INFLUENCE OF THE pH OF THE SOLUTION ON THE ADSORPTION AND INHIBITING ACTION OF SURFACE-ACTIVE SUBSTANCES ON COBALT

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UDC 541.138:541.135.8-183.24

In the process of corrosion of a metal the pH of the solution at its surface may change considerably, and this may lead to a change in the adsorption and efficiency of action of inhibitors. In [1-6] it was shown that the adsorption of a number of surface-active substances (s.a.s.) and ions decreases with increase in the pH of the solution. The decrease in the efficiency of inhibitors with increase in pH was related by the authors cited to the change in the magnitude of the steady-state potential of the metal [4] or to the change in the adsorption of OH^- ions [5]. It was of interest to make a more detailed study of the observed phenomenon.

The present paper describes a study of the influence of pH on the adsorption of a surface-active anion (the I^- ion), a surface-active cation (tetrabutylammonium sulfate,TBAS), and their simultaneous adsorption (tetrabutylammonium iodide,TBAI) on a cobalt electrode.

We recorded the potentiostatic curves and differential capacity curves for electrolytic α-cobalt* in aqueous $H_2SO_4 + Na_2SO_4$ solutions with a total concentration of 1 N and different pH values (from 0.05 to 3). The polarization curves were recorded by means of a P-5611 potentiostat. The order of measurement of the polarization curves was the same as in the measurement of the differential capacity curves. The procedure used in the capacity measurements was described in [7, 8]. The values of the capacity, measured for a series scheme, were recalculated for a parallel scheme. The potentials were measured relative to a normal hydrogen electrode.

Some results of the recording of the potentiostatic curves are given in Table 1: b_c and b_a are the slopes of the cathodic and anodic polarization curves, φ_s is the steady-state potential (mV), and i_s is the current of spontaneous dissolution (A/cm^2).

It follows from Table 1 that the slope of the cathodic curve increases and that of the anodic curve remains unchanged with increase in pH; $(\partial\varphi_s/\partial \mathrm{pH}) = -0.065$ V. The increase in b_c is due to the production of diffusion limitations in the process of hydrogen liberation.

The differential capacity curves recorded for a pure solution of the background electrolyte are given in Fig. 1a and b (curves 1). With increase in pH the rising section on the C, φ curve, associated with the adsorption of OH^- ions [7], begins at more negative values of the potential. The general form of the C, φ curve is preserved, however. In the presence of KI, a decrease in capacity as a consequence of the desorption of I^- ions is observed. From Fig. 1a and b, it may be concluded that the adsorption of I^- ions decreases as the potential of the electrode is displaced towards more negative values, and also with increase in the pH of the solution (see Table 2).

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*The composition of α-cobalt is given in [8].

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 8, No. 4, pp. 603-606, April, 1972. Original article submitted July 20, 1971.

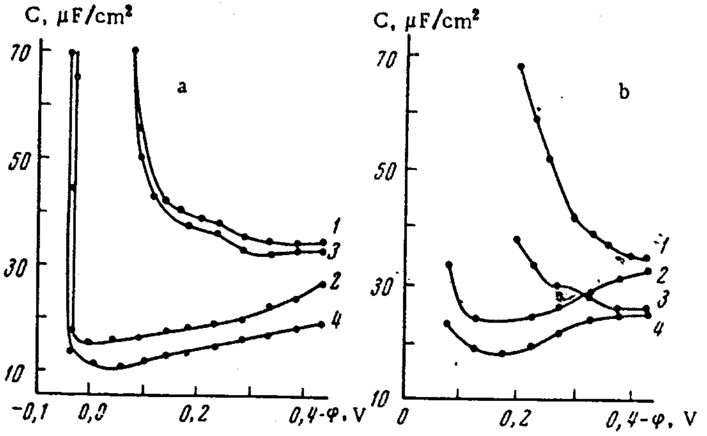

Fig. 1. Differential capacity curves recorded at a frequency of 800 Hz in $Na_2SO_4 + H_2SO_4$ (1 N) solutions at pH 0.05 (a) and 2.9 (b) with various additives: 1) pure solution; 2) 10^{-5} N KI; 3) 10^{-5} N TBAS; 4) 10^{-5} N TBAI.

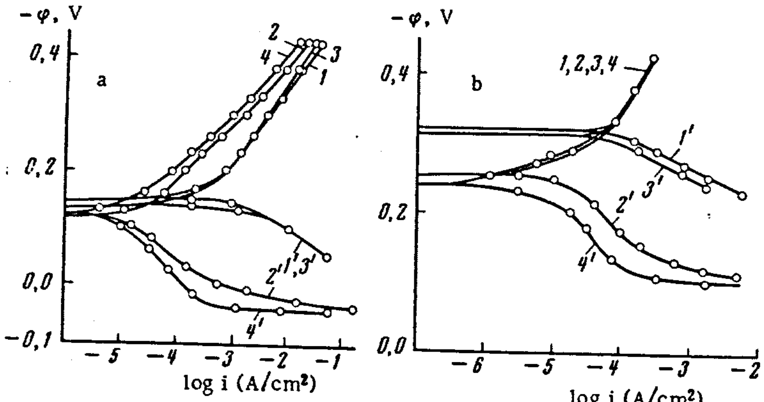

Fig. 2. Polarization curves recorded in $Na_2SO_4 + H_2SO_4$ (1 N) solutions at pH 0.05 (a) and 2.9 (b) containing various additives: 1, 1') pure solution; 2, 2') 10^{-5} N KI; 3, 3') 10^{-5} N TBAS; 4, 4') 10^{-5} N TBAI.

TABLE 1. Dependence of Various Electrochemical Characteristics of the Cobalt Electrode on the pH of the Solution

pH	b_c	b_a	φ_s	log i_s
0,05	145	50	−147	−3,35
0,92	150	45	−206	−3,6
2,14	200	45	−270	−3,8
2,9	200	45	−324	−4,1

It can be seen from Table 2 that the quantity ΔC (μF/cm²) corresponding to the decrease in capacity when KI is introduced decreases on going from acidic to weakly acidic solutions. The results of the potentiostatic measurements are in agreement with these data. Comparison of the polarization curves given in Fig. 2a and b shows that with increase in pH the retarding action of I^- ions on the process of hydrogen liberation decreases rapidly (see also Table 2, where $\Delta\varphi_c$ (mV) is the increase in the overpotential of hydrogen liberation in the presence of KI). The influence of pH on the efficiency of the action of I^- ions on the anodic dissolution of cobalt is much smaller (see Fig. 2a and b).

On the addition of KI, the steady-state potential of cobalt (φ_s) is displaced towards more positive values. The displacement $\Delta\varphi_s$ increases with increase in the pH of the solution as a consequence of the marked decrease in the retardation of the cathodic process compared with the change in the retardation of the anodic dissolution of cobalt (see Table 2). A decrease in the efficiency of the inhibiting action of KI with increase in the pH of the solution is also observed at the steady-state potential. Table 2 gives the ratios of the current for the spontaneous dissolution of cobalt in the pure solution to the current of spontaneous dissolution in the presence of KI (γ). The values of γ decrease with increase in pH. It should be noted that the determination of the current of spontaneous dissolution by extrapolation of the polarization curves in the presence of I^- ions is approximate, since the anodic and cathodic curves do not have a constant slope.

TABLE 2. Influence of KI (10^{-5} N) on Various Electrochemical Characteristics of the Cobalt Electrode

pH	ΔC at $\varphi = -0.42$ V	$\Delta\varphi_c$ at $i_c = 0.01$ A/cm²	$\Delta\varphi_s$	γ
0,05	8	65	23	35,5
0,92	4	25	41	11
2,14	2,5	5	50	17
2,9	2	0	66	5

This last feature is explained by the dependence of the adsorption of I^- ions on the potential. It is only in a fairly narrow range of potentials (see Fig. 1a and b) that the differential capacity of the cobalt electrode remains unchanged. Thus the determination of the currents of spontaneous dissolution by extrapolation is approximate in this case.

The adsorption and the action of tetrabutylammonium cations (TBAS) on the rate of the electrode processes increase with increase in the pH of the solution; this follows from the results of capacity measurements in Fig. 1a and b (the decrease in capacity in the presence of TBAS is greater at pH 2.9 than at pH 0.05) and also from the polarization curves given in Fig. 2a and b. If tetrabutylammonium cations and I^- ions are present simultaneously in the solution (TBAI), the observed decrease in capacity and the retardation of the cathodic and anodic processes are greater than those in the presence of the ions of only one kind. In this case, however, the adsorption of TBAI and its effect decrease with increase in pH, particularly in the case of the cathodic process.

The change in the adsorbability of the ions and the decrease in their influence on the anodic and cathodic processes on cobalt with increase in the pH of the solution can be attributed to the following factors.

1. As a consequence of the competing adsorption of anions, increase in the concentration of OH^- ions leads to a decrease in the adsorption of I^- ions and TBAI. At the same time, the adsorbed OH^- ions increase the adsorption of TBAS cations.

2. The displacement of the steady-state potential towards more negative values leads to an increase in the negative charge of the cobalt surface, and the adsorption of I^- ions decreases, while that of the tetrabutylammonium cation increases. The electrocapillary zero of the electrode (φ_{ez}) is apparently less dependent on the pH of the solution than the steady-state potential. Otherwise, with a marked decrease in φ_{ez} there would be a displacement of the C, φ curve recorded in the presence of KI towards more negative values,* but this is not observed experimentally (see Fig. 1a and b).

3. The production of diffusion limitations in the cathode process in weakly acidic solutions leads to the almost complete cessation of the retarding action of surface-active substances on the rate of liberation of hydrogen, despite the fact that, according to the capacity measurements, surface-active substances are present on the cobalt surface in the range of cathodic potentials, and these should be expected to influence the cathodic process.

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*It is suggested that in the adsorption of OH^- ions there may be a displacement of φ_{ez} towards more negative values, as in the case of mercury in the presence of surface-active substances.