INFLUENCE OF ANION ADSORPTION ON THE EFFECT OF INHIBITORS ON THE CORROSION OF IRON AND COBALT IN ACIDS

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The effect of inhibitors depends on their adsorption. The adsorption, in turn, is determined to a great extent by the steady potential of the corroding surface (φ_c) with respect to the zero point ($\varphi_{\varepsilon=0}$)[1-4]. By measuring the differential capacitance of the double layer in sulfuric acid solutions we found that for iron $\varphi_{\varepsilon=0} = -0.33$ to -0.37 V with respect to the normal hydrogen electrode [5]. This result was confirmed by measurements made by the method of crossed lines [6]. It follows, then, that in sulfuric acid solutions ($\varphi_c = -0.25$ V) the surface of the iron is positively charged and that this charge makes the adsorption of organic cations more difficult and the adsorption of organic anions easier.

During the adsorption of organic cations a positive adsorption ψ_1-potential is created and this potential slows down the cathodic reaction of the discharge of hydrogen ions and the anodic reaction of the ionization of the metal [1, 2]. In the case of the adsorption of organic anions these reactions must be accelerated because of the creation of the negative adsorption ψ_1-potential.*

In what follows we generalize the results of experiments in which we determined the curves of differential capacitance of the double layer which are used to measure the degree to which organic compounds of different types are adsorbed either separately or together with anions. We also studied the effect of these compounds on the corrosion rate and the electrochemical reactions determining the corrosion rates. The experiments were made in oxygen-free solutions of sulfuric acid at t = 20°C.

It was shown in [7] that the inhibitors of the cation type [tetrabutylammonium sulfate (TBAS), tribenzylamine (TBA), and others] slow down the discharge of hydrogen ions only in cases of strong cathodic polarization. On the contrary, anions of sulfoacids (benzolsulfoacid, for example) are very well adsorbed on the surface of iron from H_2SO_4 solutions, and this results in a significant decrease of the differential capacitance of the electrode recalculated for a circuit in parallel (see Fig. 1, curves 1 and 4).† This decrease is particularly large at potentials close to the steady potential. The decrease is less when the cathode potential is high, which indicates a decrease in the adsorption of anions. The degree to which the capacitance decreases, which indicates the degree to which the surface is covered with the inhibitor, increases with increasing concentrations of the inhibitor up to a certain limit corresponding to complete covering of the surface with a monomolecular layer. Experiments showed that there is a strict parallel between the decrease of the capacitance with the concentration of the inhibitor and the decrease of the corrosion rate with the concentration of the inhibitor. However, in accordance with the creation of the negative ψ'-potential, the benzolysulfoacid accelerates the corrosion instead of inhibiting it (Fig. 2, curves 1 and 5).

* This conclusion, as we shall show below, cannot be extended to inorganic anions which are chemisorbed on iron [2]; they increase the overvoltage of the electrochemical reactions indicated and, consequently, decrease the corrosion rate of iron.

† All the measurements of polarization curves and of differential capacitance were made with highly pure iron (zonal smelting), the total amount of impurities being less than 0.01% and the amount of sulfur being less than 0.0005%. The potentials φ_r are given with respect to the hydrogen electrode in a sulfuric acid solution of the same concentration.

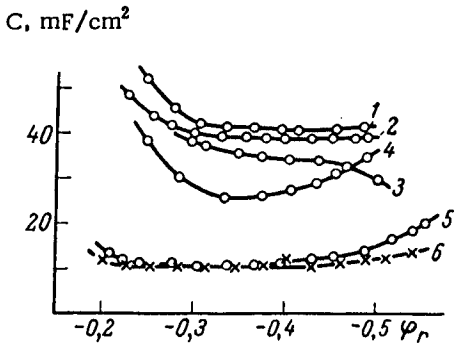

Fig. 1. Curves of differential capacitance of iron electrodes. 1) 1 N H_2SO_4; 2) 0.001 M N $(C_6H_5NH_2)_2$; 3) 0.001 N H_2S; 4) 0.01 M $C_6H_3(OH)(COOH)SO_3H$; 5) 0.01 M $C_6H_3(OH)(COOH)SO_3H$ + 0.001 M N $(C_6H_5NH_2)_3$; 6) 0.001 N H_2S + 0.001 MN $(C_6H_5NH_2)_3$ (frequency 800 Hz).

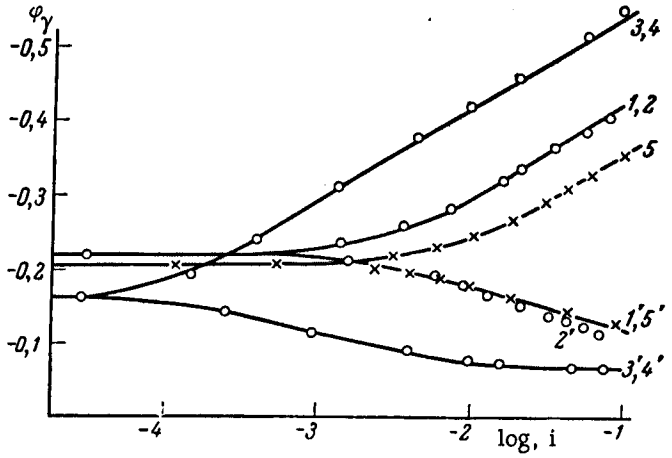

Fig. 2. Curves of cathodic and anodic polarization of iron electrodes. 1,1') 1 N H_2SO_4; 2,2') 0.5 N $C_6H_{13}OH$; 3,3') 10^{-4} N KI; 4,4') 10^{-4} N KI + 0.5 N $C_6H_{13}OH$; 5,5') 0.1 M $C_6H_3(OH)(COOH)SO_3H$.

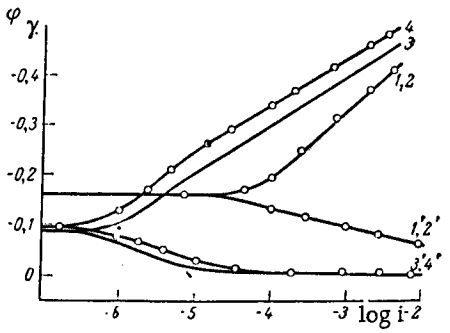

Fig. 3. Polarization curves of a cobalt electrode. 1,1') 6 N H_2SO_4; 2,2') 0.001 N N $(C_4H_9)_4+$; 3,3') 10^{-4} N KI; 4,4') 10^{-4} N KI + 0.001 N N $(C_4H_9)_4+$.

Thus, the decrease of the capacitance and the adsorption of organic substances do not answer the question of whether the organic substance acts as an inhibitor or as a stimulator. The way the inhibitor acts depends on the changes that the adsorbed substance makes in the structure of the double electric layer.

It should be noted that the stimulating action decreases and is transformed into inhibiting action with increasing molecular weight and the length of the sulfoacid molecule. For example, the solution rate of Armco iron in pure 1 N H_2SO_4 solution is 1.6 g/m^2·h. When 0.1 M $C_6H_{13}OSO_3H$ is added then the solution rate is 3.8 g/m^2·h and in the solution saturated with $C_{18}H_{37}OSO_3H$ the solution rate is 1.08 g/m^2·h. This difference is due to the screening effect of the long hydrocarbon chain of the adsorbed molecules on the discharge of ions in the double layer.

The HCl solutions in which the surface of iron has a negative charge because of the chemisorption of Cl^- ions, sulfoacids are not adsorbed and have no effect on the corrosion of iron [8].

It is interesting that uncharged molecules of aliphatic compounds [hexyl alcohol ($C_6H_{13}OH$) or capronic acid, for example], which are very well adsorbed by mercury, are not adsorbed on the iron surface and have no effect on its corrosion or its polarization curves either in pure H_2SO_4 and HCl solutions or in these solutions containing iodine ions (see Fig. 2, curves 1, 2, 3, and 4).

The fact that these substances are not adsorbed on iron must be explained by the hydrophyllic quality of the iron surface. The water molecules, which are easily adsorbed on the iron surface, displace these compounds from the surface.

COBALT ELECTRODE

Inhibitors of the cation type are not adsorbed on cobalt from H_2SO_4 solutions and do not change either the cathodic or anodic polarization curves (see curves 1 and 2 in Fig. 3).* As in the case of iron, this is explained by the fact that φ_C for the cobalt is situated at more positive potentials than $\varphi_{\varepsilon=0}$ and, consequently, the surface of cobalt is positively charged. In a 1 N H_2SO_4 solution $\varphi_C = -0.160$ V. The value of $\varphi_{\varepsilon=0}$ calculated from the work function

*We used highly pure electrolytic cobalt obtained from chlorides. The cobalt was fired in a hydrogen atmosphere before the experiments. X-ray analysis showed that the cobalt used was the α-modification and had a hexagonal structure. (The polarization and capacitance curves were obtained by the assistant, Vei Bao-min.).

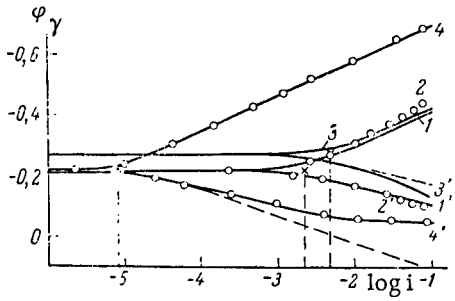

Fig. 4

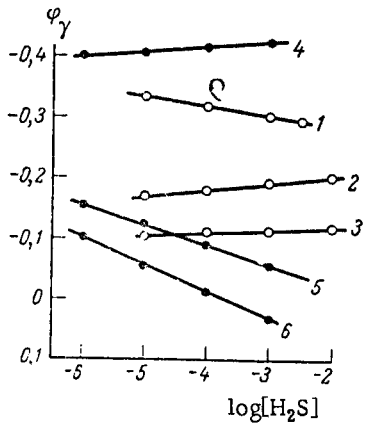

Fig. 5

Fig. 4. Polarization curves of an iron electrode. 1,1') 1 N H_2SO_4; 2,2') 1 N H_2SO_4 + 0.001 M tribenzylamine; 3,3') 1 N H_2SO_4 + 10^{-4} N Na_2S; 4,4' 1 N H_2SO_4 + 0.001 M tribenzylamine + 10^{-4} N Na_2S. The dashed line represents the M = f(t).

Fig. 5. Effect of the concentration of H_2S on the potential of a cobalt electrode not subjected to external polarization (φ_c) and also during cathodic (φ_c) and anodic (φ_a) polarization with a current of 1 mA/cm^2. 1) φ_M; 2) φ_c; 3) φ_a in 1 N H_2SO_4 + 10^{-4} M tribenzylamine; 4) φ_M; 5) φ_c; 6) φ_a.

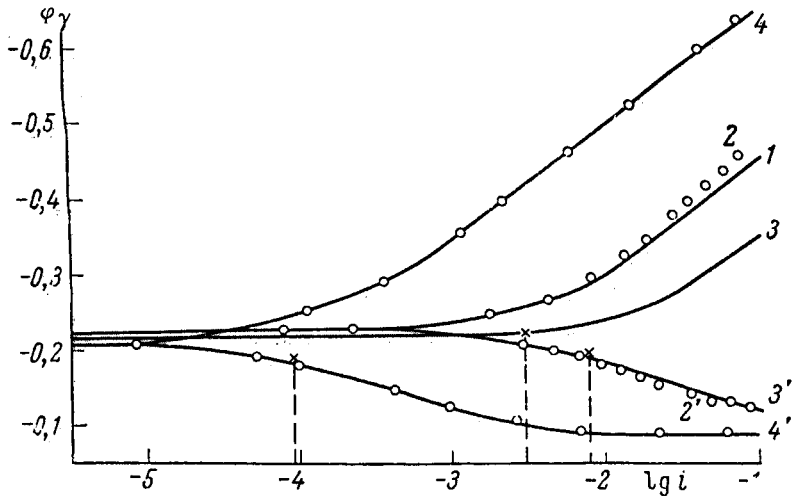

Fig. 6. Polarization curves of an iron electrode. 1,1') 1 N H_2SO_4; 2,2') 1 N H_2SO_4 + 0.001 N $N(C_4H_9)_4$; 3,3') 10^{-2} M sulfosalicilic acid; 4,4') 1 N H_2SO_4 + 10^{-2} M sulfosalicilic acid + 0.001 M $N(C_4H_9)_4$+.

of electrons is −0.68 V [9] or −0.51 V [4]. At a pH of 1-6 the experimentally found values of $\varphi_{\varepsilon=0}$ are between −0.32 and −0.48 V [10].

The halogene anions are chemisorbed on the cobalt surface in decreasing amounts: $I^- > Br > Cl^-$. As in the case of iron electrodes, they become part of the metal phase of the double layer, and this decreases the positive charge of the metal surface, which considerably facilitates the adsorption of organic cations. This effect is much weaker on cobalt than on iron and occurs only during cathodic polarization and close to φ_c, as shown by curves 3 and 4 in Fig. 3. The presence of I^- and Br^- ions during anodic polarization does not lead to any additional increase of the anode potential. This is explained by the fact that the adsorption of halogene ions does not render the cobalt surface negative, as in the case of iron, although it decreases the positive charge.

Experiments showed that small amounts of hexyl alcohol and capronic acid are adsorbed on the cobalt surface and that they slow down the electrochemical reaction and the corrosion of cobalt somewhat. We may conclude, therefore, that the cobalt surface is less hydrophyllic than the iron surface.

EFFECT OF INHIBITORS IN THE PRESENCE OF HYDROGEN SULFIDE

It is well known that H_2S stimulates the corrosion of iron and cobalt and accelerates mainly the anodic reaction. However, small amounts of H_2S favor the adsorption of inhibitors of the cation type. In the presence of inhibitors the stimulating action of H_2S is suppressed and the corrosion rate is slowed down considerably.

Polarization curves (Fig. 4) and the curves of differential capacitance (Fig. 1) confirm that tribenzylamine and H_2S separately are adsorbed very little on the iron surface; the first is an ineffective inhibitor and the second stimulates the spontaneous dissolution of iron, essentially because of the acceleration of the anodic reaction. However, when these two substances are present together in a solution of sulfuric acid then the tribenzylamine is adsorbed very intensely and the spontaneous dissolution of iron is decreased by a factor of about 800. Even when the concentration of H_2S is 10^{-6} N and that of tribenzylamine is 0.001 M, the corrosion rate of pure iron in 1 N H_2SO_4 is slowed down by about two orders. On Armco iron, on which the hydrogen overvoltage is higher, the relative effect is smaller. The presence of sulfur in industrial iron may also have an effect on the adsorption and the effect of inhibitors, since sulfur can be reduced to H_2S during the corrosion of iron in acids. This conclusion was confirmed by experiments.

Hydrogen sulfide also accelerates the cathodic and anodic reactions on cobalt but to a lesser extent than on iron (see curves 1, 2, and 3 in Fig. 5). In the presence of tribenzylamine an increase in the concentration of H_2S leads to an increase of the overvoltage of the ionization of cobalt and, to a lesser extent, to a discharge of hydrogen ions.

Many organic compounds containing sulfur (thiourea, its derivatives, sulfooxides, sulfoamides, rodanides, etc.) decrease the corrosion rate of iron because they decompose and H_2S is formed during the corrosion of iron in acids [11].

On the contrary, the aliphatic alcohols and acids which, as we said before, are not adsorbed on the iron surface and do not affect the corrosion of iron, intensify the stimulating effect of H_2S in sulfuric acid solutions [11]. The polarization curves indicate that this effect is induced essentially by the decrease of the hydrogen overvoltage.

It is also interesting that the sulfoacids themselves are stimulators of corrosion, but that together with organic bases they slow down electrochemical reactions and corrosion of iron. This effect is probably due to the formation of anion-cation pairs on the surface of the metal. The tribenzylamine is very weakly adsorbed on the iron surface from sulfuric acid at all potentials (see Fig. 1). The sulfoacid anions are well adsorbed only in a middle range of potentials close to φ_C. However, their simultaneous presence in the solution leads to strong adsorption in a wide range of potentials and, as the result, the tribenzylamine becomes an effective inhibitor (Fig. 6).

DEFORMATION OF ANODIC POLARIZATION CURVES

In pure 1 N H_2SO_4 solutions the anodic polarization curves largely follow the Tafel equation with an angular coefficient b_a = 60 mV in the case of iron obtained by zonal smelting and b_a = 30 mV for other types of iron (Armco iron, electrolytic iron).

In the presence of H_2S the logarithmic relationship ceases to be satisfied and with increasing current densities the curve begins to approach the curve relative to pure acid solutions (see curve 3, Fig. 4). This can be explained by the removal of H_2S from the solution together with the surface atoms of the metal which are being ionized and by an insufficient rate of adsorption of H_2S. As the result, the steady surface concentration of H_2S decreases and its effect is weakened. In fact, if a current i_a is applied after the iron is kept at φ_C for 1 min then the oscillogram representing the variation of φ with time has the form shown in Fig. 7a. At the moment the current is turned on the potential shifts abruptly toward more positive values, reaching φ_M, then increases slowly up to φ_a (the anode potential under steady conditions). The value of φ_M corresponds to the maximum surface concentration of H_2S existing at the moment the metal begins to dissolve. Then the surface concentration of H_2S drops and the overvoltage of the anodic process increases. The resulting anodic curve $\varphi_M = f(\log i_a)$ corresponds to the maximum concentration of the stimulator; it is shown by the dashed line in Fig. 4. At high anodic current densities the effect of inhibitors decreases; the inhibitors are adsorbed at an insufficient rate and removed from the surface together with the metal atoms which are being ionized. This is shown by the curves in Figs. 2, 3, 4, and 7. The schematic representation

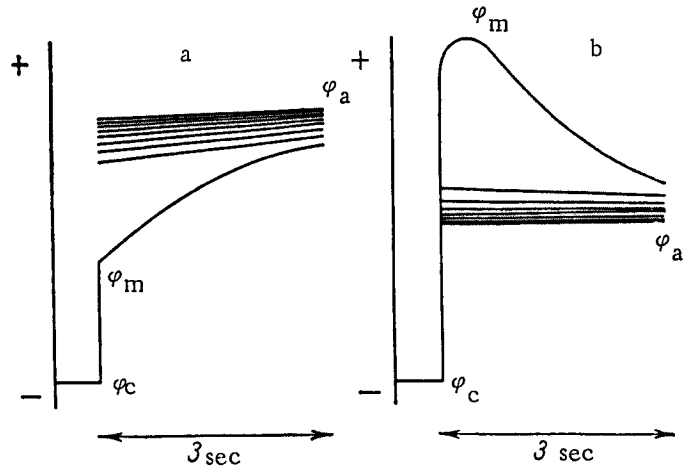

Fig. 7. Oscillograms of $\varphi = f(t)$ for iron at high anodic current densities.

of the oscillogram corresponding to this case is shown in Fig. 7b. The maximum value of the anode potential φ_M, which is rapidly stabilized when the current is turned on, corresponds to the maximum adsorption of the inhibitor. Then, because of the decrease of the surface concentration of the inhibitor the potential drops to the value φ_a corresponding to the potential under steady conditions for the given i_a. The anodic polarization curves $\varphi_M = f(\log i_a)$ obtained in this manner are shown by the dashed lines in Fig. 4.

DISCUSSION OF RESULTS

The increase in the adsorption of inhibitors and the intensification of their inhibiting action on the corrosion of iron under the effect of chemisorbed halogene anions was explained earlier [2, 12]. The effect is similar in the case of a cobalt electrode.

The accelerating effect of H_2S on the electrochemical reactions was explained in [8] by the creation of negative ψ_1-potential induced by the adsorption of HS^- ions. This explanation is inadequate. The hypothesis concerning the catalytic mechanism [13] consisting in the formation of FeS on the surface and its decomposition in acid solutions with regeneration of H_2S is also unsatisfactory. It is difficult to imagine the simultaneous formation and destruction of FeS on the surface.

Since H_2S forms chemisorbed layers close to monomolecular layers on iron [14], our explanation of its action by the formation of a surface catalyst is similar to the explanation of the accelerating action of OH^- ions on the anodic process [15-18]. We do not know the structure of this catalyst, but since the H_2S favors the adsorption of organic compounds we may assume that H_2S forms compounds of the ionic or dipole types on the surfaces of iron and cobalt and that the negative end of this dipole is toward the solution. For example, for iron we have

$$Fe + H_2S + H_2O \rightleftarrows (FeHS^-)_S + H_3O^+ \tag{1}$$

and the concentration of the catalyst is

$$[FeHS^-]_S = k' \frac{[H_2S]}{[H_3O^+]} \tag{2}$$

The anodic process is determined by the rate of the electrochemical reaction

$$(FeHS^-)_S \rightarrow FeHS^+ + 2e \tag{3}$$

The positive iron hydrosulfide ion formed as the result is hydrolyzed by the reaction

$$FeHS^+ + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O \tag{4}$$

The rate of reaction (3), taking (2) into account, is

$$i_a = k \frac{[H_2S]}{[H_3O^+]} \exp\left\{\frac{2\beta\varphi_a F}{RT}\right\} \tag{5}$$

$$\varphi_a = a_2 + \frac{RT}{2\beta F} \ln i_a - \frac{RT}{2\beta F} \ln [H_2S] + \frac{RT}{2\beta F} \ln [H_3O^+].$$

A similar mechanism can be assumed for the cobalt electrode.

Equations (2) and (6) correctly express the general tendency of the anode potential to increase and the tendency of the stimulating action of H_2S to decrease with increasing concentrations of the acid. Thus, according to the oscillograms of the type shown in Fig. 7 for Co in H_2SO_4 + 0.001 N H_2S at i = 10^{-2} A/cm^2 we have $\partial\varphi_M/\partial pH = -0.045$ V and for Fe in 0.1 N H_2SO_4 we have $\partial\varphi_M/\partial \log[H_2S] = -0.045$ V, while in 1 N H_2SO_4 solution it is equal to −0.020 V.

However, according to Eq. (6) the reaction must be a first-order reaction with respect to H_2S, so that $\partial\varphi_M/\partial \log[H_2S] = \partial\varphi_M\ \partial \log i_a$. From the polarization curves of Fe in 0.1 N H_2SO_4 we have $\partial\varphi_M/\varphi \log[H_2S] = -0.045$ V and $\partial\varphi/\partial \log i_a = 0.060$ V, i.e., the first coefficient is somewhat smaller than the second. For the cobalt electrode the first coefficient is also smaller than the second. From the experimental results we find that the order of the reaction $z = \partial \log i_a/\partial \log[H_2S] = 0.7$, i.e., is somewhat smaller than unity. This deviation from the requirement of Eq. (6) may be due to the fact that we have, in fact, never reached the adsorptional equilibrium at φ_M required by Eq. (2) in recording the $\varphi = f(t)$ oscillograms. Another cause may be the nonuniformity of the surface on which HS^- ions are adsorbed.

CONCLUSIONS

We studied the simultaneous effects of organic compounds—inhibitors—and some anions on the corrosion of iron and cobalt in sulfuric acid solutions by drawing polarization curves, differential capacitance curves, and by measuring the corrosion rate.

We have shown that halogene ions slow down the discharge of hydrogen ions on cobalt and iron and the ionization of the metal, and intensify the adsorption of inhibitors, which leads to additional slowing down of these reactions.

It was shown that H_2S and some sulfoacids, which in themselves are stimulators of corrosion, considerably increase the adsorption of inhibitors of the cation type and increase their inhibiting action on the corrosion of iron and cobalt.

We investigated the causes of the deformation of anodic polarization curves in the presence of inhibitors and stimulators of corrosion.

It is assumed that the acceleration of the anodic reaction of the ionization of iron and cobalt in the presence of H_2S is due to the formation of a surface catalyst out of chemisorbed HS^- ions and metal atoms.

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