Volatile Inhibitors of Metal Corrosion. I. Vaporization

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Abstract

This paper presents an analytical review of data on the interaction of volatile corrosion inhibitors with the atmosphere, vaporization processes, methods of experimental and computational estimation of the vapor pressure of organic compounds, and effects of vaporization conditions and compound structure on vapor pressure.

Introduction

It is difficult to determine when volatile corrosion inhibitors (VCIs) were first used in practice. Though O. I. Golyanitsky [1] refers this event to the WWII period, the ability of camphor to protect a metal in vapor phase was already well known before that [2]. Furthermore, attempts to use ammonia and volatile lower amines in the power industry [3,4] were made even in the 20s–30s of the XX century.

The facility and efficiency of metal protection by VCIs attracted the attention of researches back in the 1950s when the number of studies dealing with VCIs increased like an avalanche. Analysis of these studies allowed O. I. Golyanitsky to express the essence of vapor-phase inhibition as follows: "A volatile corrosion inhibitor exposed to the atmosphere starts to evaporate and its vapors are transferred to a metal surface by diffusion or convection. Here adsorption or condensation of inhibitor and atmospheric water vapors occurs to form a film of an aqueous solution of the inhibitor on the metal surface, which passivates the metal" [1]. Based on this scheme, let us review the main stages of VCI action.

VCI interaction with the atmosphere

The interaction of a VCI with the atmosphere comprises two processes: *i*, partial absorption of some atmosphere components by the VCI; *ii*, saturation of the atmosphere by VCI vapors or by vapors of compounds formed upon chemical conversion of the original compound [1, 5, 6].

Introduction of a VCI into the volume being protected is usually accompanied by absorption drying or adsorption drying of the atmosphere, depending on the aggregate state

of the inhibitor. Water vapors are dissolved in the inhibitor or adsorbed on its surface to give solutions that absorb atmospheric moisture until its residual vapor pressure in the system (p) becomes equal to that above the solution. The air drying can improve the corrosion resistance of metals and, according to Golyanitsky [1], can even play a decisive role in corrosion prevention.
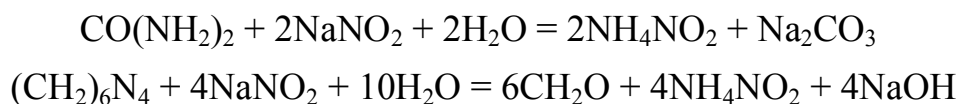
However, the latter statement is debatable, at least for solid VCIs. A simple calculation confirmed by experimental measurements suggests that air moisture does not decrease to a considerable extent upon formation of saturated solutions of salt type inhibitors, such as cyclohexylammonium carbonate, dicyclohexylammonium nitrite, *etc*. [7]. References to the surface activity of VCIs, which according to [1] favors a considerable increase in inhibitor concentration (C_{inh}) at the interface with air and decreases multi-tenfold the water vapor pressure (p) above it are hardly valid from the theoretical point of view. It is known that the vapor composition is determined by the bulk liquid phase rather than by its boundary layer. Conversely, this layer is a result of interaction between coexisting bulk phases.

Still, the drying effect of VCIs is an important co-factor in the vapor-phase protection of sealed volumes. It is favored by a high solubility (C_{sat}) and ability of a compound to undergo electrolytic dissociation that additionally reduces the molar fraction of water in solutions [8].

Many VCIs can absorb not only moisture but also other corrosive components of the medium, such as sulfur dioxide, carbon dioxide, hydrogen sulfide, hydrochloric acid vapors, and sometimes oxygen, thus diminishing the atmosphere corrosivity. The ability of amines to bind acidic gases is widely used in technology, while hydrazine and its derivatives are well known as oxygen scavengers [9]. Removal of these compounds from the atmosphere increases the critical level of atmospheric moisture below which metal protection is ensured [5]. Apparently, the majority of VCIs are inferior in terms of water and gas absorption to the usual technical agents used for this purpose. The factors listed above are important but do not determine the main VCI properties.

Vaporization processes

The ability to form vapors, *i.e.*, undergo evaporation or sublimation, commonly referred to as volatility, is a characteristic property of VCIs. It can quantitatively be expressed by saturated vapor pressure (p^0). It is well known that inhibitors with $p^0 > 10^{-5}$ mmHg (10^{-6} mmHg according to some data) can be used as VCIs [5, 10]. The required volatility can be provided by the compound itself or by its hydrolysis products. For example, the ability of nitrite-carbamide or nitrite-hexamethylenetetramine mixtures to provide vapor-phase protection is due to the formation of volatile ammonium nitrite in reactions with water [11, 12]:

$$CO(NH_2)_2 + 2NaNO_2 + 2H_2O = 2NH_4NO_2 + Na_2CO_3$$

$$(CH_2)_6N_4 + 4NaNO_2 + 10H_2O = 6CH_2O + 4NH_4NO_2 + 4NaOH$$

The vaporization of individual organic compounds containing no ionic bonds is usually accompanied by the transfer of their molecules to the gas phase. The sublimation mechanism of salt-type VCIs is more complex. There is no common point of view about it in the literature.

The vaporization processes of cyclohexylammonium carbonate were studied most thoroughly. Based on the understanding of the molecular structure of the crystals of this compound, it is stated [13] that the inhibitor is vaporized without decomposition. Conversely, other researchers [10, 14, 15] believe that its vapors mainly comprising cyclohexylamine and carbon dioxide are formed upon hydrolytic or thermal dissociation of the salt.

Considerable attention was paid in the literature to the sublimation mechanism and vapor composition of nitrites formed by various amines, dicyclohexylammonium nitrite in particular. However, the opinions of different researchers on this subject differ as well. Rozenfel'd and Persiantseva [5] came to the conclusion that a cyclic molecular complex of the amine and nitrous acid exists in its vapors. Presumably, it is either formed in the vapors upon sublimation of VCI crystal lattice ions or, more likely, it determines the structure of the crystal itself. An opposite conclusion that dicyclohexylammonium nitrite dissociates upon vaporization to give equivalent amounts of the amine and nitrous acid was made elsewhere [10, 15].

The vaporization mechanisms of amine benzoates and nitrobenzoates have been studied less thoroughly. In this case, it is also assumed [5] that the major role in this process belongs to molecular complexes "amine – carboxylic acid". However, their conclusions again rely on analytical deduction to a larger extent than on experimental facts.

The concept of dissociative vaporization of onium salts based on experimental studies seems more reasonable. However, certain facts that somewhat contradict this concept should also be mentioned. The most serious objections are drawn by the point that the vapors of these compounds consist of equivalent amounts of the corresponding acid and base. As an example, let us look at ammonium benzoate with $p^0 = 0.1$ mmHg at 20°C [16]. According to the conclusions made in [10, 15], the p of benzoic acid over this compound should be 0.05 mmHg, *i.e.*, almost two orders higher than its p^0 (0.0007 mmHg), which is impossible. However, if the possibility of non-stoichiometric acid : base ratio over the salt is assumed, the considerable differences in the p^0 values of onium-type VCIs reported in the literature, which sometimes reach several orders, become possible. They are usually attributed to the imperfection of measurement methods or to impurities, but these differences may also be due to the history of VCI specimens, *i.e.*, duration of storage in open air or evacuation during which a fraction of the more volatile component escapes and the total p of the compound decreases.

This assumption is confirmed by the results [17] that vapors of a broad range of onium salts consist of non-associated acids and bases whose p values may be nonequivalent and differ by several order, depending on the VCI nature. In fact, vapors of ammonium benzoate consist almost totally of ammonia (0.17 mmHg), whereas the p value

of benzoic acid is negligibly small in comparison ($2 \cdot 10^{-8}$ mmHg). A similar situation characterizes hexamethyleneiminium *m*-nitrobenzoate and diethylammonium *m*-nitrobenzoate. Conversely, the vapors of cyclohexylammonium benzoate and caprylate and monoetahnolammonium benzoate are enriched in the respective acids.

Effect of external conditions on the volatility of organic compounds

The volatility of VCIs changes upon interaction with the atmosphere. The absorption of moisture by a compound favors vaporization if hydrolysis of the inhibitor components produces volatile compounds. In other cases, the *p* value of a VCI decreases upon water absorption by the VCI. Normally, these processes are not considered in studies on vapor-phase protection of metals, but their mechanisms are determined by general physical chemistry laws. Based on [8, 18], it can be stated that the kinetics of this decrease depends on the mutual solubility of water and the VCI.

It occurs to the smallest extent with VCIs that are poorly water-soluble and incapable of dissolving water, *e.g.*, solid salt inhibitors. In fact, the *p* value of a VCI over the inhibitor itself is equal to the *p* over the saturated solution formed on its surface [18]. Therefore, a decrease in the volatility of such compounds can only be expected after they have absorbed an amount of water sufficient to dissolve the entire amount of the inhibitor.

The first period of exposure to a humid atmosphere of VCIs which are characterized by a limited solubility in water and a limited solubility of water in the respective inhibitor is accompanied by a decrease in volatility. This period is completed after the formation of a two-phase system "saturated solution of water in the inhibitor – saturated solution of the inhibitor in water". Further absorption of water will change the volume ratio of these phases, until one of them disappears. Only then a new decrease in the *p* of the VCI in the system is possible. The strongest and continuous volatility decrease can be expected for VCIs which are miscible in water in any ratios.

The aggregate state and mutual solubility of the inhibitor and products of its reactions with atmospheric acidic gases also affect the volatility of organic bases, *e.g.*, amines. However, the *p* value of the acidic component is more important, at least from practical point of view.

Temperature (*T*) is the most important factor that affects the volatility of compounds. The effect of temperature is determined by the Clausius – Clapeyron equation:

$$\ln p^0 = -\Delta H_{vap}^0 / RT + \Delta S_{vap}^0 / R = -\Delta G_{vap}^0 / RT , \qquad (1)$$

where $\Delta H^0{}_{vap}$ and $\Delta S^0{}_{vap}$ are the standard enthalpy and entropy of vaporization (evaporation or sublimation), respectively [8]. The linearity of $\ln p^0 - 1/T$ plots is determined by the weak dependences of ΔH_{vap} and ΔS_{vap} on *T* and is observed in rather a broad *T* range above or below the melting point of a compound (Fig. 1). The difference in the thermodynamic characteristics of vaporization of liquid and solid compounds determines the presence of an inflexion point on the plot.
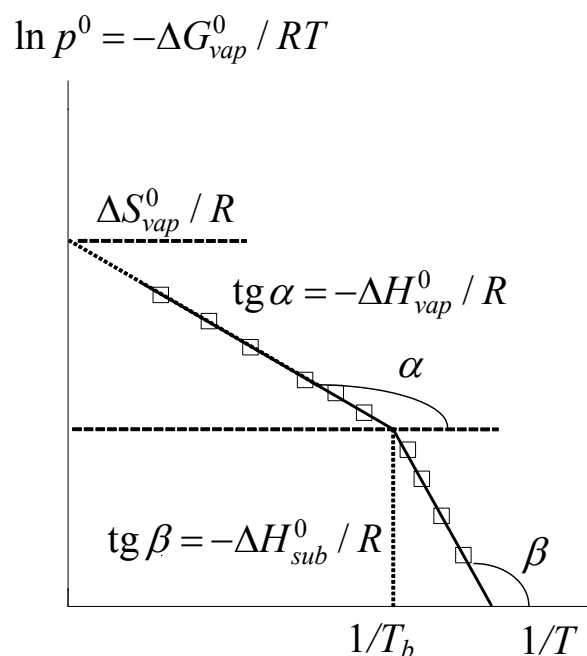
$$\ln p^0 = -\Delta G^0_{vap} / RT$$

Fig. 1. Dependence of $\ln p^0$ of compounds on $1/T$ [21].

A more accurate description of the effect of T on the p^0 of compounds is provided by empirical relationships, among which the Antoine equation is most popular:

$$\log p^0 = a + b/(c + T) \qquad (2)$$

However, the clear physicochemical meaning of the main parameters in equation (1) along with the high precision of experimental data description resulted in its predominance in the development and study of VCIs. Equation (1) is widely used [1, 5, 18, 19] to assess the p^0 of a VCI at a particular temperature needed to the researcher and to calculate the thermodynamic characteristics of vaporization.

Methods for the measurement and indirect assessment of p^0

A number of experimental methods have been developed for p^0 measurement; the most comprehensive description of these is presented in [5]. The methods are classified into static, dynamic, methods of evaporation from open surface, "boiling point" methods, and their modifications [20]. Static methods are based on direct manometric or indirect measurements of the physicochemical parameters of the gas phase related to the p^0 of the compound. Dynamic methods employ the transfer of the vapor by a stream of a gas that is inert with respect to the compound being analyzed. The p^0 of a compound is determined from compound mass (m) changes in a saturator or a condenser. The method of evaporation from an open surface involves the measurement of the evaporation or sublimation rate of a compound under atmospheric conditions or *in vacuo*. The m of a sample of the compound of interest, the reactive force of the stream of its vapors, or other

characteristics directly related to the p^0 can serve as the measurable parameter. In the measurement of p^0 by the "boiling point" method, the boiling temperature or pressure (P) of the compound are recorded when its p equals the external P.

All these methods used to assess the p^0 of VCIs in [5, 15, 21, 22] are laborious, require special equipment, and are not always accurate. This fact hindered the development of new VCIs and resulted in the propagation of simplified corrosion methods for estimation of the capability of compounds to provide vapor-phase protection.

The development of this empirical approach diverted researchers from simple, albeit not very accurate, approaches for approximate estimation of p^0 of organic compounds based on their boiling points (T_b; hereinafter, the subscript "b" denotes "boiling"). The use of such methods for VCIs is never even mentioned in the literature.

Meanwhile, these methods are quite popular in chemistry. They are based on Trouton's rule concerning the equality of $\Delta H_b/T_b$ of various chemical compounds, *i.e.*, the constancy of ΔS_b values. In graphical interpretation (Fig. 1), it means that straight lines ln $p^0 - 1/T$ for various compounds extrapolated to the infinitely high T region will intersect the Y axis in the same point. In order to reproduce the entire temperature dependence of p^0 up to the melting point (T_m), it is sufficient to know the p^0 value at some T or the T_b value at an arbitrary P. This method expressed as equations or nomograms [23, 24] is used in organic chemistry to estimate the T_b of organic compounds in the case of vacuum distillation, but it can also be used to estimate the p^0 of liquid compounds in a broad temperature range. It has to be admitted that this method is not very accurate even for weakly associated liquids. Furthermore, the ΔS_b values for polar compounds liable to form hydrogen bonds often differ considerably from the values specified by Trouton (20–21 cal/(mol K)) [8]. Yet the use of this method for the primary estimation of inhibitor suitability for vapor-phase protection would allow one to avoid laborious measurements in many cases.

The "chemical similarity method" that uses the parameters of the ln $p^0 - 1/T$ plot of a reference compound to calculate the p^0 of a compound of interest [25] has a better accuracy. It is easy to show that, if the ΔS_b values of both compounds are equal, the following equation is valid:

$$\ln p_x^0 = \frac{\Delta H_{b,r} T_{b,x}}{RT \cdot T_{b,r}} + \Delta S_{b,r} / R \qquad (3)$$

where the "x" and "r" indices refer to the compound in question and the reference compound; this equation allows one to estimate the volatility of inhibitors with a known T_b. Apparently, the above errors level off if a reference compound with a structure similar to that of the compound of interest is used.

Effect of the chemical structure of organic compounds on p^0

The methods for the estimation of liquid VCIs described above are applicable to compounds with known T_b values. This method does not allow one to predict the

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expediency of synthesizing a new compound as the basis for creating a VCI. It can only be done based on studies on the effect of the structure of organic compounds on their volatility.

The effect of the inhibitor chemical structure on volatility was apparently first studied by Rozenfel'd *et al.* [5]. They noted that p^0 decreased with an increase in molecular mass (*M*) of amines in their salts with acids. The nearly linear plots in the coordinates $\log p^0 - M$ involved a considerable number of deviating points, while the slopes of the plots were different for nitrites, benzoates, and nitrobenzoates. The deviations, that were considerable for some compounds, were attributed to changes in the VCI dipole moment. Furthermore, the changes in $\log p^0$ values resulting from changes in the nature of the amine were observed to vary linearly with $1/T_b$.

These empirical relationships with a somewhat vague physicochemical meaning provided a very limited option of synthesizing VCIs with required p^0. On the other hand, the regularities of the effect of the chemical structure of organic compounds on some thermodynamic parameters of compounds were reported in the literature, which opens better prospects for direct search and modification of the structures of liquid organic VCIs. Let us review these regularities in more detail.

The first one is based on the postulate on the additivity of the contributions of structural moieties forming a molecule to the ΔH^0_{vap} of the compound. Lebedev and Miroshnichenko [26] summarized a vast amount of experimental data and calculated averaged ΔH^0_{vap} attributable to various atom groups. This allows one to calculate the slopes of $\ln p^0 - 1/T$ plots and, provided that the coordinates of at least one point are available, reproduce the entire plot for $T > T_m$. Data on the T_b of a compound at a randomly selected pressure can be used as the reference point; however, this method is only applicable for estimating the volatility of already known compounds. Yet another option involves the restoration of the entire plot based on the slope and the Y axis intercept, *i.e.*, the ΔS^0_{vap} in Trouton's approximation. This version of the method allows one to estimate the volatility of liquid organic compounds based on their structural formula, though with low accuracy. The main sources of errors include the assumption about the constancy of ΔS^0_{vap}, the inaccuracy of calculation of fragment contributions, and the deviations from additivity noted by the same researchers [26].

Yet another semiempirical method for the estimation of the volatility of organic compounds is also based on the hypothesis on the additivity of group contributions to the ΔG^0_{vap} value. Abramzon [27] analyzed the effect of the number of C–H bonds in the aliphatic chain in compounds of various classes on ΔG^0_{vap} and found that a similar extension of the radical results in similar changes in this parameter and the related p^0 value. This allowed the volatility of simplest organic compounds to be estimated. A similar calculation of p^0 for complex compounds, primarily polar ones, involves considerable errors. For example, the contribution of the C–H bond to the ΔG^0_{vap} of nitriles and aliphatic acids differs almost 1.5-fold, which does not support the authors' hypothesis but indicates

proportional changes in ΔG^0_{vap} due to changes in the hydrocarbon chain length in different classes of compounds. This proportionality might be due to a manifestation of the Linear Free Energy (LFE) principle [28].

A series of our papers deals with a verification of this hypothesis and creation of methods for quantitative estimation of p^0 for organic VCIs [29–31]. In these papers we introduced a new scale of structural characteristics of a substituent, *viz.*, the ξ_R volatility constants, which were calculated from data on p^0 at 293 K for liquid monosubstituted benzenes taken as the standard series:

$$\xi_R = \log p^{0,R} - \log p^{0,H} \tag{4}$$

where indices "R" and "H" refer to substituted and unsubstituted compounds, respectively, and proved that $\log p^0$ changes linearly for various classes of compounds as the substituent (*R*) is varied. This allowed us to estimate the p^0 of liquid organic VCIs based on their formula and the available correlation parameters:

$$\log p^{0,R} = \alpha + \kappa \xi_R, \tag{5}$$

where $\alpha = \log p^{0,H}$ and κ is a constant that characterizes the series being analyzed. It is essential that the ξ_R scale that has been elaborated is versatile and can be used both for aromatic and aliphatic or alicyclic compounds, including polysubstituted ones. It has been found that the contributions of spatially separated *R* substituents in such compounds are independent and additive:

$$\log p^{0,R_1,R_2} = \alpha + \kappa \Sigma \xi_R. \tag{6}$$

Studies on this subject resulted in a well-developed system for the prediction and directed modification of volatility of liquid organic corrosion inhibitors. In fact, it has been shown that the manifestation of the LFE principle in the vaporization process results from the so-called isoentropicity, *i.e.*, constancy of ΔS^0_{vap} for series of related compounds. This approximation, which is much more accurate than Trouton's rule, allowed a quantitative *a priori* assessment of the volatility of organic compounds in a broad range of temperatures exceeding T_b to be carried out by correlation methods:

$$\log p^{0,R}_{(T)} = A_1 + B_1/T + C_1 \xi_R + D_1 \xi_R/T, \tag{7}$$

where A_1, B_1, C_1 and D_1 are constants. It is essential that the reference correlation relationships of this type can be derived from data on the boiling points of organic compounds under vacuum distillation conditions that are widely available in handbooks.

In the absence of data for direct calculation of p^0, the procedure elaborated for p^0 prediction combined with methods for restoration of reference functions of types (5–7) often exceeds the requirements for VCI development by providing the option of screening compounds that would show little promise prior to the synthesis. However, LFE-related methods are unsuitable for salt compounds that constitute nearly the most promising class of VCIs for atmospheric corrosion.

Some potential for the quantitative assessment of their volatility is given by the results reported in [17]. The authors analyzed the system "salt of a weak acid and a weak base – its saturated aqueous solution – vapor" and concluded that it is possible to compute the pressure and composition of saturated vapors of salt-type VCIs that do not undergo irreversible reactions with water. Such computations are based on the solubilities of the salt and its parent acid and base, as well as their p^0 and pK_a values.

Conclusions

1. The vaporization of VCIs upon interaction with the atmosphere is an important stage in the vapor-phase protection of metals. Its mechanisms as well as the composition and vapor pressure of a VCI depend on the inhibitor nature and on external conditions.
2. Beside direct measurements, the saturated vapor pressure of inhibitors can be estimated by computational methods. The use of methods based on the LFE principle ensures the most accurate *a priori* estimation of the volatility of individual liquid organic compounds under various conditions and provides the opportunity of direct modification of the inhibitor structures in order to make them capable of vapor-phase protection of metals.

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