PHYSICAL CHEMISTRY

L. N. NEKRASOV and N. P. BEREZINA

1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

L. N. NEKRASOV and N. P. BEREZINA

INVESTIGATION OF THE PROCESS OF ELECTROREDUCTION OF COPPER BY MEANS OF A DISK ELECTRODE WITH A RING

(Presented by Academician A. N. Frumkin, 27 IX 1961)

From the literature data it is known that the reduction of divalent copper to metallic copper on a dropping mercury electrode proceeds differently depending on the composition of the solution (^{1}). The reduction of simple Cu^{2+} ions in a medium of indifferent electrolytes that do not form complexes with copper is characterized by a single polarographic wave corresponding to a two-electron transition

$$Cu^{2+} + 2e^- \to Cu^0. \tag{1}$$

When a complexing agent is present in the solution, forming stable complexes with Cu^{2+} and Cu^+ ions, or only with Cu^+ ions, the polarization curve has two steps, each of which corresponds to the addition of one electron:

$$Cu^{2+} + e^- \to Cu^+; \tag{2}$$

$$Cu^+ + e^- \to Cu^0. \tag{3}$$

In the latter case monovalent copper plays the role of an intermediate product, stable in the region of the first wave and unstable in the region of the second. It is logical to assume that, even in the absence of a complexing agent, reduction also proceeds in two stages, and that the formation of only one wave is connected with the instability of Cu^+ ions in such solutions over the entire investigated range of potentials. An indirect confirmation of this point of view is provided by the observed convergence of the two reduction waves of Cu^{2+} as the concentration of Cl-ions in the solution decreases, and their complete merging if the latter does not exceed $0.02N$ (^{2}).

In connection with what has been said above, it was of interest to carry out an investigation of the mechanism of electroreduction of divalent copper in a sodium sulfate solution with the aim of directly proving the formation of monovalent copper ions as an unstable intermediate product. To solve this problem we used the rotating disk electrode with a ring described earlier (^{3}), representing a single mechanical system of two electrodes electrically independent of one another—the disk and a concentric ring—lying in one plane and separated by a thin insulating spacer. Experiments on the reduction of chloride complexes of copper also made it possible to carry out an additional test of the theoretical relations proposed for a ring-disk electrode by Yu. B. Ivanov and V. G. Levich (^{4}).

According to the authors cited, the magnitude of the current at the ring electrode I_K, in the absence of a reaction in the bulk of the solution, is expressed by the equation

$$I_K = \frac{0.8\,[1-0.75\,(r_1/r_2)^3]\,I_A}{1+k\delta_B/D_B}\frac{n_B}{n_A}\int_1^{r_3/r_2}\frac{x^2\,dx}{(x^3-1)^{1/3}\,[x^3-0.75\,(r_1/r_2)^3]}, \quad (4)$$

where I_A is the current at the disk electrode, determined by the magnitude of the diffusion flux of the initial substance to the disk; r_1 is the radius of the disk; r_2 and r_3 are the inner and outer radii of the ring; k is the rate constant of the transformation of the intermediate product into the final product at the disk electrode; D_B is the diffusion coefficient of the intermediate product; δ_B is the thickness of the diffusion boundary layer for the intermediate product; n_A and n_B are the number of electrons participating

in the reactions at the disk and ring electrodes, respectively. Combining the factors that depend on the geometrical parameters of the electrode into N, we obtain

$$I_K = \frac{n_B}{n_A}\frac{NI_A}{1+k\delta_B/D_B}. \quad (5)$$

Equation (5) can be put in another form (3):

$$I_K = Nn_BF\frac{D_Bc_B^S}{\delta_B} = N\frac{n_B}{n_A}I_A\left(\frac{D_B}{D_A}\right)^{2/3}\frac{c_B^S}{c_A^0-c_A^S}, \quad (6)$$

where c_B^S is the concentration of the intermediate product at the surface of the disk at the given electrode potential; c_A^0 and c_A^S are the bulk and surface concentrations of the initial substance; D_A is the diffusion coefficient of this substance; F is the Faraday number.

Fig. 1. A –polarization curve of the cathodic reduction of Cu^{2+} ions on a gold amalgamated disk electrode in a solution of $5\cdot10^{-4}N$ $CuSO_4 + 1N$ KCl

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Fig. 2. A —polarization curve of the cathodic reduction of Cu^{2+} ions on a platinum disk electrode in a solution of $3 \cdot 10^{-2} N$ $CuSO_4 + 1N$ Na_2SO_4 ($m = 2150$ rpm). B —corresponding curve of the dependence of the oxidation current of Cu^{+} ions at the ring electrode on the potential of the disk electrode

Figure 2: Fig. 2. A —polarization curve of the cathodic reduction of Cu^{2+} ions on a platinum disk electrode in a solution of $3 \cdot 10^{-2} N$ $CuSO_4 + 1N$ Na_2SO_4 ($m = 2150$ rpm). B —corresponding curve of the dependence of the oxidation current of Cu^{+} ions at the ring electrode on the potential of the disk electrode

($m = 5200$ rpm). *B* —corresponding curve of the dependence of the limiting oxidation current of Cu^{+} ions at the ring electrode on the potential of the disk electrode.

Fig. 2. *A* —polarization curve of the cathodic reduction of Cu^{2+} ions on a platinum disk electrode in a solution of $3 \cdot 10^{-2} N$ $CuSO_4 + 1N$ Na_2SO_4 ($m = 2150$ rpm). *B* —corresponding curve of the dependence of the oxidation current of Cu^{+} ions at the ring electrode on the potential of the disk electrode.

The experimental procedure consisted in measuring, at a gold ring electrode, the value of the limiting oxidation current of monovalent copper ions formed as a result of the reduction of Cu^{2+} ions at the disk electrode. The experiments were carried out in a nitrogen atmosphere at a temperature of $21 \pm 1^{\circ}$ over a range of rotation rates of the electrode system from 900 to 9000 rpm.

Figure 1 shows the cathodic polarization curve for the reduction of Cu^{2+} in a solution of $5 \cdot 10^{-4} N$ $CuSO_4 + 1N$ KCl on a gold amalgamated disk electrode (A) and the corresponding curve of the dependence of the magnitude of the limiting oxidation current of monovalent copper at the ring on the potential of the disk electrode (B).

Such measurements make it possible to find the value of the coefficient N entering into equation (5). For an accurate determination of this coefficient, the current recorded at the ring electrode must be corrected for the background current, determined under conditions where no Cu^{+} ions are formed at the disk electrode, which, as a rule, is fulfilled if $I_A = 0$.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

However, when an amalgamated electrode is used, the formation of monovalent copper ions on the disk surface also occurs without polarization of the electrode, as a result of the spontaneous dissolution reaction of mercury

$$2\mathrm{Hg} + 2\mathrm{Cu}^{2+} \rightarrow \mathrm{Hg}_2^{2+} + 2\mathrm{Cu}^{+}. \qquad (7)$$

As a result, a considerable current is observed at the ring electrode even at $I_A = 0$.

This difficulty was overcome by using a disk of unamalgamated gold or by measuring the background current at the ring when the current at the amalgamated disk electrode was equal to the second limiting current on the cathodic curve ($I_A = I''_d$), when the surface concentration $[\mathrm{Cu}^+]_S$ is practically equal to zero.

Fig. 3. Dependence of the limiting oxidation current of Cu^+ ions at the ring electrode in sulfate solutions on the potential of the disk electrode at CuSO_4 concentrations: **1**—$3 \cdot 10^{-2}\,N$, **2**—$3 \cdot 10^{-1}\,N$ (n.c.e.).

Fig. 4. Dependence between the magnitude of the maximum current at the ring electrode and the square root of the surface concentration of Cu^{2+} in sulfate solutions.

The value of the coefficient N found by us for an electrode with parameters $r_1 = 0.25$ cm, $r_2 = 0.276$ cm, and $r_3 = 0.359$ cm, when the rotation rates did not exceed 5000 rpm, was 0.415 ± 0.01, which improves the previously obtained data (0.38) $^{(3)}$ and agrees well with the theoretical value of this quantity, 0.41–0.42, obtained from equation (4) with the introduction of a plausible correction (5%) for the inaccuracy of formula (4). At high rates of electrode rotation, apparently as a result of the turbulence of the flow that arose, N decreased somewhat (at $m = 7200$ rpm, $N = 0.36$).

Figure 2A presents the polarization curve for the reduction of Cu^{2+} at a rotating platinum disk electrode in a solution of $3 \cdot 10^{-3}\,N$ $\mathrm{CuSO}_4 + 1N$ $\mathrm{Na}_2\mathrm{SO}_4$. As on the mercury dropping electrode, only one wave is observed on the curve. From Fig. 2B, which shows the dependence of the anodic current at the ring electrode at a potential of the latter $\varphi_K = +0.4$ V (n.c.e.) on the disk potential φ_A, it is seen that, in a certain region of disk-electrode potentials, a current different from zero is recorded at the ring; as φ_A increases, its magnitude first rises, passes through a maximum, and then falls to zero. The presence of current at the ring electrode indicates the appearance, in the reduction process at the disk, of a product capable of oxidation, which in the present case can only be monovalent copper ions. This is confirmed by the character of the polarization curve for oxidation of the indicated intermediate product at a gold ring electrode, identical to the analogous curve for oxidation of Cu^+ in a potassium chloride solution. The height of the peak at the ring increases on average by a factor of 2.5–3.

with a 10-fold increase in the concentration of divalent copper in the solution (Fig. 3). In a sodium sulfate solution containing no copper salt, the current at the ring in the investigated potential range does not exceed the background current.

Thus, in the process of reduction of divalent copper at a disk electrode in sulfate solutions, the formation of monovalent copper ions can be recorded.

The magnitude of the surface concentration of monovalent copper at the disk depends on the degree of reversibility of the stage of addition of the second electron (3). If this reaction is irreversible, then the concentration $[\mathrm{Cu}^+]_S$ exceeds the equilibrium one. In this case the rate constant of the reaction k is readily found from equation (5). If the indicated stage is reversible, then the concentration $[\mathrm{Cu}^+]_S$ corresponds to the equilibrium value and can be found from the Nernst equation.

The reversible character of reaction (3) is supported by the fact that the slope of the descending branch of the curve at the ring is equal to 58 mV, as well as by the form of the dependence of the current at the ring on the concentration of CuSO_4 in solution. According to (6), the oxidation current of Cu^+ ions at the ring is proportional to their surface concentration $[\mathrm{Cu}^+]_S$. The experimental values of the maximum current at the ring increased approximately in proportion to $[\mathrm{Cu}^{2+}]_S^{0.5}$ (Fig. 4), which is in agreement with the law of mass action

$$[\mathrm{Cu}^+]_S = \sqrt{K[\mathrm{Cu}^{2+}]_S}, \tag{8}$$

where K is the equilibrium constant.

Comparison of the value of the surface concentration $[\mathrm{Cu}^+]_S$, obtained with the aid of the ring-disk electrode at a potential corresponding to the disk-current value equal to $0.1 I_d$ ($[\mathrm{Cu}^{2+}]_S = 0.27N$), with the analogous value found for the same conditions from the value of the limiting oxidation current of Cu^+ at the disk electrode in a solution with established thermodynamic equilibrium between Cu^{2+}, Cu^+, and Cu^0 ($[\mathrm{Cu}^{2+}]_0 = 0.27N$), showed that the former value is 2.8 times larger than the latter. However, this difference is comparatively small. Hence, taking into account all the factors listed above, it may be concluded that the investigated stage of the process is reversible, but the copper deposited on the electrode surface is in a state of somewhat increased activity. The latter is probably associated with difficulties in building up the crystal lattice (5) and is confirmed by the fact that the surface concentration $[\mathrm{Cu}^+]_S$ decreases with time after interruption of the polarization of the copper-plated disk electrode. Mattson and Bockris (6) also arrived at the conclusion that the indicated stage is reversible.

The presence of a rise on the plot of I_K versus φ_A (Figs. 2B and 3) is connected with the absence of reversibility of the process of reduction of Cu^+ on the initially uncoppered surface of the platinum disk. The very steep character of the rise of the curve in this region can be explained as follows: at low current densities copper is deposited only on separate active areas of the platinum electrode (7), while the first stage of the process proceeds with considerable overvoltage. The appearance and growth of copper-plated islands lead to a substantial acceleration of the process $\mathrm{Cu}^+ \rightleftarrows \mathrm{Cu}^0$.

On a freshly copper-plated electrode it is not possible to realize the region of the rise on the curve, which serves as one more argument in favor of the view that the stage of reduction of monovalent copper is reversible.

The authors express their deep gratitude to Acad. A. N. Frumkin for discussion of the results.

Moscow State University
named after M. V. Lomonosov

Received
22 IX 1961

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