Corrosion of iron in 1 M HCl solutions containing benzhydrazide derivatives with two terminal adsorption groups as additives

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Abstract

The rate of corrosion of iron in 1 M HCl at different concentrations *C* of benzhydrazide additives was determined in a wide range of solution temperatures. The values of corrosion inhibition coefficients *K* under the conditions studied are insignificant and in some cases practically do not depend on the inhibitor concentration in the solution. An explanation is provided for these facts on the basis of the influence on these compounds of the structure and nature of the two adsorption groups in the molecule of the compounds studied and allowance for their possible vertical position during the adsorption on the surface of the iron sample. The effective activation energies of Fe corrosion in 1 M HCl inhibited by benzhydrazide derivatives were determined. They were found to be independent on the inhibitor concentration. Based on the specificity of the structure of the investigated compounds (two adsorption centers) and the possible formation of a solution layer saturated with fragments of adsorbed inhibitors, the independence of activation energy *W* on inhibitor concentration with increasing inhibitor concentration is explained. The values of *W* correspond to the mixed diffusion-kinetic control of Fe dissolution under the conditions studied and are close to the values of *W* reported in literature for the dissolution of Fe in HCl.

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Introduction

The breakthrough in the development of new advanced technologies, planned now in our country, will require additional corrosion inhibition capacities due to the inevitable growth of the country's metal fund in production processes and an increase in the corrosiveness of industrial wastes, with potentially worsening environmental conditions. In the fight against the aforementioned consequences of the growth of the industrial volume of new technologies, the inhibitory method of protecting metals from corrosion can provide an especially effective, reasonably cheap protection.

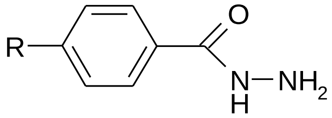
Inhibitory protection of metals from corrosion [1–11] has long and successfully been used in a variety of conditions [12–17]. An obligatory condition for its application is adsorption of inhibitor molecules on the metal surface. This simplest, at first glance, requirement is the result of a number of very complex physicochemical processes. Knowledge of the laws of adsorption, its dependence on various factors (the nature of the metal, the composition of the corrosive environment, *etc*.) and the ability to use them scientifically, are the basis for the effectiveness of this method of protection. In particular, one of the most important conditions for the use of inhibitors is the knowledge of the connection between the protective action of the inhibitor and the peculiarities of its molecular structure. In this field of science, research has been conducted for many years and very significant success has been achieved. Domestic scientists have made a significant contribution to the theory and practice of inhibitory protection. Among them, in particular, I.L. Rosenfeld, L.I. Antropov, S.A. Balezin, Yu.I. Kuznetsov, V.I. Vigdorovich, S.M. Reshetnikov with co-workers, and many others should be noted.

However, the variety of structural features that determine the specificity of an inhibitor, and together with it its protective properties, has not been fully studied and represents a wide field for new studies for the search and scientifically based synthesis of new highly efficient corrosion inhibitors. To date, the relationship between the protective action and structure of an inhibitor, the nature and location of the adsorption centers, and the changes in the concentration of the inhibitor have not been adequately studied. Solving these issues would improve the effectiveness of the protective action of inhibitors and reduce its cost.

The purpose of this study is to obtain information on the effect of possible adsorption centers on previously unknown benzhydrazide derivatives on their inhibition coefficient in the acid corrosion of Fe and its effective activation energy with increasing volume concentration of the inhibitor.

Experimental

Corrosion tests were performed on iron samples (a lamellar band for the production of batteries) measuring 1×2.5 cm in 1 M HCl solutions. Benzhydrazide derivatives (additive **B**)



(1)

with substituents R: H, Cl, CH_3O, CH_3, C_2H_5, $(CH_3)_2N$ were used as inhibitors of Fe corrosion.

For convenience, in the further presentation of the text of the article and the signatures under the figures, instead of (1), we use (2)

$$\text{R–}\mathbf{B} \qquad (2),$$

where R will represent the above-stated substituents in the test compound.

The measurements were carried out at temperatures $T = 20\text{–}60°C$. The working solutions were prepared by sequential dilution of 1 M HCl solution containing 10^{-2} M inhibitor with 1 M HCl background solution. Solutions containing additives **B** with the following concentrations (C) were studied: $1\cdot10^{-2}$; $0.5\cdot10^{-2}$; $2.5\cdot10^{-3}$; $1.25\cdot10^{-3}$; and $0.625\cdot10^{-3}$ M.

The rate of Fe corrosion was determined by the weight method using analytical scales of LV 210-A brand. The samples were subsequently degreased in ethyl alcohol, then for 10 minutes in a boiling solution for chemical degreasing of iron: NaOH 10 g/l, Na_2SiO_3 5 g/l, Na_3PO_4 25 g/l. After degreasing, the samples were rinsed with distilled water and dried with filter paper, then the samples were weighed on analytical scales, immersed in test tubes with the test solution (3 tubes for each solution without inhibitor and 3 test tubes with inhibited solution) at temperatures of 20, 30, 40, 50 and 60°C.

After holding the samples in acid solutions, they were removed, the corrosion slurry was removed with a brush. The samples were rinsed with distilled water, dried with filter paper and weighed again on analytical scales. The rate of Fe corrosion in pure 1 M HCl solutions (background solution) j_0 and inhibited j_{inh} solutions was calculated by the formulas:

$$j = \Delta m/st,\ K = j_0/j_{\text{inh}},$$

where: Δm is the mass loss of the sample, t is the duration of the corrosion test, s is the surface area of the sample, and K is the corrosion inhibition coefficient of the inhibitor.

Results and Discussion

All the compounds studied are similar in the effect on the corrosion rate of Fe in 1 M HCl. They inhibit corrosion insignificantly. The K values of the additives studied lie in the range 1.1–1.4. K weakly increases with an increase in the inhibitor concentration C. The $\lg K\text{–}\lg C$ dependences are linear (Figure 1), with approximately the same angular coefficients. Since the $\lg K\text{–}\lg C$ dependences for all the compounds studied are similar, Figure 1, further they are not given in the article. All these facts indicate that the inhibitory effects of the additives studied are practically equal, regardless of their structure.

Potentially adsorption-active fragments (unsaturated bonds, nitrogen and oxygen atoms, NH_2 group and benzene ring) in the molecule could be expected to have slightly higher values of K compared to the experimentally determined ones. Since these fragments are located differently in the molecules studied, and the value of K is practically independent of the nature of R and other factors listed above, the effect apparently established above is due to some other dominant influence factor on the value of K, which determines the behavior of K noted above for the investigated benzhydrazide derivatives at varying concentrations, solution temperatures and structures.

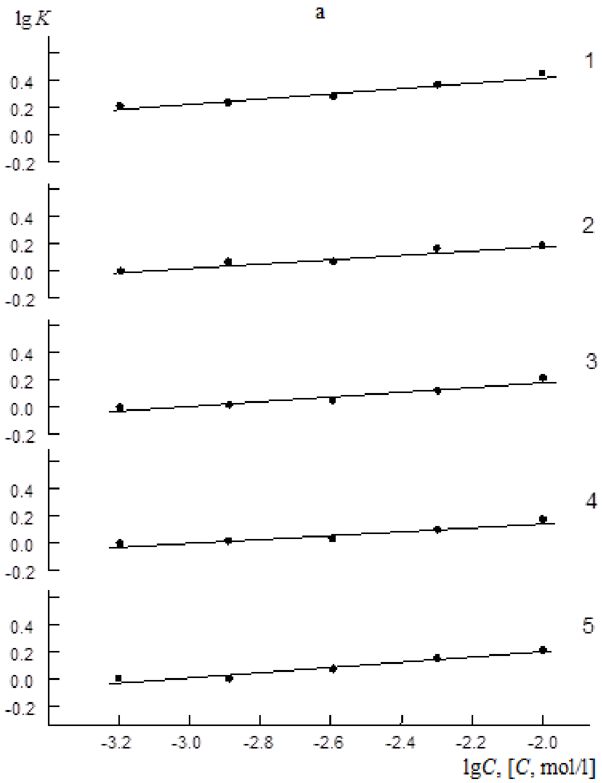


Figure 1. Logarithmic dependence of *K* on *C* for corrosion of Fe in 1 M HCl solution with the addition of: a) **B**–H, b) **B**–CH_3O, at solution temperatures: 1 – 20, 2 – 30, 3 – 40, 4 – 50, 5 – 60°C.

When presenting the results of the above experiments, the question arises. Why, for different structures of the studied **B**–R compounds, the lg*K*, *K*, and j_{cor} dependences of *C* for them are very close and even coincide.

The established regularities can be explained on the basis of the assumption that predominantly linearity (or close to it) dominates the structure of the compounds studied adsorbed on the iron surface in 1 M HCl solution. These compounds are protonated in acidic media. Thus, the terminal group NH_2 attaches the H^+ ion and passes to NH_3^+, which is an active adsorption group [6]. Another active center for the adsorption of molecules can be its benzene end fragment. Its adsorption can occur due to π-electron interaction with the metal surface; in the case of the NH_3^+ group, the interaction is electrostatically ionic. The latter provides a stronger interaction with the metal surface and a stronger Me–inhibitor adsorption bond than the π-bond. Thus, it can be assumed that the adsorption of the benzhydrazide derivatives studied on Fe will be realized mainly *via* the $Me-NH_3^+$ bond.

Through the NH_3^+ adsorption group, an inhibitor molecule is bound to the surface of the iron electrode. The rest of the adsorbed molecule, *i.e.*, the benzene moiety, remains in solution. Moreover, due to repulsive intermolecular forces, apparently, adsorbed molecules occupy a position close to vertical. Thus, a primary layer of the solution is created above the surface of the Fe electrode covered with benzhydrazide molecules by the NH_3^+–Me adsorption bond, and above it there is a secondary layer from the saturated benzene moieties of the molecules, which has considerable dimensions. These layers, due to repulsive intermolecular forces, do not allow new portions of the inhibitor to the surface of the metal with an additional increase in its volume concentration. As a result, the surface concentration of the absorbed inhibitor is constant or varies only slightly. The corrosion inhibition coefficients K remain constant, and accordingly $\lg K \neq f(C_{\mathrm{vol}})$, Figure 1. Moreover, this kind of action of the adsorption inhibitor and the layer of terminal parts of adsorbed molecules that it creates apparently remains in effect upon an increase in the solution temperature.

Obviously, if this is indeed so, then the effective activation energy of Fe corrosion with an increase in the volume concentration of the inhibitor must also remain practically unchanged. This conclusion is confirmed by certain values of W. The values of W under the investigated conditions at different inhibitor concentrations C were calculated from the formula

$$\lg j = A - (W/2.303 \cdot RT),$$

where j is the corrosion current density, A is a constant, W is the effective energy for activation of corrosion in inhibited 1 M HCl solution, R is the gas constant, T is the absolute temperature of the solution. From here, after certain transformations, the linear dependence $\lg j - 1/T$ follows, which makes it possible to determine the value of W for a given C of an inhibitor.

Figure 2 shows the experimentally found linear $\lg j - 1/T$ plots for different concentrations of inhibitors. A characteristic feature of them is a practically identical slope, which indicates the actual equality of W in all cases, regardless of the concentration and even the nature of the additives studied. Note the direct line 2 in Figure 3, which, in contrast to the other benzhydrazide derivatives, demonstrates an apparent growth of W with C. Apparently, this fact reflects additionally the effect on W not only of R–Cl in the benzene ring, but also of the Cl ions of the solution (1 M HCl). The remaining straight lines state the practical independence of W on C_{in}. The definite values of W in Figure 3 indicate a kinetic control of Fe dissolution under the conditions studied in the presence of the studied additives **B** and are consistent with the above proposed mechanism of their behavior at the metal surface. Consequently, an increase in the volume concentration C of the inhibitor will not significantly affect the value of the surface concentration of the C1 inhibitor, and the values of j_{inh}, $\lg K$, and W will not depend on the change in the bulk C and the nature of R, as noted above.

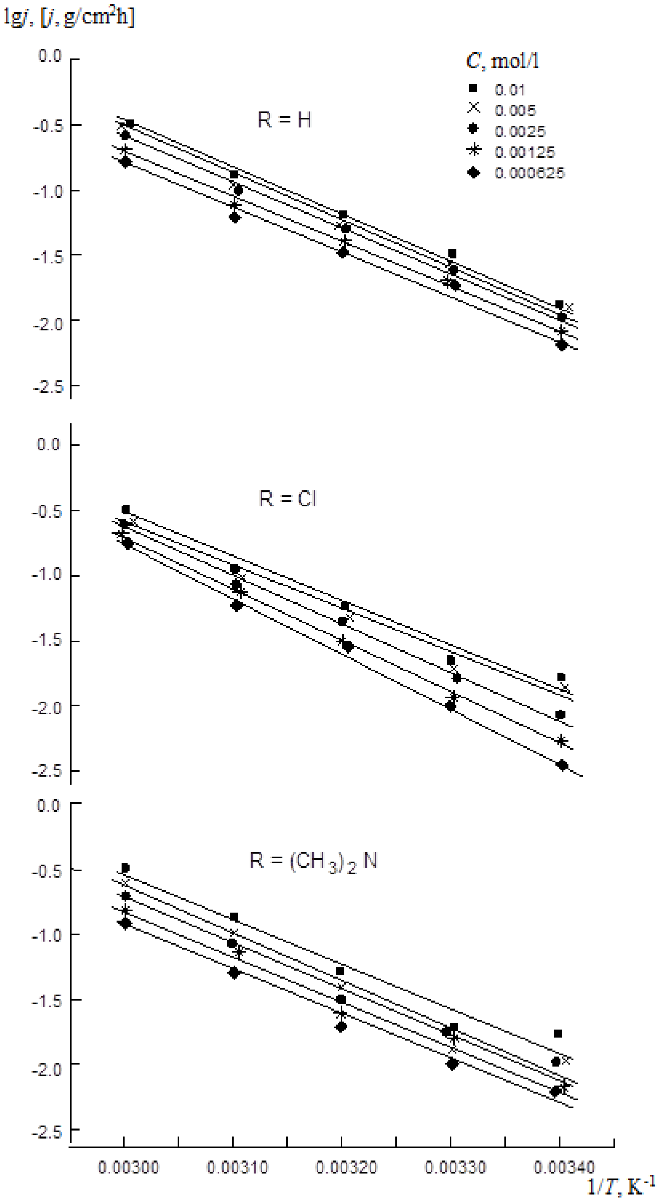


Figure 2. Dependence of the logarithm of the corrosion rate of Fe in 1 M HCl solution with the addition of **B**–H, **B**–Cl, **B**–$(CH_3)_2N$ on the inverse solution temperature 1/*T*.

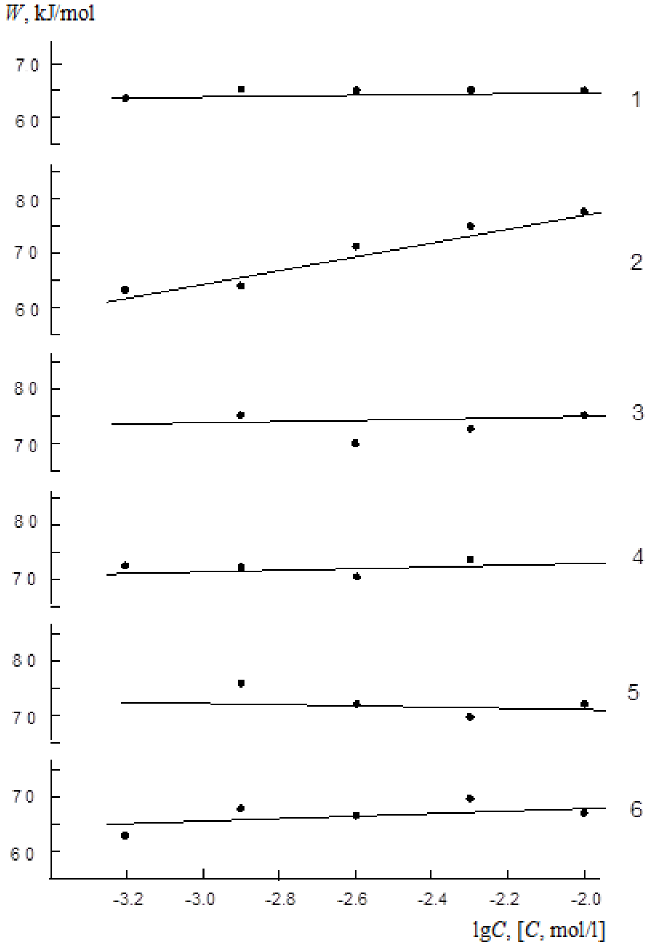


Figure 3. Dependence of the effective activation energy of Fe corrosion in 1 M HCl on the concentration of the additive with the substituent R: 1 – H, 2 – Cl, 3 – CH_3, 4 – OCH_3, 5 – $(CH_3)_2N$.

The values of *W* found in Figure 3 correspond to the mixed diffusion–kinetic control of the dissolution of Fe under the conditions studied and are close to the values of *W* for Fe dissolution in HCl reported in the literature [17].

It follows from the above study, in particular, that the development of inhibitory mixtures containing potentially possible components for vertical adsorption does not exclude the appearance of such conditions that will reduce the inhibitory efficiency of the mixture and very weakly affect its growth with an increase in the concentration of the inhibitory components of the mixture.

Conclusions

1. The values of corrosion inhibition coefficients have been found to be nearly constant, lg$K$ ~ const. This fact is explained on the basis of the assumption on the vertical (or almost vertical) orientation of the adsorbed inhibitor molecules. The latter arises from the absorption of the NH_3^+ group of molecules **B** on the surface of Fe, as a result of which a layer saturated with the rest of the molecules is formed in the solution and prevents the adsorption of new molecules of **B** with an increase in their volume concentration C. As a result, as the concentration at the electrode surface C increases, K and hence lg$K$ remain unchanged.
2. The effective activation energy of Fe corrosion in 1 M HCl containing benzhydrazide derivatives does not depend on the concentration in the range of 10^{-2}–$6\cdot10^{-4}$ mM. This fact is explained taking into account the fact that the inhibitor molecule contains two adsorption centers and the assumption on the vertical arrangement of the adsorbed inhibitor molecules.

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