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An improved method for measuring vapor pressure by DSC with automated pressure control[1]

M. Casserino[2], D.R. Blevins*, R.N. Sanders

Albemarle Corporation, P.O. Box 14799, Baton Rouge, Louisiana 70898, USA

Abstract

Vapor pressure measurements are necessary for a wide range of applications in the chemical industry. Traditional methods require 10–30 ml of sample, 6–8 h of operator time, and multiple measurements for high precision data.

With a modification to the pressure differential scanning calorimeter cell, use of hermetic-type pans with pin-holed lids, and the addition of a pressure controller, vapor pressure measurements from 5–760 torr can be obtained. These measurements use less than 1 ml of sample, take about 2 h of operator time, and achieve high precision data on a single set of measurements.

Keywords: Vapour pressure; DSC; Thermal analysis

1. Introduction

Vapor pressure is an important physical property in the chemical industry. Design of distillation columns is critically dependent on it. Vapor pressure is also required to determine the potential environmental and safety aspects of a compound or mixture.

Measurement of vapor pressure was reported as early as 1803 by J. Dalton using a head space method. Since then, improvements in head space methods have been made, the isoteniscope being a modern example of this technique. The isoteniscope is capable of providing highly accurate data. However, it is difficult to use, requires a moderate amount (about 5 ml) of sample, and because of extensive degassing requirements, is generally amenable only to pure compounds. Dynamic methods for

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* Corresponding author.

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[2] Current address: Amoco Corporation, 150 W. Warrenville Rd, Naperville, IL60566, USA

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the measurement of vapor pressure have been used since the beginning of this century. The ebulliometer has been and still is an important device for this measurement. The ebulliometer gives highly accurate data with high precision. This technique is also very time-consuming (measuring a sample can take 6–8 h) and requires large amounts of sample (greater than 10 ml). It requires the sample to be held at a high temperature for relatively long periods of time, which could lead to decomposition. To avoid this problem, the sample can be replaced after each pressure equilibrium. If this is done, the amount of sample and operator time is greatly increased.

In the modern research laboratory using micro-synthesis techniques, the quantity of sample available for a series of tests is often limited and operator time is always at a premium. Krawetz and Tovrog [1] suggested a DTA method for vapor pressure measurement in 1962. Brozena et al. [2] reviewed and improved upon thermal analysis techniques. In recent years, DSC techniques have been reported. In this paper we will describe further improvements to the DSC technique that have made this method a routine laboratory tool for use in the 5–760 torr range. It requires about 2 h of operator time, uses less than 1 ml of sample, and provides accurate results with very good precision on a single set of data. It can provide more precise data than ebulliometry on some types of samples. Minor and easily made modifications to a standard pressure DSC cell were required. Addition of a commercial pressure controller simplified the required pressure control.

2. Experimental

2.1. Apparatus

Fig. 1 shows a schematic diagram of the measuring apparatus. It consists of a TA Instruments Thermal Analyst 2000 System with general analysis program, a 910 DSC

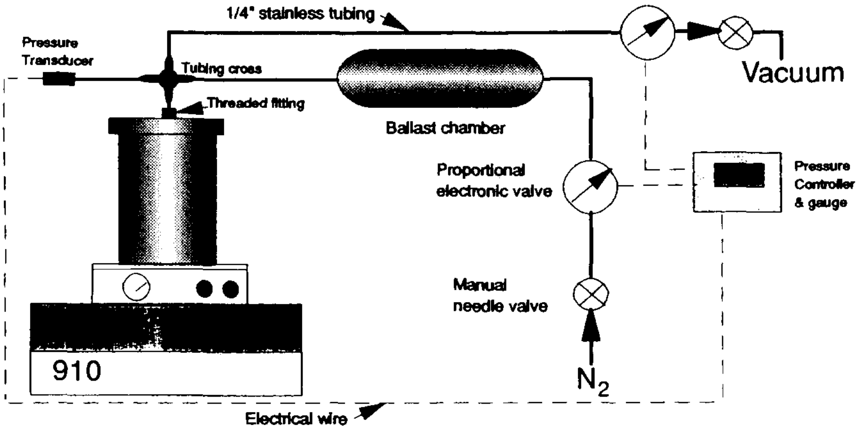

Fig. 1. DSC vapor pressure apparatus.

cell base, and a DSC pressure cell. The outer cell lid was modified by drilling and threading a hole in the center for a hose fitting to allow connection to the pressure reading device. The system is evacuated with a rotary vane pump, and the pressure is measured and automatically regulated by a combination of an electronic pressure gauge (OMEGA CN76000), pressure transducer (OMEGA PX216), and proportional valves (OMEGA PV14-SS). The ballast tank is used to stabilize the pressure control system.

2.2. Calibration

Temperature calibration of the cell is performed at 5 and 760 torr with indium ($T_m = 156.6°C$) and lead ($T_m = 327.5°C$) standards. The procedure used for calibration is identical to the sample measurement procedure except larger weights (10–20 mg) are used. The extrapolated onset temperatures (T_e) [3] are typically the same at the two pressures. Thus, for these two metals, the measured melting temperature is not affected by pressure.

The pressure regulator was calibrated at all measured pressures with a Ruska 6200 NIST-traceable secondary pressure standard device.

2.3. Materials

Decane, dodecane, and tetradecane, all 99 + %, obtained from Aldrich, were used as received. Three Albemarle research compounds were studied. Material A is a 96% pure aromatic compound, Materials B and C are 98 + % pure brominated aromatic compounds. Measurements were performed in DSC hermetic-type aluminum pans sealed with lids having a 75 μm (0.003 in) laser-machined pinhole [4].

2.4. Procedure

Sample sizes from2–5 mg are weighed into DSC pans and sealed with the laser-holed lids. The system is evacuated to the set pressure, and the pressure typically stabilizes within 60 s. The pressure control system automatically regulates the valves to nitrogen or vacuum to maintain the set pressure. Samples are equilibrated approximately 40°C below the expected boiling point, held isothermally for 3 min, then heated at a rate of 5°C min^{-1} until boiling is complete (when the endothermic curve returns to a stable baseline).

The boiling temperature (T_e) is taken as the intercept of the extrapolation of the baseline with the extrapolation of the leading side of the boiling endotherm (Figs. 2 and 3). For each compound, nine temperature–pressure data points are obtained, and the data is fitted with the Antoine equation to construct a vapor pressure curve (Fig. 4).

Note: Two deviations from the procedure are necessary below 20 torr. First, the sample size should be between 2 and 3 mg. Our experiments at 5 and 10 torr show that sample sizes greater than 3 mg frequently produced distorted boiling curves which made it difficult to measure the extrapolated onset temperature of the boiling endotherm. Others have found sample size to be an important variable, influencing the

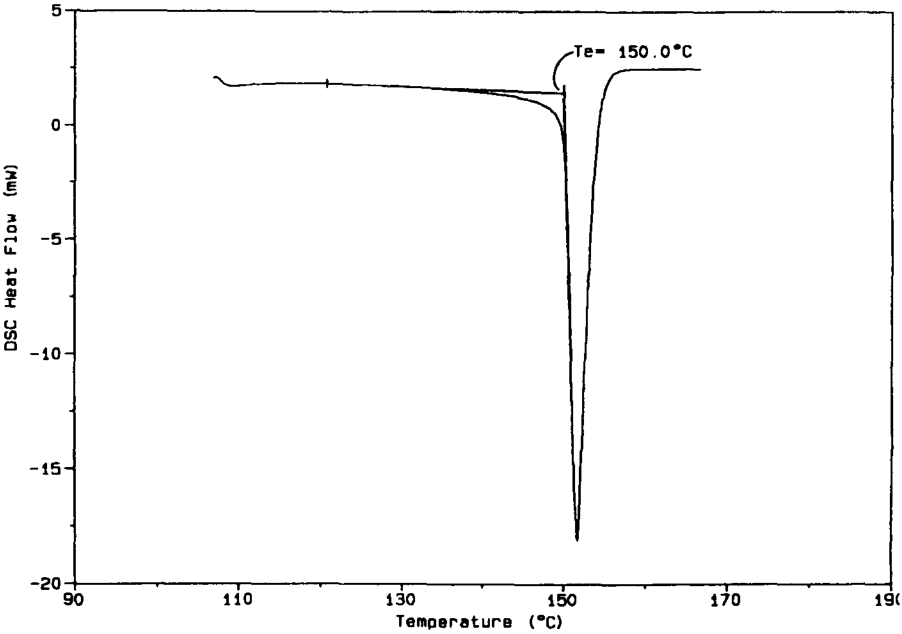

Fig. 2. DSC boiling endotherm of decane at 400 torr using 0.003-in laser-machined pinhole lid.

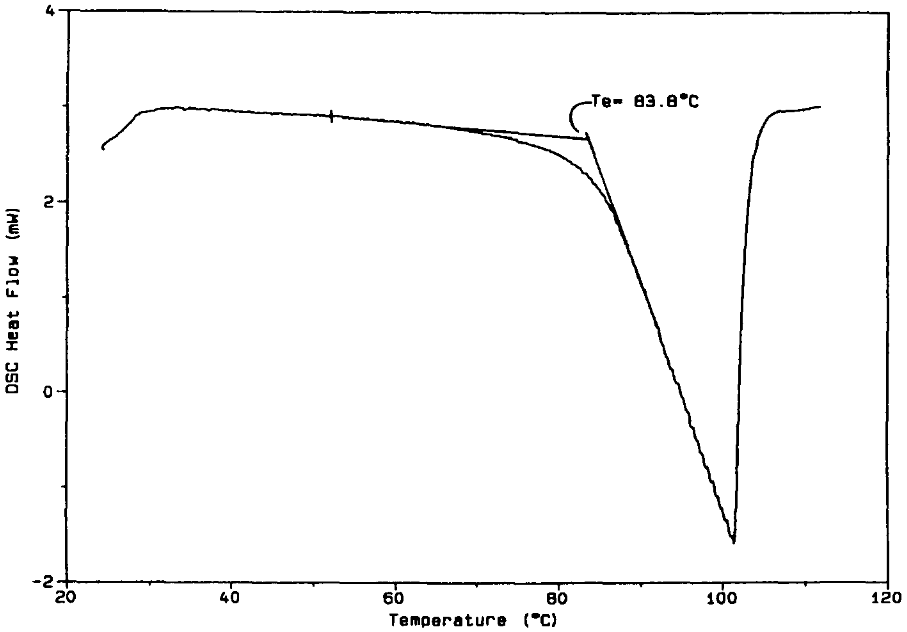

Fig. 3. DSC boiling endotherm of Material C at 400 torr using 0.003-in laser-machined pinhole lid.

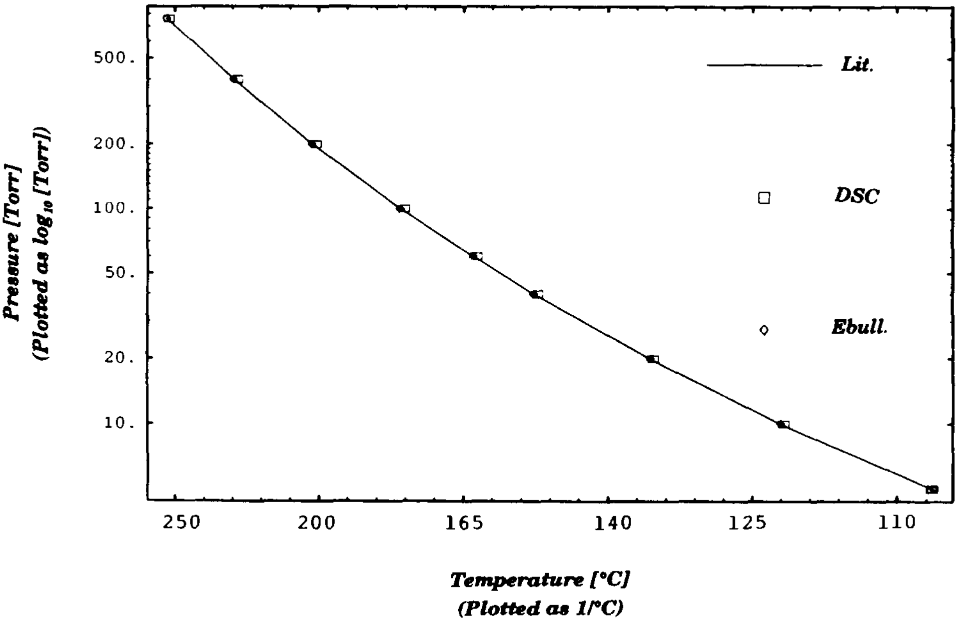

Fig. 4. Tetradecane vapor pressure data: comparision of literature, DSC, and ebulliometry.

shape of the boiling endotherm [5], [6]. Second, temperature equilibration cannot be used because it causes the temperature to "over-shoot". To avoid this problem, samples are heated from room temperature through boiling at 5°C min^{-1}.

We propose the following explanation for the temperature "over-shoot". The temperature measuring thermocouples of the DSC cell depend upon metal-to-metal thermal conductivity and thermal conductivity through the gaseous medium. At very low pressures, the contribution through the gaseous medium is decreased so that rapid temperature changes are indicated incorrectly by the thermocouples. TA Instruments apparently observed a similar phenomenon [7]. We believe there are other unidentified factors contributing to this effect.

3. Results and discussion

Table 1 compares the vapor pressure data of tetradecane using DSC and ebulliometry to literature values [8]. (All data were calculated using the Antoine equation.) Boiling temperature differences between literature, DSC, and ebulliometry are listed for each pressure. Two sets of data points were taken and averaged for the ebulliometry technique. The data from both techniques are in good agreement with literature values and both give an excellent standard error of estimate (SEE). There are three important differences between the DSC and the ebulliometry technique. DSC uses less than 1 ml of sample, takes less than 2 h of operator time, and gives high precision data on a single

Table 1
Teradecane vapor pressure data: Comparison of Literature, DSC, and ebulliometry

P/torr	T/°C		ΔT_L^1	T°C Ebull.[a]	ΔT_L^2
	Lit.	DSC			
5	108.3	108.2	−0.1	108.1	−0.2
10	122.0	121.7	−0.3	122.0	0.0
20	137.0	136.8	−0.2	137.2	+0.2
40	154.0	153.5	−0.5	154.2	+0.2
60	165.0	164.2	−0.8	165.0	0.0
100	179.6	178.8	−0.8	179.7	+0.1
200	201.8	200.8	−1.0	201.9	+0.1
400	227.0	225.9	−1.1	227.1	+0.1
760	253.6	252.5	−1.1	253.6	0.0
SEE[b]		0.2		0.2	

Key: ΔT_L^1 = (DSC − Lit.); ΔT_L^2 = (Ebull. − Lit.). [a] Average of 2 data sets. [b] Standard error of estimate.

set of measurements. Our ebulliometer takes 40 ml of sample and 12 h of operator time to measure two sets of data to obtain the same standard error of estimate as DSC. Fig. 4 clearly shows that the small differences between the data sets are insignificant.

Table 2 compares the literature values of decane and dodecane to the DSC data. Again, both sets of experimental data are in good agreement with literature values [8] and both give an excellent standard error of estimate.

The differences found between DSC results and the literature values for the standard materials, as shown in Tables 1 and 2, all have the same sign (−). This may indicate

Table 2
Comparison of literature and DSC vapor pressure data

P/torr	Decane			Dodecane		
	T/°C		ΔT_L	T°C		ΔT_L
	Lit.	DSC		Lit.	DSC	
5	45.5	44.8	−0.7	78.5	78.0	−0.5
10	57.7	56.8	−0.9	91.6	91.0	−0.6
20	71.6	70.1	−1.5	106.0	105.3	−0.7
40	86.1	84.9	−1.2	122.0	121.3	−0.7
60	95.6	64.5	−1.1	132.2	131.5	−0.7
100	108.6	107.5	−1.1	146.1	145.4	−0.7
200	128.2	127.2	−1.0	167.1	166.4	−0.7
400	150.5	149.9	−0.6	191.0	190.3	−0.7
760	174.1	174.0	−0.1	216.3	215.3	−0.6
SEE		0.1			0.3	

Key: ΔT_L = (DSC−Lit.).

Table 3
Comparison of ebulliometry and DSC vapor pressure data of research compounds

Material A				Material B			Material C		
P/torr	T°C		ΔT_E	T°C		ΔT_E	T°C		ΔT_E
	Ebull.	DSC		Ebull.	DSC		Ebull.	DSC	
5	73.4	75.1	+1.7	93.7	89.1	−4.6	86.7	82.9	−3.8
10	86.3	87.9	+1.6	105.5	102.8	−2.7	97.9	96.1	−1.8
20	100.7	102.2	+1.5	118.9	118.0	−0.9	110.8	110.8	0.0
40	116.9	118.4	+1.5	134.3	135.0	+0.7	125.8	127.4	+1.6
60	127.3	128.7	+1.4	144.4	145.9	+1.5	135.7	138.0	+2.3
100	141.5	143.0	+1.5	158.6	160.8	+2.2	149.7	152.6	+2.9
200	163.3	164.7	+1.4	181.0	183.5	+2.5	172.0	174.8	+2.8
400	188.3	189.9	+1.6	207.8	209.6	+1.8	199.3	200.5	+1.2
760	215.3	216.9	+1.6	237.9	237.4	−0.5	230.5	228.0	−2.5
SEE	1.0	0.5		1.8	0.5		2.2	0.7	

Key: ΔT_E = (DSC–Ebull.).

a bias in one of the data sets, and future work should be directed toward resolving the differences. However, the magnitude of the differences clearly shows that the DSC data are useful for R&D and engineering calculations.

Vapor pressure data generated for three research materials by DSC and ebulliometry are compared in Table 3. There is no statistically significant difference at the 95% confidence level between the results obtained by the two techniques. No significant differences were found for any of the compounds in this study.

The differences between DSC results and ebulliometer results for the research materials, as shown in Table 3, may indicate additional information about these materials. For compound A, all differences are positive, while compounds B and C follow a different pattern with increasing pressure. Whether these data sets can be correlated with the materials, purity, stability, or some other property, or even to instrumental parameters, is another area for furture work.

4. Conclusion

This study clearly demonstrates that the DSC technique applies to a wide variety of organic compounds. It always gives good precision in a single run, and its accuracy approaches that of classical methods. Vapor pressure results obtained with this technique have sufficient precision and accuracy for the intended purpose of R&D and engineering calculations. Smaller sample sizes and reduced operator time are significant advantages of the DSC technique over classical techniques.

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