

The inhibitive effects of 8-mercaptoquinoline and its iron chelate complex in the acid corrosion of iron in 1 M HCl

V. P. Grigor'ev,¹ E. V. Plekhanova,¹ E. E. Verbitskaya and L. D. Popov¹

¹ Southern Federal University, ul. Zorge 7, Rostov-on-Don, 344090 Russia

E-mail: valentgrig@mail.ru

Abstract

The inhibitive effect of a 8-hydroxyquinoline derivative (**1**) and the corresponding Fe²⁺ chelate (**2**) in the corrosion of Fe in 1 M HCl was studied. The adsorption mechanism of these compounds was considered and the post-treatment effect of these compounds was studied. An increase in the concentration of compounds **1** and **2** increases corrosion inhibition for all the compounds studied. The residual protective effect of chelates is much higher than that of the corresponding ligands. The results that we obtained were interpreted in terms of organic compounds – metal surface interactions.

Key words: corrosion, inhibitor, iron, chelates, residual protective effect.

Received: June 26, 2014.

doi: [10.17675/2305-6894-2014-3-4-215-226](https://doi.org/10.17675/2305-6894-2014-3-4-215-226)

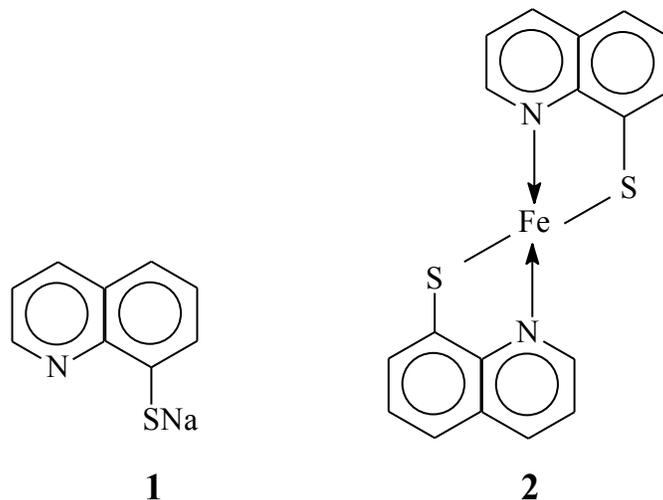
The use of metal chelates as corrosion inhibitors is very promising because they are usually poorly soluble, highly adsorbable, and have high coverage capacity due to the formation of a chelate structure containing several molecules of the original inhibitor as ligands. These factors enhance the inhibitive properties of the complex and strengthen the complex–metal surface bonds. The latter factor should also prolong the post-treatment effect (residual protective effect of the inhibitor) when a pre-inhibited metal is transferred to a noninhibited corrosive environment [1, 2].

Earlier, 8-mercaptoquinoline derivatives were tested as inhibitors of the acid corrosion of some metals. Their inhibitive effect is associated with the formation of insoluble chelate complexes between the corrosion products of metals (Fe, Cu, cast iron, etc.) and the 8-mercaptoquinoline molecules that cover the surface of a corroding metal, thus preventing access to the corrosive environment [3, 4]. We found it interesting to compare the protection mechanisms of 8-mercaptoquinoline itself and its chelate complex with a corroding metal. In the latter case, the chelate used as an inhibitor is a preformed complex (in contrast to previous tests where a chelate complex was formed during metal corrosion).

Experimental

Corrosion tests were carried out using iron band specimens (1×1.25 cm) containing the following impurities, %: P 0.035; C 0.12; S 0.045; Cr 0.15; Ni 0.2; Mn 0.45; Si 0.005; Mg 0.05.

The inhibitive effects of 8-mercaptoquinoline (inhibitor 1) and its bischelate complex (inhibitor 2) on iron corrosion in 1 M HCl were studied.



The inhibitor concentration was varied from 1 to 23 mg/l.

Complex **2** was synthesized from commercial sodium quinoline-8-thiolate and iron perchlorate by refluxing their equimolar mixture in methanol as described in [5, 6]. Elemental analysis data for complex **2** agree with those calculated from its molecular formula.

1 M HCl solution was prepared from concentrated HCl (reagent grade) and distilled water.

Samples of the inhibitors and the test electrodes were weighed on a VPR-200 analytical balance. The inhibitor was dissolved with continuous stirring and gentle heating. Solutions with lower inhibitor concentrations were prepared by successive dilution of the initial solution.

Prior to corrosion tests, iron specimens were degreased with ethanol, then by boiling for 5 min in a solution of NaOH (15 g/l), Na₃PO₄ (40 g/l), and Na₂SiO₃ (4 g/l), washed with running tap water and distilled water, and dried with filter paper.

Corrosion tests were carried out in a VB-2 water bath at 20–60°C.

For each test, at least three parallel measurements were made. Then the specimens were withdrawn, washed with distilled water, and dried with filter paper.

The protective effect was estimated by calculating the inhibition factor (1)

$$K = \frac{\Delta m}{\Delta m_{\text{inh}}}, \quad (1)$$

where Δm and Δm_{inh} are the mass losses of the electrodes due to corrosion in blank and inhibited acids, respectively, over time t .

The effective activation energy of corrosion W was determined from the linear temperature dependence of the corrosion current j by formula (2):

$$W = -2.3R \tan \alpha, \quad (2)$$

where $\tan\alpha$ is the slope of the $\log j-1/T$ plot.

The post-treatment periods τ of inhibitors **1** and **2** were determined as follows. Weighed and degreased iron specimens were kept in inhibited HCl solutions for 24 h. Then the specimens were withdrawn, rinsed with distilled water, dried with filter paper, reweighed, and immersed in a blank solution (1 M HCl). The mass losses of the specimens over time t (from 3 to 24 h) were determined. After the specified time t elapsed, the specimens were withdrawn. The post-treatment factor was calculated by formula (3)

$$K = \frac{\Delta m_{0,\tau}}{\Delta m_{\text{inh},\tau}}, \quad (3)$$

where $\Delta m_{0,\tau}$ and $\Delta m_{\text{inh},\tau}$ are the mass losses over time t from the instant the iron electrodes were immersed in blank solutions (for non-treated and inhibitor pre-treated specimens, respectively).

When an inhibited electrode was exposed to a blank 1 M HCl solution, the inhibitor became partially desorbed from the surface, thus lowering the inhibition factor. Complete desorption of the inhibitor corresponds to $K_t = 1$ and $t = \tau$.

The τ value was determined by extrapolating the K_t-t plots to $K_t = 1$.

Capacitance measurements were carried out in a temperature-controlled three-electrode cell using a P-5021 AC bridge. The electrodes were mirror-polished with glass dust.

A cylindrical platinum electrode served as the auxiliary electrode. Electrolytic hydrogen was bubbled for 20 min through the solution contained in the cell. The capacitance was measured at frequencies of 1 and 20 kHz and at a free corrosion potential versus SCE as the reference electrode when the capacitor and the resistor were connected in series. The experimental capacitance was converted to the parallel circuit scheme by formula (4):

$$C_p = C_{\text{exp}} / (1 + (R_{\text{exp}} - R_0)^2 \omega^2 C_{\text{exp}}^2), \quad (4)$$

where C_{exp} and R_{exp} are the measured capacitance and resistance, respectively, R_0 is the resistance of the solution at the frequency $f = 20$ kHz, and $\omega = 2\pi f$ is the angular frequency.

The electrode surface coverage with the inhibitor was calculated by formula (5):

$$\theta = (C_0 - C_{\text{inh}}) / C_0, \quad (5)$$

where C_0 and C_{inh} are the capacitances of the double electrical layer (DEL) in the blank and inhibited solutions, respectively.

Results and discussion

The results of the corrosion tests are given in Table 1. According to the data obtained, compounds **1** and **2** inhibit the corrosion of iron in hydrochloric media.

The K value increases with an increase in inhibitor concentration from 1 to 23 mg/l. Corrosion at higher inhibitor concentrations was not studied because $C \approx 23$ mg/l corresponds to its saturated solution. The jump in K_2 (K for inhibitor **2**) with an increase in the inhibitor concentration from 11 to 23 mg/l probably suggests that the adsorption patterns of additives **1** and **2** become different at these C values (this will be confirmed below by their adsorption isotherms).

Table 1. Dependences of the inhibition factor K on the concentrations of inhibitors 1 and 2 for iron corrosion in 1 M HCl at 20°C.

K for inhibitors 1 and 2	C , mg/l				
	23	11	6	3	1
K_1	8.1	7.0	6.3	5.3	5.3
K_2	15.0	5.3	3.2	2.7	1.9
K_2/K_1	1.85	0.76	0.51	0.51	0.36

The inhibition factors of compounds **1** and **2** (K_1 and K_2 , respectively) do not differ largely in the concentration range from 1 to 11 mg/l for each concentration studied. The low concentrations of the inhibitors and the inhomogeneous adsorbing surface of the iron electrode (see the adsorption isotherms below) seem to cancel out the structural difference between inhibitors 1 and 2, which results in comparable K_1 and K_2 values and similar dependences $K = f(C)$ (see Table 1).

Nevertheless, the chelate structure of inhibitor **2** has a dominating effect on K_2 that increases with the volume concentration of the inhibitor more rapidly than K_1 . As a result, the ratio $K_2/K_1 < 1$ observed at low concentrations of these inhibitors increases with C to $K_2/K_1 > 1$ at $C = 23$ mg/l. Therefore, the presence of a chelate structure favors the inhibition of the acid corrosion of iron.

By measuring corrosion currents at various temperatures and using the Arrhenius equation, we calculated the effective energy of activation W of iron corrosion in a blank solution and in solutions containing various concentrations of additives **1** and **2**. The W values are given in Table 2.

Table 2. Effective energies of activation W (kJ/mol) of iron corrosion in inhibited HCl

C , mg/l	1	3	6	11	23
Inhibitor 1	58.93	81.12	89.90	98.64	153.39
Inhibitor 2	67.57	69.22	70.01	77.20	205.44

At $C = 0$ (blank solution), W is 58.0 kJ/mol. In the concentration range from 0 to 11 mg/l, W increases with C . Note that the W values in the presence of inhibitor **1** are somewhat higher than those for inhibitor **2**, the difference being not very large at equal concentrations.

At $C = 23$ mg/l, W increases abruptly: by 54.75 kJ/mol (from 153.39 to 98.64 kJ/mol) for inhibitor **1** and by 129.24 kJ/mol (from 205.44 to 77.20 kJ/mol) for inhibitor **2**. The difference in ΔW between chelate complex **2** and the simple inhibitor **1** is 129.24 kJ/mol – 54.75 kJ/mol = 74.49 kJ/mol.

In the general case, the inhibition of acid corrosion of metals by organic compounds is mainly due to shielding of the metal surface (the blocking or θ -effect) and to changes in the DEL structure (chiefly caused by changes in the ψ' potential). The blocking component K_θ was estimated from the differential DEL capacitance measured using the model of two parallel capacitors and converted to a parallel circuit.

The θ values calculated by formula (5) are given in Table 3. One can see that θ increases with concentration for both inhibitors **1** and **2**.

By comparing the temperature-kinetic and capacitance data, one can interpret the gravimetric results. The low K values at low concentrations of the additive are probably due to its low surface coverage and insignificant effect on the corrosion activation energy.

The partial inhibition factor K_θ due to the blocking factor was calculated by formula (6)

$$K_\theta = 1/(1 - \theta) \quad (6)$$

and that due to the activation factor $K_{\psi'}$, under the assumption that $K \approx K_\theta \times K_{\psi'}$ [7, 8]. The results obtained are given in Table 3. One can conclude that the blocking effect is decisive in the protection of iron by compounds **1** and **2**.

Table 3. Concentration dependences of the surface coverage θ , total inhibition factor K , and partial inhibition factors K_θ and $K_{\psi'}$ for inhibitors **1** (a) and **2** (b) in iron corrosion in 1 M HCl.

a					b				
C, mg/l	θ	K_θ	K	$K_{\psi'}$	C, mg/l	θ	K_θ	K	$K_{\psi'}$
23	0.86	7.09	8.1	1.14	23	0.92	12.35	15.0	1.22
11	0.84	6.13	7	1.14	11	0.80	4.93	5.3	1.08
6	0.82	5.43	6.3	1.16	6	0.68	3.08	3.2	1.04
3	0.76	4.24	5.3	1.25	3	0.57	2.34	2.7	1.15
1	0.72	3.68	5.3	1.44	1	0.43	1.76	1.9	1.08

By linearizing the θ – C plots using appropriate functional nomographs in the first concentration range (1–11 mg/l), we found that the adsorption of inhibitor **1** obeys the Temkin isotherm characteristic of an inhomogeneous surface with uniform distribution of adsorption sites over adsorption energies (Fig. 1) and that adsorption of inhibitor **2** obeys

the Freundlich isotherm (b) characteristic of an inhomogeneous surface with exponential distribution of adsorption sites over adsorption energies (Fig. 2).

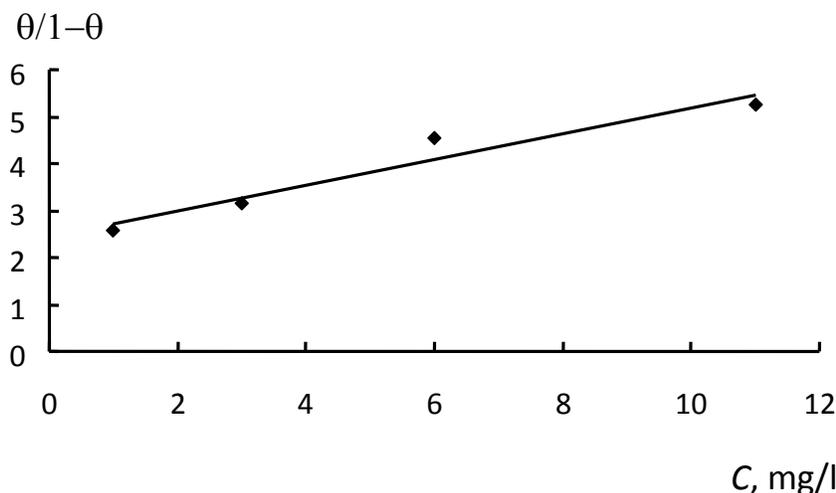


Figure 1. Plot of θ vs. C in the Temkin isotherm coordinates for inhibitor 1.

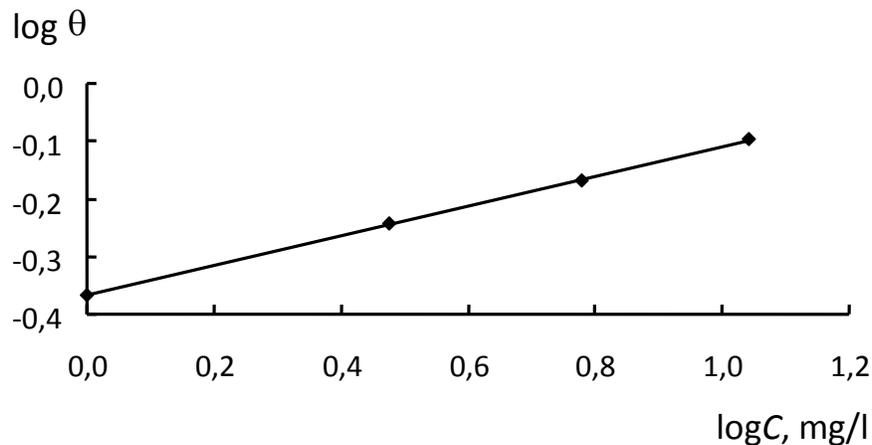


Figure 2. Plot of θ vs. C in the Freundlich isotherm coordinates for inhibitor 2.

Our subsequent study dealt with the post-treatment of organic inhibitors on iron corrosion in hydrochloric acid after transferring a specimen from an inhibited solution with a constant concentration of an additive from a blank solution of HCl. As the additive desorbs, the inhibition factor K_t monotonically decreases with t (the time of exposure of the iron specimen to the HCl solution). When K_t reaches 1, it means that $t = \tau$ (the post-treatment period). The post-treatment phenomenon is of great practical importance for determination of the period during which a pre-applied adsorption film of an inhibitor maintains its protective effect.

According to experimental data, K_t depends on the inhibitor concentration in the preadsorption bath and the time of exposure t of a specimen to the blank and inhibited solutions. K_t decreases with an increase in t (Figs. 3, 4), so K_t could be extrapolated to $K = 1$ to determine the post-treatment period τ of the organic additive for its different concentrations used for preliminary adsorption. The results obtained are given in Table 4. The higher the concentration of the additive, the longer its post-treatment period τ .

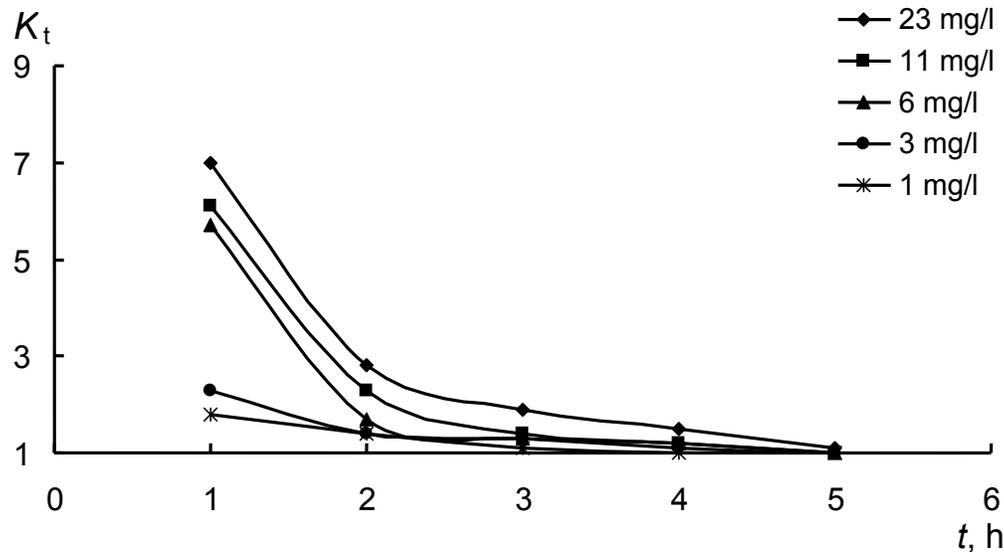


Figure 3. Plots of the post-treatment factor K_t of inhibitor 1 vs. time t for different inhibitor concentrations in the preadsorption bath.

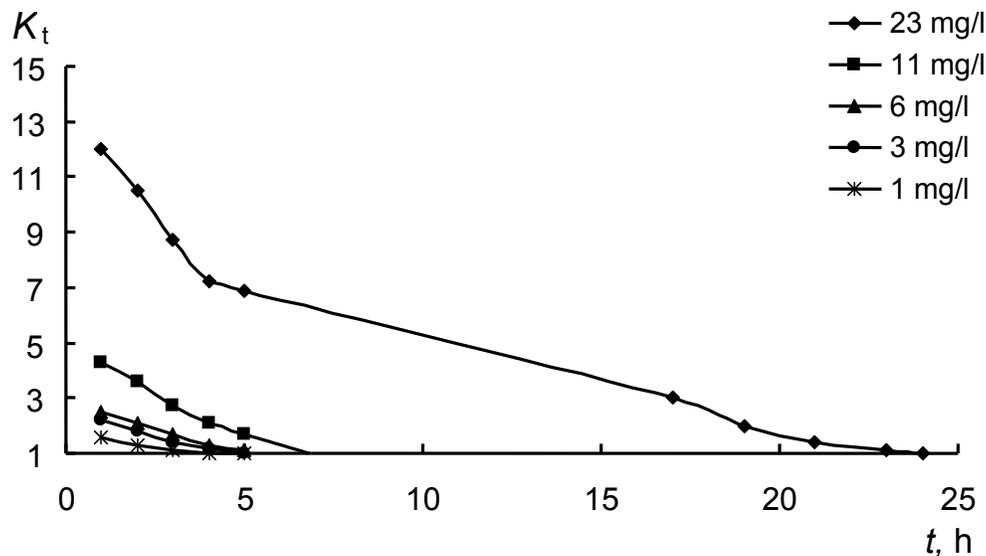
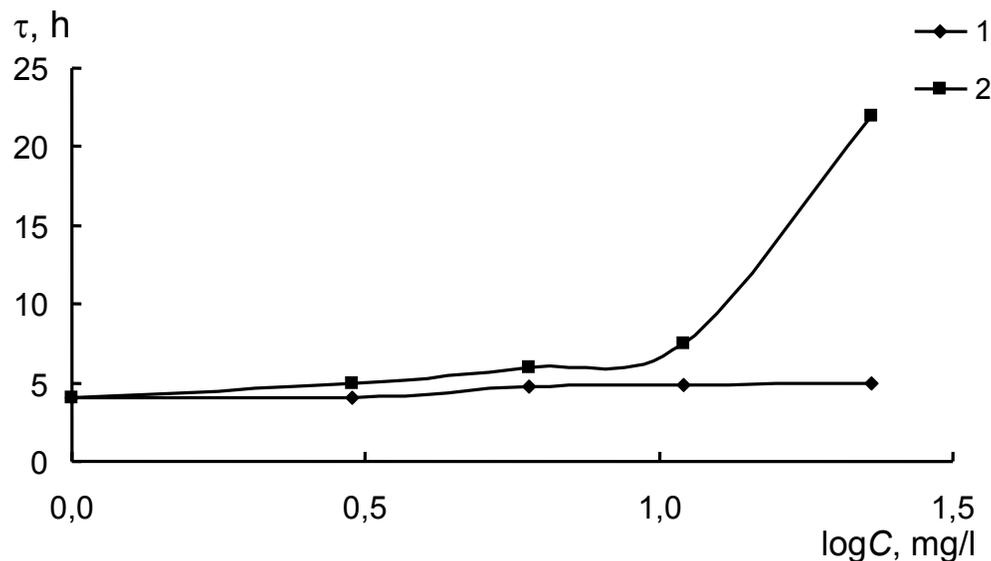


Figure 4. Plots of the post-treatment factor K_t of inhibitor 2 versus time t for different inhibitor concentrations in the preadsorption bath.

Table 4. Dependences of the post-treatment periods τ (h) of inhibitors **1** and **2** on their concentration in the preadsorption bath for iron corrosion in 1 M HCl.

Inhibitor	Inhibitor concentration, mg/l				
	23	11	6	3	1
1	5.00	4.90	4.80	4.00	4.00
2	24.00	7.50	6.00	5.00	4.00

The decrease in K_t with time t (exposure time of iron specimens to the blank solution) can be attributed only to desorption of surfactant molecules from the electrode surface. An increase in the concentration of the inhibitor enhances its adsorption and, consequently, increases the surface concentration of the preadsorbed film which is responsible for the post-treatment protective effect. The post-treatment period of inhibitor **1** linearly increases with the logarithm of its concentration and is described by the equation $\tau = a + b \log C$ (Fig. 5). A more complicated pattern observed for inhibitor **2** can probably be due to a different adsorption isotherm of inhibitor **2** compared to inhibitor **1**.

**Figure 5.** Plots of the post-treatment period of inhibitors **1** and **2** for the corrosion of iron in 1 M HCl versus their concentrations in the preadsorption bath.

The data obtained allow one, under certain assumptions, to get information on the change in the near-electrode inhibitor concentration upon its partial desorption from the electrode surface. One can assume under certain limitations that the dependence of the inhibition factor on the bulk (near-electrode) inhibitor concentration under steady-state conditions ($C = \text{const}$, $K \neq f(t)$) is much the same as that for non-steady-state conditions ($K_t = f(t)$, $C = f(t)$).

By combining the $K = f(C)$ plot (the inhibition factor as a function of the bulk or, which is the same, near-electrode concentration C_s of the inhibitor) with the $K_t = f(t)$ plot obtained in post-treatment tests, one can determine C_s from $K_t = K$ for the instant t in post-treatment tests (*i.e.*, for non-steady-state diffusion conditions). Figure 6 displays C_s-t plots for various inhibitor concentrations used for preliminary adsorption. One can see that the C_s of inhibitor **1** drops more abruptly at the initial point (corresponding to the immersion of the electrode in a blank solution) than C_s of inhibitor **2**. In addition, $C_s \approx 0$ for inhibitor **1** is achieved in a shorter period of time (2 h) compared to inhibitor **2** (~ 7.5 – 22 h, depending on the inhibitor concentration in the preadsorption bath).

This provides additional evidence that the adsorptivity of inhibitor **2** is higher than that of inhibitor **1**.

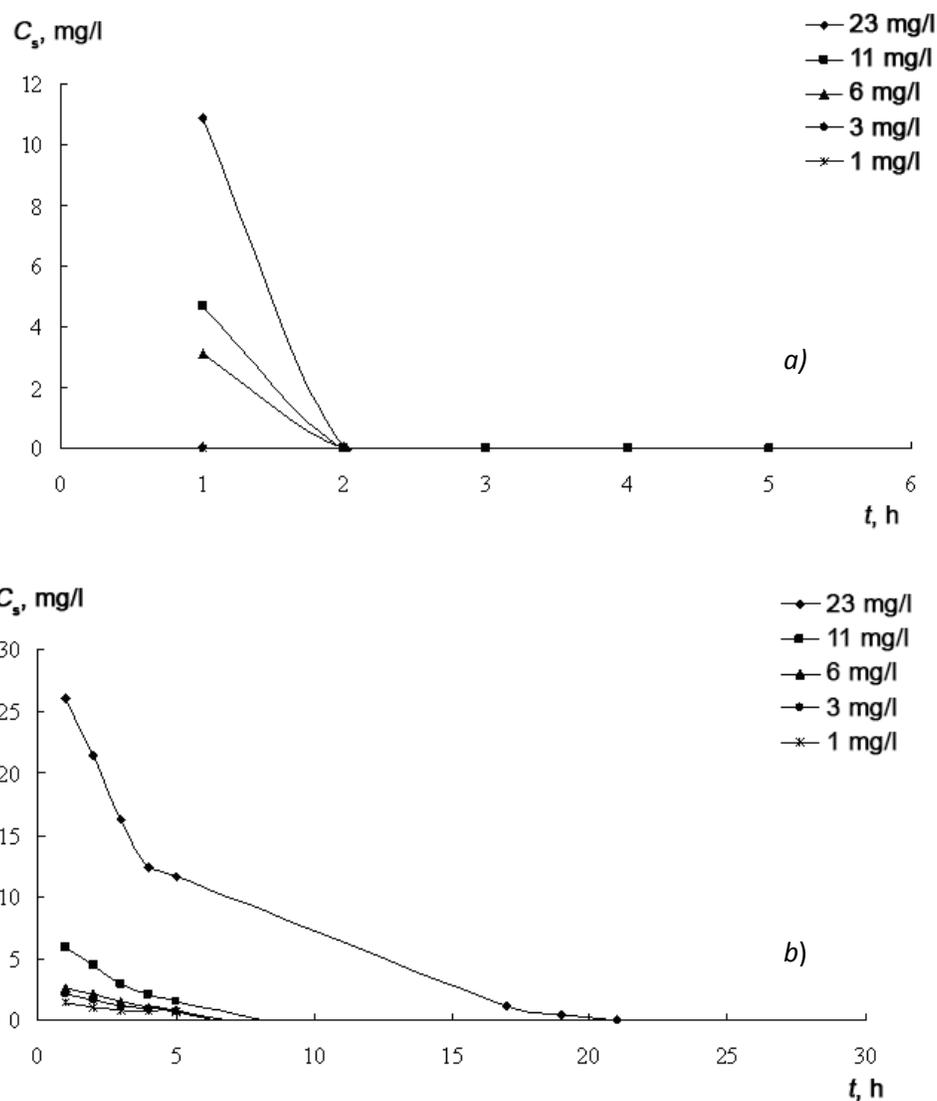


Figure 6. Time dependences of the near-electrode concentrations of inhibitors **1** (a) and **2** (b) for an iron electrode exposed to 1 M HCl after preliminary adsorption of the inhibitors ($C = 1$ – 23 mg/l) for 24 h.

It is expedient to discuss the aforementioned experiment from two standpoints:

1. Comparison of the inhibitive effects of inhibitor **1** and related chelate complex **2** on iron corrosion in inhibited solutions under steady-state conditions ($C_s = \text{const}$, $K = \text{const}$, $K \neq f(t)$).
2. Comparison of the post-treatment effects of these compounds under non-steady-state diffusion conditions ($C_s \neq \text{const}$, $K \neq \text{const}$, $K = f(t)$).

According to our experimental data, both the additives proved to be good inhibitors under the former conditions. Their K values are very close and, with allowance for a number of corrosion assumptions, may be regarded as nearly equal over the concentration range from 1 to 11 mg/l. This is largely attributable to the structures of inhibitors **1** and **2**.

Both inhibitors contain coplanar fused benzene and pyridine rings which upon adsorption seem to face the surface of the iron electrode. At low concentrations, when adsorbed molecules of these inhibitors are spaced far apart and do not interact with each other, their protective properties mainly depend on the fused rings of inhibitors **1** and **2**, although their adsorption isotherms for iron can differ, which is in fact observed experimentally. Under these conditions (low concentrations), the nature of the chelate structure is not crucial for K that is predominantly determined by the areas of the fused rings.

Apparently, inhibitor **1** dissociates to give H^+ and the corresponding anion. This prevents it from forming complex **2** with Fe^{2+} ions, contrary to the expectations. This can be inferred from the fact that inhibitor **2** cannot be prepared by mixing equimolar volumes of aqueous solutions of inhibitor **1** and an iron salt. Mixing does not produce a precipitate of the expected chelate complex (complex **2** is known to be poorly soluble). Inhibitor **2** can be obtained only by mixing nonaqueous solutions of the above starting reagents. This fact can be explained by the formation of hydrated iron ions ($\text{Fe}^{2+} \times \text{H}_2\text{O}$). Their hydration energy in aqueous solutions should be much higher than their solvation energy in nonaqueous media because the energy increases with an increase in the dielectric constant of the solution. Therefore, the solvation shell around the Fe^{2+} ion is more labile than its hydration shell and can be broken to form the corresponding chelate. This is the case when nonaqueous solutions of the aforementioned starting components are mixed, *i.e.*, these conditions are thermodynamically favorable for the formation of covalent (S–Fe–S) and coordination bonds (N→Fe←N) in the corresponding chelate complex with 8-mercaptoquinoline based ligands.

Hence, under steady-state conditions, both inhibitors act as normal adsorption-type inhibitors; their protective effects increase with concentration. At $C \approx 23$ mg/l, the role of the chelate structure becomes more significant and the adsorbed molecules are attached more firmly to the metal surface. As a result, the K of inhibitor **2** increases sharply. For inhibitor **1**, the trends of increasing K should seemingly remain unchanged and so should the pattern of the K – C plot.

This surprising fact can be explained, in terms of the aforesaid reasoning, by hydration of Fe^{2+} ions (produced by iron corrosion) in the near-electrode layer. The concentration of water in this layer is thus decreased to such a level that the resulting Fe^{2+} hydrates have more labile hydration shells than the analogous hydrates in the solution bulk. The lower energy level of “near-electrode” hydrates allows Fe^{2+} ions to form complexes with 8-mercaptoquinoline molecules (inhibitor **2**). Because of this, the K – C plots for inhibitors **1** and **2** virtually coincide at $C = 11$ – 23 mg/l.

Obviously, the nature of the metal center in chelate complexes will greatly influence their inhibition factors K , which calls for further investigations in this area.

In post-treatment effect tests, the difference in the protective effects of inhibitors **1** and **2** is more pronounced. The post-treatment period τ of compound **1** is much shorter than that of chelate complex **2** (see Fig. 6). As noted above, both inhibitors show nearly equal K_θ values under steady-state diffusion conditions, mainly because they are close in surface coverage θ .

The desorption rates of inhibitors **1** and **2** and hence the τ values will primarily depend on the strength of the bonds between their adsorption films and the iron electrode surface. The weaker these bonds, the more the surfactant molecules desorbed in a given time and the more K_t is lower than K . That is why ${}_1K \approx {}_2K$ for $t = 0$ when the initial surface coverages of both additives are equal. In post-treatment effect tests, ${}_1K_\tau < {}_2K_\tau$ at time τ because inhibitor **2** is attached to the iron surface more firmly than inhibitor **1**. As a result, the number of desorbed molecules of inhibitor **2** is lower, and hence $\tau_2 > \tau_1$.

The latter can probably be explained by physical adsorption that is most characteristic of additive **1** (electrostatic interactions of the positively charged iron surface with the π -electrons of the double bonds and the lone electron pairs of the N and S atoms of inhibitor **1**). The presence of a chelate structure in additive **2** makes it possible to involve new covalent and coordination bonds in partial interactions with the surface atoms of iron being protected. Inhibitor **2** thus becomes more strongly attached to the iron surface and, consequently, $\tau_2 > \tau_1$ (as well as ${}_1K_\tau < {}_2K_\tau$ for a given τ).

This seems to be the reason why the post-treatment periods of chelate complexes should be expected to be longer than those of organic compounds like ligand **1** (see Fig. 6). For iron specimens pretreated with inhibitors **1** and **2** ($C = 23$ mg/l), we obtained $\tau_1 \approx 2$ h and $\tau_2 \approx 24$ h.

Conclusions

1. We obtained new experimental data on the protective effects and post-treatment effects of a 8-hydroxyquinoline derivative (**1**) and its chelate complex with Fe^{2+} (**2**) on the corrosion of iron in 1 M HCl. An increase in the concentration of both inhibitors **1** and **2** enhances their protective effects. We found that the low inhibition factors K in the first concentration range is due to their low surface coverage θ as well as to only a slight change in the corrosion activation energy (ΔW).

2. The adsorption of inhibitor **1** obeys the Temkin isotherm characteristic of an inhomogeneous surface with uniform distribution of adsorption sites over adsorption energies. The adsorption of inhibitor **2** obeys the Freundlich isotherm characteristic of an inhomogeneous surface with exponential distribution of adsorption sites over adsorption energies.
3. The post-treatment period τ is a linear function of the inhibitor concentration in the preadsorption bath.
4. The post-treatment effects of the chelate complexes are much higher than those of the corresponding ligands.

References

1. V. P. Grigor'ev, S. P. Shpan'ko, V. V. Boginskaya and E. V. Plekhanova, *Fiz.-Khim. Poverkhn. Zashch. Mater.*, 2010, no. 1, 88 (in Russian).
2. V. P. Grigor'ev, E. V. Plekhanova, A. S. Burlov, I. S. Vasil'chenko and T. A. Kuz'menko, *Korrozi.: Mater. Zashch.*, 2012, no. 11, 12 (in Russian).
3. V. V. Dobrovol'skaya, T. G. Neznamova and V. P. Barannik, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1966, no. 1, 144 (in Russian).
4. Yu. A. Blankovsky, *Khimiya vnutrikompleksnykh soedinenii merkaptokhinolina i ego proizvodnykh (The Chemistry of Chelate Complexes of Mercaptoquinoline and Its Derivatives)*, Riga, Zinatis, 1978 (in Russian).
5. T. Miyate, T. Yshida, D. Hashizume, F. Jwaski and T. Nogan, *Polyhedron*, 2001, **20**, 1551.
6. P. W. Bohn and R. S. Bottei, *J. Therm. Anal. Calorim.*, 1978, 13, no. 2, 231.
7. L. I. Antropov, *Zashch. Met.*, 1977, 13, no. 4, 387 (in Russian).
8. L. I. Antropov, E. M. Makushin and V. F. Panasenko, *Ingibitory korrozii metallov (Inhibitors of Metal Corrosion)*, Kiev, Tekhnika, 1981 (in Russian).

