Rapid Measurements of Boiling Point and Vapor Pressure of Short-Chain Triglycerides by Thermogravimetric Analysis

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ABSTRACT: Temperature dependence of vapor pressure and the boiling points for tricaproin (Tcap) and tricaprylin (Tcpy) were measured by a new rapid thermogravimetric analysis (TGA) method. Results were in agreement with data from other references. The Clausius/Clapeyron model fitted Tcap and Tcpy vapor pressure data with errors of 6% or less for pressures ranging from ambient down to 20 mmHg. This agreement with the model suggests that the vapor of these compounds has a large degree of ideal gas behavior and that their vaporization enthalpies are nearly constant from 25 to 400°C. Comparable accuracy and precision were obtained with TGA and differential scanning calorimetry methods for the compounds tested; however, TGA plots had significantly straighter baselines, which made vapor pressure determinations more convenient.
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KEY WORDS: Boiling point, DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), tricaproin, tricaprylin, triglyceride, vapor pressure, vaporization enthalpy.

The temperature dependence of vapor pressure and the nominal boiling point (b.p.) at one atmosphere are of interest in predicting the pressure atomization characteristics of substitute diesel fuels based on triglycerides. From vapor pressure data, one may calculate the heat of vaporization, ΔHv, that in turn may be used to estimate atomization characteristics of fuels (1). Because it is anticipated that substitute fuels will consist of triglyceride mixtures, the vapor pressure and effective heat of vaporization of pure triglycerides are useful in selecting appropriate models for either ideal or nonideal solution behavior of triglyceride mixtures. With the correct model one can generate, for example, ΔHv values of mixtures for use in atomization simulations.

Thermogravimetric analysis (TGA) has recently been shown to be a rapid means of quantifying vapor pressure of selected organic compounds (2). The TGA method was applied to organic liquids in the 100- to 500-g molecular weight range. Boiling points and vapor pressure were found for tributyrin (Tbu), tricaprin (Tcp), 1-octanol, and oleic acid (C18:2). Samples were sealed in aluminum capsules with a laser-drilled opening in the lid. Vapor pressure data were taken at temperatures between 25 and 400°C and at pressures from ambient down to 20 mm Hg. By analogy to differential scanning calorimetry (DSC) studies (3,4), it was assumed that a liquid–vapor equilibrium was established inside the capsule at the boiling point. The laser-drilled opening permitted vapor pressure balance between the sample and the controlled environmental pressure. An inert diluent, powdered alumina, reduced the rate of vaporization as the sample approached its boiling point and reduced superheating tendencies (5). For the pressure range from ambient down to 20 mm Hg, results were within 6% of results reported by other investigators (6–8).

The primary objective of this study was to use small (approximately 5 mg) samples to obtain vapor pressures and boiling points rapidly for the short-chain triglycerides tricaproin (Tcap) and tricaprylin (Tcpy). The other study objective was to make a brief comparison between the TGA and DSC methods for obtaining vapor pressure data of triglycerides.

MATERIALS AND METHODS

Thermogravimetric analysis (TGA) data were obtained with a TA Instruments (Newcastle, DE) Model 951 thermobalance with quartz furnace tube. At ambient pressure, a 50 mL/min N_2 purge flow was used. Subatmospheric pressures were obtained with a mechanical vacuum pump (Edwards, model 5, 2 stage) and manually controlled airflow restriction valves. The platinum sample support was reshaped to accommodate the laser-drilled holders obtained from the Perkin-Elmer Corp. (Norwalk, CT) (part no. N5190788). The drilled openings were 0.050–0.100 mm in diameter (9). Thermocouple placement was immediately outside the platinum holder to follow TA Instruments recommendations. Approximately 5.0-mg samples (±1.0 mg) were placed in 20-μL pans with laser-drilled covers. To assist in achieving isothermal boiling, 1.25 mg (±0.25 mg) of alumina powder (Baker chromatography grade) was added to the sample. The heating rate was set at 10°C/min. Each experiment was conducted at constant pressure, measured with a mercury manometer. Pressure was maintained at ±1.0 mm Hg by manually adjusting a micrometer-type air bleed valve.

A plot of a typical TGA experimental run is given in Figure 1. The onset of isothermal boiling is taken as the boiling

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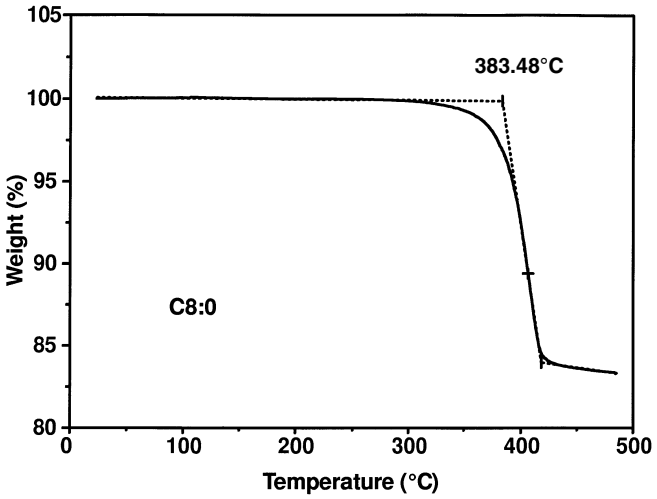

FIG. 1. Typical TGA plot for a pure short-chain triglyceride.

point at each pressure. This point is the intersection of the tangent of the isothermal weight loss slope with the initial baseline, as shown in Figure 1. The TGA data analysis software determines this onset temperature. To check the accuracy of the TGA unit for vapor pressure, a well-characterized compound, 1-octanol (6), was selected as a standard reference. In view of reports by Seyler (3,5) with the laser-drilled sample holders, reference materials were chosen to have molecular weights, boiling points, viscosities, and chemical functional groups similar to the compounds under study.

A Perkin Elmer model DSC-2 supplied boiling point data at 1 atm pressure. Nitrogen purge flow through the cell was maintained by 1.36 atm (20 psi) of pressure applied to the DSC module. Samples were enclosed in the same holders used for TGA. Approximate sample weight, alumina weight, and heating rate were also the same as those used for TGA. A plot of a typical DSC experimental run with tricaprylin is shown in Figure 2. As with TGA, the boiling point was taken to be the onset of isothermal boiling. 1-Octanol was used as a reference boiling point material.

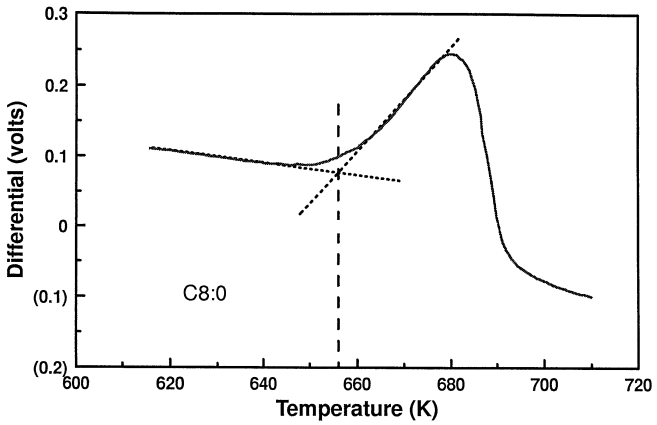

FIG. 2. Typical DSC plot for a pure short-chain triglyceride.

Vapor pressure data were collected for pure tricaproin (99%, MW 386.5 g/mole) and tricaprylin (97.5%, MW 470.7 g/mole), both supplied by Sigma Chemical Co. (St. Louis, MO). 1-Octanol (reagent grade, MW 130.2 g/mole) was obtained from Baker Chemical (Phillipsburg, NJ). Alumina powder (Baker chromatography grade) was used as diluent.

Significant errors may result from an improperly sealed sample holder. In general, if two or three replicate runs agree within 6% or less, this study suggests that one may have confidence in the accuracy of the results. If the TGA replicates have a greater variance than 6%, this often indicates that the aluminum capsules were not sealed correctly and that the sample may leak out or evaporate at excessive rates. Under these conditions, typically a low value for the boiling point will be obtained. These experimental problems may be minimized by reproducibly sealing the capsule and by use of a low-power sterioscope to examine the sealed capsule before the TGA experiment. Evidence of mechanical damage due to over- or undersealing and leaking sample liquids may be visible. After the TGA run, microscopic examination may also reveal evidence of leaking in the form of charred external films on the sides and bottom of the pans.

RESULTS AND DISCUSSION

TGA-derived vapor pressure data for 1-octanol, Tcap, and Tcpy are given in Figures 3 and 4. The data for Tcap and Tcpy are shown as Clausius/Clapeyron plots, log P vs. $-(A/T) + B$, where P is in mm Hg and T is in Kelvin. Literature data for Tcap (8) and Tcyp (8,10,11) were fitted by the linear regressions shown. 1-Octanol reference data (8) were also plotted (not shown) to obtain a model equation.

As in previous work (2), TGA data were compared to regressions developed from literature data to measure the accuracy of this TGA method. The "% error" column of Table 1 was calculated as follows. Comparison of TGA isothermal

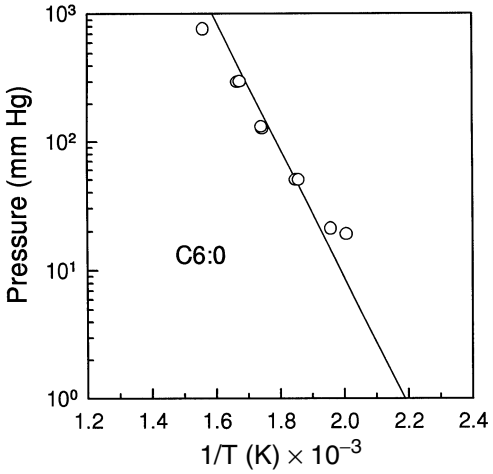

FIG. 3. TGA-derived temperature dependence of vapor pressure for tricaproin, C6:0. Regression through literature data points of Perry *et al.* (Ref. 8). $R^2 = 1$, $y = -4.997x + 10.94$.

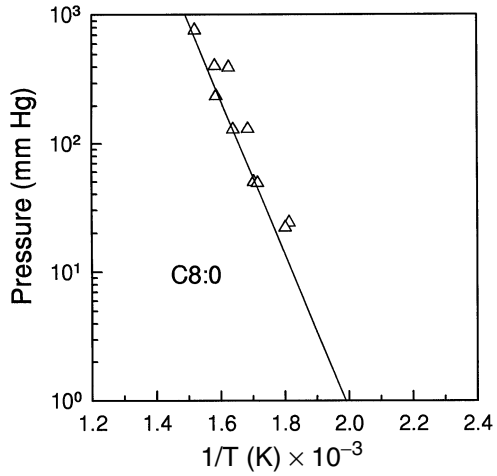

FIG. 4. TGA-derived temperature dependence of vapor pressure for tricaprylin, C8:0. Regression through literature data points of Perry *et al.* (Ref. 8), Hershberg (Ref. 11), and Strelets and Kammennov (Ref. 10). $R^2 = 0.991$, $y = -6.006x + 11.952$.

TABLE 1
TGA-Derived Vapor Pressure Data

Compound	Sample size (mg)	Pressure (mm Hg)	Boiling point (°C)	Boiling point ref. (°C)[a]	% Deviation[b]
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
Tcap[c]	5.4	21	237.8	246.5	3.5
Tcap	5.0	50	268.0	267.6	0.1
Tcap	4.5	50	265.1	267.6	0.9
Tcap	4.9	132	300.9	293.5	2.5
Tcap	4.6	127	300.3	292.3	2.7
Tcap	4.8	302	323.6	317.5	1.9
Tcap	4.9	299	326.5	317.2	2.9
Tcap	5.5	760	362.2	346.9	4.4
Tcap	4.7	760	368.1	346.9	6.1
Tcpy[d]	5.3	24	278.4	295.1	5.7
Tcpy	5.3	22	281.9	293.1	3.8
Tcpy	5.1	50	313.8	312.8	0.3
Tcpy	5.3	49	309.7	312.3	0.8
Tcpy	5.6	131	319.5	337.7	5.4
Tcpy	5.2	130	337.0	337.5	0.1
Tcpy	5.1	239	357.0	354.4	0.7
Tcpy	4.5	407	358.9	369.9	3.0
Tcpy	4.6	397	341.9	369.1	7.4
Tcpy	4.7	760	385.2	389.0	1.0
Tcpy	4.3	760	385.3	389.0	1.0

[a]Reference temperature from a linear regression fitted to literature sources: tricaproin (8), tricaprylin (8,11,10). [b]Boiling point deviation, $(T_{obs} - T_{ref})/T_{ref}$, where T_{obs} is data at pressure (x) and T_{ref} is the reference temperature pressure (x). [c]Tcap is tricaproin. [d]Tcpy is tricaprylin.

boiling temperature at pressure (x) with temperature predicted by the reference model at pressure (x) was expressed as an error of deviation from the reference: (% error) = $(T_{obs} - T_{ref})/T_{ref}$. For Tcap, the reference vapor pressure measurements were below 0.1 mm Hg. In spite of the long extrapolation of the reference regression, the TGA data of Table 1 deviated from the reference regression by 6% or less for pressures from ambient down to 20 mm Hg. For Tcpy, the TGA data of Table 1 deviated by 7% or less from the reference regression; the average deviation was 3%. Also, if the reference and TGA data above 20 mm Hg together are fitted to a linear regression, R^2 is 0.9953 for Tcap and 0.9965 for Tcpy. Thus, both TGA and reference data are in close agreement with ideal Clausius/Clapeyron linear behavior. Finally, the linear regression (R^2) factors for Clausius/Clapeyron plots of TGA data for Tcap and Tcpy range from 0.94 to 0.99.

The percent deviation of DSC-derived boiling point data for 1-octanol, Tcap, and Tcpy is compared in Table 2 with

TABLE 2
TGA- and DSC-Derived Boiling Point Data at 1 atm for 1-Octanol, Tricaproin, and Tricaprylin

Compound	Sample (mg)	TGA (°C)	DSC (°C)	Ref. boiling point	% Deviation[a]
1-Octanol	4.7		190.0		2.7
1-Octanol	4.5		192.5		1.4
1-Octanol	5.2		193.9		0.7
1-Octanol	7.4		193.1		1.5
1-Octanol	5.4		196.5		0.7
1-Octanol	5.8		200.5		2.7
Ave. 1-octanol (TGA)			198.4		1.6
Ave. 1-octanol (DSC)			192.1		1.6
1-Octanol std.				195.2[b]	
Tcap[c]	5.5		362.5		4.5
Tcap	5.8		365.0		5.2
Tcap	5.3		362.5		4.5
Tcap	5.5	368.2			6.1
Tcap	4.7	368.1			6.1
Tcap	5.8	368.4			6.2
Ave. Tcap (TGA)		368.2			6.1
Ave. Tcap (DSC)			363.3		4.7
Tcap std.				347.0[d]	
Tcpy[c]	5.8		381.5		2.0
Tcpy	4.9		374.5		3.7
Tcpy	4.7		384.0		1.3
Tcpy	4.7	385.2			1.0
Tcpy	4.3		385.3		1.0
Tcpy	5.6	382.3			1.7
Ave. Tcpy (TGA)		384.3			1.2
Ave. Tcpy (DSC)			380.0		2.3
Tcpy std.				389.1[d]	

[a]Boiling point deviation, $(T_{obs} - T_{ref})/T_{ref}$, where T_{obs} is the data at 1 atm and T_{ref} is the reference temperature at 1 atm.
[b]*Chemical Engineer's Handbook* (Ref. 6).
[c]Tcap is tricaproin and Tcpy is tricaprylin.
[d]1-atm boiling point extrapolated from Clausius/Clapeyron plot of Perry *et al.* (Ref. 8) data.
[e]1-atm boiling point extrapolated from Clausius/Clapeyron plot of Perry *et al.* (Ref. 8), Hershberg (Ref. 11), and Strelets and Kammennov (Ref. 10) data.
DSC, differential scanning calorimetry; TGA, thermogravimetric analysis.

TABLE 3
Heat of Vaporization Calculated from TGA Data

Compound	Boiling point[a] (K)	Boiling point[b] (K)	A[c]	B[c]	R^2	ΔHv[d] (J/g mole)
Tbu[e]	590.94	471.45	3272.95	8.4194	0.9939	62,555.90
Tcap[e]	646.43	519.22	3794.98	8.7808	0.9908	72,553.45
Tcpy[e]	657.76	562.19	5431.18	11.1379	0.9368	103,806.14
Tcp[e]	67.10	594.61	7680.85	14.3939	0.9908	146,795.21

[a]@ 760 mm Hg.
[b]@ 30 mm Hg.
[c]Constants A and B are from the Clausius/Clapeyron regression equation, log $P = -(A/T) + B$, where P = mm Hg and T is K. Regressions fitted to data of author.
[d]ΔHv = 2.3(A)(R), where R = 8.31 J/g·mole·K (8).
[e]Tbu is tributyrin, Tcap is tricaproin, Tcpy is tricaprylin, and Tcp is tricaprin. Data for Tbu and Tcp from Goodrum and Siesel (Ref. 2). See Table 2 for other abbreviation.

representative values for TGA-derived boiling points. Note that data from each method agree within 6% with their respective literature reference values. One striking difference between the TGA and DSC output plots is the relative simplicity of the TGA plot. Because the TGA output is sensitive to weight loss and not sensitive to heat capacity and other relatively small thermal changes occurring in the sample, the output TGA plot has much straighter baselines and an absence of peaks due to secondary thermal transitions. This makes analysis of TGA vapor pressure plots faster because there is only one clear-cut transition on the plot .

Close agreement of triglyceride data with the Clausius/Clapeyron model suggests that mixtures of the short-chain triglycerides tributyrin–tricaprin will behave as near-ideal solutions with consequent linear heat of vaporization changes as a function of mole fraction. Average vaporization enthalpies are included in Table 3.

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