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Some aspects of the mechanism of steel protection in mineral acid solutions by propargyl alcohol and propargyl chloride[†]

Ya.G. Avdeev[1]* and K.L. Anfilov[2]

[1]A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
[2]Bauman Moscow State Technical University (Kaluga Branch), Bazhenov str. 2, 248000 Kaluga, Russian Federation
**E-mail: avdeevavdeev@mail.ru*

Abstract

The specific features of iron corrosion in HCl, H_2SO_4 and H_3PO_4 solutions with addition of propargyl alcohol (PA), propargyl chloride (PC) and products of their reduction on iron in the corrosive system, namely, allyl alcohol (AA) and allyl chloride (AC), were studied by voltammetry. PA and PC have the strongest inhibitory effect on the cathodic and anodic reactions of iron in HCl solutions, while PC has such an effect in H_2SO_4 solutions as well, among the unsaturated compounds (UC) studied since these compounds form protective films of organic polymers on the metal surface. AA and AC slow down the electrode reactions of iron in HCl, H_2SO_4 and H_3PO_4 solutions much more weakly. It has been shown that the presence of adsorbed atomic hydrogen on its surface often enhances the inhibitory effect of the UCs studied on the electrode reactions. The AA and AC compounds studied are cathodically reduced on iron under diffusion control. Analysis of experimental data shows that the conversion of PA and PC to AA and AC on the metal surface in the course of inhibition of the corrosion of iron or steels in acid solutions is an undesirable process. The compounds that are formed slow down the electrode reactions and the corrosion of metals more poorly than the original inhibitors.

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Introduction

Oil and gas containing strata are usually treated with hydrochloric acid to enhance the mining of crude hydrocarbons [1–5], including the case of deposits with elevated temperatures (above 100°C). This operation is not possible without special protection of

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the steel oilfield equipment. The simplest engineering solution of this problem is to use inhibitor-based protection. Unsaturated organic compounds (UC) that primarily include acetylene alcohols are actively used as steel corrosion inhibitors in hydrochloric acid solutions [6–15]. The interest in acetylene alcohols is largely due to the possibility to use them as a base for creating mixed formulations that can protect steel in hydrochloric acid solutions against high-temperature corrosion [6–8]. Multi-component formulations that comprise propargyl alcohol (PA) $HC{\equiv}C{-}CH_2{-}OH$ are traditionally applied for these purposes. A number of PA derivatives with a fairly complex structure have been synthesized [16–20], which can also be used for the protection of steels in acids. Lately, a number of studies were reported that explored some engineering aspects of using PA for the protection of steels in acid environments at oil fields [21–26]. Of special interest is the study by Barmatov *et al.* [26] which examined PA degradation in a corrosive hydrochloric acid environment through hydrolysis.

The application areas of acetylene-based compounds are extending and are not limited to acid solutions. They are recommended for the protection of ferrous and non-ferrous metals in aqueous solutions saturated with CO_2 [27] and H_2S [28], NaCl solutions [29, 30], cooling water-based systems [31], and carbonate-bicarbonate solutions [32].

The capability of acetylene-based compounds to inhibit steel corrosion in HCl solutions at high temperatures is primarily due to the unique features of the mechanism of their action that is related to the presence of reactive $C{\equiv}C$ chemical bonds in the structure of these compounds. Experiments have shown that acetylene-based compounds present in acid solutions form protective layers of organic polymers on the surface of steels they contact, which is confirmed by IR spectroscopy [33–36] and Raman spectroscopy data [37]. The products of conversion of acetylenic alcohols [38, 39] and their halo derivatives [40] in corrosive media have been identified and the simplest formulas of these compounds have been determined. It is of importance that acetylenic compounds (for example, 1,4-butynediol [41]) that cannot form protective layers of an organic polymer on steel do not provide satisfactory protection of the metal.

Concurrently with the formation of protective layers on steel surface by acetylenic compounds, their cathodic hydrogenation occurs [41, 42]. The electrochemical reduction of acetylenic compounds on inert metals in acid solutions has been studied in detail [43–47]. PA is reduced on a Pt electrode to propane, propylene, propanol, allyl alcohol (AA) $H_2C{=}CH{-}CH_2{-}OH$, and small amounts of propyne and ethane [45]; on a Pd electrode, to propylene, propane, ethane, AA and traces of ethene and ethyne [46]; while on an Au electrode, to propylene, propine, and AA [47]. The character of PA reduction on steels is not discussed in detail in publications. Work [48] is the only study where the chromatographic method was used to show that on steel 2 in 1 M HCl, PA is reduced to AA and propanol that are found in the solution. In contrast to HCl solutions, the hydrogenation of acetylenic compounds in $HClO_4$, H_2SO_4, and H_3PO_4 solutions dominates over their surface polymerization, which frequently prevents these inhibitors from providing strong protection [42, 49].

Comparison of the electrochemical behavior of acetylenic compounds of various structure (acetylene, PA, 1,4-butynediol) has revealed that their electrochemical hydrogenation is directly related to their capability to form protective layers of an organic polymer on a metal [41]. This experimental observation allows us to determine some key points in the conversion of acetylenic compounds in a corrosive system and extend them to a more general group of corrosion inhibitors, UCs, which also includes α,β-unsaturated aldehydes and azomethines, α-alkenylphenones, chalcones, *etc.* [50]. The reactions of UC in a steel/acid solution corrosive system occur by two main pathways: formation of a protective polymer film on steel and degradation processes that reduce the content of the active substance in the corrosive environment. The degradation of UCs in such a system is determined by the following reactions:

- UC cathodic hydrogenation;
- UC polymerization in the bulk of the corrosive medium;
- UC reaction with acid solution components.

In our opinion, AA formed directly on steel surface is the most important product of PA conversion in a corrosive system. To better understand the specific features of the mechanism of the PA protective effect on corrosion of mild steel in acid solutions, it is reasonable to study the effect of these compounds on the electrode reactions of iron. Concurrently with PA and AA, propargyl chloride (PC) $HC{\equiv}C{-}CH_2{-}Cl$ and a product of its reduction, allyl chloride (AC) $H_2C{=}CH{-}CH_2{-}Cl$, have been studied, which enabled us to confirm the general character of the effect of acetylenic compounds of various composition on the corrosion of steel in acid solutions.

PC was chosen for comparison with PA since their chemical structures are very similar. Along with acetylenic alcohols, halo derivatives of acetylenic compounds are actively studied as inhibitors of steel corrosion in acids [40, 51–55]. In contrast to PA, PC itself provides protection of mild steels not only in HCl solutions but also in H_2SO_4 solutions [49]. PC is known [51] to form protective polymer layers of the inhibitor on a steel surface. The authors of [51] hypothesized that in protecting steels in HCl solutions, PA is converted to PC by the following reaction:

$$HC{\equiv}C{-}CH_2{-}OH + HCl \rightarrow HC{\equiv}C{-}CH_2{-}Cl + H_2O$$

In turn, the PC that is formed in a corrosive medium is involved in the formation of a protective polymer layer of the inhibitor on the steel surface. It should be noted that this mechanism of PA conversion is not very likely since the same study showed that in an HCl solution that contains PA, a layer of organic polymer that does not contain Cl atoms is created on steel. In contrast, in an HCl solution that contains PC or a PC+PA mixture, polymeric products containing Cl atoms are formed on steel.

In analyzing the features of the electrochemical behavior of AA [56–59] and its halo derivatives [60] on various metals in acid solutions, it was noted that they are prone to cathodic hydrogenation. In view of this, for reach a better understanding of the role of AA and AC in the inhibition of steel corrosion in acid solutions by acetylenic compounds, their capacity to undergo reduction on steels should be explored.

Experimental

Electrochemical measurements were performed on a rotating disk electrode ($n = 460$ rpm) made of annealed ARMCO Pure Iron (composition, mass%: up to 0.025 C; 0.05 Si; 0.035 Mn; 0.015 P; 0.025 S; 0.05 Cu; remainder Fe) in 1 M HCl, H_2SO_4 and H_3PO_4 deaerated with hydrogen at 25°C. The concentration of PA, AA, PC and AC was 30 mmol/L. Due to the limited solubility in water, PC and AC were added as solutions in ethanol ($C_{\text{ethanol}} = 1.2$ mol/L). The electrode was cleaned with M20 micron sandpaper and degreased with acetone. Acids of "chemically pure" grade as well as PA and AA of "pure" grade were additionally purified by distillation prior to use. PC was synthesized by the reaction of PA with PCl_3 in pyridine medium.[‡] AC was obtained by the reaction of AA with concentrated HCl in the presence of $ZnCl_2$.[¶] The solutions were prepared using distilled water.

Current-voltage curves (CVC) were recorded using a P-5827M potentiostat in potentiodynamic mode at a potential sweep rate of 0.5 mV/s. At the beginning of the experiment, the electrode was dissolved for 30 min at a potential of $E = -0.080$ V (HCl) or -0.140 V (H_2SO_4 and H_3PO_4) in order to remove the hardened hydrogenated iron layer. At this stage, the anodic current density reached $i_a \sim 100$ A/m^2. The anodic curve was recorded starting from this potential E (Figure 1a, curve 1) by decreasing the E of the electrode to the value where the current density became equal to 0 (no-current potential, $E_{\text{i}} = 0$). The cathodic curve of iron (Figure 1a, curve 2) was recorded from $E_{\text{i}} = 0$ by continuing to decrease the electrode potential until the cathodic current density reached $i_c = 100$ A/m^2. After curve 2 was recorded, the direction of iron electrode polarization was reversed. A repeated cathodic curve was recorded from the electrode potential where i_c=100 A/m^2 (Figure 1a, curve 3) by increasing its value to $E_{\text{i}} = 0$. The repeated anodic curve (Figure 1a, curve 4) was recorded by increasing the potential of the iron electrode from $E_{\text{i}} = 0$ further to the value where $i_a = 450$ A/m^2. Thus, curves 1 and 2 were obtained on an iron electrode by lowering its E from a value of -0.080 or -0.140 V to the value where $i_c = 100$ A/m^2. In contrast, repeated curves 3 and 4 were successively obtained by increasing the E of iron from the value where $i_c = 100$ A/m^2 to the value where $i_a = 450$ A/m^2. This technique for performing voltammetric measurements on an iron electrode makes it possible to obtain the most comprehensive information about the electrode reactions that occur on it and on how they are affected by the sorption of atomic hydrogen, which is released on the metal surface in the course of the cathodic reaction, by the metal [61]. Atomic hydrogen sorbed

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[‡] N.I. Podobaev, V.E. Novikov and A.G. Voskresensky, Synthesis of halogenated derivatives of the $HC{\equiv}C{-}CH_2Hal$ type and their study as corrosion inhibitors of steel in hydrochloric acid, in *Uchenyye zapiski no. 340 (Scientific notes No. 340)*, Moscow, MGPI im. V.I. Lenina, 1971, 32–46 (in Russian).

[¶] Weigand-Hilgetag, *Experimental methods in organic chemistry*, Moscow, Khimiya, 1968, 205 (in Russian). Translated from *Organisch-Chemische Experimentierkunst*, Leipzig, 1964.

by iron exists in two forms that are in equilibrium, namely, adsorbed hydrogen present on the metal surface and absorbed hydrogen located in the metal bulk. It is known that the adsorbed form of atomic hydrogen is capable of inhibiting the electrode reactions on iron. In acid solutions above a certain potential called the activation potential (E_{act}), iron is freed from adsorbed and absorbed hydrogen, and this favors an acceleration of the anodic reaction [62]. In the course of prolonged iron polarization (30 min) at $E = –0.080$ V (HCl) or –0.140 V (H_2SO_4 and H_3PO_4), which is more positive than E_{act}, the metal is freed from the sorbed hydrogen and the anodic reaction on it occurs on the surface free of adsorbed hydrogen. The subsequent decrease in the electrode potential makes it possible to study the anodic and cathodic electrode reactions on the metal with a minimum amount of sorbed hydrogen (we will tentatively assume that such iron does not contain adsorbed or absorbed hydrogen). Decreasing the E of iron electrode to values where $i_c = 100$ A/m^2 results in a significant increase in the amount of adsorbed hydrogen on its surface and dissolved hydrogen in the metal bulk. In view of this, the subsequent cathodic and anodic polarization curves recorded by increasing the potential were obtained on the metal surface where the content of adsorbed hydrogen was significant. When the repeated anodic CVC was recorded (curve 4), after reaching E_{act}, electrode activation occurred. It contained a non-polarizable region on the anodic curve, which was associated with iron freeing from sorbed hydrogen. Thus, the anodic and cathodic CVCs initially recorded by decreasing the potential were obtained at a lower content of adsorbed and absorbed hydrogen on the metal than the CVCs obtained by increasing the potential of iron.

A similar sequence of polarization measurements made it possible to reveal the effect of cathodic polarization on the polymerization of inhibitors and hydrogen sorption by iron on the anodic process. The inhibitors were added to the solution without depressurization of the cell at the electrode anodic dissolution potential, $E = –0.080$ V (HCl) or –0.140 V (H_2SO_4 and H_3PO_4), after the electrode was dissolved for 30 min. The change in the anodic current to its stationary value was followed, but for no longer than 5 min, which made it possible to judge on the inhibitor adsorption on iron containing a minimum concentration of sorbed hydrogen. Further, CVCs were recorded in the same sequence as in the background solutions.

The dependence of the cathodic current at E = –0.300 V on the electrode rotation speed (0, 460, 780, 1400 rpm) in inhibited solutions was studied. The effect of organic compounds (OC) on the electrode reactions of iron was determined from the coefficient of inhibition of the electrode reaction:

$$\gamma = i_0 / i_{in}$$

where i_0 and i_{in} are the current densities in the background solution and in the solution with an additive being studied. To determine the partial contribution of OC and hydrogen adsorbed by iron to the inhibition of the cathodic and anodic reactions, we calculated the degree of inhibition of electrode reactions by OC (Z_{OC}), by adsorbed hydrogen and OC (Z_{OC+hyd}), and by adsorbed hydrogen (Z_{hyd}):

$$Z_{OC} = \left[\left(i_0 - i_{OC}\right)/i_0\right] \cdot 100\%$$

$$Z_{OC+hyd} = \left[\left(i_0 - i_{OC+hyd}\right)/i_0\right] \cdot 100\%$$

$$Z_{hyd} = Z_{OC+hyd} - Z_{OC}$$

where i_{OC} and i_{OC+hyd} are the current densities on iron electrode in 1 M HCl defined by the adsorption of OC on the metal surface that does or does not contain adsorbed hydrogen.

All potentials of the iron electrode are given in the hydrogen scale. The corrosion rate of steel 3 (composition, mass%: 0.14–0.22 C; 0.15–0.33 Si; 0.40–0.65 Mn; up to 0.3 Cr; up to 0.30 Ni; up to 0.008 N; up to 0.30 Cu; up to 0.05 S; up to 0.04 P; up to 0.08 As; remainder Fe) in 2 M HCl, H_2SO_4 and H_3PO_4 at 25°C was determined from the mass loss of samples (at least three samples per point) measuring 50×20×3 mm. The amount of the acid solution was 50 ml per sample. Before an experiment, samples were cleaned on an abrasive wheel (ISO 9001, grit 60) and degreased with acetone. The duration of the experiments was 4 h. The efficiency of inhibitors was estimated by the inhibition coefficient:

$$\gamma = k_0/k_{in}$$

where k_0 and k_{in} are the corrosion rates in the background solution and in the solution with the additive being studied.

The article presents the results of studying the effect of UC on the electrode reactions on iron and on the corrosion of steels at 25°C. According to the experience of our experimental studies, this approach is most justified, since the process of UC conversion in a corrosive medium is hindered at this temperature.

Results and Discussion

Electrochemical studies

Hydrochloric acid

In 1 M HCl (Table 1, Figure 1), the shape of the anodic CVC of ARMCO Pure iron obtained after its activation at $E = -0.080$ V is characterized by one linear section with a slope of $b_a = 0.080$ V, which is close to the value predicted by theory and observed for annealed iron (Ferrovac-E 99.91% pure), *i.e.*, $b_a = 0.070$ V [63]. The cathodic CVC obtained by decreasing E has a slope of $b_c = 0.120$ V, which is in good agreement with the value predicted by theory for HCl solutions [63]. The cathodic CVC obtained by increasing the potential of iron electrode is characterized by the same b_c value, but the observed cathodic current densities (i_c) are smaller due to the covering of the metal surface with adsorbed hydrogen. In this case, hydrogen adsorbed on iron behaves somewhat like an inhibitor of the cathodic reaction. The anodic CVC obtained by increasing E of the metal consists of two sections. The first one ($b_a = 0.080$ V) at E more negative than

$E_{act} = –0.170$ V corresponds to the anodic ionization of iron on a surface containing adsorbed hydrogen. The inhibitory effect of adsorbed hydrogen is observed here, too. The anodic currents are significantly smaller than those observed on iron which contains the minimum amount of adsorbed hydrogen at the same potentials. On reaching E_{act}, a second linear section is observed, which is characterized by a smaller b_a value than the first one. In this section, the surface of iron is being freed from adsorbed hydrogen that slows down the metal ionization. As a result, a significant acceleration of the anodic reaction is observed. At E about 0.080 V, the anodic currents on the CVC obtained by decreasing and increasing the electrode potential become comparable, which indicates that iron is free from sorbed hydrogen. It is significant that the observed value of the zero-current potential $E_i = 0$ of iron obtained on the metal whose surface contains adsorbed hydrogen is higher than that on the surface free from it. This indicates that the inhibitory effect of hydrogen adsorbed by iron is stronger if anodic ionization of iron rather than proton reduction is hindered. In this case, the inhibition of cathodic ($E = –0.350$ V and especially anodic ($E = –0.150$ V) reactions is significant and amounts to 1.5 and 7.2 times, respectively.

Table 1. Zero-current and activation potentials $E_{i=0}$ and E_{act} of ARMCO Pure Iron in 1 M HCl, Tafel slopes b_c and b_a, cathodic and anodic current densities i_c and i_a, and inhibition factors for the cathodic and anodic reactions γ_c and γ_a at $E = –0.350$ and $–0.150$ V, respectively ($n = 460$ rpm, $t = 25$°C).

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
1 M HCl								
Decreasing *E*	–0.270	–	0.120	0.080	10	–	21	–
Increasing *E*	–0.240	–0.170	0.120	0.080	6.5	–	2.9	–
1 M HCl + 30 mM PA								
Decreasing *E*	–0.220	–0.120	0.170	0.170	2.7	3.7	1.2	18
Increasing *E*	–0.250	–0.080	0.170	0.220	2.0	3.3	1.1	2.6
1 M HCl + 30 mM AA								
Decreasing *E*	–0.270	–	0.120	0.080	4.0	2.5	14	1.5
Increasing *E*	–0.270	–0.130	0.120	0.180	2.3	2.8	1.7	1.7
1 M HCl + 1.2 M ethanol								
Decreasing *E*	–0.265	–0.110	0.120	0.080	9.7	1.0	12	1.8
Increasing *E*	–0.240	–0.170	0.120	0.080	6.3	1.0	2.9	1.0

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
1 M HCl + 1.2 M ethanol + 30 mM PC								
Decreasing *E*	–0.195	–0.100	0.200	0.125	3.8	2.6	0.55	38
Increasing *E*	–0.205	–0.110	0.200	0.200	2.9	2.2	0.60	4.8
1 M HCl + 1.2 M ethanol + 30 mM AC								
Decreasing *E*	–0.270	–0.100	0.120	0.080	8.7	1,1	8.2	2.6
Increasing *E*	–0.260	–0.140	0.120	0.130	4.8	1.4	2.3	1.3

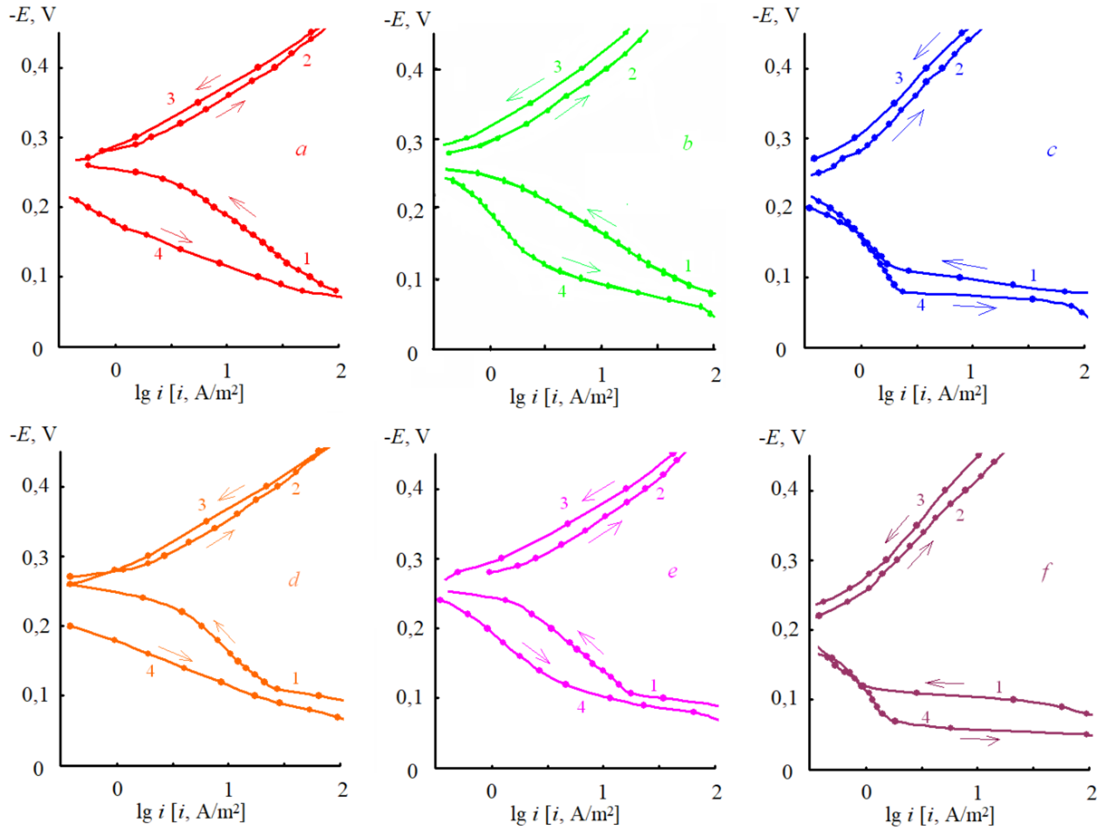

Figure 1. Current–voltage curves of ARMCO Pure Iron in 1 M HCl without (*a*) and in the presence of 30 mM AA (*b*); 30 mM PA (*c*); 1.2 M ethanol (*d*); 1.2 M ethanol + 30 mM AC (*e*); 1.2 M ethanol + 30 mM PC (*f*). Curves *1*, *2* - decreasing potential; *3*, *4* - increasing potential. The directions of polarization of the iron electrode are indicated by arrows.

Individual ethanol, which is used as a solvent to introduce PC and AC insoluble in aqueous media does not exert a significant effect on the electrode reaction of steel in HCl solutions.

The presence of 30 mM PA in the corrosive medium changes the shape of the CVC on iron significantly. The anodic CVC obtained by decreasing E contains two linear sections. The first one with a low b_a slope results from PA adsorption on the iron surface with a minor amount of adsorbed hydrogen. Inhibitor adsorption leads to a rapid decrease in the anodic current. After completion of PA adsorption on iron, a process is established that is characterized by the second linear section with $b_a = 0.170$ V. In this section, the anodic ionization of iron occurs on the metal surface inhibited by a protective PA layer with a minimum hydrogen content. The fact that the Tafel slope of the anodic reaction is high and significantly exceeds its value in the background solution is in favor of the formation of a protective layer of inhibitor molecules. The cathodic CVC recorded by decreasing and increasing the iron potential are also characterized by a high slope, $b_c = 0.170$ V. Such a high polarization Tafel slope also indicates that the cathodic reaction occurs on iron surface coated with a protective inhibitor layer. The anodic CVC obtained by increasing E of iron comprises two sections. The linear section adjacent to the zero current potential is characterized by an even greater Tafel slope. In our opinion, such a slope increase results from the joint inhibitory effect of the protective layer of the inhibitor and adsorbed hydrogen on the anodic reaction. In addition, cathodic polarization of iron coated with PA can stimulate polymerization of the inhibitor in the surface layer [64] that should improve its protective properties. The improvement of the protective efficiency of the surface layer of the organic inhibitor by adsorbed hydrogen present on the surface is also supported by the fact that the value of E_{act} of iron coated with adsorbed hydrogen is by 0.040 V more positive than without it. The phenomenon of anodic activation of steels in inhibited solutions of acids is discussed in publications [65]. The reason of iron anodic activation in HCl solution containing PA is that adsorbed hydrogen is removed from the metal surface and the organic inhibitor is partially desorbed, leading to the development of pit corrosion on the freed metal surface [61, 62]. The $E_i = 0$ value is more positive for the iron surface containing the minimum amount of adsorbed hydrogen than in the background medium, which indicates that the anodic process is hindered predominantly. Cathodic polarization of the electrode decreases $E_i = 0$ to a value close to the background values. The inhibitor layer formed on iron surface under these conditions slows down both electrode reactions on the metal to an equal extent. Addition of PA significantly decreases the cathodic and anodic polarization currents. Moreover, they are lower on iron surface containing adsorbed hydrogen.

Addition of PC affects the electrode reactions of steel in qualitatively the same way as the PA addition, *i.e.*, the reactions slow down considerably. This inhibitor primarily slows down the anodic reaction of metal by shifting $E_{i=0}$ to higher potentials. In comparison with PA, it inhibits the anodic reaction of steel more significantly. In its presence, the Tafel slopes b_a and especially b_c are significantly larger than in the background medium. This is indicative of the formation of a protective layer on iron by this compound. Most probably, its formation is facilitated by the cathodic polarization of the metal.

Addition of AA and AC weakly affects the electrode reactions on iron. In the presence of these inhibitors, the b_c slope matches that in the background medium, while the value of b_a is higher than in the background medium only for the anodic CVCs obtained by increasing E. The result obtained indicates that it is unlikely that AA and AC forms a protective inhibitor film on iron. It is important to note that the protective effect of AA and AC is significantly enhanced in the presence of adsorbed hydrogen on iron surface.

It seems important to give a qualitative estimate of the contribution of hydrogen adsorbed by the metal, organic inhibitor, and their combination on the effect on the electrode reactions on iron (Table 2). It can be seen that in background 1 M HCl itself, the effect of adsorbed hydrogen on the cathodic and, especially, anodic reactions on iron is significant. Its effect is the weakest in the case of PA and PC. In the case of AA and AC, it is more significant and observed for both electrode reactions.

Table 2. The degree of inhibition of the cathodic (–0.350 V) and anodic (–0.150 V) reactions of ARMCO Pure Iron in 1 M HCl by OC (Z_{OC}), adsorbed hydrogen (Z_{hyd}), adsorbed hydrogen and OC (Z_{OC+hyd}). t = 25°C.

***E*, V**	–0.350	–0.150	–0.350	–0.150	–0.350	–0.150
Inhibitor	–		**30 mM PA**		**30 mM AA**	
Z_{OC}, %	0	0	73.0	94.3	60.0	33.3
Z_{hyd}, %	35.0	86.2	7.0	0.5	17.0	58.6
Z_{OC+hyd}, %	–	–	80.0	94.8	77.0	91.9
Inhibitor	**1.2 M ethanol**		**1.2 M ethanol + 30 mM PC**		**1.2 M ethanol + 30 mM AC**	
Z_{OC}, %	3.0	42.9	62.0	97.4	13.0	61.0
Z_{hyd}, %	34.0	43.3	9.0	–	39.0	28.0
Z_{OC+hyd}, %	37.0	86.2	71.0	97.1	52.0	89.0

The reduction of PA and PC on iron in solutions of mineral acids occurring in diffusion mode was observed previously [42]. Studies on the effect of the convective factor on the cathodic reaction rate of iron in acid solutions containing AA and AC allows us to estimate their tendency to undergo cathodic reduction. It has been found that the dependence of cathodic current density in the presence of the UC being studied on the rotation frequency of an iron disk is described by the Levich equation (Table 3). It is reasonable to assume that in the absence of additional oxidizers in an acid solutions containing AA and AC, the increase in cathodic current with increasing electrode rotation rate results from the reduction of these compounds. The reduction of the UC being studied occurs in diffusion mode and accelerates the cathodic reaction.

Table 3. Constants *c* and *d* in the equation i_c (A/m^2) = $c + dn^{1/2}$ at $E = –0.300$ V in mineral acids inhibited by AA and AC. $t = 25°C$.

Inhibitor	**2 M HCl**		**2 M H_2SO_4**		**2 M H_3PO_4**	
	c	***d***$\cdot 10^2$	***c***	***d***$\cdot 10^2$	***c***	***d***$\cdot 10^2$
30 mM AA	0.6	2.0	9.8	1.1	2.7	1.2
30 mM AC	2.0	0.4	8.0	3.0	2.6	2.6

According to electrochemical studies, PA and PC significantly affect the electrode reactions of iron in HCl solution. In contrast, the effect of AA and AC on the electrode reactions is smaller and differs slightly.

Sulfuric acid

In 1 M H_2SO_4 (Table 4, Figure 2), the shape of the anodic CVC of ARMCO Pure iron obtained after its activation at $E = –0.140$ V features three linear segments. The segment closest to $E_{i=0}$ has the slope $b_a = 0.040$ V, a value typical of sulphate media [63]. In our understanding, this anodic CVC (Figure 2a, curve 1) consists of a segment of anodic iron ionization on the surface free from adsorbed hydrogen. It is followed by a segment of electrode non-polarizability where the anodic current sharply drops due to the emergence of adsorbed hydrogen on iron surface and its accumulation to a certain stationary value. After that, up to $E_{i=0}$, the anodic CVC exhibits a segment characteristic of iron ionization on a surface that contains adsorbed hydrogen. The slope of the cathodic CVC (Figure 2a, curve 2) obtained by decreasing E is $b_c = 0.100$ V, which is close to the values previously observed in these media [63]. As the potential of iron electrode is increased, the cathodic CVC (Figure 2a, curve 3) is characterized by the same b_c value, but no inhibiting effect of the evolved hydrogen on the cathodic process is observed. In contrast, the released hydrogen affects the anodic process significantly (Figure 2a, curve 4). It is inhibited to the extent that $E_{i=0}$ is shifted to the positive region up to E_{act}. The anodic CVC obtained as E of metal is increased consists of two parts. The first part ($b_a \rightarrow 0$) is related to the release of adsorbed hydrogen from the metal and onset of pitting. The second part observed at larger E values is characteristic of anodic ionization of iron on a surface free from adsorbed hydrogen. An unusual effect is observed here: due to the strong inhibition of the anodic reaction by the released hydrogen, no segment associated with the occurrence of this reaction on the surface containing adsorbed hydrogen is observed on the anodic CVC. Some slowdown of the anodic reaction observed on the curve obtained by decreasing E compared to that obtained with increasing it is apparently due to the contamination of the metal surface with sludge formed during the anodic dissolution of the electrode. It is indicative that the observed value of the zero current potential $E_{i=0}$ of iron obtained on a metal whose surface contains adsorbed hydrogen is higher than that obtained on a hydrogen-free surface. This indicates that the inhibitory effect of hydrogen adsorbed by iron manifests itself when the anodic ionization of iron is slowed down. Similar CVCs were obtained by us in 1 M H_2SO_4 + 1.2 M ethanol, the only difference being that the current densities of the anodic and cathodic reactions are slightly smaller.

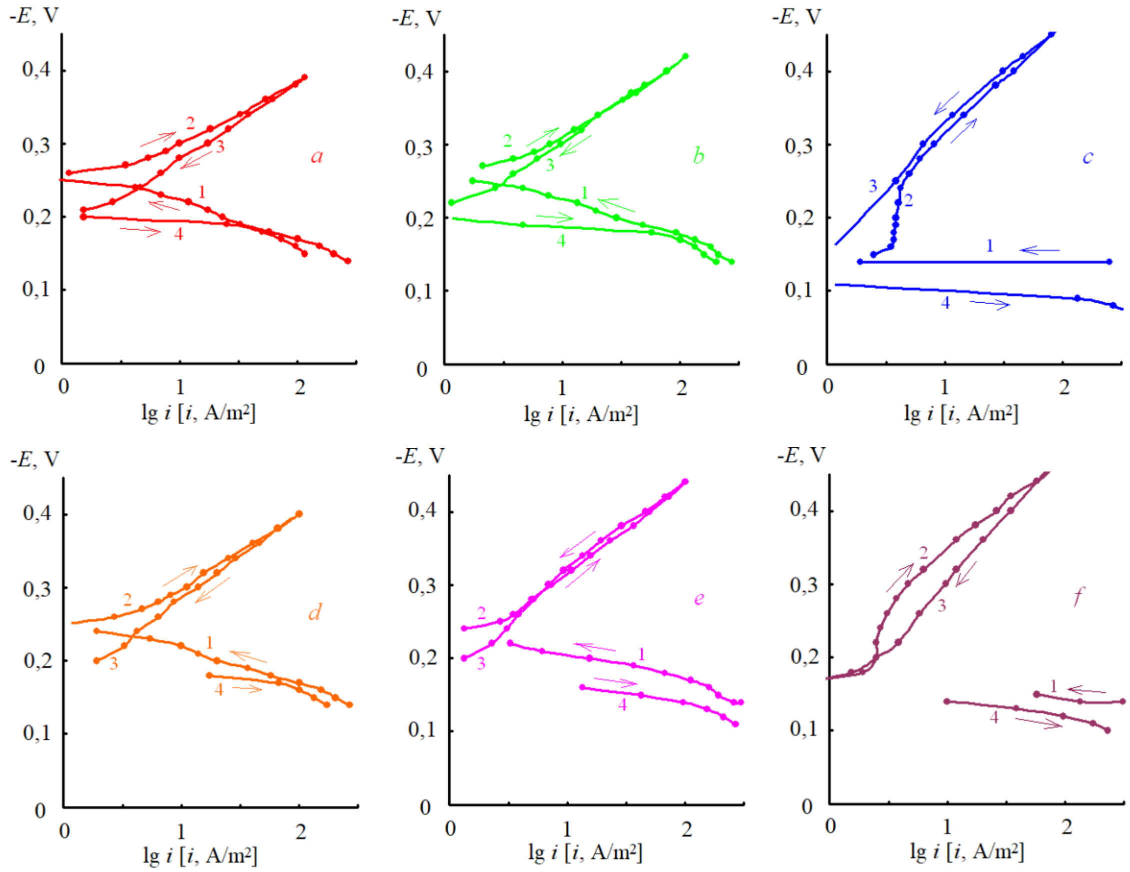

Figure 2. Current-voltage curves of ARMCO Pure Iron in 1 M H_2SO_4 without (*a*) and in the presence of 30 mM AA (*b*); 30 mM PA (*c*); 1.2 M ethanol (*d*); 1.2 M ethanol + 30 mM AC (*e*); 1.2 M ethanol + 30 mM PC (*f*). Curves *1*, *2* – decreasing potential; *3*, *4* – increasing potential. The directions of polarization of the iron electrode are indicated by arrows.

Table 4. Zero-current and activation potentials $E_{i=0}$ and E_{act} of ARMCO Pure Iron in 1 M H_2SO_4, Tafel slopes b_c and b_a, cathodic and anodic current densities i_c and i_a, and inhibition factors for the cathodic and anodic reactions γ_c and γ_a at E = –0.350 and –0.150 V, respectively (n = 460 rpm, t = 25°C).

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
				1 M H_2SO_4				
Decreasing *E*	–0.255	–0.195	0.100	0.040	41	–	210	–
Increasing *E*	–0.200	–0.195	0.100	→ 0**	50	–	180	–

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
1 M H_2SO_4 + 30 mM PA								
Decreasing *E*	–0.145	–0.145	→ ∞*	–	21	2.0	–	–
Increasing *E*	–0.120	–0.120	→ ∞	→ 0	14	3.8	25***	7.2
1 M H_2SO_4 + 30 mM AA								
Decreasing *E*	–0.260	–0.195	0.100	0.040	25	1.6	210	1.0
Increasing *E*	–0.210	–0.195	0.110	→ 0	25	2.0	160	1.1
1 M H_2SO_4 + 1.2 M ethanol								
Decreasing *E*	–0.245	–0.195	0.100	0.040	33	1.2	200	1.1
Increasing *E*	–0.190	–0.190	0.110	→ 0	38	1.3	135	1.3
1 M H_2SO_4 + 1.2 M ethanol + 30 mM PC								
Decreasing *E*	–0.165	–0.165	→ ∞	→ 0	10	4.1	58	3.6
Increasing *E*	–0.150	–0.150	→ ∞	→ 0	17	2.9	18***	10
1 M H_2SO_4 + 1.2 M ethanol + 30 mM AC								
Decreasing *E*	–0.230	–0.175	0.110	0.040	19	2.2	190	1.1
Increasing *E*	–0.180	–0.170	0.120	→ 0	16	3.1	42	4.3

* Limiting diffusion current region.

** Region of anodic non-polarizability of steel electrode.

*** Found by extrapolation of the first linear region of the $E - \lg i_a$ plot to $E = -0.150$ V.

Addition of 30 mM PA to 1 M H_2SO_4 causes a significant drop in the anodic current on anodically polarized steel ($E = -0.140$ V), which is observed for 5 min. A slight decrease in the *E* value of steel leads to a rapid change from an anodic reaction (Figure 2c, curve 1), which occurs on iron, to a cathodic one (Figure 2c, curve 2). After reaching $i_c = 100$ A/m^2 with decreasing *E*, we obtain a cathodic curve (Figure 2c, curve 3) characterized by currents lower than those on cathodic curve 2. Immediately after $E_{i=0}$ of iron, a segment of anodic non-polarizability of the metal follows, which is replaced by an anodic CVC region where iron ionization occurs on a non-poisoned surface (Figure 2c, curve 4). It can be seen that at any direction of iron electrode polarization, its $E_{i=0}$ value shifts up to E_{act}, which may result from the inhibition of the anodic reaction on the metal by the inhibitor with concurrent stimulation of the cathodic reaction [49]. Indeed, PA slows down both electrode reactions on iron, but in the region of cathodic potentials adjacent to $E_{i=0}$, there is a limiting current segment. This limiting current is associated with PA reduction, which accelerates the cathodic reaction and is responsible for shifting the value of $E_{i=0}$ to E_{act}. In addition, the reduction of an unsaturated inhibitor in a corrosive environment is often the reason for its low efficiency in inhibiting steel corrosion. In general, hydrogen absorption by an iron electrode has a positive effect on slowing down the electrode reactions by PA. This is indicated by lower currents on the cathodic CVC obtained by increasing the potential compared to the curve obtained by decreasing it. Also, the value of $E_{i=0}$ observed after cathodic polarization is higher than the value without it. If the cathodic reaction slows down more strongly, this can only be the result of an even stronger inhibition of the anodic reaction. It should be noted that the enhancement of the inhibitory effect of PA on electrode reactions is not only the result of the combined action of the hydrogen adsorbed by the metal and the organic inhibitor, but can also be caused by stimulation of PA polymerization by hydrogen being reduced, which results in the formation of a protective film of the inhibitor. The formation of protective polymer layers by PA on iron surface is indirectly indicated by the high slope of the cathodic CVCs in the regions in the E region below the limiting current.

The qualitative nature of the cathodic and anodic CVCs of iron in the presence of PC is similar to that in the presence of PA. The inhibitory effect of this inhibitor on the electrode reactions of iron is usually stronger than in the case of PA. The limiting current observed in the presence of PC and caused by its reduction is smaller than for PC. It should be noted that the inhibition of the cathodic reaction by PC after cathodic polarization of iron electrode becomes poorer. It may be assumed that this effect results from reduction of PC molecules by released hydrogen to give compounds that are weaker inhibitors. In general, the data of current-voltage measurements make it possible to expect that the inhibition of iron corrosion by PC in H_2SO_4 solutions would be stringer than by PA.

Compared to the corresponding acetylenic inhibitors, the effect of AA and AC on the electrode reactions of iron is less significant. In their presence, the b_c and b_a slopes are close to the values observed in the background medium, indicating the absence of their polymerization on iron to form a protective film. In the presence of both compounds, especially AC, the presence of adsorbed hydrogen on iron surface enhances their effect on the electrode reactions. It should be noted that AA and AC undergo cathodic reduction on iron in 1 M H_2SO_4 that occurs in diffusion mode (Table 3).

Phosphoric acid

The character of iron CVC in 1 M H_3PO_4, both in the background medium and in the presence of the compounds under study, is qualitatively close to that observed in 1 M H_2SO_4 (Figure 3, Table 5). It should be noted that both acetylenic and ethylenic compounds virtually do not slow down the electrode reactions of iron. In addition, in the presence of PC, in contrast to the H_2SO_4 solution, a high value of the limiting cathodic current is observed, that is close to the value observed in the presence of PA. These observations suggest the low efficiency of the UCs under consideration in inhibiting the corrosion of iron in H_3PO_4 solutions. It should be noted that AA and AC undergo cathodic reduction on iron in 1 M H_2SO_4, which occurs in diffusion mode (Table 3).

Table 5. Zero-current and activation potentials $E_{i=0}$ and E_{act} of ARMCO Pure Iron in 1 M H_3PO_4. Tafel slopes b_c and b_a. cathodic and anodic current densities i_c and i_a. and inhibition factors for the cathodic and anodic reactions γ_c and γ_a at E = –0.350 and –0.150 V, respectively (n = 460 rpm. t = 25°C).

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
1 M H_3PO_4								
Decreasing *E*	–0.290	-	0.120	0.040	9.6	–	170	–
Increasing *E*	–0.250	–0.230	0.120	$\to 0$**	7.4	–	170	–
1 M H_3PO_4 + 30 mM PA								
Decreasing *E*	–0.200	–	$\to \infty$*	0.040	6.2	1.5	89	1.9
Increasing *E*	–0.200	-0.175	$\to \infty$	0.060	4.6	1.6	81	1.9
1 M H_3PO_4 + 30 mM AA								
Decreasing *E*	–0.280	–	0.120	0.040	6.8	1.4	170	1.0
Increasing *E*	–0.240	–0.230	0.120	$\to 0$	6.0	1.2	170	1.0
1 M H_3PO_4 + 1.2 M ethanol								
Decreasing *E*	–0.290	–	0.120	0.040	9.5	1.2	130	1.3
Increasing *E*	–0.250	–0.230	0.120	$\to 0$	5.8	1.3	120	1.4
1 M H_3PO_4 + 1.2 M ethanol + 30 mM PC								
Decreasing *E*	–0.210	–0.210	$\to \infty$	0.040	6.7	1.4	100	1.7
Increasing *E*	–0.200	–0.200	$\to \infty$	$\to 0$	6.7	1.1	96	1.8
1 M H_3PO_4 + 1.2 M ethanol + 30 mM AC								
Decreasing *E*	–0.275	–0.175	0.130	0.040	9.6	1.0	110	1.5
Increasing *E*	–0.235	–0.230	0.130	$\to 0$	9.6	0.77	100	1.7

* Limiting diffusion current region. ** Region of anodic non-polarizability of steel electrode.

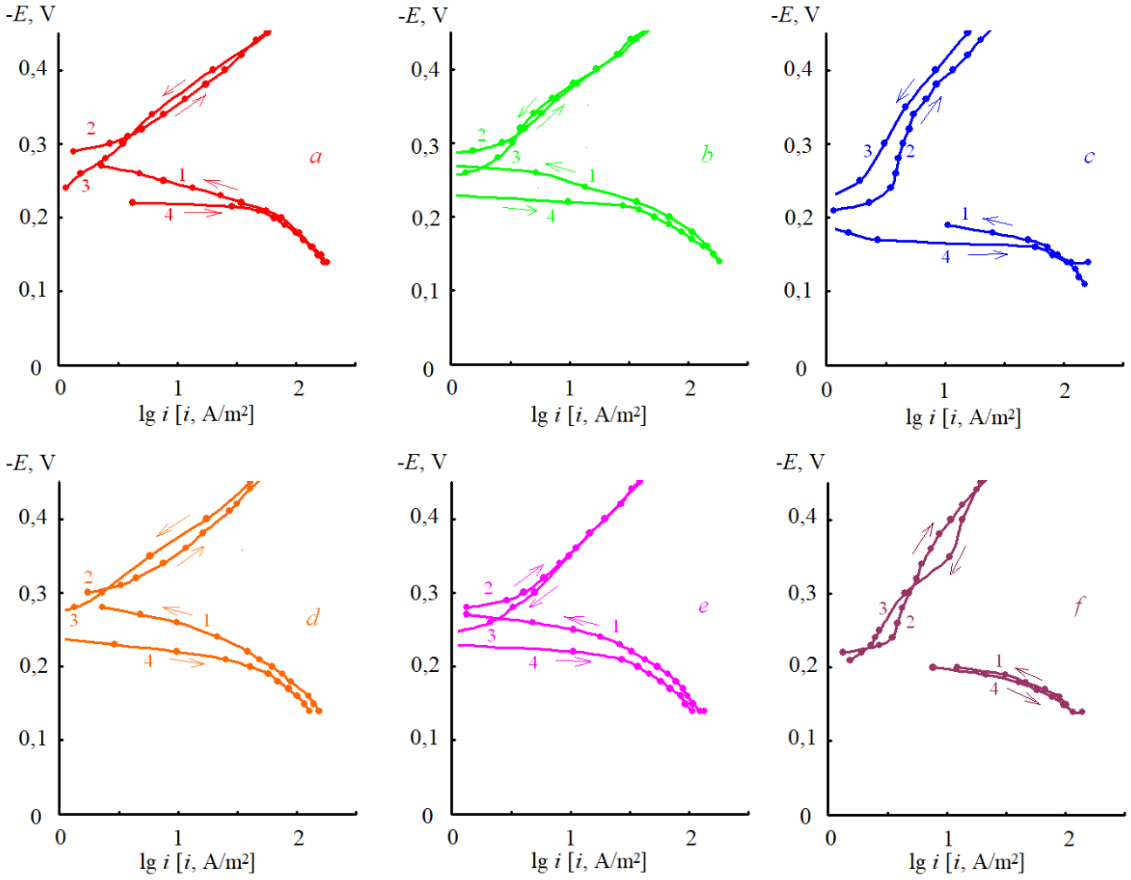

Figure 3. Current-voltage curves of ARMCO Pure Iron in 1 M H_3PO_4 without (*a*) and in the presence of 30 mM AA (*b*); 30 mM PA (*c*); 1.2 M ethanol (*d*); 1.2 M ethanol + 30 mM AC (*e*); 1.2 M ethanol + 30 mM PC (*f*). Curves *1, 2* – decreasing potential; *3, 4* – increasing potential. The directions of polarization of the iron electrode are indicated by arrows.

Corrosion studies

Studies on the corrosion rate of steel in acid solutions containing UC would help verify our conclusions (Table 6). As it could be expected, PC provides the best corrosion inhibition of steel 3 in 2 M HCl. The protective effect of PA is somewhat weaker, while that of AA and AC is the weakest. Among the UCs studied, only PC provides effective protection of steel in 2 M H_2SO_4; in 2 M H_3PO_4, no compounds provide such a protection.

Among the compounds studied, PA and, especially, PC hinder the electrode reactions of iron most strongly due to the formation of a protective film of organic polymer on the metal surface by these compounds. The products of their reduction (AA and AC) are inferior to them in the efficiency of inhibiting the electrode reactions of iron, which is reflected in the weak inhibition of steel corrosion. The electrochemical reduction of PA and PC on iron surface in HCl solutions to give AA and AC is certainly a harmful process in terms of metal protection as it leads to products with poorer protective effects. A similar conclusion should be drawn in the case of iron protection in H_2SO_4 solutions by PC.

Table 6. Corrosion rates (k·g/(m^2·h) of steel 3 and corrosion inhibition coefficients (γ) of unsaturated compounds (30 mM) in mineral acids (t = 25°C).

Inhibitor	**2 M HCl**		**2 M H_2SO_4**		**2 M H_3PO_4**	
	k	**γ**	***k***	**γ**	***k***	**γ**
–	7.0	–	16	–	18	–
PA	0.46	15	6.4	2.5	5.0	3.6
AA	3.5	2.0	4.0	4.0	7.2	2.5
PC	0.14	50	0.18	89	3.8	4.7
AC	1.8	3.9	2.2	7.3	6.9	2.6

A fundamentally different situation is observed in H_2SO_4 and H_3PO_4 solutions inhibited by PA and in solutions of H_3PO_4 inhibited by PC. In these systems, the acetylenic compounds under consideration are rather quickly reduced on iron, forming ethylene compounds that are weak inhibitors, rather than polymerization products that would slow down the corrosion of iron in acid solutions most strongly.

The role of AA and AC formation from PA and PC in the corrosive environment needs clarifying. This process results in products that are inferior to the initial inhibitors in the protective effect. However, at the initial stage of the iron corrosion inhibition process, these compounds formed on the metal surface can slow down its corrosion. Such a process is likely to favor faster adsorption of acetylenic compounds on iron, facilitating the formation of a protective film.

In general, it should be noted that, other conditions being equal, the more hydrophobic PC and AC molecules are more efficient in corrosion inhibition than PA and AA, respectively. The results of the study confirm the pattern established by us previously [49] that acetylenic compounds can only be efficiently used for the protection of steels in HCl solutions. In H_2SO_4 solutions, only acetylenic compounds with hydrophobic molecules, such as PC, provide satisfactory protection. The most challenging system in terms of steel protection is represented by H_3PO_4 solutions [66]. Most likely, in this medium, there is a competitive adsorption of phosphate anions and OC molecules on the steel surface, due to which satisfactory inhibition by such substances is not possible. The results on the protection of steels in H_3PO_4 solution with PA and PC additives confirm these conclusions.

The AA and AS additives, despite the presence of an unsaturated C=C bond in their structure, do not significantly affect the b_c and b_a slopes of iron electrode in all the acid solutions. This indicates the reluctance of these compounds to form protective polymer films, which would provide the most efficient inhibition of electrode reactions and corrosion in general, on the metal surface. On the contrary, these compounds are capable of reduction on iron, which should have a negative effect on their ability to inhibit corrosion.

The study of UC conversion processes in the metal/corrosive medium system is extremely important for understanding the mechanism of their protective action. Without understanding the chemical processes involving UCs that occur in a corrosion system, it is not possible to provide efficient protection of the metal. It should be taken into account that only the processes of polymerization of UC on the metal surface ensure a high efficiency of these compounds in protecting steels in acid environments, even under conditions of high-temperature corrosion ($t > 100°C$) [67]. All other processes of chemical transformation of UCs, including their reduction considered in our study, are undesirable. To ensure efficient protection of a metal with an UC, conditions should be selected where the fraction of these processes is negligible. Unfortunately, when considering the protection of metals with UCs, their chemical transformations in a corrosive environment, including the important process of polymerization on the metal surface, have been completely ignored lately. The high efficiency in the protection of steels in acid solutions with cinnamic aldehyde is known to be due to its polymerization on the metal surface [67–69]. However, in recent works [70, 71], in considering the features of the mechanism of the protective effect of this UC on steel corrosion, this effect was ignored. In this regard, the study by Barmatov and Hughes [72] who explored the hydrolysis of azomethines during the protection of steels in acid solutions is of importance. Accounting for the destruction of this group of inhibitors in a corrosive environment is of importance for understanding the nature of their protective action.

Conclusions

1. The inhibitory effect of PA and PC on the electrode reactions of iron and on the corrosion of steels in acid solutions is determined by the anionic composition of the latter. In the case of PA, efficient inhibition of the electrode reactions of iron and corrosion of steels is only observed in HCl solutions, while for PC, in HCl and H_2SO_4 solutions. The strong inhibitory effects provided by these UCs are explained by the formation of a protective film of an organic polymer on the surface of a corroding metal. In acid environments where a strong protective effect of these UCs is not observed, their cathodic reduction occurs predominantly. The molecules of PC that is more hydrophobic than PA inhibit the corrosion of steels much more strongly.
2. The products of PA and PC reduction, namely ethylenic compounds AA and AC, exhibit a low protective effect in the inhibition of electrode reactions of iron and corrosion of steel in solutions of mineral acids, regardless of their anionic composition. The result obtained indicates a negative effect of the reduction of acetylenic compounds in the corrosive system, since the resulting ethylenic compounds are weaker inhibitors of steel corrosion. In addition, further reduction of ethylenic compounds is possible on the surface of corroding steel in acid solutions.
3. The electrode reactions of iron in acid solutions, including those in the presence of UCs, are shown to be sensitive to the accumulation of adsorbed hydrogen on the metal surface. The accumulation of adsorbed hydrogen on the metal surface often enhances the effect of UC on the electrode reactions.

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