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THERMOGRAVIMETRIC ANALYSIS FOR BOILING POINTS AND VAPOUR PRESSURE

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Abstract

A TGA instrument has been adapted for rapid measurement of boiling points and vapour pressure at temperatures from ambient up to 400°C and pressures from ambient down to 20 mm Hg. Samples were contained in sealed holders having a laser-drilled aperture. Several organic liquids in the 100 to 300 g *MW* range showed good agreement with reference vapour pressure data. Sample mass, heating rate, and use of inert diluents were important variables affecting accuracy of vapour pressure measurements.

Keywords: boiling points, DSC, TGA, vapour pressure

Introduction

Recent DSC studies [1, 2] have shown that rapid and accurate boiling point and vapour pressure data may be obtained with a new design of sealed sample holder with a uniform and reproducible laser-drilled aperture. The authors conclude that the laser-drilled hole must be small enough to restrict diffusion out of the sample container to a rate less than the vaporization rate inside the container, yet have sufficient diameter to prevent any self-pressurization. The above reports are summaries of a cooperative research program intended to systematically evaluate the dependence of vapour pressure measurements on aperture size, heating rate, and vapour pressure magnitude.

For the DSC, Jones and Seyler [1] recommend for pure liquids that hermetic containers (less than 50 μl capacity) with samples of 2–4 mg, heating rates of 5–10°C min^{-1}, and pinhole diameter of 0.0125–0.127 mm be used. Seyler [3] observed that the addition of inert diluents such as 100 micron glass beads or powdered alumina measurably assist in achieving isothermal sample boiling. This is somewhat analogous to the "boiling stone" effect well known to chem-

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ists. The diluent is reported to increase liquid surface area, reduce vaporization before boiling by retention of sample through surface tension, and to act as nucleation sites for boiling which minimizes superheating.

Thermogravimetric analysis (TGA) has also been used to determine the temperature dependence of vapour pressure for solids and pure liquids, but only at pressures below 1 mm Hg. A Knudsen effusion cell attachment replaces the sample holder [4, 5]. The method allows for measurement of weight loss of an evaporating substance due to exit of its molecules through a calibrated orifice. The effusion cell is a rather complex sample holder with a pinhole orifice which must be calibrated. According to Weidemann [4], the pinhole restricts diffusion of vapour molecules from the cell to a rate less than the diffusion rate through the vapour space inside the effusion cell.

The determination of vapour pressure by both the DSC and TGA methods is referred to as the "boiling point" method. The isothermal boiling temperature of a pure liquid is measured as a function of pressure. The boiling temperature is taken from a plot of thermal differential or weight loss *vs.* sample temperature. The extrapolated onset of isothermal boiling is taken as the boiling point corresponding to the pressure outside the sample holder [3]. DSC vapour pressure data may be shown as a straight-line Clausius-Clapeyron plot of $\log P$ *vs.* $1/T$ (K), where P is pressure (mm Hg) and T is temperature (K). If the vapour does not behave as an ideal gas or if the heat of vaporization is not constant over the temperature range of interest, the Antoine equation will more accurately fit the DSC data [1].

The DSC and TG methods as described above are very similar in many respects. Since the TA Instruments TGA unit readily operates at ambient and subambient pressures [6], the use of laser-drilled capsules in a conventional TGA unit was investigated as a potential method for obtaining vapour pressures of selected triglycerides. If successful, the TGA laser-drilled capsule method would provide a rapid, simple method of obtaining vapour pressures and boiling points at or below atmospheric pressure.

The general objective of this study then was to evaluate the accuracy of boiling point and vapour pressure measurements made with a standard TGA unit, laser-drilled sample holders, and inert diluents. The effects of pressure, sample size and heating rate were also observed.

Equipment and procedure

The TA Instruments Model 951 thermobalance with quartz furnace tube was used with 50 ml/min N_2 flow at ambient pressure. Below atmospheric pressure, selected pressures were obtained with the system shown schematically in Fig. 1. The platinum sample support was reshaped to accommodate the laser-drilled capsules obtained from the Perkin-Elmer Corp. (part no. N5190788). The

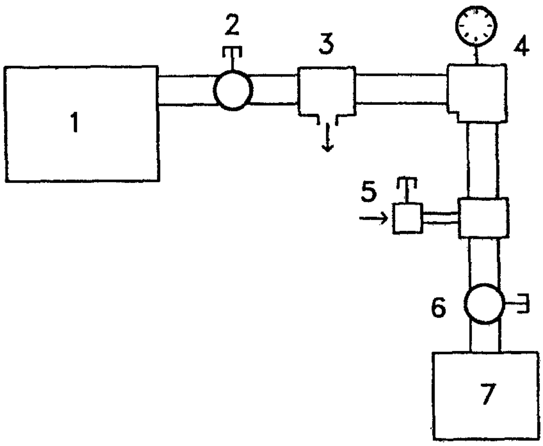

Fig. 1 Schematic of vacuum system; (1) TGA unit, (2) glass valve, (3) manometer, (4) mechanical pressure gage, (5) micrometering valve for air bleed, (6) flow restriction valve, (7) vacuum pump

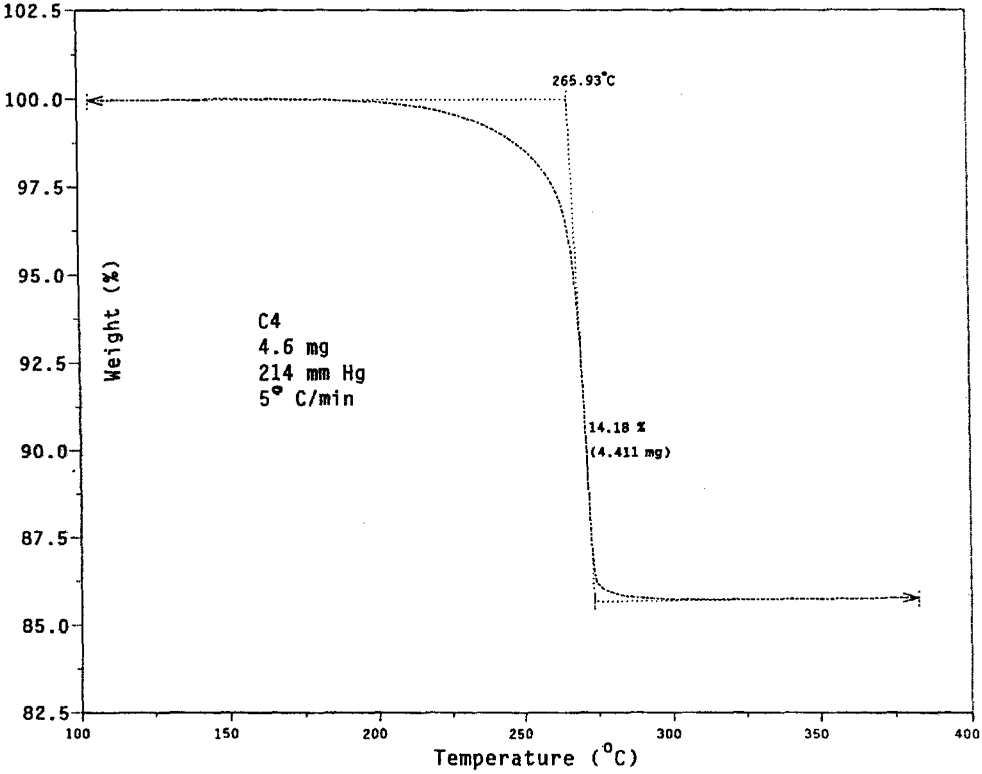

Fig. 2 Example data plot from TGA, showing tangents used to locate onset temperatures

drilled openings are 0.050 to 0.100 mm diameter [7]. Thermocouple placement was immediately outside the platinum holder, following TA Instruments recommendations. Approximately 5.0 mg samples (±1 mg) were placed in 20 μl pans with laser-drilled covers. To assist in achieving isothermal boiling, 0.5 mg of alumina powder (Baker chromatography grade) was added to the sample. The heating rate was set at 5°C $\min^{-1}$. Each experiment was conducted at constant pressures measured with a mercury manometer. Pressure was maintained at ±0.5 mm Hg by manually adjusting a micrometer-type air bleed valve. Beginning with an initial pressure of one atmosphere, each experiment was repeated at steps of decreasing pressure to 20 mm Hg.

The sample weight loss is determined as the difference between the initial and final weight. The boiling point at each pressure is taken as the onset of isothermal boiling. This point is the intersection of the tangent of the isothermal

Table 1 TGA-derived vapour pressures for 1-octanol and tributyrin

Sample	Sample size/ mg	Pressure/ mm Hg	Onset/ °C	Expected *T*/ °C	%Error
1-octanol	7.4	763	198.1	190.3	4.1
1-octanol	5.4	764	196.5	190.3	3.3
1-octanol	4.3	399	172.5	171.8	0.4
1-octanol	4.8	198	152.5	153.3	0.5
1-octanol	5.8	197	156.8	153.2	2.3
1-octanol	5.1	98	132.7	136.2	2.6
1-octanol	4.8	51	114.2	121.6	6.0
1-octanol	5.2	49	115.9	120.7	4.0
1-octanol	5.9	49	115.9	120.7	4.0
1-octanol	5.4	20	97.6	102.3	4.6
1-octanol	5.1	19	101.0	101.3	0.3
tributyrin	5.6	763	317.4	311.2	2.0
tributyrin	4.8	763	315.0	311.2	1.2
tributyrin	4.6	214	266.0	268.6	0.9
tributyrin	5.5	213	264.8	268.4	1.3
tributyrin	4.3	132	247.1	253.9	2.7
tributyrin	5.7	131	249.0	253.7	1.9
tributyrin	5.8	108	241.0	248.1	2.8
tributyrin	5.4	97	237.3	245.0	3.1
tributyrin	4.6	51	212.7	227.3	6.4
tributyrin	4.7	51	215.5	227.3	5.2
tributyrin	5.2	22	183.4	205.9	10.9
tributyrin	5.2	20	191.2	203.6	6.0

weight loss slope with the initial baseline as shown in Fig. 2. The TA Instruments data analysis software quickly determines this onset temperature.

To survey the potential accuracy of the TGA unit with the new pans, several compounds with known vapour pressure curves were examined, namely, 1-octanol, oleic acid, tributyrin, and tricaprin, over the range of ambient pressure to as low as 20 mm Hg. The 1-octanol of 99% purity, *MW* 130.2 g, was obtained from J. T. Baker. Oleic acid (99%), *MW* 282.5 g, and tricaprin (99%), *MW* 554.0 g, were supplied by Sigma. Tributyrin (98%), *MW* 302.4 g, was supplied by Aldrich Chemical Co.

Table 2 TGA-derived vapour pressure for tricaprin and oleic acid

Sample	Sample size/ mg	Pressure/ mm Hg	Onset/ °C	Expected *T*/ °C	%Error
tricaprin	4.5	764	395.3	419.3	5.7
tricaprin	4.3	764	394.3	419.3	6.0
tricaprin	4.3	127	346.9	368.5	5.9
tricaprin	4.8	125	356.0	368.1	3.3
tricaprin	4.5	22	319.7	325.5	1.8
tricaprin	5.5	21	312.4	324.4	3.7
oleic acid	4.9	767	352.1	357.2	1.4
oleic acid	4.8	765	351.1	357.1	1.7
oleic acid	5.4	350	322.6	328.1	1.7
oleic acid	5.3	149	297.5	299.4	0.6
oleic acid	5.3	149	295.7	299.4	1.2
oleic acid	4.6	74	272.1	277.8	2.1
oleic acid	5.4	51	259.6	267.0	2.8
oleic acid	4.7	22	227.4	244.0	6.8
oleic acid	5.0	21	223.8	242.8	7.8

Results and discussion

The data for TGA experiments is given in Tables 1 and 2 for vapour pressures from ambient to 20 mm Hg. Repeatability of the TGA data is greater than 99% at pressures as low as 20 mm Hg. In order to evaluate the accuracy of the TG data, observed values were compared to models developed from reference data. Reference compounds selected were either low *MW* triglycerides or compounds with similar physical and chemical properties.

The reference models are shown in Figs 3 and 4. These are Clausius-Clapeyron plots of log pressure *vs.* $1/T$ (K). Reference data for each of the compounds

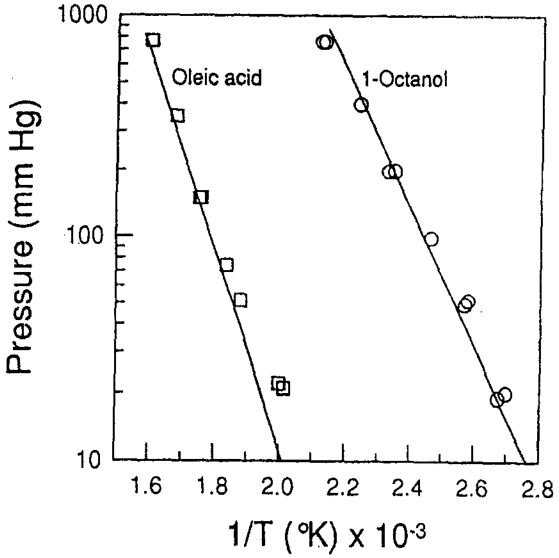

Fig. 3 Log pressure (mm Hg) *vs.* $1/T$ (K). Linear regression (lines) for data of Perry [8] compared to TGA data (points) for 1-octanol and oleic acid

is fitted by the linear regressions shown, typically with an R^2 fit of 0.99. Reference data is as follows: 1-octanol [8], oleic acid [8], tributyrin [9, 10] and tricaprin [10].

The "% error" columns of Tables 1 and 2 were calculated as follows. Comparison of TGA isothermal boiling temperature at pressure (i) with temperature predicted by the reference model at pressure (i) may be expressed as an error of deviation from the reference:

$$\% \text{error} = \frac{T_{\text{obs}} - T_{\text{model}}}{T_{\text{model}}}$$

In Fig. 3 the TGA data for oleic acid and 1-octanol are compared to their respective reference models. For these two compounds there are many pressure measurements from ambient down to 1 mm Hg. Reference vapour pressure data fits these two linear regressions with R^2 values of 0.999 and 0.998 respectively. For oleic acid, the TGA data deviates less than 6% from the model down to 50 mm Hg. For 1-octanol, the TGA data deviates less than 6% from the reference line down to 20 mm Hg.

In Fig. 4 the TGA data for C4, tributyrin, and C10, tricaprin are compared to their respective reference models. For C4 there are many pressure measurements from ambient down to less than 1 mm Hg. Deviations from the reference are less than 6% at pressures above 70 mm Hg. For C10, the reference regres-

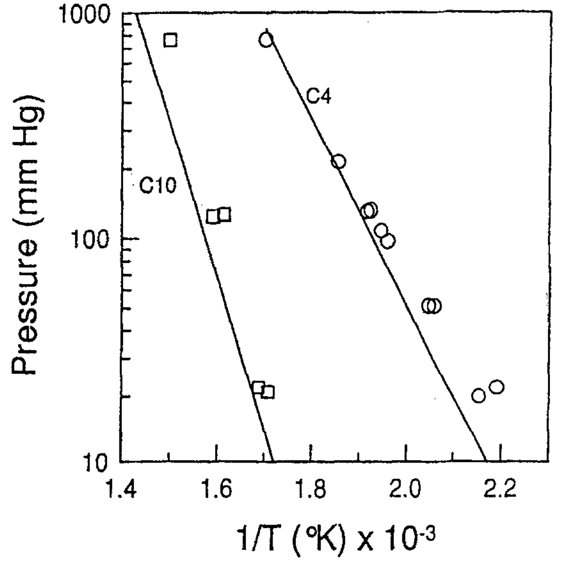

Fig. 4 Log pressure (mm Hg) *vs.* 1/*T* (K). Linear regression (line) for tributyrin (C4): Perry [10], Weatherby [9], and Newmann [11] compared to TGA data (points). Linear regression (line) for Tricaprin (C10): Perry [10], compared to TGA data (points)

sion is based on three points, 763 mm, 0.5 mm and 0.001 mm (R^2 = 0.9996). The fit of the TGA data to this very limited model is predictably poor (Table 2). However, if the reference and TGA data above 20 mm Hg together are fitted to a linear regression, the R^2 is 0.9991. Thus, the TGA data in this case is also in close agreement with ideal Clausius-Clapeyron behaviour.

At lower pressures, depending on the compound studied, the TG data has deviation errors greater than 6%. The observed temperatures in several compounds are consistently lower – fitting a second order regression – than the true isothermal boiling point which follows a linear regression. It is suggested that sample pans with different sizes of laser-drilled orifices may be helpful. Another alternative is to fit TGA data with the Antoine equation if there is evidence that the vapour does not behave as an ideal gas or if the heat of vaporization is not constant over the temperature range of interest.

Conclusions

A preliminary study using TGA with laser-drilled pans suggests that one may obtain quick and accurate measurements of vapour pressure over selected broad pressure ranges.

For the TA Instruments Model 951 TGA unit, vapour pressures from ambient down to 20 mm Hg were measured by attachment of a vacuum system.

From ambient down to 20 mm Hg, 1-octanol and tricaprin had measured values of temperature/vapour pressure that were within a 6% error of deviation from the Clausius-Clapeyron equation for reference values. For oleic acid and tributyrin, vapour pressures as low as 50 mm and 100 mm, respectively, followed the above 6% error criterion.

For the compounds studied, optimal conditions for DSC determination of vapour pressure (sample size, heating rate, and use of inert diluents) appear to be equally suitable for TGA measurement of vapour pressure, if laser-drilled pans are used.

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