ADSORPTION OF ALLYLPHENYLTHIOUREA AND TETRABUTYLAMMONIUM IODIDE ON COBALT IN SULFURIC ACID

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The authors performed adsorption measurements on α-cobalt in sulfuric acid for allylphenylthiourea and tetrabutylammonium iodide, which are inhibitors of cobalt corrosion, and constructed the adsorption isotherms for these compounds. The adsorption kinetics of allylphenylthiourea were studied.

Judging from polarization curves measured in the presence of inhibitors, cobalt and iron have similar adsorption properties [1, 2]. However, direct measurements of inhibitor adsorption on cobalt have not been performed.

The present paper deals with the adsorption and inhibiting properties of allylphenylthiourea (APTU) and tetrabutylammonium iodide (TBAI) on α-cobalt.* Corrosion measurements revealed that TBAI and, in particular, APTU effectively inhibit cobalt corrosion (see Table 1).

The adsorption of APTU and TBAI was determined from capacitance measurements by means of an R-568 impedance bridge on cylindrical specimens (diameter 0.3 mm) of area 2-4 mm^2. The solutions were prepared in doubly distilled water and were subjected to adsorption purification by platinized platinum and to cathodic purification on cobalt, in the measuring cell itself, with a current of 10 mA/cm^2 for 2-3 h. Before an experiment, the test electrode was cleaned with glass powder or a scraper, washed with ethyl alcohol and water, polarized for 1 h by a cathodic current of 10 mA/cm^2, and then kept for 10-15 min without current until the steady potential was established. We then obtained the (C, φ) curves in the pure solution, and with added APTU or TBAI, in the direction from cathodic to anodic potentials. The measurements were performed with series-connected capacitance and resistance at 800 Hz; in accordance with the analysis in [3, 4], the value of the capacitance was then converted to a parallel circuit, allowing for the solution resistance by the formulas:

$$C_u = \frac{C_u}{1+(R_u-R_0)^2C_u^2\omega^2}; \quad R_1 = (R_u-R_0)\left(1+\frac{1}{(R_u-R_0)^2C_u^2\omega^2}\right), \tag{1}$$

* Composition of α-cobalt (%): Cd, Mn, Pb < $1\cdot10^{-4}$; Sn, Bi, P < $5\cdot10^{-5}$; Fe ~ $6\cdot10^{-4}$; Ni, Zn, Si, Al < $1\cdot10^{-3}$; As < $3\cdot10^{-3}$; Cu, Sb < $2\cdot10^{-4}$; S — $8\cdot10^{-4}$; C — $7\cdot10^{-3}$.

TABLE 1. Mean Rate of Corrosion of Cobalt in 1 N H_2SO_4, g/cm^2·h

Method of determination	Composition of solution		
	1 N H_2SO_4	1 N H_2SO_4 + $5.2\cdot10^{-6}$ M APTU	1 N H_2SO_4 + $9.3\cdot10^{-5}$ M APTU
Weight losses	$3.3\cdot10^{-5}$	$8.0\cdot10^{-7}$	$1.4\cdot10^{-6}$
Colorimetric measurements	$3.5\cdot10^{-5}$	$9.3\cdot10^{-7}$	$1.6\cdot10^{-6}$

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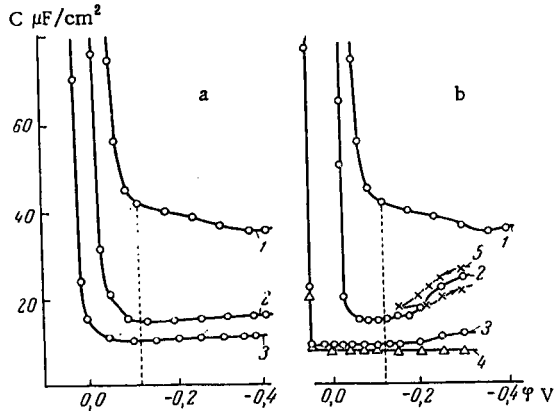

Fig. 1. Differential capacitance versus potential for a cobalt electrode in 1 N H_2SO_4: a – 1) in the pure solution; 2) $5 \cdot 10^{-6}$ M; 3) $2 \cdot 10^{-5}$ M APTU; b – 1) in the pure solution; 2) $1 \cdot 10^{-6}$ M; 3) $1 \cdot 10^{-5}$ M; 4) $5 \cdot 10^{-3}$ M TBAI; 5) $3.5 \cdot 10^{-6}$ M KI. The dashed line denotes the steady potential.

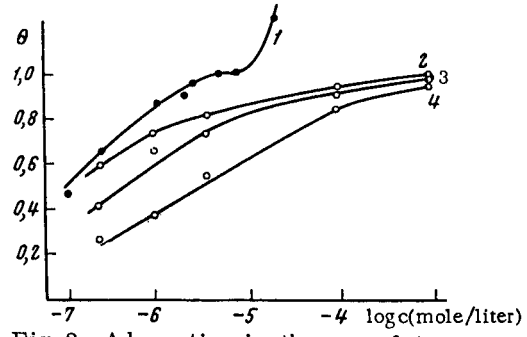

Fig. 2. Adsorption isotherms of APTU at $\varphi = -0.2$ V (1) and TBAI at $\varphi = -0.15$ V (2); –0.2 V (3); –0.3 V (4) on cobalt in 1 N H_2SO_4.

where C_u and R_u are the measured values of the capacitance and resistance, respectively, R_0 is the solution resistance, and ω is the angular frequency.

For APTU the measurements were performed in the concentration range from $1 \cdot 10^{-7}$ to $2 \cdot 10^{-5}$ M, and for TBAI from $2 \cdot 10^{-7}$ to $5 \cdot 10^{-3}$ M. These compounds were added at cathode potentials corresponding to the origin of the (C, φ) curve. Since the capacitance measurements were performed on electrodes with different coefficients of roughness, the values of the capacitance in the cathode potential range fluctuated from 35 to 50 $\mu F/cm^2$ in the base electrolyte. To construct composite (C, φ) curves, we introduced a correction factor allowing for variation of the surface roughness. We took the capacitance in pure 1 N H_2SO_4 as 35 $\mu F/cm^2$. The potential was measured relative to a normal hydrogen electrode.

It will be seen from Fig. 1 that adsorption of APTU is virtually independent of potential, whereas the amount of TBAI adsorbed increases markedly as the potential shifts towards the positive side, particularly at low concentrations. At higher positive potentials we observe desorption of the molecules of the organic substance, together with a marked increase in the capacitance due to the reverse course of the reaction

$$Co + OH^- - e \rightleftarrows CoOH_{ads},$$

which is the first stage of anodic solution of the metal.

From the capacitance measurements we calculated the surface coverage by the organic substance, θ, and constructed the adsorption isotherms (Fig. 2). For this purpose we used the formula

$$\theta = \frac{C_0 - C_c}{C_0 - C_\infty}, \qquad (2)$$

where C_0, C_c, and C_∞ are the double-layer capacitances in the pure base electrolyte, in the electrolyte with added organic compound (concentration c), and in the electrolyte with an organic concentration corresponding to monolayer coverage. Coverage by APTU and TBAI obeys the Temkin isotherm. In the case of APTU, at concentrations above $5 \cdot 10^{-6}$ M we apparently have polymolecular adsorption because the isotherm has a characteristic inflection. The possibility of polymolecular adsorption of thiourea derivatives on iron was noted in [5]. However, by analogy with phenylthiourea [6] we can assume that adsorption of APTU on cobalt and iron is accompanied by partial decomposition of the molecules of the substance and therefore has a more complex character.

It will be seen from Fig. 2 that surface coverage of cobalt by APTU molecules takes place in a narrower concentration range and at lower concentrations than in the case of TBAI. The difference between the adsorption mechanisms of APTU and TBAI is revealed from a comparison of the (C, φ) curves, measured in dilute solutions of the organic compounds (see Figs. 1a and 1b).

Adsorption of TBAI apparently takes place as follows. The iodide anions, which appear during dissociation of TBAI in the electrolyte, are chemisorbed on the metal surface and displace the zero charge

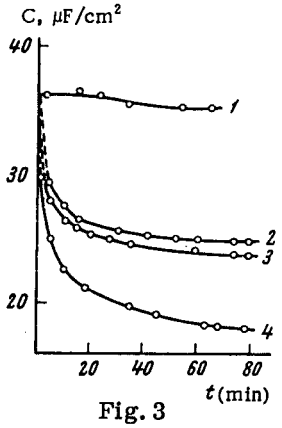

Fig. 3

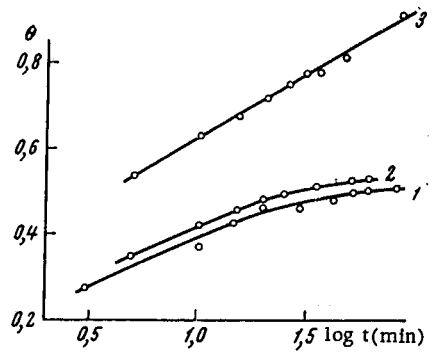

Fig. 4

Fig. 3. Capacitance versus time with addition of APTU to 1 N H_2SO_4: 1) pure electrolyte; 2) $1 \cdot 10^{-7}$ M; 3) $2 \cdot 10^{-7}$; 4) $5 \cdot 10^{-6}$ M APTU.

Fig. 4. Semilogarithmic time dependence of θ : 1) $1 \cdot 10^{-7}$ M; 2) $2 \cdot 10^{-7}$; 3) $5 \cdot 10^{-6}$ M APTU.

potential towards the positive side [7, 8]. The charge of the cobalt surface becomes more negative and the TBAI cations are adsorbed on the metal surface under the effect of electrostatic forces. It is of interest that adsorption of TBAI changes with potential in the same way as that of I^- ions, as may be judged from the similar shape of the (C, φ) curves. It follows from Fig. 1b (curve 5) that adsorption of I^- ions is effectively irreversible and on retracing the (C, φ) curves towards more negative potentials we observe only their partial desorption.

Adsorption of APTU on cobalt is apparently accompanied by frequent decomposition of the organic substance to form HS^- ions. Part of the undecomposed molecule adds on a hydrogen ion and is present in the solution as cations. The adsorption mechanism of the latter is the same as for TBAI. On the metal surface we may also observe adsorption of APTU molecules not subjected to chemical changes owing to interaction of the free pair of electrons at the sulfur or nitrogen atom with the unfilled d-shell of the cobalt atoms.

However, in the initial period adsorption of APTU is apparently markedly linked with electrostatic forces since the adsorption rate is largely dependent on the electrode potential and increases at more positive potentials. We assessed the adsorption rate from the change in the double-layer capacitance on the cobalt electrode with time when APTU was added to the solution (Fig. 3). From the curves in Fig. 3, we calculated by (2) the dependence of θ on the adsorption time. It was found that the experimental data agree with the Roginskii-Zel'dovich equation [9]:

$$\frac{d\theta}{dt} = k_1 c \exp[-k_2\theta], \tag{3}$$

where k_1 and k_2 are constants and c is the concentration of the adsorbate.

In the integral form, (3) is as follows:

$$\theta = \frac{1}{k_2} \ln\left[\frac{k_1}{k_2} t + 1\right] \tag{4}$$

or with a fairly long adsorption time $[(k_1/k_2)t \gg 1]$.

$$\theta = \frac{1}{k_2} \ln\left[\frac{k_1}{k_2} t\right]. \tag{5}$$

If the concentration is not too small, the experimental data on APTU adsorption obey (5) satisfactorily (Fig. 4). For TBAI similar processing of the experimental data is difficult owing to the high rate of adsorption.

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CONCLUSIONS

1. The concentration dependence of the amount of APTU and TBAI adsorbed is described by the Temkin isotherm.

2. Adsorption of APTU is virtually independent of the electrode potential, by adsorption of TBAI depends on the latter. This dependence is largely due to the change in the amount of adsorbed I^- ions with a change in the potential.

3. In the case of APTU the dependence of θ on the adsorption time obeys the Roginskii-Zel'dovich equation.

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