Solid Vapor Pressure and Enthalpy of Sublimation for Perfluorooctanoic Acid

Catherine A. Barton,[*,†] **Miguel A. Botelho,**[‡] **and Mary A. Kaiser**[‡]

DuPont Engineering Research and Technology, 1007 Market Street, Brandywine Building 9432, Wilmington, Delaware 19898, and DuPont Corporate Center for Analytical Sciences, Experimental Station 402, Wilmington, Delaware 19880

A modified gas saturation method was used to determine the solid vapor pressure of perfluorooctanoic acid (PFOA) at ambient temperatures. Measurements were made over the temperature range from (25 to 45) °C. Pressures ranged from (5.2 to 40.7) Pa. The enthalpy of sublimation was calculated as 88.9 $\mathrm{kJ \cdot mol^{-1}}$.

Introduction

Fluorinated compounds have unusual chemical properties that are much different than their hydrocarbon counterparts, due to the great strength of the C−F bond and the high electronegativity and small size of the fluorine atom. The perfluoroalkyl moiety is both oleophobic and hydrophobic. Because of this feature, it has been suggested that perfluorinated compounds should be considered a third class of material, distinct from those that are solely hydrophobic or oleophobic. The uniqueness of the chemical properties in perfluorinated compounds manifests itself in analytical challenges that have driven the development of new analytical techniques.[1] Thus, it cannot be assumed that the properties and behavior of PFOA follow conventional "rules" such as those that apply to hydrocarbons.

Vapor pressure is an important property for modeling the behavior of substances in the environment. Perfluorooctanoic acid (PFOA) is a low volatility material that is a solid at environmentally relevant temperatures of (10 to 35) °C. For low vapor pressure materials, measurements are often collected at elevated temperatures and extrapolated to lower temperatures of interest. However, because of the variability in vapor pressure values expressed in the literature, because PFOA experiences a phase change at approximately 53 °C, and because of the importance of assessing environmental behavior of PFOA, direct measurement of vapor pressure at ambient temperatures was undertaken.

The gas saturation method is appropriate for vapor pressure measurements in the range of 10^{-8} Pa to 10^{3} Pa.[2,3] This study used a modified gas saturation method to measure the vapor pressure of PFOA at ambient temperatures. The heat of sublimation was then derived from the temperature dependence of the vapor pressure.

Experimental Section

Materials. PFOA (CAS Registry No. 335-67-1) is a white solid at room temperature. PFOA used in this experiment was obtained from Oakwood Products (West Columbia, SC) with a purity of 98.7 %.

Apparatus and Procedures. Vapor pressure was measured using the EPA gas saturation method.[4] A schematic of the apparatus is given in Figure 1. The entire experimental apparatus was set up in a ventilated enclosure. Approximately 5 g (weighed to ± 0.00001 g) of the finely ground acid was placed in a preweighed glass column (gas chromatographic inlet liner 19251-60540, Agilent, Little Falls, DE). Preweighed deactivated borosilicate glass wool (Restek Corporation, Bellefonte, PA) was used to contain the powder within the column. The glass column was placed in a gas chromatographic oven (HP series 6890, Agilent, Little Falls, DE). The temperature was set with the oven controls and verified by a National Institute of Standards and Technology (NIST, Gaithersburg, MD) traceable thermometer (catalog number 62344-7364, VWR International, Inc., West Chester, PA). The oven temperature was held constant within 0.4 °C. The column was connected to the nitrogen supply and the flow set at the desired flow rate. The nitrogen passed through a gas moisture trap (catalog number MT120-4-D, Agilent, Little Falls, DE), a NIST-traceable 65 mm aluminum flow controller (catalog number 32044-00, Cole-Palmer, Vernon Hills, IL), and a gas mass-flow meter with flow totalizer (catalog numbers K-32648-04 and K-32650-70, Cole-Palmer, Vernon Hills, IL). Latex tubing (6.35 mm, VWR International, Inc., West Chester, PA) connected the nitrogen source to the gas moisture trap and the gas moisture trap to the flow controller. All other connections were made with low-density polyethylene tubing (6.35 mm, Cole-Palmer, Vernon Hills, IL). Approxi-

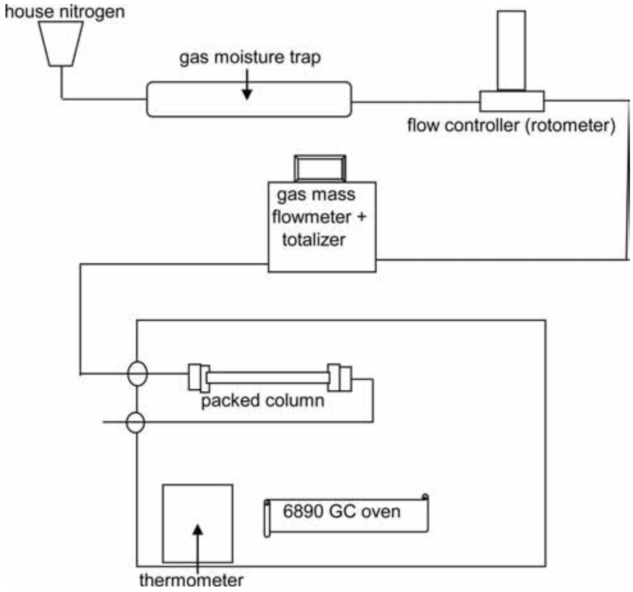

Figure 1. Schematic of the gas saturation method test apparatus.

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[*] Corresponding author. E-mail: catherine.a.barton@usa.dupont.com.
[†] DuPont Engineering Research and Technology.
[‡] DuPont Corporate Center for Analytical Sciences.

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mately 30 min was required for the flow to stabilize at the set point. The measured pressure drop across the apparatus was 14.7 Pa.

The unmodified gas saturation method calls for the transported substance to be trapped for analysis, or in-line analysis can be used. Due to difficulties in finding a sufficiently adsorbent trapping medium, this study used a modified method to quantify the mass of transported material in lieu of direct analysis. In some cases, up to 70 h was required to collect a single data point. These long time periods in addition to the unusual properties of PFOA described previously made it difficult to find an adsorption medium to efficiently trap the low levels of PFOA.

The quantity of transported material was measured as the difference in mass of PFOA in the packed column before and after the inert carrier gas flowed through the column. To determine the mass lost after the desired time interval, the nitrogen flow was stopped and the packed column disconnected. At ambient temperatures, the column was then weighed to the nearest 0.01 mg, and the loss of mass was calculated. The accuracy of the balance was verified before taking each measurement. A 5 g Class S-1 (NIST Classification) calibration mass was weighed at the same time and recorded to ensure consistency in the mass measurement. In this experiment, the temperature measurement uncertainty was +1 °C, and the pressure measurement uncertainty was +4.9 Pa.

Data Reduction. The vapor pressure of PFOA (P_{org}) can be computed using the following equations[3]

$$m_{\text{gas}} = \frac{Q_{\text{D}}}{0.0224\left[\frac{273.15 + t_{\text{exh}}}{273.15}\right]\left[\frac{101325}{P_{\text{T}}}\right]} \tag{1}$$

$$m_{\text{org}} = W_{\text{org}}/M \tag{2}$$

$$y = m_{\text{org}}/(m_{\text{org}} + m_{\text{gas}}) \tag{3}$$

$$P_{\text{org}} = y(P_{\text{amb}} + \Delta P) = y(P_{\text{T}}) \tag{4}$$

where m_{gas} = moles of carrier gas; Q_{D} = volume of dry gas in m^3; t_{exh} = exhaust temperature in °C; P_{amb} = ambient air pressure, 101 325 Pa; m_{org} = moles of sublimed PFOA; W_{org} = mass of sublimed PFOA in grams; M = molar mass of PFOA, 414.1 in g·mol^{-1}; P_{org} = vapor pressure in Pa; y = mole fraction of test chemical in carrier gas, dimensionless; ΔP = pressure drop through the system, 14.7 Pa; and P_{T} = total pressure = ($P_{\text{amb}} + \Delta P$) in Pa.

For the modified method used in this work, the mass of PFOA sublimed, W_{org}, was determined based on measured mass loss in the apparatus before and after testing at a given temperature and flow rate. Measurements were made at 1 mL·min^{-1} and 3 mL·min^{-1} and at temperatures ranging from approximately (25 to 45) °C.

The enthalpy of sublimation is the heat required to change one mole of solid into one mole of gas. The enthalpy of sublimation of PFOA can be derived from the Clausius–Clapeyron equation that shows the temperature dependence of the vapor pressure[1]

$$\ln(p) = \frac{-\Delta_{\text{vap}}H + C}{RT} \tag{5}$$

where p = vapor pressure; $\Delta_{\text{vap}}H$ = the enthalpy of sublimation; R = the universal gas constant, 8.314 J·mol^{-1}K^{-1}; T = absolute temperature; and C is a constant which includes the entropy of sublimation.

Table 1. Solid Vapor Pressures for PFOA Measured at Three Temperatures by the Modified Gas Saturation Method

mean t/°C[a]	mean p/Pa[a]	SE/Pa[b]	precision[c]
27.1	5.2	0.58	0.39
35.4	18.0	2.08	0.40
45.7	40.7	3.52	0.30

[a] Mean temperatures and vapor pressures were calculated from 12 individual measurements (n = 12). [b] SE, the standard error, is the standard deviation of the difference between the measured values and the mean value. [c] Precision defines the repeatability of the test measurement within the same laboratory and with the same operator and is calculated as the relative standard deviation of each batch of 12 samples.

Using the vapor pressure measurements determined at various temperatures, the Clausius–Clapeyron equation can be solved to obtain a mean value for $\Delta_{\text{vap}}H$ within the temperature range tested.

Results and Discussion

Vapor Pressure of the Control Sample. To ensure the validity of the test apparatus, the vapor pressure of naphthalene was measured using the modified gas saturation method and equations presented above. At 45 °C, a vapor pressure of 79 Pa was measured for naphthalene. This value is consistent with other published values measured using gas saturation methods of 79.7 Pa at 46.85 °C[5] and 71.1 Pa at 45.35 °C.[6]

Vapor Pressure of PFOA. PFOA vapor pressure measurements were made using eqs 1 to 4. Experimental results and uncertainties are shown in Table 1. The standard errors (standard deviations in the mean) were calculated from the scatter of the individual determinations. Reported relative standard deviations (S_{r}) are a measure of the repeatability or precision of the measurement equipment. The precision reported in this work (0.30 to 0.40) is within the range of precision values for the gas saturation method published by the American Society of Testing and Materials (ASTM), reported as 0.31 to 0.55 for materials with similar vapor pressure.[3]

The measured vapor pressure for PFOA at ambient temperature can be compared with the predicted subcooled vapor pressure using previously published Antoine equation constants for PFOA[7]

$$\ln(p/\text{kPa}) = 14.73 + \frac{(-3397.98)}{t/^\circ\text{C} + 142.69} \tag{6}$$

Using eq 6, the subcooled vapor pressure at 27 °C is 5.0 Pa, which compares favorably with the measured value in this work of 5.2 Pa.

Enthalpy of Sublimation of PFOA. The enthalpy of sublimation for PFOA was calculated using eq 5. A plot of ln(p) vs 1/T is shown in Figure 2, which is represented by the following equation (with R^2 = 0.974)

$$\ln(p/\text{Pa}) = \frac{-10695}{T} + 37.292 \tag{7}$$

The enthalpy of sublimation is calculated from the slope of eq 7 resulting in a value of 88.9 kJ·mol^{-1}. This value is similar to the enthalpy of sublimation values reported for naphthalene of 73.9 kJ·mol^{-1} and 72.9 kJ·mol^{-1}.[8,9] Error bars shown in Figure 2 represent the 95 % confidence intervals of the data.

Conclusions

The present work provides vapor pressure measurements for PFOA at ambient temperatures using a modified gas saturation method. It also presents a calculated enthalpy of sublimation.

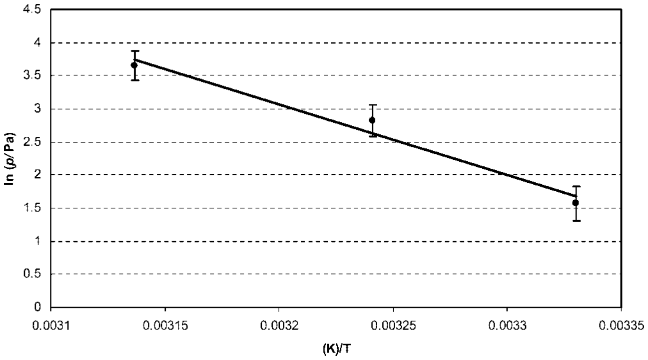

Figure 2. Clausius−Clapeyron relationship for PFOA, used to derive the enthalpy of sublimation ($\Delta_{vap}H$) using eq 5. Uncertainty is represented by error bars showing the 95 % confidence intervals ($n = 12$).

Previous measurements of vapor pressure have been published; however, these measurements were collected at elevated temperatures that exceed ambient conditions. Efforts to estimate ambient vapor pressures in the past have been confined to extrapolations from conditions above the melting point. Because vapor pressure−temperature relationships are different for sublimation and vaporization, a more accurate representation of the vapor pressure under ambient conditions is provided in this work through actual measurements. Vapor pressure measurements made in this work compared favorably with subcooled vapor pressure predictions extrapolated from Antoine constants that were presented in a previous work, showing that the vapor pressure relationship of PFOA with temperature does follow convention.

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Supporting Information Available:

Flow, temperature, and calculated vapor pressure for individual measurements are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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