V. F. IVANOV and Z. A. IOFA

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V. F. IVANOV and Z. A. IOFA

ON THE FORMATION OF AMALGAMS OF METALS OF THE IRON GROUP ON A MERCURY DROPPING ELECTRODE

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The possibility of formation of amalgams of metals sparingly soluble in mercury during their reduction on a mercury dropping electrode (m.d.e.) has been discussed in the literature up to the present time. In works ([1–3]) the authors assume that metals of the iron group (Cr, Mn) do not form amalgams and coat the mercury with a layer of the deposited metal. On the other hand, in works ([4]) the reason for the high overvoltage of the metals of the iron group on the m.d.e. is explained by difficulty in the formation of amalgams. From data obtained on a stationary mercury electrode (s.m.e.), it is known that by electrolysis of salts of Fe, Ni, and Co one can obtain the corresponding amalgams with a concentration up to 1% ([5]). The systems obtained, however, are not single-phase and are colloidal solutions of metals in mercury.

According to the data of work ([6]), the use of the hanging mercury drop method and continuous recording of the reverse branch of the polarographic curve makes it possible to judge the anodic solubility of Ni and Co. But in work ([7]), by an oscillographic method with a reverse sweep, it is stated that, during reduction of metals of the iron group, anodic peaks of their dissolution are not formed. Thus, the data of the published works do not agree with one another.

In the present work an attempt was made to clarify the character of the metal reduced on mercury as a function of the conditions of the cathodic process.

Preliminary observations carried out on the s.m.e. at a current density of 0.1 a/cm^2 showed that electrodeposition of iron from 0.05 N $FeSO_4$ against the background of a saturated Na_2SO_4 solution during the first 10–15 min after switching on the current is not accompanied by visible evolution of hydrogen. The current, therefore, is consumed in the formation of an amalgam, which apparently is in the colloidal state. After the indicated time has elapsed, hydrogen evolution begins. At the same time the mercury surface swells and becomes nodular. After the experiment the mass of cathodic mercury has the viscosity of a paste, but retains the luster characteristic of mercury. When the sulfate solutions are replaced by chloride solutions (10 N $CaCl_2$ or 10 N LiCl) at the same acidity, concentration of Fe^{2+}, and current density, visible hydro-

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

gen evolution begins almost immediately after the current is switched on. After the experiment the cathodic mercury is comparatively easily separated from a dark-gray, powdery mass of reduced iron. Experiments with acidified solutions of 10 N $Ca(ClO_4)_2$ gave a result not differing from the results obtained with sulfate solutions.

Thus, the character of the reduced metal depends on the nature and concentration of the background anion, which influences the structure of the double layer and the composition of the discharging ion ([8]). Measurements of the dependence of the metal-reduction potential on the nature of the background and on the electrolysis time on the s.m.e. lead to the same conclusion. In the case of discharge against the background of concentrat-

···chlorides (Fig. 1, 1, 2), a lower polarization and a shorter delay before the onset of hydrogen evolution are observed than in concentrated sulfates (curve 3) at the same current density. The arrows in the figure indicate the time at which visible hydrogen evolution begins*.

To determine the nature of the reduction products of the iron-group metals at the dropping mercury electrode, we used the method of single-cycle reverse sweep on a TsLA-01 oscillographic polarograph of the Zfasman system. A potential of −1.8 V (delay potential φ_3) was applied to the growing mercury drop (drop time 5-6 sec) for 2-3 sec (delay period t). The sweep rate V was varied from 1 to 8 V/sec.

Fig. 1. Dependence of the reduction potential of Fe^{2+} and of the time of onset of visible hydrogen evolution on the nature of the supporting electrolyte and on the duration of electrolysis at the dropping mercury electrode. $[Fe^{2+}] = 0.05$ N; pH $\sim$ 1; $i = 4 \cdot 10^{-4}$ A/cm^2. 1 –10 N $CaCl_2$; 2 –5 N $CaCl_2$; 3 –saturated Na_2SO_4 solution.

In Fig. 2, 1 is shown the oscillogram for Ni in 1 N KCl during the reverse sweep from −1.8 to 0 V, switched on after the indicated delay. The oscillogram shows the cathodic wave of nickel reduction ($\varphi_{1/2} = -1.2$) and the anodic peak of nickel dissolution ($\varphi = -0.3$ vs. the normal calomel electrode). In 10 N $CaCl_2$ (curve 2) the cathodic wave passes smoothly into the anodic peak in the potential region −0.6-−0.4. Consequently, the reduction process of Ni becomes practically reversible, which agrees with the data of ([9]). For iron and cobalt at $\varphi_3 = -1.8$ V, it was not possible to obtain an anodic wave of dissolution of the metals deposited on mercury.

Figure 3

Figure 3: Figure 3

Fig. 2. Oscillograms of the reverse sweep in the case of reduction of Ni^{2+} at the dropping mercury electrode. pH $\sim$ 4.7; t = 2 sec; V = 1.0 V/sec. 1 – background 1.0 N KCl; 2 –background 10 N $CaCl_2$.

Using the oscillographic method described above, experiments were also carried out on a hanging mercury drop (h.m.d.)–Kemula electrode. The concentration of the solutions studied was of the order of $1 \cdot 10^{-3}$-$5 \cdot 10^{-3}$ N. The supporting electrolytes were 0.01 and 0.1 N KCl solutions, for which oscillograms were recorded beforehand; t was varied from 2 sec to 2 min, $V = 0.125$ V/sec.

As at the dropping mercury electrode, at $\varphi_3 = -1.6$ to -1.8 V and t from 14 sec to 1 min, reverse-sweep oscillograms in the case of Fe at the hanging mercury drop did not reveal a peak of anodic dissolution of the metal, except for a notch on the negative branch of the mercury dissolution peak ($\varphi = +0.06$ V), which perhaps belongs to iron (Fig. 3, 1). It was noted that the height and area of the mercury dissolution peak depend on $[Fe^{2+}]$ and t. This can be explained by the joint dissolution of Fe and Hg (curve 2). The data obtained agree with those of ([6]).

However, if φ_3 was set equal to -1.1 to -1.2 V, then on the oscillogram (Fig. 3, 4) a peak of anodic dissolution of iron was observed at $\varphi = -0.47$ V. This peak cannot be detected if φ_3 is more negative than -1.4 V. The magnitude of the peak depends on $[Fe^{2+}]$ and t (curves 3, 4). The peak can

* When a stationary mercury drop is polarized, the formation of microcrystals and the evolution of H_2 from them can be observed under a microscope.

can be detected even at t = 2-3 sec. Verification showed the possibility of reproducing these peaks on the d.m.e. It should be noted that in acidified solutions this peak is not observed. Upon neutralization of the solution the peak

Fig. 3. Oscillograms of the reverse sweep in the case of reduction of Fe^{2+} at the Kemula electrode. Background 0.1 N KCl; V = 0.125 V/sec.; t = 14 sec.; 1–$\varphi_3 = -1.6$ V; $[Fe^{2+}] = 1 \cdot 10^{-3}$ N; 2–$\varphi_3 = -1.6$ V; $[Fe^{2+}] = 5 \cdot 10^{-3}$ N; 3–$\varphi_3 = -1.1$ V; $[Fe^{2+}] = 1 \cdot 10^{-3}$ N; 4–$\varphi_3 = -1.1$ V; $[Fe^{2+}] = 5 \cdot 10^{-3}$ N; 5–same as 4, but after disconnecting the cell for 10 sec.

can be detected again. The peak disappears if, after holding at $\varphi_3 = -1.2$ V, $\varphi_3 = -1.8$ V is set. If the cell is disconnected from the instrument, the peak decreases in accordance with the duration of disconnection (compare curves 4, 5).

Fig. 4. Oscillograms of the reverse sweep in the case of reduction of Co^{2+} at the Kemula electrode. Background 0.1 N KCl; V = 0.125 V/sec.; t = 14

Figure 4

Figure 4: Figure 4

sec.; $[Co^{2+}] = 5 \cdot 10^{-3}\, N$; 1–$\varphi_3 = -1.5$ V; 2–$\varphi_3 = -1.1$ V; 3–same as 2, but background $5\, N$ $CaCl_2$

The peak of anodic dissolution of cobalt appears at a more positive potential ($\varphi = -0.15$ V). The conditions for its formation are the same as for iron (Fig. 4, 1, 2).

At very negative holding potentials ($\varphi_3 = -1.5$ V) the indicated peak does not appear, while the height and area of the peak corresponding to mercury dissolution increase and its potential shifts in the positive direction. As in the case of iron, the latter is apparently connected with the simultaneous dissolution of Co and Hg. If $\varphi_3 = -1.1$ V is first set, then the presence of a peak at $\varphi = -0.15$ V is checked, and afterward $\varphi = -1.6$ V is set, one can observe its gradual disappearance after several successive sweeps.

The deposition of nickel on the r.d.e. has certain special features. On a fresh drop the anodic peak ($\varphi = -0.3$ V) appears even at sufficiently negative φ_3 (Fig. 2, 1). On the d.m.e., after a series of successive sweeps

with an interval of 10-14 sec the peak disappears. It can be detected again on the same drop only at lower φ_3 and t, not less than 1 min.

Thus, the data obtained show that metals deposited at low cathodic polarizations dissolve anodically at potentials more negative than the dissolution potential of mercury: -0.47, -0.3, -0.15 V for Fe, Ni, and Co, respectively. It may be considered that the indicated peaks are peaks of anodic dissolution of the solid phase of the corresponding metal. Evidence for the existence of a solid phase under these conditions may be the absence of similar peaks at sufficiently negative φ_3. In the latter case the metal apparently passes into mercury, forming colloidal solutions or suspensions, and its anodic dissolution proceeds at potentials close to the dissolution potentials of mercury. It follows from this that the conditions determining the magnitude of the cathodic polarization of the reduction process of metals of the iron group at the dropping mercury electrode (the nature and concentration of the supporting electrolyte, the possibility of complex formation, the shift of the ψ_1-potential, the presence of surface-active substances, etc.) can to a considerable extent also determine the character of the final products of deposition of these metals.

The results of the experiments can be explained if it is assumed that, at first, during electrodeposition of metals of the iron group on the surface of the dropping mercury electrode, irrespective of the magnitude of the polarization, a solid phase is formed–microcrystals of Fe, Ni, or Co. The subsequent process of transfer of the metals into mercury depends on the wettability of the microcrystals by mercury and, consequently, on the increase in the difference of surface

tensions at the boundaries microcrystal | solution and mercury | solution; this may be connected with a certain difference in potentials on mercury and on the microcrystals, since on the latter the reduction of metal and hydrogen ions proceeds more readily than on mercury, and also with the difference in the positions of the zero points of Fe and Hg. A significant role in the wetting process is probably played by the degree of oxidation of the microcrystals, which increases with decreasing cathodic polarization and acidity of the solution. With increasing acidity or polarization of the cathodic process, the surface of the crystals is cleaned of the oxide film, and their wetting by mercury is intensified, which leads to the disappearance of anodic peaks on the oscillograms of the reverse sweep. When using data from polarization measurements it is necessary to take into account the possibility that the states of the metal deposited on the dropping mercury electrode may differ at different potential values.

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Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.