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Abstract

Full Text

PHYSICAL CHEMISTRY

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INVESTIGATION OF THE KINETICS OF THE ELECTROREDUCTION OF IRON AT A DROPPING MERCURY ELECTRODE

(Presented by Academician A. N. Frumkin, 30 XI 1960)

A large number of works have been devoted to the study, by the polarographic method, of the reduction of divalent iron ions at the dropping mercury electrode (DME) ([1]). However, almost all of them pursue analytical aims. J. Heyrovský ([2]) was the first to point out the high overvoltage in the reduction of iron ions at the DME. He assumes ([3]) that Fe^{2+} is reduced reversibly, since the reduction potential obeys the equation $\varphi = \text{const} + 0.029 \lg[Fe^{2+}]$. The very negative values of the potential are explained by him by the formation of a metastable amalgam containing highly active atomic iron. This also explains the absence, on the anodic branch of the oscillographic curve, of a delay associated with dissolution of iron from the amalgam. The reversibility of the process is also indicated in work ([4]). However, Kolthoff and Lingane ([5]) consider that iron does not form an amalgam at the DME and that the reduction proceeds irreversibly.

In the present work we investigated the degree of irreversibility of this reaction, the influence of the concentration of iron ions and hydrogen ions, and also the influence of the concentration and nature of the supporting background on the kinetics of the process.

The investigation was carried out on a visual polarographic setup. The potential of the DME was measured by a compensation method. A 1 N calomel electrode served as the reference electrode. A feature of the cell used was the presence of hydrogen and glass electrodes mounted on ground joints, which made it possible to monitor the pH of the solution at any moment of the experiment. The accuracy of pH determination was ± 0.05. The temperature of the experiments was $25 \pm 0.15^{\circ}$. In order to separate the closely lying half-wave potentials for the discharge of iron ions and hydrogen ions, some experiments were carried out on a TsLA-01 oscillographic polarograph of Heyrovský' s system. With the aid of this oscillograph, the peak potentials φ_p of differential polarograms were measured.

A study of the dependence of the limiting current I_d on the concentration of Fe^{2+} ions in the range from 10^{-4} to $10^{-2}N$ showed that in neutral and weakly acidic solutions (at pH > 4.5) I_d obeys the Ilkovič equation with sufficient accuracy, if

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Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

one takes $n = 2$, and the diffusion coefficient as $0.76 \cdot 10^{-5}$ cm^2/sec (calculated from conductivity data). The experimental data are presented in Fig. 1, 1. In the pH region from 4.5 to 2.8 the limiting currents for iron and hydrogen become comparable. From Fig. 1, 2, 3 it is seen that within the pH range from 7 to 2.8 the limiting diffusion current is equal to the sum of the currents for hydrogen and iron.

The investigation confirmed the conclusions of works ([3,5]) that $\varphi_{1/2}$ of the iron wave shifts toward more positive potentials when the concentration of iron ions is increased (see Fig. 1, 4). According to literature data ([6]), no corresponding change of $\varphi_{1/2}$ with the concentration of Ni and Co was found. The magnitude of the shift of $\varphi_{1/2}$, in the general case, is not constant and is in a complex dependence on the values of the concentrations of iron ions and hydrogen ions in the solution.

In Figs. 2, 1-3 are shown the results of determining the influence of the concentration and nature of the supporting electrolyte on $\varphi_{1/2}$ of iron at pH > 4.5, when the presence of H^+ ions has no noticeable effect on the iron wave. Curve 4, showing the dependence of the coefficient $a = 0.029/b^*$ on the concentration of the supporting electrolyte (KCl), is plotted there as well. As is seen from curve 4 of Fig. 2, the value of a decreases with increasing supporting-electrolyte concentration, which indicates the irreversibility of the process.

This decrease in the values of a, as well as the shift of $\varphi_{1/2}$ to the right, is evidently caused by a decrease in the negative values of the ψ_1-potential with increasing

Fig. 1. Dependence curves: **1** $-I_d$ on $[Fe^{2+}]$, supporting electrolyte $2\,N$ KCl, pH 5.5; **2** $-I_d$ on pH, supporting electrolyte $1\,N$ KCl, $[Fe^{2+}] = 10^{-3}\,N$; **3** $-I_d$ on pH, supporting electrolyte $1\,N$ KCl, $[Fe^{2+}] = 0$; **4** $-\varphi_{1/2}$ on $[Fe^{2+}]$, supporting electrolyte $2\,N$ KCl, pH 5.5.

Fig. 2. Dependence curves of $\varphi_{1/2}$ on supporting-electrolyte concentration: **1** $-$ KCl, **2** $-$KCl; **3** $-K_2SO_4$. $[Fe^{2+}] = 10^{-3}\,N$, pH 5.5. **4** $-$curve of the dependence of $a = 0.029/b$ on [KCl]. $[Fe^{2+}] = 10^{-3}\,N$, pH 5.5.

the concentration of the supporting electrolyte. This effect is especially noticeable when sulfates are used as the supporting electrolyte.

Concentrated solutions of $CaCl_2$ exert the opposite influence. In the presence of a $5\,M$ $CaCl_2$ solution as supporting electrolyte, a shift of $\varphi_{1/2}$ to the positive side by up to 300 mV is observed (see Fig. 4). If, instead of $CaCl_2$, a concentrated solution of $Ca(ClO_4)_2$ (sp. gr. ~ 1.4) is taken as the supporting electrolyte, then the value of $\varphi_{1/2}$ remains approximately the same as in KCl solutions.

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The results of our studies on the influence of pH on $\varphi_{1/2}$ of the electroreduction of Fe^{2+} are presented in Fig. 3A. As is seen from curves 4 and 6, the half-wave potentials of the combined discharge of iron ions and hydrogen ions in the pH range from 4.5 to 2.8 lie considerably more positive than $\varphi_{1/2}$ for the discharge of hydrogen ions (see curves 1, 3, 5), but more negative than the values of $\varphi_{1/2}$ for the discharge of iron ions at pH > 5 (see curve 2). With decreasing pH, $\varphi_{1/2}$ of the combined wave, as is seen from curves 2, 4, 6, 7, approaches the value of $\varphi_{1/2}$ of the hydrogen wave ($\varphi_{1/2} = -1.620$ V).

If, from the currents of the total wave, the currents of the hydrogen wave at different potential values are subtracted, then from the current differences one can construct the wave of iron discharge (for the given pH value). The half-wave potentials $\varphi_{1/2}$ of the curves of discharge of Fe^{2+} ions in acidic solutions obtained in this way

* b from the equation $\varphi = \varphi_{1/2} + b \lg \frac{i_d - i}{i}$.

turn out to be more negative than in neutral media (see curves 8 and 9 in Fig. 3B).

The validity of such construction of the curves and of the indicated conclusion was confirmed by differential polarography data:

Background	1 N KCl	1 N KCl	1 N KCl	1 N KCl	10 N $CaCl_2$	10 N $CaCl_2$	10 N $CaCl_2$	10 N $CaCl_2$	10 N $Ca(ClO_4)_2$	10 N LiCl
pH	6.5;	4.5;	3.5;	3.0;	5.0*;	3.5*;	5.0;	3.5	4.5	5.8
$-\varphi_{1/2}$, V	1.42;	1.45;	1.49;	1.55	–	–	1.13;	1.14	1.42**	1.27**
$-\varphi_p$, V	1.45;	1.50;	1.55;	–	1.33*;	1.24*;	1.27;	1.27	1.4	–

* Data of work (8).
** From the polarographic wave.

These data showed that the peak potential φ_p on the differential curves for the discharge of hydrogen ions is not changed by the presence of iron ions in the solution and is practically independent of changes in pH. At the same time, φ_p for the discharge

Fig. 3. A–curves of the dependence $I-\varphi$, $[Fe^{2+}] = 0$, background 1 N KCl: 1–pH 6.6, 3–pH 3.8, 5–pH 3.3; curves of the dependence I on φ, $[Fe^{2+}] = 10^{-3}$ N, background 1 N KCl: 2–pH 6.6; 4–pH 3.8; 6–pH 3.3; 7–pH 2.8. B–dependence of $\varphi_{1/2}$ on pH, background 1 N KCl: 8–$[Fe^{2+}] = 0$; 9–$[Fe^{2+}] = 10^{-3}$ N.

Fig. 4. Curves $I - \varphi$ against a background of 5 M $CaCl_2$: 1–$[Fe^{2+}] = 0$, pH 3.65; 2–$[Fe^{2+}] = 10^{-3}$ N, pH 4.9; 3–$[Fe^{2+}] = 10^{-3}$ N, pH 3.6; 4–$[Fe^{2+}] = 10^{-3}$ N, pH 2.9.

of iron ions on these same differential curves, as pH decreases, shifts toward negative potentials: when the pH changes from 6.5 to 3.5, $\Delta\varphi_p \simeq 100$ mV. In very acidic solutions (pH 2.2), the peak of the wave for the discharge of iron ions merges with the peak for the discharge of hydrogen ions. In the general case, the magnitude of the shift of $\varphi_{1/2}$ and φ_p depends on the ratio of the concentrations of iron ions and hydrogen ions; with increasing concentration of iron ions, $\Delta\varphi_{1/2}$ decreases.

According to literature data, an increase in polarization with decreasing pH has been observed in the electrodeposition of zinc, nickel, cobalt, lanthanum, indium, and some other metals (7). For the process of discharge of iron ions at the DME, there are no such data, with the exception of work (8), in which the reverse course of this dependence is noted against the background of a 5 M $CaCl_2$ solution. However, the latter does not agree with the results of our experiments carried out under analogous conditions (see Fig. 4).

The totality of the experimental data obtained by us can be explained if the following mechanism is assumed for the process of electroreduction of iron at the DME. In aqueous solution, through the reaction:

$$\underbrace{[Fe(H_2O)_n]^{2+}}_{A} + H_2O \rightleftarrows \underbrace{[FeOH(H_2O)_{n-x}]^{+}}_{B} + H^+ + x(H_2O) \qquad (1)$$

less hydrated oxo complexes B are formed. In the double layer, at a definite ratio of concentrations, both ions A and ions B are present. If it is assumed that the discharge of the more hydrated aquo complexes A is more difficult, then the rate of the process must be determined by the slowness of the discharge step of the less hydrated complexes B:

$$[FeOH(H_2O)_{n-x}]^{+} + 2e \rightarrow Fe^0 + OH^- + (n-x)H_2O, \qquad (2)$$

Thus, reaction (2) is the stage determining the rate of the process. The consumption of ions B can be replenished by diffusion of ions A and their rapid conversion into ions B as the equilibrium $A \rightleftarrows B$ in the near-electrode layer is shifted. The magnitude of the limiting current is determined not by ions B, but by the total concentration of iron ions in the bulk.

In accordance with the proposed mechanism of the electrode reaction, a decrease in the pH of the solution should cause a shift of the equilibrium of the bulk reaction (1) toward a decrease in the concentration of ions B and thereby cause an increase in polarization. On the other hand, it would seem that any measure leading to a decrease in the degree of hydration of iron ions should facilitate the process of their discharge and make it more reversible. In highly concentrated $CaCl_2$ solutions we did, indeed, observe a decrease in the polarization of this process. However, replacement of the $CaCl_2$ background by a concentrated $Ca(ClO_4)_2$ solution showed that Ca^{2+} ions do not play the decisive role. The

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reason for the large shift of $\varphi_{1/2}$ toward positive values in the indicated case is probably connected not with additional dehydration of the aquo complexes, but with the replacement of oxo complexes by chloro complexes.

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