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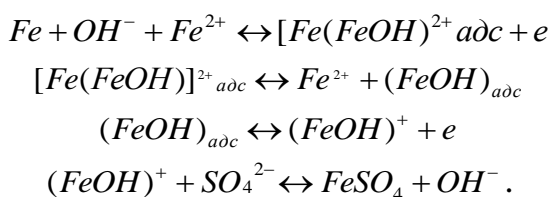
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## **Influence of Fe<sup>2+</sup> ions on protective action mechanism of acid corrosion inhibitors**

At etching process, including closed cycles, inhibitors are used to protect metals from corrosion. The given inhibitors (C-5 (mixed of stillage residue after coke gas purification and mixed of heavy pyridine bases), KH-I (polybenzylpyridinibchloride), TM (thiourea)) belong to surface-active agents, and are able to absorb on metal surface. Inhibitor absorption causes the changing both single reaction, which is the basis for corrosion process, and surface condition particularly, the active surface value.

The Ferrous ions presence in etching solution of closed cycles effects greatly on cathode and anode stage kinetics of corrosion process. This condition has to be taken into consideration when studying the action mechanism of acid corrosion inhibitors. Thus, the influence of cathode inhibitors in this case can occur by means of interaction between H<sub>3</sub>O<sup>+</sup> ions reduction reaction, and also sedimentation process of ferrous iron ions, as well as iron ionization process behavior in cathode area<sup>1</sup>. Our investigations show that ferrous ions also take part in anode steel dissolution process on kinetics scheme<sup>2</sup>:



In [3] kinetic equations for current density of general kind are obtained

$$I_k = b_0 [H] b_1 [Fe] b_2 \exp(b_3 / T) ,$$

order;  $b_3$  – temperature coefficient. The value of kinetic parameters  $b_0$ ,  $b_1$ ,  $b_2$ ,  $b_3$  depends upon steel grade.

Thus, cathode process speed, despite other factors, is defined by the reaction of ferrous iron ion electrodeposition.

Therefore, the inhibitor efficiency changing or even changing of its mechanism of action is possible as a result of competitive adsorption.

The quantitative characteristic of inhibitor efficiency is expressed by inhibition coefficient  $\gamma$  or protective degree  $z$ . By Antropov<sup>4</sup> the inhibition coefficient of corrosion rate can be calculated by the product of four multipliers – single inhibition coefficient

$$\gamma = \gamma_1 \gamma_2 \gamma_3 \gamma_4 \quad (1)$$

Single coefficient  $\gamma_1$  and  $\gamma_2$  is called kinetic inhibition coefficient,  $\gamma_3$  – blocking inhibition coefficient, and  $\gamma_4$  – absorption or bilayer inhibition coefficient.

Kinetic inhibition coefficient enacts only at low inhibitor concentrations, i.e. in the region of small filled surface, when exchange currents changes greatly with filling growth due to exception of the most active centers, forcing accelerator and etc. With surface concentration growth of inhibitor  $\gamma_4$  plays higher role and, at relatively small values  $\Delta\phi_1$ , can 10 times or higher exceed values  $\gamma_1$  и  $\gamma_2$ . At the highest filling  $\gamma_3$  plays the highest role<sup>4</sup>. We can suppose, that in the investigated inhibitor concentration interval at initial approximation the shadow and  $\phi_1$  effect will have the highest value.

Basically the relation between inhibitor absorption and inhibition grade of metal acid corrosion is established due to function relation between inhibition coefficient (or protection grade) and  $\theta$  surface filling grade<sup>5</sup>. The  $\theta$  definition when the metal undergoes corrosion, has loose characteristic and refers to methodology difficulties. In<sup>6</sup> tries to define the inhibition mechanism and metal surface inhomogeneity character using the interdependence of  $\gamma$  or  $z$  and bulk concentration of inhibitor  $C$ .

a) uniform surface

$$\lg(\gamma - 1) = \lg b + \lg c, \quad (2)$$

b) evenly nonuniform surface

$$z = a_1 + 1/f \ln c, \quad (3)$$

c) exponent nonuniform surface

$$\lg z = \lg b + n_1 \lg c_1. \quad (4)$$

If only  $\varphi_1$  – effect, then the concentration of inhibitor protective action with its bulk concentration is defines by equations:

a) uniform surface

$$1/\lg \gamma = 1/k' + 1/k' \lg c, \quad (5)$$

b) evenly nonuniform surface

$$\lg \gamma = k' + (k_1' / f) \lg c, \quad (6)$$

c) exponent nonuniform surface

$$\lg \lg \gamma = \lg k_1' b + n_1 \lg c. \quad (7)$$

If to suppose that ferrous ions in etching solution does not effect on the inhibitor efficiency, than the inhibitor action mechanism in acid, containing ferrous iron sulphate, has to be the same as in the pure acid.

Transferring the obtained  $\gamma$  values in equation coordinates (2 – 7), we can define the inhibitor mechanism of action and metal surface character as absorbent.

Let show, for example, the action mechanism of KI-I inhibitor in pure sulphuric acid and in sulphuric acid, containing ferrous ion. For 20 %  $H_2SO_4$  experimental values lies on line in coordinates  $\lg \lg \gamma - \lg c$ , which shows the fulfillment of equation (7) (fig. 1). In coordinates of other equations these values does not give linear dependence. It shows that  $\varphi_1$  – action mechanism of KI-I inhibitor and absorption in accordance with Freundlich isotherm for exponent nonuniform surface.

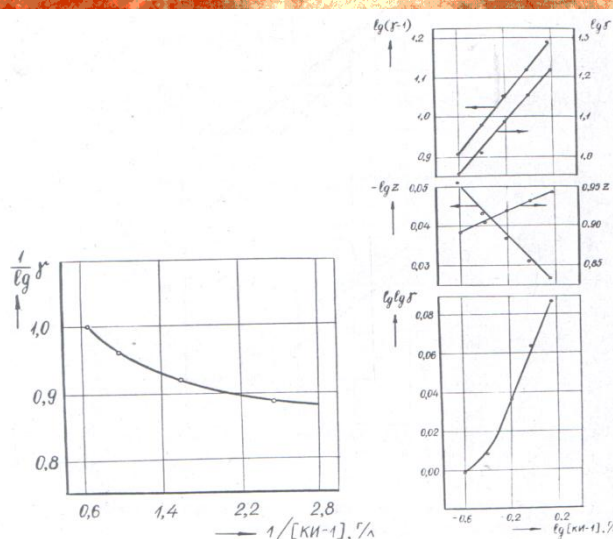


Fig. 1 Graphic interpretation of KI – I inhibitor action for performing equation (2 – 7); 20 % H<sub>2</sub>SO<sub>4</sub>, 80 °C, steel 10 кп

For sulphuric acid, containing ferrous iron (240 g/l H<sub>2</sub>SO<sub>4</sub> + 90 g/l FeSO<sub>4</sub>) (fig. 2), correspondent graphical construction shows, that linear dependence can be in all above mentioned cases, except the dependence  $\lg \lg \gamma - \lg c$  and  $1/\lg \gamma - \lg c$ .

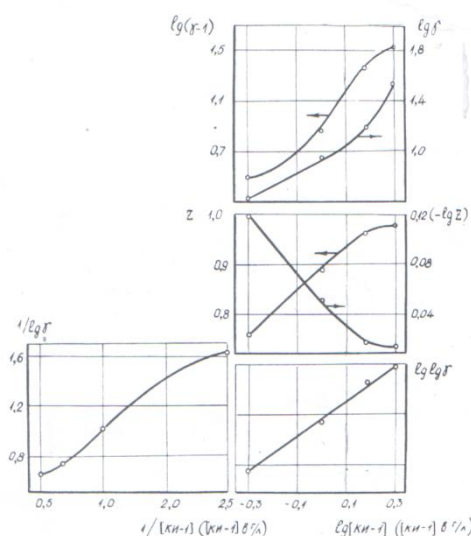


Fig. 2. Graphic interpretation of KI-1 inhibitor action for performing equation (2 – 7); 240 g/l H<sub>2</sub>SO<sub>4</sub> and 90 g/l FeSO<sub>4</sub>; 80 °C, steel 10 кп

Experimental values can be characterized by equation (2) and equation (6), i.e. the same results can be explained by both blocking inhibiting mechanism on uniform surface and  $\phi_1$  – mechanism on nonuniform surface.

containing surface-active cations and anions (fig. 3): linear dependence obtained in coordinates  $\lg \gamma - \lg c$  and  $\lg(\gamma - 1) - \lg c$ , assuming different mechanisms.

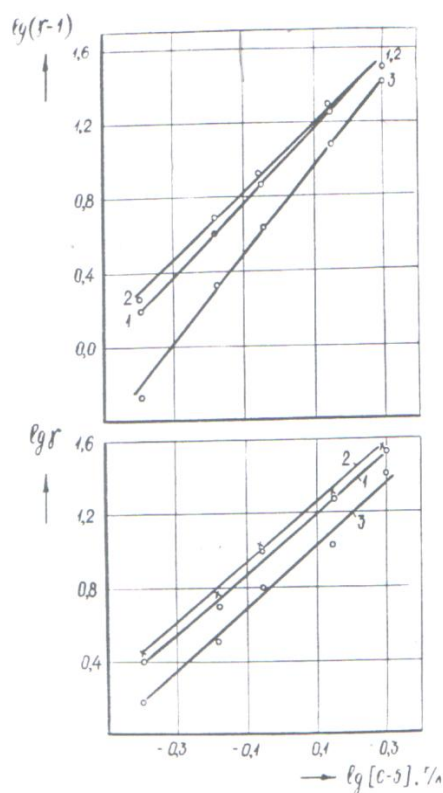


Fig. 3 Graphic interpretation of C – 5 inhibitor action for performing equation (2) and (6); 240 g/l  $H_2SO_4$  and 90 g/l  $FeSO_4$ ; 80 °C, 1 – steel 10 кп; 2 – steel 45; 3 – steel A12

Thus, define the inhibitor mechanism using the method provided in<sup>5</sup> in acid containing ferrous ions is impossible.

It should be noted that in the analyzed papers concerning the acid corrosion inhibitor efficiency of different type and on different metals in pure acids depending upon bulk concentration, explained by Reshetnikov<sup>6</sup>, in most cases the interpretation of experimental values in accordance with one of equations (2 – 7).

Therefore, the difficulties, which arise at interaction of absorption and inhibition of steel acid corrosion in acid, containing ferrous ions, shows the presence of some complicating factor, which, as per our decision, can be the parallel process of ferrous ions electrodeposition, and  $Fe^{2+}$  participation in anode

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