article submitted February 23, 1966.

in the presence of TBA against a background of 10 N $CaCl_2$ and $Ca(ClO_4)_2$ on a hanging drop at two-second intervals (figure).



Oscillograms of catalytic maxima in the joint reduction of nickel and cobalt on an electrode in the form of a hanging mercury drop: 1) 10 sec after the beginning of the life of the drop; 2) after 60 sec; 3) after 90 sec.

In these experiments, a sequence of the appearance and disappearance of peaks on the I versus φ curves, related to the evolution of hydrogen on microcrystals of nickel and cobalt, could be observed with time: after 5-10 sec from the time of suspension of the drop, a catalytic peak is formed on the oscillographic I versus φ curve, associated with the appearance of microcrystals of cobalt ($\varphi = -1.6$ V). And only at a later development does a peak associated with microcrystals of nickel ($\varphi = -1.47$ V) appear and begin to grow from development to development, reaching a maximum height on the development taken after 65 sec (TBA concentration $\approx 1.4 \cdot 10^{-5}$ N). The two peaks disappeared on the development taken after 80-85 sec (see figure).

We attempted to calculate the degree of surface coverage θ of the electrode by TBA cations at various moments of the life of the hanging drop, using the equation of diffusion for the case of a stationary sphere after its reduction to the form:

$$\frac{dN}{dt} = SDc_0\left\{\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0}\right\},$$

from which

$$N = SDc_0\int_0^t \left\{\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0}\right\} dt,$$

$$\Gamma = \frac{N}{S} = Dc_0 t\left(\frac{2}{\sqrt{\pi Dt}} + \frac{1}{r_0}\right) \qquad \theta = \frac{\Gamma}{\Gamma_\infty} = \frac{Dc_0 t}{\Gamma_\infty}\left(\frac{2}{\sqrt{\pi Dt}} + \frac{1}{r_0}\right),$$

where Γ_∞ is the limiting degree of surface coverage by TBA, equal to $2.07 \cdot 10^{-10}$ moles/cm^2 [3]. The calculation indicated that under the experimental conditions (c_0 – volume concentration of TBA, equal to $1.4 \cdot 10^{-8}$ moles/cm^3; $D = 1.3 \cdot 10^{-6}$ cm^2/sec for TBA in 10 N $CaCl_2$; r_0 – radius of the drop, equal to $5 \cdot 10^{-2}$ cm), the formation of a peak on the I versus φ curves in the case of a solution of cobalt and iron salt occurs at $\theta = 0.28$ (t = 10 sec), while in the case of a nickel salt, $\theta = 0.85$ (t = 65 sec). In all cases the peaks disappear at $\theta \to 1$ (t = 85-90 sec).

Thus, on a hanging mercury drop, discharging of water molecules on microcrystals of cobalt begins at an earlier time and at a more negative potential ($\varphi = -1.6$ V), i.e., at a lower degree of coverage. On microcrystals of nickel, discharging of hydrogen is possible only at a sufficiently high degree of coverage of the mercury surface by TBA cations, which corresponds to a less negative potential ($\varphi = -1.47$ V).

To explain these data, we should assume that microcrystals of nickel are more easily amalgamated and their retention on the surface requires a larger degree of coverage of the mercury electrode by TBA cations. On the other hand, the appearance of catalytic properties under conditions of a high degree of coverage of the mercury by TBA cations, responsible for the low reduction currents of nickel and low concentration of its microcrystals on the mercury surface, is evidence of a very low electrocatalytic activity of nickel. The manifestation of catalytic properties of cobalt, on the other hand, requires a high concentration of its microcrystals on the mercury surface, which can be ensured by sufficiently high reduction currents of cobalt, i.e., at low degrees of coverage of the surface of the dropping mercury electrode by TBA cations.

Iron occupies an intermediate position between nickel and cobalt in its properties in these processes.

In preliminary experiments conducted in solutions of salts of Cr^{+3} and Mn^{+2} against a background of 10 N $CaCl_2$ in the presence of TBA, no maxima on the I versus φ curves analogous to those described above could be obtained.

The authors would like to thank B. B. Damaskin for his valuable advice during the performance of the work and in the examination of the manuscript.

LITERATURE CITED

1. V. F. Ivanov and Z. A. Iofa, DAN SSSR, 140, 1368 (1961); ZhFKh, 36, 1080 (1962); 38, 1026 (1964).
2. L. M. Roshchupkina, V. F. Khonina, V. F. Ivanov, and Z. A. Iofa, Élektrokhimiya, 1, 982 (1965).
3. B. B. Damaskin, S. Vavrzhichka, and N. B. Grigor'ev, ZhFKh, 36, 2531 (1962).