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ELECTROREDUCTION OF ANIONS AND POLAROGRAPHIC MAXIMA OF THE 2nd KIND

(Presented by Academician A. N. Frumkin on 1 VII 1961)

In the investigation of the electroreduction of anions at a mercury dropping electrode, a sharp inhibition of the reaction is observed on passing to potentials corresponding to negative charges of the surface, associated with the repulsion of negatively charged particles from the negatively charged electrode surface. At still more negative potentials the reaction rate again increases (^{1}). It seemed of interest to us to study the reduction reaction of the anion $S_2O_8^{2-}$ under conditions of a sharp increase in the reaction current caused by tangential motions of the surface of the mercury electrode at high rates of mercury outflow, i.e., in the presence of a maximum of the 2nd kind. It could be assumed that under the conditions of a maximum of the 2nd kind, when mixing of the solution is great, the reduction current of $S_2O_8^{2-}$ would be determined by the kinetics of the electrochemical process, and the diffusion limitations arising under the conditions of ordinary recording of $I–\varphi$ curves would be removed.

For the work a capillary with constants $m = 6.18$ mg/sec, $\tau = 1.35$ sec was used in a 0.1 M KCl solution with open circuit. All potentials in the work are given relative to the normal calomel electrode.

Figure 1 shows the $I–\varphi$ curve for the reduction of $4.4 \cdot 10^{-4}$ M $K_2S_2O_8$ in the presence of 0.001 M KCl. At positive charges of the surface a sharply expressed current maximum is observed. Since the rate of mercury outflow was high and the conductivity of the solution low, the observed maximum is the result of interaction of motions of the first and second kind, i.e., it should be regarded as an inverted maximum of the 1st kind (^{2}).

On passing from positive values of the electrode surface charge to negative ones, a sharp drop in current occurs; it decreases by approximately a factor of 100 and begins to grow again only at negative potentials. In the present case a sharper inhibition of the reaction was obtained than in other works, since the reaction rate before the current drop is considerably higher owing to the presence of additional stirring by tangential motions of the surface of the mercury drop.

Fig. 1 and Fig. 2: polarization curves

Figure 1: Fig. 1 and Fig. 2: polarization curves

When $6 \cdot 10^{-4}$ M tetraamylammonium bromide (TAA) is introduced into the solution under investigation, we obtain a normal polarization curve with a well-defined limiting-current plateau (Figs. 1, 2). This change in the shape of the $I-\varphi$ curve is connected with the fact that adsorption of TAA leads to inhibition of the motions of the surface of the mercury drop, and the maximum current falls to the values of the normal limiting current (^{3}); at the same time the TAA cation increases the rate of reduction of the anion, and therefore the minimum on the $I-\varphi$ curve disappears upon addition of TAA (^{4}).

Analogous effects were also obtained in the case of solutions in which 0.01 M KCl served as the background. However, the current drop in this case is somewhat smaller, since

as the inhibition of the reduction reaction of $S_2O_8^{2-}$ is partly removed by the cations K^+ (Figs. 2, 3). In the region of the maximum, the magnitude of the reaction current is several times greater than the value of the limiting current, and it could be assumed that the current at the maximum is determined by the kinetics of the electrochemical process and is not complicated by concentration-polarization phenomena. To test this assumption, curves for the reduction of $S_2O_8^{2-}$ were recorded at different rates of mercury outflow (Fig. 2). If the current at $\varphi = -1.0$ is cor-

Fig. 1. Polarization curves for the reduction of $4.4 \cdot 10^{-4}$ M $K_2S_2O_8$ + 0.001 M KCl:
1 —without additive, 2 —with addition of $6 \cdot 10^{-4}$ M $[(C_8H_{17})_4N]Br$.

Fig. 2. Polarization curves for the reduction of $4.4 \cdot 10^{-4}$ M $K_2S_2O_8$ + 0.01 M KCl at different τ: 1—2.75 sec, 2—2.2 sec, 3—1.7 sec, 4—1.2 sec.

rected for concentration polarization, the current at the minimum will practically not depend on the height of the mercury column H*, i.e., it will be deter-

is controlled by the rate of the electrochemical reaction. In the region of the limiting current, I is proportional to $\sqrt{H}$, and, consequently, is determined by the rate of the diffusion process. As is seen from Fig. 2, the current at the maximum depends on H, and the diffusion limitations, even with substantial stirring of the solution in the case of high mercury outflow rates, cannot be completely removed.

Indeed, as was shown by Yu. M. Povarov,* even when a current density of $1.5 \cdot 10^{-3}$ A/cm^2 was reached on a rotating amalgamated copper electrode in a solution of the same composition as that studied by us, the reaction rate is

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* In Fig. 2 the dependence $I - \varphi$ of the curves is given not on H, but on the formation time of one drop, $\tau = \dfrac{K}{H}$.

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

controlled by diffusion. In our experiments the largest current at the maximum of the curve was only $\sim 1 \cdot 10^{-5}$ A/cm^2, i.e., the reaction in the present case proceeds according to diffusion kinetics.

Fig. 3. Polarization curves for the reduction of $4.4 \cdot 10^{-4}$ M $K_2S_2O_8$ in the presence of: 1—0.1 M KCl; 2—0.1 M KCl + $6 \cdot 10^{-4}$ M $[(C_5H_{11})_4N]Br$

Fig. 4. Polarization curves for the reduction of $4.4 \cdot 10^{-4}$ M $K_2S_2O_8$ in the presence of: 1—2.0 M KCl; 2—2.0 M KCl + $6 \cdot 10^{-4}$ M $[(C_5H_{11})_4N]Br$

As is known, increasing the concentration of background cations removes the inhibition of the reduction reaction of $S_2O_8^{2-}$, and in this case we do not observe a current decline. In Fig. 3, 1 the I—φ curve is shown for the reduction of $4.4 \cdot 10^{-4}$ M $K_2S_2O_8$ in the presence of 0.1 M KCl. The maximum of the second kind is most developed in the region of the potential of zero charge. An increase in the charge of the mercury surface inhibits motion, and the current falls almost to the value of the limiting diffusion current. Introduction of the TAA cation into the solution leads to inhibition of motions of the mercury surface, and no maximum of the second kind is observed on the I—φ curve. At the desorption potential of TAA, a small rise in current is observed, which makes it possible to estimate the magnitude of the stirring effect at this potential (Fig. 2, 2).

In concentrated background solutions the charges inhibit the motion of the surface much less, and a maximum of the second kind is observed over the entire potential range of the I—φ curve (Fig. 4, 1). Addition of the TAA cation leads to inhibition of motions, and the current in a certain potential region (1.0—1.5) falls to the values of the limiting diffusion current. At $\varphi = -1.58$, desorption of the TAA cation from the surface of the mercury electrode occurs, the motions of the surface develop again, and the current reaches the same values as in solutions without addition of the organic substance [3]. At positive and weakly negative charges of the surface, on the I—φ curve for the reduction of $S_2O_8^{2-}$ in the presence of KCl and $6 \cdot 10^{-4}$ M TAABr, pronounced inhibition of the reduction reaction of $S_2O_8^{2-}$ is observed (Fig. 4, 2). In this case the phenomenon of inhibition of the reaction is associated with drawing into the electrical double

* Unpublished.

the layer of background anions by surface-active organic cations, as was shown earlier (^{5}).

Thus, the effects observed previously in the reduction of multiply charged anions may be found in still more distinct form in the presence of intense tangential motions of the surface of the mercury electrode.

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