Nitrogen-containing six-membered heterocyclic compounds as corrosion inhibitors for metals in solutions of mineral acids – A review

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Abstract

The current state of studies on metal protection from corrosion in mineral acid solutions by six-membered *N*-containing heterocyclic compounds is reviewed. Literature data on the protection of various metals in acid solutions by these compounds are summarized. The specific features of their protective action mechanism are discussed. The feasibility of metal protection by formulations containing these compounds, even in high-temperature corrosion, is noted. *N*-Containing six-membered heterocyclic compounds are prone to adsorption on metal surfaces from mineral acid solutions. Based on the free adsorption energy values of these corrosion inhibitors (CIs) on metal surfaces, it can be deemed with high probability that they are mostly bound to a metal by physical forces, but upon adsorption on its surface they slow down the cathodic and anodic reactions, and eventually inhibit its corrosion. Compounds containing S atoms or bulky substituents are most interesting. These compounds are adsorbed on metals more strongly and behave as more efficient CIs. It often happens that such CIs hinder metal corrosion in HCl solutions but do it much more weakly in H_2SO_4, $HClO_4$, and H_3PO_4. A known method for improving the protective effect of *N*-containing six-membered heterocyclic CIs in these media involves combining them with anionic additives, *e.g.*, halide or rhodanide anions. The heterocycles discussed behave as CIs in "cold" solutions but lose these properties at higher temperatures. Examples of the use of six-membered *N*-containing heterocycles as CIs of various steels and non-ferrous metals (Al, Cu, Sn, Zn and their alloys) are available in literature. The industrial application of individual six-membered *N*-containing heterocycles and their derivatives for metal protection in acid media is of little promise and is unjustified. It is more appropriate to use these compounds as components of inhibitor mixtures. Mixed CIs containing these compounds can hinder corrosion even in such corrosive media as high-temperature HCl solutions or hot H_3PO_4 solutions. The base for creating prospective mixed corrosion inhibitors for metals in acids should be searched for among six-membered heterocyclic compounds containing two or more nitrogen atoms or compounds obtained from natural raw materials. The bibliography includes 150 references.

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Introduction

Solutions of mineral and organic acids currently find extensive use in various spheres of human activity, including the metal industry, housing maintenance and utilities, and oil-and-gas sector. Mineral acids are used for scale removal from steels by pickling. Various acid formulations serve for efficient removal of mineral deposits and rust from internal surfaces of various process equipment, including that made of metals. Oil-bearing, gas-bearing and water-bearing strata are often treated with acid solutions to stimulate extraction of hydrocarbons and water. During these process operations, the acid contacts metal parts of the equipment used. As a result, metal parts of the equipment are degraded and the acid consumption increases. The only acceptable method of metal protection in these environments involves the use of inhibitors (CIs), *i.e.*, chemical compounds or formulations that, "when present in sufficient concentration in the system, reduce the corrosion rates of metals without changing significantly the concentration of any corrosive reagent" [1]. The general issues of the protection of metals and alloys in aqueous media by inhibitors, as well as the specific mechanisms of action of various CI groups in these media are covered in a monograph [2] and in reviews [3–9]. However, the specifics of CI application for the protection of metals in acid solutions are not considered in those publications.

Metal protection by CIs in acid solutions was covered in most detail in monographs [10, 11] and in a review [12], but more than 30 years passed since they were issued. A number of reviews dealing with certain specific CI groups in acids have been published in the past 15 years. They dealt with unsaturated organic compounds [13], acetylenic compounds [14], unsaturated carbonyl compounds [15] and azomethines [15, 16], as well as the specific features of their protective mechanisms.

Phosphoric acid solutions are media where inhibitory protection is difficult. The physicochemical aspects of CI creation for these media are considered in Ref. [17]. Reviews [18, 19] deal with a description of the protective properties of CIs recommended for the oil and gas industry. Helpful information is contained in articles, which were claimed to be reviews, dealing with the effect of organic CIs on the electrochemical behavior of steels in acid solutions [20] or considering specific CI groups, such as formulations of organic compounds with halide anions [21], thiourea and thiodiazole derivatives [22], polymeric compounds [23], pharmaceutical agents [24], environmentally-friendly products [25], and plant extracts [26].

Though numerous reviews dealing with corrosion inhibitors in acid media are available, an important group of organic compounds, namely, nitrogen-containing heterocycles, was covered insufficiently to date. The few available publications include article [13] where data on corrosion inhibition in acid media are briefly generalized and the review [27] dealing with the inhibition of steel corrosion in acids by pyrimidine derivatives. It appears important to generalize data on the protection of metals in acid media by six-membered nitrogen-containing heterocyclic compounds (Figure 1), analyze the possible ways for enhancing the protective action, and consider the specific features of the mechanism of their inhibitive action and areas of practical application.

Inhibition of metal corrosion in acid media by six-membered nitrogen-containing heterocyclic compounds

Simple ring systems

Pyridine poorly inhibits the corrosion of mild steel in 1.0 M HCl (25°C). The protective effect it provides at C_{in} = 2 mM concentration in the corrosive medium is Z = 14.8%. Replacement of hydrogen atoms in the pyridine molecule by substituents (R) can considerably enhance its protective action. For example, under the same conditions, 2-(4-pyridyl)-benzimidazole provides Z = 94.5%, though benzimidazole itself, whose radical was used as the R, provides Z = 23.9% [29]. However, this effect is not always observed: 2-acetylpyridine and 2-benzoylpyridine weakly affect the corrosion of mild steel [30, 31] and aluminum [32] in cold HCl solutions.

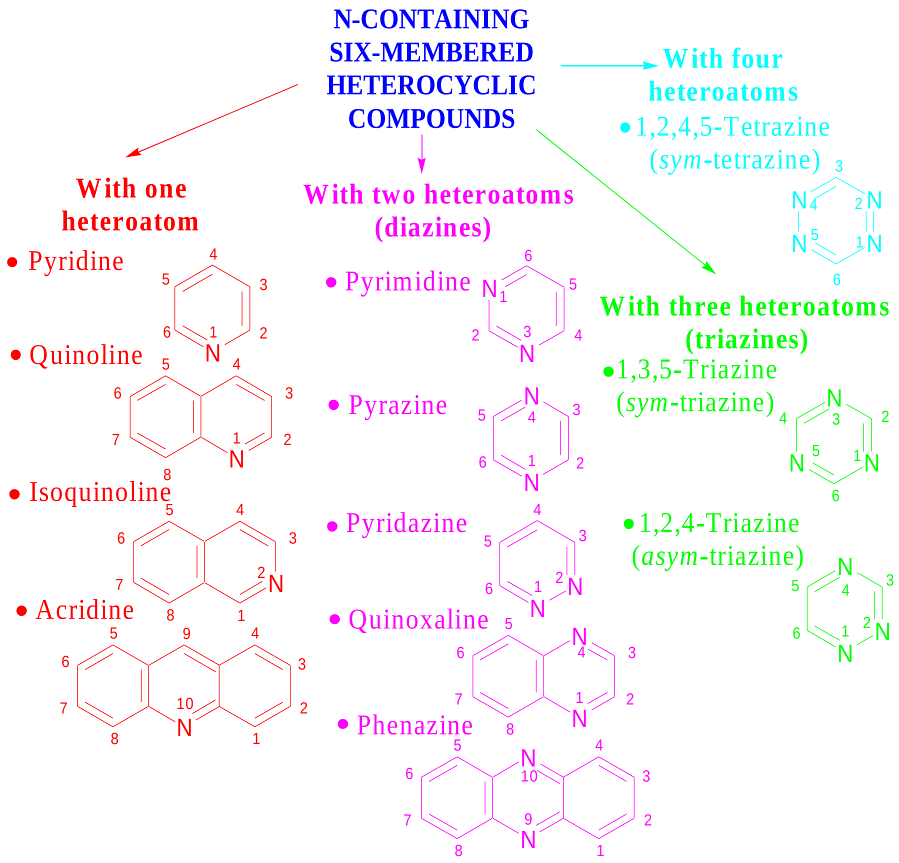
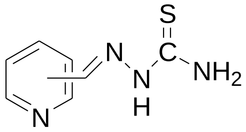


Figure 1. The most important nitrogen-containing six-membered organic heterocycles used as part of corrosion inhibitors [28].

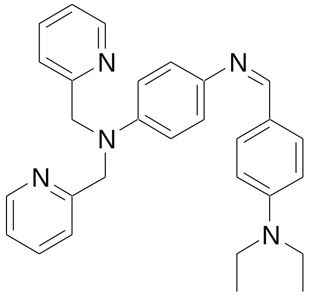
The inhibitive properties of sulfur-containing pyridine derivatives have been studied extensively. Pyridine-2-thiol and 2-pyridyl disulfide slow down the corrosion of mild steel in 0.1 M HCl at room temperature [33]. Isomeric compounds



were studied as corrosion inhibitors of mild steel in 1 M HCl (30°C) [34, 35]. According to electrochemical data, their efficiency at C_{in} = 0.15–1.5 mM depends on the position of R in the pyridine ring as follows: *ortho* > *meta* > *para*. An increase in *t* from 30 to 50°C can decrease the protective effect of the *o*-isomer and especially the *p*-isomer. The same CIs were studied for aluminum protection in 1.0 M HNO_3 (25°C). According to electrochemical impedance spectroscopy (EIS) data, it decreases in the series of isomers: *meta* > *para* > *ortho*. The most efficient of them provides *Z* = 44.3–88.4% at C_{in} = 0.1–10 mM [36]. According to mass loss measurements, 4-pyridinecarboxaldehyde-4-phenyl-thiosemicarbazide and especially 3-pyridine-carboxaldehyde-4-phenylthiosemicarbazide (C_{in} = 0.1–1.0 mM) efficiently inhibit the corrosion of mild steel in 1 M HCl (30–50°C), though there protective effects also decrease somewhat with a temperature growth [37]. 2,5-*bis*(4-Pyridyl)-1,3,4-thiadiazole (*C* = 0.2–1.2 mM) slows down the corrosion of mild steel in 1 M HCl (30°C). Its efficiency is somewhat lower in 0.5 M H_2SO_4, and it can stimulate corrosion in 1 M $HClO_4$. According to voltammetric curves of steel, the increase in the corrosion rate in 1 M $HClO_4$ in the presence of this compound may be due to a cathodic reduction of this CI [38]. According to EIS data, 2,5-*bis*(2-pyridyl)-1,3,4-thiadiazole and especially 2,5-*bis*(3-pyridyl)-1,3,4-thiadiazole are more efficient in corrosion inhibition. Their protective action also decreases in the series of acids: 1 M HCl > 0.5 M H_2SO_4 > 1 M $HClO_4$. In this case, 2,5-*bis*(2-pyridyl)-1,3,4-thiadiazole in 1 M $HClO_4$ is rather a strong stimulator of steel corrosion [39].

According to electrochemical studies, including EIS, 2-pyridinecarbonitrile (C_{in} = 0.5–10 mM) inhibits the corrosion of mild steel in 0.1 M HCl (25°C) [40]. Under these conditions, pyridine carbonitriles with more complex compositions inhibit the corrosion and electrode reactions of steel in more concentrated solutions: 1–2 M [41, 42] and even 15% HCl [43].

Low efficiency in the inhibition of the corrosion of Q235 mild steel (composition, mass%: C 0.14-0.22; Mn 0.30-0.65; Si up to 0.3; S up to 0.5; P up to 0.045) in 1 M HCl (35–55°C) is observed for the high-molecular compound 4-[((4-(bis(pyridin-2-ylmethyl)-amino)phenyl)imino)methyl]-*N*,*N*-diethylaniline (C_{in} = 0.1–1 mM)



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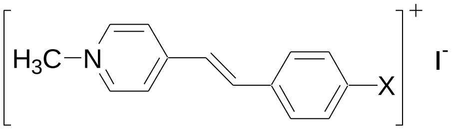
whose *Z* is ≤ 92% [44].

In USSR, corrosion inhibitors of Katapin series were developed for the protection of various steels in acid solutions [11, 45]. They were obtained from pyridine and produced on industrial scale. Katapins A ($n = 8–10$) and K ($n = 4–6$) were produced on the basis of *para*-alkylbenzylpiridinium chlorides ($[H_3C–(CH_2)_n–CH_2–C_6H_4–CH_2–NC_5H_5]Cl$), while Katapins B-300 ($n = 6–8$, $m = 2–5$), BPV and EPV differing in the production technology were obtained from alkylpolybenzylpyridinium chlorides ($C_nH_{2n+1}–CH_2–(C_6H_4–CH_2)_m–NC_5H_5]Cl$). Furthermore, corrosion inhibitors of brands I-A, I-V, and I-E were produced on the basis of polyalkylpyridines with different degrees of modification, as well as the KPI-3 inhibitor was obtained from a quaternary pyridinium salt.

Pyridinium salts with the composition

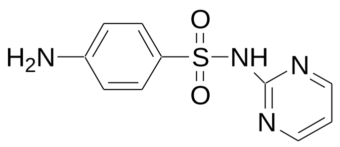


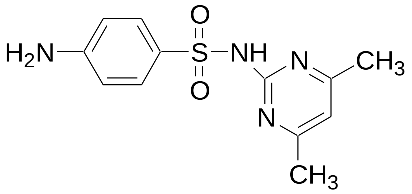
X = H, Cl, OH

were studied as CIs for an Al–Cu alloy (composition, mass%: Cu 4.32; Mg 0.21; Pb 0.072; Fe 0.099; Mn 0.223; Si 0.634) in 0.5 M HCl. According to the data of EIS, mass loss and voltammetric studies, these compounds provide $Z > 94\%$ at $C_{\text{in}} = 0.25$ mM and $t = 30$°C. The protective effects of the CIs increase in the series of R: H > Cl > OH. The protective effects of these compounds decrease with an increase in temperature. For the most efficient CI, 1-methyl-4[4′(-OH)-styryl]pyridinium iodide, an increase in *t* from 30 to 70°C decreases *Z* from 98.2 to 82.8% [46].

Among *pyrimidine* derivatives, compounds with amino groups have been studied most thoroughly. The protective effect of 1 mM 2-aminopyrimidine for Armco iron in 2 M HCl (40°C) is as low as $Z = 28\%$. Even poorer protection ($Z = 24\%$) is provided by 2,4,6-triaminopyrimidine. The protective effect of substituted pyrimidines can be enhanced by combining a few amino and thiol groups in their structures (*Z*(2,4-diamino-6-mercaptopyrimidine) = 39%, *Z*(2,6-dimercapto-4,5-diaminopyrimidine) = 40%), though thiols are more efficient: 2,4-dimercaptopyrimidine, $Z = 43\%$; 2-mercaptopyrimidine, $Z = 62\%$ [47–49]. In 1 M HCl (20°C), 0.5 mM 2-amino-4,6-dihydroxypyrimidine provides good protection of carbon steel, $Z = 94.5\%$, but at $t = 50$°C it decreases to 79.5% [50]. According to electrochemical studies, in 0.5 M H_2SO_4 (20°C) 10 mM 2-aminopyrimidine and 2,4-diaminopyrimidine hinder the corrosion of cold rolled steel (composition, mass%:

C 0.07; Si 0.01; Mn 0,3; P 0.022; S 0,010; Al 0.030) to reach *Z* = 82.0 and 89.6%, respectively [51]. In dilute 0.05 M HNO_3 (30°C) on 1018 carbon steel (composition, mass%: C 0.2; Si 0.003; Mn 0.6; P 0.04) at C_{in} = 17 μM, protection increases in the series: 2-aminopyrimidine < 2,4-diaminopyrimidine < 2,4-diamino-6-hydroxypyrimidine < 2,4,6-triaminopyrimidine, the observed effects being *Z* = 36.3, 42.7, 48.5 and 53.3%, respectively. The protective effects of these compounds can be improved by addition of 1 mM KI to reach Z_{mix} = 51.0, 62.0, 66.0 and 75.0% [52]. The simplest way of chemical modification of amines is to convert them to azomethines. According to mass loss measurements, in 2 M HCl (25°C) the inhibitive effect on the corrosion of carbon steel (composition, mass%: C 0.2; Si 0.003; Mn 0.35; P 0.024) of azomethines obtained from 4,6-dimethylpyrimidine-2-amine decreases in the series: *N*-benzylidene-4,6-dimethylpyrimidine-2-amine > 2-[(3,6-Dimethylpyridimine-2-ylimino)methyl]-4-nitrophenol > 4,6-Dimethylpyrimidine-2-amine. At C_{in} = 5 mM, *Z* = 93.3, 73.4 and 70.6%, respectively [53]. Substituted 2-aminopyrimidines



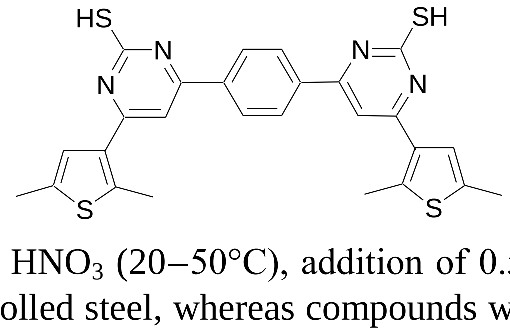


have been studied as corrosion inhibitors of mild steel in 1 M HCl and 0.5 M H_2SO_4 (25°C). The first compound is more efficient in both acids, and both CIs hinder the corrosion in 1 M HCl much better [54].

4-Phenylpyrimidine is more efficient than 5-phenylpyrimidine in corrosion inhibition of cold rolled steel (composition, mass%: C 0.07; Si 0.01; Mn 0.3; P 0.022; S 0.010; Al 0.030) in HCl solutions. Their protective effects decrease even on increasing *t* to 50°C and C_{HCl} from 1 to 5 M [55].

Compounds with more complex structures containing a pyrimidine residue were also studied as CIs of various steels in cold HCl solutions. For example, vitamin B_1 [56, 57] in 0.5 M HCl provides *Z* = 91.5% only at high C_{in} = 10 mM.

In HNO_3 and H_2SO_4 solutions, steel protection could be ensured only in the case of sulfur-containing pyrimidine derivatives, such as 2-mercaptopyrimidine [58] and more complex compounds:

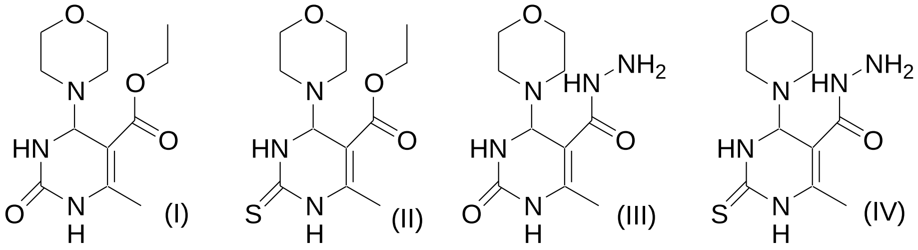


[59].

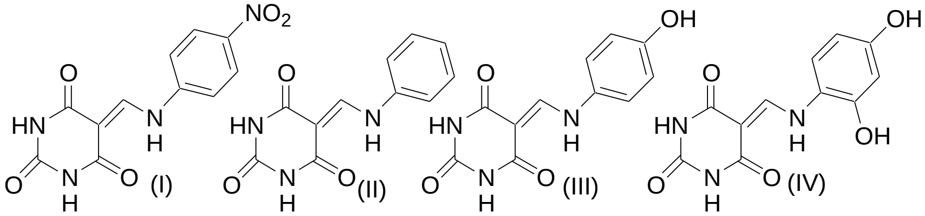
For example, in 0.1 M HNO_3 (20–50°C), addition of 0.5 mM 2-mercaptopyrimidine provides *Z* ≤ 95% for cold rolled steel, whereas compounds with similar structures such as

2-chloropyrimidine, 2-hydroxypyrimidine, 2-bromopyrimidine, and 2-aminopyrimidine provide low protection ($Z \leq 35\%$) even at C_{in} = 10 mM.

Corrosion inhibitors based on a hydrogenated pyrimidine ring are known. Hydrogenated pyrimidines (3,4-dihydropyrimidine) and their low-molecular derivatives (2-mercapto-3,4-dihydropyrimidine, 2-mercapto-3,4-dihydro-6-methylpyrimidine, 2-mercapto-4-amino-1,6-dihydropyrimidine, 2,5,6-triamino-3,4-dihydropyrimidine, and 2-mercapto-4-amino-5-nitro-1,6-dihydropyrimidine) in 2 M HCl (40°C) almost do not affect the corrosion of Armco iron or even accelerate it [47, 48]. Corrosion of mild steel is inhibited more strongly in 2 M HCl (35–65°C) by compounds with bulky substituents R, *viz.*, 4-substituted 5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-ones with phenyl or nitrophenyl substituents. According to mass loss studies at 10 mg/l of the most efficient one of them, 5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one, Z = 99.0% at t = 35°C but as small as 91.0% at t = 65°C [60]. Tetrahydropyrimidine derivatives are even more interesting. According to mass loss measurements and EIS data obtained in 1 M HCl (25°C), 5 mM 5-benzoyl-4-(4-carboxphenyl)-6-phenyl-1,2,3,4-tetrahydro-2-imino-pyrimidine or 5-benzoyl-4-tolyl-6-phenyl-1,2,3,4-tetrahydro-2-thioxopyrimidine inhibit the corrosion ($Z \geq 90\%$) of stainless steel (composition, mass%: C 0.0425; Si 0.421; Mn 2.13; P 0.0133; S 0.113; Cr 18.51; Mo 0.563; Ni 8.34; Al 0,0334; Co 0.0901; Cu 0.358) [61]), a material that is difficult to protect. Some tetrahydropyrimidine derivatives



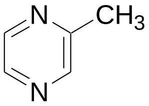
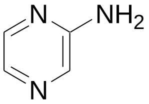
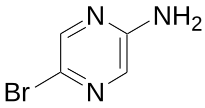
can enhance steel protection with rising temperature. For example, compound IV provides Z = 89.4% on mild steel in 0.5 M HCl at t = 30°C but Z = 92.4% at t = 60°C. The efficiency of the CIs increases in the series: I < II < III < IV. Other conditions being equal, the inhibitive effect of such CIs is improved upon replacement of an oxygen atom with sulfur or an ethoxy group with a hydrazine residue [62]. Conversely, the efficiency of compounds with the structures



decreases with an increase in t from 35 to 65°C and increases in the following series for mild steel protection in 1 M HCl: (I) < (II) < (III) < (IV) [63].

Substituted *pyrazines* than do not show outstanding protective effects in H_2SO_4 solutions (Table 1) [64] have been studied less thoroughly. The protective effects of these CIs are considerably higher in HCl solutions [65]. The efficiency of CIs decreases in the series 2-amino-5-bromopyrazine (ABP) > 2-aminopyrazine (AP) > 2-methylpyrazine (MP), which is in good agreement with the data of quantum-chemical DFT calculations for the molecules of these compounds, as well as by molecular dynamics simulation of interactions between pyrazine molecules and iron surface using materials from Studio 6.0 software [66]. The –C=N– atomic group, the N atom of the amino group, and the Br atom are considered as the active centers for the adsorption of these CIs. It is assumed that they and π-electron systems can bind with the metal surface, forming donor-acceptor bonds or providing electrons for the formation of a coordination bond with incomplete d-orbitals of the metal. More rarely, a CI can also be an electron acceptor that accepts electrons from a metal.

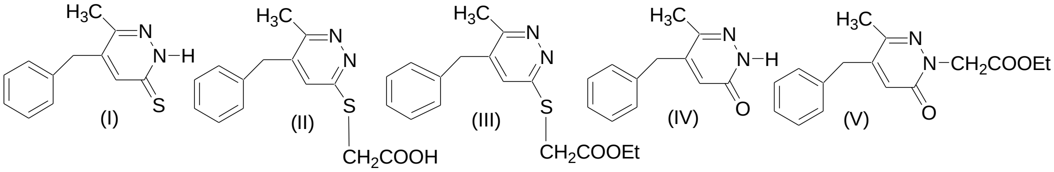
Table 1. Binding energies of substituted pyrazine molecules with Fe(110) surface (E_{binding}) based on data of molecular dynamics simulations [66]; protection degree of cold rolled steel* by substituted pyrazines (1.0 mM) in acid solutions (25°C) based on EIS data (Z); free adsorption energy of pyrazines on steel from acid mixtures (ΔG_{ads}) [64, 65].

Compound	**Structural formula**	**E_{binding}, kJ/mol**	**1.0 M H_2SO_4**		**1.0 M HCl**	
			***Z*, %**	**ΔG_{ads}, kJ/mol**	***Z*, %**	**ΔG_{ads}, kJ/mol**
2-methylpyrazine		127.5	60.5	–28.3	–	–
2-aminopyrazine		194.6	69.6	–29.0	93.0	–36.1
2-amino-5-bromopyrazine		236.2	75.3	–29.7	96.0	–37.5

* composition, mass%: C 0.07; Si 0.01; Mn 0.3; P 0.022; S 0.010; Al 0.030.

The data obtained show that the energy of pyrazine interaction with the Fe(110) surface is negative, hence good adsorption of such compounds on the metal surface can be expected. The energy of binding of pyrazines with iron surface increases in the series: MP < AP < ABP. ABP provides the highest energy of binding with iron surface, which indicates its strong adsorption on the metal surface, hence it should be a more efficient CI than AP and MP. In the case of MP adsorption on iron, the methyl group prevents a parallel orientation of its molecule on the surface. It can be the reason of the lower binding energy obtained for MP adsorption on iron surface in comparison with ABP and AP. Despite the data of quantum-chemical calculations, the experimentally determined adsorption energies of the CIs in question on steel surface from acid solutions are high, but insufficient for making the conclusion on the chemisorption nature of their interaction with the surface.

Substituted *pyridazines* constitute a CI group that is studied better. Of the compounds with similar structures studied



(I) (II) (III) (IV) (V)

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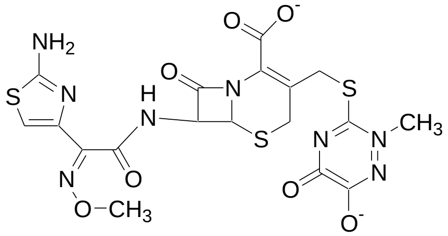
at C_{in} = 0.1 mM, according to mass loss measurements, the corrosion of pure iron (99.5%) in 1 M HCl (25°C) is inhibited most efficiently by sulfur-containing compounds (Z_I = 98%, Z_{II} = 85%, Z_{III} = 81%). In this case, R substituents at the S atom weaken the protective effect of CIs. Replacement of an S atom with O in a CI molecule decreases the protective effect (Z_{VI} = 74%). A stronger adverse effect on the CI properties is caused by a substituent at a nitrogen atom in the heterocycle (Z_V = 64%) [67, 68]. An increase in the protective effect of pyridazines upon the use of S as the R was noted in [69, 70]. The inhibitory effect of pyridazines decreases with an increase in temperature: the *Z* value of 5-(2-chlorobenzyl)-2,6-dimethylpyridazin-3-one (1 mM) in 1.0 M HCl for S38 steel (composition, mass%: C 0.21; Si 0.38; Mn 0.05; P 0.09; S 0.05; Al 0.01) decreases from 96.1 to 82.8% upon a temperature increase by 35°C [71, 72]. 5-[(2-Chlorophenyl)(hydroxy)-methyl]-6-methylpyridazin-3(2*H*)-one can slow down the corrosion of copper (composition, mass%: Cu 99.5; Ni 0.001; Al 0,019; Mn 0.004; S 0.116) in 2.0 M HNO_3 (30°C), giving Z = 94.3%, but Z = 77.6% at t = 70°C [73].

According to corrosion tests in 1 M HCl (6 h, 25°C) on mild steel, a derivative of hydrogenated pyridazine, 6-methyl-4,5-dihydro-2*H*-pyridazine-3-one (C_{in} = 0.1–10 mM), provides Z = 92–98%, but in 0.5 M H_2SO_4, Z = 21–55% even at C_{in} = 0.1–50 mM [74]. More recent studies performed under similar conditions [75] have shown that mild steel protection by 0.5 mM of this compound is even weaker: Z = 17.7%. However, replacement of the methyl in its molecule with the more hydrophobic phenyl and replacement of the O atom with S results in Z = 98.0%. An increase in the protective effect is noted in the series of compounds: 6-methyl-4,5-dihydro-2*H*-pyridazine-3-one < 6-phenyl-2*H*-pyridazine-3-one < 6-phenyl-2*H*-pyridazine-3-thione.

A few *triazine* based compounds studied as CIs of metals in acids were reported. It was shown that symmetrical 2,4,6-trisubstituted triazines with various structures weakly inhibited the corrosion of mild steel even in 0.1 M HCl (20°C) [76]. 1,3,5-Triazine 2,4,6-triaminoethoxylate (0.05%) is more efficient: according to electrochemical measurements, it provides Z = 91.3% in 1 M HCl (25°C) on carbon steel (composition, mass%: C 0.3; Si 0.02; Mn 0.03; P 0.04; Sn 0.045) [77]. An *asymm*-triazine derivative, the ceftriaxone antiobiotic (10 mM)

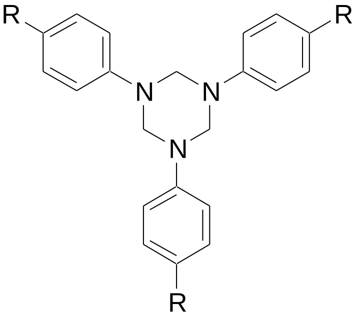


provides *Z* = 94.1% on mild steel in the same medium according to mass loss measurements, *versus* 80.3% for the amoxicillin antibiotic [78].

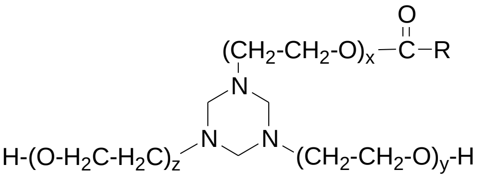
Voltammetric and mass loss measurements were used to study the corrosion of St3 (according to ISO 630-80, St3 steel is an analogue of Fe360 steels) in HCl and H_3PO_4 solutions (t = 25–95°C) in the presence of *N*-(2-chlorophenyl)-1,3,5-triazine-2,4-diamine derivatives. They considerably slow down the electrode reactions of St3 steel in 2 M HCl (t = 60°C), but their efficiency in 2 M H_3PO_4 at the same temperature is low. *N*-(2-Chlorophenyl)-6-linoleyl-1,3,5-triazine-2,4-diamine is the most promising CI for steel. It hinders the corrosion of St3 in 2 M HCl 15–75 fold at t = 25–80°C. In this case, the coefficient of corrosion inhibition with this CI increases with a t increase. Conversely, this CI poorly hinders corrosion in 2 M H_3PO_4 according to electrochemical studies [79].

The protective properties of hydrogenized triazine derivatives were also studied. It was shown that the protection of mild steel in 1 M HCl (27°C) with 6-R-4-amino-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-ones improved in the R series: methyl < *tert*-butyl < benzyl. According to voltammetry and EIS data, the most efficient inhibitor of this series provided $Z > 99\%$ at C_{in} = 0.02% [80]. The same compounds with methyl and benzyl R were studied as corrosion inhibitors of aluminum in 1 M HNO_3 (at room temperature), where Z = 93.3 and 97.7% was reached at C_{in} = 0.01% according to EIS data [81].

Derivatives of trihydro-1,3,5-triazine were studied more thoroughly. For example, according to electrochemical studies, compounds with the composition



slowed down mild steel corrosion in 1 M HCl (35°C), where the protection increased in the R series: $NO_2 < H < CH_3 < OCH_3 < NH_2$. The Z values of these CIs (0.03%) were 84.8, 92.7, 93.7, 95.0 and 97.0%, respectively [82, 83]. Surface active compounds with the composition shown below (1 mM) are less efficient in the corrosion inhibition of CS37 carbon steel (composition, mass%: C 0.11; Si 0.25; Mn 0.45; P 0.04; S 0.05) in 1 M HCl (25°C).

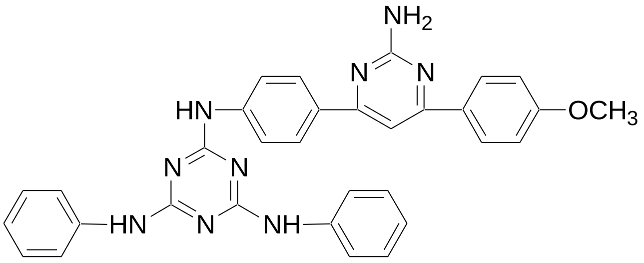


, where x + y + z = 9 (I), 13 (II), 23 (III).
R from oleic acid.

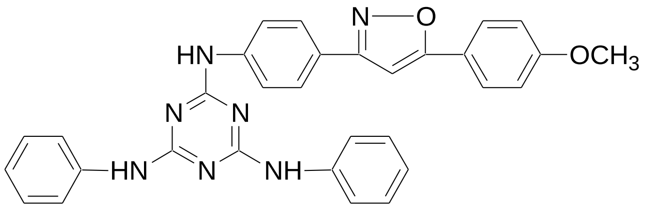
The *Z* values of these compounds are 87.1 (I), 90.7 (II) and 93.1% (III) [84]. It was shown that corrosion inhibition of mild steel in a H_2SO_4 solution with 1,3,5-tribenzyltrihydro-1,3,5-triazine results from the adsorption of this CI on the metal and suppression of cathodic hydrogen evolution due to the creation of an adsorption potential jump and a change in the process rate, but not from surface blocking by the inhibitor [85, 86].

According to mass loss, voltammetry and EIS data, a hydrogenized derivative of *tetrazine* – 3,6-*bis*(2-methoxyphenyl)-1,2-dihydro-1,2,4,5-tetrazine – is an efficient CI of mild steel in 1 M HCl (30°C) but has poor efficiency in 0.5 M H_2SO_4: at C_{in} = 0.1 g/l it provides $Z < 95.8\%$ and $Z > 68.2\%$, respectively. According to voltammetry data, an increase in temperature of 1 M HCl from 25 to 60°C increases *Z* from 94.5 to 96.4% [87].

Compounds whose structures involved a few simple nitrogen-containing six-membered heterocycles at once were reported. 3,6-*bis*(3-Pyridyl)pyridazine (C_{in} = 0.2–1.2 mM) can slow down the corrosion of C35E carbon steel (composition, mass%: C 0.37; Si 0.23; Mn 0.68; S 0.016; Cr 0.077; Ti 0.011; Ni 0.059; Co 0.009; Cu 0.16) in 1 M HCl (30°C), giving *Z* = 87.4–92.8% [88]. According to voltammetry and EIS data, 2,4,6-*tris*(2-pyridyl)-1,3,5-triazine poorly inhibits the corrosion of mild steel in 1 M HCl at room temperature ($Z < 90\%$), being inferior to a trisubstituted tetrazole derivative, 2,3,5-triphenyl-2*H*-tetrazolium chloride [89]. This triazine inhibits the corrosion of Sn, In and their alloy (5% In) in the same medium. According to electrochemical data, the inhibition effect at C_{in} = 0.001 mM decreases in the series: alloy > In > Sn, while at C_{in} = 1 mM, in the series Sn > In > alloy [90]. The 1,3,5-triazine-2,4,6-triamine derivative containing a pyrimidine ring



protects N80 steel (composition, mass%: C 0.34–0.38; Si 0.20–0.35; Mn 1.45–1.7; P up to 0.02; S up to 0.015; Cr up to 0.15; V 0.11–0.16) in 15% HCl (30°C), providing *Z* = 93.0–94.6% at C_{in} = 0.015% according to gravimetry, voltammetry and EIS data [91]. A compound with a similar structure



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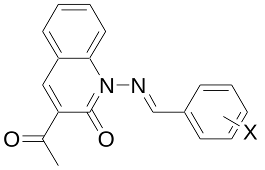
which contains a 1,2-oxazole ring instead of a pyrimidine one, is inferior in protective properties to the former compound.

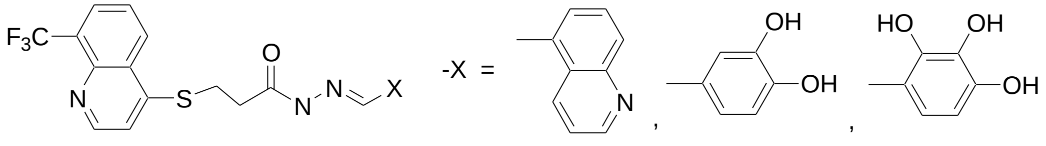
Complex systems

Quinoline poorly inhibits steel corrosion on its own. Even at C_{in} = 0.1 M on mild steel in 0.5 M HCl (30−40°C), $Z \leq 88.7\%$. 2-Methylquinoline and quinoline-2-carboxylic acid provide somewhat better protection under the same conditions ($Z \leq 91.4\%$ and $Z \leq 94.2\%$, respectively) [92]. The observed effect is in full agreement with the quantum-chemical calculations performed by the same researchers [93], according to which quinoline-2-carboxylic acid should provide the maximum protection of steel in acid media. Low protective effects under similar conditions are provided by quinoline derivatives with small substituents: 8-hydroxyquinoline, 3-formyl-8-hydroxyquinoline [94], 2-chloro-6-nitroquinoline-3-carbaldehyde [95], 2,6-dichloro-8-nitroquinoline-3-carbaldehyde [95], 2-chloro-3-formylquinoline [96], and 3-formyl-2-chloroquinoline [97, 98]. It is interesting that modification of the latter compound by conversion to higher-molecular azomethines only worsens the steel protection [97]. Only the Schiff base obtained in the reaction of 3-formyl-2-chloroquinoline with *p*-methylaniline protects steel with $Z > 90\%$ [98]. Azomethines with the composition



X = CH_3, OH, NO_2

on N80 steel in 15% HCl (35°C) are more interesting. According to EIS data, they provide $Z \geq 91.3\%$. However, according to mass loss studies, their efficiency decreases strongly with a temperature increase [99]. Sulfur-containing azomethines [100−102]



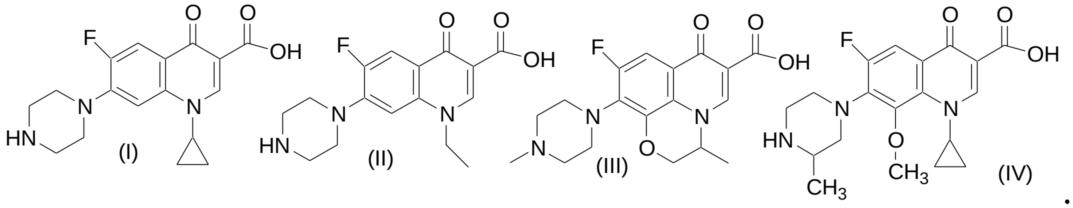
(I) (II) (III)

containing the hydrophobic CF_3 group were studied as CIs in HCl. For example, according to gravimetry data, 0.05% of compound (I) in 1 M HCl solution (30°C) strongly inhibits the corrosion of mild steel (Z = 93.6%), but the protective effect of the CI decreases with an increase in temperature to 60°C (Z = 84.4%) or C_{HCl} to 2 M (Z = 91.6%) [100].

According to mass loss, voltammetry and EIS data, 6-benzylquinoline and 6-(quinolin-6-ylmethyl)benzene-1,2,3,4,5-pentasulfonic acid inhibit the corrosion of mild steel in 1 M HCl (25°C), providing Z = 94.7 and 97.2%, respectively, at C_{in} = 1.0 mM [103].

4-Substituted 2-amino-7-hydroxy-1,4-dihydroquinoline-3-carbonitriles are strong corrosion inhibitors of mild steel in 1 M HCl (35°C). Their efficiency increases in the series: 2-amino-7-hydroxy-4-phenyl-1,4-dihydroquinoline-3-carbonitrile < 2-amino-7-hydroxy-4-(*p*-tolyl)-1,4-dihydroquinoline-3-carbonitrile < 2-amino-7-hydroxy-4-(4-methoxyphenyl)-1,4-dihydroquinoline-3-carbonitrile < 2-amino-4-(4-(dimethylamino)-phenyl)-7-hydroxy-1,4-dihydroquinoline-3-carbonitrile [104].

In "cold" HCl solutions, the corrosion of carbon steel is efficiently hindered by some antibiotics, *viz.*, ciprofloxacin (I), norfloxacin (II), ofloxacin (III) [105], and gatifloxacin (IV) [106]:



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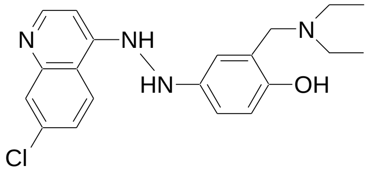
It has been shown for gatifloxacin as an example that that a temperature increase decreases the inhibitory properties [106].

Quaternization is an important method to increase the protective efficiency of quinolines. For example, according to EIS data, *N*-benzylquinolinium chloride (37 mM) provides Z = 94.6% in 15% HCl for N80 steel at 20°C, but already at 90°C, Z = 79.4% according to mass loss data [107].

The studies on quinoline derivatives as CIs of metals in H_2SO_4 have not been systematized and are fragmentary. The substituted quinoline with the structure

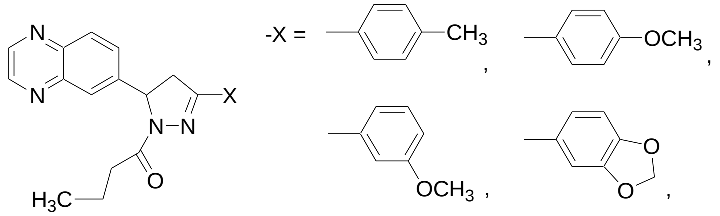


poorly inhibits the corrosion of mild steel in 0.5 M H_2SO_4 even at C_{in} = 0.01 M (Z = 79.4%) [108]. Good protection of steel in H_2SO_4 can be reached using CIs such as substituted quinolinium iodides or bromides [109], which is a result of synergistic action of the cationic surfactant and halide ions, as well as sulfur-containing quinoline derivatives [102].

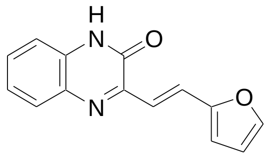
Of *isoquinoline* derivatives, 1-methylisoquinoline has been studied. Like low-molecular quinoline derivatives, it poorly protects mild steel in HCl [110].

Acridine is known as a steel corrosion inhibitor in HCl and H_2SO_4 solutions, but the protective effects of this compound are low. Higher protection is provided by its substituted derivatives and acridinium salts [45]. It is noted that acridine can be used to protect aluminum and its alloys with copper [45] and zinc [111] in hydrochloric acid. For example, Z = 80−98% for an alloy containing 4.5−6.5% zinc.

Data on the protection of metals in acid media with *quinoxalines* are more abundant. Both quinoxaline itself and its derivatives containing the Cl, SH and C_6H_4−OH groups at position 2 poorly inhibit the corrosion of mild steel in 1 M HCl (25°C) at C_{in} = 1 mM: Z = 69.9, 72.6, 79.3 and 85.0%, respectively [112]. The authors [112] believe that this result correlates rather well with the binding energies of these compounds (321, 344, 370 and 523 kJ/mol) with Fe(110) surface calculated by molecular dynamics simulations. Higher protective effects are demonstrated by quinoxalines with bulky substituents:



[113]



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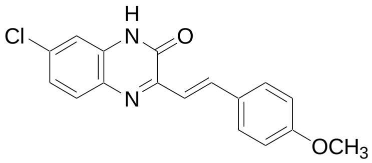
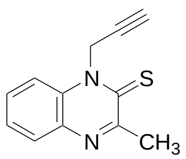


[115, 116].

According to corrosion studies, 3-methyl-2-phenylquinoxaline and 2,3-diphenylquinoxaline (1 mM) considerably inhibit the corrosion of mild steel in 1 M H_2SO_4 at 30°C (Z = 95.1 and 96.4%), but their more hydrophilic analogues, 3-methyl-2(2′-hydroxyphenyl)quinoxaline and 3-phenyl-2(2′-hydroxyphenyl)quinoxaline, have low efficiency (Z = 80.3 and 88.9%) [117].

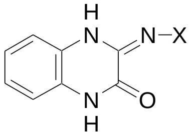
Among quinoxaline derivatives, 3-methyl-1-prop-2-ynylquinoxaline-2(1*H*)-thione should be distinguished:



[118].

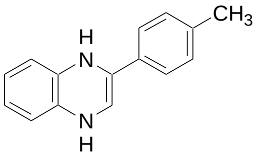
Its protective effect on mild steel in 1 M HCl is preserved fairly well in the *t* range of 35–80°C. The presence of 1 mM of this CI in the solution hinders corrosion at least 20-fold. This kind of dependence of the protective effect on *t* is not typical of *N*-containing six-membered heterocyclic compounds and is due to the propargyl moiety present in the molecule. It is known [13, 14, 119] that organic compounds containing a propargyl moiety protect steel in hydrochloric acid solutions in a broad range of temperatures up to 100°C. The presence of a C≡C unsaturated bond in these compounds predetermines their adsorption–polymerization mechanism of action [120–122], according to which inhibitor molecules are first adsorbed on a metal surface and then a protective film is formed by polymerization processes on the surface. An increase in *t* accelerates the formation of the protective film and thus enhances the protective effects. A similar action mechanism is typical of compounds with conjugated unsaturated C=C and C=O bonds [123]. Compounds containing such groups often show protective effects in heated HCl solutions. It is logical to assume that a similar protective mechanism should work in the case of 3-methyl-1-prop-2-ynylquinoxaline-2(1*H*)-thione.

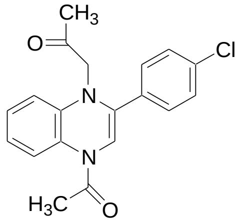
Substituted 1,4-dihydroquinoxalines (1,4-dihydroquinoxaline-2,3-dione ($Z_{0.5\ \mathrm{mM}}$ = 87%) [124], (*E*)-3-(4-methoxystyryl)-7-methylquinoxalin-2(1*H*)-one ($Z_{1\ \mathrm{mM}}$ = 90%) [125], 2-(4-methylphenyl)-1,4-dihydroquinoxaline ($Z_{1\ \mathrm{mM}}$ = 91%) [126], and 2-[3-(2-oxo-2-phenylethylidene)-1,4-dihydroquinoxaline-2(1*H*)-ylidene]-1-phenylethanone ($Z_{0.1\ \mathrm{mM}}$ = 81%) [127]) inhibit the corrosion of mild steel in 1 M HCl at nearly room temperatures. Under the same conditions, mild steel is protected in 1 M H_2SO_4 by the compounds:

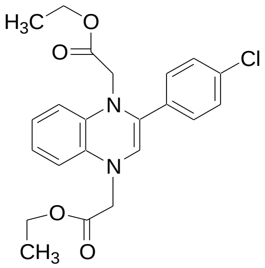


-X = $-C_6H_5$ (I), $-C_6H_4CH_3$ (II), $-C_6H_4OCH_3$ (III) [128],
$-NH_2$ (IV), -CO-NH_2 (V), -CS-NH_2 (VI) [129].

Strong inhibitory properties are shown by compounds I-III, VI.

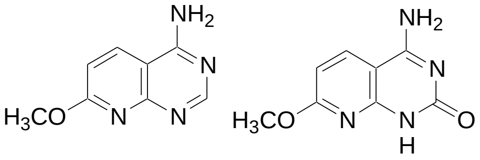




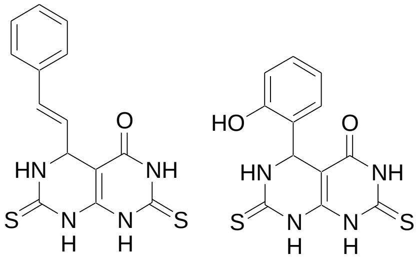


Some of the compounds (1 mM) inhibit copper corrosion in 2 M HNO_3 (30°C): *Z* = 82.8, 91.8 and 97.0% [130].

The inhibitive action of CIs containing two fused six-membered rings with three and four nitrogen heteroatoms was reported. 7-Methoxypyrido[2,3-*d*]pyrimidin-4-amine and 4-amino-7-methoxypyrido[2,3-d]pyrimidin-2(1*H*)-one

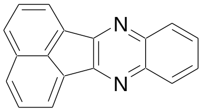


at 0.02% concentration in 15% HCl (60°C) provide *Z* no. worse than 92.4% [131], though their protective action decreases with an increase in temperature. Under the same conditions, 5-styryl-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-*d*]pyrimidin-4(1*H*)one and 5-(2-hydroxyphenyl)-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-*d*]pyrimidin-4(1*H*)one



inhibit the corrosion of N80 steel much worse, though they contain sulfur atoms [132].

Phenazine even at C_{in} = 0.1 M weakly inhibits the corrosion of mild steel in H_2SO_4 at 30°C (Z = 80%), being inferior in this respect to 1,12-phenathroline, phenothiazine, and phenoxazine [133]. A higher protective effect is shown by 2,3-diphenylbenzoquinoxaline that provides Z = 99% on mild steel in 0.5 M H_2SO_4 (30°C) at C_{in} = 10 μM [134]. Under the same conditions, the *Z* value provided by acenaphtho[1,2-*b*]quinoxaline



is as low as 80% [135], while Z = 90% in the presence of this compound in 1 M H_2SO_4 (30°C) is reached at C_{in} = 10 mM [136].

It should be noted in this review that we deliberately did not cover organic compounds containing both six- and five-membered nitrogen-containing organic rings, including fused ones. To our understanding, the inhibitory action of such compounds is largely determined by the properties of five-membered heterocycles [5, 13] that require a separate consideration. The same corresponds to compounds incorporating five-membered rings with O and S heteroatoms.

Thus, six-membered nitrogen-containing heterocyclic compounds can inhibit the corrosion of carbon steels in HCl solutions. As a rule, their inhibitive action is improved by incorporation of bulky R or mercapto groups in their molecules. Conversely, in $HClO_4$, H_2SO_4, and H_3PO_4 solutions, these CIs often have low inhibitory effects, except for the cases where mercapto derivatives of heterocycles are used. It often happens that an increase in the temperature of an acid solution at least to 60°C decreases the protective action of these CIs considerably. Apart from inhibition of mild steels, they can be used to inhibit the corrosion of stainless steels and non-ferrous metals (Al, Cu, Sn, Zn and their alloys) in HCl and HNO_3 solutions. Analysis of literature shows that individual six-membered nitrogen-containing heterocycles are rarely used in acids as industrial CIs of metals, since it is important in these cases to provide efficient metal protection at $t \geq 60°C$.

Specifics of the action mechanism of nitrogen-containing six-membered heterocyclic CIs of metals in acid media

Important information about the mechanism of CI action can be obtained by analyzing the processes of CI adsorption on metals. As a rule, the stronger the adsorption of a CI on a metal, the higher its protective effects that can be expected. The best protective effects are provided by CIs that chemically interact with a metal surface. It is believed that if the standard free adsorption energy $(-\Delta G_a^0)$ is less than 20 kJ/mol, then it is of physical nature. Only if $(-\Delta G_a^0) \geq 40$ kJ/mol, one can state with high probability that the inhibitor is chemisorbed. Unfortunately, the literature sources that we studied contain data on the adsorption of nitrogen-containing six-membered heterocyclic compounds on metals from acid solutions (Tables 1 and 2) calculated only from the results of corrosion studies on these metals based on the mass loss of specimens, which is a rough approximation that gives considerable errors. The majority of researchers adhere to the opinion that adsorption of such CIs on metals is most adequately described by the Langmuir isotherm, which they choose formally from the list of existing isotherms. The reported data indicate the high adsorption activity of six-membered nitrogen-containing heterocycles on steels and non-ferrous metals, but in most cases the observed $(-\Delta G_a^0)$ values are insufficient for an unambiguous conclusion that they are chemisorbed on a metal surface. Only for some sulfur-containing heterocyclic compounds or heterocycles with bulky R, $(-\Delta G_a^0) \geq 40$ kJ/mol, which is evidence in favor of chemisorption. Comparison of data on adsorption of nitrogen-containing six-membered heterocyclic CIs with the results of corrosion studies allows the conclusion to be made that the nature of interaction of the majority of these compounds with metals is predominantly of physical nature, since such compounds are generally low-efficiency CIs or easily lose the protective effect as the temperature increases.

As a result of adsorption interaction of these compounds with metal surfaces, they decrease the double electric layer capacity, strongly hinder both electrode reactions and increase the polarization resistance. These factors ultimately determine the protective effect of these CIs. The literature that we analyzed reveals no. information that six-membered nitrogen-containing heterocyclic compounds form polymolecular protective layers on the metal surface that are characteristic of triazoles, *i.e.*, another group of heterocycles. As we have shown previously [137–139], the fact that triazoles form such layers on steel surface allows the highest protective effects to be reached. The fact that triazoles form protective layers on metal surfaces makes it possible to use them for the protection of mild and chromium-nickel steels even under high-temperature acid corrosion conditions [140–142].

Table 2. Free adsorption energies of nitrogen-containing six-membered heterocyclic compounds on metals from acid media.

Inhibitor	Type of metal	Type of corrosive medium	Standard adsorption free energy (-ΔG_{ads})*, kJ/mol	Ref.
Pyridines				
2-(4-Pyridyl)-benzimidazole	Mild steel	1.0 M HCl (25°C)	32.4	29
Pyridine-2-thiol and 2-pyridyl disulfide	Mild steel	0.1 M HCl (25°C)	34.3, 37.2	33
o,*m*,*p*-Pyridinecarboxaldehyde thiosemicarbazones	Mild steel	1 M HCl (30°C)	37.2, 35.8, 33.1	34, 35
	Aluminum (Puratronic, 99.999%)	1.0 M HNO_3 (25°C)	27.7, 28.7, 27.8	36
4-Pyridinecarboxaldehyde-4-phenylthiosemicarbazide; 3-pyridinecarboxaldehyde-4-phenylthiosemicarbazide	Mild steel	1 HCl (30–50°C)	41.2–41.6, 43.1–48.6	37
2,5-*bis*(*o*,*m*,*p*-Pyridyl)-1,3,4-thiadiazoles	Mild steel	1 M HCl, 0.5 M H_2SO_4, 1 M $HClO_4$ (30°C)	38.4, 40.4, 34.9 (HCl), 35.4, 36.4, 32.7 (H_2SO_4), 34.4 ($HClO_4$, *m*–isomer)	38
2-Pyridinecarbonitrile	Mild steel	0.1 M HCl (25°C)	34.9	40
2-Amino-6-methoxy-4-phenylpyridine-3,5-dicarbonitrile; 2-Amino-6-methoxy-4-(4-methylphenyl)pyridine-3,5-dicarbonitrile; 2-Amino-6-methoxy-4-(4-methoxylphenyl)pyridine-3,5-dicarbonitrile	Mild steel	1 M HCl (35–65°C)	33.2–37.4; 32.6–35.8; 31.8–33.9	42
2-Amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile; 2-Amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl)nicotinonitrile	N80 steel	15% HCl (35°C)	30.6; 29.9	43

Inhibitor	**Type of metal**	**Type of corrosive medium**	**Standard adsorption free energy ($-\Delta G_{ads}$)*, kJ/mol**	**Ref.**
4-[((4-(bis(pyridin-2-ylmethyl)amino)phenyl)imino)-methyl]-*N*,*N*-diethylaniline	Q235 mild steel	1 M HCl (35–55°C)	31.4–32.7	44
1-Methyl-4[4´(-X)-styryl]-pyridinium iodides (X: H, Cl, OH)	Al–Cu alloy	0.5 M HCl (30°C)	36.1, 36.8, 37.4	46
Pyrimidines				
4,6-Diamino-2-pyrimidinethiol	Mild steel	0.1 M HCl (25°C)	34.0	49
2-Amino-4,6-dihydroxypyrimidine	Carbon steel	1 M HCl (20–50°C)	20±2	50
2-Aminopyrimidine and 2,4-diaminopyrimidine	Cold rolled steel	0.5 M H_2SO_4 (20°C)	23.5, 24.9	51
4-Phenylpyrimidine and 5-phenylpyrimidine	Cold rolled steel	HCl (30°C)	29.2, 28.5	55
2-Mercaptopyrimidine	Cold rolled steel	0.1 M HNO_3 (20–50°C)	38.2–41.0	58
bis-Pyrimidin-2-thiol derivative	Mild steel	1 M H_2SO_4 (room temperature)	40.5	59
5-Acetyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)-one, 5-acetyl-6-methyl-4-(3-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)-one and 5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one	Mild steel	1 M HCl (30–60°C)	39.1–39.9, 40.1–42.1, 45.2–47.9	60
5-(((4-nitrophenyl)amino)-methylene)pyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione; 5-((phenylamino)methylene)-pyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione; 5-(((4-hydroxyphenyl)amino)-methylene)pyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione; 5-(((2,4-dihydroxyphenyl)amino)-methylene)pyrimidine-2,4,6-(*1H*,*3H*,*5H*)-trione	Mild steel	1 M HCl (35–65°C)	32.2–34.0; 32.6–34.6; 32.9–35.5; 33.7–37.3 (Temkin adsorption isotherms)	63

Inhibitor	**Type of metal**	**Type of corrosive medium**	**Standard adsorption free energy ($-\Delta G_{ads}$)*, kJ/mol**	**Ref.**
Pyridazines				
5-Benzyl-6-methylpyridazine-3-thione	Pure iron (99.5%, from Good Fellow, Cambridge, UK)	1 M HCl (25–80°C)	48 (Frumkin isotherm adsorption)	67
Ethyl(6-oxo-3-phenylpyridazin-1(6*H*)-yl)acetate and ethyl(3-phenyl-6-thioxopyridazin-1(6*H*)-yl)acetate	C38 Mild Steel	1 M HCl (30°C)	39.5 и 39.5	70
6-Phenyl-2H-pyridazine-3-thione	Mild steel	1 M HCl (35–65°C)	40.1	75
Triazines				
Ceftriaxone	Q235 Mild steel	1 M HCl (25°C)	45.6	78
2,4,6-*tris*(2-Pyridyl)-1,3,5-triazine	Tin	0.5 M HCl	73.5 (Frumkin isotherm adsorption)	90
1,3,5-Triazine-2,4,6-triamine derivatives	N80 steel	15% HCl (30–60°C)	38.6–41.6	91
Quinolines and related structures				
Quinoline, 2-methylquinoline, quinoline-2-carboxylic acid	Mild steel	0.5 M HCl (25°C)	23.5, 27.5, 37.4	92
8-Hydroxyquinoline and 3-formyl-8-hydroxyquinoline	Mild steel	1 M HCl (30–60°C)	9.8–11.0, 11.9–13.2	94
2,6-Dichloroquinoline-3-carbaldehyde; 2-chloro-6-nitroquinoline-3-carbaldehyde; 2,6-dichloro-8-nitroquinoline-3-carbaldehyde	Mild steel	1 M HCl (30°C)	36, 35, 34	95
2-Chloro-3-formylquinoline	Mild steel	1 M HCl (30–60°C)	27.9–33.2 (Freundlich adsorption isotherm)	96

Inhibitor	Type of metal	Type of corrosive medium	Standard adsorption free energy (-ΔG_{ads})*, kJ/mol	Ref.
3-Formyl-2-chloroquinoline and 2-chloro-quinoline-3-yl-methylene)-*p*-tolylamine	Mild steel	1 M HCl (30–60°C)	33.4, 35.0	98
3-Acetyl-1-(4-methylbenzylideneamino)quinolin-2-one; 3-acetyl-1-(4-hydroxybenzylideneamino)-quinolin-2-one; 3-acetyl-1-(3-nitrobenzylideneamino)quinolin-2(1*H*)-one	N80 steel	15% HCl	34	99
Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propanohydrazide	Mild steel	1–2 M HCl (30–60°C)	33.2–38.3	100
N′-Benzylidene-3-(quinolin-4-ylthio)propanohydrazide	Mild steel	1–2 M HCl. 0.5–1 M H_2SO_4 (30–60°C)	33.5–38.0 (HCl), 35.2–41.4 (H_2SO_4)	101
3-{[8-(trifluoromethyl)quinolin-4-yl]thio}-N’- (2,3,4,-trihydroxybenzylidene)propano-hydrazide	Mild steel	1–2 M HCl. 0.5–1 M H_2SO_4 (30–60°C)	34.6–39.4 (HCl), 33.4–41.5 (H_2SO_4)	102
6-Benzylquinoline; 6-(quinolin-6-ylmethyl)benzene-1,2,3,4,5-pentasulfonic acid	Mild steel	1 M HCl (25–55°C)	34.2–36.4, 35.1–37.0	103
2-Amino-7-hydroxy-4-phenyl-1,4-dihydroquinoline-3-carbonitrile; 2-amino-7-hydroxy-4-(p-tolyl)-1,4 dihydroquinoline-3-carbonitrile; 2-amino-7-hydroxy-4-(4-methoxyphenyl)-1,4 dihydroquinoline-3 carbonitrile; 2-amino-4-(4-(dimethylamino)phenyl)-7-hydroxy-1,4-dihydroquinoline-3-carbonitrile	Mild steel	1 M HCl (35°C)	35.8–36.4; 36.4–37.9; 36.6–37.9; 37.8–39.8	104
Ciprofloxacin, norfloxacin, ofloxacin and gatifloxacin	Mild steel, L-52 carbon steel (gatifloxacin)	1 M HCl (30°C)	48.5, 47.7, 46.6, 39.8	105, 106

Inhibitor	**Type of metal**	**Type of corrosive medium**	**Standard adsorption free energy (-ΔG_{ads})*, kJ/mol**	**Ref.**
N-Benzylquinolinium chloride	N80 steel	15% HCl (90°C)	30.3	107
1-Substituted quinolin-1-ium iodide	Mild steel	0.5 M H_2SO_4 (25–60°C)	33.4–41.6	109
Quinoxalines and related structures				
3-Methyl-1-prop-2-ynylquinoxaline-2(1*H*)-thione	Mild steel	1 M HCl (35°C)	38.8–44.5	118
(E)-3-(4-Methoxystyryl)-7-methylquinoxalin-2(1*H*)-one	C35 carbon steel	1 M HCl (30°C)	34.9	125
1,4-Dihydroquinoxaline-2,3-dione derivatives	Mild steel	1 M H_2SO_4 (30°C)	23±1 (Langmuir adsorption isotherm). 27 (Temkin adsorption isotherm)	128
7-Methoxypyrido[2,3-d]pyrimidin-4-amine; 4-amino-7-methoxypyrido[2,3-d]pyrimidin-2(1*H*)-one	Mild steel	15% HCl (30–60°C)	35.0–37.5, 36.7–38.2	131
5-Styryl-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido [4,5-d] pyrimidin-4(1*H*)one; 5-(2-hydroxyphenyl)-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-*d*]-pyrimidin-4(1*H*)one	N80 steel	15% HCl (35°C)	32.7, 32.3	132

*Adsorption energy data presented without additional clarification were calculated from the Langmuir isotherm.

Composite CIs based on nitrogen-containing six-membered heterocyclic compounds

Due to the drawbacks of *N*-containing six-membered heterocyclic CIs considered above, a more interesting approach involves the creation of mixed CIs on their basis. This approach is easy to implement and it does not require a chemical modification of the starting *N*-containing heterocycles. The literature that we reviewed contains a few successful implementations of this approach, including the creation of industrial corrosion inhibitors.

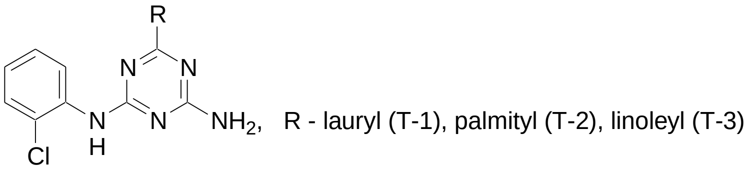
The "ChM" inhibitor that consisted of two components, *i.e.*, a pickling regulator (a mixture of quinoline bases) and a foaming agent, was the first CI for metals in acids produced in the USSR . It was used in the pickling of ferrous metals in H_2SO_4 solutions with $t \leq 60°C$. Based on a modified pyridine – Katapin B-300 – the “KI-1” corrosion inhibitor (25% Katapin, 25% urotropine, balance water) was produced, which was recommended for the protection of carbon steels in HCl, H_2SO_4, H_3PO_4 and HF solutions (20–100°C). It provided $Z \geq 97\%$ in HCl and H_2SO_4 solutions. CIs of S-5 series are synergistic mixtures of heavy pyridine and quinoline bases (cationic component) with bottom products from coke gas treatment (anionic component) in 1 : 4 component ratio. Modification of S-5U corrosion inhibitor makes it possible to protect carbon steels in solutions of HCl, H_2SO_4, H_3PO_4, HNO_3, acetic, formic and citric acids [11].

The active base of the BA-6 inhibitor is a mixture of 1,3,5-tribenzyltrihydro-1,3,5-triazine and *N*-methylbenzylamino-*N*′-benzyliminomethylene. This CI well protects carbon steels in HCl solutions, but it is not always sufficiently efficient in H_2SO_4 [11]. Synergism was also noted in the action of an equimolar mixture of 1,3,5-tribenzyltrihydro-1,3,5-triazine and benzylanilinium chloride on mild steel corrosion in HCl and H_2SO_4 solutions [143]. The authors believe that the synergism of action of these mixed components results from the positive attractive interaction of their molecules on steel surface resulting in the mutual enhancement of CI adsorption.

N-Dodecylpyridinium bromide, which is marketed by its developers as a surfactant [144–149], is an important component of CIs for high-temperature hydrochloric acid corrosion of steels based on unsaturated organic compounds. Probably, the role of the additive in such mixtures is not so unambiguous, since the multicomponent high-temperature CIs for steels in acids that were produced in USSR contained BA-6 [150] that also incorporated a nitrogen-containing heterocycle, *viz.*, 1,3,5-tribenzyltrihydro-1,3,5-triazine.

Unlike in hydrochloric media, six-membered *N*-containing heterocycles often weakly hinder the corrosion of steels in H_2SO_4, $HClO_4$, H_3PO_4 and HNO_3 solutions. A known method for improving the protective effect of organic CIs in these media involves combining them with anionic additives, *e.g.*, halide anions [21]. We already discussed above the possibility of improving the protective effect of substituted pyrimidines in corrosion of carbon steel in HNO_3 solutions by KI addition [52]. The synergism of action of the components of a mixture containing a substituted quinoline and halide ions on the corrosion of mild steel in 0.5 M H_2SO_4 is noted [108].

In our opinion, it is more promising to protect steels in these acids by combinations of nitrogen-containing heterocycles with S-containing compounds. For example, a small addition of KNCS to triazines with the formula



R - lauryl (T-1), palmityl (T-2), linoleyl (T-3)

makes it possible to obtain CIs capable of hindering mild steel corrosion in H_3PO_4 solutions at $t \leq 80°C$ (Table 3). Voltammetric measurements show that the efficient inhibition of steel corrosion by the formulations studied results from a considerable hindrance of the cathodic and anodic reactions on steel in H_3PO_4 by these mixtures in comparison with the CI components taken separately (Figure 2) [79].

Table 3. Corrosion rates of St3 mild steel (k, g/(m^2·h)) and coefficients of corrosion inhibition (γ) in 2 M H_3PO_4 by substituted triazines and their compositions with KNCS at various temperatures. Test duration: 2 h.

Inhibitor	***k*, γ**	**Temperature**				
		25°C	**40°C**	**60°C**	**80°C**	**95°C**
–	*k*	5.8	20	38	141	518
5.0 mM T-1	*k*	3.0	5.0	21	–	–
	γ	1.9	4.0	1.8	–	–
5.0 mM T-2	*k*	4.2	11	83	–	–
	γ	1.4	1.8	0.46	–	–
5.0 mM T-3	*k*	2.7	4.7	15	320	–
	γ	2.1	4.3	2.5	0.45	–
0.5 mM KNCS	*k*	6.6	16	31	78	315
	γ	0.88	1.3	1.2	1.8	1.6
4.5 mM T-1+ 0.5 mM KNCS	*k*	0.50	0.73	1.3	3.7	596
	γ	12	27	29	38	0.87
4.5 mM T-2 + 0.5 mM KNCS	*k*	0.69	0.95	1.6	12	606
	γ	8.4	21	24	12	0.85
4.5 mM T-3 + 0.5 mM KNCS	*k*	0.35	0.53	0.93	1.6	251
	γ	17	38	41	88	2.1

The ecological effect of the industrial application of the CI group under consideration is worthy of attention. Pyridine, quinoline, and their derivatives are toxic by themselves, which limits their usage at modern industrial plants that maintain stringent requirements for labour conditions and ecological safety of the plants. We cannot agree with W.W. Frenier and D.G. Hill who consider *N*-dodecylpyridinium bromide as a “green” CI [149]. In this context, it seems promising to search for CIs from among six-membered heterocycles with two or more N atoms. CIs obtained by modification of natural raw materials show promise. For example, 6-substituted *N*-(2-chlorophenyl)-1,3,5-triazine-2,4-diamines (T-1, T-2 and T-3) are synthesized from methyl esters of fatty acids derived from plant oils, such as coconut, palm and sunflower oils [79].

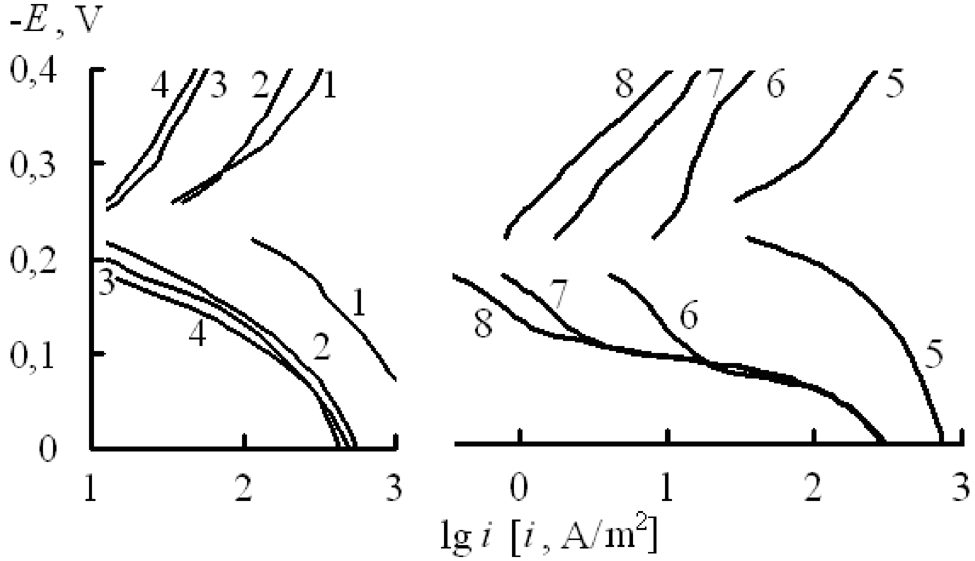


Figure 2. Polarization curves on St3 mild steel at $t = 60°C$ in 2 M H_3PO_4 (*1*) with addition of 5.0 mM T-1 (*2*), 5.0 mM T-2 (*3*), 5.0 mM T-3 (*4*), 0.5 mM KNCS (*5*), 4.5 mM T-1 + 0.5 mM KNCS (*6*), 4.5 mM T-2 + 0.5 mM KNCS (*7*), 4.5 mM T-3 + 0.5 mM KNCS (*8*).

Conclusion

N-Containing six-membered heterocyclic compounds are prone to adsorption on metal surfaces from mineral acid solutions. Based on the $(-\Delta G_a^0)$ values of these CIs on metal surfaces, it can be deemed with high probability that they are mostly bound to a metal by physical forces, but upon adsorption on its surface that slow down the cathodic and anodic reactions, and eventually inhibit its corrosion. Compounds containing S atoms or bulky substituents are most interesting. These compounds are adsorbed on metals more strongly and behave as more efficient CIs. It often happens that such CIs hinder metal corrosion in HCl solutions but do it much more weakly in H_2SO_4, $HClO_4$, and H_3PO_4. The heterocycles discussed above behave as CIs in “cold” solutions but lose these properties at higher temperatures. Examples of the use of six-membered *N*-containing heterocycles as CIs of various steels and non-ferrous metals (Al, Cu, Sn, Zn and their alloys) are available in literature.

The industrial application of individual six-membered *N*-containing heterocycles and their derivatives for metal protection in acid media is of little promise and is unjustified. It is more appropriate to use these compounds as components of inhibitor mixtures. Mixed CIs containing these compounds can hinder corrosion even in such corrosive media as high-temperature HCl solutions or hot H_3PO_4 solutions. The base for creating prospective mixed corrosion inhibitors for metals in acids should be searched for among six-membered heterocyclic compounds containing two or more nitrogen atoms or compounds obtained from natural raw materials.

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