

Protection of nickel-chromium steel in sulfuric acid solution by a substituted triazole

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Abstract

The corrosion of 12Kh18N10T nickel-chromium steel in 2.0 M H₂SO₄ ($t = 20\text{--}100^\circ\text{C}$) was studied using mass loss, potentiometric, and polarization methods. It was shown that the corrosion resistance of this material in H₂SO₄ solutions is low, particularly at temperatures close to 100°C. Efficient steel protection in sulfuric acid solutions can be achieved using mixtures of IFKhAN-92 (a triazole derivative) with KI (molar ratio of the components 1 : 1), KBr (1 : 9), or KCNS (4 : 1) as corrosion inhibitors. Of the IFKhAN-92 formulations studied, the highest corrosion inhibition coefficients are provided by the equimolar mixture with KI, despite an antagonism in the action of its components. Decreasing the concentration of this formulation to 0.005–0.025 mM (depending on temperature) does not considerably decrease the protective effect. Mixed inhibitors based on the substituted triazole protect the metal in the acid solution for at least 8 h. The presence of the inhibitors being studied in the solution considerably increases the contribution of diffusion control to the corrosion process, as indicated by a significant decrease in the activation energy from 60 ± 1 to 35 ± 2 kJ/mol in the presence of these compounds. Steel corrosion occurs in the active dissolution region both in background and inhibited acid solutions. A correlation was noted between the free corrosion potential of steel (E_{cor}) in an acid solution containing an inhibitor and the protective effect of the latter (γ): the higher the γ value of the inhibitor, the more positive the potential of steel. The corrosion inhibition of stainless 12Kh18N10T steel in H₂SO₄ solutions by formulations based on IFKhAN-92 results from strong hindrance of electrode reactions on the metal by these compounds in a broad temperature range (up to 100°C). The strongest inhibition of electrode reactions on stainless steel is provided by the IFKhAN-92+KI mixture. As a result, it has the maximum efficiency in suppression of metal corrosion. A considerable effect on the characteristics of electrode reactions on stainless steel in background and inhibited acid solutions results from selective dissolution of metal surface components.

Keywords: *acid corrosion, corrosion inhibitors, stainless steel, triazoles.*

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Our previous studies [1] have shown that the corrosion resistance of nickel-chromium stainless steels in hydrochloric acid solutions is low. An efficient method to protect 12Kh18N10T stainless steel in these media at temperatures $t \leq 100^\circ\text{C}$ is to use a corrosion inhibitor of triazole class, namely, IFKhAN-92 or its formulation with urotropin.

Sulfuric acid solutions are yet another corrosive media where nickel-chromium steels have low corrosion resistance. These steels are resistant to corrosion only in very dilute H_2SO_4 solutions. A traditional method to enhance the corrosion resistance of this kind of steels in sulfuric acid solutions involves alloying with 2–3% Mo (up to 5–6% in some cases). The enhancement of corrosion resistance of these steels by molybdenum is attributed to preservation of the passive state in dilute acid solutions and a decrease in its dissolution rate in the active state [2, 3]. Nickel-chromium steels can be passivated in H_2SO_4 by adding an oxidant (*e.g.*, HNO_3) to the solution. As a result, the concentration and temperature ranges where the metal is corrosion-resistant are expanded considerably. Anodic protection is also used for steel passivation and corrosion resistance improvement in H_2SO_4 [2].

The use of organic corrosion inhibitors is an alternative method of nickel-chromium steel protection on H_2SO_4 solutions. Various derivatives of nitrogen-containing heterocycles, such as pyridine [4, 5], pyrimidine [6], diazoles [7, 8], and triazoles [9–11], are suggested for this purpose. Some of them (N-methyl-N'-pyridin-2-ylthiourea [5], 5-benzoyl-4,6-diphenyl-1,2,3,4-tetrahydro-2-thiopyridine [6], N-vinylimidazole [8], 1,2,3-benzotriazole [9], derivatives of triazoleisoquinoline [10] and 1,2,4-triazole [11]) can provide degrees of protection $Z > 90\%$ on stainless steels. It is noted in the case of hexadecylpyridinium bromide [4], N-methyl-N'-pyridin-2-ylthiourea, and a triazoleisoquinoline derivative that the protective effect decreases with an increase in temperature t . The protective effect is preserved in heated acid solutions only in the case of 1,2,3-benzotriazole and an 1,2,4-triazole derivative. Rather often, sulfur-containing organic compounds act as efficient corrosion inhibitors on nickel-chromium steels [5, 6, 12]. Attempts of some researchers to use various amino acids for protection of nickel-chromium steels [13, 14] should be considered unsuccessful, because Z is below 90% for these inhibitors. Unfortunately, only individual chemical compounds were used to create corrosion inhibitors for nickel-chromium steel in H_2SO_4 solutions, but the feasibility of enhancing their protective effect by various additives was not considered. We have shown previously [15] that creation of mixed inhibitors is a promising approach for corrosion protection of various steels in corrosive acidic media. For example, inhibiting formulations created on the basis of substituted triazoles protect low-carbon steel from corrosion in sulfuric acid solutions even under high-temperature conditions (up to 200°C) [16, 17].

It seems appropriate to create a series of mixed inhibitors based on a substituted triazole (IFKhAN-92 inhibitor) to protect 12Kh18N10T nickel-chromium stainless steel in H_2SO_4 solutions in a broad temperature range (up to 100°C). We studied KI, KBr, and KCNS, which enhance the protective effect of triazoles in corrosion of low-carbon steel in mineral acid solutions [18, 19], as additives to IFKhAN-92 inhibitor.

Experimental procedure

The corrosion rate of nickel-chromium 12Kh18N10T steel (composition, mass%: C up to 0.12; Si up to 0.8; Mn up to 2; Ni 9–11; S up to 0.02; P up to 0.035; Cr 17–19; Cu up to 0.3; Ti up to 0.5; Fe balance) in H₂SO₄ solutions was determined from the mass loss of specimens (at least three specimens per point) sized 25.0 mm × 25.0 mm × 1.0 mm, 50 ml of acid solution per specimen, in the temperature range of $t = 20\text{--}100^\circ\text{C}$. Prior to a test, specimens were cleaned on abrasive discs with varying grain size (finest grit P600) and degreased with acetone.

Solutions were prepared from H₂SO₄ of “chemically pure” grade and distilled water. The base concentration of individual and mixed inhibitors was $C_{\text{in}} = 5.0$ mM. The following additives enhancing the protective effect of IFKhAN-92 have been studied: KI (reagent grade), KBr (reagent grade), and KCNS (reagent grade). Due to the low solubility of IFKhAN-92, it was added to the acid solution as a solution in ethanol. The resulting ethanol concentration in the pickling solution did not exceed 1.2 mol/l.

The efficiency of inhibitors was estimated from the inhibition coefficient, $\gamma = k_0/k_{\text{in}}$, and the degree of protection $Z = [(k_0 - k_{\text{in}})/k_0] \cdot 100\%$, where k_0 and k_{in} are the corrosion rates in the non-inhibited solution and in the solution with the compound being studied, respectively.

In order to quantitatively estimate the effect of the additive on the inhibitor, the mutual influence coefficients of the mixture components were calculated [9]:

$$K_m = \frac{\gamma_{\text{mix}}}{\prod_{i=1}^m \gamma_i},$$

where γ_{mix} is the corrosion inhibition coefficient for the inhibitor mixture and $\prod_{i=1}^m \gamma_i$ is the product of the corrosion inhibition coefficients for individual mixture components. If $K_m < 1$, the protection coefficients of the inhibitor components are mutually reduced; at $K_m = 1$, they show an additive behavior; and only at $K_m > 1$ it should be concluded that the components of the inhibitor mixture mutually enhance protection.

Electrochemical measurements were carried out using a stationary electrode from 12Kh18N10T steel (5.0 mm × 5.0 mm × 1.0 mm) in a three-electrode thermally controlled glass cell (working solution volume 60 ml) with naturally aerated 2.0 M H₂SO₄. The steel electrode potentials were measured against a silver chloride electrode and converted to the normal hydrogen scale. Prior to each experiment, a steel electrode was cleaned with emery paper (P600 grit) and degreased with acetone. During a potentiometric study, a steel electrode was placed in a solution to be studied and the electrode potential was recorded at certain time intervals with an EL-02.061 potentiostat until the potential reached a constant value, but for no less than 2 h. To perform a voltammetric study, a potentiostat was used to record anodic and cathodic polarization curves at a dynamic potential scanning rate of

0.0005 V/s. The curves were recorded in 1, 30, and 120 min after a steel electrode was placed in the working solution.

Experimental results and discussion

Corrosion studies

Addition of 5.0 mM IFKhAN-92 to 2.0 M H₂SO₄ (60°C) slows down the corrosion of stainless 12Kh18N10T steel 2.2-fold (Table 1). Of the anionic additives studied (5.0 mM), the maximum protection was provided by I⁻, whereas Br⁻ and CNS⁻ inhibited corrosion much worse (the *k* value in the presence of Br⁻ and CNS⁻ was 18 and 31 times higher, respectively, than in the solution containing I⁻).

Table 1. Coefficients of 12Kh18N10T steel corrosion inhibition by the IFKhAN-92 + anion-active compound (KAn) formulation at $C_{\text{mix}} = 5.0$ mM and the mutual effects of the inhibitor mixture components in 2.0 M H₂SO₄ (60°C). Test duration: 2 h.

$C_{\text{IFKhAN-92}}$, mM	0.0	0.5	1.0	2.5	4.0	4.5	5.0
C_{KAn} , mM	5.0	4.5	4.0	2.5	1.0	0.5	0.0
KI							
k^* , g/(m ² ·h)	0.42	0.32	0.22	0.21	0.34	0.37	45
γ	240	310	460	480	290	270	2.2
K_m	–	0.59	0.87	0.91	0.55	0.51	–
KBr							
k , g/(m ² ·h)	7.4	1.0	2.3	2.4	4.7	7.9	45
γ	14	100	44	42	21	12	2.2
K_m	–	3.2	1.4	1.4	0.68	0.39	–
KCNS							
k , g/(m ² ·h)	13	1.9	1.3	1.2	1.0	1.6	45
γ	7.7	53	77	83	100	63	2.2
K_m	–	3.1	4.5	4.9	5.9	3.7	–

* The corrosion rate of 12Kh18N10T steel in 2.0 M H₂SO₄ at 60°C is 100 g/(m²·h).

The IFKhAN-92 + KI mixture shows the highest protective effects, despite the antagonism in the action of its components ($K_m = 0.51$ – 0.91). The maximum protective effect is shown by the formulation containing the components in equimolar ratio. The IFKhAN-92 + KBr mixture is less efficient, though it shows a synergism of the component effects at high Br⁻ concentrations in solution. The highest inhibition coefficient is observed in the mixture with 1 : 9 molar ratio of the components. Unlike the other mixtures, the

IFKhAN-92+KCNS formulation shows only synergistic action of the components ($K_m = 3.1–5.9$), whereas the maximum γ value is observed for the 4 : 1 component ratio.

The corrosion rate of 12Kh18N10T steel in 2.0 M H₂SO₄ increases with temperature (Table 2), whereas the k value increases 184-fold upon temperature increase by 80°C. Addition of 2.5 mM IFKhAN-92+2.5 mM KI decreases the k of steel 57- to 560-fold. An increase in temperature by 80°C in a solution inhibited with this mixture accelerates corrosion 24-fold. The 0.5 mM IFKhAN-92+4.5 mM KBr formulation slows down the corrosion of stainless steel 48- to 380-fold. With this mixture, the k value at 100°C is 24 times higher than at 20°C. The 4.0 mM IFKhAN-92+1.0 mM KCNS mixture slows down corrosion only 32- to 200-fold, while a t increase by 80°C increases the k value 72-fold. The temperature maxima of the γ coefficients for all the mixed corrosion inhibitors studied are observed at t values close to 80°C, which formally allows them to be considered as high-temperature inhibitors [20].

Table 2. Corrosion rates (k , g/(m²·h)), corrosion inhibition coefficients (γ) and steady-state potentials* (E_{cor} , V) of 12Kh18N10T steel in 2.0 M H₂SO₄ at various temperatures. Test duration: 2 h.

Inhibitor	k, γ	Temperature, °C				
		20	40	60	80	100
–	k	5.7	29	100	450	1050
	E_{cor}	–0.14	–0.12	–0.10	–0.08	–0.05
2.5 mM IFKhAN-92+ 2.5 mM KI	k	0.10	0.19	0.21	0.80	2.4
	γ	57	150	480	560	440
	E_{cor}	–0.05	–0.05	–0.04	–0.04	0.00
0.5 mM IFKhAN-92 + 4.5 mM KBr	k	0.12	0.58	1.0	1.2	2.9
	γ	48	50	100	380	360
	E_{cor}	–0.04	–0.07	–0.13	–0.05	–0.03
4.0 mM IFKhAN-92 + 1.0 mM KCNS	k	0.18	0.47	1.0	2.2	13
	γ	32	62	100	200	81
	E_{cor}	–0.11	–0.10	–0.09	–0.07	–0.07

*Steady-state E_{cor} values established after 2 h of electrode exposure to a solution.

Analysis of the temperature dependence of steel corrosion rate in H₂SO₄ using the Arrhenius equation allowed us to estimate the effective activation energies (E_a) of this process. The calculation was based on the analysis of the $\ln k - T^{-1}$ plot (Figure 1). In 2.0 M H₂SO₄, the effective activation energy of the corrosion process, E_a , amounts to 60 ± 1 kJ/mol, which indicates that the reaction occurs in a mixed kinetics zone. The

presence of mixed inhibitors in the solution based on the substituted triazole increases the contribution of the diffusion component to the process ($E_a = 35 \pm 2$ kJ/mol).

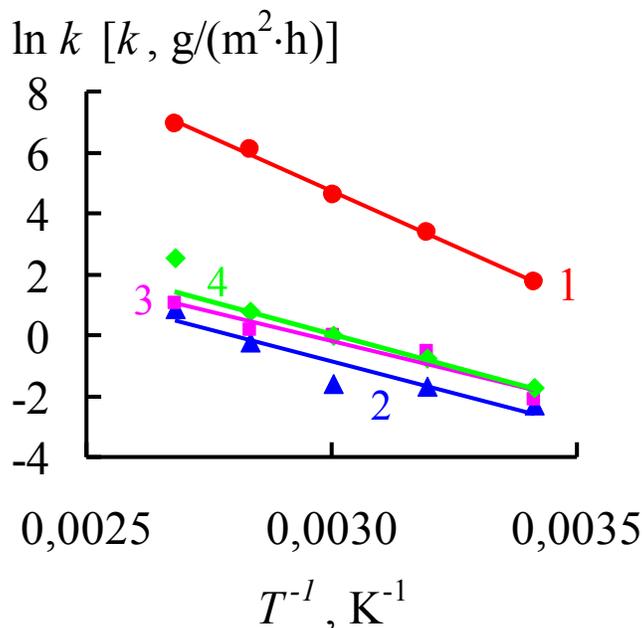


Figure 1. Dependence of $\ln k$ on T^{-1} for corrosion of 12Kh18N10T steel in 2.0 M H_2SO_4 (1) containing 2.5 mM IFKhAN-92 + 2.5 mM KI (2), 0.5 mM IFKhAN-92 + 4.5 mM KBr (3), or 4.0 mM IFKhAN-92 + 1.0 mM KCNS (4).

The corrosion rate of 12Kh18N10T steel in 2.0 M H_2SO_4 ($t = 60^\circ C$) systematically increases with time during at least 8 hours (Table 3). In this case, the k value found from 8-hour tests is 2.1 times higher than the corrosion rate calculated from 0.5-hour corrosion tests. In the presence of the most efficient mixture, *i.e.*, IFKhAN-92 + KI, the k_{in} value decreases after 0.5 h of the test and then remains stable for at least 2–8 h, while $k_{in} \leq 0.5$ g/($m^2 \cdot h$). The IFKhAN-92 + KBr and IFKhAN-92 + KCNS formulations are somewhat inferior to it, with $k_{in} \leq 1.8$ and 1.2 g/($m^2 \cdot h$), respectively. In the presence of these mixtures, corrosion gradually accelerates for 4 h and then slows down to some extent.

The Z – C plots for mixed inhibitors based on IFKhAN-92 in H_2SO_4 solutions for the steel being studied are Γ -shaped (Figure 2). Decreasing the C of the IFKhAN-92 + KI formulation (equimolar mixture) from 10 mM to 0.005–0.025 mM (depending on t) does not considerably decrease its Z . A similar concentration range for the IFKhAN-92 + KBr formulation (1 : 9) is from 10 to 0.05–0.25 mM. This range is the narrowest, *viz.*, 10 to 0.25–0.5 mM, in the case of the IFKhAN-92 + KCNS formulation (4:1). Probably, these parts of the curves correspond to the regions of the maximum surface coverage by the inhibitor. At lower concentrations of the mixed inhibitors in solution, a considerable loss of their protective effect is observed, even up to corrosion stimulation. The higher the solution temperature, the higher the C_{in} where it loses its protective action considerably. In this case, the Z values observed in the C_{in} range corresponding to the maximum coverage

of the metal surface by the inhibitor are higher where the temperature of the H_2SO_4 solution is higher.

Table 3. Corrosion rates of 12Kh18N10T steel (k , $g/(m^2 \cdot h)$) and coefficients of corrosion inhibition (γ) in 2.0 M H_2SO_4 by formulations of IFKhAN-92 at various exposure times. $t = 60^\circ C$.

Inhibitor	k, γ	Specimen exposure times				
		0.25	0.5	1	4	8
–	k	71	72	76	130	150
2.5 mM IFKhAN-92+	k	0.40	0.50	0.30	0.20	0.20
2.5 mM KI	γ	180	144	250	650	750
0.5 mM IFKhAN-92 +	k	0.83	0.92	0.95	1.8	1.4
4.5 mM KBr	γ	86	78	80	72	110
4.0 mM IFKhAN-92 +	k	0.85	1.0	1.1	1.2	1.0
1.0 mM KCNS	γ	84	72	69	110	150

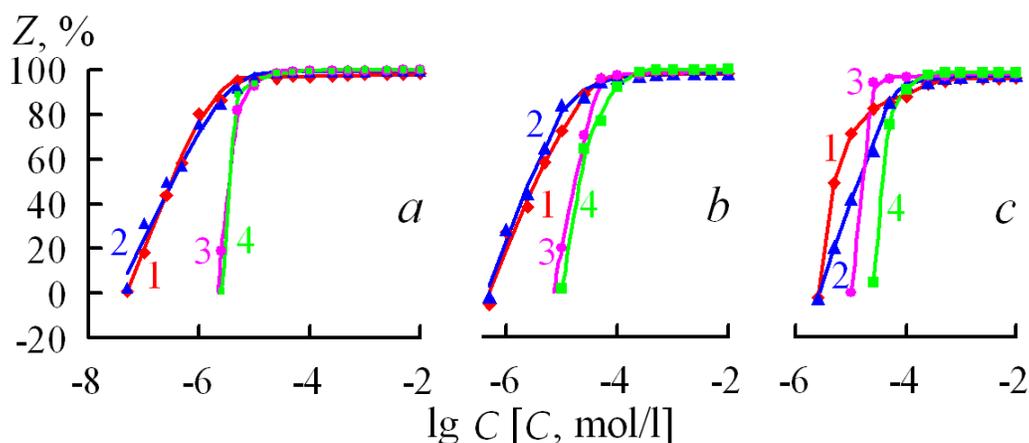


Figure 2. Dependence of the protective effect of IFKhAN-92 + KI formulation (1 : 1) (a), IFKhAN-92 + KBr formulation (1 : 9) (b), and IFKhAN-92 + KCNS formulation (4 : 1) (c) on concentration for corrosion of 12X18H10T steel in 2.0 M H_2SO_4 at various temperatures, $^\circ C$: 20 – 1, 40 – 2, 60 – 3, 80 – 4. Test duration: 2 h.

The reason of the stimulating effect of low C_{in} values on the corrosion of steels in mineral acid solutions was discussed in detail in our previous paper [21], namely, the nitrogen-containing organic compounds decrease the solution surface tension, thus facilitating the removal of hydrogen bubbles from the metal surface, while the electrode reactions are only slightly hindered by the inhibitor.

Thus, a series of inhibitor formulations, namely IFKhAN-92 + KI (molar component ratio 1 : 1), IFKhAN-92 + KBr (1 : 9), and IFKhAN-92 + KCNS (1 : 1), have been

developed. They provide the protection of 12Kh18N10T steel in H_2SO_4 solutions in a wide temperature range. The proposed formulations ensures metal corrosion inhibition in the acid solution for at least 8 h.

Electrochemical studies

The corrosion potentials (E_{cor}) of 12Kh18N10T steel in background 2.0 M H_2SO_4 solution ($t = 20–100^\circ C$) indicate that metal corrosion occurs in the active dissolution region (Figure 3, Table 2). The E_{cor} value increases with time to reach a steady value in no more than 100 min. It is only at $t = 100^\circ C$ that a steady potential is established at once. In this case, its value is higher than the steady E_{cor} values for steel observed at lower temperatures. The increase in E_{cor} noted above may be due to unhindrance of the cathodic process and/or inhibition of the anodic reaction.

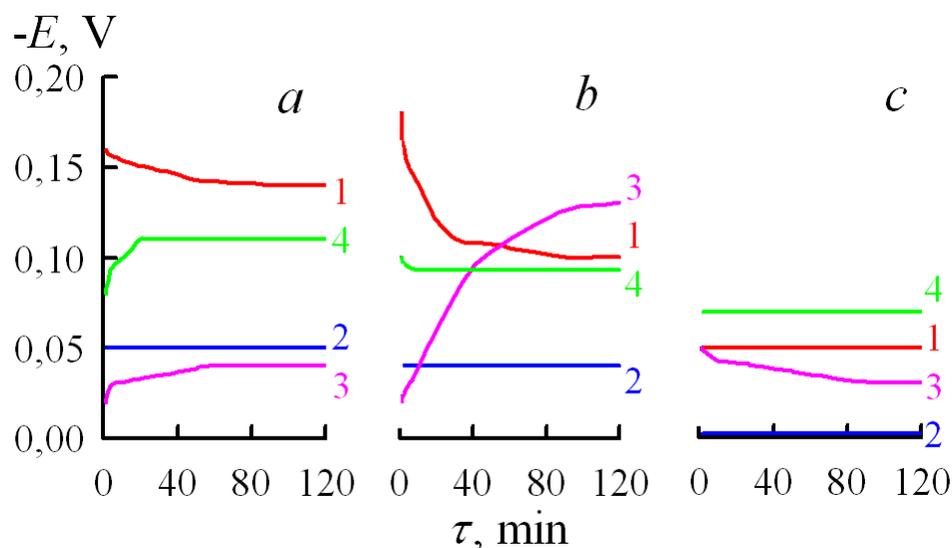


Figure 3. Dependence of corrosion potential of 12Kh18N10T steel in 2.0 M H_2SO_4 (I) on time at various temperatures, $^\circ C$: 20 – *a*; 60 – *b*; 100 – *c*. Curves 2 – with addition of 2.5 mM IFKhAN-92 + 2.5 mM KI; 3 – with addition of 0.5 mM IFKhAN-92 + 4.5 mM KBr; and 4 – with addition of 4.0 mM IFKhAN-92 + 1.0 mM KCNS.

In H_2SO_4 solutions inhibited by 2.5 mM IFKhAN-92 + 2.5 mM KI, like in background solutions, corrosion of 12Kh18N10T steel occurs in the region of active steel dissolution, but the E_{cor} values are more positive, which indicates that this inhibitor preferentially slows down the anodic reaction of the metal. The E_{cor} values do not change in time. An increase in E_{cor} with a temperature rise is noted. Decreasing the C of the IFKhAN-92 + KI mixture (1 : 1) in H_2SO_4 solution at $20^\circ C$ decreases the efficiency of steel protection (Figure 4a). In parallel, E_{cor} of steel decreases to become comparable to the value in the background solution at $C_{in} \leq 5 \cdot 10^{-6}$ M. In total, a correlation between E_{cor} of steel in inhibited acid solution and the protective effect of the inhibitor is evident: the higher the γ value of the inhibitor, the more positive the steel potential. At $t = 80^\circ C$, a more positive E_{cor} of steel than in the background solution in acid solutions inhibited by the IFKhAN-92 + KI mixture

is observed at $C_{in} \geq 2.5 \cdot 10^{-5}$ M (Figure 4b). Decreasing the inhibitor concentration below this value decreases γ and E_{cor} of steel to the values observed in the background solution. Like at $t = 20^\circ\text{C}$, a correlation between E_{cor} of steel and γ is observed in the inhibited acid solution.

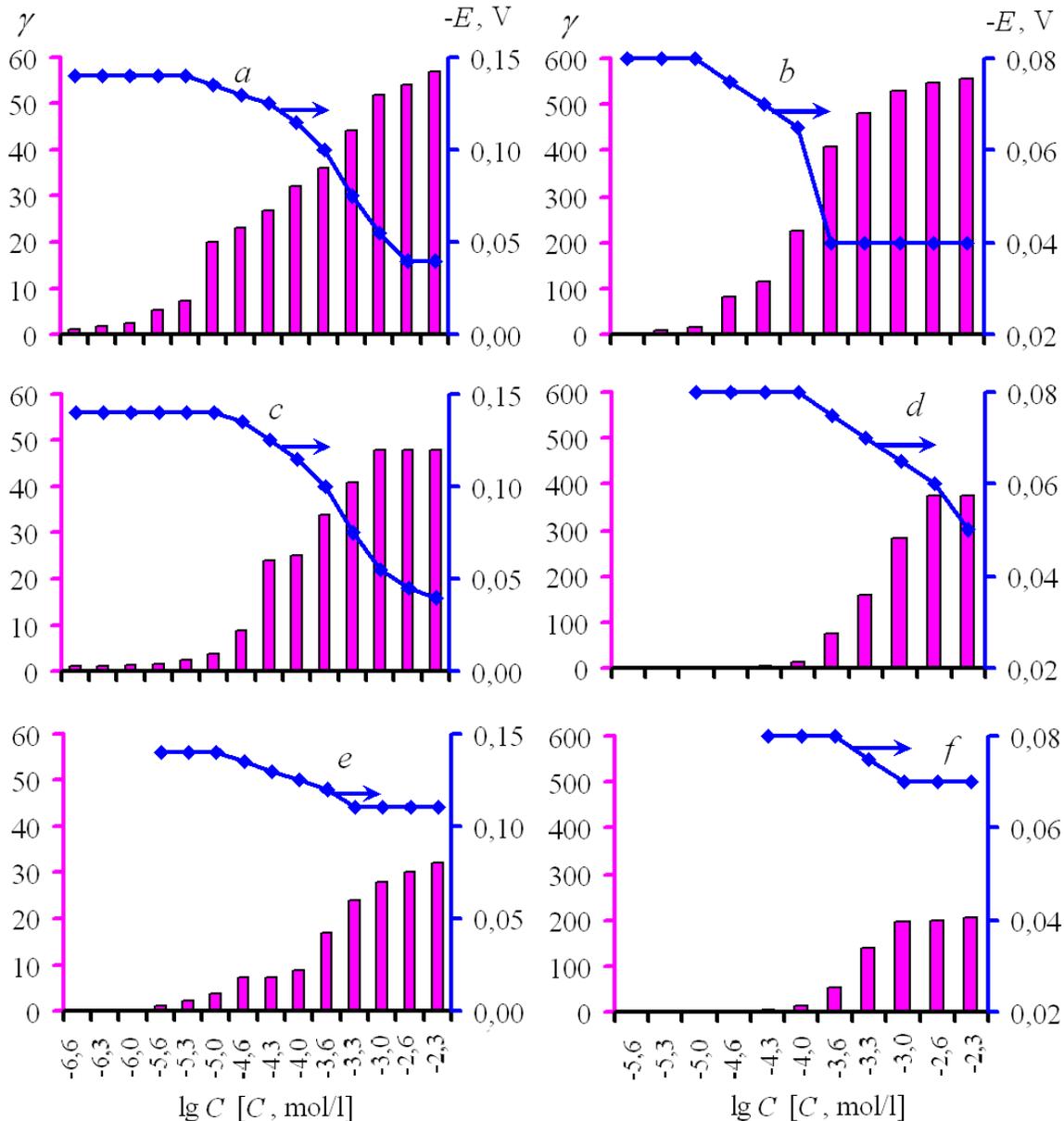


Figure 4. Corrosion potentials of 12Kh18N10T steel in 2.0 M H_2SO_4 and corrosion inhibition coefficients by the IFKhAN-92 + KI formulation (1 : 1) (*a, b*), by the IFKhAN-92 + KBr formulation (1 : 9) (*c, d*), and by the IFKhAN-92 + KCNS formulation (4 : 1) (*e, f*) at various inhibitor concentrations in the solution at various temperatures, $^\circ\text{C}$: 20 – *a, c, e*; 80 – *b, d, f*.

In the presence of 0.5 mM IFKhAN-92 + 4.5 mM KBr, the potential of nickel-chromium steel in the acid solution is in the active dissolution range. A temperature increase to 60°C decreases E_{cor} , but the latter increases at higher temperatures. The

decrease in E_{cor} at 60°C is so significant that it becomes more negative than the background value. In a solution inhibited by 0.5 mM IFKhAN-92+4.5 mM KBr, E_{cor} decreases with time, which may be due to stronger inhibition of the cathodic process on the metal by the mixture and/or weaker inhibition of the anodic process. It is only at $t = 100^\circ\text{C}$ that E_{cor} increases with time.

In the H_2SO_4 solution containing 4.0 mM IFKhAN-92+1.0 mM KCNS, like in all the other cases, the steel is in the active dissolution range. At $t \leq 80^\circ\text{C}$, this inhibitor preferentially inhibits the anodic process and/or accelerates the cathodic one, judging by the more positive E_{cor} values in comparison with the background solution. The E_{cor} value increases with temperature.

A correlation between the plots of γ and E_{cor} versus C_{in} is observed for the IFKhAN-92+KBr (1:9) and IFKhAN-92+KCNS mixtures (4:1), like for the mixture with KI (Figure 4c–f), with the only exception that lower γ values are observed and the difference between the E_{cor} values in the background solution and in the inhibited solution is somewhat smaller.

More comprehensive information about the processes that occur on stainless steel surface in H_2SO_4 , both in the absence and in the presence of the inhibitors in question, can be obtained by studying the regularities of the electrode reactions occurring in the system.

As a rule, the cathodic polarization slopes of stainless steel in 2.0 M H_2SO_4 background solution (Figs. 5–7, Table 4) are close to the values observed for an individual alloy component, nickel (0.12 V), whereas the anodic polarization slopes are close to the values typical of iron (0.04 V) [22]. Increasing the exposure time of the steel electrode accelerates the cathodic reaction, which is due to surface enrichment with nickel which has a lower hydrogen evolution overvoltage than the other alloy components, *viz.*, Cr and Fe. As noted previously [23], Ni has a lower dissolution rate at E_{cor} of chromium steels in H_2SO_4 than Cr or Fe and can be accumulated on steel surface. Since Ni has a lower hydrogen evolution overvoltage than chromium steel, accumulation of Ni on the surface shifts E_{cor} in the positive direction, as shown for the corrosion of 25Cr6NiTi steel in H_2SO_4 .

In background solutions, the anodic polarization curves (PCs) have a complex shape that is an overall result of the anodic ionization and passivation of the alloy components. Since the metal surface is selectively dissolved with time in acid solutions, the shape of anodic PCs recorded on steel changes. The anodic reaction can become either slower or faster in the course of time. Most probably, these effects also result from enrichment or depletion of the metal surface in nickel content, *i.e.*, the alloy component which is most resistant to dissolution.

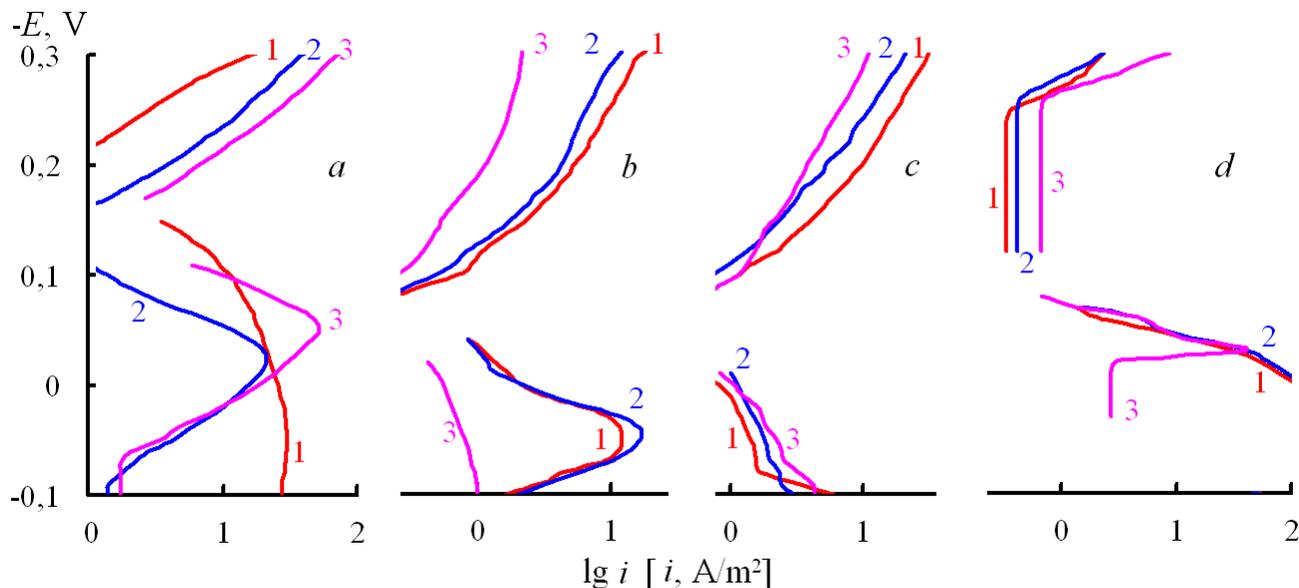


Figure 5. Polarization curves on 12Kh18N10T steel at $t = 20^\circ\text{C}$ in 2.0 M H_2SO_4 (a) with addition of 2.5 mM IFKhAN-92 + 2.5 mM KI (b), 0.5 mM IFKhAN-92 + 4.5 mM KBr (c) and 4.0 mM IFKhAN-92 + 1.0 mM KCNS (d). Time of preliminary electrode exposure to the solution, min: 1 – 1, 30 – 2, 120 – 3.

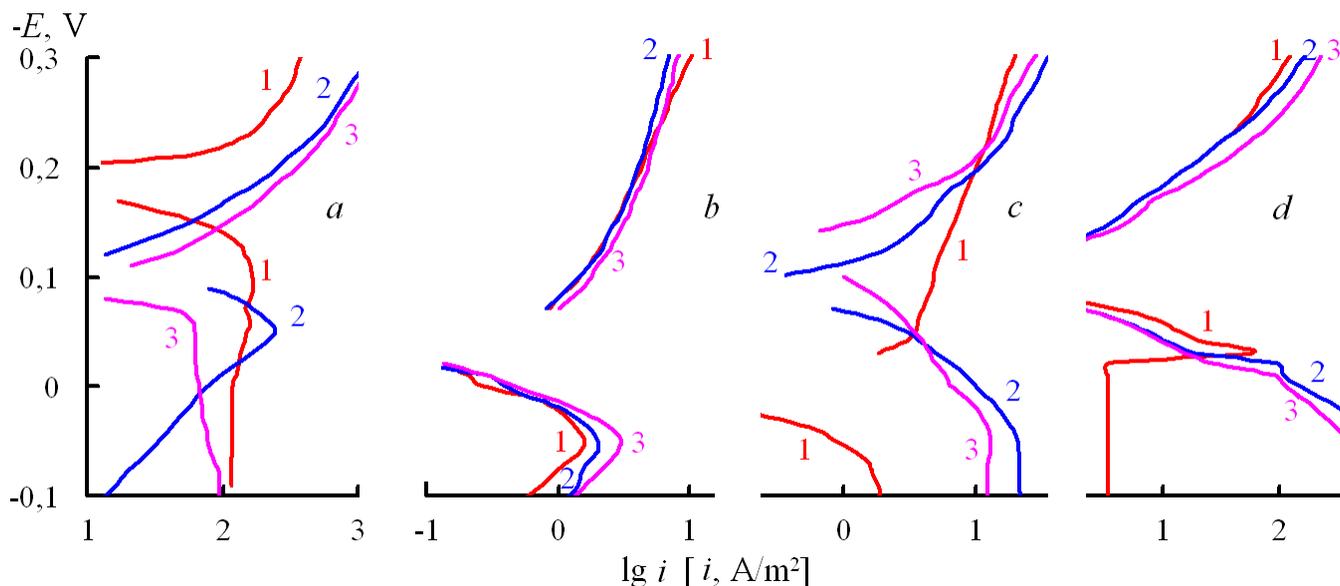


Figure 6. Polarization curves on 12Kh18N10T steel at $t = 60^\circ\text{C}$ in 2.0 M H_2SO_4 (a) with addition of 2.5 mM IFKhAN-92 + 2.5 mM KI (b), 0.5 mM IFKhAN-92 + 4.5 mM KBr (c) and 4.0 mM IFKhAN-92 + 1.0 mM KCNS (d). Time of preliminary electrode exposure to the solution, min: 1 – 1, 30 – 2, 120 – 3.

Thus, an increase in E_{cor} of steel with time in background solutions can mainly be due to metal surface enrichment with Ni, which results in acceleration of the cathodic reaction and inhibition of the anodic one.

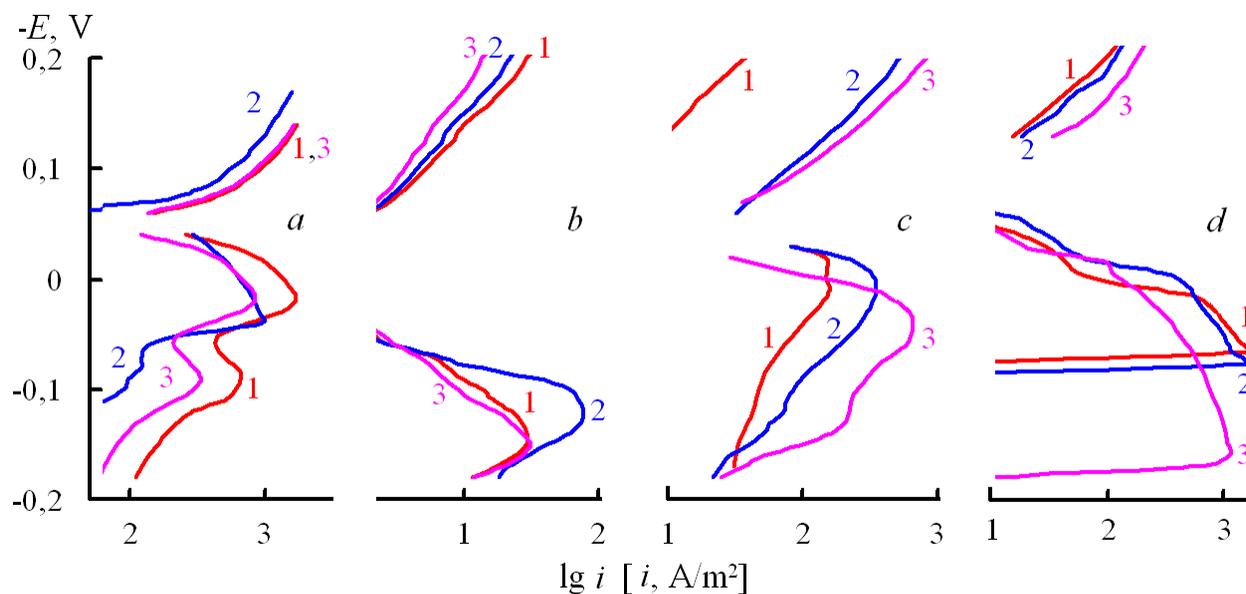


Figure 7. Polarization curves on 12Kh18N10T steel at $t = 100^\circ\text{C}$ in 2.0 M H_2SO_4 (a) with addition of 2.5 mM IFKhAN-92 + 2.5 mM KI (b), 0.5 mM IFKhAN-92 + 4.5 mM KBr (c) and 4.0 mM IFKhAN-92 + 1.0 mM KCNS (d). Time of preliminary electrode exposure to the solution, min: 1 – 1, 30 – 2, 120 – 3.

In general, addition of IFKhAN-92 based formulations to an H_2SO_4 solution considerably hinders the electrode reactions on steel in the entire temperature range studied. In hot solutions, the strongest inhibition of both electrode reactions on steel is provided by the IFKhAN-92 + KI mixture. This is the reason of the very strong corrosion inhibition shown by mass loss measurements. The cathodic PCs in the presence of IFKhAN-92 formulation can have a limiting diffusion current region that is typical of inhibitors that form polymolecular protective layers on a metal surface.

It should be noted that anodic PCs on stainless steel in inhibited acid solutions have a complex shape determined not only by ionization and passivation of alloy components, but also by the effect of the inhibitor on these processes. Like in the background solution, the shape of anodic PCs changes due to selective dissolution of stainless steel surface components with time.

Thus, efficient corrosion inhibition of stainless 12Kh18N10T steel in H_2SO_4 solutions by formulations based on IFKhAN-92 results from strong hindrance of electrode reactions on the metal by these compounds in a broad temperature range (up to 100°C). The strongest inhibition of electrode reactions can be reached using the IFKhAN-92 + KI mixture. A considerable effect on the characteristics of electrode reactions on stainless steel in background and inhibited acid solutions results from selective dissolution of metal surface components that enriches the surface with Ni.

Table 4. Free corrosion potentials (E_{cor}), Tafel slopes b_c and b_a , cathodic and anodic current densities (i_c and i_a), and inhibition coefficients for the cathodic and anodic reactions (γ_c and γ_a) of 12Kh18N10T steel in 2.0 M H_2SO_4 as a function of electrode exposure time (τ) at $E_c = -0.25$ V (20–60°C) or -0.15 V (100°C) and $E_a = 0.05$ V (20–60°C) or 0.00 V (100°C).

Inhibitor	τ , min	E_{cor} , V	b_c , V	b_a^* , V	i_c , A/m ²	i_a , A/m ²	γ_c	γ_a
20°C								
–	1	–0.16	0.10	0.07	2.7	18.7	–	–
	30	–0.15	0.12	0.04	13.7	12.0	–	–
	120	–0.14	0.12	0.04	31.3	43.7	–	–
2.5 mM IFKhAN-92 + 2.5 mM KI	1	–0.05	0.13	0.10	10.0	0.67**	0.27	28
	30	–0.05	0.13	0.10	6.7	0.67**	2.0	18
	120	–0.05	0.17	i_d^{***}	1.8	0.40**	17	109
0.5 mM IFKhAN-92 + 4.5 mM KBr	1	–0.02	0.12	i_d	18.3	0.63	0.15	30
	30	–0.04	0.14	i_d	11.2	0.79	1.2	15
	120	–0.04	0.16	i_d	6.8	1.0	4.8	44
4.0 mM IFKhAN-92 + 1.0 mM KCNS	1	–0.08	i_d	0.04	0.37	6.0	7.3	3.1
	30	–0.11	i_d	0.04	0.41	7.2	33	2.6
	120	–0.11	i_d	0.04	0.67	7.3	47	6.0
60°C								
2.5 mM IFKhAN-92 + 2.5 mM KI	1	–0.18	0.12	0.04	222	150	–	–
	30	–0.11	0.12	0.04	648	245	–	–
	120	–0.10	0.12	0.04	739	62.3	–	–
0.5 mM IFKhAN-92 + 4.5 mM KBr	1	–0.04	i_d	0.04	6.7	0.010**	33	15000
	30	–0.04	i_d	0.04	5.5	0.013**	118	12000
	120	–0.04	i_d	0.04	6.4	0.016**	115	3900
4.0 mM IFKhAN-92 + 1.0 mM KCNS	1	–0.02	i_d	0.04	14.0	–	16	–
	30	–0.08	0.12	0.10	20.8	2.8	31	88
	120	–0.13	0.12	I_d	16.6	3.3	45	19
2.5 mM IFKhAN-92 + 2.5 mM KI	1	–0.10	0.10	0.04	59.0	14.0	3.8	11
	30	–0.09	0.10	0.04	68.3	7.3	9.5	34
	120	–0.09	0.10	0.04	110	6.7	6.7	9.3

Inhibitor	τ , min	E_{cor} , V	b_c , V	b_a^* , V	i_c , A/m ²	i_a , A/m ²	γ_c	γ_a
100°C								
–	1	–0.05	0.12	0.04	1871	1408	–	–
	30	–0.05	0.12	0.12	1278	658	–	–
	120	–0.05	0.12	0.04	1871	700	–	–
2.5 mM IFKhAN-92 +	1	0.00	0.12	0.08	13.5	0.63**	139	2200
2.5 mM KI	30	0.00	0.14	0.04	10.6	0.063**	121	10000
	120	0.00	0.16	0.08	7.4	0.79**	253	890
0.5 mM IFKhAN-92 +	1	–0.05	0.10	0.04	13.7	150	137	9.4
4.5 mM KBr	30	–0.04	0.10	0.04	227	340	5.6	1.9
	120	–0.03	0.10	0.04	327	153	5.7	4.6
4.0 mM IFKhAN-92 +	1	–0.07	0.10	0.05	35.3	56.7	53	25
1.0 mM KCNS	30	–0.07	0.10	0.05	43.3	302	30	2.2
	120	–0.07	0.15	0.05	93.3	112	20	6.3

* b_a values determined for the first linear section of anodic polarization curve.

** The data are found by extrapolating the first linear segment of the E , $\log i_a$ curve to $E = 0.05$ V (20–60°C) or 0.00 V (100°C).

*** i_d is the limiting diffusion current.

Conclusions

- Mixed inhibitors containing a triazole derivative (IFKhAN-92) combined with KI, KBr, or KCNS have been suggested. They offer a more efficient protection of 12Kh18N10T steel in H₂SO₄ solutions in a broad temperature range, $t = 20$ – 100 °C. Of the inhibiting formulations studied, the highest corrosion inhibition coefficients are provided by the equimolar IFKhAN-92 + KI mixture.
- At $t = 20$ – 100 °C, corrosion of 12Kh18N10T steel in H₂SO₄ solution, both in the absence and in the presence of IFKhAN-92 based formulations, occurs in the region of mixed diffusion–kinetic control. If the inhibitors being studied are present in the solution, the contribution of diffusion control increases, as indicated by a decrease in the process activation energy in the presence of these compounds.
- Corrosion of 12Kh18N10T steel in the H₂SO₄ solutions studied, including those inhibited by mixtures based on IFKhAN-92, occurs in the active dissolution region. Mixtures of IFKhAN-92 with KI, KBr, or KCNS slow down the electrode reactions on 12Kh18N10T steel in H₂SO₄ solution in a broad temperature range (up to 100°C), which determines the efficiency of these inhibitors in corrosion suppression.

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