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# Physicochemical aspects of the action of volatile metal corrosion inhibitors

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**Abstract. The state-of-the-art of investigations into the development and perfection of volatile corrosion inhibitors is analysed. The characteristic features of metal protection by these compounds and the effects of their chemical structures on the properties are discussed. The problems of adsorption and protective post-effect of volatile corrosion inhibitors are considered. The bibliography includes 133 references.**

## I. Introduction

Atmospheric corrosion, which occurs not only under thick (phase-type) films but also under thin (adsorption-type) water films, is the most common type of corrosion.[1–6] The use of volatile corrosion inhibitors (VCIs) for metal protection from atmospheric corrosion started in the 1940s when Shell Co. patented the use of amine nitrites for this purpose.[1]

Volatility is the main distinctive feature of VCIs in comparison with traditional metal corrosion inhibitors in aqueous solutions.[7–12] The ability of VCIs to propagate, upon evaporation, throughout a system to be protected predetermines their major advantage: it is unnecessary to apply such inhibitors on metal surfaces and no special measures are needed to remove them.[1] The latter feature is of importance where VCIs are used to protect military equipment during long-term storage, since this can quickly be put into operation as required.[13,14]

In the storage and transportation of articles (the so-called temporary protection) or operation of bulky extended constructions and pipelines that contact corrosive vapours and gases, VCIs that spontaneously enter various crevices and interstices are adsorbed on metal surfaces from the vapour phase and create there thin protective films. It is important that the VCI vapour can saturate a corrosive liquid that is often condensed in hardly accessible places, thus ensuring the required protection in the liquid phase as well. It is due to this feature that VCIs are used in power engineering† and for the protection of inner surfaces of pipelines.

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Depending on the structure that determines the saturated vapour pressure ($p^0$) together with other characteristics, VCIs form adsorption layers of different thicknesses on the surface to be protected. In the corrosion protection of high-precision metal articles (for example, bearings, electrical or radio equipment and particularly electronic equipment that usually operates in moderately-corrosive environments), certain classes of VCIs form nanosized protective layers upon adsorption, which is the most attractive feature. These VCIs can be used to protect 'clean' metallic surfaces where paint coatings are unacceptable. It was also reported [15] that in some cases VCIs improve the efficiency of organic coatings as well.

The majority of complex articles consist of various metals and alloys; for this reason, the so-called versatile VCIs have been developed. Both individual chemical compounds, such as hexamethyleneimine *m*-nitrobenzoate, benzoimidazole and certain thiazoles as well as mixtures, *e.g.*, of 1,2,3-benzotriazole (BTA) which is an efficient corrosion inhibitor of many non-ferrous metals with VCIs that reliably protect only ferrous metals (amines, amine nitrites, *etc.*), became popular.[1,2,16,17] However, the majority of these VCIs have low volatility, which limits their scope. In view of this, functionalised alkylamines were studied as VCIs and it was proved that incorporation of an additional functional group into an alkylamine molecule increases the protective ability of VCIs with respect to a wide range of metals and alloys and also makes it possible to optimise their volatility. As a result of these studies, versatile new-generation VCIs have been elaborated: dialkylamino ketones,[1,18] dialkylamino nitriles,[19] *etc.*[15]

The scope of VCIs has expanded considerably over recent years. In addition to the traditional packing papers and porous carriers,[1,2,20] polymeric films containing volatile inhibitors as additives find general use.[21–25] The advantages of such materials over paper are obvious, though the introduction of a VCI into a polymer has some specific features, and not every inhibitor maintains its highly protective properties upon thermal treatment during the film preparation. Water-soluble VCIs were also recommended for modifying acrylate or alkyd films that have been suggested instead of preservative oils or paint coatings applied from organic solvents.[26,27] Modified thin coatings ($\delta \leqslant 25$ μm) can be used for the protection of metal articles during sea transportation or storage in air. Such coatings are advantageous due to their environmental safety, as regards both their application and removal, which is effected by aqueous washing solutions.

† The use of ammonia and volatile amines for the anti-corrosion protection of inner surfaces of steam-power plants and tubes started back in the 1920s.[6]

Volatile corrosion inhibitors are often used in combination with usual (contact-type) inhibitors to protect pipelines and equipment of water-supply systems. They are used to slow down corrosion not only in liquids but also in vapours.[28,29] Such protection becomes necessary where tanks or pipes are partially filled with water or where they are operated intermittently, for example, in seasonal operation. Sometimes, during shutdowns of boilers, turbines and other equipment, they are dried with air saturated with VCI vapour; this is more efficient in terms of corrosion protection than ordinary drying.[30] We have found that compounds that form azeotropic mixtures with water can be employed as VCIs,[31] which should help broaden the scope of VCIs. Under certain conditions, such VCIs ensure the metal protection even under heavy condensation of water vapour. In closed systems, aqueous solutions of these VCIs that protect the metal surface without deliberate drying will be convenient for hydrotesting, for example, of power equipment and other types of bulky equipment.

Increasing interest in VCIs is also being felt in the gas industry where they are used to protect the inner surfaces of steel pipelines, both as such and as part of film-forming blends.[32–39] It is important that VCIs are applicable for steel protection from hydrogen sulfide corrosion and from the quite peculiar carbon dioxide corrosion. An efficient method was described [40] for the use of VCIs for protecting the outside surface of an oil pipeline where it crossed a roadway. Mechanical damage is avoided in such cases by mounting a special duct around the pipeline; a VCI is introduced into the annular space in-between.

Volatile corrosion inhibitors were used as the basis for development of a novel type of anticorrosion agents, *viz*., migrating corrosion inhibitors (MCIs).[41–45] These have been developed for the protection of steel reinforcement in concrete against corrosion, which is a pressing scientific and technical problem of current city- and bridge-building. For example, according to data from Ref. 43, $\sim$200 million dollars is spent annually in the USA to repair bridges where chloride-induced destruction of reinforced concrete has occurred. The first MICs contained volatile amine carboxylates or alkanolamine carboxylates as the most important components that diffused through concrete pores (including vapour diffusion), reached the surfaces of reinforcing steel and inhibited its corrosion. Such inhibitors should not only possess high self-diffusion coefficients, be poorly adsorbed on cement stone and be well adsorbed on steel, but should also be competitive in these parameters with chlorides, which induce most often the corrosive destruction of reinforcing steel in concrete. It should be remembered that reinforcing steel could be corroded initially and that corrosion stimulation that often occurs due to its localisation is unacceptable in reinforced-steel structures, particularly in strained ones.

To date, the mechanism of action of MCIs has been studied insufficiently and its discussion is beyond the scope of this review. However, there is no doubt that this mechanism has much in common with that of VCIs. Obviously, the development of more efficient VCIs would also favour progress in the protection of reinforced-steel structures.

The requirements for corrosion protection have increased during the last decade, especially in terms of environmental safety. This certainly gives impetus to the development of new efficient and environmentally safe compositions and protective agents and favours the development of the theoretical basis of the VCI action. This provides prospects for rapid progress in this field.

## II. Specific features of vapour-phase metal protection by inhibitors

If the space to be protected can be sealed, at least partially, this is a direct indication for the use of VCIs. Depending on the conditions, VCI vapour fills the entire volume by diffusion or with a gas stream. It is the diffusability of the inhibitor vapour that determines the advantages of VCIs over other types of inhibitors and governs some of their specific parameters, such as the protection radius ($l_{pr}$), passivation time, *etc*.[46–50]

The kinetics of VCI vapour diffusion plays an important role in anti-corrosion protection from the onset of its contact with the metal. Volatile corrosion inhibitors are often used to preserve complex items that may fail due to even minor damage.[25,51] Therefore, it is a prerequisite of protection that an inhibitor be accumulated on a metal surface in an amount sufficient to suppress corrosion before the first corrosion sites appear on the surface. It should be noted that, though the mathematical tools for the description of diffusion processes have been developed to a considerable extent, the first attempts to simulate this condition were undertaken from the late 1980s to the early 1990s.[46–50] A series of studies [47–50] on quasi-steady evaporation of a VCI droplet inside a metallic sphere coated with a water film were the most successful. This model assumed that the surface electrolyte contained an inhibitor in a minimum protective concentration ($C_{pr}$) to prevent metal corrosion.

The analytical solution for the problem has the form

$$l_{pr} = \lambda\sqrt{\frac{Dp^0}{C_{sat}\ln(1 - C_{pr}/C_{sat})}} \quad (1)$$

and defines the relationship between the VCI efficiency expressed as a function of $l_{pr}$, the diffusion coefficient ($D$) of VCI vapour in air, the saturation pressure $p^0$, the solubility ($C_{sat}$) and the $C_{pr}$ value under conditions affecting the coefficient $l$ (temperature, thickness of the moisture film on the metal, *etc*.). Analysis of the possible variation ranges of these parameters [52] showed that $D$ affects the protection efficiency the least.

This model provides a fairly good description of the trend of the effects of the base parameters on the protective properties of VCIs provided heat exchange and mass exchange with the environment can be neglected, *e.g*., in the conservation of metal articles under atmospheric conditions. Generally,[1,53] after the article and a VCI source are sealed, the system is kept for some time at a constant temperature in order to allow the inhibitor vapour to reach the surface. Thus $l_{pr}$ can be regarded as the main criterion of the VCI efficiency, and approaches to enhance protection that follow from Eqn (1) (an increase in the inhibitors' $p^0$ and their protective capability in thin electrolyte films, uniform spatial distribution of VCI sources, *etc*.) prove to be efficient.

On the other hand, sealed systems where protection is only determined by the initial period of contact of a metal with a VCI are rather rare in real technics. The role of heat transfer and mass transfer processes in initiating corrosion of real systems protected by VCIs consists of violation of the protection conditions ($C_{inh} > C_{pr}$) due to a decrease of the inhibitor concentration in the surface electrolyte ($C_{inh}$) or an increase in $C_{pr}$ with time.[31,54]

Evaporation of VCI from the space that is protected through a permeable packing is a reason for a decrease in $C_{inh}$. Hence, inhibitors with $p^0 > 13.3$ Pa cannot normally ensure long-term vapour-phase protection.[1] However, corrosion can also be initiated in an unsealed system due to the ingress of aggressive atmospheric components, including water, into such a system.

The introduction of VCIs into a space that is protected is accompanied by their interaction with water contained in the internal environment, formation of solutions, and a decrease in the humidity of the gas phase. These processes usually affect only slightly the corrosivity of the environment [55] but they favour the diffusion of water into the system. Obviously, if the relative humidity of the environment exceeds that above a VCI solution with a concentration of $C_{pr}$, gradual dilution of the latter with atmospheric moisture will result in the initiation of corrosion even if the inhibitor is not removed from the space that is protected.

Analysis of basic models has shown that the rate of water diffusion into a space that is protected can appreciably exceed the rate of VCI evaporation and determine the kinetics of its dilution in a system and the protection period. In fact, mass exchange of a quasi-equilibrium system containing a VCI that is miscible with

water in all proportions, with a water-saturated external atmosphere is described [54] by the following equation

$$\frac{N_{H_2O}}{N_{inh}} = \frac{D_{H_2O} p^0_{H_2O}}{D_{inh}\, p^0_{inh}}, \quad (2)$$

where $N$ is the number of moles of the inhibitor or water, respectively (depending on the subscript) that diffuse through the barrier material per unit time. An approximate calculation showed that in the case of mass transfer through open pores and violated integrity of the barrier material, the $N_{H_2O}/N_{inh}$ ratio can reach $10^5$. The success in the combined use of VCIs and desiccants for metal protection shows that diffusion of water contributes the most to the rate of a decrease in the $C_{inh}$, at least for VCIs with comparatively small $p^0$ values.[30]

If the ingress of water into the system decreases $C_{inh}$, the diffusion of acid gases ($SO_2$, $NO_2$, $CO_2$, $H_2S$, *etc.*) into it increases the corrosivity of the medium and hence increases $C_{pr}$. This can also result in the corrosion initiation. Binding of such gases by inhibitors, many of which are organic bases (or contain them as components), favours their diffusion into the space that is protected.[1, 16, 52, 56]

Metal protection by a volatile inhibitor can also be violated by heat exchange between the system and the environment. It is well known that abundant condensation of water vapour due to temperature fluctuations is very unfavourable for vapour-phase protection.[18, 57] However, the majority of researchers had previously limited themselves merely to the statement of this fact and simulation of such conditions in VCI efficiency preliminary tests.[16, 51, 56]

The analysis of mechanisms of corrosion initiation by heat exchange that we have carried out [31] has shown that the temperature gradient on a metal results in a redistribution of water and a VCI in the surface electrolyte, similar to that occurring during distillation of solutions. The evaporation is intensified on heated areas and the vapour phase is enriched in the more volatile component of the mixture and its surface concentration decreases. If $p^0_{inh} > p^0_{H_2O}$, a decrease in $C_{inh}$ below $C_{pr}$ can stimulate corrosion. On the other hand, on cooled surfaces where vapour condenses the surface electrolyte becomes enriched in the volatile component. This may result in the violation of vapour-phase protection if $p^0_{inh} < p^0_{H_2O}$.

There are a number of ways to prevent corrosion that appears by this mechanism. One of them involves the use of VCIs that are irreversibly adsorbed on the metal and have a protective post-effect. If the temperature difference on the metal occurs occasionally and afterwards the system comes to a near-equilibrium state, such a post-effect can protect the article. However, this does not guarantee that the article will remain preserved. No matter what the VCI post-effect, possible heat-exchange can initiate corrosion.

Yet another possibility for vapour-phase metal protection under heat-exchange conditions is the use of VCIs with $p^0$ and vaporisation enthalpy ($\Delta H_v$) values similar to those of water. In this case, the composition of the surface electrolyte is identical to that of the vapour above it. Evaporation and condensation can neither change $C_{inh}$ nor cause corrosion. However, perfect ideal matching of $p^0$ and $\Delta H_v$ is only realised for optical isomers and it is practically impossible to select a VCI that satisfies this condition.

The third way, new in principle, for metal protection by volatile corrosion inhibitors under heat exchange conditions is the above-mentioned one, *viz.*, the use of inhibitors that form azeotropic mixtures with water. If the content of these VCIs allows their equilibrium concentrations in the surface electrolyte to exceed the concentrations of the azeotropic mixtures ($C_{az}$) and $C_{az} > C_{pr}$, no heat-exchange mode initiating corrosion can be attained in the entire possible temperature range of the environment. In fact, irrespective of whether the azeotropic mixture is characterised by a maximum or minimum in the composition–pressure diagram, the surface electrolyte that meets the condition

$$C_{inh} > C_{az} > C_{pr}, \quad (3)$$

can be distilled to give pure VCI and its solution with a concentration of $C_{az}$. If $C_{az} > C_{pr}$, the vapour-phase protection cannot be violated by heat exchange. The specific features of metal protection by such inhibitors have been little studied to date, but the prospects associated with them make these studies of high priority.

## III. The effect of chemical structures of volatile corrosion inhibitors on their protective properties

In practice, systems protected by VCIs are as a rule subject to a complex of external effects that alter the metal storage life. However, an analysis of the mechanisms of violation of vapour-phase protection described above allowed us to mark the most important characteristics that determine the VCI efficiency, *viz.*, evaporability; inhibitory properties in the surface electrolyte, including the anticorrosion post-effect; solubility in water and ability to form azeotropic mixtures. These characteristics are determined by the chemical structure of VCIs.

An analysis of structure–property relationships plays an important role in the development of efficient corrosion inhibitors for various media.[7, 11, 20, 37, 58, 59] Since the characteristic features of a VCI include its volatility and ability to form protective layers on the metal from the vapour phase, the assessment of the effect of the inhibitor's chemical structure on $p^0$ is of particular importance in the case of vapour-phase protection.

### 1. Vaporisation of volatile corrosion inhibitors and dependence of their volatility on the chemical structure

The ability to form vapours (due to evaporation or sublimation), which is often (not quite correctly) called volatility, is a characteristic property of VCIs.[1, 10, 16] Volatility is quantitatively expressed as $p^0$. The volatility required for the vapour-phase protection ($p^0 > 1.3 \times 10^{-3}$ Pa, or $1.3 \times 10^{-4}$ Pa according to other data)[1, 16] can come from the compound itself or from its hydrolysis products. For example, nitrite–carbamide or nitrite–hexamethylenetetramine mixtures owe their ability to provide vapour-phase protection to the formation of volatile ammonium nitrite in reactions with water:[16, 20]

$$(NH_2)_2CO + 2\,NaNO_2 + 2\,H_2O = 2\,NH_4NO_2 + Na_2CO_3, \quad (4)$$

$$(CH_2)_6N_4 + 4\,NaNO_2 + 10\,H_2O = 6\,CH_2O + 4\,NH_4NO_2 + 4\,NaOH. \quad (5)$$

Vaporisation of individual organic compounds devoid of ionic bonds usually consists of the transfer of their molecules to the gas phase.

Sublimation of salt-type VCIs is associated with their dissociation. The vapours of onium salts consist of non-associated acids and bases;[16, 59] partial pressures of the vapours of these compounds can differ by several orders of magnitude. For example, the vapour of ammonium benzoate consists almost completely of ammonia for which the vapour pressure is $p = 22.7$ Pa. The value of $p$ for benzoic acid ($2.67 \times 10^{-6}$ Pa) is negligibly small. A similar situation characterises hexamethyleneimmonium and diethylammonium *m*-nitrobenzoates. Conversely, vapours of cyclohexylammonium benzoate and octanoate and monoethanolammonium benzoate are enriched in the respective acids.

Several experimental methods have been developed for measuring $p^0$ that depend on the nature of the compound and on the temperature. Unfortunately, they are rather laborious, require special instruments, and are not always accurate. Therefore, semiempirical computational methods are used to assess the volatility of organic compounds. They are mainly based on measurements of boiling points ($T_b$) of compounds.[60–64]

The effect of temperature on $p^0$ obeys the Clausius–Clapeyron equation

$$\ln p^0 = -\frac{\Delta H_v^\circ}{RT} + \frac{\Delta S_v^\circ}{R} = -\frac{\Delta G_v^\circ}{RT}, \quad (6)$$

where $\Delta H_v^\circ$, $\Delta S_v^\circ$, $\Delta G_v^\circ$ are the standard enthalpy, entropy and free energy of vaporisation (evaporation or sublimation), respectively. The equation is fairly well approximated by linear relationships $\ln p^0 - 1/T$. The linearity results from weak temperature dependences of $\Delta H_v^\circ$ and $\Delta S_v^\circ$; it is observed in a wide temperature range above or below compounds' melting points. In accordance with Trouton's rule of the approximate constancy of the boiling entropies for different chemical compounds, it is possible to assess $\ln p^0$ roughly, based on $T_b$.[63]

A greater accuracy is achieved by methods that take into account the specific features of compounds (*e.g.*, chemical similarity method and simulation methods).[60–65] Models implemented as equations, nomograms or special software products[64] facilitate considerably the search for efficient VCIs. However, one cannot use these methods to predict the expediency of synthesising new compounds for creating VCIs. This can be done provided one has knowledge of the regularities relating the chemical structure of an organic compound to its volatility.

In recent years, quantitative structure–activity relationships (QSAR) have been used rather extensively to assess the volatility of organic compounds. These relationships are commonly obtained using quantum mechanical calculations,[64,66] structural topological and/or topochemical analysis.[64,67–72]

The prediction of $p^0$ makes use of the principle of additivity of the contributions of molecular structural fragments to the thermodynamic characteristics[73–76] that determine the volatility of organic compounds. However, this postulate has recently been called into question, at least with respect to the free energy of vaporisation. In fact, it has been shown[77,78] that variation of substituents in different classes of liquid organic compounds results not in equal but rather in proportional changes of this parameter and the related $p^0$ value, *i.e.*, linearity of the free energy (LFE) of evaporation.

There is a series of papers[77–80] dealing with the development of methods for the quantitative assessment of $p^0$ values for organic VCIs based on the LFE principle. A new scale of structural characteristics of substituents, *viz.*, the scale of volatility constants $\xi_R$, has been introduced. The $\xi_R$ values were computed using $p^0$ data at 293 K for liquid monosubstituted benzenes chosen as the standard series

$$\xi_R = \log p^{0,R} - \log p^{0,H}, \quad (7)$$

where indices R and H refer to substituted and non-substituted compounds, respectively. This approach made it possible to assess $p^0$ values for liquid organic VCIs from their formulae and data required for calculating correlations of the type

$$\log p^{0,R} = \alpha + \kappa\xi_R, \quad (8)$$

where

$$\alpha = \log p^{0,H},$$

and $\kappa$ is a constant characterising the series in question. It is important that the $\xi_R$ scale that has been elaborated is versatile and can be used for both aromatic and aliphatic/alicyclic compounds, including polysubstituted ones. The contributions of spatially separated substituents ($R^1$ and $R^2$) in such compounds are independent and additive

$$\log p^{0,R^1,R^2} = \alpha + \kappa\sum\xi_R. \quad (9)$$

Adjacent substituents can partially shield each other from intermolecular interactions, affecting $\alpha$ and $\kappa$ values and sometimes impairing the accuracy of data description. However, in most cases, the accuracy is sufficient for predicting the volatility of VCIs. This statement is demonstrated in Fig. 1.

Studies in this field resulted in the creation of an advanced system for the prediction and directed modification of the volatility of liquid organic corrosion inhibitors.[77–80] It was shown that the fulfilment of the LFE principle for the evaporation process results from the isoentropicity, that is, constancy of the standard entropy for a series of related compounds. This allowed a quantitative *a priori* assessment of the volatility of organic compounds in a broad temperature range above the boiling points by correlation methods,

$$\log p_{(T)}^{0,R} = A_1 + \frac{B_1}{T} + C_1\xi_R + \frac{D_1\xi_R}{T}, \quad (10)$$

where $A_1$, $B_1$, $C_1$ and $D_1$ are constants. It is important that this type of correlation relationship can be derived from data on boiling points of organic compounds under vacuum distillation conditions.

The approach elaborated for the prediction of $p^0$, together with the methods for reconstructing relationships of types (8)–(10) in the absence of data allowing one to determine them directly, often makes it possible to reject non-promising VCIs before synthesising them.

However, this system is unsuitable for salts of organic acids and bases that are perhaps the most promising class of volatile inhibitors of atmospheric corrosion. The results of a recent study (Ref. 59) provide possibilities for the quantitative assessment of their volatility. An analysis of a system 'salt of a weak acid and a weak base–its saturated aqueous solution–vapour' has led to the conclusion that it is possible to compute the pressure and composition of the saturated vapour of salt-type VCIs that do not undergo irreversible reactions with water. Computation is based on the solubilities of the salt and its constituent acid and base, as well as their $p^0$ and $pK_a$ values.

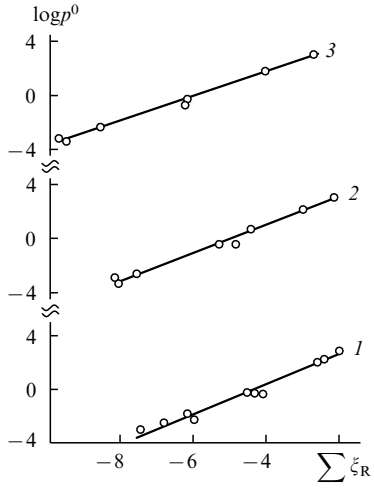



**Figure 1.** Dependences of $\log p^0$ on $\sum\xi_R$ for primary (*1*), secondary (*2*) and tertiary amines (*3*).

## 2. Effects of basicity and hydrophobicity on the functional properties of volatile corrosion inhibitors

Obviously, by no means every volatile compound can provide vapour-phase protection of a metal. An inhibitor should possess properties required for slowing down (or suppressing) surface reactions that cause metal corrosion. No matter for what purpose and in what form a VCI is used, other conditions being equal, it will protect the metal the more reliably the more strongly it inhibits corrosion in the surface (phase- or adsorption-type) moisture. Therefore, studies on the effect of the chemical structures of organic compounds on their inhibitory properties are of primary importance for developing new VCIs.

Diverse semiempirical QSAR approaches to this problem exist. They have been analysed in relation to metal corrosion inhibitors in aqueous and aqueous–organic solutions in a number of papers.[7,11,57,58,81] One can distinguish two main directions of

these studies. One of these, which has been developing intensely over the past decade, is based on the use of quantum chemical methods.[81–87] However, these methods are not yet used to create VCIs. Yet another direction, which has been developed more thoroughly, is based on Pearson's concept of hard and soft acids and bases and on the LFE principle.[7, 11, 57, 58, 83, 88–90]

The effect of the chemical structure of a VCI on its inhibitory properties depends considerably on the metal that is protected and on corrosion conditions. Perhaps, the relationship between the protective properties of organic compounds and their $pK_a$ values is deduced most often; in the majority of cases, the efficiency of inhibitors similar in chemical nature increases with an increase in the basicity of compounds.

For ammonia and lower amines, which constitute the most common class of VCIs, corrosion protection of metals is to some extent associated with the ability of VCIs to alkalify aqueous solutions.[1, 6, 10, 17, 91] A moderate increase in pH of surface moisture films decreases the corrosivity of the medium with respect to both steel and other materials. In this case, corrosion problems appear only for aluminium and only under conditions of abundant condensation of water. The alkalification factor is important not only in the protection against atmospheric corrosion, but also in the protection of steel equipment from carbon dioxide-induced corrosion in steam-condensate systems, refinery units, and oil-and-gas pipelines.[92–95]

One should not underestimate the possibility of pH control of the protective properties of salt-type VCIs as well. It is not incidental that hydrolysis of the majority of them produces alkaline medium; their anions are often oxidants that alkalify the near-surface layer upon reduction.

On the other hand, it has long been known[1, 17, 18] that the effect of $pK_a$ on the protective properties, even for individual amines, is not reduced to an increase in pH by these compounds. Following adsorption on the metal surface, they ensure metal protection at lower pH values than an alkali.[96, 97] It should be noted that the increase in the protective effect of volatile amines with an increase in their $pK_a$ often remains high in electrolytes with the same pH.[96] This can be explained by an increase in the amine adsorptivity with an increase in the electron density on the nitrogen atom, as can be measured by the ability of the compound to bind a proton. In this case, the beneficial effect of the amine basicity on the steel protection by these compounds is observed not only in solutions, but also in a humid atmosphere.[52]

The importance of the VCI adsorption itself has been demonstrated[38, 39, 97] in the protection of steel from carbon dioxide-induced corrosion, *i.e.*, under conditions where pH control was traditionally considered to play the major role.[92] It turned out that the order of steel protection efficiency of amines in the vapour phase differs from the basicity series. For instance, dibutylamine ($pK_a = 11.25$) is the best VCI among butylamine derivatives, whereas tributylamine ($pK_a = 11.04$) is the worst, and its protection efficiency is even lower than that of butylamine ($pK_a = 10.78$).[97] It is of note that VCIs that are efficient in a carbon dioxide atmosphere include not only amines but also some carboxylic acids that cannot decrease the acidity of the medium but are readily adsorbed on steel, such as lauric acid.[38, 98] This suggests that basicity is not always the dominant parameter of the inhibitory action of VCIs. This conclusion is not unexpected. It is well known that the reactivity of organic compounds cannot be described by basicity alone.[99–101]

Therefore, different characteristics of substituents were considered in studies on organic inhibitors. In particular, correlations between the efficiency of metal corrosion inhibition and electronic σ-constants of substituents have repeatedly been established.[7, 37, 57, 58, 102] The type of constants that describe such relationships and the character of their effect change depending on the charge-transfer effects occurring in the compounds, the nature of adsorption bonds and the specific features of inhibitors' protective action. It is unlikely that VCIs are different from other organic inhibitors in this respect, and it is not by chance that both salts of substituted benzoic acids[7] and volatile Schiff bases[11, 102] are among the compounds studied in most detail.

On the other hand, the use of σ-constants of substituents for the description of the protective properties of inhibitors by LFE methods is not always sufficient. One of the reasons is that adsorption of an inhibitor from an aqueous solution can be accompanied by partial dehydration of its molecules or ions, hence the affinity of an inhibitor for water is very important for metal protection.[7, 11] In order to take these factors into account, hydrophobicity constants derived from the distribution ratios of substituted organic compounds in the biphasic system octanol–water[101] are often used in addition to electronic parameters of substituents. This approach allows one to improve the accuracy of quantitative 'structure–protective effect' relationships, *e.g.*, in the case of salts of substituted aromatic acids.[7] An increase in Hansch's hydrophobicity of substituents also increases the ability of inhibitors to stabilise oxide films on metals, including those formed in air.

The hydrophilic–hydrophobic balance of VCIs becomes particularly important in the case of vapour-phase protection. The ability of inhibitors adsorbed from the vapour phase to hydrophobise a metal surface is considered to be an additional protection factor. While it is sufficient to use the $pK_a$ values of volatile amines for describing their inhibitory effect with respect to steel in chloride solutions,[96] the role of hydrophobicity may become considerable in the case of vapour-phase protection.

The reasons for the beneficial effect of the VCI hydrophobicity on the efficiency of steel protection in humid atmospheres are clear.[103] It is known that the physical adsorption on non-porous adsorbents is enhanced with an increase in the length of the alkyl substituent. The non-specific interaction of VCIs with a metal surface increases in parallel with the hydrophobicity, since introduction of a hydrophobic hydrocarbon fragment into an organic molecule increases its polarisability and attraction to the adsorbate caused by electron density fluctuations.[104] Furthermore, an increase in hydrophobicity increases the ability of VCIs to displace adsorbed water from the metal surface and impart water-repellent properties to it. However, the contribution of the hydrophobising action of VCIs should not be overestimated. If organofluorine and organosilicon compounds that are not widely used as VCIs are excluded from consideration, this is not a major contributing factor in metal-protection processes.

The basicity and hydrophobicity also affect the solubility of VCIs in surface water films and in condensed phases, which affects the kinetics of VCI propagation in the space that is protected,[47–50, 52] mass exchange with the environment,[54] interphase distribution of the inhibitor, and eventually protection efficiency. The effect of VCI solubility on vapour-phase metal protection is complex and depends on specific conditions. However, it is obvious that a VCI should be soluble in aqueous electrolyte solutions in order to provide fast and efficient corrosion inhibition.

The solubility of VCIs, many of which are weak electrolytes, also depends on their ability to undergo ionisation in water. However, the solubilities of compounds belonging to the same reaction series and possessing similar $pK_a$ values, often differ considerably. For example, an increase in the length of the hydrocarbon substituent in primary amines, starting from propylamine, almost does not affect their basicities but decreases the solubility. According to Abramzon,[105] changes in the hydrophilic–hydrophobic balance of monofunctional aliphatic compounds upon increase in the number of C—H bonds by one result in the increase in the standard free energy of dissolution ($\Delta G^\circ_{sol}$) by $\sim 1.76 \times 10^6$ kJ mol$^{-1}$. Accordingly, the saturation concentration ($C_{sat}$) for compounds rather poorly soluble in water, which is described by Eqn (11)

$$\ln C_{sat} = -\frac{\Delta G^\circ_{sol}}{RT}, \qquad (11)$$

also changes. From the structural formula and solubility of one member of the series one can assess $C_{sat}$. Unfortunately, this approach does not allow one to predict the solubility changes when heteroatoms are introduced in a molecule and is of little use for aromatic compounds.

In the latter case, it is reasonable to use correlations based on the LFE principle. It has been shown [106] that the change in $C_{sat}$ due to structure variation for liquid aromatic compounds that are not ionised in water is described by the Hansch equation

$$\ln C_{sat} = a + b\pi_R, \quad (12)$$

where $a$ and $b$ are constants for a given series, $b < 0$; and $\pi_R$ is the substituent's hydrophobicity.

Combination of the methods described makes it possible to optimise the properties of VCIs in a certain range (which is currently rather narrow) by modifying their chemical structures. It should be taken into account here that a decrease in the inhibitor's solubility with an increase in hydrophobicity may result in the loss of protective properties. This situation is particularly characteristic of corrosive media where the $C_{pr}$ values of inhibitors are high. However, it was noted [96] that complete protection of steel in 0.005 M aqueous solution of NaCl, *e.g.*, by tributylamine, was impossible, due to the low $C_{sat}$ value. A similar situation has been reported in vapour-phase protection.[103] Steel corrosion was not suppressed in the vapour phase even above saturated solutions of n-nonylamine and n-decylamine, whereas butylamine which is more hydrophilic and has a similar basicity prevents corrosion at a concentration as low as 0.14 mol litre$^{-1}$.

It is impossible to optimise the chemical structure of organic compounds for creating more efficient VCIs without revealing the specific features of their adsorption on metals that are protected. Furthermore, it has become clear in recent years that VCIs can have a rather prolonged protective post-effect. This opens new prospects for their application and calls for studies of VCI desorption from the surface of metals and oxides.

## IV. Adsorption and desorption of volatile corrosion inhibitors

From the very first years of investigations into VCIs, their adsorption was studied by both direct and indirect methods, among which electrochemical methods, including those applied to processes occurring under thin moisture films,[1] were of considerable importance. It has been shown that, first, it takes a long time (hours or even days) to form protective films on metals placed in a VCI atmosphere and, second, once such films have been formed, corrosion on these samples begins, following removal of VCI vapour, later than on metals that have not been subjected to pre-treatment with the VCI. Unfortunately, the advantages of employment of this phenomenon in the practice of vapour-phase anti-corrosion protection were underestimated for a long time.

Obviously, the reason for the VCIs' post-effect is determined by the character of their adsorption on metals. If we take into account that this effect is much more pronounced on iron and steels than on zinc and aluminium, it is reasonable to assume that chemisorption of the VCIs on the surface occurs. However, not only chemisorption prevents desorption of VCIs.

In fact, the adsorption of *N*,*N*-diethylaminoethanol vapour (in the range of $p/p^0$ from 0.1 to 0.9) on the surface of naturally oxidised iron powder results virtually in a monolayer but increases 4–5-fold at $p/p^0 = 1.0$ (Fig. 2).[107] This is close to the ellipsometric estimate of its adsorption on an iron surface in air.

Evacuation of the inhibitor vapour resulted in its total desorption, which suggests the reversibility of adsorption, at least in the absence of an access of air and in a relatively short-term experiment (~5 days). On the other hand, adsorption of water on an iron powder that has preliminarily adsorbed no more than a monolayer of this VCI occurs in a different way than on its clean surface. Despite VCI desorption, the maximum mass gain is ~5 times smaller than that upon water adsorption by a surface

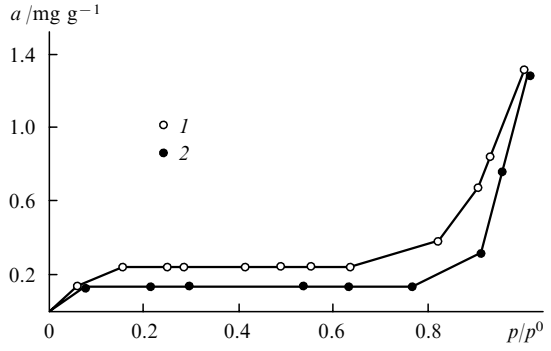



**Figure 2.** Adsorption isotherms of *N*,*N*-diethylaminoethanol on the surface of naturally oxidised iron powder at 13 (*1*) and 22 °C (*2*).[107]

free from the inhibitor (Fig. 3). Evacuation results in a 'zero' mass for a given experiment, that is, the mass of the sample that has already adsorbed the VCI (0.14 mg g$^{-1}$). Hence, the VCI studied decreases the limiting adsorption of water even at low inhibitor coverage, which may be explained by the adsorption of water molecules on the same surface-active centres as the VCI. This property of VCIs is of key importance, since it is known that a considerable increase in the corrosion rate of a metal in water vapour occurs after at least 2–4 monolayers of adsorbed water have been formed on the metal surface.

If iron powder has first adsorbed 0.26 mg g$^{-1}$ of the VCI, which corresponds to the plateau on the adsorption isotherm of *N*,*N*-diethylaminoethanol at 13 °C (see Fig. 2), evacuation of the vapour does not restore the original mass of the sample. This suggests that either partially irreversible VCI adsorption occurs under the effect of water vapour or that additional oxidation of iron with water stimulated by traces of the VCI takes place. Obviously, under real conditions of anticorrosion protection, the adsorption of VCIs is complicated by the presence of oxygen and other gases in the atmosphere. A volatile corrosion inhibitor can react with them, while the surface can catalyse the process.

In fact, the results of studies on the adsorption–desorption kinetics of various VCIs on the surface of naturally oxidised iron (Fig. 4) by ellipsometric methods confirm that the formation of adsorption layers takes rather a long time (several days are required even for fairly volatile compounds). Furthermore, these results suggest the polymolecular adsorption of amine-type VCIs and adsorption irreversibility to a considerable degree for many well-known VCIs. Attention should be paid to the fact that the

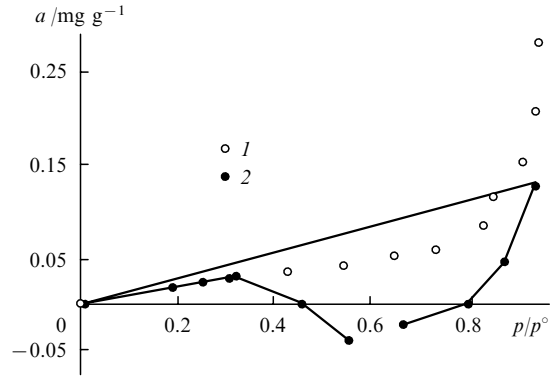



**Figure 3.** Adsorption isotherms of water vapour on the original sample of iron powder (*1*) and on a sample with preliminary adsorption of *N*,*N*-diethylaminoethanol (*2*).[107]
For convenience in the comparison of isotherms, the changes in the sample mass refer to the zero coordinate corresponding to the original mass of the sample that has adsorbed the VCI (0.14 mg g$^{-1}$).

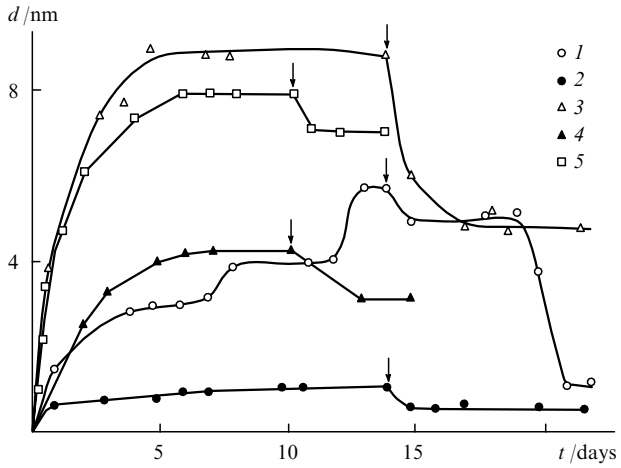



**Figure 4.** Kinetics of VCI adsorption – desorption on iron surface under atmospheric conditions.[107]
(*1*) 2-Aminoethanol, (*2*) *N*-ethyldiethanolamine, (*3*) *N*,*N*-diethylaminoethanol, (*4*) *N*,*N*-diethylaminopropionitrile, (*5*) 4-diethylamino-3-methylbutan-2-one. The variations in ellipsometric angle $\Delta$ have been converted to the thickness of adsorption layers $d$ using Drude's approximation: $d = -\alpha(\Delta - \Delta_0) = -\alpha\delta\Delta$.

irreversibility of *N*,*N*-diethylaminoethanol adsorption was clearly higher than that measured in the above adsorption measurements *in vacuo*. In this case, longer exposure of a sample in VCI vapour favours not only the chemisorption of the amine, but also increases the probability of formation of a structured polymolecular adsorption film by the inhibitor. This follows from the results of studies on the mechanism of action of yet another well-known amine-type VCI, *viz*., *N*,*N*-diethylaminopropionitrile.[19]

The interaction of *N*,*N*-diethylaminopropionitrile with an iron surface was studied by XPS and ellipsometry.[108] In addition, IR spectra of a $\gamma$-$Fe_2O_3$ powder impregnated with the VCI were measured immediately after drying following exposure in air for different periods of time. These studies resulted in the conclusion that a film consisting of a chemisorbed and a physically adsorbed layer is formed on the oxidised iron. The formation of the first layer is due to hydrolysis of *N*,*N*-diethylaminopropionitrile; as a result, compounds that are less volatile than the original compound but have a higher protective effect in aqueous solutions, that is, diethylaminopropionamide and possibly the diethylaminopropionate anion, are adsorbed on the surface. This chemisorbed layer is formed in 1.5 – 2 days; it does not undergo desorption *in vacuo* and it is not removed upon washing with ethanol or upon prolonged (up to 8 months) exposure to a dry atmosphere.

The physically adsorbed layer is also non-uniform. Taking into account the ability of the CN group in *N*,*N*-diethylaminopropionitrile to add another VCI molecule due to the formation of both a donor – acceptor bond with the nitrogen atom of the amino group and a 'paired dipole bond' with the CN group oriented antiparallel, it was assumed that associates with increased viscosity are formed atop the chemisorbed layer. They are soluble in ethanol but almost cannot be removed *in vacuo*. This layer should provide good screening of the metal surface preventing the penetration of a corrosive medium. On the other hand, *N*,*N*-diethylaminopropionitrile remains partly unbound and, being rather volatile, is desorbed from the surface not only *in vacuo*, but also on storage in air.

A study on the formation of adsorption layers in *N*,*N*-diethylaminopropionitrile vapour [109] showed that the characteristic electron binding energies in the spectra of an iron surface are almost the same irrespective of whether the VCI is adsorbed from the liquid or vapour phase. However, the spectra of O1s electrons change as the exposure time increases. As in the case of VCI application by the contact technique, the intensity of lines in the high-energy region of the spectrum ($E_b$ = 532 – 534 eV) increases, which is explained by the adsorption of oxygen-containing hydrolysis products on iron. The spectra of rinsed and non-rinsed samples were identical after exposure for 30 h. After exposure for 300 h, the high-energy region of the spectrum becomes predominant. However, unlike the case of VCI adsorption from the liquid phase, the low-energy region of the spectrum corresponding to iron oxides is retained.

After adsorption of *N*,*N*-diethylaminopropionitrile vapour on iron, as upon contact application of the inhibitor, the $Fe2p_{3/2}$ spectrum contains both the lines corresponding to the original iron sample ($E_b$ = 707 and 711.5 eV) and, when exposed for periods from 10 min to 300 h, 'shoulders' in the region of 708 – 710 eV due to the appearance of nucleophilic species on the iron surface. For samples washed with ethanol, the intensities of lines in the spectrum of $Fe2p_{3/2}$ electrons remain virtually unchanged for all exposure times. For non-washed samples, the spectrum of $Fe2p_{3/2}$ electrons after the first 30 h of exposure differs only slightly from the corresponding spectrum for the washed samples. After exposure for 48 hours, the content of iron in the layer in question on non-washed samples quickly decreases and then remains unchanged (Fig. 5). The maximum in the spectrum ($E_b$ = 711.5 eV) also persists after exposure for 300 h. This makes it different from the spectra obtained upon contact application of the VCI. In the latter case, a low-energy shift of the maximum was observed as early as after 36 h of exposure. Furthermore, the high-energy region of the spectrum corresponding to oxides was retained after exposure of iron in the vapour phase.

The kinetic regularities of variations in the relative content of the elements analysed are the same as for adsorption of this VCI from the liquid phase. Starting from the first minutes of exposure, the concentrations of nitrogen, oxygen and carbon (the curves for carbon are not shown in Fig. 5), measured on the surfaces washed with a solvent, increase abruptly, whereas the content of iron decreases. After ~30 h, these parameters level off. After the first 30 h of adsorption, the curves for washed and non-washed samples almost do not differ from each other, but for non-washed samples the relative concentrations of the elements stabilise after a longer period, as a rule, after 2 days.

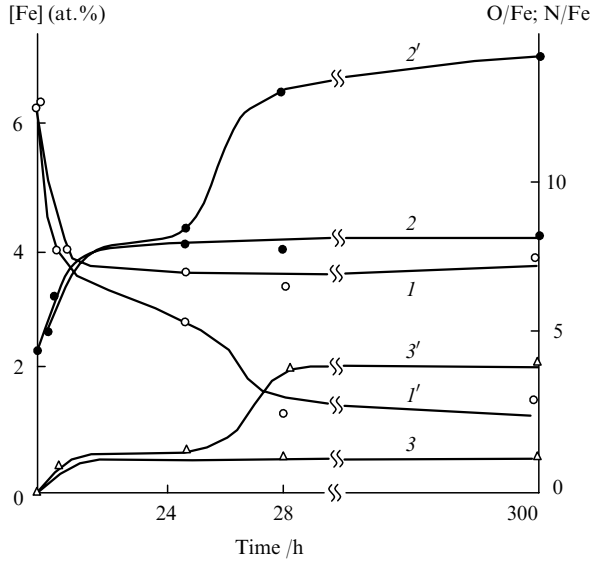



**Figure 5.** Variation in the concentration of iron (*1*, *1*′) and the relative content of oxygen (*2*, *2*′) and nitrogen (*3*, *3*′) on an iron surface exposed to *N*,*N*-diethylaminopropionitrile vapour.
(*1* – *3*) After washing with ethanol (*1*′ – *3*′) without washing.

A comparative analysis of the effect of the VCI from the liquid and vapour phases on iron showed that the mechanism of formation and growth of protective layers does not depend on the way the inhibitor was applied on the surface. However, it affects the ratio of the chemisorbed and physically adsorbed VCI. In fact, chemisorption of the inhibitor after a 300-hour exposure is higher if the film is formed from the vapour phase, whereas the physically adsorbed VCI layer is thicker upon contact application. This is probably due to the fact that, unlike the case of gradual adsorption of *N*,*N*-diethylaminopropionitrile vapour, the contact application of the inhibitor favours the association of VCI molecules. In the latter case, the thickness of the physically adsorbed layer prevents the access of water from the atmosphere followed by hydrolysis of the VCI. This can explain the smaller concentration of chemisorbed species.

The results of ellipsometric measurements (Fig. 4) showed that, once a polymolecular film of *N*,*N*-diethylaminopropionitrile has been formed from the vapour phase, its desorption does not exceed 28% and occurs most intensively during the first three days. The remaining film is strongly bound to the surface of the iron sample.

We also observed an important contribution of chemical transformations to the protective effect of VCIs for one of the most efficient versatile inhibitors of atmospheric corrosion, *viz*., 4-diethylamino-3-methylbutan-2-one.[110] The adsorption of this VCI on iron also results in a polymolecular protective film. The adsorption is largely irreversible (see Fig. 4) due to oxidation, dimerisation, condensation and perhaps more profound chemical transformations of unsaturated ketones formed upon the dissociative adsorption of the VCI. It is no wonder that this inhibitor has a long post-treatment effect (Table 1).

It was previously assumed that lower amines are prone to desorption. Hence, metal protection requires that they are always present in the corrosive medium, whereas their higher homologues can provide metal protection due to the post-treatment effect, *i.e.* by irreversibly adsorbed molecules.[111] Most often, this is actually the case. For example, allylamine ($pK_a = 9.42$) does not show any protective post-treatment effect and even stimulates copper corrosion. However, diallylamine ($pK_a = 9.29$) or n-heptylamine, which possess higher hydrophobicities, show post-treatment effects not only on steel but also on zinc. n-Octylamine protects steel even more efficiently. In fact, a steel sample exposed for 12 days in n-octylamine vapour did not undergo corrosion for over 30 days in a VCI-free atmosphere with a 100% relative humidity.[110]

**Table 1**. Protective post-effect of VCIs under 100% relative humidity in the absence of forced condensation of moisture on the samples.

| Volatile inhibitor | $\tau$ /months | Sample | | |
|---|---|---|---|---|
| | | St.3 | Cu | Zn |
| Allylamine | 0.5 | – | – – | – |
| | 1.0 | – | – – | – |
| Diallylamine | 0.5 | + + | – – | + + |
| | 1.0 | + + | – – | + + |
| | 2.0 | + | – – | – |
| | 3.0 | + | – – | – |
| Heptylamine | 1.0 | + + | – – | + |
| | 2.0 | + | – – | + |
| | 3.0 | – | – – | + |
| Ethylenediamine | 0.5 | + + | – – | + |
| | 1.0 | + + | – – | ± |
| | 2.0 | + + | – – | – |
| | 3.0 | + | – – | – |
| | 0.5 | + + | + + | + |
| *N*,*N*-Diethylaminoethanol | 1.0 | + + | + + | – |
| | 2.0 | + + | – | – |
| | 3.0 | + | – | – |
| 4-Diethylamino-3-methyl- | 0.5 | + + | + + | ± |
| butan-2-one | 1.0 | + + | + + | ± |
| | 2.0 | + + | + + | – |
| | 3.0 | + | + + | – |

**Note**. The following notation is used: $\tau$, exposure time; two plus signs, absence of corrosion; one plus sign, small corrosion damage; one plus-minus sign, poor metal protection; one minus sign, no protection; two minus signs, corrosion stimulation.

Such a strong adsorption of amines on the surface of oxidised steel depends on their nature and agrees well with our concepts about interactions of a hard base with a hard acid; the role of the latter, unlike iron itself, is played by its oxidised surface.[103] The energy characteristics of such an interaction have not yet been studied in sufficient detail. So, its calorimetric estimate based on the integral heat of adsorption of both liquid amines (heat of immersion) and their vapours deserves attention. It has been shown[112] that the amino group in n-octylamine provides the major contribution to the heat of adsorption on a naturally oxidised iron powder. The value of this parameter for n-octylamine is noticeably higher than those of non-polar n-undecane and even polar octanol. Therefore, both the high potential of dispersive interaction with the $C_8$ hydrocarbon radical and the specific interaction of the amino group with electron-withdrawing surface sites are responsible for the high energy of adsorptive interaction of the alkylamine with the iron powder studied.

Such sites can include coordination-unsaturated ion-atoms of iron with incomplete d-shells, which enter into donor–acceptor interactions with nitrogen atoms of the amino groups. It has been shown that Fe(II) and Fe(III) sites are present on the surface of oxidised finely dispersed iron, *e.g.*, in an IR-spectroscopic study of CO and NO adsorption.[113] Under atmospheric conditions, these centres are blocked with water molecules that cannot be removed by low-temperature evacuation and are desorbed only partially upon evacuation at 100 °C. It should be noted that the collective properties of the surface and adsorbate are strongly affected by the formation of donor–acceptor bonds by these compounds and the ionisation potential of the organic compound.[114]

According to estimates,[112] the total heat of adsorption and condensation of n-octylamine is as high as 44 kJ mol$^{-1}$; this can suggest its ability to be chemisorbed on an oxidised iron surface (taking into account partial irreversibility of amine adsorption). Interestingly, the irreversibility of adsorption increases in the series n-octylamine < cyclohexylamine < primary aliphatic amines $C_{10}$–$C_{13}$. In these cases, the fractions of strongly adsorbed compounds are 25%, 40% and 60% of their total content, respectively. It was noted that the adsorption energies are virtually the same for amines with different hydrocarbon radicals. Hence, electron-withdrawing sites are arranged rather sparsely on the surface, which allows them to easily interact with the amino groups despite considerable size differences in the 'landing sites' that are about 30, 60 and 80–90 Å$^2$ for cyclohexylamine, n-octylamine and aliphatic amines $C_{10}$–$C_{13}$, respectively.

In this case, it was also noted that the adsorption of water on the surface of a powder modified by n-octylamine was lower than that on the original adsorbent. It would seem that this difference is attributable to the fact that water cannot totally displace chemisorbed VCI molecules. However, the fact of the partially irreversible adsorption of water implies that its interaction with the surface is more complex. Presumably, the adsorbed VCI facilitates additional oxidation of iron or undergoes protonation to give the octylammonium ion and a surface hydroxy group.

On the other hand, elongation of the alkyl fragment in the molecules decreases the volatility of amines and their solubility in water; therefore, higher amines can only be used at high temperatures, *e.g.* , in the protection of power plants. It is more efficient to use certain heteroalkylated amines as VCIs: under ordinary conditions, even hydrophilic ethylenediamine can provide a long-

lasting protective post-treatment effect on low-carbon steel (Table 1).

Thus, by creating adsorption layers from a VCI-containing vapour phase, it is possible to provide a prolonged post-treatment metal-protection effect. This refers not only to protection from atmospheric corrosion. Studies on a VCI in a carbon dioxide atmosphere have shown [115] that the irreversibility of VCI adsorption is much higher than in air. In fact, the adsorption of 2-aminoethanol is enhanced according to a power law in both cases, though it is somewhat more slow in a carbon dioxide atmosphere. After the cell has been unsealed and the VCI has been removed from it, 2-aminoethanol is desorbed gradually (Fig. 4). However, in air, desorption is incomplete even after 14 days, though the irreversibility of its adsorption is not high: the desorption coefficient $K_d$ that expresses the fraction of the desorbed VCI exceeds 80%. The desorption of 2-aminoethanol becomes even less ($K_d \approx 14\%$) if the protective film on the metal surface was formed in a carbon dioxide atmosphere.[115]

This suggests the formation of stronger bonds of the VCI with carbonate compounds that are formed on iron.[116] The results of FTIR studies on the reaction of $CO_2$ with 2-aminoethanol on naturally oxidised iron confirmed that amino alcohol carbonates could be formed on the surface.[115] Presumably, the long-term protective post-treatment effect of some other VCIs in the carbon dioxide atmosphere is due to similar reasons. For example, after exposure of low-carbon steel electrodes to vapour of aliphatic amine 'A' ($K_d \approx 7\%$), the corrosion current in the corrosive aqueous solution containing (per litre) 0.25 g AcOH + 5 g NaCl + 0.04 g $Na_2S$ ($p_{CO_2} = 1$ atm) changes only slightly during the first 200 hours, whereas it increases almost threefold for the electrodes that have not been treated with the inhibitor.[39] Subsequently, the corrosion current gradually increases due to the inhibitor desorption, but even after 350 h, it is still 1.5-fold smaller than that for the untreated metal. Similar results that prove the possibility of the long-term post-treatment effect of VCIs were obtained in a study [117] where protective films were obtained using comparatively concentrated aqueous solutions (4 g litre$^{-1}$) of the same VCIs. The data obtained are still insufficient for drawing the conclusion that it is preferable to create protective VCI layers from the vapour phase, but the prospects of using 'self-organisation' effects for this purpose deserve attention. In recent years, these effects have attracted the particular attention of scientists in various fields of chemistry,[118] including those who deal with the anti-corrosion protection of metals.[119–124]

In this respect, the formation of protective layers on metals by benzotriazole (BTA), which is one of the most famous copper alloy corrosion inhibitors,[7,10,11] commonly used for corrosion prevention in aqueous solutions, is of interest. For this reason, the interaction of its solutions with copper is usually studied. However, despite its relatively low volatility ($p_s \approx 1.3\ 10^{-3}$ Pa at 25 °C), it is an excellent VCI and is used to suppress the corrosion of copper, zinc and their alloys.[1,16] The protective properties of BTA have long been attributed to the formation of a polymolecular film of its complex with metal cations. Numerous justifications for this point of view have been considered in reviews.[125–128] However, the opinions regarding the structure of the resulting film remained controversial, which was partially due to differences in the conditions of film formation and the impossibility of detailed determination of their composition and morphology by *in situ* methods.

The adsorption of BTA was studied [128,129] from the vapour phase on the 110 face of a copper single crystal in an ultrahigh vacuum directly in the chamber of an instrument that makes it possible to analyse the surface by a scanning tunnel microscope, as well as by slow-electron diffraction and UV photoemission methods. It was shown that in ~85 min a monolayer was formed on copper where the BTA molecules were arranged parallel to the metal surface ('planar adsorption'). After that, slow changes in the spectra were observed during 125 min of exposure; the changes became noticeable between 120 and 185 min due to the formation of a second layer where two BTA molecules are arranged on one BTA molecule of the first layer binding with it through nitrogen atoms. It is believed that this kind of polymerisation of the adsorbate changes the orientation of its molecules on the surface and favours π-bonding of the molecules with the surface, while the ligand's electrons are transferred to the lowest unoccupied d-orbitals of copper.

It is of note that, as shown by X-ray photoelectron spectroscopy (XPS),[130,131] certain azoles that are less volatile but more hydrophobic than BTA, *e.g.*, 3,5-diphenyl-4*H*-1,2,4-triazole or 2,5-bis(2-pyridyl)-1,3,4-oxadiazole, can also be chemisorbed on a steel surface.

Of sulfur-containing volatile compounds, thiophene ($p^0 = 2.3$ Pa) has long been known as a steel corrosion inhibitor; its adsorption from the vapour phase on the faces of single-crystal iron was studied [132] by several methods in an ultravacuum chamber. This compound, when chemisorbed on an iron surface through S–Fe bonds, first loses hydrogen α-atoms and then β-atoms. α-Dehydrogenation results in polymeric chain structures where the thiophene rings are oriented horizontally or vertically, depending on the temperature.

Although adsorption studies from the vapour phase in an ultra-high vacuum are undoubtedly valuable, it should be noted that the results obtained do not always allow one to draw conclusions on the nature and character of a bond between a VCI and an oxide-coated hydroxylated metal surface under atmospheric conditions. If water is present in the gas phase, the situation can be different as well. An obvious example is the adsorption of silanes on hydroxylated iron from the vapour phase which is not accompanied by chemisorption even at elevated temperatures (up to 80 °C).[133] In the case of joint adsorption of silanes and water vapour, the former are hydrolysed to give silanols $R_{4-n}Si(OH)_n$ that undergo condensation with the hydroxylated surface followed by polymerisation.

* * *

The scope of VCI application has been rapidly expanding over recent years. However, this is hindered by the insufficient development of the theory of vapour-phase protection. Many physicochemical aspects of mechanisms of action of VCIs are still understood only roughly. Therefore, it should be acknowledged that total algorithmisation of designing optimal molecular structures of VCIs for solving particular practical problems remains a task for tomorrow. In the authors' opinion, the current priority tasks include the development of methods for predicting the formation of azeotropes of organic compounds with water, mathematical description and experimental simulation of conditions of vapour-phase metal protection, development of the theory of the mutual influence of components of mixed inhibitors and studies on the VCI adsorption and mechanisms of the post-treatment effect.

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