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Physicochemical aspects of metal corrosion inhibition in aqueous solutions

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Contents

I.	Introduction	75
II.	Oxidising inhibitors	75
III.	Adsorption inhibitors	77
IV.	Complexation-type inhibitors	80
V.	Polymeric inhibitors	84

Abstract. The state-of-the-art of research dealing with the development and perfection of metal corrosion inhibitors in aqueous solutions is analysed. The main mechanisms involved in formation of protective layers on metals by inhibitors are discussed. Ways of creating mixed corrosion inhibitors with high protective properties are considered. The bibliography includes 150 references.

I. Introduction

The method of prevention of metal corrosion based on the use of corrosion inhibitors (henceforth referred to as inhibitors), *i.e.*, chemical compounds or compositions 'which, when present in a system at sufficient concentrations, decrease the corrosion rate without causing considerable changes in the concentration of any corrosive reagent', has been known for several centuries.[1] However, it was only in the middle of the twentieth century that a scientific concept about the mechanism of the inhibitor action was created and first achievements in the directed synthesis of inhibitors appeared after that. Corrosion inhibitors are used in numerous systems, from water supply systems and virtually any power plants to the protection of microelectronics and contemporary military equipment. Considering that losses from metal corrosion exceed 5% of the gross national product in industrial countries, the development and application of inhibitors, which is one of the main methods of corrosion protection, should be considered as a scientific and engineering task of current interest.

The action of inhibitors is always associated with changes in the state of the surface being protected due to adsorption or formation of poorly soluble compounds with metal cations. Such compounds decrease the area of active metal surface and/or increase the corrosion activation energy; as a rule, corrosion is of electrochemical nature in aqueous media. It is no wonder that the first classification of inhibitors was based on their ability to slow down cathodic or anodic (or both) electrochemical reactions. Later, a group of inhibitors capable of suppressing corrosion by accelerating rather than slowing down cathodic reactions was added to this classification.[2] In the latter case, the action of an inhibitor is based on its electrochemical conversion, *viz.*, reduction. This process provides conditions for the thermodynamic stability of a thin protective oxide film, which, in turn, slows down the anodic reaction. A modern classification includes oxidants as well as adsorption, complexation and polymeric inhibitors.[3] Such a division suggests that inhibition mechanisms are diverse and that achievements in different fields of chemistry can be utilised for corrosion protection.

Only inhibitors used in aqueous solutions are considered in this review. The use of inhibitors in other systems has specific features which, from a chemist's viewpoint, deserve a separate discussion. However, the action of inhibitors is almost always based on their ability to prevent metal corrosion caused by the presence of water in a system, hence the leading role rightfully belongs to water-soluble corrosion inhibitors.

II. Oxidising inhibitors

Salts of chromic acid are the best-known oxidising inhibitors; they show protective properties toward many metals in a broad pH range. An important role in the mechanism of their action belongs to the reduction of chromate ions, *e.g.*, according to the reaction

$$CrO_4^{2-} + 4H_2O + 3e \longrightarrow Cr(OH)_3 + 5OH^-, \; E^0_{cor} = -0.13 \text{ V}.^{\dagger} \qquad (1)$$

Judging by the values of its standard potential and the free corrosion potential of iron in water (E_{cor} is -0.3 to -0.4 V), this reaction can occur even in neutral aqueous solutions. However, chromate undergoes reduction only at the initial instant when a metal contacts with the solution; after a film of hardly soluble chromium and iron hydroxides has been formed on its surface, reaction (1) virtually ceases [2] and a kind of equilibrium between Cr^{3+} compounds and adsorbed chromate ions is established. If a defect appears in the passivating film for some reason, chromate migrates into such a defect, undergoes reduction and 'heals' the film. This is one of the main reasons for the continuing use of chromates in conversion and protective paint coatings in spite of serious environmental restrictions.[4, 5]

Naturally, chromates manifest their oxidising properties more readily in acid solutions, especially on those metals whose E_{cor} is more negative than E_{cor} of iron, *e.g.*, on aluminium. However, acceleration of the cathodic reaction can also stimulate corrosion if an oxidant cannot create conditions for the formation of a passive film on a metal surface. The effect of oxidants is consid-

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† Hereinafter, the electrode potentials are presented *versus* the standard hydrogen electrode.

erably affected by the solution pH (especially in the case of aluminium due to its amphoteric properties). At certain stoichiometric ratios of components involved in electrochemical reactions, conditions can be created such that only foreign or mixed oxide layers are formed on the aluminium surface, whereas other oxoanion reduction products capable of loosening the oxide structure are absent.[6] Judging by the changes in the corrosion inhibition coefficient

$$\gamma = \frac{K_0}{K_{in}}$$

(where K_0 and K_{in} are the corrosion rates in a reference solution and in a solution containing the additive under study), chromate acts as a corrosion activator at $2.0 < pH < 6.0$ (Fig. 1), whereas its inhibiting effect is more pronounced in more acidic (or more alkaline) solutions.

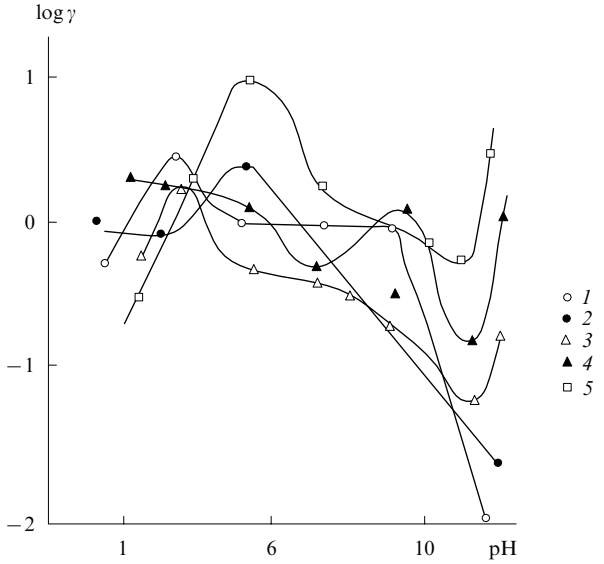


Figure 1. Effect of pH in a solution containing 0.01 N SO_4^{2-}, 0.1 N Cl^-, 0.1 N F^- and oxoanion additives on the inhibition coefficient of aluminium corrosion.[6]
Additive: (*1*) 0.1 N $Cr_2O_7^{2-}$, (*2*) 0.1 N MnO_4^-, (*3*) 0.05 N VO_4^{3-}, (*4*) 0.05 N WO_4^{2-}, (*5*) 0.05 N MoO_4^{2-}.

It has long been an important problem to find inhibitors that are less environmentally hazardous than toxic chromates. Most commonly, molybdates are used as substitutes; their oxidising properties are inferior to those of chromates (see Fig. 1). Thermodynamic calculations showed[7] that molybdate forms a barely soluble salt at potentials of active dissolution of iron in weakly acidic solutions (at $pH < 6.0$),

$$Fe + HMoO_4^- = FeMoO_4 + H^+ + 2e,\ E = E^0 - 0.0295\,pH. \quad (2)$$

The oxidising properties of molybdate with respect to steel do not manifest themselves in neutral media, so efficient protection of the steel surface requires the presence of yet another oxidant.[8] Black MoO_2 films are formed at $pH < 5$, which suggests that reduction of molybdate or, more accurately, isopolymolybdate compounds occurs. However, passivation phenomena manifest themselves only slightly even at pH 3. On metals whose free corrosion potentials are more negative than that of steel, the effect of molybdate is also observed in neutral media, let alone in weakly acidic solutions. In fact, the protective properties of molybdate with respect to zinc attain a maximum in solutions with pH 5.0; however, the following reaction is possible at pH 7:

$$MoO_4^{2-} + 2H_2O + 2e = MoO_2 + 4OH^-. \quad (3)$$

Corrosion inhibition occurs due to the formation of a thin layer of a molybdate reduction product on the zinc surface.

In the past, molybdates have attracted the attention of researchers as compounds that can prevent pitting of various steels, including stainless steels. The effect of MoO_4^{2-} as a corrosion inhibitor is even compared with the effect of molybdenum as an alloying component of ferrite iron–chromium alloys.[9,10] However, MoO_4^{2-} acts as an adsorption inhibitor rather than an oxidant, since the nucleation and development of pits occur in the passive region of potentials where molybdenum can, in fact, be oxidised into MoO_4^{2-}.

In a discussion of molybdates, tungstates and similar salts, one cannot neglect their ability to form heteropoly compounds.[11] Many of them are stronger oxidants than molybdate, hence they can be regarded as suitable compounds for the protection of metals in highly corrosive media. For example, salts of phosphomolybdic acid have long been known as corrosion inhibitors in hot brines, but some specific features of their protection mechanism have been revealed only recently.[12] It was proven that phosphomolybdic acid is an efficient corrosion inhibitor of steel in acid brines (65% LiBr) only at temperatures above 120 °C. Its addition to brine accelerates the cathodic reaction on steel and thus increases E_{cor} by 0.1–0.15 V. In weakly alkaline brines (pH 8.5), this acid can decrease the corrosion rate of steel by an order of magnitude in a broad temperature range (80–220 °C). The effect of phosphomolybdic acid on the effective activation energy of corrosion (ΔG^*_{ef}) depends on the solution pH: the value of ΔG^*_{ef} decreases at pH 5.0 but increases at pH 8.5; this suggests that the mechanism changes due to decomposition of the acid and incorporation of its fragments into the oxide film. Thus, the mechanism of steel protection is not limited to the increase in the oxidative properties of the solution upon addition of phosphomolybdic acid; to a considerable extent, it results from changes in the composition of oxide films resulting in an increase in their corrosion resistance.

Inhibition of metal corrosion in solutions of acids by inhibitor reduction products is typical of weaker oxidants, too. Iron protection by phenylarsonic acid ‡ is believed to occur according to this mechanism.[13]

Oxidants that do not form oxides (hydroxides) upon reduction can also be efficient inhibitors.§ Organic nitro compounds that are reduced at high rates even in neutral media can serve as examples. For example, the current density in the reduction of 3,5-dinitrobenzoate (> 10 mA cm^{-2}) exceeds considerably the passivation current density (i_p) of iron in borate buffer solution.[2] An oxidant of this kind does not affect directly the anodic reaction of iron dissolution, but it can increase the pH of the near-electrode layer due to generation of hydroxyl anions, which favours passivation. The efficiency of this type of inhibitor (*e.g.*, derivatives of benzoic acid, phenol, naphthol, *etc.*) was proven in numerous studies generalised in a monograph by Rozenfeld and Persiantseva.[15]

Trabanelli[16] correctly noted that reduction of organic inhibitors in acids can give chemical compounds some of which can protect metal surfaces whereas others can stimulate metal dissolution. Reduction of sulfoxides to organic sulfides, which are more efficient inhibitors, is a typical example of secondary inhibition.

‡ However, this acid inhibits the corrosion of titanium for a different reason, *viz.*, due to the formation of insoluble complex compounds with its cations.

§ The reference to steel protection by sodium nitrite leaves room for discussion. Some authors ascribed its protective effect in neutral solutions solely to adsorption of the NO_2^- anion on the metal, relating passivation in acid media only to the oxidation properties of nitrite.[2] However, it has already been proven that the oxidation properties of nitrite may not be ignored in the former case, near the free corrosion potential, as well.[14]

III. Adsorption inhibitors

If a protective layer is formed by adsorption-type inhibitors, adsorption is not only the first but also the main step. Obviously, it can play an important role in mechanisms of action of other inhibitors as well, but their interactions with metals are not limited to adsorption.

The kinetics of metal corrosion depends on many factors (local phase and chemical equilibria, surface tensions and activities of components in interphase layers), but the most important role belongs to the electric and energy characteristics of the surface. It is not surprising that one can slow down metal corrosion by affecting the adsorption of a medium component, since adsorption can change the above characteristics considerably. On the other hand, the majority of studies were performed with polycrystalline metal surfaces where it is difficult to detect the reconstructing effect of an inhibitor on the near-surface layer and on the electronic structure of the adsorbent. Therefore, though admitting the importance of studies on such effects,¶ let us limit ourselves to consideration of the 'macro effects' of an inhibitor that is adsorbed, *i.e.*, how it affects the rates of electrode reactions and the metal corrosion itself. If an adsorption-type inhibitor is used, an exceptionally important role belongs to the redox properties of the medium components and their adsorptivity.

The processes of adsorption and formation of protective layers on a metal substantially depend on the charges of the surface and inhibitor species. As a rule, cation-active inhibitors slow down cathodic reactions and active metal dissolution. Local corrosion is more efficiently prevented by anion-active inhibitors. However, the electrostatic interaction of an inhibitor with a metal surface is not the only motive force of adsorption. Some contributions to it can made by 'squeezing-out' of inhibitor species from the interionic space [18] and by hydrophobic interaction of non-polar inhibitor fragments with water.[19] Donor–acceptor interactions between a metal and an inhibitor can result in a stronger chemisorption binding of the latter to the surface.

If a metal is dissolved from the active state, which is usually the case in acids, then, for moderate metal surface coverages (θ), it is possible to single out two main contributions to the corrosion inhibition coefficient, *viz.*, related to changes in the ψ_1-potential and to surface blocking:

$$\log\gamma = \text{const} \times \Delta\psi_1 - \log(1-\theta). \qquad (4)$$

Even this simplified approach proposed by Antropov back in the 1970s [20] proved to be useful for formulating the concept of inhibitor action. However, it does not answer the important question: what structure should a compound have in order to be an efficient inhibitor?

Other approaches are required to establish the inhibitor structure–efficiency relationship. The majority of adsorption inhibitors are organic compounds; that is why many researchers used the linear free energy (LFE) relationship to reveal the role of the inhibitor structure.[14, 21–25]

Grigoriev and Ekilik [21] studied this problem in most detail in relation to acid corrosion, which usually occurs in the active dissolution region of potentials. They showed that if the inhibitor species are small and their adsorption increases the corrosion activation energy ($\Delta G^{\neq}$) due to charge redistribution in the double electric layer, the following equation is valid:

$$\log\gamma_R = \log\gamma_H + \rho\sigma, \qquad (5a)$$

where ρ is the reaction parameter, which is assumed to be equal to unity for a standard reaction series and which depends on the nature of the reaction being studied and on the conditions under which it occurs; σ is a constant of a substituent R, which accounts for its electron-donor ($\sigma < 0$) or electron-acceptor ($\sigma > 0$) effect on the reaction centre in comparison with hydrogen. In the general case of inhibitors capable of partial blocking of the active sites, equation (5a) assumes the form

$$\log\left(\frac{\gamma_R}{\gamma_H}\right) = \rho\sigma - \log\left(\frac{\theta_R}{\theta_H}\right), \qquad (5b)$$

where θ_H and θ_R are the degrees of coverage of the metal surface by the non-substituted and substituted inhibitor of the given reaction series, respectively. Similar regularities were also observed by many authors, not only in acidic but also in other media. For example, the efficiency of *N*-benzylideneaminoethanol derivatives in neutral medium containing hydrogen sulfide increases linearly with an increase in the electron-donor effect of the substituent R taken into account by its Wepster's σ^n-constant (Fig. 2).[24] According to Eqn (5b), substituents affect the protective properties of organic compounds solely by increasing the inhibitor adsorption; as a result, the value $\Delta G^{\neq}$ increases, whereas the surface area of the metal that undergoes corrosion decreases. For example, if the inhibitor being adsorbed is an electron donor, the inhibitor–surface binding strengthens with an increase in the electron density on the reaction site. Other mechanisms of inhibitor adsorption are also possible (see, *e.g.*, the monographs [14, 20]).

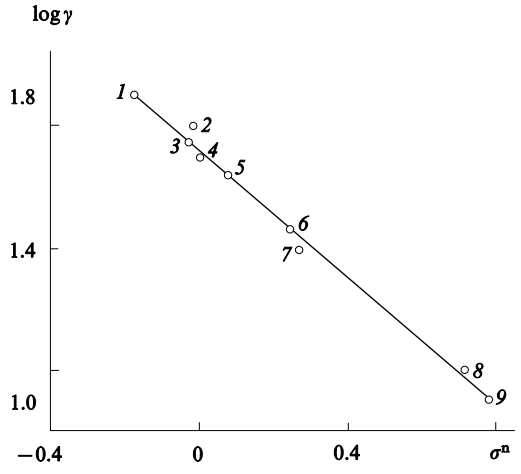


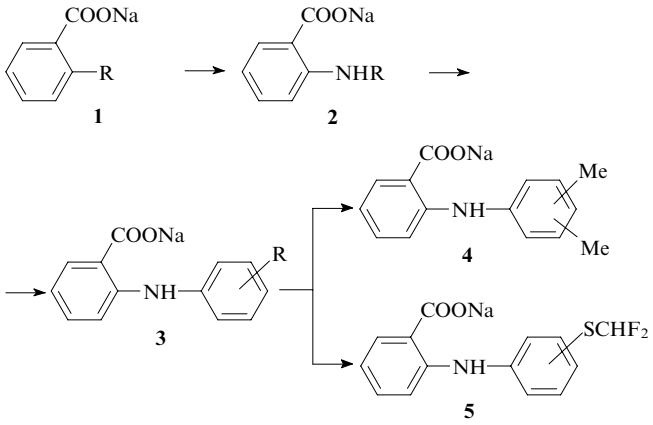
Figure 2. Dependence of the inhibition coefficient of steel corrosion in aqueous solution (0.5% NaCl, 0.25 g litre^{-1} CH_3COOH, 0.4 g litre^{-1} H_2S, pH 6.0) by substituted *N*-benzylidenaminoethanols with general formula $HO(CH_2)_2N=CH-C_6H_4-R$ on Wepster's constants of substituents.[24]
Substituents: (*1*) *p*-$N(CH_3)_2$; (*2*) *m*-OH, *p*-OCH_3; (*3*) *m*-OCH_3, *p*-OCH_3; (*4*) H; (*5*) *m*-OCH_3; (*6*) *p*-Br; (*7*) *p*-Cl; (*8*) *m*-NO_2; (*9*) *p*-NO_2. The inhibitor concentration is 0.004 mol litre^{-1}.

The approach considered above can also be applied for describing the effect of organic compounds on the passivation current density of metals, though the surface blocking in the active–passive transition region can be caused by oxide formation to a greater extent than by the inhibitor adsorption. Both linear and more complex dependences of $\log\gamma_p$ (here, $\gamma_p = i_p^0/i_p$, i_p^0 and i_p are the current densities in the reference and inhibited solutions, respectively) on substituent σ-constants were obtained for acidic [21] and neutral [14] media.

Studies of the effect of the organic anion structure on iron passivation in neutral solutions made it possible to find [14] new efficient adsorption-type inhibitors. Benzoate (**1**) hinders passivation; however, by introducing various substituents in the benzene ring, it was found that anthranilates (**2**) facilitate passivation. In the series of *N*-substituted anthranilates **2**, sodium *N*-phenyl-

¶ An attempt to generalise them was undertaken previously.[17]

anthranilate (SPA) **3** is notable for its passivating capability. It is in an aqueous solution of this corrosion inhibitor that the possibility of iron passivation without the formation of an oxide film was shown for the first time.[26] The discovery of this phenomenon, which was called adsorption passivation,[14,27] inspired a search for novel, even more efficient passivators; of the compounds tested, salts of mefenamic acid **4** (MEF) and isodiftorant **5** are noteworthy.



The linear free energy relationship principle was successfully used to describe the inhibition of local corrosion of metals, which is an even more complex process. In this case, the displacement of the electrode local depassivation potential [or the potential of the formation of the first pit (E_{pit})] to more positive values

$$\Delta E = E_{\text{pit}} - E_{\text{pit}}^{\text{background}}$$

was used as the inhibitor efficiency criterion. This value is determined from potential–time dependences or from anodic polarisation curves. In many cases, V-shaped dependences of ΔE on substituent σ-constants were observed, *i.e.*, the value of ρ changed its sign within a reaction series; this is caused by a change in the rate-determining step of the process. For example, this is typical of passive state stabilisation of the D16T aluminium alloy by *o*-substituted benzoates.[3] In this case, the branches corresponding to electron-donor and electron-acceptor substituents can have different sensitivities to the nature of the corrosive anion,† pH and solution temperature.

If solvation effects for a reaction series in question and a standard reaction series differ considerably, it is worthwhile to take into account, aside from the substituent σ-constant, its hydrophobicity π- or *f*-constants calculated from distribution factors of compounds in an octanol–water system

$$P = \exp\frac{\Delta G_{\text{o-w}}}{RT},$$

where $\Delta G_{\text{o-w}}$ is the distribution free energy for a compound.[28] This approach, which takes into account the electronic and hydrophobic properties of a substituent simultaneously, was originally used in biochemical studies; however, it also proved to be useful for description of efficient inhibitors.

Using quantitative prediction methods, it was shown that the efficiency of metal protection is limited if adsorption inhibitors that are individual chemical compounds are only used. This is connected with the tightening of environmental requirements. In many systems, the best protection is achieved by surfactants with high hydrophobicity ($\log P > 3$), *i.e.*, compounds poorly soluble in water and therefore unsafe ecologically.[29] In view of this, it becomes ever more urgent to develop inhibitor mixtures from components that could improve metal protection more efficiently than any of its components.

† Not only Cl^- but also other anions (I^-, Br^-, NCS^-) can cause depassivation in the system studied.[3]

The majority of such inhibitors for acidic media were created on the basis of the double electric layer recharging effect by some anions discovered back in the 1950s. The essence of this effect is as follows: an anion adsorbed on a surface that was initially charged positively gives some negative charge to that surface. Large organic cations that have considerable shielding effects can be adsorbed on such a surface; this improves the metal protection. There are many examples of successful corrosion inhibition by this method in complex systems. Schmitt *et al.*,[30] who considered the synergism and antagonism of various inhibitors of carbon dioxide-induced corrosion of steels, found that, though the surfaces to be protected contain carbonate deposits, the inhibition efficiency is largely determined by cooperative adsorption of anions and alkylammonium cations. According to results obtained by Shikai and Yufen,[31] the activity of anions in mixed inhibitors containing organic cations depends on the nature of the acid and decreases in the following series:

H_2SO_4	$I^- > SCN^- > HS^- > Br^- > Cl^-$;
HCl	$I^- > HS^- > Cl^- > SCN^- > Br^-$;
HF	$SCN^- > I^- > HS^-$;
CH_3COOH	$HS^- > SCN^- > I^- > Br^- > Cl^-$.

The mutual effects of components in a mixed inhibitor are usually evaluated by comparing the product of their corrosion inhibition coefficients ($\Pi\gamma_i$) with a similar value measured in the presence of the corresponding mixture (γ_{mix}). If the mutual effect coefficient *m* of the components

$$\kappa_m = \frac{\gamma_{\text{mix}}}{\Pi\gamma_i} \tag{6}$$

is larger than 1, one can say that their protective effect is enhanced, whereas if it is lower than 1, the protective effect is weakened.

A similar criterion was suggested [32] for the analysis of the concentration dependences γ of individual and mixed inhibitors. For example, if *n* portions of an individual inhibitor Δc_i are introduced successively (with its zero initial concentration), the overall concentration effect coefficient is expressed by the formula

$$\kappa_c = \frac{\gamma_{\Sigma c}}{(\gamma_{\Delta c_i})^n}, \tag{7a}$$

where the subscripts show whether the measured values reflect the effect of the total inhibitor amount (Σc) or of its certain portion (Δc_i). In the case of the power-law dependence common for adsorption inhibitors

$$\gamma = \gamma_0 c^{\beta},$$

where γ_0 and β are constants, Eqn (7a) assumes the form

$$\kappa_{\Sigma c} = \gamma_0^{1-n} n^{\beta} (\Delta c_i)^{\beta(1-n)}. \tag{7b}$$

For *m* inhibitors in a mixture and a variable concentration (c_i) of one inhibitor, designating the $\gamma_{\Delta ci}$ for the mixed inhibitor as $\gamma_{\Delta ci,\Sigma}$, the following equation is obtained:[32]

$$\kappa_m = \frac{\kappa_{\Sigma c}(\gamma_{\Delta c_i,\Sigma})^n}{\Pi\gamma_i}. \tag{8}$$

Ekilik and Ekilik [32,33] analysed the equation they derived for the inhibition of iron corrosion in 1 M H_2SO_4 by 2-(2-pyridyl)-benzoimidazole, NaCl, NaF, NaSCN and their binary and ternary mixtures. They concluded that the effect of chloride on the protective action of the azole exceeds the mutual effect coefficients for all other combinations studied. It was also shown that evaluation of mutual effects of mixture components in the case of iron acid corrosion inhibition requires that not only the kinetic equations of partial electrode reactions but also the free corrosion potential be taken into account. If changes in E_{cor} are ignored, erroneous conclusions about the mutual enhancement of mixture components can be drawn.

It is in much more rare cases that the presence of certain cations increases the protective effect of organic anions. For example, local depassivation of iron in weakly alkaline solutions is more strongly inhibited by phenylanthranilic acid if this inhibitor is combined with hexamethylenediamine.[34] However, this kind of synergy of protective effects of inhibitors is not versatile. Selective dissolution of binary alloys (45% Ni + 55% Zn, 70% Cu + 30% Zn, 90% Cd + 10% Zn, 97% Sn + 7% In) in weakly acidic solutions of mixtures of cation-active organic compounds (acridine, substituted pyrylium salts, 2-aminobenzoimidazole) and halides [35] was found to involve mainly an antagonism of the mutual effects of inhibiting mixture components caused by their competitive adsorption.

The approach based on the linear free energy relationship is also used to study the mutual effects of inhibitors and to search for more efficient inhibitor mixtures.[36–38] For a mixture of inhibitors corresponding to the same reaction series and at their constant total concentration

$$c_1 + c_2 + \ldots + c_i = \text{const}$$

the following relationship is valid:

$$\log\gamma = a + \rho\sum_{i=1}^{n} N_i\sigma_i\,, \qquad (9)$$

where a is a constant and N_i is the molar fraction of the ith compound in the mixture (*i.e.*, $\Sigma N_i = 1$). If the inhibitors present in the system and corresponding to m different reaction series are designated by the left subscript 1, 2, ..., m, then for an ideal system, *i.e.*, a system where no mutual effects of the inhibitors exist, one can write:

$$\log_m\gamma_c = $$

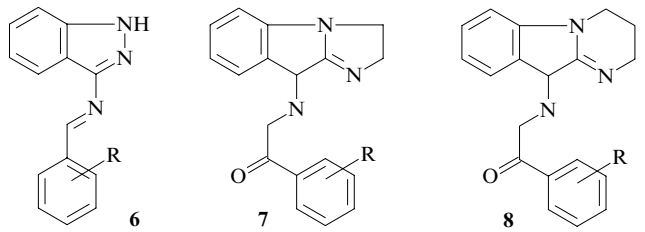
$$= \sum_{1}^{m} a + {}_1\rho\sum_{i=1}^{{}_1n}\left({}_1N_i \times {}_1\sigma_i\right) + \ldots + {}_m\rho\sum_{i=1}^{{}_mn}\left({}_mN_i \times {}_m\sigma_i\right). \qquad (10)$$

In a similar equation for real corrosion systems, the first term and the coefficients do not match those in Eqn (10). Taking this into account, Grigoriev *et al.*[38] assumed that, provided that the concentrations of the components are unchanged, *i.e.*, N = const, the ρ values, which are different for different reaction series, become equal for mixtures of these compounds. In such a case, the following equation is valid:

$$\log_m\gamma_{\text{mix}} = $$

$$= {}_m a_{\text{mix}} + {}_m\rho\left[\sum_{i=1}^{{}_1n}\left({}_1N_i \times {}_1\sigma_i\right) + \ldots + \sum_{i=1}^{{}_mn}\left({}_mN_i \times {}_m\sigma_i\right)\right]. \qquad (11)$$

In fact, Eqn (11) is well obeyed for mixtures of azomethine **6**, imidazobenzoimidazole **7** and pyrimidobenzoimidazole **8** derivatives



in 1 M H_2SO_4 + 0.25 M NaCl solution at different temperatures and with different numbers of components (m). It was found that the concentration of a mixed inhibitor (consisting of representatives of the above reaction series) ensuring the required corrosion inhibition coefficient ($_{\text{mix}}c$) can also be found using substituent σ-constants and taking the molar fractions of each mixture component into account

$$\log {}_{\text{mix}}c = a + \rho\sum N_i\sigma_i. \qquad (12)$$

To optimise the composition of inhibitor mixtures, it is necessary to establish the reasons for deviations of their action from 'additivity'. This requires additional studies, primarily on joint adsorption of mixture components on metal surfaces. In this respect, attention should be paid to effects of mutual enhancement of inhibiting effects and adsorption of organic anions.

For example, experiments on corrosion protection of steel by mixtures of hydroxynaphthoates (HNP) with substituted anthranilates showed [39] the synergistic effect of these inhibitors, which is only observed if the anion of the aromatic amino acid has high hydrophobicity, *e.g.*, in mixtures with MEF anions (Fig. 3). Ellipsometric studies showed that the synergism results from the ability of one of the anions (at its low concentration) to initiate the adsorption of the other anion. In this case, the free adsorption energy ΔG_a° increases, *i.e.*, the bond between the inhibitor and the oxidised iron surface strengthens. This effect is expressed even more clearly for SPA – sodium oleate mixtures; however, in this case an adduct, which interacts with the surface through chemisorption, is formed in the solution bulk; the ΔG_a° value reaches 40 ± 4 kJ mol^{-1} (see Ref. 40), which is more than two times higher than $\Delta G_a^\circ = 16.8 \pm 0.3$ kJ mol^{-1} for SPA.

The hard – soft acid – base (HSAB) principle is widely used to estimate possible interactions involved in joint adsorption of inhibitors.[14, 31, 41–46] This approach mainly relies on the nature of the reaction centres rather than on the nature of the substituent.

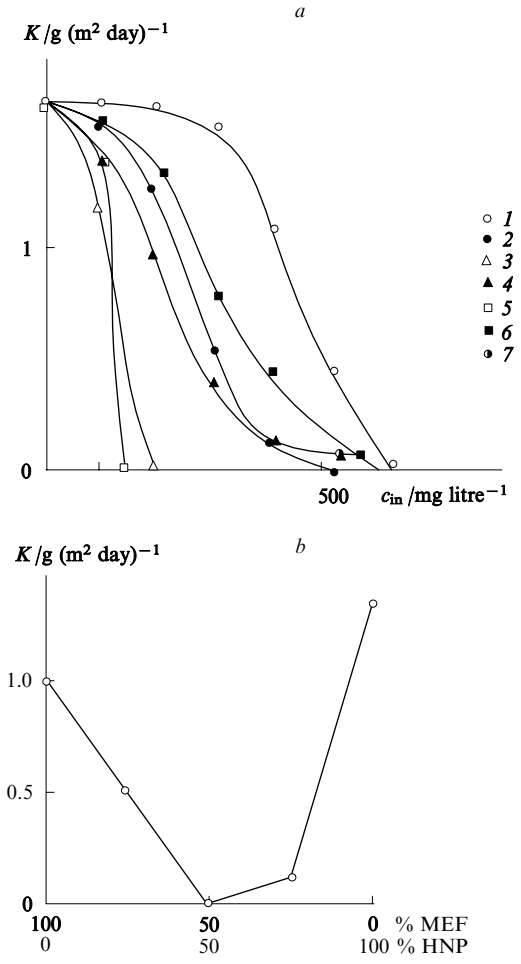


Figure 3. Dependence of the corrosion rate of St.3 steel in water containing 30 mg litre^{-1} NaCl and 70 mg litre^{-1} Na_2SO_4 on the inhibitor concentration (*a*) and on the component ratio in HNP – MEF mixtures at c_{in} = 200 mg litre^{-1} (*b*).[39]
Inhibitor: (*1*) SPA, (*2*) HNP, (*3*) sodium *N*-methylanthranilate (SMA), (*4*) MEF – HNP mixture (1 : 1), (*5*) MEF, (*6*) SMA, (*7*) SPA.

The surfaces of metals, primarily d-metals, are comparatively 'soft' reagents; however, they become 'hard' reagents upon oxidation, at least when Fe_2O_3, Al_2O_3 or MgO is formed. In the former case, strong adsorption can be expected for compounds with readily polarisable (soft) reaction centres; in the latter case, adsorption is mainly determined by electrostatic (*i.e.*, hard) interaction of the adsorbate with the surface.

In corrosion studies, estimation of hard and soft properties of reagents became possible owing to the use of the equation for nucleophile reactivity [14]

$$S = \alpha \log \mathrm{MR} + \beta \mathrm{H} + \gamma\pi, \tag{13a}$$

where S is a kinetic parameter of the process reflecting the relative change in the activation energy due to changes in the nucleophile nature; α, β, and γ are coefficients; MR is the molar refraction of the nucleophile's reaction centre,‡ and H is its relative basicity

$$H = \mathrm{p}K_\mathrm{a} + 1.74.$$

The parameter π characterises the hydrophobicity of an atom or a group of atoms with respect to the hydrogen atom; this is calculated from distribution coefficients,

$$\pi = \log P_{\mathrm{C_6H_5R}} - \log P_{\mathrm{C_6H_6}}.$$

The effect of the nucleophile basicity on the reactivity is weak; therefore, it is possible to use only two parameters, *viz.*, molar refraction and hydrophobicity

$$S = \alpha \lg \mathrm{MR} + \beta + \gamma\pi, \tag{13b}$$

which certainly simplifies the verification of this equation and its use for interpretation of mechanisms of complex heterogeneous reactions, such as corrosion, anodic dissolution of metals, *etc*. For example, the increase in polarisability of halides in the series $F^- < Cl^- < Br^- < I^-$ should increase the degree of charge transfer in the adsorbed complex, which facilitates covalent binding and blocking of the electrode surface. Taking into account that the hydrophobicity of anions increases in the same series, it becomes clear why not only Cl^- and Br^- but also I^- (to an even greater extent) being adsorbed on the iron surface from acidic solutions slow down its dissolution. It is important that the highest protective effect in acids is shown by organic cations combined with soft bases, *viz.*, I^- and CNS^-. The F^- anion, which is a hard base, is weakly adsorbed by the non-oxidised iron surface (which can be considered as a soft acid) and therefore does not enhance the protective effects of organic cations.

However, such a joint corrosion inhibition results not only from surface recharging. It was noted a long time ago that a metal surface can undergo partial hydrophobisation upon chemisorption of anions and can become somewhat 'softer' upon adsorption of soft bases.[3] Both factors can facilitate subsequent adsorption of large organic molecules or ions on a metal; those molecules or ions which are capable of covalent interactions through π-electrons of an aromatic ring or unsaturated bonds are the most efficient inhibitors.

The application of the HSAB principle to metal dissolution and corrosion inhibition processes has been considered in detail in a number of reviews.[43–46] It will only be noted here that the use of this principle is especially efficient if medium components interact with a metal surface more strongly than in the case of physical adsorption. Self-assembling molecules that chemically modify a metal surface can serve as an example. It is no coincidence that the use of alkanethiols for the protection of iron [49–52] or copper [50, 53] requires special surface cleaning to remove oxides and enable soft interaction of the SH group with the metal. Except for specific cases where surface preparation is performed *in vacuo* or using the Langmuir–Blodgett technique, alkanethiols are inefficient as corrosion inhibitors since chemisorption of these molecules only occurs on non-oxidised surfaces.[54] It is possible that the use of alkanethiols combined with other corrosion inhibitors can improve protective properties of self-assembling surface layers, as shown for dodecane-1-thiol and Schiff's bases (*N*-2-hydroxyphenyl- or *N*-2-octadecyl-3-methoxysalicylideneimine);[55] however, practical implementation of this kind of inhibition could be hampered considerably by the toxicity of alkanethiols.

Less toxic alkylphosphonates deserve attention in this connection: they can form oriented layers on oxidised surfaces of aluminium [56] and iron.[57, 58] However, metal surface modification by this method has been studied insufficiently. Further studies in this direction are needed to reveal advantages of adsorption of alkylphosphonates in comparison with that of more common inhibitors, *e.g.*, dialkyl phosphates that are also capable of irreversible adsorption on an oxidised iron surface.[59]

IV. Complexation-type inhibitors

It is not easy to draw a border between adsorption-type and complexation-type inhibitors, since inhibition by a single compound can involve different mechanisms depending on the metal to be protected and the pH of the medium. On the other hand, taking complexation into account, it is often possible to explain corrosion inhibition that is inexplicable within the adsorption theory. The antagonism of action of two depassivators, which was originally discovered on nickel and then on other metals and alloys,[60–62] can serve as an example. For example, the E_pit of nickel in solutions of corrosive sodium caproate ($C_5H_{11}COONa$) does not depend any more on the activator concentration if the concentration of the first anion is $c_{\mathrm{an},1} > c_\mathrm{c}$.[60] Seemingly, the addition of as little as 10^{-8} mol litre^{-1} of NaCl, which is less corrosive under these conditions, to a comparatively concentrated (0.05 M) $C_5H_{11}COONa$ solution should not affect E_pit; however, this value does increase, *i.e.*, nickel depassivation is hindered. Chloride cannot activate nickel at such a low concentration (c_Cl); furthermore, adsorptive displacement of caproate by chloride is impossible at the ratio $c_{\mathrm{an},1}/c_\mathrm{Cl} = 5 \times 10^6$. As c_Cl is increased to 0.1 mol litre^{-1}, the inhibition effect becomes obvious, since the E_pit values in the individual solutions of both activators are lower than those in mixed solutions. The effect of low Cl^- concentrations can be explained as follows: although chloride cannot displace caproate, it can prevent hydration of the complex by replacing a weaker nucleophile, *viz.*, water, in this complex. The changes in the complex composition probably decrease its solubility, which can result in a change in the rate-determining step of depassivation and in the blocking of some of the active sites; as a result, E_pit increases. As the chloride concentration is increased, the inhibiting effect increases until chloride becomes capable of displacing caproate. In such a case, depassivation is inhibited by caproate until c_Cl becomes sufficiently high to displace $C_5H_{11}COO^-$ completely, and E_pit becomes equal to that in pure chloride solutions. This effect was also observed with other carboxylates, $RCOO^-$, where R = H, C_nH_{2n+1} ($n = 1–9$), $HC{\equiv}C$, $CClH_2$ and CF_3. The inhibiting effect of Cl^- increases with an increase in the substituent hydrophobicity expressed through its f-constant,

$$\Delta E = E_{(\mathrm{an}+\mathrm{Cl})\,\mathrm{pit}} - E_{(\mathrm{an})\,\mathrm{pit}} = 0.05 + 0.17f, \tag{14}$$

which does not contradict the explanation proposed for such an unusual inhibiting effect.

Two groups of complexation-type inhibitors can be distinguished. The first group comprises heterocyclic compounds that can form insoluble complexes with copper, zinc and other metals in aqueous solutions. The second group includes complexones (chelating reagents) and their complexes with metal cations.

In the first group, the widely used azoles (imidazoles, triazoles, thiazoles, *etc*.) are notable for their efficiency. Azoles, particularly

‡ Equation (13a) differs from the widely known Edwards equation, which was considered in detail in a number of publications,[14, 47, 48] by the third term. Like in Edwards' calculations, it is legitimate here to use the MR of the entire nucleophile, rather than its reaction centre, for comparatively small nucleophiles.

benzotriazole and its derivatives, have almost no competitors for protection of copper and copper alloys. Their recent uses include the protection of electronic equipment,[63,64] in cooling systems (inhibitors resistant to chlorine have been developed [65]) as well as in brines,[66] for modification of conversion coatings on copper,[67] steel,[68] zinc [69] and silver.[70]

The mechanisms of action of these inhibitors differ considerably from those considered above; they are discussed in several reviews.[71–73] In most cases, azoles form thin insoluble surface films of complex compounds with cations of those metals that are often present on oxidised surfaces.[74–76] The interest in azoles has not weakened during the past decade; their ability to form thin self-assembling layers on copper, observed, *e.g.*, for 2-mercaptobenzoxazole [77] or *N*-vinylcarbazole,[78] opens new prospects for corrosion prevention by these compounds.

Other heterocyclic inhibitors that can form insoluble metal complexes, *e.g.*, certain macrocyclic compounds (porphyrins, phthalocyanines), are also worthy of attention.[79] The number of publications dealing with this group of inhibitors is growing steadily, and they should probably be reviewed in a separate paper. It will only be noted here that the efficiency of copper and zinc protection with azoles is closely related to the ability of these metals to form different bonds in complexes and can be estimated using the linear free energy relationship approach.[71] The increase in the electron density on the reaction centre in 2-substituted benzoimidazoles (BI), which is reflected by substituent induction constants (Fig. 4), strengthens the σ-bond in protective zinc complexes and increases the protection efficiency. In contrast, copper, which can act as an electron donor owing to its low ionisation potential and high electronegativity, forms π-complexes with BI; therefore, electron-acceptor substituents enhance copper protection.

The leading position in the second group of inhibitors belongs to phosphorus-containing complexones, such as 1-hydroxyethanediyldiphosphonic acid (HEDP), nitrilotri(methylphosphonic acid) (NTP), ethylenediamine-*N*,*N*,*N*′,*N*′-tetra(methylphosphonic acid) (EDTP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) as well as their metal complexes. The mechanism of their protective action is rather complex. It is possible to distinguish (maybe, somewhat arbitrarily), as has been done elsewhere,[80] three types of systems 'metal–solution of a complex-forming reagent' with the following features:

(1) ligands are hydrophilic, and their complexes are highly soluble in the corrosive medium;

(2) ligands are rather hydrophobic, while their complexes are either poorly soluble or insoluble;

(3) metal corrosion is controlled by interaction with complexes (soluble in the medium) of the same or some other metal.

In the former case, complexones often accelerate corrosion; if it occurs at potentials of the active metal dissolution range, carboxyl-containing complexones are most dangerous, whereas phosphonic acids are most dangerous for oxidised metal as they can cause the formation of small pits.[14,81] If the value of E_{cor} is outside the potential range where metal ionisation with formation of a soluble complex is thermodynamically possible, adsorption of a suitable ligand can block the corroding surface (at least partially), change the ψ_1 potential of the electrode, *etc.* Furthermore, many phosphonic complexones form barely soluble polynuclear complexes at high metal/ligand activity ratios

$$m = [M^{n+}]:L$$

Since *m* should be high in the near-electrode layer at low complexone concentrations and active metal dissolution, it is such complexonates that can be formed on the surface. This results in corrosion inhibition, though the inhibition is unlikely to be highly efficient because mononuclear highly soluble complexes, in particular those with iron, are formed as *m* decreases.[82] In fact, the i_p of iron in a borate buffer (pH 7.36) initially decreases and then increases with an increase in the concentrations of many complexones.[14] It was noted [83] that HEDP, NTP and similar complexones show no passivating properties for steel even in oxygen-saturated neutral solutions.

However, more hydrophobic phosphorus-containing complexones do not cause pitting on iron, *i.e.*, they can be attributed to the second type of the systems in question. For example, pits on iron were not formed up to oxygen evolution potentials in a borate buffer containing 10^{-3}–10^{-6} mol litre^{-1} hexamethylenediamine-*N*,*N*,*N*′,*N*′-tetra(methylphosphonic acid) (HMDTP).[81] In comparison with HNP and EDTP, the HMDTP complexone is less hydrophilic and more surface-active; it can even hinder iron depassivation by chlorides: at equimolar NaCl : HMDTP ratio and their concentrations equal to 0.01 mol litre^{-1}, the E_{pit} increases by 0.08 V. This effect is comparable to the action of the

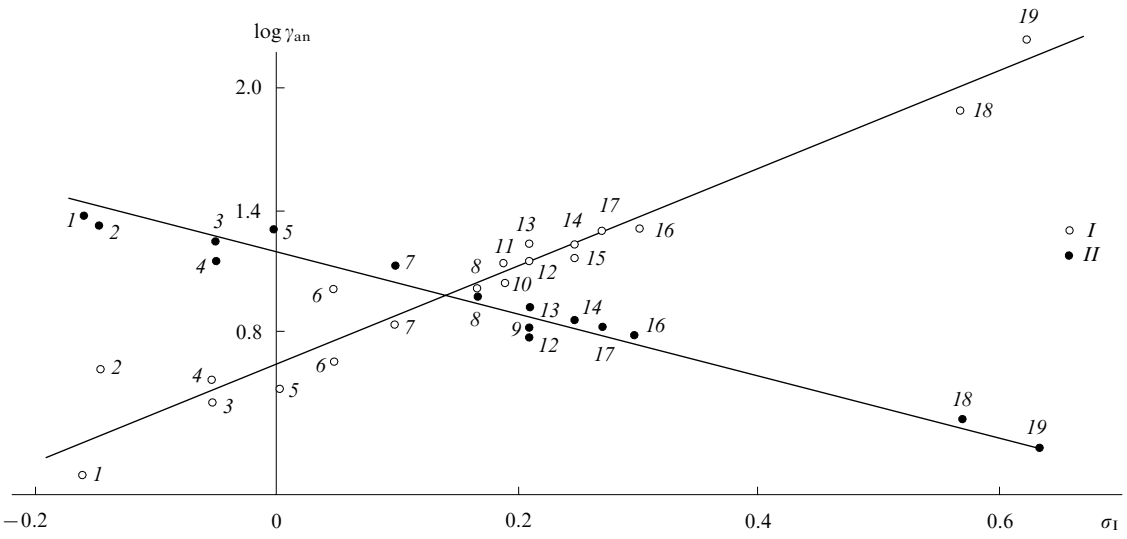


Figure 4. Effect of the inhibition coefficient of anodic dissolution of copper (*I*) and zinc (*II*) in 0.5 M phosphate solution at pH 11.4 on the induction constants of substituents in benzoimidazole.[71]
(*I*) $c_{in} = 5 \times 10^{-4}$ mol litre^{-1}, $E = -0.14$ V; (*II*) $c_{in} = 5 \times 10^{-3}$ mol litre^{-1}, $E = 1.0$ V.
Substituent: (*1*) OH, (*2*) COO^-, (*3*) C_2H_5, (*4*) CH_3, (*5*) H, (*6*) CH_2SCH_3, (*7*) NH_2, (*8*) NHC_2H_5, (*9*) $CH_2SO_2C_4H_9$, (*10*) $NHCH_3$, (*11*) SCH_3, (*12*) $SCH=CH_2$, (*13*) $CH_2SO_2C_6H_5$, (*14*) SH, (*15*) SC_6H_5, (*16*) OCH_3, (*17*) OC_3H_5, (*18*) CN, (*19*) NO_2.

caproate anion, but it is lower than that in the case of higher alkanecarboxylates [14] or dialkyl phosphates.[59]

In acid solutions (0.5 M H_2SO_4), nitrilotri(methylphosphonic acid) does not act as a corrosion inhibitor with respect to iron, (2-hydroxyethyl)iminodi(methylphosphonic acid) shows weak protective properties, whereas the more hydrophobic diethylenetriamine-*N*,*N*,*N*′,*N*″-penta(methylphosphonic acid) (DTPP) and (2-hydroxyethyl)iminodi(methylphosphonic acid) are rather good inhibitors.[84] It is of note that the addition of small amounts of iodide anions, as well as of ethylenediamine or diethylenetriamine, enhances the protective properties of aminophosphonic acids. These complexones probably behave as cation-active adsorption-type inhibitors in acidic media.

It was shown [85] that DTP and EDTP taken at optimum concentrations passivate steel in weakly alkaline carbonate solutions (pH 9.8) but do not hinder its pitting in the presence of chloride ions.

Complexones become rather good corrosion inhibitors of steel in hard water due to the presence of Ca^{2+} and Mg^{2+} ions. Probably, these cations partially neutralise the negative charge of complexones and thus decrease the adsorbate hydrophilicity and increase adsorption.[14,41] It is likely that these systems correspond to the third type of system, metal–solution of a complex-forming reagent, though calcium complexonates are usually characterised by the lowest stability constants among similar complexes of divalent metals. It was found [86,87] that even small Ca^{2+} concentrations strongly affect the efficiency of steel protection with HEDP or hydroxyphosphonoacetic acid (HPA), but not with PBTC. In fact, the efficiency increases from 64% to 88% as the Ca^{2+} : HPA concentration ratio increases from 0 to 1.0 due to stronger inhibition, first of the cathodic reaction and then of the anodic reaction as well. It was shown [88] that in stirred aqueous solution with low concentrations of corrosive anions (8.2 and 14 mg litre^{-1} Cl^- and SO_4^{2-}, respectively) but with a comparatively high content (130.2 mg litre^{-1}) of calcium ions, HEDP displays protective properties for low-carbon steel at as low a concentration as 1 mg litre^{-1}. The protection efficiency increases up to the concentration of 50 mg litre^{-1}; however, HEDP accelerates corrosion at concentrations $\geqslant$ 100 mg litre^{-1}. This fact was explained by decomposition of the protective oxide film. The best protection of steel in 0.5 M $NaClO_4$ solution (pH 7) is achieved with the molar ratio Ca : HEDP = 0.5. Using an atomic force microscope, the formation of a relatively uniform protective film was observed on the surface under these conditions.[89]

Neagle [86] analysed steel surfaces after exposure to hard water in the presence of HPA as the inhibitor. It was concluded that Ca^{2+} facilitates HPA transport and adsorption and is incorporated in the thin (20–40 nm) protective film that almost does not weaken heat transfer. In an alkaline solution [$Ca(OH)_2$, pH 12.5] simulating the concrete pore-filling liquid, the presence of calcium facilitates steel protection by NTP.[90] Studies of a steel surface by FT-IR spectroscopy and XPS revealed the formation of an NTP film with polymeric structure, in which Ca^{2+} is bound with three phosphonic groups.

Important information about the mechanism of steel protection by complexonates can be obtained by studying the dependence of the inhibitor concentration, which provides the maximum degree of protection, on the stability constant (K_s). It was shown [14,91] that in water containing no hardness salts (*i.e.*, in soft water), Ca^{2+} and especially Mg^{2+} phosphonate complexes are often more efficient corrosion inhibitors than the corresponding acids themselves. For example, complexes of NTP with magnesium or calcium can prevent completely the corrosion of steel in soft water. Complexes of HEDP, 1-carboxy-1-hydroxypropane-3-aminodi(methylphosphonic acid) (CHADP) or EDTP with these metals are more efficient than the acids themselves.[92,93] However, HMDTP and PBTC are more efficient than their complexes with Ca^{2+}, and complexes of HMDTP with Ca^{2+} and Mg^{2+} maintain the ability to suppress the corrosion of steel in water completely. In contrast, although imino-*N*-acetic-*N*,*N*-di(methylphosphonic acid) is more efficient than its magnesium complex, its protective efficiency is lower than that of its calcium complex.[81]

In order to explain the entire data on the efficiency of complexonates, one should take into account that the stability constants of magnesium and calcium phosphonates are usually lower than those of the corresponding iron complexonates, hence electrophilic substitution of the complex-forming agent is thermodynamically favourable.[91] It results in the precipitation of barely soluble hydroxides

$$MH_kL^{2-a} + Fe^{2+} = FeH_kL^{2-a} + M^{2+} \xrightarrow{2OH^-} M(OH)_2, \qquad (15)$$

which, along with the inhibitor adsorption, facilitates steel protection. However, if the stability constant is low, the complexonate is dissociated to a considerable extent and its actual concentration in solution is lower. It is no wonder that the left branch of the $\log c - \log K_s$ dependence (Fig. 5) is ascending, which indicates that the inhibitor efficiency increases with an increase in the complexonate stability to a certain threshold. If it is exceeded, the inhibitor efficiency decreases, probably due to the kinetic hindrance of electrophilic substitution of complex-forming cations by iron.

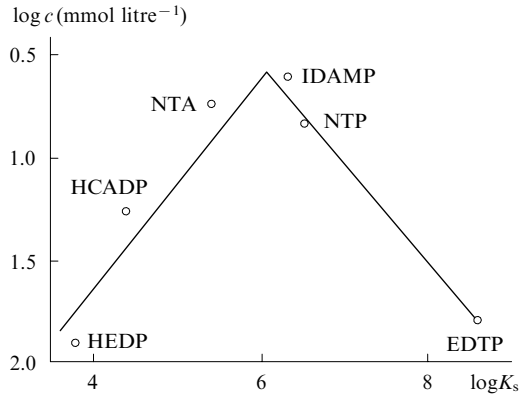


Figure 5. Dependence of the concentration of calcium complexonates providing the maximum protection of steel in water containing 30 mg litre^{-1} NaCl + 70 mg litre^{-1} Na_2SO_4 on their stability constants.[81]
IDAMP is imino-*N*,*N*-diacetic-*N*-methylphosphonic acid.

The presence of hardness salts in water can decrease the inhibiting effect of complexones, therefore zinc phosphonates are often used as inhibitors. The effect of mutual enhancement of the protective action of zinc salts and phosphonic acids has been known for a long time,[14,41] but studies of this effect are still under way for different complexones and metals to be protected.

The zinc–HEDP complex can passivate steel not only in pure water but also in a borate buffer (pH 7.4) containing 0.03 mol litre^{-1} Na_2SO_4.[14] According to XPS data, washing of a steel surface with water after its exposure for 16 h to a solution of this complex (200 mg litre^{-1}, pH 7.6) did not completely remove the inhibitor from the film. The film was rather thin, as the X-ray photoelectron spectrum recorded before ion etching of the sample clearly displayed a signal of metallic iron. The film contained phosphorus in the outer layer only, whereas zinc, which has been in excess with respect to its content in the inhibitor, was still detected during layer-by-layer argon etching of the sample. Probably, the complex is decomposed, at least partially, during the initial stages of film formation, *e.g.*, due to displacement of Zn^{2+} by iron ions. The zinc ions that are released react with hydroxyl ions generated in the cathodic reaction to give barely soluble $Zn(OH)_2$, which shields the surface and slows down corrosion. As the corrosion rate decreases, the deposition of $Zn(OH)_2$ slows down, and

predominant adsorption of the inhibiting complex on the surface starts.

It was found [89] that zinc salts synergistically enhance steel protection by an inhibitor such as HEDP in 0.5 M $NaClO_4$ solution; the strongest effect was observed with the molar ratio Zn : HEDP = 3. It was shown that $Zn(OH)_2$ deposition is responsible to a considerable extent for the higher effect of zinc on the protective properties of HEDP in comparison with calcium. This fact agrees with results of earlier studies.[14,91] The ability of HEDP – Zn^{2+} mixtures to hinder the anodic dissolution of steel was also confirmed for aqueous solutions containing up to 0.01% Cl^- (see Ref. 94). For static conditions, it is recommended to use a binuclear complex with Zn : HEDP = 2, since HEDP anions themselves are corrosive with respect to steel. On the other hand, an excess of zinc ions favours hindering of the cathodic reaction of oxygen reduction.

In sea water, HEDP itself has poor protective properties, whereas its complex with zinc protects steel more efficiently, especially at high flow rates ($V = 3$ m s^{-1}).[95] In this case, high degrees of protection ($\geqslant 95\%$) are reached at a complex concentration equal to 0.1 mmol litre^{-1} (this value is by an order lower than that at $V = 1$ m s^{-1}).

The synergistic effect of components in mixtures of zinc salts with NTP used for steel protection was observed by different researchers.[91,96] The inhibitor forms a thin compact film on the metal surface, which comprises both $Zn(OH)_2$ and NTP – zinc complexes. It was shown [97] that the NTP – zinc complex prevents pit corrosion of Kh18N9T steel in chloride-containing water, though it does not suppress it completely.

Enhancement of the protection of low-carbon steel due to synergism was also found for mixtures or complexes of zinc with EDTP,[92] CHADP,[93] PBTC,[98] *N*,*N*-di(phosphonomethyl)glycine,[99] ethyl- and chloroethylphosphonic,[100] phenylphosphonic,[101] 2-dimethylamino-2-hydroxypropylenediphosphonic and benzyliminodi(methylphosphonic) acids.[14] A similar effect was observed [101] for protection of brass [14,102] and aluminium alloys.[103]

Thus, the mechanism of metal protection by complexonates involves not only adsorption but also surface reactions of electrophilic substitution of complex-forming cations, deposition of barely soluble hydroxides and formation of hetero- and polynuclear complexes. No wonder that the dependences of their efficiency on chemical composition are rather complex in many cases. For example, the concentration of a complexonate-type inhibitor required to manifest protective properties depends on its stability constant: if the nature of the complex-forming cation is the same, *e.g.*, for zinc complexes (Fig. 6 *a*), this value increases with an increase in the stability constant, since the possibility of the formation of zinc hydroxide decreases. If the complex-forming cation is varied while the complexone remains the same, the dependence of the inhibitor efficiency on the solubility product of the hydroxide formed upon electrophilic substitution passes through a maximum (Fig. 6 *b*).[3] The protective properties of phosphonates of divalent metals are enhanced with a decrease in the solubility of their hydroxides and an increase in the stability of their complexonates, until their stability constants exceed those of iron(II) phosphonates. The mechanism of protection by more stable complexonates also involves the electrophilic substitution of a divalent metal ion, but probably due to the formation of more stable iron(III) complexonates.

The protection mechanism considered above, which we proposed and described in detail previously,[14,91] is also valid for complexonates of metals other than divalent ones. Cations of rare-earth metals (REM), which are recommended as metal corrosion inhibitors more and more often due to environmental problems,[104–107] are worthy of attention. The mechanism of steel protection by REM phosphonates was first studied for NTP derivatives.[108] Electrophilic substitution of REM by Fe^{2+} cations is thermodynamically unfavorable due to the high stability of the phosphonates [their stability constants are 4 – 8 orders larger than

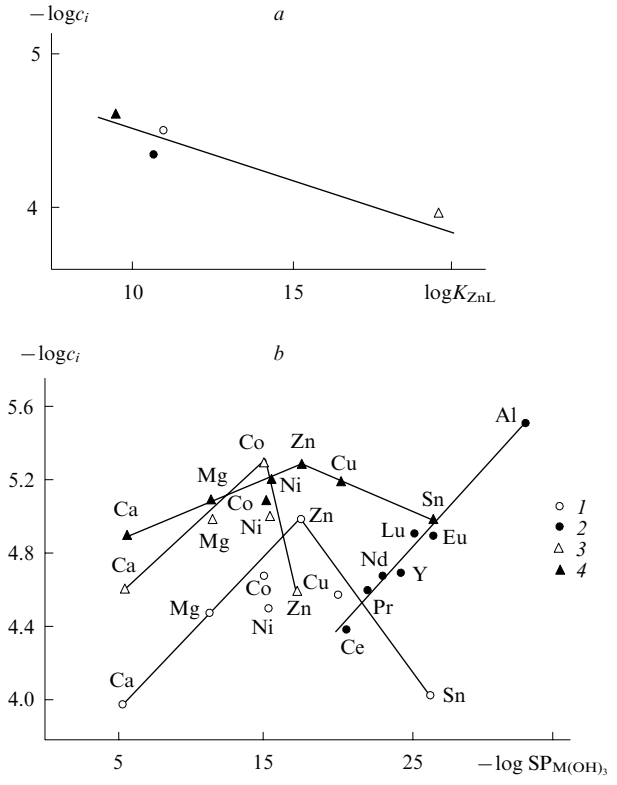


Figure 6. Effect of the stability constants of zinc complexes with phosphonic acids (*a*) and of the solubility products of hydroxides of complex-forming metals in phosphonate corrosion inhibitors (*b*) on their protective concentrations for St.3 in water containing 30 mg litre^{-1} NaCl and 70 mg litre^{-1} Na_2SO_4. The speed of solution movement relative to steel cylinders is 0.8 m s^{-1}.
Phosphonic acids: (*1*) HEDP, (*2*) NTP, (*3*) EDTP, (*4*) CHADP.

that of the similar iron(II) complex]. However, in neutral solutions, the Fe^{2+} ion is readily oxidised to Fe^{3+}; the latter forms a complexonate whose stability is comparable to that of the yttrium – NTP complex, which is the most stable of all REM – NTP complexes. Hence, in this case, electrophilic substitution can occur according to the following scheme:

$$MH_kL^{3-a} + Fe^{3+} = FeH_kL^{3-a} + M^{3+} \xrightarrow{2OH^-} M(OH)_3. \qquad (16)$$

Simultaneously, competing formation of $Fe(OH)_3$ occurs; the latter is characterised by weak protective properties. Thus, reaction (15), which, at least partially, prevents Fe^{2+} oxidation, does not occur, and the protective effects of REM complexonates are appreciably inferior to those of NTP complexes with divalent metals. Auger electron spectroscopic studies of the surface film on iron formed in water containing a cerium – NTP complex showed that the film was enriched with cerium. The Ce : Fe ratio was close to 1.0 throughout the film thickness and even somewhat higher in the inner layer. On the other hand, P : Ce $\leqslant$ 0.6 (this ratio equals 3.0 in the inhibitor); it is smaller in deeper layers, which are less accessible to washing water, than in the outer layers. This suggests that hydroxides play an important role; it is therefore not surprising that the efficiency of NTP complexes with trivalent metals increases with a decrease in the solubility product of $M(OH)_3$ (see Fig. 6 *b*).

It is of note that the protective film formed by the less stable aluminium(III) complexonate, which can undergo reaction (15), is more perfect and probably free of the adverse effect of $Fe(OH)_3$. Therefore, the NTP – aluminium complex is one of the most efficient inhibitors in soft water with low chloride content.

Metal complexonates are used in the reagent-based treatment of aqueous systems,[14, 109] in acid washing solutions, in cutting fluids, *etc*. Small additions of such complexonates facilitate the cathodic protection of steel in sea water [110] and improve the protective properties of magnetite coatings when added to oxidising nitrate solutions.[111] The nature of complex-forming cations is also important in magnetite coatings modified by complexonates. Complexonates which form barely soluble hydroxides are preferable; yet another condition should be met, *viz*., complexonates should not be too large, otherwise the structure of a magnetite coating can be violated and its defectiveness can increase.

The comparatively high cost of reagents and the tightening of environmental requirements for the content of phosphorus in water restrict the usage of phosphonate inhibitors in water consumption systems. To decrease the concentration of phosphonates, it was recommended to use them as mixtures with inexpensive additives, *e.g*., adsorption-type inhibitors (aliphatic amines,[112] phthalic anhydride,[113] and other compounds [14]), complex-forming reagents (tartrates,[114] gluconates [115]) or extracts from certain plants.[116]

The combined use of phosphonates and oxidants is justified by their mechanism of action. Since reduction of some oxidants can increase pH of the near-surface solution layer, metal phosphonates are destabilised: in effect, nucleophilic substitution of the ligand by hydroxyl groups occurs, which results in the deposition of $M(OH)_x$ hydroxides poorly soluble in water. Furthermore, it is known that the addition of nitrite enhances steel protection by complexones (HEDP [117] or PBTC [118]); at elevated temperatures, small amounts of sodium *m*-nitrobenzoate (SNB) act similarly. It was shown [119] that both oxidants can also enhance the inhibiting effect of the HEDP–zinc complex in hot water (80 °C). This is only possible at a certain ratio of the complexonate and oxidant concentrations, which depends on the nature of the oxidant. Although SNB is a stronger oxidant than $NaNO_2$, its inhibiting effect is weaker. Both oxidants play an auxiliary role, that is, they only provide better conditions for the protective layer formation by the phosphonate.

However, though numerous patents on mixed inhibitors based on complexonates have been issued, the scientific grounds for formulating such mixtures are still poorly explored. Aside from the methods for improving the efficiency of complexonate inhibitors considered above, yet another promising method should be noted, *viz*., their joint use with water-soluble polymers.

V. Polymeric inhibitors

It was known back in the 1930s that the addition of polyphosphates to water (a few milligrams per liter) inhibits not only scaling but also steel corrosion. However, while the anti-scaling effect of polyphosphates results from their adsorption and dispersing ability, their inhibiting properties are associated with the ability to form poorly soluble compounds with metal cations. Polyphosphates are most efficient in mixtures with Zn^{2+}, Ca^{2+} or Ni^{2+}; steel corrosion is mainly hindered due to inhibition of the cathodic reaction. The use of water-soluble polymers, along with polyphosphates, for the anti-scaling protection of aqueous systems started in the 1970s; these polymers containing COOH and OH groups (and mostly based on derivatives of acrylic and maleic acids) had high hydrolytic stability. Water treatment with mixtures of zinc phosphates or phosphonates with such polymers became popular 10–15 years later; a short time after that, the ability of polymers to inhibit metal corrosion was also discovered. In the early 1980s, the first 'phosphorus-free' (zinc-polymeric) water treatment programmes were developed in Japan due to restrictions on the content of phosphates (even non-toxic ones) in waste water. Suzuki and Kawamura [120] presented a brief review of these programmes and concluded that, despite certain achievements, 'phosphate-free' water treatment still cannot be widely used.

Studies on the mechanism of action of an acrylic acid–2-hydroxyethyl methacrylate–methyl methacrylate copolymer (MM = 3000) showed that adsorption of the polymer on a calcium phosphate film slows down the film growth, makes it less porous and thinner, and improves its protective properties. Presumably, in order to improve the efficiency of polymeric reagents that can eventually become leaders in scaling and corrosion prevention in cooling systems, it is necessary to study the dependence of their efficiency on the most important characteristics of polymers (molecular mass, number of functional groups, *etc*.). Analysis of the results of such studies has led to the conclusion [121] that polymers with molecular masses not exceeding 10 000–12 000 are most efficient for scaling inhibition. Unfortunately, these polymers have been little studied in application to metal corrosion inhibition, though numerous publications are available on the properties of new polymeric inhibitors.

Zinc salts are added in almost all cases to carboxylic [29] or sulfonate [122] polymers in order to confer on them corrosion-inhibiting properties with respect to steel in water, while phosphonate polymers do not require such addition. On the contrary, the efficiency of steel corrosion inhibition in water without stirring with polyvinylpyrrolidone (MM = 40 000) decreases in the presence of Zn^{2+} (see Ref. 123), suggesting that the activities of the polymers' functional groups differ considerably. Certain bipolar polypeptides, primarily polyasparaginates with MM = 1000–2000, are efficient inhibitors of carbon dioxide corrosion of steel [124] and scaling.[125] Reaction products of polysuccinic acid with aliphatic amines, particularly poly(succinimides) and poly(dodecyl-succinamides), proved to be rather efficient inhibitors of hydrogen sulfide-induced corrosion of steel. Owing to low toxicity, such polymers are likely to have considerable promise for application in oil-extracting and petrochemical industries.[126]

Apart from the nature of a polymer's functional groups and molecular mass, its protective properties can be affected by the presence of hydrophobic radicals. For example, in weakly alkaline solutions (pH 8–10), the efficiency of aluminium protection with a maleic acid–styrene–acrylic ester copolymer increases with an increase in the number of carbon atoms in the ester alkyl chain.[127]

Polymers containing acid groups are more commonly used as scaling inhibitors, whereas cation-active polymers are used to prevent the metal corrosion. It was shown, for example,[128] that the ultra-thin film (70 nm) obtained by layer-by-layer deposition of poly(diallyldimethylammonium chloride) or poly(*N*-octyl-4-vinylpyridinium iodide) and poly(styrenesulfonate) inhibits considerably the dissolution of 316L steel in 0.6–0.7 M NaCl solution and suppresses pitting on its surface, despite the high water content in the film and its high ionic permeability.

Even thinner conductive polyaniline films (which can be obtained not only by chemical techniques but also by anodic polarisation of a metal) show passivating properties toward stainless steels in acids. This was originally shown by De Berry [129] and then confirmed by many researchers. Protective polyaniline films were also obtained on aluminium,[130, 131] copper [132, 133] and titanium.[134] However, for a long time, similar protective films could not be obtained on low-carbon steel in aqueous solutions, partially due to the corrosion of the anode. To avoid corrosion, Yagova *et al*.[135, 136] applied films from a 0.4 M aniline solution containing arenecarboxylate inhibitors, *e.g*., 0.08 M solution of salicylic acid. As a result, they obtained a film that protected steel in 0.05 M H_2SO_4 and in humid atmosphere. Polyaniline films on iron were also obtained in the presence of phosphates and 3-aminobenzenesulfonic acid (ABSA).[137, 138] The protective properties of the film increased in both cases; however, whereas ABSA formed a copolymer with polyaniline, phosphates were just incorporated in the passivating layer of iron oxides but did not react with the polymer. However, some researchers do not acknowledge the protective properties of films based on polyaniline, polypyrrole, *etc*. on iron or steel, and discussions on this subject continue.[139, 140]

Polyhexamethyleneguanidinium (PHMG) $-[(CH_2)_6-NH-C(=NH^+)-NH]_n-$ is also a polymeric cation worthy of note, as well as its salts synthesised by Antonik *et al.*[141] and Tomin *et al.*[142] At $n = 10-100$, PHMG is a strong base and a biocide; its anticorrosion properties depend strongly on the counter-ion. PHMG phosphate mixed with small amounts of sodium nitrite and tetraborate provides good protection of steel in non-stirred aqueous solutions but is inefficient against scaling. The PHMG–HEDP salt shows both protective and technological properties required for its usage in cooling systems of oil refineries. Tomin *et al.*[142] also reported good protective properties of a polymer synthesised by the reaction of hexamethylenediamine with phosphoric acid and urea in the presence of glycerol.

Yet another group of this class of inhibitors includes hydrophilic monomers that can polymerise upon adsorption on a metal surface rather than polymers. This kind of polymerisation can decrease the solubility of the adsorption layer, increase the protective effect and make adsorption irreversible. Acetylene derivatives known since the 1940s as corrosion inhibitors of steel in acids are examples of such compounds. Brief reviews on the mechanism of action of these inhibitors, starting from the first experiments with iron powder, which showed that corrosion inhibition in HCl with acetylene results from the formation of a hydrophobic film of a hydrogenation and polymerisation product, are known.[2, 3, 143]

Aliphatic acetylenic alcohols in protonated form are relatively stable in acids and undergo various reactions only in the presence of an electrochemically active metal surface. There is no doubt at present that alkynols first undergo reduction and then dehydration and polymerisation, and that protective films formed by them consist of products of not only polymerisation but also other chemical transformations. It was shown [144, 145] that the susceptibility of alkynols to electrochemical reduction correlates with their ability to undergo polymerisation on iron in acids. According to Frignani *et al.*,[146] the inhibiting effects of alkynols can be enhanced by replacing the acetylenic hydrogen by a halogen. Small anodic polarisation of iron in a 1 M HCl solution facilitates the formation of a chemisorption layer, whereas cathodic polarisation accelerates the growth of a polymeric film.[147]

Aromatic acetylenic alcohols are reactive in acids.[148] They form products that are also efficient inhibitors and that undergo further reactions; as a result, steel is coated with a poly(phenyl ketone) protective film.

It was shown in a number of studies that preliminary application of certain monomers on a metal surface from aqueous solution can protect it in a corrosive medium owing to the formation of a polymeric structure. For example, immersion of aluminium samples for 15 min in 0.5% solution of methacryloyloxypropylmethoxysilane (at 80 °C) results in an alumosiloxane film stable even in 3.5% NaCl solution.[149]

The results of these studies give a reason to assume that the achievements of polymer chemistry, especially if they are used to search for ways of controlling the polymerisation of inhibitors in thin adsorption layers, will make it possible to create a new approach for efficient protection of metals by inhibitors. However, the currently known inhibitors of this type, *viz.*, acetylenic alcohols or alkenals, have a noticeable toxicity (the maximum permissible concentrations of propynol and acrolein are 1.0 and 0.7 mg m^{-3}, respectively); besides, they present fire and explosion hazards. In view of this, attention should be paid to the less toxic cinnamaldehyde, which is adsorbed on steel and protects it from acid corrosion by forming a polymeric film.[29] Probably, the efficiency of protection of monomers can be increased by using them together with polymerisation initiators, as was observed for methacrylonitrile and potassium persulfate used to protect steel in 1 M HCl solution.[150]

* * *

Intense studies on the mechanism of metal corrosion inhibition and its dependence on the composition and properties of inhibitors have continued in the past decade. Unfortunately, it is impossible to discuss all physicochemical aspects of corrosion inhibition within a single paper. Achievements of the quantum-chemical approach to the description of this complex process undoubtedly deserve a special discussion. The development of the theory of action of quite specific volatile inhibitors and the mechanisms of metal protection in organic solvents, paint and conversion coatings were also left outside the scope of this review. However, the author hopes that the presented material on the current state of corrosion inhibitor science, whose development has been one of the most important fields of research at the Institute of Physical Chemistry, will attract the attention of not only physicochemists already working in this field but also researchers in other fields of chemistry.

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