Effect of urotropine on the potential of the Fe(III)/Fe(II) redox couple in mineral acid solutions

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Abstract

2.0 M HCl, 2.0 M H₂SO₄ and 2.0 M H₃PO₄ solutions and their mixtures containing Fe(III) and Fe(II) cations were studied by the potentiometry method at 20–95°C. It was shown that addition of urotropine to the HCl+H₃PO₄+Fe(III)+Fe(II) system containing at least 20% H₃PO₄ of the total acid amount decreased the oxidizing ability of the system. The decrease in the oxidizing ability of the system upon addition of urotropine is the stronger, the higher the content of H₃PO₄ in the acid mixture. In the H₂SO₄+H₃PO₄+Fe(III)+Fe(II) system, the effect of urotropine on the decrease in the oxidizing properties is weaker. The decrease in the oxidizing ability of the Fe(III)-containing acid mixtures being studied upon addition of urotropine can result from binding of Fe(III) into complex compounds with phosphate anions and urotropine. Such Fe(III) complexes have low oxidizing ability. The two-component inhibitor IFKhAN-92+KNCS is recommended for the inhibitory protection of steels in mixtures of mineral acids based on H₃PO₄ if there is a potential for the accumulation of Fe(III) salts in these solutions which significantly increases the system corrosivity. Addition of urotropine is used to increase the efficiency of this inhibitory formulation. It was found that urotropine causes a more considerable increase in the protection of low-carbon steel by this formulation in the HCl+H₃PO₄+Fe(III) system than in the H₂SO₄+H₃PO₄+Fe(III) system due to a stronger decrease in the oxidizing ability of the former system by this compound.

Keywords: corrosion inhibitors, potentiometry, hydrochloric acid, sulfuric acid, phosphoric acid, redox couple Fe(III)/Fe(II), iron(III) chloride, iron(III) sulfate, iron(III) phosphate.

Received: April 20, 2020. Published: May 4, 2020

doi: [10.17675/2305-6894-2020-9-2-12](https://doi.org/10.17675/2305-6894-2020-9-2-12)

Introduction

The commercial utilization of mineral acid solutions is often accompanied by accumulation of Fe(III) salts in them, which significantly increases their corrosivity toward steel structures which they contact. In the acid pickling of steels for the removal of thermal scale, Fe(III) salts are primarily accumulated due to dissolution of scale constituents such as magnetite (Fe₃O₄) and hematite (Fe₂O₃). In the acid washing of inner surfaces of process equipment made of steel, rust (FeO(OH)) is the main source of Fe(III) salts transferred into solutions.

The corrosion of low-carbon steels in acid solutions containing Fe(III) salts results from the reaction of metallic iron with an acid:

and with a Fe(III) salt:

The accumulation of Fe(III) salts in solutions of mineral acids makes the inhibitory protection of metals inefficient in these media [1]. Inhibitors of acid corrosion of steels can significantly reduce the rate of the cathodic reaction of proton reduction but only slightly inhibit the reduction of Fe(III) cations, which adversely affects the inhibition of the corrosion process in general [2].

The Fe(III) cations present in solutions of mineral acids are often bound into complex compounds with anions of acid residues formed upon acid dissociation. As a result, the oxidizing ability of these cations decreases. In HCl and H₂SO₄ solutions, the oxidizing ability is reduced only slightly, whereas this effect is strong in H₃PO₄ [3, 4]. This is sufficient to ensure that in H₃PO₄ solutions containing FePO₄, the addition of a composite inhibitor comprising a 3-substituted 1,2,4-triazole derivative (IFKhAN-92) and KNCS provides efficient protection of low carbon steel [2]. In solutions of individual HCl or H₂SO₄ containing Fe(III) salts, this mixed inhibitor protects steel unsatisfactorily under the same conditions. However, the protection of steels by the mixed inhibitor is maintained in H₂SO₄+H₃PO₄ solutions containing Fe(III) salts. Efficient protection of the metal is observed if the H₃PO₄ content in a mixture of acids is no lower than 40% of their total amount. Unfortunately, in HCl+H₃PO₄ solutions containing Fe(III) salts, the IFKhAN-92+KNCS formulation does not provide the necessary inhibition of steel corrosion [5]. This is largely due to the weaker decrease in the oxidizing ability of Fe(III) cations in this mixture of acids (Figure 1) [3, 4].

Additional modification of the 4.5 mM IFKhAN-92+0.5 mM KNCS mixed inhibitor by addition of 0.2 M urotropine not only improves the protection of low carbon steel in H₂SO₄+H₃PO₄ solutions containing Fe(III) salts but also provides a good inhibitory effect in HCl+H₃PO₄+Fe(III) systems containing no less than 40% H₃PO₄. We put forward the hypothesis [6, 7] that the effect of urotropine on the corrosion process is associated with its ability to additionally bind Fe(III) cations to complex compounds whose oxidizing ability is even lower. Information on the formation of Fe(III) and Fe(II) complex compounds with urotropine is available [8]. In particular, the following Fe(III) complex compounds are known: [Fe(C₆H₁₂N₄)₂(H₂O)₃(NO₃)](NO₃)₂·2H₂O [9], [Fe(C₆H₁₂N₄)]Cl₃ and [Fe(C₆H₁₂N₄)₂]Cl₃ [10]. The following Fe(II) complexes have been obtained: [Fe(C₆H₁₂N₄)₂]Cl₂ [11], [Fe(H₂O)₆](NO₃)₂·2C₆H₁₂N₄·4H₂O [12]. These data allow us to believe that Fe complexes are formed in solutions of mineral acids containing Fe salts in the presence of urotropine.

Figure 1. Platinum electrode potential in argon-deaerated 2 M mineral acids containing 0.05 M Fe(III) and 0.05 M Fe(II) at various temperatures [3, 4].

It is most convenient to use the redox potential of the Fe(III)/Fe(II) couple in these solutions as a quantitative estimate of the oxidizing ability of acid solutions containing Fe(III) salts. Earlier [3, 4], this parameter was used to characterize the oxidizing ability of HCl–H₃PO₄–Fe(III), H₂SO₄–H₃PO₄–Fe(III), HCl–HF–Fe(III), and H₂SO₄–HF–Fe(III) systems.

In view of the above, it seems appropriate to estimate the oxidizing ability of mineral acid solutions containing Fe(III) and Fe(II) salts in the presence of urotropine. To study the complexation processes in these redox systems, we used the potentiometry method that is widespread, highly sensitive, simple, inexpensive, and convenient [13, 14]. The real potential was used as the quantitative characteristic of the processes that occur in solutions of acids containing Fe(III) and Fe(II) cations. It is interpreted as the potential of a redox system established in a particular solution when the initial concentrations of the oxidized and reduced forms of potential-determining ions are equal, without taking into account the corrections for the processes of complexation, hydrolysis, *etc.* [15]. It is also very convenient in interpreting the results of an experiment related to the complexation of potential-determining ions.

Experimental

Solutions were prepared from acids (HCl, H₂SO₄, H₃PO₄) of “chemically pure” grade and distilled water. Acid solutions containing Fe(III) salts were prepared by reactions of Fe(OH)₃, which was precipitated with NaOH (chemically pure) from a FeCl₃ solution, with an excess of the corresponding acid. The Fe(III) chloride solution was prepared from FeCl₃·6H₂O (“pure” grade). Solutions of H₂SO₄ containing Fe(II) sulfate were prepared from

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (“chemically pure”). Due to the technical difficulties in obtaining solutions of the remaining acids containing the corresponding Fe(II) salts suitable for potentiometric studies, they were replaced with acid solutions containing an equivalent concentration of FeSO_4 . With this approach, the maximum unaccounted-for content of SO_4^{2-} and the acid anion itself was 2.4% of the total concentration of anions in the solution, which allowed us to neglect this fact in further discussions.

The base concentration of urotropine added to test media was 0.20 M.

The potentiometric studies were performed in a YaSE-2 thermostatically controlled glass electrochemical cell. The accuracy of maintaining the temperature in the cell was $\pm 1^\circ\text{C}$. Smooth platinum (1.5 cm^2) was used as the working electrode; a saturated silver chloride electrode served as the reference electrode. The potential difference between the working and reference electrodes was determined using a PI-50 potentiostat. The error in determining the potential did not exceed 0.01 V. The working solutions were deaerated with argon (“chemically pure”) before (30 min) and during the experiment. The potential of the platinum electrode in the working solution was measured 30 minutes after the target temperature (t) was established in the cell. In this mode of measurement, the potential of the working electrode remained unchanged for at least the last 20 minutes. All electrode potentials in the article are given in the standard hydrogen electrode scale.

The effect of urotropine on the oxidizing ability of acid solutions containing Fe(III) and Fe(II) was estimated as the variation in the platinum electrode potential in the test medium 5 hours after the addition of this compound:

$$\Delta E = E^{0h} - E^{5h}$$

where E^{0h} is the potential of the platinum electrode in the test solution 30 minutes after the specified t was established in the cell and E^{5h} is the potential of the platinum electrode in the same system 5 hours after the addition of urotropine.

Results and Discussion

The platinum electrode potential in a solution containing Fe(III) and Fe(II) is determined by the reaction:

and can be calculated from the active concentrations of the corresponding cations using the Nernst equation:

$$E_{\text{Fe(III)/Fe(II)}} = E_{\text{Fe(III)/Fe(II)}}^0 + \frac{RT}{F} \ln \frac{a_{\text{Fe(III)}}}{a_{\text{Fe(II)}}}$$

The standard electrode potential is $E_{\text{Fe(III)/Fe(II)}}^0 = 0.771\text{ V}$ at 25°C , $\frac{dE_{\text{Fe(III)/Fe(II)}}^0}{dT} = 0.00119\text{ V/K}$ [16]. In 2 M acids containing 0.05 M Fe(III) and 0.05 M Fe(II) that we studied,

the electrode potentials of platinum in the selected t range are lower, which indicates that the Fe cations in these media are bound by acid anions into complexes (Table 1). The values of these $E_{\text{Fe(III)/Fe(II)}}^0$ are in full agreement with the values that we obtained previously (Figure 1) [3, 4].

Table 1. Effect of addition of 0.20 M urotropine on the potential of the Pt electrode in acid solutions.

Potential, V	Temperature, °C				
	20	40	60	80	95
2.0 M H ₂ SO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.66	0.68	0.71	0.72	0.75
E^{5h}	0.67	0.69	0.71	0.72	0.74
ΔE	–0.01	–0.01	0	0	0.01
1.0 M H ₂ SO ₄ +1.0 M H ₃ PO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.55	0.56	0.57	0.59	0.60
E^{5h}	0.53	0.54	0.55	0.54	0.55
ΔE	0.02	0.02	0.02	0.05	0.05
2.0 M HCl+0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.67	0.68	0.70	0.71	0.71
E^{5h}	0.69	0.69	0.70	0.71	0.71
ΔE	–0.02	–0.01	0	0	0
1.6 M HCl+0.4 M H ₃ PO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.61	0.64	0.65	0.67	0.69
E^{5h}	0.60	0.62	0.64	0.65	0.66
ΔE	0.01	0.02	0.01	0.02	0.03
1.4 M HCl+0.6 M H ₃ PO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.59	0.61	0.63	0.65	0.67
E^{5h}	0.57	0.58	0.60	0.61	0.61
ΔE	0.02	0.03	0.03	0.04	0.06
1.2 M HCl+0.8 M H ₃ PO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.58	0.60	0.61	0.63	0.65
E^{5h}	0.55	0.55	0.56	0.58	0.57
ΔE	0.03	0.05	0.05	0.05	0.08

Potential, V	Temperature, °C				
	20	40	60	80	95
1.0 M HCl+1.0 M H ₃ PO ₄ +0.09 M Fe(III)+0.01 M Fe(II)					
E^{0h}	0.61	0.63	0.65	0.66	0.68
E^{5h}	0.57	0.57	0.56	0.58	0.57
ΔE	0.04	0.06	0.09	0.08	0.11
1.0 M HCl+1.0 M H ₃ PO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.56	0.57	0.59	0.61	0.63
E^{5h}	0.52	0.52	0.51	0.54	0.54
ΔE	0.04	0.05	0.08	0.07	0.09
1.0 M HCl+1.0 M H ₃ PO ₄ +0.01 M Fe(III)+0.09 M Fe(II)					
E^{0h}	0.52	0.53	0.54	0.55	0.57
E^{5h}	0.47	0.45	0.46	0.45	0.46
ΔE	0.05	0.08	0.08	0.10	0.11
2.0 M H ₃ PO ₄ +0.05 M Fe(III)+0.05 M Fe(II)					
E^{0h}	0.44	0.44	0.45	0.45	0.46
E^{5h}	0.40	0.39	0.38	0.35	0.33
ΔE	0.04	0.05	0.07	0.10	0.13

The highest $E_{\text{Fe(III)/Fe(II)}}^0$ values are observed in 2.0 M H₂SO₄+0.05 M Fe(III)+0.05 M Fe(II). The addition of 0.20 M urotropine into such media nearly does not change their oxidizing properties (Figure 2). A similar situation is observed after the addition of 0.20 M urotropine to 2.0 M HCl+0.05 M Fe(III)+0.05 M Fe(II). In 2.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II), the $E_{\text{Fe(III)/Fe(II)}}^0$ value is the lowest compared to 2.0 M H₂SO₄+0.05 M Fe(III)+0.05 M Fe(II) and 2.0 M HCl+0.05 M Fe(III)+0.05 M Fe(II). Despite this fact, the addition of 0.20 M urotropine to 2.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II) decreases the redox potential of the system by 0.040–0.13 V in 5 hours. The decrease in the potentials of the system is the stronger, the higher the solution temperature, and their values are 0.33–0.40 V against 0.44–0.46 V in the solution without urotropine. A decrease in the potential of the platinum electrode in 2.0 M H₃PO₄ upon addition of urotropine can be explained by the fact that in this medium, Fe cations from phosphate complexes are converted to stronger complexes with more complex structures that simultaneously contain phosphate anions and urotropine as the ligands. The oxidizing ability of such Fe(III) complexes is significantly lower than that of phosphate complexes. In sulfate or chloride media, the addition of urotropine does not result in a decrease in potential, which indicates the specific role of

phosphate anions in the formation of these complexes. It should be noted that the platinum electrode potentials that are established in $\text{H}_3\text{PO}_4 + \text{Fe(III)} + \text{Fe(II)}$ 5 hours after the addition of urotropine should not be considered as equilibrium values. Despite their relative stability in time after 5 hours, the established E is not an equilibrium value. This is demonstrated by the fact that the platinum electrode potential is the lower, the higher the solution temperature. Apparently, at low t there are some kinetic limitations on the formation of Fe(III) complexes with phosphate anions and urotropine. Because of that, the decrease in the E of the system is relatively low. In contrast, the formation of the compounds in hot solutions is relatively fast. As a result, the potential decrease is stronger. It is important to note that in solutions of H_3PO_4 alone and acid mixtures based on it that will be discussed below, the oxidizing ability of systems decreases quickly upon addition of urotropine and persists for at least 5 hours.

Figure 2. Platinum electrode potential in 2.0 M $\text{H}_2\text{SO}_4 + 0.05 \text{ M Fe(III)} + 0.05 \text{ M Fe(II)}$ (a), 2.0 M $\text{HCl} + 0.05 \text{ M Fe(III)} + 0.05 \text{ M Fe(II)}$ (b) and 2.0 M $\text{H}_3\text{PO}_4 + 0.05 \text{ M Fe(III)} + 0.05 \text{ M Fe(II)}$ (c) after addition of 0.20 M urotropine to the solution.

It should be understood how the presence of H_3PO_4 in acidic sulfate and chloride media containing Fe(III) and Fe(II) affects the response of these media to the addition of urotropine. The addition of 0.20 M urotropine to 1.0 M $\text{H}_2\text{SO}_4 + 1.0 \text{ M H}_3\text{PO}_4 + 0.05 \text{ M Fe(III)} + 0.05 \text{ M Fe(II)}$ decreases the E of the system by only 0.02–0.05 V (Figure 3). In contrast, in 1.0 M $\text{HCl} + 1.0 \text{ M H}_3\text{PO}_4 + 0.05 \text{ M Fe(III)} + 0.05 \text{ M Fe(II)}$, the decrease in E is larger, *i.e.*, 0.04–0.09 V. In $\text{HCl} + \text{H}_3\text{PO}_4$, already at $C_{\text{H}_3\text{PO}_4} = 20\%$, the addition of urotropine provides $\Delta E = 0.01$ –0.03 V (Figure 4). Increasing $C_{\text{H}_3\text{PO}_4}$ to 30 and 40% systematically increases ΔE to 0.02–0.06 and 0.03–0.08 V. Thus, the addition of urotropine more strongly decreases the oxidizing ability of the $\text{HCl} + \text{H}_3\text{PO}_4 + \text{Fe(III)} + \text{Fe(II)}$ system in comparison with the

$\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4 + \text{Fe(III)} + \text{Fe(II)}$ system. The effect of urotropine addition to a mixture of acids becomes more pronounced with an increase in the H_3PO_4 content.

Figure 3. Platinum electrode potential in 1.0 M $\text{H}_2\text{SO}_4 + 1.0$ M $\text{H}_3\text{PO}_4 + 0.05$ M $\text{Fe(III)} + 0.05$ M Fe(II) (a) and 1.0 M $\text{HCl} + 1.0$ M $\text{H}_3\text{PO}_4 + 0.05$ M $\text{Fe(III)} + 0.05$ M Fe(II) (b) after addition of 0.20 M urotropine to the solution.

Figure 4. Platinum electrode potential in 1.6 M $\text{HCl} + 0.4$ M $\text{H}_3\text{PO}_4 + 0.05$ M $\text{Fe(III)} + 0.05$ M Fe(II) (a), 1.4 M $\text{HCl} + 0.6$ M $\text{H}_3\text{PO}_4 + 0.05$ M $\text{Fe(III)} + 0.05$ M Fe(II) (b) and 1.2 M $\text{HCl} + 0.8$ M $\text{H}_3\text{PO}_4 + 0.05$ M $\text{Fe(III)} + 0.05$ M Fe(II) (c) after addition of 0.20 M urotropine to the solution.

An increase or decrease in the Fe(III) content in 1.0 M HCl+1.0 M H₃PO₄+Fe(III)+Fe(II) has practically no effect on the E response upon urotropine addition to the solution (Figure 5). At the highest $C_{\text{Fe(III)}}=0.09$ M, $\Delta E=0.04$ – 0.11 V.

Figure 5. Platinum electrode potential in 1.0 M HCl+1.0 M H₃PO₄+0.09 M Fe(III)+0.01 M Fe(II) (a) and 1.0 M HCl+1.0 M H₃PO₄+0.01 M Fe(III)+0.09 M Fe(II) (b) after addition of 0.20 M urotropine to the solution.

The effect of urotropine addition on the electrode potential of platinum electrode in 1.0 M HCl+1.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II) (60°C) becomes significant at $C_{\text{urotropine}}=0.10$ M, which results in $\Delta E=0.03$ V (Figure 6). At $C_{\text{urotropine}}=0.30$ M, the ΔE value is significant, *viz.*, 0.18 V. A further increase in the urotropine content in the solution does not significantly affect the ΔE value.

It seems important to understand how a further accumulation of Fe(III) would affect the oxidizing ability of the system containing 0.20 M urotropine+1.0 M HCl+1.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II). It is interesting that the platinum electrode potential in 1.0 M HCl+1.0 M H₃PO₄ after urotropine addition is significantly lower than that in 1.0 M HCl+1.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II) under the same conditions (Figure 7). Sequential introduction of 0.05 M FeCl₃ to the 1.0 M HCl+1.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II) system containing 0.20 M urotropine causes an abrupt increase in the platinum electrode potential. The effect of the decrease in the E of the system upon addition of 0.2 M urotropine disappears completely upon subsequent addition of 0.15 M FeCl₃. The total content of Fe(III) in the system is 0.20 M.

Figure 6. Platinum electrode potential in 1.0 M HCl+1.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II) after addition of various concentrations of urotropine to the solution. $t = 60^{\circ}\text{C}$.

Figure 7. Platinum electrode potential in 1.0 M HCl+1.0 M H₃PO₄ (1) and 1.0 M HCl+1.0 M H₃PO₄+0.05 M Fe(III)+0.05 M Fe(II) (2 and 3) after addition of 0.20 M urotropine to the solution. Curve 3 – with sequential addition of 0.05 M FeCl₃. $t = 60^{\circ}\text{C}$.

As we expected, the addition of urotropine to solutions of mixtures of mineral acids containing Fe(III) salts decreases their oxidizing ability. The effect that we detected allows us to explain the effect of urotropine addition to HCl+H₃PO₄+Fe(III) and H₂SO₄+H₃PO₄+Fe(III) systems on the protection of low-carbon steels in these media by the IFKhAN-92+KNCS formulation. In mixtures of acids containing H₃PO₄, Fe(III) cations are bound into complexes with phosphate anions and urotropine. The oxidizing ability of these complexes

is extremely low, which favors the inhibition of corrosion by the IFKhAN-92+KNCS formulation in their presence. Thus, the decrease in the oxidizing ability upon urotropine addition to the $\text{HCl}+\text{H}_3\text{PO}_4+\text{Fe(III)}$ system is stronger than in the $\text{H}_2\text{SO}_4+\text{H}_3\text{PO}_4+\text{Fe(III)}$ system. This is in good agreement with the fact that the addition of urotropine to the IFKhAN-92+KNCS mixture affects the protection of steel in the $\text{HCl}+\text{H}_3\text{PO}_4+\text{Fe(III)}$ system much more strongly than in the $\text{H}_2\text{SO}_4+\text{H}_3\text{PO}_4+\text{Fe(III)}$ system.

This result is important for the development of theoretical concepts in the field of inhibitory protection of metals. We have previously found [1] that the inhibitory protection of steels in solutions of mineral acids where accumulation of Fe(III) cations as an additional oxidizing agent occurs is possible under two conditions. First, the oxidizing ability of Fe(III) cations should be decreased by binding them into complex compounds by anions formed upon acid dissociation. Individual H_3PO_4 or its mixtures thereof with other acids can be used as such acids. Second, a sufficiently efficient acid corrosion inhibitor must be selected, which can simultaneously slow down the reduction of protons and Fe(III) complex compounds with anions of acid residues. Composite inhibitors based on triazole derivatives and sulfur-containing compounds possess this property to a considerable extent. An additional way for affecting this system appears, which makes it possible to increase the efficiency of steel protection in it. An additional complexing component must be introduced in the inhibitor to bind Fe(III) into even stronger complex compounds with extremely low oxidizing ability. The effect of an even greater decrease in the oxidizing ability of Fe(III) cations will facilitate the inhibition of their reduction by an inhibitor. Urotropine is the most convenient additional complexing component for the systems we are studying. In addition, it is also interesting because it can act as an effective inhibitor of steel corrosion in formulations with other compounds.

Conclusions

1. The addition of urotropine to the $\text{HCl}+\text{H}_3\text{PO}_4$ and $\text{H}_2\text{SO}_4+\text{H}_3\text{PO}_4$ systems containing Fe(III) and Fe(II) salts decreases their oxidizing ability. This effect is most pronounced in the $\text{HCl}+\text{H}_3\text{PO}_4+\text{Fe(III)}+\text{Fe(II)}$ system.
2. The decrease in the oxidizing ability of the acid mixtures being studied containing Fe(III) and Fe(II), which is observed upon addition of urotropine, can result from binding of Fe(III) into complex compounds with phosphate anions and urotropine. Such Fe(III) complexes have low oxidizing ability.
3. The more considerable increase in the protection of low-carbon steel by urotropine by the IFKhAN-92+KNCS formulation in the $\text{HCl}+\text{H}_3\text{PO}_4+\text{Fe(III)}$ system in comparison with the $\text{H}_2\text{SO}_4+\text{H}_3\text{PO}_4+\text{Fe(III)}$ system results from a stronger decrease of the oxidizing ability of the former system by this compound.

Acknowledgments

This study was carried out within the framework of the Program of Basic Scientific Research of the State Academies of Sciences for 2013–2020, topic “Development of the fundamental scientific basis of the protective effect of inhibitors of metal corrosion in gas and condensed media, nanocomposites, paintwork and conversion coatings” (state registration number AAAA-A18-118121090043-0).

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