



Estimating the gas permeability of commercial volatile corrosion inhibitors at elevated temperatures with thermo-gravimetry

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Abstract

Volatile corrosion inhibitors (VCIs) are incorporated into packaging paper or film to protect metals against atmospheric corrosion. The vapour pressure determines the equilibrium concentration of a volatile corrosion inhibitor (VCI) in the surrounding atmosphere. However, the rate at which the VCI can be delivered across the air gap to a metal surface is determined by the gas permeability. This is the product of the vapour pressure and the diffusion coefficient: $S_A = P_A D_{AB}$. The gas permeability of commercial VCIs was estimated at elevated temperatures from vaporisation rates measured using a simple thermo-gravimetric method (TG).

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Nomenclature

C	concentration, mol/m ³
D	diffusion coefficient, m ² /s
M	molar mass, kg/mol
m	sample mass, kg
N	molar flux, mol/(m ² s)
P	vapour pressure, Pa
R	universal gas constant, J/mol K
S	permeability, Pa m ² /s
T	temperature, K
t	time, s
z	diffusion path length, m

Subscripts

A	sample compound A (corrosion inhibitor)
B	gas

1. Introduction

Atmospheric corrosion is caused by the oxygen and moisture in air. It is aggravated by the presence of corrosive gases and adventitious impurities, e.g. pollutants, dust and acidic compounds. The following strategies are available for the protection of metal surfaces against the corrosive effects of the atmosphere during storage or transit [1]:

- (i) *Drying agents*. Good protection requires reducing the relative humidity of the surrounding air. Below a critical humidity, approximately 40–50% RH for most common metals, corrosion rates drop to very low values [2]. Drying adsorbents such as silica gel or zeolites can reduce humidity to the required levels.
- (ii) *Inert atmospheres*. Use of nitrogen atmospheres reduces corrosion owing to the decrease or absence of oxygen. This is not a common strategy because as little as 3% oxygen in the gaseous environment can cause corrosion [3]. However, active packaging systems that prevent the transmission of moisture and/or corrosive gases such as H₂S and SO₂ are finding increasing application.
- (iii) *Protective coatings*. Water displacing surface coatings based on oils, waxes or lacquers, may be used. However, the need for a subsequent removal process poses problems of inconvenience and waste disposal.
- (iv) *Volatile corrosion inhibitors (VCIs)*. Corrosion inhibitors are substances which, when added to corrosive environments in relatively small dosages, will drastically reduce corrosion rates. Vapour phase corrosion inhibitors or VCIs, also labelled vapour phase inhibitors (VPIs), are similar to the organic

adsorption-type inhibitors. Owing to a relatively high vapour pressure, they can be used to inhibit atmospheric corrosion of metals without coming into direct contact with the metal surface.

VCI sources are placed in the vicinity of the metal to be protected. In current commercial practice VCIs are incorporated in the paper or plastic film packaging used to wrap or encapsulate parts [4]. The active is transferred to the metal surface to be protected by a diffusion process. The protection mechanism may involve a combination of passivating the surface and rendering it hydrophobic [3].

Protection of metal containing components with VCIs is an elegant solution to the problem of atmospheric corrosion. The technical simplicity of a “once only” low dosage application, combined with the fact that humidity need not be controlled and that other materials of construction are usually not affected, has definite advantages. Suitable barrier materials are required to prevent loss of inhibitor to the outside atmosphere.

A wide range of chemical compounds has been proposed as VCI corrosion inhibitors [2,4–9]. Commercially, the most commonly used inhibitors are either salts of moderately strong, volatile organic bases with weak volatile acids, or complex organic nitrogen compounds, e.g. tolyltriazole [5,6].

The VCI compound present on the surface of the packaging film reaches the metal surface via a series of steps: evaporation (or sublimation), diffusion and adsorption. The VCI should be sufficiently volatile to ensure rapid protection of the metal surfaces. However, too high a volatility may lead to premature loss of inhibitor. In some instances it may be desirable to combine VCIs with different volatilities to achieve a combination of rapid and long-term protection [5,9]. Previous investigators have used the vapour pressure as a measure of a VCIs volatility [4]. According to Rozenfeld [2] the vapour pressure should be in the range of 0.002–1 Pa at 20 °C.

The air that surrounds the metal part to be protected acts as a secondary reservoir for VCI molecules. In fact, if ideal gas behaviour can be assumed, the equilibrium concentration is given by

$$C_A = P_A/RT \quad (1)$$

It is therefore of interest to know the vapour pressure of VCIs at application temperatures. Price and Hawkins [10] and others [11–16] have proposed thermo-gravimetric (TG) methods for estimating the volatility or the vapour pressure of compounds such as UV absorbers and dyes. Compared to conventional measurement techniques, the TG method utilizes a simple experimental set-up. It also allows rapid and convenient estimation using relatively small amounts of substance. Since VCIs are effective over a broad range of vapour pressures, the lower accuracy of the TG method is tolerable.

The purpose of this investigation is to explore the effects of operating variables, such as scan rate, sample size and purge gas flow rate on the performance of the TG method and to obtain estimates for the volatility of some commercial VCIs.

2. Theory

Consider the situation where a metal surface needs to be protected with a VCI source present as a surface layer on plastic packaging film. The simplest geometry consists of two parallel sheets separated by an air gap of thickness z . The following simplifying assumptions make the problem mathematically tractable: All the vapours behave as ideal gases. The partial pressure of the VCI (compound A) in the air (gas B) follows Raoult's law. The concentration of A assumes a constant value at the sample surface that equals the equilibrium concentration at the prevailing temperature and pressure as defined by Eq. (1). All relevant physical properties, e.g. the diffusion coefficient, D_{AB} , are concentration independent. The gas layer is quiescent, that is, convective transport owing to bulk motion of the gas is neglected. With this assumption the rate of mass transport is limited by diffusion across the gas layer. The highest rate of mass transfer is obtained under steady state conditions when the concentration of VCI near the metal surface approaches zero. This applies during the early stages of metal surface protection when irreversible adsorption of the VCI on the metal surface takes place. The steady state solution of Eq. (3), as applied to this problem, yields a linear concentration profile. At isothermal conditions the steady state flux is given by [15,16]

$$N_A = \frac{P_A D_{AB}}{zRT} \quad (2)$$

The same equation applies to the situation where the compound evaporates out of a TG sample cup [15,16]. Such an experimental set-up is illustrated schematically in Fig. 1. The sample cup shape is idealised as a cylindrical tube. The cup is partially

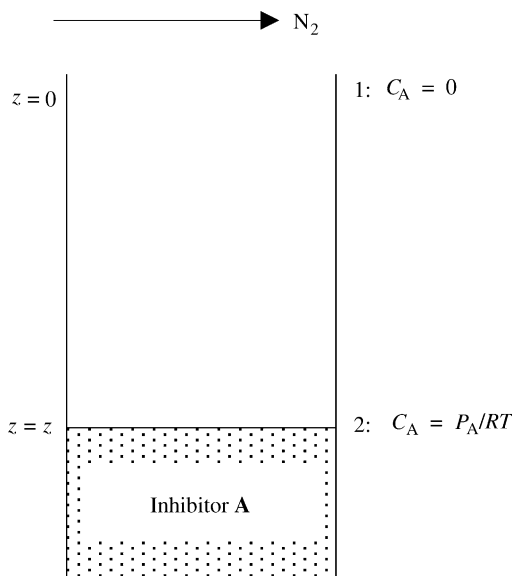


Fig. 1. Schematic of the experimental set-up.

filled with the sample liquid (or compressed solid) A. Inert gas B (e.g. air or nitrogen) flows rapidly across the open end of the tube, sweeping away any molecules of A emerging from the cup. This causes the concentration of vapour A to approach zero at the top of the cup. Consequently, the mass transfer in this system also corresponds to one-dimensional diffusion through a stagnant gas layer and Eq. (2) applies. Since the concentration of the sample compound in the gas phase is very low, the gas permeability is connected to the mass loss rate as follows:

$$S_{AB} \equiv P_A D_{AB} = \frac{zRT}{M_A A} \frac{dm_A}{dt} \quad (3)$$

Strictly speaking, Eq. (3) is only valid for isothermal–isobaric conditions. However, Price and Hawkins [10] found that the mass loss rates measured at low scan rates of approximately 1 °C/min were similar to those measured under isothermal conditions. Pieterse and Focke [16] used an approximate analysis and found that the equilibration time for shallow pans is very fast and that mass loss measurements obtained under dynamic conditions can provide pseudo-steady state mass loss values even when scan rates of 20 °C/min are used.

3. Experimental

Samples of commercial copper VCIs, i.e. benzotriazole and tolyltriazole (actually a mixture of 4- and 5-methyl benzotriazole) were obtained from Bayer. Three novel liquid VCIs, suitable for protecting mild steel, were supplied by the CSIR.

For comparison purposes the evaporation rates of pure naphthalene, vanillin and dibutyl phthalate were also determined. Following the recommendation of Van der Linde et al. [17], naphthalene was chosen as primary reference substance. It is thermally stable and easy to obtain in the pure state. Caldwell [18] and Cho et al. [19] have reported diffusion coefficients for naphthalene. Other diffusion coefficients were estimated using Fuller's method as described by Reid et al. [20]. Density and vapour pressure data were also obtained using Reid et al. [20].

Mass loss determinations were done on a Mettler Toledo TGA/SDTA 851e simultaneous TGA/DTA thermal analyser. Scans were performed in a dry nitrogen atmosphere. The purge gas flow rate was controlled electronically. According to Alexander et al. [13], the main factors that must be included and reported for every thermal analysis experiment are the sample mass, crucible, heating rate and the atmosphere used. These parameters also influence the rate of evaporation.

- (i) *Sample mass.* Sample mass was varied to investigate the effect of the diffusion path length (z).
- (ii) *Crucible/sample cup.* Solid or liquid samples weighing 10–70 mg were placed in open 70 μ l cylindrical ceramic pans (see Fig. 1). The inside diameter was 4.7 mm and the depth 4.0 mm.
- (iii) *Heating rate (dT/dt).* Heating rates of 2, 5, 10 and 20 °C/min were used.

- (iv) *Atmosphere*. To avoid sample oxidation, dry nitrogen was chosen as sample atmosphere instead of air. The effect of the purge gas flow rate was investigated at 10, 20, 50 and 100 ml/min.

Two methods for heating the samples were used. Liquid samples were directly heated from ambient temperature to 300 °C at the specified heating rate. Solid samples were first heated (at 10 °C/min) to just above the melting point and then cooled to 25 °C. The sample was then reheated from 25 to 300 °C at a specified heating rate. This was done to ensure a uniform and consolidated sample at the bottom of the sample cup before the run was started. The temperature was ramped up linearly with time and the rate of mass loss recorded. As the sample evaporates, the diffusion path length, z , increases. This change was determined from the amount evaporated and the density of the material.

4. Results and discussion

The TG evaporation method was validated using naphthalene and dibutyl phthalate as reference materials. Eq. (3) assumes that the diffusion of the inhibitor through the gas in the sample cup is rate limiting. The depth of this gas layer depends on the residual amount of sample inside the sample cup, the sample density and the cup dimensions. Fig. 2 shows the effect of initial sample size on apparent N_2 gas permeability of naphthalene and dibutyl phthalate. Reasonable agreement between expected and experimental results is obtained for sample sizes of 50 mg and below.

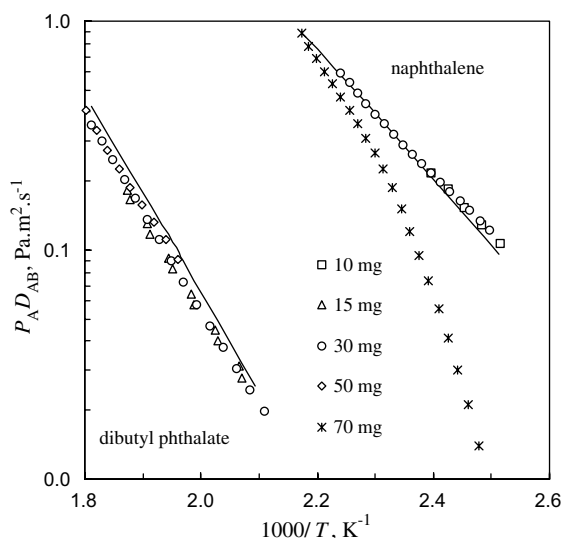


Fig. 2. The effect of the initial sample mass on the N_2 permeability of naphthalene and dibutyl phthalate. The heating rate was 10 °C/min and the purge gas flow rate 50 ml/min.

Large deviations are observed for the 70 mg naphthalene sample. This indicates that the cup was too full initially, i.e. the diffusion path length inside the cup was insufficient to be rate limiting. Note, however, that the permeability approaches the expected curve as the sample is depleted towards the end of the experiment, i.e. at high temperatures.

Fig. 3 shows the effect of the gas flow rate on the apparent N_2 gas permeability of naphthalene. The driving force for mass transfer is the difference in the concentrations at the top of the sample cup and at the upper level of the inhibitor inside the cup. At too low gas flow rates the emerging volatiles are not swept away fast enough and the concentration of volatile at the top of the cup will assume a finite value. This implies a reduction in the driving force. The result is a lowering of the mass loss rate. This effect was in fact observed at a flow rate of 10 ml/min. If on the other hand the gas flow rate is too high, it could generate an eddy inside the cup. This would enhance the mass loss rate via a convection mechanism. This effect was not observed presently: The experimental values at flow rates of 20, 50 and 100 ml/min are in reasonable agreement.

Fig. 4 shows that the scan rate has no effect on the gas permeability. The measured values for naphthalene agree to within $\pm 15\%$ with the expected curve (absolute average deviation was 4%). With dibutyl phthalate, the error band is larger and the measured values for fall in a band between -25% and $+5\%$ of the expected curve. However, in this case there is some uncertainty about the validity of the theoretical curve as the diffusion coefficients for dibutyl phthalate had to be estimated from Fuller's correlation since experimental data were not available.

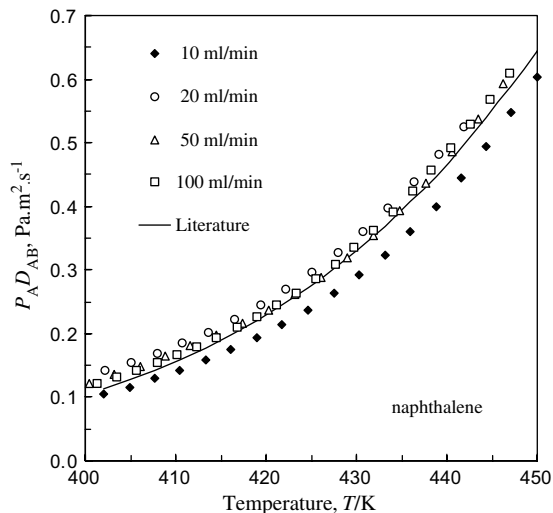


Fig. 3. The effect of purge gas flow rate on the permeability of naphthalene. The heating rate was $10\text{ }^\circ\text{C}/\text{min}$ and the initial sample mass 30 mg.

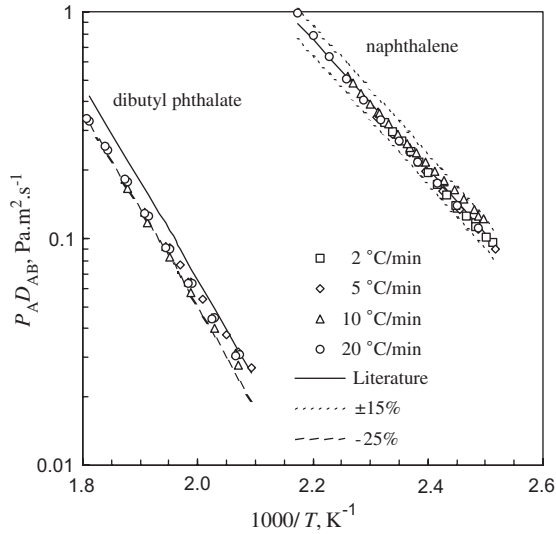


Fig. 4. The effect of heating rate on the N_2 permeability of naphthalene and dibutyl phthalate. The purge gas flow rate was set at 50 ml/min. Sample masses were 30 and 15 mg for naphthalene and dibutyl phthalate, respectively.

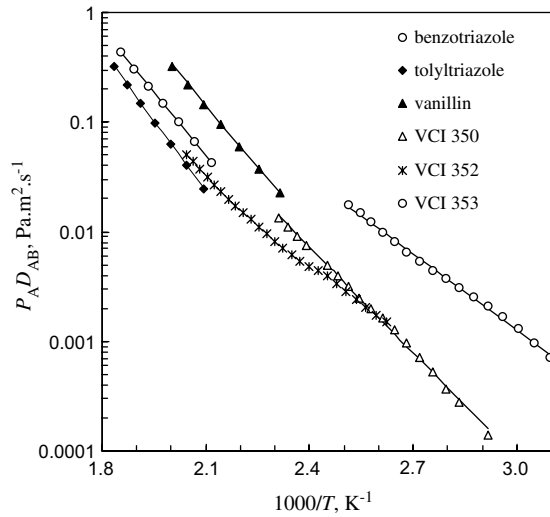


Fig. 5. N_2 gas permeability of vanillin and commercial VCIs: benzotriazole and tolyltriazole ex Bayer and VCI 350: 1-(dimethylaminomethyl)-1H-tolyltriazole; VCI 352: 1-(dibutylaminomethyl)-1H-tolyltriazole, and VCI 353: 4-(*N,N*-dibutylaminomethyl)morpholine ex CSIR.

Fig. 5 compares the data obtained for vanillin, three CSIR VCIs, benzotriazole and tolyltriazole. The latter two are used to protect copper and copper alloys. The

results show that their N₂ permeabilities are of the same order of magnitude as dibutyl phthalate but that their volatility is much lower than that of naphthalene. It is unfortunate that the method is limited to measurements at elevated temperatures for VCIs. However, this is the direct consequence of the low vapour pressures of these compounds.

5. Conclusions

The rate at which a VCI traverses a stagnant gas layer is determined by its gas permeability. The permeability combines the effects of vapour pressure and diffusion coefficient into a single parameter: $S_A = P_A D_{AB}$. A simple TG method for estimating the gas permeability of VCIs at elevated temperatures was developed. In essence the method entails the dynamic measurement of the mass loss rate from a partially filled cylindrical sample cup. During the experiment purge gas is swept horizontally across the cup opening. The method was validated on a Mettler Toledo TGA/SDTA 851e simultaneous TGA/DTA thermal analyser using naphthalene as primary reference and diffusing through nitrogen. Reasonable agreement between experiment and theory was obtained for scan rates between 2 and 20 °C/min when the 70 µl cup was filled to less than 50% of its volume at a gas flow rate of 50 ml/min. The results suggest that the permeability of tolyltriazole is comparable to that of dibutyl phthalate. At this stage the method can only provide order of magnitude comparisons at elevated temperatures for inert gas permeabilities of pure components.

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