Volatile inhibitors of atmospheric corrosion
of ferrous and nonferrous metals
I. Physical and chemical aspects of selection
of starting reagents and synthetic routes

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Abstract
The paper discusses the relationship between the physicochemical and electronic
characteristics of various metals and molecular parameters of inhibitors that allows a better
prediction of the efficiency of volatile inhibitors of atmospheric corrosion (VIACs) of
ferrous and nonferrous metals. The high efficiency of commercial VNKh-L inhibitors
based on Schiff and Mannich bases as VIACs is substantiated. It is demonstrated by
analyzing the main molecular characteristics that products of complex condensation of
nitrogen-containing compounds with aldehydes can serve as highly efficient VIACs.

Key words: physical and chemical aspects; volatile inhibitors; atmospheric corrosion;
ferrous and nonferrous metals; Schiff and Mannich bases.

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According to the current concepts adopted by most researchers [1–16], the efficiency of a
volatile inhibitor of atmospheric corrosion (VIAC) generally depends on the pressure of its
saturated vapor \( P^0 \) at a given temperature, the diffusivity \( D \) determined by the
molecular mass, and the minimum protective concentration \( C_{\text{min}} \) in water with respect to
a metal to be protected. The first two factors, unlike the third one, are independent of the
metal nature. The minimum protective concentration depends on the properties of an
inhibitor as well as on the metal nature. The mere existence of such a term as “radius of
VIAC protective action” can prove that diffusion of an inhibitor across the air layer from
the surface of evaporation to the surface of a water film on the metal is the slowest step [7].
Otherwise, the efficiency of VIAC would be independent of the thickness of the air layer
[9–13].

A detailed analysis of the plot of the efficiency of VIAC vs. \( D \) and \( P^0 \), which has been
performed for inhibitors used to preserve metallic parts in the last 40–50 years [1, 9–13,
15, 17], revealed that the vapor pressure of a “perfect” VIAC should range from \( 1 \cdot 10^{-6} \) to
1·10^{−2} \text{ mmHg}. \text{ Diffusivity varies only slightly among inhibitors. For instance, the diffusivity of inhibitors with molecular masses of 200–300 at 20°C ranges within 0.05–0.04 cm^2/s [1, 9–12].}

The trends of the adsorption of corrosion inhibitors on metals and their effect on the kinetics of partial electrode reactions and the corrosion process as a whole, which determine the efficiency of an inhibitor, depend on many factors, notably the electronic structures of the adsorbate and adsorbent. Let us consider the set of main physicochemical properties of metals and inhibitors that determine their anticorrosion properties.

From the viewpoint of accounting the electronic features, VIACs do not differ from other organic corrosion inhibitors. However, knowledge of the electronic structures and volatility alone is insufficient for understanding and predicting the protective properties of inhibitors. One reason is that the adsorption of an inhibitor on a metal from a thin moisture film (or an aqueous solution) can be accompanied by dehydration of its molecules; that is why the affinity of an inhibitor for metal and water, which is characterized by hydrophobicity constants [18], is very important for protection of metals from atmospheric corrosion [7].

Sufficiently distinct quantitative correlations between the inhibitive efficiency and the properties associated with the electronic structure of a compound were found mostly for series of related compounds with respect to the same metal; as a rule, these correlations do not hold for another metal and should be applied with caution.

It is generally accepted that the formation of an “inhibitor–metal” bond occurs by redistribution of electrons of the occupied and vacant orbitals of the metal and the inhibitor. This is based on estimation of the inhibitor adsorptivity from the ionization potential (IP): the lower IP, the easier adsorption occurs. The donating properties of a compound increases with decreasing IP, which is explained by easy transfer of a lone electron pair of a compound with a low IP to a metal.

Generally, a combination of a compound with a low IP and a metal with a high IP or vice versa is required. A sufficient condition for the formation of an adsorption bond is believed [19] to be as follows:

- a high electron work function of the metal and a low IP of the adsorbate, or
- a low electron work function of the metal and a high IP of the adsorbate.

However, we will demonstrate below that application of these general concepts does not provide an unambiguous prediction of the efficiency of VIACs with respect to dissimilar metals.

Nechaev and Kuprin [20, 21] proposed a new approach to the estimation of the adsorptivity of compounds based on IP. Unlike the generally adopted concepts of the formation of adsorption bonds by redistribution of electrons of the occupied and vacant orbitals of the adsorbent and adsorbate, the new approach considers the interaction of two
occupied orbitals to give a common electronic system. It has been demonstrated in [20, 21] that the plot of the adsorption of molecules on metals and metal oxides versus their first adiabatic IPs passes through a maximum named the “resonance” potential, which is essentially a sorption characteristic of a solid. According to Nechaev and Kuprin, the “resonance” potentials of metals and metal oxides allow one to predict the adsorptivity and inhibitive efficiency of a compound.

However, the high adsorptivity of a compound seems to produce the reverse effect as well: it can stimulate corrosion, especially for metals protected via dative bonds, as we will show below. We believe that Nechaev’s concept should be applied to corrosion inhibition in a more careful and detailed manner. When predicting the inhibitive efficiency of a compound based on its adsorptivity, one should consider that not only the first adiabatic IP of the compound but also the adiabatic IPs of all the “anchor” atoms in its molecule should match (be close to) the “resonance” potentials of the metal to be protected and its oxide.

Undoubtedly, other physicochemical characteristics of metals should also be taken into account. The ability of a metal to adsorb chemical compounds depends on both its donor-acceptor properties and the mobility of its surface atoms. The higher the vibrational frequency of the surface atoms of a metal (below the melting point), the more difficult it is for chemical compounds to be adsorbed on it. That is why light metals are less susceptible to corrosion protection by inhibitors. According to this concept, protection of cadmium or zinc by inhibitors is more difficult than that of copper or iron, which generally agrees with published data on corrosion inhibitors.

When using inhibitors for metal protection from atmospheric corrosion, one should consider the presence of metal oxides and hydroxides on the metal surface; they inevitably form in a moist atmosphere and have different compositions on different metals. According to the Pourbaix diagrams [22], the metal surface at pH ~7 mainly contains hydroxides for Zn and Cd, oxides and hydroxides for Cu and Fe, and oxides for Mg and Al. Therefore, one can expect that the adsorption of the same compound on a metal and subsequent corrosion inhibition would be similar for such pairs of metals as zinc and Cd, Cu and Fe, Mg and Al.

Thus, we believe that prediction of the inhibitive properties of compounds on various metals should be based on a whole set of physicochemical characteristic of metals (Table 1).

To meet modern specifications, VIACs should be thermally stable up to 160–180°C, which will allow incorporating them into polyolefin films during manufacture. For this reason, coordination compounds should be excluded from the list of new possible inhibitors because they are highly hydrolyzable and thermally unstable.

Unlike the previously developed domestic and imported inhibitors based on quaternary ammonium bases, new volatile inhibitors of the series IFKhAN and VNKh are molecular compounds and hence can be used at high temperatures and incorporated into
polymer films during manufacture. We believe that the most promising synthetic route involves the preparation of such molecular compounds as Schiff and Mannich bases.

**Table 1.** Selected physicochemical properties of the metals to be protected from atmospheric corrosion.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electronic configuration</th>
<th>IP, eV</th>
<th>“Resonance” IP according to Nechaev, eV</th>
<th>Melting point, °C</th>
<th>Surface characteristic at pH 7 (from the Pourbaix diagram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>3s²</td>
<td>7.64</td>
<td>–</td>
<td>651</td>
<td>oxides</td>
</tr>
<tr>
<td>Al</td>
<td>3s²p¹</td>
<td>5.98</td>
<td>7.24</td>
<td>660.1</td>
<td>oxides</td>
</tr>
<tr>
<td>Fe</td>
<td>3d⁶4s²</td>
<td>7.87</td>
<td>7.3 and 7.9</td>
<td>1550</td>
<td>oxides + hydroxides</td>
</tr>
<tr>
<td>Cu</td>
<td>3d¹⁰4s¹</td>
<td>7.72</td>
<td>7.2 and 7.9</td>
<td>1083</td>
<td>oxides + hydroxides</td>
</tr>
<tr>
<td>Zn</td>
<td>3d¹⁰4s²</td>
<td>9.39</td>
<td>9.2–9.4</td>
<td>419.5</td>
<td>hydroxides</td>
</tr>
<tr>
<td>Cd</td>
<td>4d¹⁰5s²</td>
<td>8.99</td>
<td>7.5–7.7</td>
<td>321</td>
<td>hydroxides</td>
</tr>
</tbody>
</table>

To synthesize new VIACs, we used cyclohexylamine (CHA), morpholine (MP), and benzotriazole (BTA) as the starting materials. We obtained two homologous series of compounds by condensation of formaldehyde (FA) or benzaldehyde (BA) with cyclohexylamine (Schiff bases) and morpholine (Mannich bases) as well as by complex condensation of the following mixtures: cyclohexylamine + morpholine, cyclohexylamine + benzotriazole, and morpholine + benzotriazole with aldehydes.

Tables 2 and 3 show the chemical and conventional names, the total electron densities on the heteroatoms in the molecules (Σq), the calculated saturated vapor pressures, and the Hansch hydrophobicity constants for the products obtained and for inhibitors developed by us previously that are currently manufactured on commercial scale.

The pressures of saturated vapors were calculated as described in [7, 8] using the ξR constants introduced by N. Andreev for taking account of the contribution of substituent (R) to the change in the Gibbs energy of vaporization. The hydrophobicity constants of the compounds obtained were calculated by the Hansch method [18, Ch. IV] from the data on the πx of fragments with consideration for the total fragment constants and geometrical factors [18, pp. 23, 24]. Quantum chemical calculations of molecular diagrams were performed using the HyperChem Version Professional Release 6.03 program (Hypercube Inc.) by the CNDO/2 method without optimization; standard bond lengths and bond angles were set for the Build model in the Single Point mode.
Table 2. Selected characteristics of the VIACs obtained by condensation with formaldehyde (FA).

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Chemical name</th>
<th>$\Sigma q$ on the heteroatoms</th>
<th>Calculated $P^0$, mmHg, at 20°C</th>
<th>Calculated hydrophobicity constants</th>
<th>Conventional no. of the inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHA + FA</td>
<td>Methylidene-cyclohexylamine</td>
<td>1.140</td>
<td>1.1 $^a$</td>
<td>1.21</td>
<td>VNKh-L-111</td>
</tr>
<tr>
<td>MP + FA</td>
<td>Dimorpholino-methane</td>
<td>4.823</td>
<td>12.2$\cdot 10^{-2} b$</td>
<td>0.52</td>
<td>VNKh-L-112</td>
</tr>
<tr>
<td>CHA + MP + FA</td>
<td>1-Morpholinomethylcyclohexylamine</td>
<td>3.591</td>
<td>8.9$\cdot 10^{-2}$</td>
<td>2.33</td>
<td>VNKh-L-113</td>
</tr>
<tr>
<td>CHA + BTA + FA</td>
<td>1-Cyclohexylaminomethylbenzotriazole</td>
<td>4.388</td>
<td>0.12$\cdot 10^{-4}$</td>
<td>1.86</td>
<td>VNKh-L-405</td>
</tr>
<tr>
<td>MP + BTA + FA</td>
<td>1-Morpholinomethylbenzotriazole</td>
<td>5.576</td>
<td>0.19$\cdot 10^{-4}$</td>
<td>–0.15</td>
<td>VNKh-L-406</td>
</tr>
</tbody>
</table>

$^a$ The experimental value is $2\cdot 10^{-4}$ at 40°C.

$^b$ The experimental value is $4\cdot 10^{-2}$ at 20°C.

Table 3. Selected characteristics of the VIACs obtained by condensation with benzaldehyde (BA).

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Chemical name</th>
<th>$\Sigma q$ on the heteroatoms</th>
<th>Calculated $P^0$, mmHg, at 20°C</th>
<th>Calculated hydrophobicity constants</th>
<th>Conventional no. of the inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHA + BA</td>
<td>1-Benzylidene-cyclohexylamine</td>
<td>1.189</td>
<td>2.88$\cdot 10^{-3} a$</td>
<td>3.91</td>
<td>VNKh-L-49</td>
</tr>
<tr>
<td>MP + BA</td>
<td>(Dimorpholino)-(phenyl)methane</td>
<td>4.808</td>
<td>2.88$\cdot 10^{-5} b$</td>
<td>1.90</td>
<td>VNKh-L-20</td>
</tr>
<tr>
<td>CHA + MP + BA</td>
<td>1-Morpholinomethyl-1-phenylcyclohexylamine</td>
<td>3.600</td>
<td>3$\cdot 10^{-5}$</td>
<td>3.91</td>
<td>VNKh-L-21</td>
</tr>
<tr>
<td>CHA + BTA + BA</td>
<td>1-Cyclohexylaminomethyl-1-(phenyl)benzotriazole</td>
<td>4.401</td>
<td>0.15$\cdot 10^{-5}$</td>
<td>3.44</td>
<td>VNKh-L-407</td>
</tr>
<tr>
<td>MP + BTA + BA</td>
<td>1-Morpholinomethyl-1-(phenyl)benzotriazole</td>
<td>5.584</td>
<td>0.23$\cdot 10^{-7}$</td>
<td>1.43</td>
<td>VNKh-L-408</td>
</tr>
</tbody>
</table>

$^a$ The experimental value is $2.95\cdot 10^{-3}$ at 20°C.

$^b$ The experimental value is $3\cdot 10^{-5}$ at 20°C.
Let us analyze and compare data on the commercial and new corrosion inhibitors. It follows from Tables 2 and 3 that

- BA derivatives are more hydrophobic and less volatile than FA derivatives;
- CHA derivatives are more hydrophobic than MP derivatives;
- products of complex condensation involving BTA are less hydrophobic and less volatile than the similar derivatives obtained from CHA + MP.

These trends are quite understandable and are due to the presence of hydrophilic fragments in the inhibitors (the O atom of morpholine and the group of three N atoms of benzotriazole) and to the molecular masses of the products.

In terms of volatility, the least promising inhibitors for “perfect” VIACs are VNKh-L-112 with \( P^0 = 12.2 \cdot 10^{-2} \) mmHg and VNKh-L-113 with \( P^0 = 8.9 \cdot 10^{-2} \) mmHg (Table 2) and BTA derivatives: VNKh-L-407 with \( P^0 = 0.15 \cdot 10^{-7} \) mmHg and VNKh-L-408 with \( P^0 = 0.23 \cdot 10^{-7} \) mmHg (Table 3). In terms of hydrophobicity, the least promising inhibitors are VNKh-L-112 with \( \pi = 0.52 \) and hydrophilic VNKh-L-406 with \( \pi = -0.15 \) (Table 2).

However, a high or, in contrast, low volatility of an inhibitor in combination with a low minimum protective concentration in water [9, 10] do not necessarily mean that an inhibitor should be rejected. Compound with high protective properties and high volatility can be used with due sealing for preservation of metallic parts, while compounds with low volatility can be used for extended storage time of preserved parts in a warehouse before transportation [13]. The high hydrophobicity of such low-volatile compounds as VNKh-L-408 and its analog VNKh-L-407 is worth noting (Table 3).

Molecular diagram calculations showed that the condensation of nitrogen-containing compounds with FA or BA considerably changes the electron densities on the heteroatoms (\( \Sigma q \)) for products of complex condensation, which is evident from comparison of data for MP, CHA, BTA, and the compounds obtained (Tables 2, 3). The changes are substantial for the adiabatic IPs of the “anchor” atoms and groups of atoms:

- morpholine: IP of \( n_a(N) = 8.3 \pm 0.1 \) eV; IP of \( n_a(O) = 9.6 \pm 0.1 \) eV; \( \Sigma q = 2.394 \);
- cyclohexylamine: IP of \( n_a(N) = 8.07 \pm 0.1 \) eV; \( q = 1.221 \);
- benzotriazole: IP of \( \pi(b_1) = 7.98 \pm 0.1 \) eV; IP of \( n_a(N) = 8.72 \pm 0.1 \) eV; \( \Sigma q = 3.209 \);
- dimorpholinomethane (VNKh-L-112): IP of \( n_a(N) = 8.0 \pm 0.1 \) eV; IP of \( n_a(O) = 9.4 \pm 0.1 \) eV;
- (dimorpholino)(phenyl)methane (VNKh-L-20): IP of \( n_a(N) = 7.65 \pm 0.1 \) eV; IP of \( n_a(O) = 9.4 \pm 0.1 \) eV; IP of \( \pi(b_1) = 8.8 \pm 0.1 \) eV;
- methylidene cyclohexylamine (VNKh-L-111): IP of \( n_a(N) = 8.99 \pm 0.1 \) eV; IP of \( \pi(C=N) = 9.35 \pm 0.1 \);
- benzyldene cyclohexylamine (VNKh-L-49): IP of \( \pi(b_1) = 8.34 \pm 0.1 \) eV; IP of \( n_a(N) = 9.1 \pm 0.1 \) eV; IP of \( \pi(C=N) = 10.0 \pm 0.1 \) eV;
1-morpholinomethyl-1-phenylbenzotriazole (VNKh-L-408): IP of π(b₁) = 7.5 ± 0.1 eV; IP of nₓ(N) = 8.1±0.1 eV; IP of nₓ(O) = 9.4±0.1 eV.

The first adiabatic IPs of the starting compounds and their assignments were taken from [24–26]. Kuznetsov obtained data on the IPs of the first four inhibitors and made their assignments [27]; data for 1-morpholinomethyl-1-phenylbenzotriazole were calculated with allowance for the current concepts of the influence of substituents on IP [25, 26].

The inhibition factors of commercial VIACs estimated in corrosion tests simulating the conditions of atmospheric corrosion are given in Table 4. The inhibitor concentrations were ~100 g/m³ of air.

Table 4. Inhibition factors of atmospheric corrosion of metals in the presence of commercial VIACs (the full chemical names of the compounds are listed in Tables 2 and 3). The concentration of the inhibitors is ~100 g/m³ of air; t = 20–40°C; humidity 98±2%. The test includes 15 cycles.

<table>
<thead>
<tr>
<th>Inhibitor trade name</th>
<th>Metal surface contains, in addition to Meₓ⁺ (from the Pourbaix diagram):</th>
<th>oxides + hydroxides</th>
<th>hydroxides</th>
<th>oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Steel St3</td>
<td>Copper M3</td>
<td>Zinc Ts1</td>
<td>Cadmium KD0</td>
</tr>
<tr>
<td>VNKh-L-111</td>
<td>220</td>
<td>75</td>
<td>corrosion</td>
<td>corrosion</td>
</tr>
<tr>
<td>VNKh-L-49</td>
<td>125</td>
<td>60</td>
<td>corrosion</td>
<td>4</td>
</tr>
<tr>
<td>VNKh-L-112</td>
<td>250</td>
<td>100</td>
<td>corrosion</td>
<td>corrosion</td>
</tr>
<tr>
<td>VNKh-L-20</td>
<td>250</td>
<td>60</td>
<td>corrosion</td>
<td>2.5</td>
</tr>
<tr>
<td>VNKh-L-408</td>
<td>125</td>
<td>150</td>
<td>3.9</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Let us consider the applicability of the above general approaches to estimation of the adsorptivity of compounds on metals and their protective properties from the first IPs and the electron work function of the metal. In terms of electron work function, the metals can be arranged in the order:

\[ \text{Mg} < \text{Cd} < \text{Al} < \text{Zn} < \text{Cu} < \text{Fe} \]  

(series 1)

Series (1) shows that the IP of a compound that well adsorbs on magnesium should be higher than the IP of another compound that adsorbs well on copper and iron. According to the data on the first adiabatic IPs of commercial inhibitors, the adsorptivity of VNKh-L-49 on magnesium should be the highest, while that of VNKh-L-408 should be the lowest. However, it follows from Table 4 that all the inhibitors but VNKh-L-408 promote magnesium corrosion.

In terms of the first IP, the metals can be arranged in the order:
Al < Mg < Cu < Fe < Cd < Zn  

(Series 2)

Series (2) shows that the IP of a compound that adsorbs well on cadmium and zinc should be lower that the IP of another compound that adsorbs well on aluminum. It follows from Table 4 that zinc and cadmium are protected by VNKh-L-408 only, while the compounds with higher IPs promote the corrosion of these metals. This approach is mostly not applicable to aluminum.

Moreover, the surface coverage and the Gibbs energy of adsorption even on the same metal (St3 steel) show no distinct correlation with the first IPs of commercial inhibitors of VNKh series [27]. Table 5 shows data taken from [27] that support this concept for the inhibitors in question.

Table 5. Surface coverage \( \theta \) for St3 steel (from capacitance measurements) and the Gibbs energy of adsorption from a mixed solvent (0.05 N NaCl + 0.05 N Na\(_2\)SO\(_4\)) in the presence of commercial inhibitors of the VNKh series.

<table>
<thead>
<tr>
<th>Inhibitor trade name</th>
<th>( \theta = 0.9 ) at concentration, mol/dm(^3)</th>
<th>Gibbs energy of adsorption, kJ/mol ( ^{a} )</th>
<th>First adiabatic IP, eV (with assignment)</th>
<th>( \gamma ) for St3 steel from Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNKh-L-49</td>
<td>( 1 \cdot 10^{-5} )</td>
<td>44.17</td>
<td>8.34 ( \pi(b_{1}) )</td>
<td>125</td>
</tr>
<tr>
<td>VNKh-L-20</td>
<td>( 1 \cdot 10^{-7} )</td>
<td>55.60</td>
<td>7.65 ( n_{s}(N) )</td>
<td>250</td>
</tr>
<tr>
<td>VNKh-L-112</td>
<td>( 2.5 \cdot 10^{-7} )</td>
<td>63.94</td>
<td>8.0 ( n_{s}(N) )</td>
<td>250</td>
</tr>
<tr>
<td>VNKh-L-111</td>
<td>( 5 \cdot 10^{-7} )</td>
<td>108.31</td>
<td>8.99 ( n_{s}(N) )</td>
<td>220</td>
</tr>
</tbody>
</table>

\( ^{a} \) From the Frumkin adsorption isotherm.

However, the Gibbs energies of adsorption of molecular inhibitors (Table 5) are substantially higher than those of commercial salt type inhibitors (NDA, G-2, etc. [1]) and are nearly five times higher than the Gibbs energy of adsorption of water on the oxidized iron surface, which suffices to displace water by adsorbed molecules of inhibitors. Because of this, these inhibitors are highly efficient.

Thus, the general approach to the estimation of the adsorptivity of compounds on metals and hence their inhibiting properties from the general electronic characteristics of compounds and metals (IP and electron work function) fails to provide an unambiguous prediction of the inhibitive effects of compounds on dissimilar metals.

Let us consider whether the adsorption and inhibitive effect of compounds can be predicted from the match of the “resonance” IPs of metals and metal oxides with the first adiabatic IPs of the compounds. Comparison of the “resonance” IPs of metals and metal oxides and the first adiabatic IPs of commercial inhibitors with different assignments shows that (provided that the adsorption and inhibitive effect are the same):
- VNKh-L-111 is expected to protect none of the metals in Table 4;
- VNKh-L-112 is expected to protect iron, copper, zinc, and aluminum (it can be adsorbed on iron, aluminum, copper oxide, and zinc oxide);
- VNKh-L-49 is expected to protect zinc and aluminum (it can be adsorbed on their oxides);
- VNKh-L-20 is expected to protect iron, copper, and cadmium (it can be adsorbed on iron, copper, and cadmium);
- VNKh-L-408 is expected to protect iron, copper, aluminum, and cadmium (it can be adsorbed on iron, copper, cadmium, and aluminum).

The protective effects of the inhibitors predicted from the first adiabatic IPs are in conflict with experimental data. Let us apply this approach taking not only the first adiabatic IP of a compound but also the adiabatic IPs of all the “anchor” atoms into consideration.

Table 6. Inhibition factors of atmospheric corrosion of St3 steel in the presence of commercial VIACs (from Table 4) and the Δ values (differences between the “resonance” IPs of iron and iron oxide and the adiabatic IPs of the “anchor” atoms in the structures of the inhibitors). For the designations of Δ, see text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>VNKh-L-408</th>
<th>VNKh-L-49</th>
<th>VNKh-L-111</th>
<th>VNKh-L-112</th>
<th>VNKh-L-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibition factors</td>
<td>125</td>
<td>125</td>
<td>220</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Δ₁</td>
<td>0.3</td>
<td>0.4</td>
<td>1.9</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Δ₂</td>
<td>0.1</td>
<td>0.4</td>
<td>0.5</td>
<td>1.5</td>
<td>1.85</td>
</tr>
<tr>
<td>Δ₃</td>
<td>2.2</td>
<td>1.5</td>
<td>–</td>
<td>–</td>
<td>2.2</td>
</tr>
<tr>
<td>Δ₄</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Δ₅</td>
<td>0.3</td>
<td>0.4</td>
<td>1.14</td>
<td>0.44</td>
<td>–</td>
</tr>
<tr>
<td>Δ₆</td>
<td>2</td>
<td>1.16</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
</tr>
<tr>
<td>Δ₇</td>
<td>–</td>
<td>2.8</td>
<td>2.1</td>
<td>2.15</td>
<td>1.45</td>
</tr>
<tr>
<td>Δ₈</td>
<td>–</td>
<td>0.5</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Data in Table 6 allow analyzing the protective effects of commercial inhibitors on iron (steel). The parameters taken into account include the adiabatic IPs of atoms and groups of atoms (nₓ(N), nₓ(O), π(b₁), π(C=N)) and the “resonance” IPs (RIPs) of iron (7.2 and 7.9 eV) and iron oxide (9.4–9.6 eV). Symbols Δ denote: Δ₁ = IP of nₓ(N) – RIP_{Fe}; Δ₂ =
IP of $n_d(N) - RIP_{ox}; \Delta_3 = IP of n_d(O) - RIP_{Fe}; \Delta_4 = IP of n_d(O) - RIP_{ox}; \Delta_5 = IP of \pi(b_1) - RIP_{Fe}; \Delta_6 = IP of \pi(b_1) - RIP_{ox}; \Delta_7 = IP of \pi(C=N) - RIP_{Fe}; \Delta_8 = IP of \pi(C=N) - RIP_{ox}$.

Table 6 contains two $\Delta$ values related to the RIP of iron (7.2 and 7.9 eV). For the RIP of iron oxide, we used an average of 9.5 eV for calculations.

Based on the data in Table 6, one can assume that the inhibitive effect is determined by the following factors:

- mostly adsorption of the unpaired electrons of the N atoms and the $\pi$-electrons of the C=N group on iron oxides (for VNKh-L-111 and VNKh-L-49); to some extent, also adsorption of the ring $\pi$-electrons on iron (for VNKh-L-49);
- mostly adsorption of the unpaired electrons of the N atoms at iron (for VNKh-L-112 and VNKh-L-20) and adsorption of oxygen and ring $\pi$-electrons on iron oxides (VNKh-L-20);
- mostly adsorption of the unpaired electrons of the N atoms on both iron and iron oxides (for VNKh-L-408) and adsorption of oxygen and ring $\pi$-electrons on iron.

A similar analysis of the protective effects of the inhibitors on copper suggests predominant formation of adsorption bonds between the heteroatoms of the inhibitors and copper oxides. The most efficient inhibitor of copper corrosion, VNKh-L-408 ($\gamma = 150$), which seems to be adsorbed (through its heteroatoms) on non-oxidized sites of copper as well, is an exception.

All the inhibitors (except for VNKh-L-408) promote the corrosion of zinc (Table 4). Apparently, this is due to the fact that the IPs of the “anchor” atoms of the inhibitors are close to the “resonance” potential of metallic zinc (rather than zinc oxide): strong adsorption bonds with metal sites on the zinc surface cause corrosion stimulation rather than inhibition. An exception is shown by VNKh-L-408, whose structure contains two adsorption sites with IPs close to the “resonance” IP of oxidized zinc (the $\pi$-electrons and three N atoms of the ring).

Cadmium is similar to zinc in all characteristics and hence its protection by inhibitors is also difficult. The inhibitive effect of VNKh-L-408 is probably due to adsorption of the $\pi$-electrons on non-oxidized sites of metallic cadmium areas and to adsorption of the unpaired electrons of oxygen on cadmium oxide areas. The weaker protective effects of VNKh-L-49 and VNKh-L-20 may be due to possible participation of only the unpaired electrons of nitrogen and the $\pi$-electrons of the C=N group in the adsorption bond with oxidized areas (VNKh-L-49) or to the adsorption bond of nitrogen with metallic cadmium (VNKh-L-20). The failure of the VNKh-L-111 and VNKh-L-112 inhibitors to protect cadmium cannot be explained only by possible formation of adsorption bonds between the “anchor” atoms and the metal and calls for other hypotheses.

Protection of aluminum by inhibitors is complicated by the catalytic properties of aluminum oxide bearing active sites where many adsorbed molecules undergo complex transformations. Aluminum oxide is surface-active and can react with electron-donating
molecules, which all the compounds in question belong to. Active aprotic sites at its surface can act as Lewis acids and are highly electronegative, which is evident from data on the adsorption of ammonia, pyridine, methylamine, diethylenetriamine, and other nitrogen-containing compounds on Al₂O₃ [28].

Of the compounds studied, aluminum can be protected only by VNKh-L-49 and VNKh-L-408. Apparently, this is due to possible adsorption of VNKh-L-408 on both the non-oxidized metal surface and aluminum oxide through the unpaired electrons of the N atoms and the ring π-electrons. In terms of this concept, it remains unclear why VNKh-L-112 and VNKh-L-20 promote rather than inhibit the corrosion of aluminum: for VNKh-L-112, the IP of n₄(N) is exactly the same as the RIP of aluminum oxide; for VNKh-L-20, the IP of n₄(N) is close to the RIP of the aluminum metal and its oxide. A similar pattern of the corrosive and inhibitive behavior of the compounds under study is true for magnesium, which is not surprising for the electronic and other characteristics of these metals are similar.

Thus, there is no distinct correlation between the inhibitive efficiency of VIAC (atmospheric corrosion inhibition coefficients) and the difference (low or high) between the “resonance” IP of a metal (metal oxide) and the first adiabatic IP of a compound.

We believe that data on the relations between the “resonance” potentials, the first adiabatic IPs, and the IPs of the “anchor” atoms in a molecule can be used only to predict possible forms of adsorption bonds between a molecule and a metal and to explain facts of the reverse phenomenon, namely, corrosion stimulation.

Now let us consider the results from another point of view. According to the concept adopted by many researchers, surfactant–metal interactions should be analyzed with allowance for the substantial role of water molecules capable of adsorbing on a metal in two ways: Me – OH₂ (here the metal atom acts as an acceptor of the lone electron pair of the O atom in the water molecule) and Me – H–O–H. Accordingly, the adsorption of an inhibitor on a metal surface covered with a water film follows the electron-donating or proton-donating mechanism. Electron-donating surfactants displace water adsorbed by to the former type. Proton-donating surfactants can either add to water or displace it from the metal surface. Thus, the surface activity of corrosion inhibitors under these conditions is determined by both the electron density on the heteroatoms and the presence of active H atoms in their structures.

Therefore, one can assume that compounds containing an acidic H atom would be better inhibitors. The predicted protective ability of VNKh-L inhibitors with similar structures is as follows:

- VNKh-L-113 is superior to VNKh-L-112;
- VNKh-L-405 is superior to VNKh-L-406;
- VNKh-L-21 is superior to VNKh-L-20;
• VNKh-L-407 is superior to VNKh-L-408.

Thus, the principal molecular characteristics of products obtained by complex condensation of nitrogen-containing compounds with aldehydes give grounds to predict their high inhibitive efficiency as VIACs.

Conclusions

1. Physical and chemical aspects of selection of the starting reagents and synthetic routes for the preparation of volatile inhibitors of atmospheric corrosion (VIACs) of ferrous and nonferrous metals were discussed for Schiff and Mannich bases as examples. Relationships between the physicochemical and electronic characteristics of various metals and the molecular parameters of inhibitors that allow prediction of their efficiency were considered.

2. The general approach to estimation of the adsorptivity of compounds on metals and, consequently, their inhibitive properties from the general electronic characteristics of the compound and the metal (ionization potential and electron work function) does not allow an unambiguous prediction of the inhibitive effects of compounds toward various metals.

3. Estimation of the inhibitive effect based on the match between the first adiabatic potentials of compounds and “resonance” potentials of metals and metal oxides can be used only to predict possible forms of adsorption bonds between a compound and a metal and to explain facts of the reverse phenomenon, namely, simulation of corrosion of ferrous and nonferrous metals.

4. Thermally stable molecular compounds like Schiff and Mannich bases were shown to be promising volatile inhibitors of atmospheric corrosion of ferrous and nonferrous metals.

5. The main physicochemical parameters that characterize VIACs, commercial inhibitors of the VNKh-L series, and new inhibitors obtained by complex condensation of nitrogen-containing compounds with aldehydes were determined.

6. The main molecular characteristics of the compounds obtained by complex condensation of nitrogen-containing compounds with aldehydes provide the basis for prediction of their high inhibitive efficiency as VIACs.

References


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