Some aspects of the mechanism of steel protection in hydrochloric acid solutions by propargyl alcohol♣

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Abstract

The specific features of iron corrosion in HCl solutions with addition of propargyl alcohol (PA) and products of its conversion in the corrosive system, namely, acrolein and allyl alcohol (AA), were studied by voltammetry. PA has the strongest inhibitory effect on the cathodic and anodic reactions of iron in acid solutions among the unsaturated compounds (UC) studied since PA forms a protective film of an organic polymer on the metal surface. Acrolein and AA slow down the electrode reactions of iron much more weakly. It has been shown that the presence of adsorbed atomic hydrogen on iron surface enhances the inhibitory effect of the UCs studied on the electrode reactions of iron. The UCs studied are cathodically reduced on iron surface under diffusion control. This result is an experimental confirmation of PA and acrolein to AA conversion on iron surface. The corrosion rate of mild steel calculated from the mass loss of metal samples in HCl solution in the presence of the UCs studied decreases in the series: AA > acrolein > PA, which is consistent with the results of electrochemical studies of these compounds on iron. Analysis of experimental data shows that the conversion of PA by isomerization to acrolein or by reduction to AA on the metal surface in the course of inhibition of the corrosion of iron or steels in HCl solutions is an undesirable process. The compounds formed slow down the electrode reactions and the corrosion of metals more poorly than the original inhibitor. We identified the main pathways of UC conversion in the course of steel corrosion inhibition in acid solutions, namely, the formation of a protective polymer film from an UC on steel and UC degradation processes that diminish the content of the reactive compound in the corrosive environment. The degradation of UCs is determined by reactions of their cathodic hydrogenation, polymerization in the bulk of the corrosive medium, and reactions with components of the acid solution.

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Introduction

Organic unsaturated compounds (UC), including acetylenic compounds, α,β-unsaturated aldehydes and azomethines, α-alkenylphenones, chalcones, *etc*., are extensively studied as steel corrosion inhibitors in mineral acid solutions [1–10]. The interest in these compounds is determined to a considerable extent by the possibility of creating mixed formulations based on them that can protect steels in hydrochloric acid solutions under high-temperature corrosion conditions [1–3]. Formulations of this kind are in demand in the oil and gas industry which urgently needs to intensify the production of hydrocarbons by hydrochloric acid treatment of oil and gas bearing strata [11–15], including those with elevated temperatures. This operation cannot be performed without special measures to protect the steel oilfield equipment. Protection by inhibitors is the simplest technical solution to this problem. Formulations containing propargyl alcohol (PA) are used most commonly for these purposes. In recent years, a number of rather complex UCs have been synthesized, namely, PA derivatives [16, 17] and cinnamic aldehyde (CA) [16, 18–21], that were suggested for the protection of steels in acids. The applications of UCs are expanding and are not limited to acid solutions. They are recommended for the protection of ferrous and nonferrous metals in aqueous solutions saturated with CO_2 [22, 23], in NaCl solutions [24, 25], cooling water systems [26], citrate solutions [27], and carbonate-bicarbonate solutions [28].

The ability of UCs to inhibit the corrosion of steels in HCl solutions under high-temperature conditions is largely due to the unique features of their mechanism of action, which is determined by the presence of reactive C≡C and/or C=C chemical bonds in the structure of these compounds. It has been found experimentally that UCs present in acid solutions form protective layers of organic polymers on the surface of steels in contact with these solutions. The polymerization of acetylenic compounds [29–32] as well as unsaturated aldehydes and ketones [33, 34] on steel surfaces is confirmed by IR spectroscopy data. Similar results were obtained by Raman spectroscopy for PS steel protection in an HCl solution [35]. The products of the conversion of acetylenic alcohols [36, 37] and their halogenated derivatives [38] in a corrosive medium were identified and the simplest formulas of these compounds were determined. The most comprehensive information on the composition of the products formed by unsaturated aldehydes on the surface of the steel being protected was obtained by chromato-mass spectrometry [34, 39]. It is important that the UCs that are incapable of forming protective layers of an organic polymer on steel (1,4-butynediol [40], α-amyl-CA [39]) fail to provide satisfactory metal protection.

In parallel with the formation of protective layers on the steel surface by UCs, the latter undergo cathodic hydrogenation [39, 40]. For example, PA is reduced to AA on steel in HCl solutions, as shown by the chromatographic method [41]. In contrast to HCl solutions, UC hydrogenation in $HClO_4$, H_2SO_4, and H_3PO_4 solutions prevails over the their polymerization on the surface, which often prevents these inhibitors from providing high protective effects [39, 42]. Comparison of the electrochemical behavior of acetylenic compounds with various structures (acetylene, PA, 1,4-butynediol) showed that the electrochemical hydrogenation of

UCs is directly related to their ability to form protective organic polymer layers on the metal [43].

This experimental fact allowed us [44] to identify some of the most important aspects of the mechanism of UC action. Compounds incapable of hydrogenation fail to form protective inhibitor films. Unsaturated compounds capable of hydrogenation can undergo the following reactions:

1. cathodic reduction that accelerates the cathodic reaction and causes consumption of the inhibitor;
2. bulk polymerization that removes the inhibitor from the corrosive environment;
3. formation of a protective polymer film firmly bound to the steel surface on the metal surface. The film is formed through the stage involving the formation of complexes of surface metal atoms with UC molecules and the film structure changes with time.

It should be noted that the bulk polymerization of an inhibitor in a corrosive environment is an undesirable process. When discussing the mechanism of the protective action of PA, we assumed that the bulk polymerization of this inhibitor resulted from its isomerization into acrolein, which, in turn, underwent resinification [45].

In recent years, a number of studies have been published that consider some technological aspects of the use of PA in the protection of steels in acid environments at oil fields [46–51]. Among these studies, attention should be paid to Ref. [51] where not only the process of PA degradation in corrosive hydrochloric acid medium is considered but also an attempt is made to determine the specific features of the process mechanism. The hydrolysis of PA in HCl solutions leading to the formation of weak corrosion inhibitors such as 1-hydroxypropan-2-one and 2-chloroprop-2-en-1-ol is considered. In contrast, acrolein, a product of PA isomerization, has a high inhibitory effect comparable to that of PA in the protection of steels in hydrochloric acid. The k value of carbon steel in 7.83 M HCl (80°C) in the presence of PA (0.2%) is about 33 mm/year, while in the presence of the same amount of acrolein it is slightly higher, namely, 50 mm/year. It is important to note that, unlike the first two products, acrolein was not detected in HCl solutions containing PA by ^{1}H NMR spectroscopy used in that work. The authors explained this by the extremely high reactivity of this product in acid solutions resulting in the formation of polymeric products. According to their data, the half-life of acrolein in 3.6 M HCl (80°C) is more than three orders of magnitude lower than the half-life of PA in the same environment.

We believe that AA and acrolein are the most interesting products of PA conversion in the corrosion system. In order to better understand the features of the mechanism of the protective effect of PA on the corrosion of mild steel in HCl solutions, it seems expedient to study the effect of these compounds on the electrode reactions on iron. It should be noted that AA can be formed in a corrosion system not only by PA reduction on the metal but also by acrolein reduction.

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 deaerated with hydrogen at 25°C. The concentration of PA, AA and acrolein was 30 mmol/L. The electrode was cleaned with M20 micron sandpaper and degreased with acetone. Acids of "chemically pure" brand as well as PA and AA of "pure" grade additionally purified by distillation were used. Acrolein was synthesized by dehydration of glycerol** and further purified by distillation. Solutions were prepared using distilled water.

Polarization curves (PC) 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 in order to remove the hardened and hydrogenated iron layer. At this stage, the anodic current density reached i_a~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, $E_{i=0}$). The cathodic curve of iron (Figure 1a, curve 2) was recorded from $E_{i=0}$ 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 $E_{i=0}$. The repeated anodic curve (Figure 1a, curve 4) was recorded by increasing the potential of the iron electrode from $E_{i=0}$ 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 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 [52]. Atomic hydrogen sorbed 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 [53]. In the course of prolonged iron polarization at E=–0.080 V, which is more positive than E_{act}, the metal is released from 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

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** Acrolein, *Sintez organicheskikh preparatov (Organic syntheses)*. Vol. 1., Ed. B.A. Kazanskii, Moscow, Gosudarstvennoye izdatel'stvo inostrannoi literatury, 1949, 17–20 (in Russian).

the metal with a minimum amount of sorbed hydrogen (we will tentatively assume that such iron does not contain adsorbed or absorbed hydrogen). The decrease in 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 PC 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 PCs initially recorded by decreasing the potential were obtained at a lower content of adsorbed and absorbed hydrogen on the metal than the cathodic and anodic PCs obtained by increasing the potential of iron.

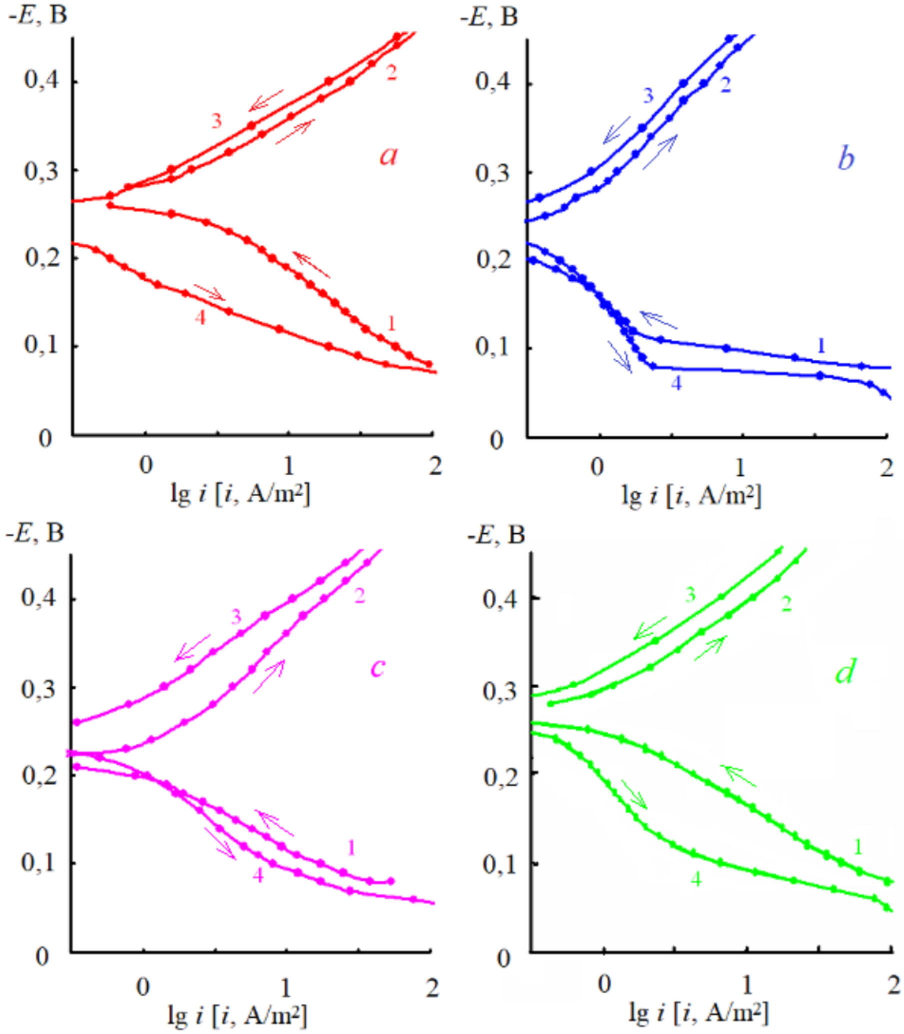

Figure 1. Polarization curves of ARMCO Pure Iron in 1 M HCl without (a) and in the presence of 30 mM unsaturated compounds: b – PA; c – acrolein; d – AA. Curves 1, 2 – decreasing potential, 3, 4 – increasing potential. The directions of polarization of the iron electrode are indicated by arrows.

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, after the electrode was dissolved for 30 minutes. The change in the anodic current to its stationary value was followed, but no longer than for 5 min, which made it possible to judge on the inhibitor adsorption on iron containing a minimum concentration of sorbed hydrogen. Further, PCs 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 (460, 780, 1400 rpm) in inhibited solutions was studied. All potentials of the iron electrode are given in the hydrogen scale. The effect of UC on the electrode reactions of iron was determined from the coefficient of inhibition of the electrode reaction:

$$\gamma = \frac{i_0}{i_{\text{inh}}},$$

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

$$Z_{\text{UC}} = \frac{i_0 - i_{\text{UC}}}{i_0} \cdot 100\%,$$

$$Z_{\text{UC+hyd}} = \frac{i_0 - i_{\text{UC+hyd}}}{i_0} \cdot 100\%,$$

$$Z_{\text{hyd}} = Z_{\text{UC+hyd}} - Z_{\text{UC}},$$

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

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 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 hours. The efficiency of inhibitors was estimated by the inhibition coefficient:

$$\gamma = \frac{k_0}{k_{\text{inh}}},$$

where k_0 and k_{inh} 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

In 1 M HCl (Table 1, Figure 1), the shape of the anodic PC 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 [54]. The cathodic PC 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 [55]. The cathodic PC 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 covering the metal surface with adsorbed hydrogen. In this case, hydrogen adsorbed on iron behaves somewhat like an inhibitor of the cathodic reaction. The anodic PC 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 operates 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 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 PC 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.

The presence of 30 mM PA in the corrosive medium changes the shape of the PC on iron significantly. The anodic PC 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 PC recorded by decreasing and increasing the iron potential are also characterized by a high slope, b_c=0.170 V. Such a high Tafel slope of polarization also indicates that the cathodic reaction occurs on iron surface coated with a protective inhibitor layer. The anodic PC 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 [56] 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 0.040 V more positive without it. The reason of iron anodic activation in HCl solution inhibited by PA is that adsorbed hydrogen is removed from the metal surface and the organic inhibitor is partially desorbed, leading to the development of pitting corrosion on the freed metal surface [52, 53]. The $E_{i=0}$ value is more positive for 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.

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

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
				1 M HCl				
E decrease	–0.270	–	0.120	0.080	10	–	21	–
E increase	–0.240	–0.170	0.120	0.080	6.5	–	2.9	–
				1 M HCl+30 mM PA				
E decrease	–0.220	–0.120	0.170	0.170	2.7	3.7	1.2	18
E increase	–0.250	–0.080	0.170	0.220	2.0	3.3	1.1	2.6

Iron polarization	$E_{i=0}$	E_{act}	b_c	b_a	i_c	γ_c	i_a	γ_a
1 M HCl+30 mM acrolein								
E decrease	–0.220	–0.120	0.160	0.080	8.7	1.1	4.4	4.8
E increase	–0.250	–0.090	0.130	0.130	3.9	1.7	3.0	0.97
1 M HCl+30 mM AA								
E decrease	–0.270	–	0.120	0.080	4.0	2.5	14	1.5
E increase	–0.270	–0.130	0.120	0.180	2.3	2.8	1.7	1.7

Addition of acrolein has a qualitatively similar effect on the electrode reactions on steel, with the only difference that the effect of this compound on the electrode reactions is less significant than in the case of PA addition. The Tafel slope of the anodic PC obtained by decreasing *E* corresponds to the background acid solution. The b_c and b_a values are significantly higher than the background ones only on the cathodic PC and on the repeated anodic PC. This result allows one to assume that this compound forms a protective film on iron. Most likely, its formation is favored by cathodic polarization of the metal.

Addition of AA has the weakest effect on the electrode reactions on iron. In the presence of this inhibitor, the b_c slope matches that in the background medium, and the value of b_a is higher than in the background medium only for the anodic PC obtained by increasing *E*. The result obtained indicates that it is unlikely that AA forms a protective inhibitor film on iron. It is important to note that the protective effect of AA 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 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. In the case of acrolein, the effect of adsorbed hydrogen on the cathodic reaction is significant. In the case of AA, it is observed for both electrode reactions, but primarily for the anodic reaction.

Studies on the effect of the convective factor on the cathodic reaction rate of iron in acid solutions containing UC 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 solution containing a UC, the increase in cathodic current with increasing electrode rotation rate results from the reduction of these compounds. AA is the most likely product of PA and acrolein reduction. Moreover, AA is also capable of further reduction. The reduction of the UC being studied occurs in diffusion mode and accelerates the cathodic reaction.

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 UC (Z_{UC}), adsorbed hydrogen (Z_{hyd}), adsorbed hydrogen and UC ($Z_{\text{UC+hyd}}$).

Inhibitor	**–**		**30 mM PA**		**30 mM acrolein**		**30 mM AA**	
E, V	–0.350	–0.150	–0.350	–0.150	–0.350	–0.150	–0.350	–0.150
Z_{UC}, %	0	0	73.0	94.3	13.0	79.0	60.0	33.3
Z_{hyd}, %	35.0	86.2	7.0	0.5	48.0	6.7	17.0	58.6
$Z_{\text{UC+hyd}}$, %	35.0	86.2	80.0	94.8	61.0	85.7	77.0	91.9

According to electrochemical studies, PA significantly affects the electrode reactions of iron in HCl solution. In contrast, the effect of acrolein and AA on the electrode reactions is smaller and differs only slightly in some respects. It is more likely that acrolein forms protective inhibitor layers on the metal. As a result, acrolein should provide stronger corrosion inhibition than AA.

Table 3. Constants c and d in the equation $i_c(\text{A/m}^2) = c + dn^{1/2}$ at $E = -0.300$ V in inhibited 1 M HCl.

Inhibitor	c	$d \cdot 10^2$
30 mM PA	1.8	1.8
30 mM acrolein	2.3	1.5
30 mM AA	0.6	2.0

Corrosion studies

Studies on the corrosion rate of steel in HCl solution containing UC will help verify our conclusions (Table 4). As it could be expected, PA provides the best corrosion inhibition of steel 3. The protective effect of acrolein is somewhat weaker, while that of AA is the weakest. At first glance, one might think that this result contradicts the data of electrochemical studies, according to which the effects of acrolein and AA on iron electrode are similar. However, on iron whose surface contains a minimum amount of hydrogen, the effect of acrolein on the anodic reaction is significantly higher than that of AA. Probably, it is what ultimately determines its superior efficiency in corrosion suppression. In contrast, the maximum effect of AA on the electrode reactions appears after a significant cathodic polarization of iron that does not occur under real corrosion conditions.

Table 4. Corrosion rates (k, g/(m^2·h) of steel 3 and corrosion inhibition coefficients (γ) of unsaturated compounds (30 mM) in 2 M HCl.

Inhibitor	***k***	**γ**
–	7.0	–
PA	0.46	15
acrolein	0.66	11
AA	3.5	2

* * *

Among the compounds studied, PA hinders the electrode reactions of iron most strongly due to the formation of a protective film of organic polymer on the metal surface by this compound. The products of its isomerization (acrolein) and reduction (AA) are inferior to it in inhibition efficiency, which is reflected in the weak hindrance of steel corrosion. Comparison of the electrochemical behavior of these compounds shows that acrolein, unlike AA, is capable of forming protective layers of organic polymer on iron. This polymer layer is inferior in efficiency to the protective layers formed by PA but would provide stronger corrosion inhibition compared to AA that does not form such layers. Thus, the electrochemical reduction of PA and acrolein on iron surface in HCl solutions to give AA is certainly a harmful process in terms of metal protection that leads to a product with a poorer protective effect.

The role of acrolein formation from PA in the corrosive environment needs clarifying. This process results in a product that is inferior to the initial inhibitor in the protective effect. Due to high acrolein reactivity, it can participate in the polymerization of the corrosion inhibitor in the bulk of the corrosive medium, thus reducing its content in the medium. Poling [29] notes that as the content of C=O groups in the polymer formed by PA on steel surface increases, its protective properties decrease. We believe that the observed effect originates from the copolymerization of PA and acrolein on the metal surface. The larger amount of acrolein is formed in the corrosive environment, the larger its amount will be included in the copolymer, thus impairing steel protection.

It should be noted that the results obtained in [51] are important for understanding the mechanism of UC action. The example of PA shows the need to take into account the reactions that UC undergo due to chemical interaction with the corrosive environment. The need to take into account the hydrolysis of an organic inhibitor in the protection of steel in acid solutions by Schiff bases was noted previously [57]. The data provided in those studies make it possible to enrich the understanding of UC conversion pathways in the protection of steels in acid solutions suggested previously [44, 57]. The reactions of UC in a steel/acid solutions 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 UC in such a system is determined by the reactions:

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

Conclusions

1. Among the UC studied (PA, acrolein, AA), PA has the strongest inhibitory effect on the cathodic and anodic reactions of iron in acid solutions. The observed effect results from the formation of a protective film of organic polymer by this compound on the metal surface. According to electrochemical studies, acrolein also forms an organic polymer layer on iron in hydrochloric acid, but its protective properties are poorer than those of the polymer formed by PA. AA does not form a protective layer on iron, so it has the weakest effect on the electrode reactions.
2. Atomic hydrogen adsorbed on iron surface inhibits the electrode reactions of the metal in HCl solution, both in the absence and in the presence of an UC in the corrosive medium. In UC-inhibited media, the greatest contribution to the inhibition of electrode reactions by adsorbed hydrogen is observed in the presence of AA.
3. PA and acrolein undergo cathodic hydrogenation on iron in hydrochloric acid in diffusion mode. This result is an experimental confirmation that these UC are converted to AA on iron surface. At the same time, AA can undergo further reduction on iron surface and thus can stimulate the cathodic process, which is undesirable.
4. The corrosion protection of steel in HCl solution by the UC studied decreases in the series: PA>acrolein>AA, which is consistent with the results of electrochemical studies of these compounds on iron.
5. It has been shown experimentally using the capabilities of electrochemical methods that conversion of PA to acrolein or AA during corrosion inhibition of iron or steels in HCl solutions is a process that is undesirable for their protection. The compounds that are formed are poorer corrosion inhibitors than the original inhibitor. Reduction of PA to AA followed by hydrogenation of the latter adversely affect the iron cathodic reaction that is accelerated as a result. This increases the consumption of the initial UC.

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