Effect of anionic composition of solutions of mineral acids containing Fe(III) on their oxidizing properties

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Abstract

Solutions of $HClO_4$, HBr, H_2SO_4, HCl, H_3PO_4, HF and some of their mixtures containing Fe(III) and Fe(II) cations were studied at 20–95°C by potentiometry. The oxidizing ability of such solutions of individual acids decreases in the series: $HClO_4 > HBr > H_2SO_4 > HCl > H_3PO_4 > HF$. This effect is the result of the enhancement in this series of the ability of anions of acids to bind Fe(III) cations into complex compounds that are less prone to reduction in comparison with its aqua complexes. To decrease the oxidative ability of acid solutions (HCl and H_2SO_4) with a weak ability of anions to bind Fe(III) cations to complex compounds, it is possible to add acids (H_3PO_4 or HF) that generate anions binding Fe(III) into stable and hardly reducible complexes. In the H_2SO_4–H_3PO_4–H_2O, H_2SO_4–HF–H_2O, HCl–H_3PO_4–H_2O, and HCl–HF–H_2O systems containing Fe(III) and Fe(II), the dependence of the redox potential of the Fe(III)/Fe(II) couple on the anionic composition of the medium showed that H_3PO_4 is the most promising additive that reduces the oxidizing properties of HCl and H_2SO_4 in solutions. In the HCl–H_3PO_4–H_2O system taken as an example, the main regularities of changes in the oxidizing properties of two-component acid mixtures containing Fe(III) and Fe(II) are revealed. Variation in the total content of an equimolar Fe(III)+Fe(II) mixture (C = 0.01–0.10 M) in 1 M HCl + 1 M H_3PO_4 nearly does not affect its oxidative ability. Conversely, an increase in the relative content of Fe(III) in the system considerably increases its oxidative potential. At a fixed concentration of the Fe(III) + Fe(II) mixture (0.04 M) in the HCl + H_3PO_4 system, an increase in the concentration of these acids from 1 to 4 M slightly reduces the oxidative properties of the system. Improving the corrosion protection of steel in HCl or H_2SO_4 solutions containing Fe(III) salts with a composite inhibitor (IFKhAN-92 + KNCS + hexamine) can be effective when H_3PO_4 is added. This effect is largely determined by the binding of Fe(III) cations to phosphate complexes, which have a lower oxidizing capacity compared to its aqueous, sulfate and chloride complexes.

Keywords: *corrosion inhibitors, potentiometry, perchloric acid, hydrobromic acid, hydrochloric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, Fe(III)/Fe(II) redox couple.*

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The use of mineral acids solutions under various industrial conditions often results in the accumulation of Fe(III) salts. Corrosion of steel items in these media results not only from the reaction of the metal with the acid but also with a Fe(III) salt. The gain in corrosion losses due to the presence of Fe(III) cations may be considerable, especially in cold solutions [1–4]. Reduction of Fe(III) cations with metallic iron that occurs in diffusion mode is usually poorly hindered by corrosion inhibitors, which makes steel protection by this method inefficient [5].

It was previously shown [6] that a decrease in the oxidizing ability of acids containing Fe(III) salts makes it possible to effectively use corrosion inhibitors in these environments to protect mild steel. A decrease in the oxidizing ability of these solutions is possible by binding these cations into complex compounds, which have a lower oxidizing potential in comparison with hydrated Fe(III) ions. Mineral acids, that generate at dissociation anions that are ligands with good binding ability, can be used as additives, converting Fe(III) cations into complexes. Analysis of literature data (Table 1) on the stability of Fe(III) complexes with anions of mineral acids shows that solutions of phosphoric and especially hydrofluoric acids are most promising in terms of diminishing the oxidizing ability of Fe(III) salts. It can be assumed that the oxidizing ability of Fe(III) cations in solutions of these acids would be minimal. Introduction of ligand-generating acids that bind Fe(III) cations into hardly reducible complex compounds to solutions of acids that do not possess such properties would reduce the oxidizing ability of Fe(III) therein. This approach would allow one to create mixtures of solutions of mineral acids containing salts of Fe(III) with low oxidizing ability and would make it possible to effectively protect steel with corrosion inhibitors.

In view of the above, it is expedient to evaluate the oxidative ability of mineral acid solutions containing Fe(III) and Fe(II) salts. To study the processes of complex formation in these redox systems, we used the potentiometry method [12, 13], which is highly sensitive, inexpensive and experimentally simple. The processes occurring in solutions of acids containing Fe(III) and Fe(II) cations were quantitatively characterized using the real potential, which is interpreted as the redox potential of the system established in a particular solution at equal starting concentrations of the oxidized and reduced forms of the potential-determining ions, without corrections for complexation, hydrolysis, and other processes [14]. The real potential is very convenient when interpreting the results of an experiment related to the complexation of potential-determining ions.

Experimental

Solutions were prepared from $HClO_4$, H_2SO_4, H_3PO_4, HF, HCl and HBr of “chemically pure” grade and distilled water. Acid solutions containing Fe(III) salts were obtained using the reaction of an excess of an acid with $Fe(OH)_3$ precipitated with NaOH (“chemically pure” grade) from a $FeCl_3$ solution. The Fe(III) chloride solution was prepared from $FeCl_3{\cdot}6H_2O$ (“pure” grade). H_2SO_4 solutions containing Fe(II) sulfate were prepared from $FeSO_4{\cdot}7H_2O$ (“chemically pure” grade). Due to technical difficulties in the preparation of solutions of the other acids containing the corresponding Fe(II) salts for potentiometric studies, they were replaced by solutions containing an equivalent concentration of $FeSO_4$. In this approach, the maximum unaccounted-for concentration of SO_4^{2-} and the anion of the corresponding acid was 2.4% each of the total concentration of anions in a solution, which allowed us to neglect this fact in the further discussion.

Potentiometric studies were performed in a YaSE-2 temperature-controlled glass electrochemical cell. The accuracy of temperature control in the cell was ±1°C. A smooth platinum (1.5 cm^2) working electrode and a saturated silver chloride reference electrode were used. Potentiometric studies of solutions containing HF were performed in a temperature-controlled polyethylene electrochemical cell. The design of the cell completely prevented the contact of its glass elements made from the solutions being studied. The connecting elements of the cell are made of silicone. The reproducibility of experimental results obtained in both electrochemical cells was shown using some model solutions as examples. The potential difference between the working and reference electrodes was determined using a PI-50 potentiostat. The working solutions were deaerated with argon ("chemically pure" grade) for 30 min both before and during the entire experiment. The potential of the platinum electrode in the working solution was measured in 30 min after the required temperature in the cell was established. In this measurement mode, the potential of the working electrode remained constant for at least the last 20 min. All electrode potentials in the article are given relative to the standard hydrogen electrode.

Experimental results and discussion

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

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} = \mathrm{Fe}^{2+}.$$

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

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

The standard electrode potential is $E^{0}_{\mathrm{Fe(III)/Fe(II)}}$ = 0.771 V at 25°C, while $\frac{\mathrm{d}E^{0}_{\mathrm{Fe(III)/Fe(II)}}}{\mathrm{d}T}$ = 0.00119 V/K [15]. In the 2 M acid solutions studied containing 0.05 M Fe(III) and 0.05 M Fe(II) (Figure 1) and in the absence of interaction of Fe cations with anions formed during their dissociation, the potential values of the platinum electrode should match the reference data [15]. In practice, for all the studied solutions in the selected temperature (t) range, the electrode potential of platinum is lower, which indicates that binding of Fe cations into complexes occurs in such media. The oxidative capacity of 2 M acid solutions containing an equimolar mixture of Fe(III) and Fe(II) can be arranged in the series: $HClO_4$ > HBr > H_2SO_4 > HCl > H_3PO_4 > HF. This series is in satisfactory agreement with the data on the complexing ability of Fe(III) cations with the anions of mineral acids presented in Table 1. Fluoride and phosphate anions bind Fe(III) cations into stable complexes; therefore, in 2 M H_3PO_4 and 2 M HF, the potentials of the platinum electrode are the lowest in comparison with the reference values. Accordingly, in 2 M $HClO_4$ and 2 M HBr, the potentials of the platinum electrode are close to the reference values. Similar data on the decrease in the oxidative ability of the same 1 N acids, containing an equimolar mixture of Fe(III) and Fe(II), were reported in [16].

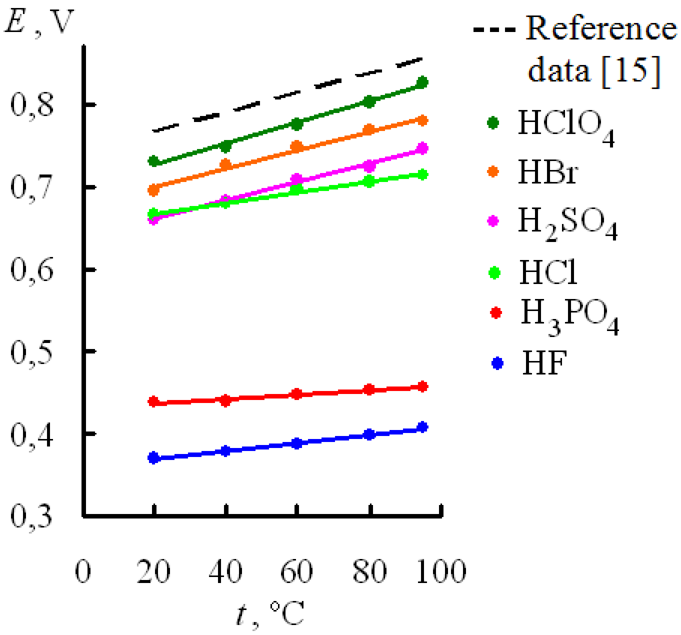

Figure 1. Potentials of a platinum electrode in argon-deaerated 2 M mineral acids containing 0.05 M Fe(III) and 0.05 M Fe(II) at various temperatures.

In HF and H_3PO_4 solutions is observed the strongest decrease in the potential of the Fe(III)/Fe(II) redox couple ($E_{Fe(III)/Fe(II)}$). In practice, the most widely used solutions are HCl and H_2SO_4, in which $E_{Fe(III)/Fe(II)}$ is not so much reduced as compared with reference values. In this regard, it is advisable to lower $E_{Fe(III)/Fe(II)}$ in these media by introducing HF or H_3PO_4 into them.

In 2 M H_2SO_4 + H_3PO_4, containing 0.05 M Fe(III) and 0.05 M Fe(II), with an increase of the molar fraction of H_3PO_4, the oxidizing potential of the system decreases (Figure 2 a). As the H_3PO_4 content in the acid mixture increases, the oxidizing ability of the solutions decreases. A similar dependence is observed in 2 M H_2SO_4 + HF containing 0.05 M Fe(III) and 0.05 M Fe(II), but the most intense decrease in the oxidizing potential of this system is observed for solutions with a high mole fraction of HF (Figure 2 b). In addition, the mixture H_2SO_4 + HF is more sensitive to the increase in *t*. For such a system, containing

50% H_2SO_4 from the total molar fraction of acid in mixture, an increase in t by 75°C increases the potential by 0.08 V, and in H_2SO_4 + H_3PO_4 mixture by only 0.06 V.

Table 1. Instability constants (pK_i) of Fe(III) complexes with some inorganic ligands. t = 20–30°C.

Ligands	pK_{i1}	$pK_{i1,2}$	$pK_{i1\text{-}3}$	$pK_{i1\text{-}4}$	$pK_{i1\text{-}5}$	$pK_{i1\text{-}6}$	**Ref.**
ClO_4^-	1.15	–	–	–	–	–	7
	1.0	–	–	–	–	–	8
SO_4^{2-}	4.18	7.4	–	–	–	–	7
	4.02	5.38	–	–	–	–	9
HSO_4^-	2.48	–	–	–	–	–	10
HPO_4^{2-}	3.5	–	–	9.15	–	–	7
$H_2PO_4^-$	9.75	–	–	–	–	–	7
F^-	6.04	10.74	13.74	15.74	16.10	~16.10	7
Cl^-	1.45	2.10	1.10	−0.85	–	–	7
	1.52	2.22	–	–	–	–	8
	1.48	2.13	1.13	–	–	–	11
Br^-	0.55	0.82	–	–	–	–	7

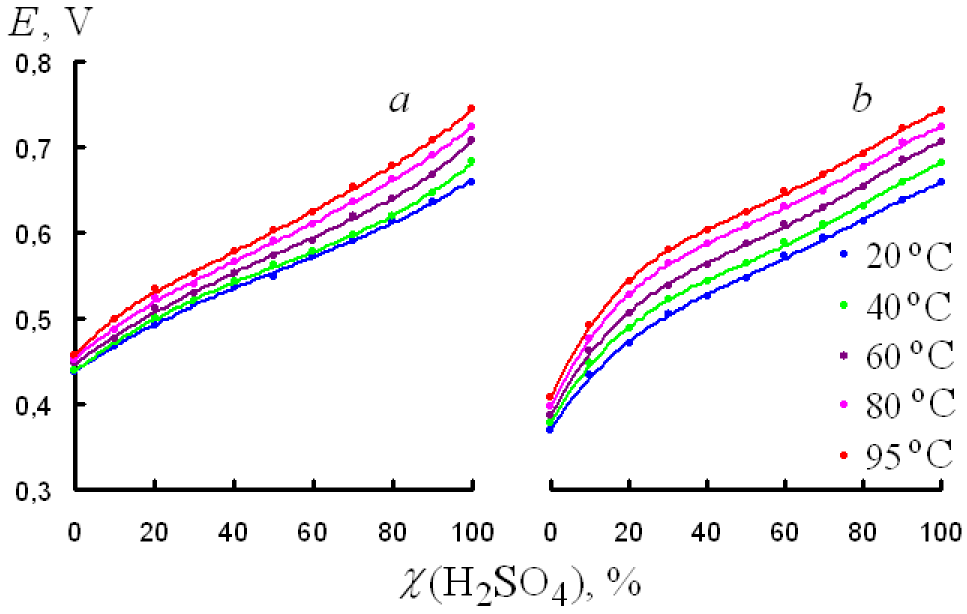

Figure 2. Potentials of a platinum electrode in argon-deaerated 2 M H_2SO_4 + H_3PO_4 (a) and 2 M H_2SO_4 + HF (b) solutions containing 0.05 M Fe(III) and 0.05 M Fe(II) depending on the H_2SO_4 molar fraction in acid mixtures at various temperatures.

As in the above systems based on H_2SO_4, in 2 M HCl + H_3PO_4 and 2 M HCl + HF containing 0.05 M Fe(III) and 0.05 M Fe(II) the oxidizing potential decreases with a decrease in the molar fraction of HCl (Figure 3). The strongest decrease in the oxidizing potential of the HCl + HF mixture is observed in solutions with a high molar fraction of HF. The same mixture is more sensitive to increasing *t*. For such a system containing 50% HCl of the total molar fraction of the acid in the mixture, an increase in *t* by 75°C increases the potential by 0.10 V, and in HCl + H_3PO_4 mixture, by 0.07 V.

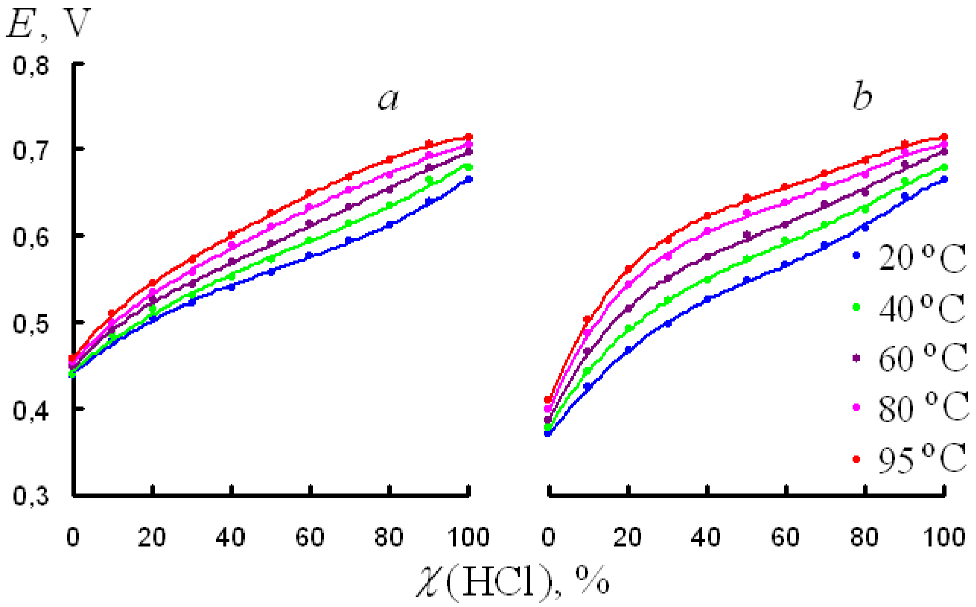

Figure 3. Potentials of a platinum electrode in argon-deaerated 2 M HCl + H_3PO_4 (a) and 2 M HCl + HF (b) solutions containing 0.05 M Fe(III) and 0.05 M Fe(II) depending on the HCl molar fraction in acid mixtures at various temperatures.

The difference in the values of platinum electrode potentials in 2 M H_3PO_4 and 2 M HF containing 0.05 M Fe(III) and 0.05 M Fe(II), depending on *t*, is 0.05–0.07 V. We expected a more significant effect of the addition of hydrogen fluoride, in comparison with phosphoric acid, on HCl and H_2SO_4 solutions containing Fe(III) and Fe(II). Our data show that these differences are significant only when the content of H_3PO_4 and HF additives in hydrochloric or sulfuric acid is high. Solutions in which the content of H_3PO_4 and HF additives is low are interesting from the practical point of view. There is no significant difference in oxidizing ability for such media. Taking into account the high toxicity of hydrofluoric acid additives and the lack of a significant difference in its action from H_3PO_4 in reducing the oxidizing ability of HCl and H_2SO_4 solutions containing Fe(III), it is more practically important to use inhibitor protection of steels in acidic solutions with addition of phosphoric acid.

The main regularities of changes in the oxidizing properties of binary compositions of acids containing Fe(III) and Fe(II) were revealed using the example of the HCl + H_3PO_4 mixture. A tenfold decrease in the content of the equimolar mixture of Fe(III) and Fe(II) in

1 M HCl + 1 M H_3PO_4 nearly does not affect the potential of the Pt electrode in this solution (Figure 4), which well agrees with the Nernst relationship of potential *versus* the ratio of active concentrations of the oxidized and reduced forms of a redox couple. Its small growth is observed (*ca*. by 0.02 V), which apparently results from the different capability of Fe(III) and Fe(II) cations to undergo complexation with phosphate and sulfate anions. This simultaneously and to a different extent decreases the content of free Fe(III) and Fe(II) cations in the solution. Conversely, variation of the Fe(III)/Fe(II) ratio in the acid mixture considerably affects the oxidizing ability of the system (Figure 5). An increase in the Fe(III)/Fe(II) ratio by 4 orders increases E by 0.19–0.22 V. In this case, the higher the Fe(III) content in the solution, the more considerably the potential of the Pt electrode grows with an increase in t. In fact, at $C_{Fe(III)} / C_{Fe(II)}$ = 0.01, an increase in solution temperature by 75°C increases $E_{Fe(III)/Fe(II)}$ by 0.05 V, while at $C_{Fe(III)}/C_{Fe(II)}$ = 100, by 0.08 V.

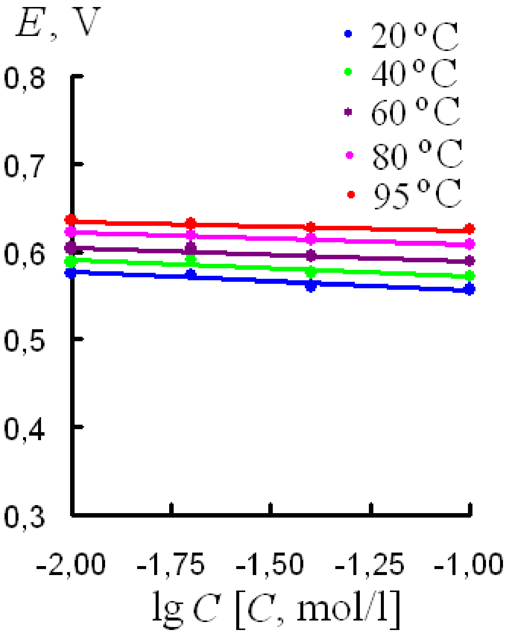

Figure 4. Potentials of a platinum electrode in argon-deaerated 1 M HCl + 1 M H_3PO_4 solutions containing an equimolar Fe(III) + Fe(II) mixture depending on the total concentration of Fe cations.

At a fixed content of the equimolar mixture Fe(III)+Fe(II) in solution, an increase in the content of the HCl+H_3PO_4 mixture (1:1) somewhat decreases the potential of a Pt electrode (Figure 6). An increase in the content of the acids mixture from 1 M to 4 M decreases E by 0.01–0.03 V. This is a result of more efficient binding of Fe(III) cations into complexes in their concentrated solutions.

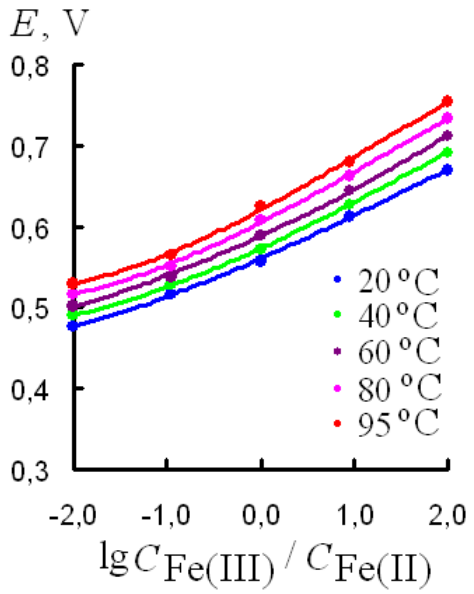

Figure 5. Potentials of a platinum electrode in argon-deaerated 1 M HCl + 1 M H_3PO_4 solutions containing an 0.1 M Fe(III) + Fe(II) mixture depending on the Fe(III) / Fe(II) concentration ratio.

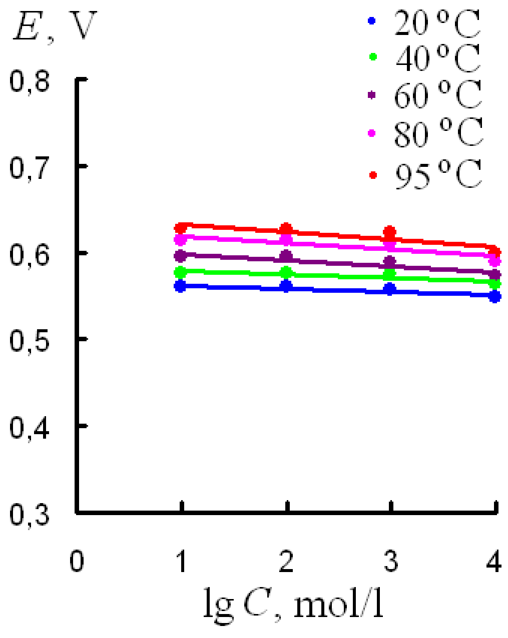

Figure 6. Potentials of a platinum electrode in argon-deaerated HCl + H_3PO_4 (1 : 1) solutions containing an 0.02 M Fe(III) + 0.02 M Fe(II) mixture depending on the total concentration of acids.

Experimental results on reducing the oxidizing ability of HCl and H_2SO_4 solutions containing Fe(III) by introducing H_3PO_4 additives explain our earlier data [3, 4] on inhibitory protection of mild steel in these media with the composition of a triazole derivative – IFKhAN-92, KNCS and urotropine (the molar ratio of the components is

9:1:400). In the case of the protection of steel in H_3PO_4 solution, this inhibitors composition is resistant to the accumulation of Fe(III) cations. On the contrary, in HCl or H_2SO_4 solutions containing Fe(III), the protective effect of this inhibitor is significantly reduced. The observed phenomenon is well explained by the fact that in phosphoric acid cations of Fe(III) are linked into stable complexes and have a lower oxidizing ability in comparison with HCl and H_2SO_4 solutions. The decrease in the oxidizing ability of the medium is sufficient for the inhibitor to exert a protective action against the corrosion of steel. The addition of H_3PO_4 to hydrochloric or sulfuric acid containing Fe(III) also reduces their oxidizing ability by binding Fe(III) cations to phosphate complexes. As a result, in these media, the protective effect of the composite inhibitor in the presence of Fe(III) salts is maintained at a high level up to 60% HCl or H_2SO_4 content of the total amount of the acid in the mixture.

We have shown that the oxidizing properties of solutions of acids containing Fe(III) salts are largely determined by the anionic composition of the solution. By affecting the anionic composition of the medium, for example, by creating acid mixtures, it is possible to significantly reduce $E_{\mathrm{Fe(III)/Fe(II)}}$ in them. As additives that reduce $E_{\mathrm{Fe(III)/Fe(II)}}$, acids should be used, the dissociation of which produces anions that firmly bind Fe(III) into complexes. These acids are HF and H_3PO_4. From a practical point of view, H_3PO_4 is most interesting. At low concentrations of H_3PO_4 in solution, it is comparable with HF in effectiveness of decreasing $E_{\mathrm{Fe(III)/Fe(II)}}$ and is not toxic as HF. Controlling the anionic composition of solutions of acids containing Fe(III) salts opens a way for regulating the protective properties of inhibitors in such media.

Conclusions

1. The oxidizing ability of 2 M acids solutions containing 0.05 M Fe(III) and 0.05 M Fe(II) decreases in the series: $HClO_4 > HBr > H_2SO_4 > HCl > H_3PO_4 > HF$. The observed effect in this series is the result of an enhancement of the ability of acid anions to bind Fe(III) cations into complex compounds that are less prone to reduction.
2. To reduce the oxidizing ability of acid solutions (HCl and H_2SO_4) with a weak ability of anions to bind Fe(III) cations into complexes, acids (H_3PO_4 and HF) that generate anions binding Fe(III) into stable and hardly reducible complexes should be added. The oxidizing ability of the H_2SO_4–H_3PO_4–H_2O, H_2SO_4–HF–H_2O, HCl–H_3PO_4–H_2O, and HCl–HF–H_2O systems containing Fe(III) and Fe(II) decreases as the relative content H_3PO_4 or HF, respectively, increases. The observed effect is the result of the formation of Fe(III) complexes with phosphate and fluoride anions, which are weaker oxidizing agents than the aqueous, sulfate and chloride complexes of Fe(III) cations. Analysis of the dependence of $E_{\mathrm{Fe(III)/Fe(II)}}$ in the systems studied on the anionic composition of the medium showed that H_3PO_4 is the most promising additive that reduces the oxidizing properties in HCl and H_2SO_4 solutions.
3. The main regularities of changes in the oxidizing properties of binary mixtures of acids containing Fe(III) and Fe(II) were revealed using the HCl + H_3PO_4 mixture as an

example. Variation in the total content of an equimolar Fe(III)+Fe(II) mixture (*C* = 0.01–0.10 M) in 1 M HCl + 1 M H_3PO_4 nearly does not affect its oxidative ability. Conversely, an increase in the relative content of Fe(III) in the system considerably increases its oxidative potential. At a fixed concentration of the Fe(III) + Fe(II) mixture in the system (0.04 M), addition of an equimolar mixture of HCl and H_3PO_4 (up to 4 M) somewhat decreases the oxidative properties of the system.

4. Addition of H_3PO_4 is an effective way to increase the protective effect of the composite inhibitor – IFKhAN-92 + KNCS + urotropine (9:1:400) on the corrosion of mild steel in HCl and H_2SO_4 solutions containing Fe(III). The observed effect is largely determined by binding of Fe(III) cations into phosphate complexes that have a lower oxidizing capacity than its water, sulfate and chloride complexes.

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References

1. Ya.G. Avdeev, O.A. Kireeva, Yu.I. Kuznetsov and I.G. Gorichev, *Korroz.: mater., zashch.*, 2016, no. 5, 27–35 (in Russian).
2. Ya.G. Avdeev, O.A. Kireeva, Yu.I. Kuznetsov and I.G. Gorichev, *Int. J. Corros. Scale Inhib.*, 2016, **5**, no. 4, 333–346. doi: 10.17675/2305-6894-2016-5-4-4
3. Ya.G. Avdeev, O.A. Kireeva, D.S. Kuznetsov and Yu.I. Kuznetsov, *Prot. Met. Phys. Chem. Surf.*, 2018, **54**, no. 7, 1298–1304. doi: 10.1134/S2070205118070055
4. Ya.G. Avdeev, O.A. Kireeva, D.S. Kuznetsov and Yu.I. Kuznetsov, *Korroz.: mater., zashch.*, 2018, no. 7, 22–28 (in Russian). doi: 10.31044/1813-7016-2018-0-7-22-28
5. Ya.G. Avdeev, M.V. Tyurina and Yu.I. Kuznetsov, *Korroz.: mater., zashch.*, 2014, no. 1, 18–25 (in Russian).
6. Ya.G. Avdeev, T.E. Andreeva and Yu.I. Kuznetsov, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 3, 366–375. doi: 10.17675/2305-6894-2018-7-3-7
7. Yu.Yu. Lurie, *Spravochnik po analiticheskoy khimii (Handbook of Analytical Chemistry)*, Khimiya, Moscow, 1971, pp. 255–265 (in Russian).
8. X. Zhu, D.K. Nordstrom, R.B. McCleskey, R. Wang and X. Lu, *Chem. Geol.*, 2017, **460**, 37–45. doi: 10.1016/j.chemgeo.2017.04.010
9. J.M. Casas, G. Crisóstomo and L. Cifuentes, *Hydrometallurgy*, 2005, **80**, no. 4, 254–264. doi: 10.1016/j.hydromet.2005.07.012
10. G. Yue, L. Zhao, O.G. Olvera and E. Asselin, *Hydrometallurgy*, 2014, **147–148**, 196–209. doi: 10.1016/j.hydromet.2014.05.008
11. H. Majima and Y. Awakura, *Metall. Trans. B*, 1985, **16**, 433–439.

12. M.M. Rakhimova, T.M. Nurmatov, N.Z. Yusupov, M.A. Ismailova and E. Faizullaev, *Russ. J. Inorg. Chem.*, 2013, **58**, no. 6, 719–723. doi: 10.1134/S003602361306020X
13. M.M. Rakhimova, N.Z. Yusupov, K.Dzh. Suyarov, K.G. Khasanova and Sh. Bekbudova, *Russ. J. Inorg. Chem.*, 2013, **58**, no. 8, 972–975. doi: 10.1134/S0036023613080196
14. V.A. Zakharov, O.A. Songina and G.B. Bekturova, *Zh. Anal. Khim.* 1976, **31**, no. 11, 2212–2221 (in Russian).
15. *Techniques of electrochemistry: Electrode Processes*, V. 1., Eds. E. Yeager and A.J. Salkind, John Wiley & Sons Inc., New York, 1972, 592 pp.
16. A.V. Kuzin, I.G. Gorichev and Yu.A. Lainer, *Russian Metallurgy (Metally)*, 2013, **2013**, no. 9, 652–657. doi: 10.1134/S0036029513090073

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