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Physicochemical aspects of inhibition of acid corrosion of metals by unsaturated organic compounds †

Ya G Avdeev, Yu I Kuznetsov

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Abstract. The state-of-the-art in the development and improvement of methods for protecting metals from corrosion in mineral acid solutions using unsaturated organic compounds is considered. Characteristic features of the mechanism of their protective action on metal corrosion in acidic media are discussed. The bibliography includes 203 references.

I. Introduction

The search for efficient methods for anticorrosive protection of metals and alloys stems not only from the damage that corrosion causes for technology and economy [1–3] but also from the environmental pollution by corrosion products [4] or toxic compounds that result from the corrosion of chemical production equipment and pipelines.[5] One of the efficient methods for anticorrosive protection of metals is the use of corrosion inhibitors (hereinafter, inhibitors), *i.e.*, chemical compounds or compositions 'which being present in the system in a sufficient concentration reduce the rate of metal corrosion without considerable changes in the concentration of any corrosive reagent'.[6] Among the most corrosive production media are solutions of mineral acids (non-oxidants) used for acidizing of oil-bearing [7,8] and water-formations,[9] descaling of metal surface, and washing of internal surfaces of pipelines and other metallic equipment from mineral deposits.[10]

Practically, two groups of organic compounds are used for protection of metallic constructions in mineral acid solutions. The first group includes amines and quaternary ammonium salts, which are adsorbed on the protected metal surface intactly. The second group of inhibitors comprises unsaturated organic compounds, the multiple bonds in the molecules of which are highly reactive. Thus, acetylenic compounds can undergo addition reactions, readily isomerize and polymerize, and form organometallic compounds.[11,12] The chemical transformations of unsaturated compounds in a corrosive medium result in certain cases in the formation of a hydrophobic protective film on the metal surface, substantially inhibiting corrosion. The adsorption of such compounds on the metal surface occurs, as a rule, *via* interaction of the atoms forming the multiple bond with the surface metal atoms. In this respect, of particular interest are organic compounds in which a multiple bond is formed by different atoms (*e.g.*, azomethine bonds), since for such molecules the additional possibilities of adsorption on the metal surface emerge. Nitrogen-containing heterocyclic systems with conjugated double bonds are also promising for creation of corrosion inhibitors. On the whole, such compounds are more stable, which is very important for their application as inhibitors.[13] Many nitrogen-containing heterocyclic systems readily form complexes with metal cations.[13,14]

The protective action of acid corrosion inhibitors is usually studied by the gravimetric and electrochemical methods, while to determine the compoisition, structure, and thickness of protective layers or to elucidate the nature of metal – inhibitor bonds, physicochemical methods are used such as IR spectroscopy, ellipsometry,[15] X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), laser mass spectrometry (LMS),[16,17] combined chromatography – mass spectrometry,[15] and scanning tunnelling (STM) [18] and atomic force (AFM) [19] microscopy.

A promising trend in investigations of the inhibition of acid corrosion is the application of molecular modelling methods for the calculation of electronic structures of

Ya G Avdeev, Yu I Kuznetsov A N Frumkin Institute of Physical Chemistry and Eletrcochemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119071 Moscow, Russian Federation. Fax/tel. (7-495) 334 95 55, e-mail: avdeevavdeev@mail.ru (Ya G Avdeev), tel. (7-495) 334 95 90, e-mail: kuznetsov@ipc.rssi.ru (Yu I Kuznetsov)

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molecules and explanation of the inhibition mechanism. The assessment of the possibilities of molecule orientation, favourable configuration, steric and electronic effects is important to gain a better understanding of the mechanism of inhibitor action. The quantitative analysis of the structure–activity relationships for the molecules of organic compounds facilitates the development of more efficient inhibitors.[20–22]

The present review deals with acyclic organic inhibitors having multiple C≡C, C=C, C=O (aldehydes), and C=N bonds in the molecules and nitrogen-containing compounds (triazoles and tetrazoles). Many of these compounds have proven themselves as efficient inhibitors long ago, other compounds form the basis for the creation of a new generation of inhibitors.

II. Inhibition of metal corrosion in aicdic media by unsaturated organic compounds

1. Acetylenic compounds

The most extensively studied group of unsaturated inhibitors for acid solutions are acetylenic compounds. Some of them relate to the high-temperature inhibitors, *i.e.*, they are capable of protecting steel in solutions of mineral acids without reduction in efficiency up to 110 °C. This property is rarely common to inhibitors of acid corrosion. Let us consider in more detail the behaviour of the most important types of acetylenic corrosion inhibitors among which are acetylenic hydrocarbons, acetylenic alcohols and glycols, acetylenic halocarbons, halogen-substituted acetylenic alcohols, and acetylenic alcohol ethers.

Acetylenic hydrocarbons with a terminal triple bond are weak inhibitors of iron corrosion in hydrochloric and sulfuric acids, and their protective action at moderate temperatures reduces with an increase of molecular weight. As the temperature in hydrochloric solutions increases, their protective action decreases to be completely lost at 100 °C (Table 1). In the presence of acetylene, the polymeric products are formed on the surface of corroding iron, which is not observed for hex-1-yne. The abnormally high protective action in HCl is characteristic of diacetylene (buta-1,3-diyne), but other representatives of this series which do not contain conjugated bonds, *e.g.*, dipropargyl (hexa-1,5-diyne) are less efficient. The efficient corrosion inhibitors in HCl are vinylacetylenic and particularly divinylacetylenic hydrocarbons of variable structure. They form a polymeric film on iron. The radical polymerization initiators (benzoyl peroxide, UV irradiation) as well as temperature rise facilitate the polymerization of inhibitors on the metal surface and enhance their protective action. The vinylacetylenic compounds feature an afteraction effect.[23,24]

Acetylenic alcohols far surpass alkynes in the protective action and can be used for the protection of various steels, nickel and copper.[23,25–31] In steel protection in hydrochloric acid solutions, most efficient are normal primary and secondary alkynols [HC≡CCH(OH)R] (see Table 1). As the molecular weight increases, the protective action of primary alcohols somewhat decreases and that of secondary alcohols increases. Starting from non-1-yn-3-ol, the protective action of secondary alcohols decreases due to the reduction of their solubility. In sulfuric, perchloric, and phosphoric acids,[32] acetylenic alcohols are very weak inhibitors and, in some cases, they promote corrosion. In HCl the protective action of primary and secondary acetylenic alcohols increases with temperature rise, with time and with increase in the acid concentration, which is explained by the formation of polymeric films that protect metal. A low inhibition coefficient of tertiary alcohols is associated with their high reactivity leading to the polymerization of alcohols in the acid bulk rather than on the metal surface. Dihydric acetylenic alcohols are inefficient inhibitors. For instance, but-2-yne-1,4-diol is not efficient for the protection of iron in hydrochloric and sulfuric acids;[33,34] at the same time, hexa-2,4-diyne-1,6-diol is an excellent inhibitor in HCl.[35]

The high proptective action is exhibited by vinylacetylenic and allylacetylenic alcohols.[36–38] In all cases, the effect of inhibitor afteraction is observed. The efficiency of alcohols is enhanced by initiators that facilitate the radical polymerization of vinylacetylenic alcohols on the metal surface.

Table 1. Protective action of acetylenic compounds (c_{inhib} = 30 mmol litre^{-1}) in the corrosion of low-carbon steel in 4 M HCl depending on temperature.[23]

Inhibitor	Formula	T /°C	k [a]	Z [b] (%)
None		25	10.7	
		60	223	
		100	2310	
Acetylene	HC≡CH	25	0.40	96.3
		60	7.1	96.8
		100	1000	56.7
Hex-1-yne	HC≡C(CH$_2$)$_3$CH$_3$	25	0.52	95.1
		60	18.9	91.5
		100	2200	4.8
Prop-2-yn-1-ol	HC≡CCH$_2$OH	25	1.0	90.7
		60	4.1	98.2
		100	13.8	99.4
But-3-yn-1-ol	HC≡CCH$_2$CH$_2$OH	25	1.8	83.2
		60	8.0	96.4
		100	18.7	99.2
But-3-yn-2-ol	HC≡CCH(OH)CH$_3$	25	0.93	91.3
		60	3.8	98.3
		100	13.4	99.4
Hex-1-yn-3-ol	HC≡CCH(OH)(CH$_2$)$_2$CH$_3$	25	0.88	91.8
		60	1.6	99.3
		100	4.4	99.8
Non-1-yn-3-ol	HC≡CCH(OH)(CH$_2$)$_5$CH$_3$	25	0.90	91.6
		60	2.7	98.8
		100	6.0	99.7
2-Methyl)but-3-yn-2-ol	HC≡CC(OH)(CH$_3$)$_2$	25	6.3	41.1
		60	17.3	92.2
		100	160	93.1
But-2-yn-1,4-diol	HOCH$_2$C≡CCH$_2$OH	25	1.8	83.2
		60	12.4	94.4
		100	68.0	97.1
Dipropargyl ether	HC≡CCH$_2$OCH$_2$C≡CH	25	0.9	91.6
		60	2.5	98.9
		100	12.8	99.4

[a] In g (m^2 h)$^{-1}$; [b] $Z = \frac{k_0 - k_{in}}{k_0} 100\%$, where k_0 is the rate of corrosion in the supporting solution, k_{inhib} is the rate of corrosion in the presence of an inhibitor.

The protective action of dipropargyl ether only slightly differs from that of propargyl alcohol and is manifested only in HCl (see Table 1). However, its analogue, dipropargyl thioether, is an order of magnitude more efficient than propargyl alcohol in HCl solution and 40 times more efficient in H_2SO_4 solutions. Diol propargyl ethers are efficient inhibitors in HCl. As the temperature increases from 20 to 80 °C, their protective action enhances. The best inhibitor is dipropargyl ether of propane-1,3-diol.[35]

The halogen-containing acetylenic compounds were studied as inhibitors mostly by the example of propargyl halides. In hydrochloric solutions, the protective action of $HC\equiv CCH_2Hal$ increases in the series Cl < Br < I and exceeds the protective action of propargyl alcohol. As the temperature increases to 60 °C, the protective action of propargyl halides enhances, but subsequently it weakens by 100 °C.[39] A possibility of application of propargyl halides in solutions of oxygen-containing acids was shown with propargyl chloride. It is efficient in steel corrosion in sulfuric and perchloric acids but is not efficient in phosphporic acid. In H_2SO_4 the inhibition coefficient ($\gamma = k_0/k_{in}$) increases with temperature rise and in the course of time.[32, 40]

Halogen-substituted acetylenic alcohols $HalC\equiv CCR.(R')OH$ (Hal = Cl, Br, I; R, R′ = H, Alk) are inferior in efficiency to the corresponding halocarbons but can surpass analogous acetylenic alcohols.[39, 41] Propargyl halides and α-halogenated propargyl alcohols polymerize on iron surface.

For acetylenic inhibitors pertaining to various classes of organic compounds, a particular dependence of the protective action on the triple bond position in the molecule can be followed. The highest efficiency among the compounds of one class is manifested by those containing terminal triple bonds.

It is possible to define the scope of applicability of acetylenic compounds possessing rather high protective action (primary and secondary alk-1-yn-3-ols, dipropargyl ether and thioether and propargyl halides) as inhibitors of acid corrosion of iron. Most of them are efficient in hydrochloric acid solutions and are not efficient in solutions of oxygen-containing acids (sulfuric, perchloric, and phosphoric). The exception may comprise such compounds as dipropargyl thioether and propargyl chloride, which retain their efficiency in solutions of H_2SO_4 and $HClO_4$. The coefficients of corrosion inhibition for acetylenic inhibitors are often >100 and in some cases >1000. For example, at 80 °C in 15% aq. HCl for hex-1-yn-3-ol (0.3%), γ = 1880; in 25% aq. H_2SO_4, the addition of 0.2% of dirpopargyl thioether provides for γ = 1050.[35]

In the behaviour of acetylenic inhibitors for steel in hydrochloric acid solutions, some common regularities can be pointed out. As the acid concentration increases, their protective action enhances, which allows for their efficient application in highly concentrated (25% – 30%) solutions of HCl. The strengthening of the protective action of acetylene derivatives is observed with temperature rise up to a maximum after which the value of γ is drastically reduced. The value of this maximum for high-temperature acetylenic inhibitors (propargyl alcohol, hex-1-yn-3-ol, non-1-yn-3-ol, phenyl propargyl ether, *etc.*) ranges from 100 to 110 °C. The protective action of acetylene derivatives increases with time (up to 20 days) and maintains the high level for ~30 days. Hence, the acetylenic compounds can be recommended as inhibitors for iron corrosion in hydrochloric acid solutions with high acid concnetrations and at relatively high temperatures. The most frequently used range of concentrations of acetylenic inhibitors comprises 1 – 100 mmol litre^{-1} (Ref. 35). Currently, the application scope of acetylenic inhibitors for acid corrosion is extending. The information appeared on the use of propargyl alcohol and 2-butyne-1,4-diol for the protection of aluminium alloy 3003 in 0.5% aq. solution of NaCl.[42, 43] For mixtures containing up to 0.4 mmol litre^{-1} of acetylenic alcohol, the protection degree is >90% (25 °C).

2. Aldehydes

Aldehydes are used most often for the corrosion protection of steels. In hydrochloric acid solutions, aliphatic (isovaleric aldehyde, 7-hydroxy-3,7-dimethyloctanal) and aromatic (benzaldehyde, furfural) inhibitors retain their efficiency at temperatures ⩽ 60 °C. In solutions of H_2SO_4 and H_3PO_4, such compounds provide a low level of metal protection and even can promote the corrosion.[44–47] Among them, a particular attention should be drawn to α,β-unsaturated aldehydes (acrolein, crotonaldehyde, citral, and cinnamaldehyde), which surpass aliphatic and aromatic aldehydes in protective action in HCl (Table 2). Some of α,β-unsaturated aldehydes (citral and cinnamaldehyde) are compounds of plant origin and, hence, they can be considered to be relatively eco-friendly. The best results on the steel protection in hydrochloric acid medium were obtained with cinnamaldehyde, which, similarly to acetylenes, behaves as a high-temperature inhibitor.[44, 48, 49] This allowed Frenier and Hill[48] to suggest it as an alternative to rather expensive and toxic acetylenic inhibitors.

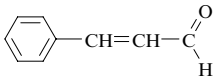
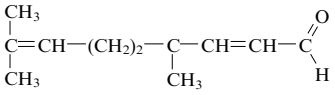
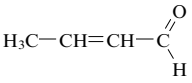
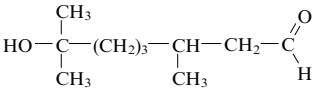
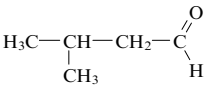
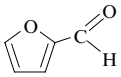
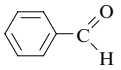
In recent years cinnamaldehye and its derivatives have found ever-growing application in the protection of metals from corrosion. Thus, it is recommended for the protection of carbon steel in acidic media.[50] The introduction of cinnamaldehyde into a solution of citric acid, which is used for the chemical rinsing of the primary coolant circuit of nuclear reactors, affords the protection of metallic constructions for 24 h. Therewith, the metal surface was noted to be coated by a protective layer consisting of iron(II) complexes and molecules of cinnamaldehyde.[51]

Attempts were made to use derivatives of cinnamaldehyde and some related compounds as corrosion inhibitors. Thus, *p*-dimethylaminobenzylideneacetone was tested as a potential inhibitor for the protection of soft steel in 1 M H_3PO_4.[52] The possibility of application of cinnamic acid *N*-phenylamides to inhibit the corrosion of lead in 0.1 M HCl was shown.[53] However, it should be noted that, as a rule, on going from cinnamaldehyde to its substituted analogues the protective action of an inhibitor declines.[49]

3. Azomethines

Azomethine compounds are used for the protection of a wide range of metals in a diversity of corrosive media. In hydrochloric acid solutions, azomethines of various structures (methoxyaniline,[54] *p*-anisidine, *p*-toluidine, and dinitroaniline[55] derivatives) efficiently inhibit steel corrosion, their protective action being enhanced as the acid concentration increases. At low concentrations (c_{HCl} = 0.1 – 0.5 mol litre^{-1}), none of the explored azomethines provided Z > 85% at the content of 0.04 g litre^{-1}; at the same time, in 2.0 M HCl, all of them showed high efficiency in the protection of metal from corrosion (up to

Table 2. Protective action of aldehydes (c_{inhib} = 10 mmol litre^{-1}) in the corrosion of steel St3 in 2 M HCl and H_2SO_4.[44]

Aldehyde	Formula	Acid	T/°C	k/g (m^2 h)$^{-1}$	Z (%)
None		HCl	25	5.5	
			60	64.0	
			80	378	
			95	995	
		H_2SO_4	25	11.7	
			60	91.4	
Cinnamaldehyde		HCl	25	1.6	70.9
			60	7.0	89.1
			80	22.9	93.9
		H_2SO_4	25	20.1	−71.8
			60	180	−96.9
Citral		HCl	25	2.4	56.4
			60	17.8	72.2
			80	187	50.5
		H_2SO_4	25	15.8	−35.0
			60	126	−37.9
Crotonaldehyde		HCl	25	2.5	54.5
			60	22.0	65.6
			80	210	44.4
		H_2SO_4	25	11.7	0.0
			60	57.7	36.9
Hydroxycitronellal		HCl	25	2.9	47.3
			60	34.4	46.3
3-Methylbutanal		HCl	25	5.0	9.1
			60	40.7	36.4
Furfural		HCl	25	3.3	40.0
			60	35.5	44.5
Benzaldehyde		HCl	20	3.4	38.2
			60	40.6	36.6

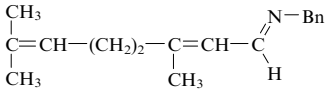
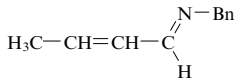
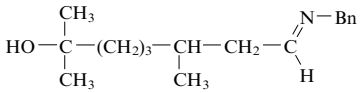
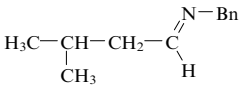
Z = 98%). It should be noted that under the same conditions the initial components used for the synthesis of azomethines possess weak protective properties ($Z \leqslant 50\%$). An analogous effect was noticed in another work,[56] where it was shown that in 0.5 M HCl the inhibiting action of *p*-aminobiphenyl comprised 92.6% at c_{inhib} = 0.04 g litre^{-1}, and the efficiency of the azomethine derived from it [2-(3-hydroxybenzylidene)-*p*-aminobiphenyl] at the same concentration was 97.2%. A high degree of protection by various azomethines in hydrochloric acid solutions was also mentioned in other works.[57–61] It was found that enhanced efficiency is characteristic of azomethines containing sulfur atoms.[62–64]

Among different types of azomethines, α,β-unsaturated azomethines prepared by condensation of various amines with crotonaldehyde, citral[65,66] or cinnamaldehyde[54,67] stand out. These compounds considerably surpass, in the protective action, azomethines with a related structure that do not contain the additional C=C bond (Table 3). The azomethine prepared by condensation of cinnamaldehyde and *p*-methoxyaniline provides $Z > 88\%$ for steel when present in solution in only 0.2 g litre^{-1} concentration. For the product of condensation of vanillin and *p*-methoxyaniline, such a protective effect is observed only at twice higher concentration of the inhibitor, and for azomethine formed by salicylaldehyde, $Z \leqslant 68\%$ even at c_{inhib} = 0.5 g litre^{-1}. α,β-Unsaturated azomethines retain their protective action at temperatures of < 80 °C.

A series of works showed a possibility of application of azomethines for the inhibition of corrosion of nonferrous metals in HCl solutions. Thus, they essentially inhibit the corrosion of aluminium and its alloys in 0.1–4.0 M HCl[68–71] as well as copper in 1.0 M HCl.[72] The furfural derivatives can be used for the protection of zinc in HCl, the protective action of such inhibitors being enhanced with time and being retained at temperatures of up to 75 °C.[73]

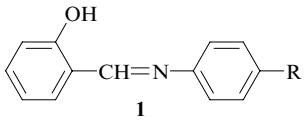
In sulfuric acid solutions, other conditions being equal, the protective action of azomethines is lower than in HCl.[55] Even promotion of steel corrosion was observed in 2 M H_2SO_4 (see Table 3).[65,66] However, this does not mean that azomethines themselves cannot serve as inhibitors in sulfuric acid media, since there are data on their inhibition of steel corrosion in more dilute solutions, namely, at $c_{H_2SO_4} \leqslant 1.5$ mol litre^{-1} (Refs 74–80).

Table 3. Effect of the products of benzylamine condensation with various aldehydes (c_{inhib} = 10 mmol litre^{-1}) on the rate of corrosion and the degree of protection of steel St3 in 2 M HCl and H_2SO_4 at 60 °C.[65]

Initial aldehyde	Azomethine	Acid	k /g (m^2 h)$^{-1}$	Z (%)
Citral		HCl	1.7	97.3
		H_2SO_4	130	−42.0
Crotonaldehyde		HCl	4.1	93.6
		H_2SO_4	176	−92.1
Hydroxycitronellal		HCl	15.7	75.5
		H_2SO_4	135	−47.4
3-Methylbutanal		HCl	21.2	66.9
		H_2SO_4	122	−33.2

Note. The rate of corrosion of steel St3 in 2 M HCl and H_2SO_4 is 64.0 and 91.6 g (m^2 h)$^{-1}$, respectively.

It is known that not so many organic inhibitors are efficient for the protection of zinc from corrosion in sulfuric acid. In this respect, a particular attention should be drawn to the works of Indian researchers,[81–85] who studied the inhibition of zinc corrosion in 0.25 and 0.5 M H_2SO_4 by azomethines based on ethylenediamine. Azomethines obtained from salicylaldehyde inhibit the corrosion of copper in 0.5 M H_2SO_4.[86] Grigor'ev *et al.*[87–89] demonstrated inhibition of sulfuric acid corrosion of nickel with derivatives of *o*-hydroxyazomethine **1**.



1

R = H, OH, Me, OMe, OEt, CO_2H, CO_2Et, Cl, NMe_2

An important property exhibited by azomethines is their afteraction in the metal protection in solutions of mineral acids.[90–93] It was established that aluminium and steel samples that have been kept in an acid solution inhibited by azomethine (for preliminary adsorption), after being transferred into a solution of the same acid without the inhibitor, are dissolved for several hours at the rates similar to those in the inhibited solution. In particular, for aluminium in H_2SO_4 solution (20 °C), the inhibiting aftereffect of *o*-hydroxyazomethines **1** is retained for 50 to 100 h. The duration of the aftereffect of such azomethines increases as the polarity of the substituents R enhances. The introduction of KCNS, KBr, KCl or thiourea additives into the solution for preliminary adsorption of an inhibitor may produce either increase or reduction of the azomethine aftereffect time, depending on the metal nature. The revealed effect offers new opportunities for the construction of more effecient protective layers of inhibitors on the metal surface, as was recently demonstrated for less corrosive neutral media.[94, 95]

In conclusion, compare the behaviours of different unsaturated acyclic inhibitors.[96] Among unsaturated compounds, the least inhibiting activity against acid corrosion of metals was found for compounds with one double C=C bond (alkenes and their derivatives),[97] C=O bond (aldehydes and ketones) or C=N bond (azomethines). The protective action of compounds with the C=C bond conjugated with C=O (α,β-unsaturated aldehydes) or C=N (unsaturated azomethines) groups is somewhat higher. The most efficient corrosion inhibition is observed in the case of compounds with the triple C≡C bond. Moreover, the following regularities in the protective action of inhibitors of the acid corrosion of steel can be noted:

— the protective action of unsaturated compounds increases with increase in their unsaturation;

— the presence of the halogen or sulfur atoms in the unsaturated compound has a positive effect on its protective propertes.

4. Azole derivatives

In the last decade, numerous reports appeared devoted to the protection of metals in solutions of mineral acids by azole derivatives. 1,2,4-Triazole[98] and 3-amino-1,2,4-triazole[99] possess low protective ability towards steel in HCl solutions. Triazoles with more intricate substituents[100–110] are efficient inhibitors of steel corrosion in hydrochloric acid and, as a rule, provide for 90% metal protection at the concentration in solution of >1 mmol litre^{-1}. Many of these triazole deriavtives relate to thiols[106–109] or sulfides.[110] Analogous results on the protection of steel by triazole derivatives were obtained in sulfuric acid solutions.[111–114] The improvement of the efficiency of iron protection in 1 M HCl or H_2SO_4 in the presence of a hydrophobic substituent in triazoles was exemplified by 4-amino-3,5-di(*p*-tolyl)-1,2,4-triazole,[115, 116] 4-dodecyl-1,2,4-triazole[117] and 4-amino-3-n-propyl-1,2,4-triazole-5-thiol.[118]

The triazole derivatives can be used for the protection of high-strength[113] and stainless steels[114] in mineral acids. Upon steel etching, triazoles reduce the hydriding of metals[109, 113] and hamper the deterioration of their mechanical properties. They are stable against the accumulation of iron(II) and iron(III) ions in the etching slution[119] and do not inhibit the removal of thermal cinder from the metal

surface.[120] The triazole derivatives may protect low-carbon steel in solutions of hydrochloric [105] and sulfuric [121] acids at temperatures above 120 °C and retain the thermal stability in such media up to 160 °C. An aromatic derivative of 1,2,4-triazole [105, 121] in the concentration of 20 mmol litre^{-1} at 120 °C inhibits the corrosion 313-fold in 2 M H_2SO_4 and somewhat less effectively, 55-fold, in 2 M HCl.

The application scope of triazoles for the protection of steel in acidic media is not restrcited to mineral acids, they appear to be also efficient in solutions of organic acids. Quraishi and co-workers [122–124] showed a possibility of use of substituted 1,2,4-triazole-5-thiols for the protection of steels in 20% aq. acetic and formic acids. The derivatives of 1,2,4-triazole-5-thiol [125] and 5-substituted 4-phenyl-4*H*-1,2,4-triazole-3-thiols [126] retain the protective action at elevated temperatures.

Triazoles can also find application in the protection of nonferrous metals in mineral acids. For example, in 2 M HCl, the addition of an aromatic derivative of 1,2,4-triazole [127] in the concentration of 5 mmol litre^{-1} reduces the rate of corrosion of copper more than 35-fold, whereas an equimolar amount of the known corrosion inhibitor for nonferrous metals, namely, 1,2,3-benzotriazole (BTA) promotes the corrosion. In 2 M HCl and H_2SO_4 (95 °C), the degree of brass protection is over 80%. Unlike the commercially produced inhibitors, catamine AB and BTA, it does not cause dezincification of the metal surface. The novel inhibitor also considerably inhibits the corrosion of zinc in HCl, H_2SO_4, and, what is particularly valuable, H_3PO_4 solutions at 25–40 °C. It is efficient also in the corrosion protection of aluminium alloys in hydrochloric acid solutions at temperatures $\leqslant$ 40 °C.

Along with triazoles, a good inhibiting action is manifested by substituted oxadiazoles retatding steel corrosion in hydrochloric acid solutions.[128, 129]

A relatively new class of inhibitors are tetrazoles inhibiting steel corrosion in HCl,[130–132] H_2SO_4 (Refs 132–134), and H_3PO_4 [134] solutions and, furthermore, the high degree of protection is achieved at low inhibitor concentration. In particular, nitrotetrazolium blue chloride [133] at c_{inhib} = 50 μmol litre^{-1} provides for 93% protection of steel in 0.5 M H_2SO_4. The possibility of harnessing 5-(2-dimethylaminoethyl)tetrazole [135] derivative for the protection of low-carbon steel in 2 M HCl and H_2SO_4 at 25–95 °C was demonstrated. Thus, at the concentration of this inhibitor of 5 mmol litre^{-1}, the rate of steel St3 corrosion is reduced more than 100 times even at 95 °C.

Various substituted phenyltetrazoles found application in the protection of copper and brass in dilute HCl (Ref. 136) and HNO_3,[137–139] zinc in dilute HNO_3 (Ref. 138) and aluminium in 1 M HCl.[140] In the corrosion of copper, brass and aluminium, the protective action of susbtituted tetrazoles increases in the series 1*H*-tetrazole < 5-amino-1*H*-tetrazole < 1-phenyl-1*H*-tetrazole < 1-phenyl-1*H*-tetrazole-5-thiol.

Besides triazoles and tetrazoles, steel corrosion in mineral acid solutions is inhibited by pyridine,[141–143] pyrazole,[144–149] pyrimidine,[150] pyridazine,[151] indole,[152, 153] benzimidazole,[154–157] quinoline,[158] purine [159–161] and 1*H*-imidazo[4,5-*f*][1,10]phenanthroline [162] derivatives. Along with them, heterocyclic compounds containing, apart from nitrogen atoms, also oxygen (oxazolidine,[163, 164] benzoxazole,[165] oxadiazole [166–168]) or sulfur (thiodiazole,[169–173] thiazole [174, 175]) find application. It is noted that the introduction of a sulfur atom into the heterocycle enhances the inhibiting action; at the same time, the presence of an oxygen atom in the heterocycle structure reduces the inhibitory properties of a compound.[132]

Hence, the compounds of azole class, especially triazoles and tetrazoles, are versatile corrosion inhibitors, capable of protecting a wide range of steels and nonferrous metals in different acidic mdedia. It is important that in the individual form such compounds have a broad temperature range of operation (above 100 °C). Most promising are azoles with bulky substituents bearing a thiol group.

III. Modern concepts of the mechanism of anticorrosive action of unsaturated compounds

1. Acetylenic compounds, aldehydes, and azomethines

The mechnaism of action of acid corrosion inhibitors pertaining to the unsaturated compounds has been discussed in scientific literature for more than half a century. The currently suggested mechanisms can be divided into two groups: adsorption and adsoprtion-polymerization.

According to the former, corrosion inhibition is caused by adsorption of an inhibitor on metal at a multiple bond; the contribution of polymerization processes is not taken into account. Unfortunately, the information on the adsorption of unsaturated compounds on the metal surface is unsystematic and fragmentary. For acetylenic compounds, in some cases, the presence of chemisorptive interactions between an inhibitor and metal surface can be assumed. Based on the quantum mechanical analysis of the models suggested for the adsorption of propargyl alcohol on iron surface, Kuteja *et al.*[176] concluded that its adsorption from the acid solution is accomplished by the interaction of the triple bond carbon atom with the surface iron atoms. The adsorption of but-2-yn-1-ol on austenite chromium nickel steel from 0.5 M H_2SO_4 is described by the Temkin isotherm, and the adsorption energy lies in the range of 60–90 kJ mmol^{-1} depending on the temperature, which supports the assumption about the chemical character of interactions between the inhibitor molecules and protected metal.[27] Under the same conditions, the adsorption of propargyl alcohol on platinum also follows the Temkin isotherm, and the adsorption energy is 49 kJ mol^{-1} (Ref. 177).

In acid solutions, the adsorption of aldehydes and their derivatives on steel is governed by the electrostatic forces. Thus, the adsorption of 3,4-dihydroxybenzaldehyde on cold-rolled steel in 1.0 M H_2SO_4 (Ref. 45) and vanillin in 3.0 M H_3PO_4 (Ref. 46) is described by the Temkin isotherm, and the adsorption energy falls within the range of 34.0–38.8 kJ mol^{-1}. The adsorption energy of *N*-phenylcinnamide on lead from 0.1 M HCl is $\leqslant$14.8 kJ mol^{-1}, which is typical of physical adsorption.[53]

The adsorption of azomethines on steels in HCl and H_2SO_4 solutions is described by the Langmuir isotherm [58, 61, 64, 75, 76, 78–80, 178, 179] and rarely obeys the Temkin equation.[62, 78, 180] For the azomethines tested, the value of adsorption energy is between 19 and 40 kJ mmol^{-1}, which does not confirm their ability to be chemisorbed on steel. The adsorption of azomethines on aluminium in hydrochloric acid and zinc in sulfuric acid follows the Langmuir isotherm, and the adsorption energy does not exceed 27 and 10 kJ mol^{-1}, respectively.[69, 71, 82]

Among the classes of acyclic unsaturated compounds described in Section II, only acetylene derivatives are amenable to chemisorption on the metal surfaces, which agrees well with their relatively high protective properties. Aldehydes and azomethines are bound to the metal surface by electrostatic forces, which, to a certain extent, causes their lower efficiency.

The adsorption theory does not account for the experimentally observed fact of enhancement of the inhibiting action of some unsaturated compounds with the course of time and with temperature rise. These facts are explained by the adsorption-polymerization theory. The molecules of an unsaturated inhibitor, specifically adsorbed on the metal surface, react with analogous molecules in solution, which leads to the formation of a polymeric protective film on the metal. Thus, in HCl, propargyl alcohol forms a polymeric film on iron, which grows in time. The limiting thickness of the film is reached in 25 h and comprises 60 Å. A monomolecular film provides for 80% – 90% protection; as its thickness increases, the protective action reaches >99%.[35] The formation of a polymeric film occurs both in hydrochloric acid solutions,[181] where propargyl alcohol is efficient, and in sulfuric acid,[182] where its efficiency is extremely low. The film that forms in hydrochloric acid contains carbonyl groups, double C=C bonds, hydroxy groups, and represents a resin-like product of $(C_6H_6O)_n$ composition, where $n = 2-10$ (the n value depends on the reaction conditions).[35] At the same time, there are no triple bonds in the polymer.[183] The organic phase contains iron(II) oxide and chloride inclusions.[181] The oligomer forming in sulfuric acid solutions is similar in composition to the films obatined in HCl; it does not contain triple bonds and has a stereoregular structure.[182] In HCl, polymerization is likely to proceed as an electroinitiated process [181] and in H_2SO_4, it is chemically initiated.[182] According to the former mechnaism, the polymerization of propargyl alcohol is initiated by the radical anions generated upon electroreduction of its molecule on the metal surface. In the chemical mechanism, the polymerization proceeds in the adsorption layer of an inhibitor on the catalytic metal surface. The analogous resin-like products of polymeric transfromations containing the atoms of the corresponding halogen were obtained for propargyl halides and halogenated propargyl alcohols in hydrochloric acid solutions. All the resins are deprived of triple C≡C bonds and contain double bonds.[39]

An important stage in the development of the concept of adsorption-polymerization mechanism is the work of O'Bockris and Yang,[184] in which the authors outlined the main causes for inhibition of electrode reactions by acetylenic compounds: the blocking effect, change in the electrical double layer structure by an inhibitor, change in the mechanism of electrode reactions by an inhibitor, and formation of a three-dimensional protective film of the polymerization and condensation products. The inhibiting action of a particular acetylenic inhibitor is determined by the ratio of the contributions of four different factors to the overall inhibition process. Depedning on which factors predominate, the mechanism can vary from the adsorption to adsorption-polymerization mechanism.

The formation of protective polymeric films is not a unique feature of only acetylenic inhibitors. The formation of such films in acid solutions in the presence of α,β-unsaturated aldehydes and azomethines is indirectly indicated by the high slope angles of the cathodic and anodic polarization curves of a steel electrode.[44, 66] Using cinnamaldehyde as an example, it was shown by infrared spectrsocopy [49] and combined chromatography – mass spectrometry [15] that its chemical transformations on steel in hydrochloric acid are possible. As a result, the steel surface is coated with an organic film conatining dimeric and trimeric products of transformations of cinnamaldehyde that may be aldehydes, semiacetals, phenylalkenes and arenes.[15]

In some investigations,[185, 186] the possibility of isomerization of acetylenic alcohols into α,β-unsaturated aldehydes in the corrosion medium is noted, which in certain cases can strengthen or weaken the protective action of an inhibitor. Such isomerization transformations of acetylenic alcohols in a corrosion medium can explain the presence of aldehyde groups in a protective film of an inhibitor formed on the metal surface.[186]

The investigation of the effect of unsaturated compounds on the kinetics of electrode processes shows that their ability to form a protective polymeric film is a necessary but not a sufficient condition for efficiency. Many acetylenic,[187, 188] aldehyde,[44] and azomethine [66] inhibitors are amenable to eletrochemical hydrogenation on iron in acid solutions. The process can proceed so readily that some of them completely lose the inhibiting action. In particular, propargyl alcohol in hydrochloric acid solutions efficiently inhibits the electrode reactions proceeding on iron (hydrophobic adsorbed chloride ion retards the hydrogenation of unsaturated alcohol). The metal surface is coated by a protective polymeric film, which is indicated by an increase of the Tafel slopes of polarization curves.[189] The situation changes for iron corrosion in solutions of oxygen-containing acids (perchlroic, sulfuric and phosphoric) possessing hydrophilic anions. Being reduced on the iron surface, propargyl alcohol facilitates the cathodic process; therewith, an increase in the corrosion potential up to the pitting potential takes place. This leads not only to a drop in the inhibitor efficiency but also to the corrosion localization. Propargyl chloride is less prone to the hydrogenation than propargylic alcohol and polymerizes more readily, which provides for its efficiency in HCl and oxygen-containing acids.[32] It is hard to escape the conclusion that hydrogenation of unsaturated compounds is adverse for the inhibition of acid corrosion. It is enough to find an unsaturated compound stable to hydrogenation, and it will equally well inhibit corrison in all acids. However, the inclination of unsaturated compounds to hydrogentaion is directly related to their polymerization ability. The compounds that are not susceptible to hydrogenaion do not polymerize on iron. These are inhibitors acting by the adsorption mechanism and having low protective effect in all acids. An example of such inhibitors is but-2-yne-1,4-diol. It weakly inhibits the electrode processes on iron in H_2SO_4 and HCl, practically does not change the Tafel slopes of polarization curves; no polymeric film is formed on iron.[188] Hence, in solutions of oxygen-containing acids, only those unsaturated compounds can be efficient for which the polymerization process predominates over hydrogenation. Moreover, an inhibitor must polymerize on metal rather than in the acid bulk.

The key point in elucidation of the mechnaism of action of unsaturated compounds is the relationship between hydrogenation and polymerization of such compounds. The compounds that are not inclined to hydrogenation do

not form protective inhibitor films. The unsaturated compounds prone to reduction can undergo the follwoing transformations:

1) cathodic reduction accelerating the cathodic reaction and causing inhibitor consumption;

2) polymerization in solution bulk removing the inhibitor from the corrosion medium;

3) formation of a protective polymeric film on the metal that is strongly bound to the steel surface. It is formed *via* the generation of complexes between the surafce metal atoms and molecules of the unsaturated compound and changes its structure in the course of time.

Considering the possible transformations, unsaturated ihibitors can be divided into five groups.[96]

1. Unsaturated compounds that do not polymerize on iron. The mechanism of action of such inhibitors is adsorption; their inhibiting action is not very high and does not depend on the acid anionic composition. An example is but-2-yne-1,4-diol.

2. Unsaturated compounds that are prone to hydrogenation and do not polymerize are represented by compounds with one double bond. Upon reduction, such inhibitors form saturated products and are not prone to further chemical transformations. The representatives are allyl alcohol and allyl chloride.

3. Unsaturated compounds that are prone to hydrogenation and do polymerize. The group joins the compounds containing a triple bond or conjugated double bonds. These compounds are efficient in HCl and can be characterized by high protective action at elevated temperatures. In solutions of acids with hydrophilic anions, they are not efficient and can promote the corrosion. The representatives include propargyl alcohol, hex-1-yn-3-ol, unsaturated azomethines and α,β-unsaturated aldehydes.

4. Unsaturated compounds that polymerize but are hard to be hydrogenated. The group is formed by acetylenic inhibitors the molecules of which contain a hydrophobic fragment. They are efficient in all acids at elevated temperatures. The representatives include propargyl chloride and dipropargyl thioether.

5. Unsaturated compounds that polymerize in the acid bulk. The highly reactive compounds the chemical transformations of which are catalyzed by acids; they exhibit low protective action in all acids. An example is dimethylethynylmethanol.

2. Azole derivatives

A distinctive feature of the azole class inhibitors compared to the above compounds is their chemical resistance in the corrosion medium. As a rule, azoles efficiently inhibit both electrode reactions of steel,[102, 103, 110, 111, 132, 133, 190] copper,[136–138] zinc,[138] and aluminium[140, 191] in solutions of mineral acids. They essentially reduce the capacity of the electrical double layer of metallic electrodes and increase the polarization resistance.

The quantum mechanical investigations of the models of disposition of azole molecules on the metal surface show that the adsorption of such compounds must proceed *via* the interaction of the surface metal atoms with the azole ring.[110, 129, 137–139, 162, 192, 193] In the presence of azole inhibitors, the metal surface is covered with the layers consisting of complexes of metal cations with inhibitor. It is assumed that the surface layers arising on metals provide for the high efficiency of inhibition of the metal corrosion by azoles.

The investigation of azole adsorption on the surface of steel[103, 110, 111, 132, 133, 190] and aluminium[140, 191] shows it can be satisfactorily described by the Langmuir isotherm. In the case of copper, the adsorption data can be described by the Frumkin isotherm.[137, 194] On different steels,[102, 111, 112, 132, 133, 162, 190] high adsoprtion energy of azoles (30–40 kJ mol^{-1}) is often observed, but this result does not allow for unambiguous conclusion on the chemisorption character of interaction of such inhibitors with the metal surface. The energy of azole adsorption on aluminium is even lower: 29–34 kJ mol^{-1} (Refs 140 and 191). Only in the case of adsorption of 1-phenyl-1,2,3,4-tetrazole-5-thiol from 0.1 M HNO_3, the adsorption energy comprises 68 kJ mol^{-1}, which suggests the chemisorption of the inhibitor on metal.[137]

In a number of cases, physicochemical methods are able to detect the formation of layers of a chemical compound formed by the inhibitor (azole) and metal on the surface. In HCl inhibited by 5-(3-aminophenyl)tetrazole, Raman spectroscopy shows the presence of surface layers of copper(I) complex with the inhibitor.[136] On the surface of carbon steel, in sulfuric acid containing 3-alkyl-1-vinylimidazolium bromides, the formation of the inhibitor protective layers was revealed by atomic force microscopy.[190]

The chemical unsaturation of azoles offers additional opportnities for the formation of protective layers on the metal surface that hamper the corrosive destructrion of metals. As a rule, the adsorption of such compounds on the metal surface is caused by electrostatic forces, and the inhibitor molecules are situated in the adosrption layer in the unchanged form (except for the cases of formation of complexes from the inhibitor molecules and corrosion products). Most often, azoles are not removed from the corrosion medium due to polymerization processes in the solution bulk, which is typical of acyclic unsaturated inhibitors prone to chemical transformations.

IV. Means of improving the efficiency of metal protection in acid solutions by unsaturated compounds

There are two means of improving the efficiency of metal protection by inhibitors. The first one consists in the creation of novel inhibitors *via* chemical modification of already known compounds and imparting desired properties to them. In our opinion, it is much more economical to create the inhibiting compositions possessing higher protective effects compared to the individual components and extended ranges of operation.

Of particular interest is the search for additives that will enhance the efficiency of already known acetylenic inhibitors, especially, at elevated temperatures. The additives strengthening the protective action of acetylenes must be those substances that initiate the polymeric transformations on the metal surface and those decreasing the cathodic hydrogenation of inhibitors. As additives of the first group, in the case of vinylacetylenic compounds, radical polymerization initiators are used. The second group comprises metal cations that increase the overvoltage of hydrogen ion reduction; nitrogen-containing corrosion inhibitors;

sulfur-contining compounds; halide ions. The highest synergistic effect is manifested by the additives that hydrophobize iron surface (halide and thiocyanate ions, sulfur-containing compounds). There is a number of mixtures based on acetylenes in which a role of additives cannot be explained by the considered mechanisms, *e.g.*, mixtures consisting of several acetylenic compounds and mixtures of high-molecular acetylenic alcohols and organic solvents.

In some cases, mixtures of acetylenic compounds may exert a higher inhibiting effect on the corrosion than individual compounds. For example, in 15% aq. HCl in the presence of 0.2% propargyl alcohol, the rate of corrosion was 0.5 g cm^{-2} day^{-1}, and in the presence of 0.2% hept-1-yn-3-ol, it was 0.0039 g cm^{-2} day^{-1}. Upon addition to the acid of 0.2% of a 1 : 1 mixture of these alcohols, the rate of corrosion comprised 0.0005 g cm^{-2} day^{-1}. Even higher efficiency is observed upon the application of a mixture of alcohols with carbon chains differing by more than four atoms.[35] The synergism of action is noted for mixtures of propargyl alcohol with propargyl halides ($HC\equiv CCH_2Hal$), but the combined action of propargyl and 3-halopropargyl ($HalC\equiv CCH_2OH$) alcohols is additive.[39]

The protective action of acetylenic alcohols poorly soluble in HCl increases upon the introduction of up to 5 vol.% of a water-soluble organic solvent (methanol, ethanol, ethanal, *etc.*) into acid solution, the effect being enhanced with temperature rise. The observed effect is explained by the increase in the solubility of acetylenic alcohol in acid in the presence of these additives.[35] However, there is information suggesting taht the formation of a protective film of the unsaturated inhibitor molecules on the metal surface involves the molecules of organic solvents, even when there are relatively chemically inert such as methanol or ethanol.[15]

As organic additives for acetylenic inhibitors in HCl, the following organic compounds of various classes are recommended: liquid hydrocarbons, different pyridine and quinoline derivatives, amines and quaternary ammonium salts, dimethylformamide, 2-amino-6-chlorobenzothiazole and benzothiazole-2-thiol. To enhance the protective action of acetylenic alcohols at tempeartures of >100 °C, metal halides (Cu, Cr, Fe, Bi, Mn, Pb, Ba, Li) are recommended. The strongest effect is achieved upon the harnessing of CuI. The addition of Cr^{3+}, As^{3+} and Ni^{2+} increases the inhibiting action of propargyl alcohol in refluxing HCl. A particular attention should be drawn to soluble compounds of arsenic(III). The observed effect is explained by the fact that As^{3+} ions, being reduced on iron, increase the overpotential of hydrogen ion reduction.[35]

The strongest effect can be achieved by the combined application of organic and inorganic additives. Thus, the application of nitrogen-conatining inhibitors (BA-6, PKU)‡ as additives in the presence of Sn^{2+}, Cr^{3+} cations and I^- anion makes it possible to use hex-1-yn-3-ol and propargyl alcohol for the protection of low-carbon steel in HCl at temperatures of up to 250 °C.[35] A five-component composition including different acetylenic alcohols, phenyl vinyl ketone, mixture of amines, industrial solvent and surfactant additive was recommended for the protection of carbon steels J55 and N80 and chromium stainless steel L80§ in HCl solutions and its mixtures with HF at temperatures of $\leqslant 150$ °C.[48]

It is essential that high-temperature inhibiting compositions can be created not only based on acetylenic compounds but also based on unsaturated aldehydes and ketones.[48] A composition including cinnamaldehyde, quaternary ammonium salt, industrial solvent and surfactant is used to protect the same steels at temperatures of up to 120°C. A mixture of phenyl vinyl ketone, amines, aromatic solvent, industrial solvent and surfactant allows the protection of chromium (13% Cr) and laminated steel in HCl and HCl + HF solutions up to 200 °C.

The disclosure of specific features of the inhibition mechanism allows, in certain cases, targeted selection of additives to improve the inhibitor protective properties. As it was mentioned above, a vast majority of acetylenic inhibitors lose the efficiency in H_2SO_4 solutions due to their cathodic hydrogenation. To enhance the protective action of propargyl alcohol, it was proposed[195] to use a range of relatively hydrophobic additives [Cl^-, Br^-, I^-, and CNS^- anions; thiourea, benothiazol-2-thiol (captax), catapine BPV] that suppress the cathodic process. All the studied additives appeared to have a positive effect on the inhibiting properties of propargyl alcohol in H_2SO_4. Most efficient were mixtures of propargyl alcohol with captax and thiocyanate ions, but some authors prefer to use mixtures of acetylenic alcohols with I^- (Refs 196–198) or hydrogen sulfide.[199, 200]

Like acetylenes, azomethines and aldehydes are also not efficient in sulfuric acid solutions due to the cathodic hydrogenation. In the presence of hydrophobic anions (I^-, CNS^-, diethyldithiocarbamate), azomethines and aldehydes in H_2SO_4 turn from corrosion promoters into inhibitors providing $Z \geqslant 90\%$.[44, 65, 66] In particular, equimolar mixtures of cinnamaldehyde with KI or sodium diethyldithiocarbamate (10 mmol $litre^{-1}$) reduce the rate of steel St3 corrosion in 2 M H_2SO_4 (at 60 °C) more than 50-fold, synergism in the component action being observed.

An interesting method for modification of azomethine inhibitors is their introduction into solution not in the individual form but in the form of complex compounds with transition metals. Often a complex compound appears to be more efficient than azomethine itself. Nickel(II) complex of *N*-(4-ethoxybenzylidene)-2-aminophenol in the

‡ BA-6 and PKU are products of urotropine condensation with benzylamine and benzyl chloride, respectively.

§ The compositions of the listed steels are presented (in mass %).

Element	Steel brand		
	J55	N80	L80
C	0.34–0.39	0.34–0.38	0.15–0.20
Si	0.20–0.35	0.20–0.35	$\leqslant$1.00
Mn	1.25–1.5	1.45–1.7	0.25–1.00
P	$\leqslant$0.02	$\leqslant$0.02	$\leqslant$0.02
S	$\leqslant$0.015	$\leqslant$0.015	$\leqslant$0.010
Cr	$\leqslant$0.15	$\leqslant$0.15	12.0–14.0
Ni	$\leqslant$0.20		$\leqslant$0.20
Cu	$\leqslant$0.20		$\leqslant$0.20
V		0.11–0.16	

Table 4. Effect of mixtures of substituted triazole (ST) with the molecular additive (MA) and KI on the rate of steel St20 corrosion in 2 M HCl and H_2SO_4 (test duration 0.5 h).[105, 121]

T/°C	HCl				H_2SO_4			
	inhibitor: ST + MA /mmol litre^{-1}	k_0 /g (m^2 h)$^{-1}$	k_{in} /g (m^2 h)$^{-1}$	γ	inhibitor: ST + MA /mmol litre^{-1}	k_0 /g (m^2 h)$^{-1}$	k_{in} /g (m^2 h)$^{-1}$	γ
100	10 + 10	1550	10.5	148	5 + 5	2260	2.0	1130
120	20 + 20	4990	16.0	312	5 + 5	3160	2.6	1215
140	20 + 100	8060	49.6	163	5 + 5	4040	4.5	898
160	20 + 100	12400	248	50	10 + 5	6780	19.2	353
200	–	–	–	–	10 + 5	15300	78.4	195

concentration of 10 μmol litre^{-1} can protect aluminium in 0.1 M HCl (25 °C). Under these conditions, azomethine itself practically does not inhibit the corrosion.[201]

To enhance the protective action of nitrogen-containing heterocyclic inhibitors, the addition of d-metal cations in low concentrations (< 0.1 mmol litre^{-1}) is often used.[147, 202, 203] For example, copper(II) cations increase the protective action of substituted tetrazoles (in particular, phenyltetrazole) towards steel in 2 M H_2SO_4 (60 °C).[135] This effect is explained by the formation of a protective layer from copper cation complexes with azoles on the metal.

The combined application of substituted triazoles and cheap molecular additives of the class of amines protects low-carbon steel in 2.0 – 6.0 M HCl at temperatures of ⩽160 °C. A composition of triazole derivative and the molecular additive provides the protection degree not lower than 99.3% upon steel St20 corrosion in 2 M HCl (⩽140 °C) (Table 4). Under the same conditions, the individual compounds of this mixture practically do not inhibit steel corrosion.[105]

An interesting result was obtained upon application of mixtures based on triazoles in inhibition of steel corrosion in H_2SO_4. A mixture of substituted triazole with KI or KBr protects low-carbon steel at temperatures of ⩽200 °C. In 2 M H_2SO_4 (200 °C), the most efficient mixture containing 10 mmol litre^{-1} of triazole derivative and 5 mmol litre^{-1} of KI (see Table 4) inhibits the corrosion almost 200-fold.[121] It should be noted that this is the first investigation on the inhibition of steel corrosion in H_2SO_4 at so high temperatures.

Compositions containing triazoles offer a range of technological advantages as high-temperature inhibitors compared with mixtures based on other unsaturated compounds. First of all, they are stable and do not undergo resinification with time, which is particularly characteristic of cinnamaldehyde.[125]

The inhibiting compositions based on acyclic and cyclic unsaturated compounds find wide applicaion in the protection of metals, especially steels in solutions of mineral acids. An important feature of these compounds is a possibility of high-quality protection of steels under conditions of high-temperature corrosion (up to 200 °C), which is particularly valuable for oil production with well acidizing producing high bottomhole temperatures.

V. Conclusion

The application of unsaturated compounds and mixtures based on them as corrosion inhibitors can provide high-quality protection of ferrous and nonferrous metals in solutions of mineral acids and, in some cases, also in organic acids. The most studied inhibition mechanism is that of the corrosion of ferrous and nonferrous metals by unsaturated acyclic compounds which are able to form protective coatings in the form of organic polymers on the metal surface. The substantially less studied inhibition mechanism is that of the metal corrosion by azoles, although there is a basis to assume the formation by such inhibitors of nanoscale coatings containing a polymeric complex compound of inhibitor and metal cation on the metal surface.

The quality of metal protection by unsaturated compounds is determined not only by the structure of their molecules but also by the chemical reactions in the corrosion medium and on the metal surface. The knowledge of these properties creates conditions for an optimal selection of inhibitors for metal protection in a particular corrosion medium. The investigation of the mechanisms of formation of protective layers by unsaturated compounds offers opportunities for their design *via* selection of the initial monomeric inhibitors, which provides polymeric films of the inhibitor with specified properties on the metal surface.

The efficiency of metal protection by azoles is determined by the elemental composition and structure of the heterocyclic fragment and by the hydrophobicity of the substitutents and their electronic effect on the ring. The application of hydrophobic azole compounds as inhibitors provides layers with high protective properties on the metal surface. Tetrazoles are rather little studied as inhibitors; the high reactivity and high thermal stability give hope that compounds able to protect metals under acid corrosion conditions will be found among them.

Compared to other classes of organic inhibitors of acid corrosion, unsaturated compounds possess a valuable advantage, namely, they can protect ferrous metals under conditions of high-temperature acid corrosion. The combined application of such compounds with additives of various nature ensures high-quality protection of metals in solutions of mineral acids at temperatures of up to 200 °C.

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