Vapor Pressures of Volatile Corrosion Inhibitors by the Torsion-Effusion Method

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The vapor pressures of dicyclohexylammonium nitrite, cyclohexylammonium benzoate, diisopropylammonium nitrite, and morpholine carbonate were determined between 15 and 26° C. by the torsion-effusion method. The vapor pressures of the first 3 compounds were represented by the equation $\log_{10} P = A - B/T$. The corresponding heats of sublimation were also calculated from these data.

VOLATILE corrosion inhibitor is the name applied to compounds which have the ability to vaporize and condense on a metal surface making it less susceptible to corrosion. One of the most important properties of these compounds is vapor pressure. Cyclohexylammonium carbonate, for example, has a high vapor pressure of 0.4 mm. of mercury at 25° C. and is a very effective corrosion inhibitor. The protective time is very short because of rapid depletion of the inhibitor. There are also inhibitors with low vapor pressures on the order of 10^{-5} mm. of mercury. These compounds, however, cannot vaporize quickly enough before corrosion occurs. Therefore, vapor pressure is important, since it determines the usefulness of the compounds.

To utilize volatile corrosion inhibitors it is also important to know the rate of vaporization or the vapor pressure change with temperature. A vapor pressure–temperature curve with $1/T$ *vs.* the $-\log P$(mm. of Hg) will provide information which can later be related to the effectiveness of the various volatile inhibitors.

Most of the information on volatile corrosion inhibitors in the literature does not pertain to their physico-chemical properties, and some of the data are conflicting. For example, the value for the vapor pressure of dicyclohexylammonium nitrite at 21° C. determined by Rozenfeld (*4*) and by Wachter (*7*) is different by a factor of 10. Therefore, it seemed necessary to find a method which would accurately determine the vapor pressures of these compounds and their rates of change with temperature.

EXPERIMENTAL

For this work, a less commonly used effusion method, originated by Volmer (*6*) was selected because it can be used to determine vapor pressures in the range characteristic of volatile inhibitors (less than 1 mm. of Hg). The torsion-effusion method (*8*) is based on the measurement of the recoil force developed when molecules at saturated vapor pressure effuse through holes into a vacuum. If a sample is placed in an effusion vessel suspended from a fiber and the vapor escapes in a horizontal direction from two eccentrically placed holes, the fiber will be twisted through an angle. This angle of deflection is measured and the vapor pressure is calculated from Equation 1:

$$P_t = \frac{2KB}{f_1 d_1 a_1 + f_2 d_2 a_2} \tag{1}$$

where

P_t = vapor pressure
K = the torsion constant of the fiber
B = the steady angle of torque produced by effusion at constant temperature
$f_1 f_2$ = correction factors (ratio of the force in effusion of vapor through a hole of finite length to the force expected if the hole had infinitesimal length)
$d_1 d_2$ = the distances of holes 1 and 2 from the axis of rotation
$a_1 a_2$ = the areas of holes 1 and 2

Since the geometric factors K, f, d, and a were difficult to determine with sufficient precision, the apparatus was calibrated using a compound with known vapor pressures at different temperatures. Therefore, the equation becomes

$$P_1 = K_1 B$$

where

P_1 = vapor pressure of known compound
K_1 = constant
B = steady angle of torque produced

The constant, K_1, was calculated, and it was used to determine vapor pressures of other compounds within the same range of temperatures.

The apparatus used is similar to that of Balson (*1*). A diagram of the torsion-effusion apparatus is shown in Figure 1. It consists of the torsion system enclosed within a vertical vacuum chamber. The upper part of the vacuum chamber has a ground glass turnable joint supporting the indicator needle and the torsion system. A side arm through which the system is evacuated is near the lower end of the chamber. Sealed in the side arm are the leads for the small heater located under the effusion vessel. Opposite the side arm is the crank attached to a ground joint which is used to raise or lower the heater. The lower portion of the vacuum chamber consists of a round bottomed flask which can be removed without disturbing the torsion system.

Sealed in the side arm of the flask is the copper-constantan thermocouple. The thermocouple was calibrated at the ice point against a N.B.S. calibrated thermometer. The accuracy of the calibrated thermocouple was ±0.05° C. Measurements of the e.m.f. were made with a Leeds and Northrup Millivolt Potentiometer with limits of error better than ±0.01° C.

The entire flask was immersed in a vacuum-jacketed water bath which could be controlled to ±0.01° C.

The chamber was evacuated by a 3-stage mercury diffusion pump connected to the side arm through 2 liquid nitrogen traps. The diffusion pump was backed by a 2-stage rotary pump. Measurements of the vacuum were made using a cold cathode-type gage. Vacuums on the order of 2×10^{-6} mm. of mercury were obtained.

The torsion system consisted of four parts. The suspension was tungsten wire of 1.9-mil diameter. The tungsten wire was attached to the turnable ground glass joint and to it was fixed a 1-mm. diameter quartz rod. A galvanometer

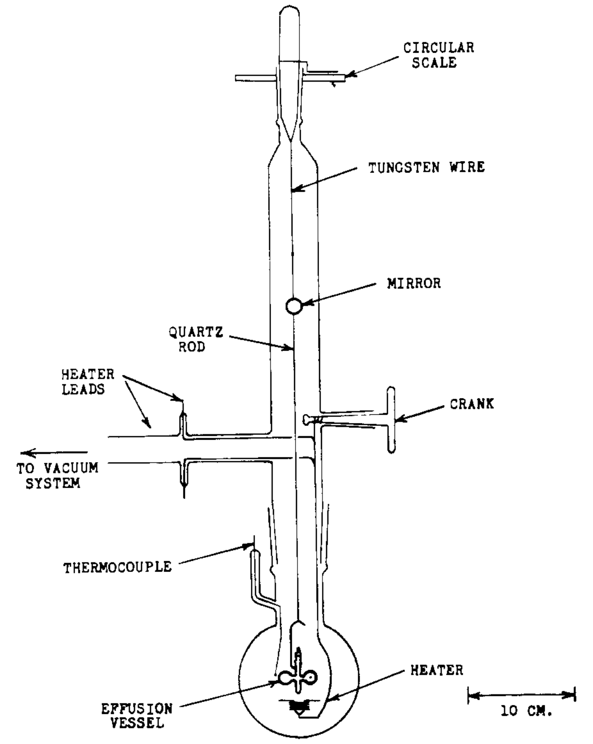

Figure 1. Torsion-effusion apparatus

mirror, 1-cm. diameter, was mounted on the quartz rod, and the effusion vessel hung from a hook at the lower end of it.

The details of the effusion vessel are shown in Figure 1. The holes were made in the bulbs by very carefully grinding the front surfaces of the bulbs on a glass plate using a paste of silicon carbide and water. The surface was ground until a small hole could be punched using a steel needle. The hole was then abraded to the desired size. Holes from 0.9 to 1.8-mm. diameter were formed using this method.

The small heater located under the effusion vessel was made from 1-mm. diameter quartz rod. The circular disk on top was made by coiling the rod with adjacent turns touching. The disk serves as a radiation shield for the bulbs. The heater winding was made from 30 gage chromel wire. The entire heater assembly could be raised by turning the crank at the side of the chamber.

The angle of deflection was determined from the position on a curved 30 cm. scale of an image reflected from the galvanometer mirror by a lamp. A diverging lens was placed in front of the mirror to obtain a sharp image on the scale located 1 meter from the mirror. If, during the course of a run, the image moved off the scale, it could be brought back onto the scale by turning the adjustable joint at the top of the chamber. The circular scale at the top of the chamber was marked in 1° increments for 360°. Therefore, the position of the pointer on the circular scale could be noted before and after the changing of the hairline image.

SAMPLE PURITY

It was essential that the compounds used would be pure. Prior to determining the vapor pressure, the purity of each substance was established as follows: The compounds used in this work, dicyclohexylammonium nitrite (VPI 260) and diisopropylammonium nitrite (VPI 220) were obtained from Shell Development Co. Cyclohexylammonium benzoate and morpholine carbonate were obtained from Eastman Organic Chemicals, Distillation Products Industries.

Recrystallization was conducted on all of the compounds, and a melting point was determined after each recrystallization. Diisopropylammonium nitrite, cyclohexylammonium benzoate, and morpholine carbonate showed no change in melting point after successive recrystallization, which indicated the compounds to be pure as received. The melting points were 139–140° C., 185–186° C. (with decomposition), and 99–100° C., respectively.

The dicyclohexylammonium nitrite was yellow in color, as received, and further recrystallization showed increases in the melting point until a constant value of 179–180° C. (with decomposition) was obtained. The crystals became whiter as the purity increased.

PROCEDURE

The following steps were taken in making vapor pressure measurements. A small amount of the material was placed in the tube projecting from the bottom of the effusion vessel. The vessel was cemented to the hook of the quartz rod with Apiezon wax. The round bottomed flask was placed carefully around the vessel onto the ground joint. The flask was immersed in a water bath cooled to 14° C. The chamber was evacuated to 10^{-4} mm. of Hg. After 10 minutes the heater was lifted around the bottom of the effusion vessel, and it was heated until the sample was sublimed into each bulb. After the sample was completely sublimed, the heater was turned off and lowered from the vessel. If there was an insufficient amount of compound present on the inside surface of the bulbs to make initial readings, the effusion vessel had to be removed and more of the sample placed in the stem. This sample was sublimed until the compound completely covered the inside surface of the bulbs.

Since all of the compounds were heated in a vacuum to have sublimation occur, the temperatures to which they were heated were obviously lower than their melting points. However, to confirm this, a thermocouple was inserted into the stem of the effusion vessel and heated to the temperature required to sublime the compounds. The temperatures obtained were 20 to 40° C. lower than the compounds' melting points.

The movement of the vessel was damped by raising the heater to touch the bottom of the vessel, then lowering it, until the oscillation was reduced to less than 1 cm. The mean position or midpoint of the image was then determined. The temperature of the water bath was increased by 1 to 2° C. increments until the range was covered. Readings at six to eight temperatures could be determined before the compound was depleted. At the end of the run, the vacuum system was closed off and air was admitted into the chamber. The water bath was removed from around the chamber, and the zero point was determined when the image stopped oscillating.

The apparatus was first calibrated using mercury whose vapor pressure data is available in the literature (*2*). The value of K_1 was determined as 0.92. The accuracy and reliability of the calibration was then checked using benzophenone whose vapor pressure has been established. It can be seen from the data in Table I that the value obtained for benzophenone at 26° C. is in good agreement with the value listed in the literature (*3*).

Using this calibration data and the effusion vessel, the vapor pressure measurements were made with 4 volatile corrosion inhibitor-type compounds.

RESULTS AND DISCUSSION

The results are listed in Table I along with data obtained from the literature. The vapor pressure temperature curves for dicyclohexylammonium nitrite, cyclohexylammonium benzoate, and diisopropylammonium nitrite are shown in Figure 2. The values obtained for dicyclohexylammonium nitrite at 21° and 25° C. agree with the data obtained by

Table I. Vapor Pressures of Compounds Investigated

Compound	Temp., °C.	Vapor Pressure Data, 10^{-4} Mm. of Hg RIA Data	 Literature
Benzophenone	26.0	6.75	6.859(3)
Dicyclohexylammonium nitrite	17.3	0.72	
	19.1	0.97	
	21.0	1.20	1.2(7) 0.1(4)
	21.2	1.23	
	22.7	1.47	
	24.4	1.91	
	25.0	2.0	2.0(5)
Diisopropylammonium nitrite	15.6	36.2	
	17.6	39.8	
	19.6	44.8	
	21.0	48.4	47(7)
	22.5	52.8	
	24.8	60.3	
	25.0	59.6	50(5)
Cyclohexylammonium benzoate	16.5	0.41	
	19.3	0.64	
	20.8	0.76	
	22.7	1.04	
	24.6	1.32	
Morpholine carbonate	21.0	77	

Table II. Constants of $\log_{10}P = A - B/T$ and the Heats of Sublimation (Temp. Range 15 to 26° C.)

Compound	A	B	ΔH_s, Kcal./per Mole	Std. Deviation
Dicyclohexylammonium nitrite	13.69	5178	23.65	0.78
Cyclohexylammonium benzoate	14.21	5384	24.59	1.29
Diisopropylammonium nitrite	4.61	2035	9.29	0.85

Wachter (*7*) and by Turnbull (*5*). Rozenfeld's (*4*) value is lower by a factor of 10.

The original effusion vessel used was not satisfactory for compounds of higher vapor pressure (10^{-3} mm. of Hg) because the sample would vaporize completely before any measurements could be made. Another effusion vessel was made with smaller holes and also calibrated using mercury. The value of K for this effusion vessel was 2.63. This vessel was used for vapor pressure measurements of diisopropylammonium nitrite and morpholine carbonate.

The data obtained for diisopropylammonium nitrite at 21° and 25° C. agree with that of Wachter (*7*) and Turnbull (*5*).

Cyclohexylammonium benzoate and morpholine carbonate were investigated as possible volatile corrosion inhibitors. Their vapor pressure values are within the useful range as volatile inhibitors.

The dependence of the vapor pressures of the compounds on temperature is shown in Figure 2. The data plotted for the compounds gave satisfactory straight lines. The vapor pressure–temperature graph for morpholine carbonate was not plotted because of insufficient data above 21° C. The compound has a high vaporization rate so that the sample was depleted before enough measurements could be made.

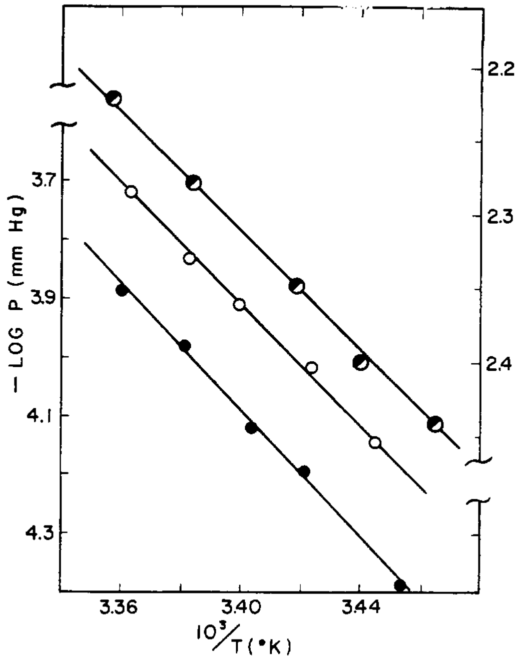

Figure 2. The $-\log P$(mm. of Hg) of the vapor pressure as a function of $10^3/T$(° K.)

○ Dicyclohexylammonium nitrite
● Cyclohexylammonium benzoate
◓ Diisopropylammonium nitrite

In the cases where the points gave a straight line obeying the equation $\log_{10}P = A - B/T$, the constants A and B were calculated and are shown in Table II. Using this data, the vapor pressure of the compound can be calculated for any temperature within the range indicated.

Listed in Table II are the heats of sublimation as calculated from the slopes of the curves in Figure 2.

The results demonstrate that the torsion-effusion technique is useful in the determination of the vapor pressures of organic compounds selected as volatile corrosion inhibitors. The advantages of the method are that a small amount of substance is required and knowledge of the molecular weight of the compound is not necessary to calculate the vapor pressure.

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