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DSC enthalpy of vaporization measurements of high temperature two-phase working fluids[1]

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Abstract

The enthalpies of vaporization, saturated pressure–temperature behavior, and melting points for high-temperature (300–400°C) two-phase working fluids were measured using high-pressure DSC methodologies similar to those currently under development by ASTM E37. The materials, biphenyl, decafluorobiphenyl, *o*-terphenyl, naphthalene, quinoline, and perfluoro-1,3,5-triphenylbenzene, were studied at seven pressures between 50 kPa and 1.4 MPa. The experimental measurements employed the use of a Mettler Pressure DSC and sealed aluminum sample/reference pans having a laser-drilled (0.10–0.13 mm orifice) lid. The vaporization pressure–temperature data were curve fitted to the Antoine equation using Marquardt–Levenberg non-linear regression, and the enthalpy of vaporization was then computed from the Clapeyron equation. The results were compared to literature values, where available, and water was also included in the study at each DSC-scan pressure to evaluate the accuracy of the method. Overall, the technique produced saturated pressures which were within 6% (2 standard deviations, 2σ) of literature values, and the standard deviation (σ) associated with the Antoine curve fits was less than 3%. Enthalpy of vaporization data computed from the Clapeyron equation were within 4% of literature values for biphenyl, naphthalene, quinoline, and water, and within 12% for *o*-terphenyl.

Keywords: DSC; Enthalpy; Vaporization; High-temperature two phase working fluid

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1. Introduction

The objective of this effort was to evaluate the fusion and vaporization thermodynamic properties of high-temperature working fluids. Some materials which were identi-

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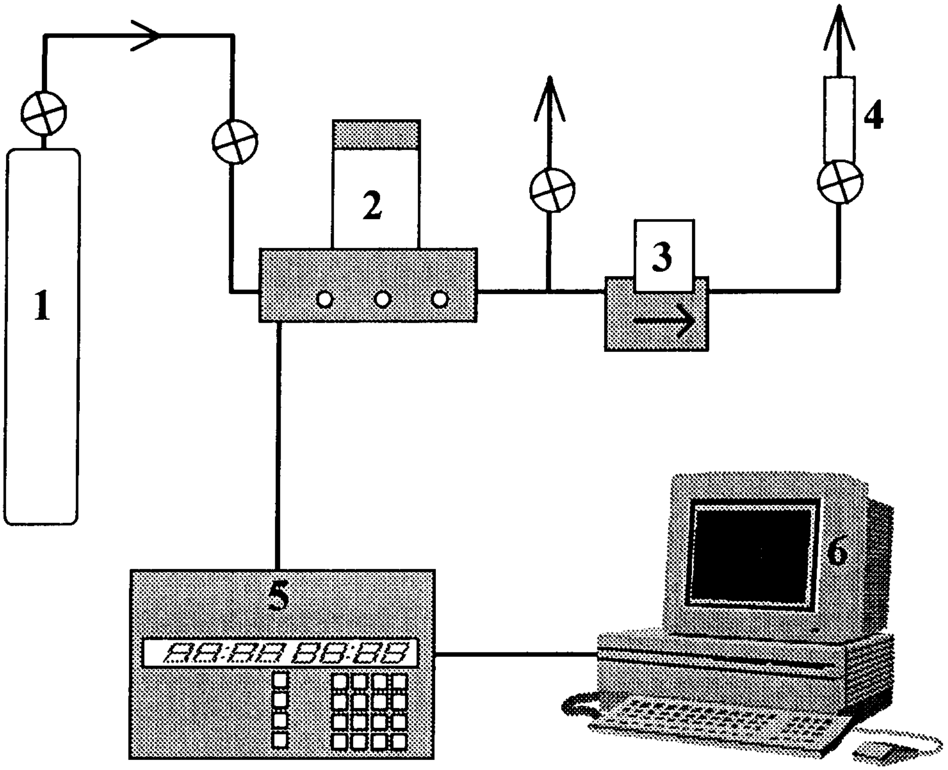

Fig. 1. Schematic of experimental setup: 1, nitrogen cylinder for purge gas; 2, Mettler DSC 27HP; 3, Brooks 5866 pressure controller; 4, rotameter; 5, Mettler TC11 TA processor; 6, PC running Mettler Graphware TA72 analysis software.

fied for use in specific space application thermal management systems had not yet been characterized, or not characterized in the temperature and pressure ranges of interest. Six organic materials were identified and procured for this study. The specific thermodynamic properties of interest included melting points, boiling points, and enthalpies of vaporization. The authors began developing a technique utilizing high-pressure DSC and sample vaporization with the objective of measuring enthalpies of vaporization directly over a pressure range from vacuum to several atmospheres. However, the difficulties associated with mass uncertainties through the vaporization endotherm and pressure uncertainties associated with sealed samples pans made this task non-trivial. In developing an alternate approach of indirectly calculating the enthalpy of vaporization with pressure–temperature points and an Antoine equation, it was learned that ASTM E37 was in the final stages of detailing such a method [1]. The general procedures under development by ASTM E37 were integrated into the working-fluid characterization study described here. This work thus describes the results of a study aimed at determining the pressure–temperature relationship and enthalpy of vaporization for six high temperature working fluids and water using a high-pressure DSC and finely drilled aluminum crucible lids.

2. Experimental method, instrumentation, and materials

A Mettler 27HP DSC was used for the measurements with a Brooks 5866 Pressure Controller downstream of the DSC module. The DSC cell was continuously purged with N_2 between 0.5 and 1 l min^{-1} (STP) while the cell was maintained at constant pressure. A schematic of the experimental setup is shown in Fig. 1. The pressure controller is rated at an accuracy of 0.5% full scale (±6.9 kPa) and 0.1% repeatability (±1.5 kPa). Temperature scan rates β of 5°K min^{-1} were used for all calibration and experimental runs. The temperature accuracy of the DSC system and repeatability are assumed to be ±0.5–1.0°K as measured by standard material checks during the experimental runs and also from correspondence with Mettler application specialists.

Following the method currently under development by ASTM E37, aliquots (2–20 mg) of the materials were weighed and sealed in 40 μl aluminum crucibles with a lid having a 0.10–0.13 mm laser-drilled orifice (Lasertron, Sun Rise, Florida). Samples were ramped in temperature at 5°K min^{-1}, and the phase-change endotherms were recorded. Melting and boiling points were then evaluated using Mettler TA72 GraphWare software, and transferred through the QNX operating system to DOS running graphics/statistics software for display and curve fitting.

The materials evaluated in this study were: biphenyl (C_6H_5–C_6H_5, purity 99%, RN 92-52-4), *o*-terphenyl (C_6H_5–C_6H_4–C_6H_5, 99%, RN 84-15-1), naphthalene ($C_{10}H_8$, 99%, RN 91-20-3), and quinoline (C_9H_7N, 98%, RN 91-22-5), all procured from Aldrich and distilled at Mainstream Engineering; perfluoro-1,3,5-triphenylbenzene (C_6F_3–$[C_6F_5]_3$, RN

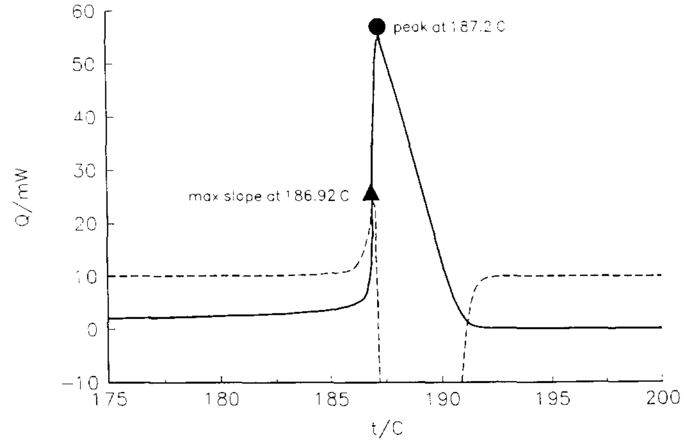

Fig. 2. DSC temperature scan (5°C min^{-1}) for naphthalene at 47.6 kPa with maximum-slope boiling temperature (▲) and peak boiling temperature (●). DSC $Q/mW - t/C$ scan and dQ/dt curve are represented by the solid and dashed curves, respectively.

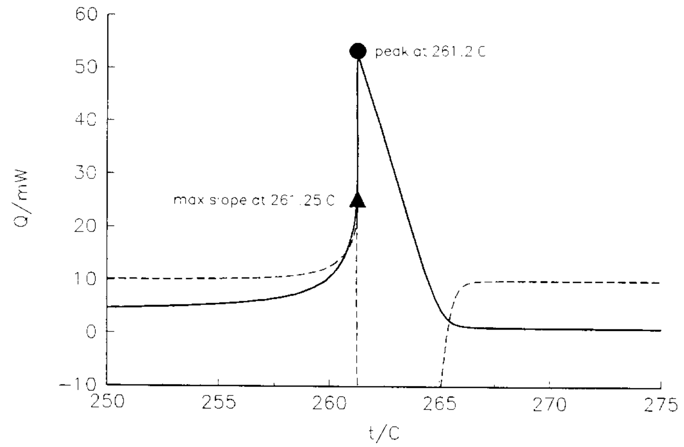

Fig. 3. DSC temperature scan (5°C $\min^{-1}$) for decafluorobiphenyl at 343.4 kPa with maximum-slope boiling temperature (▲) and peak boiling temperature (●). DSC *Q/mW – t/C* scan and d*Q*/d*t* curve are represented by the solid and dashed curves, respectively.

612-71-5), synthesized and purchased from FAR Research, Palm Bay, FL, and recrystallized at Mainstream Engineering; and, decafluorobiphenyl (C_6F_5–C_6F_5, 99%, RN 434-90-2), purchased from Ryan Scientific and distilled at Mainstream Engineering.

The DSC was calibrated with three temperature points over the range of 30–420°C using gallium (m.p. 29.8°C, purity 99.9999%, Aldrich, RN 7440-55-3), bismuth (m.p. 271.3°C, purity 99.99%, Aldrich, RN 7440-69-9), and zinc (m.p. 419.6°C, purity

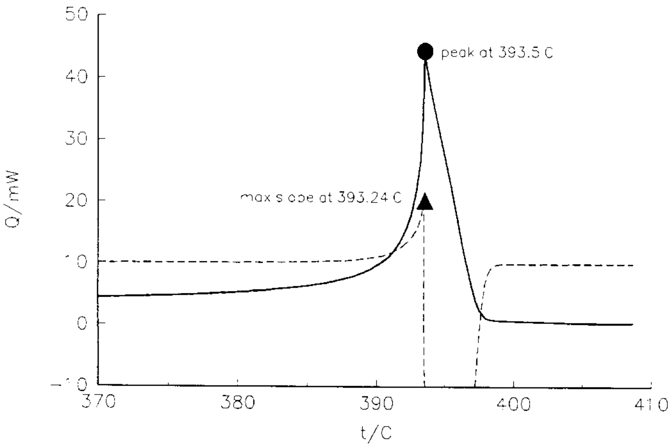

Fig. 4. DSC temperature scan (5°C $\min^{-1}$) for biphenyl at 1.034 MPa with maximum slope boiling temperature (▲) and peak boiling temperature (●). DSC *Q/mW – t/C* scan and d*Q*/d*t* curve are represented by the solid and dashed curves, respectively.

99.998%, Aldrich, RN 7440-66-6). The true melting points of these standards used in the calibration of the DSC were assumed invariant with pressure.

The protocol for selecting melting and boiling points, and the calibration temperatures, was the maximum in the heat flow-temperature derivative (d*Q*/d*t*) curve. Example vaporization scans for naphthalene at 47.6 kPa, decafluorobiphenyl at 343.4 kPa, and biphenyl at 1.034 MPa are shown in Figs. 2–4, respectively. The maximum in the heat flow curve is denoted by the symbol ●, and the maximum first derivative (or slope) in the heat flow curve is denoted by ▲. The maximum first derivative protocol for temperature selection was recommended by Mettler specialists as having a high degree of repeatability, and was therefore used for all calibration and sample runs. Other temperature selection protocols such as onset and peak temperatures should not alter the applicability of the DSC method described in this study, provided the method is used consistently with calibration and sample studies.

3. Experimental results and data treatment

Six organic materials and water were examined using this DSC method to characterize both the melting and boiling points at pressures ranging from 50 kPa to 1.4 MPa. The vaporization data were then curve fitted to the Antoine equation:

$$\log_{10}(P/\mathrm{kPa}) = a - \frac{b}{(t/^\circ\mathrm{C}) + c} \tag{1}$$

using linear-least-squares procedures within DOS-PC Microsoft Excel spreadsheet software, and then with Marquardt–Levenberg [2] non-linear least squares regression software (AXUM by TriMetrix, Inc.). In Eq. (1), P is pressure in kPa, t is temperature in °C, and a, b, and c are Antoine equation constants. The data were fitted to Eq. (1) in order to minimize the residual error function ε in pressure estimates [3] defined as

$$\varepsilon = \sum_{i=1}^{N}\left(\frac{P_i^{\mathrm{calc}} - P_i}{P_i}\right)^2 \cong \sum_{i=1}^{N}\left(\log\frac{P_i^{\mathrm{calc}}}{P_i}\right)^2 \quad \text{as} \left|P_i^{\mathrm{calc}} - P_i\right| \to 0 \tag{2}$$

where N is the number of data points fitted, ε is the residual error function, P_i^{calc} is the pressure estimate from the curve fit, and P_i is the actual pressure data point. Note that the equality in Eq. (2) is a very close approximation when the relative error $(P_i^{\mathrm{calc}} - P_i)/P_i$ is small (i.e. less than 0.15, or 15%). Substituting Eq. (1) into Eq. (2), the resulting error function equation can be rewritten as

$$\varepsilon = \sum_{i=1}^{N}\left(\log\frac{P_i^{\mathrm{calc}}}{P_i}\right)^2 = \sum_{i=1}^{N}(\log P_i^{\mathrm{calc}} - \log P_i)^2 = \sum_{i=1}^{N}\left(a - \frac{b}{t_i/^\circ\mathrm{C} + c} - \log P_i\right)^2 \tag{3}$$

where t_i is the experimental temperature (in °C) of vaporization corresponding to pressure P_i. Consequently, minimizing the residual of the Antoine equation with P expressed non-linearly as $\log_{10} P$ results in the constants a, b, and c which minimize the error function ε, or percent error of the fit. The specific convergence criterion used for the Marquardt–Levenberg non-linear regression was a 0.01% or less change in the sum of squared residuals after each iteration relative to the sum of squared residuals at the current iteration of Eq. (3). The standard deviation percent error ($\sigma_{\%}$) associated with the minimized error function of Eq. (3) can be defined as

$$\sigma_{\%} = 100\sqrt{\frac{\varepsilon}{N-1}} \tag{4}$$

with $2\sigma_{\%}$ therefore being a measure of the expected percent error of the fit at 95% confidence.

The complete least squares regression analysis was carried out by first calculating the "initial" constant values a_0, b_0, and c_0, from a linear least squares curve fit of the rearranged Antoine equation (Eq. 1):

$$t \log_{10} P = a_0 t - c_0 \log_{10} P + (c_0 a_0 - b_0) \tag{5}$$

which is linear in constant coefficients a_0, b_0, and c_0. Note that a linear least squares analysis of Eq. (5) minimizes the residual of ($t \log_{10} P$), not P or $\log_{10} P$. The values of a_0, b_0, and c_0 were then used as starting values for a non-linear regression of the Antoine equation (Eq. 1), minimizing the residual of Eq. (3) to determine the constants a, b, and c of Eq. (1). Non-linear regression of Eq. (1) leads to values for a, b, and c which differed only slightly from a_0, b_0, and c_0. A summary of the non-linear regression results are given in Table 1. The $2\sigma_{\%}$ error of the fit is given, in addition to the 2σ percent error of the measured pressures relative to correlations reported in DIPPR [4] at the same temperatures. The non-linear Antoine equation curve fits and data points are given for naphthalene, biphenyl, and *o*-terphenyl in Fig. 5, decafluorobiphenyl, quinoline, and per-

Table 1

Summary of non-linear least squares curve fits to the Antoine equation

Fluid	Antoine constants			t range in °C	2σ percent errors	
	a	b	c		Curve fit	DIPPR [4]
Biphenyl	6.493	2123.12	217.76	222–415	1.85	2.60
Decafluoro-biphenyl	7.025	2239.78	239.15	180–335	6.26	–
o-Terphenyl	6.718	2639.94	222.61	303–513	4.10	5.24
Naphthalene	6.464	2035.46	238.13	187–374	1.46	3.10
Perfluoro-TPB	7.223	2550.04	140.97	319–476	16.41	–
Quinoline	6.357	1938.13	208.03	207–395	1.30	2.93
Water	6.995	1572.27	214.97	81–193	2.98	5.46

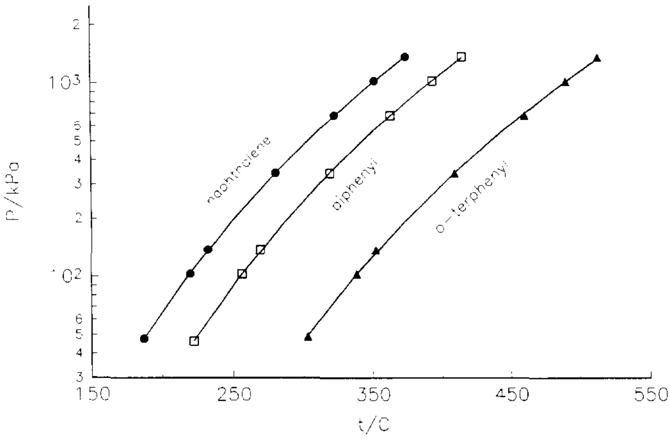

Fig. 5. Antoine equation curve fits (solid lines) and DSC pressure–temperature data points for naphthalene (●), biphenyl (☐), and *o*-terphenyl (▲).

fluoro-1,3,5-triphenylbenzene in Fig. 6, and water in Fig. 7. In Fig. 7, several steam table points [5] are also given for comparison to the DSC data and Antoine regression curve.

It should be noted that the minimization of a residual function linear in pressure (i.e. Eq. (2) without P_i in the denominator) does not minimize the percent error. Accordingly, the authors concluded that a curve fit based on minimizing the pressure residual (i.e. $P_i^{\mathrm{calc}} - P_i$) resulted in over-leveraged high pressure curve-fit estimates at the expense of large relative errors for low pressure estimates (e.g. 10–30%).

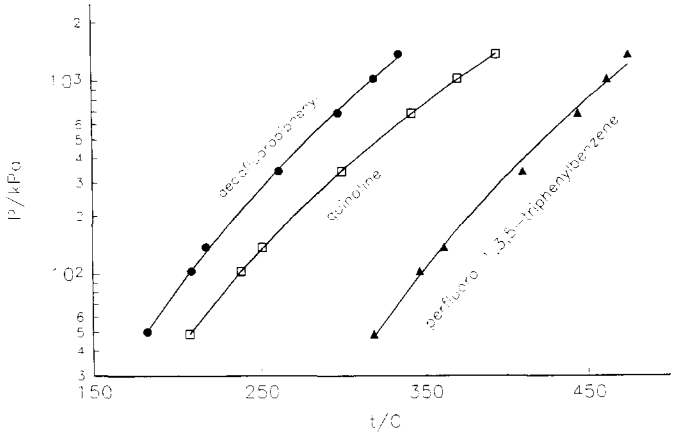

Fig. 6. Antoine equation curve fits (solid lines) and DSC pressure–temperature data points for decafluorobiphenyl (●), quinoline (☐), and perfluoro-1,3,5-triphenylbenzene (▲).

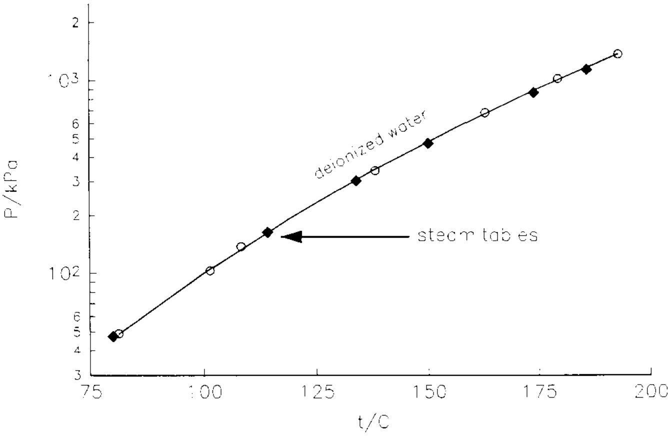

Fig. 7. Antoine equation curve fits (solid lines) and DSC pressure–temperature data points for deionized water (O), and selected steam table [5] pressure–temperature points (◆) for comparison.

4. Discussion and conclusions

The use of high-pressure DSC for the determination of phase-change thermodynamic properties has been found to provide accurate vapor pressure–temperature and enthalpy of vaporization data in agreement with literature values. Two thermodynamic properties were measured for each fluid at each pressure setting: melting point and boiling point. The boiling temperatures were then used with each DSC pressure to construct an Antoine equation over the pressure range of 50 kPa to 1.4 MPa. This method, currently under development by ASTM E37, can be used to generate vaporization data suitable for chemical/thermal system design or the assimilation of tables.

As shown in Table 1, the non-linear Antoine curve fits yielded $\pm 2\sigma_{\%}$ errors of 1–7%, excluding the results for perfluoro-1,3,5-triphenylbenzene. Also shown in Table 1, the experimental pressure data fell within 6% ($\pm 2\sigma$) of literature and other correlation values at the same temperatures. The regression errors of the DIPPR correlations for saturated pressure of biphenyl, *o*-terphenyl, naphthalene, quinoline, and water are reported as ±3%, ±10%, ±1%, ±3%, ±0.2%, respectively, which are comparable to the standard errors ($\sigma_{\%}$) of the curve fits developed in this study.

Perfluoro-1,3,5-triphenylbenzene was found to decompose at the higher pressures and temperatures of the study as evidenced by a black residue in the aluminum sample crucible after completion of the temperature scan. The temperature scans for perfluoro-1,3,5-triphenylbenzene were also characterized by noisy baselines for pressures exceeding about 345 kPa (corresponding to a boiling point of 410.4°C). Consequently, the Antoine equation may only adequately fit the data over a limited range at low pressures (and temperatures) for perfluoro-1,3,5-triphenylbenzene. Similar baseline noise in DSC scans was encountered for *o*-terphenyl at pressures exceeding 1.03 MPa, which corresponds to a vaporization temperature for the fluid of 492°C or greater. The curve in Fig. 6 for perfluoro-1,3,5-triphenylbenzene, and the curve in Fig. 5 for *o*-terphenyl, compared to the other materials in Figs. 5–7, also suggests anomalous behavior of perfluoro-1,3,5-triphenylbenzene and *o*-terphenyl due to more scatter in the data about the Antoine curve fit. These two materials had the highest boiling points among the group of materials studied, so the baseline instabilities and pressure–temperature data scatter are believed to be either directly (e.g. thermal instabilities within the DSC cell) and/or indirectly (e.g. decomposition) related to the high DSC temperatures.

The enthalpy of vaporization was of central interest in this study. Since the DSC does not in itself provide a means to directly measure the enthalpy of vaporization ΔH_{vap} due to mass loss during the process, the exact thermodynamic relationship of Clapeyron [5] was used to calculate ΔH_{vap} from pressure–temperature data. The Clapeyron equation is expressed as

$$\Delta H_{\text{vap}} = T(V^{\text{v}} - V^{\text{l}})\frac{\mathrm{d}P}{\mathrm{d}T} \tag{6}$$

where V^{v} is the molar vapor volume, V^{l} is the molar liquid volume, T is temperature in K, and T and P are the saturated pressure and temperature. The vapor and liquid volumes as a function of temperature were experimentally determined in previous studies, and the derivative in Eq. (6) is determined from the Antoine expression of Eq. (1). The final expression for ΔH_{vap}, after substituting $\mathrm{d}P/\mathrm{d}t$ per the Antoine equation, is given as

$$\Delta H_{\text{vap}}(T,P) = 2.303(V^{\text{v}} - V^{\text{l}})\frac{b(T/\text{K})(P/\text{kPa})}{[t/^{\circ}\text{C}+c]^2} \tag{7}$$

A summary of enthalpy of vaporization results is given in Table 2 for selected temperatures and pressures. Values found in the literature [4] are also given for comparison at the same temperatures and pressures.

As shown in Table 2, the enthalpy of vaporization values predicted from the Antoine curve fit are similar to those found in literature [4]. The regression errors of the DIPPR

Table 2

Summary of enthalpy of vaporization data computed from Antoine and Clapeyron equations

Fluid	t in °C	P in MPa	ΔH_{vap} in kJ mol^{-1}		% Diff.
			Curve fit	Literature [4]	
Biphenyl	351	0.5756	42.19	40.56	4.0
Decafluoro-biphenyl	321	1.0629	10.94	–	–
o-Terphenyl	351	0.1305	50.62	57.29	11.6
Naphthalene	351	1.0209	33.57	32.30	3.9
Perfluoro-TPB	362	0.1379	103[a]	–	–
Quinoline	351	0.7764	38.22	38.12	0.3
Water	100	0.1007	41.31	40.80	1.3

[a] Value estimated from the endotherm area of the DSC scan.

Table 3

Comparison of measured melting points to literature values

Fluid	Experimental			Literature		% Diff.
	T_{fus} (in °K)	T_{fus}–1σ (in °K)	P range (in MPa)	T_{fus} (in °K)	P range (in MPa)	
Biphenyl	340.84	±0.59	0.05–1.4	342.27	0.1	0.4
Decafluoro-biphenyl	339.74	±0.90	0.05–1.4	342.15[a]	0.1	0.7
o-Terphenyl	328.02	±1.84	0.05–1.4	329.35	0.1	0.4
Naphthalene	352.21	±0.62	0.05–1.4	353.37	0.1	0.3
Perfluoro-TPB	422.25	±0.66	0.05–1.4	–	–	–

[a] Average value reported by Ryan Scientific.

correlations for the heat of vaporization of biphenyl, *o*-terphenyl, naphthalene, quinoline, and water are reported as ±5%, ±10%, ±1%, ±5%, ±1%, respectively. The differences between the curve fit generated values and those calculated from the DIPPR correlations are generally within, or at the limits of, these published regression errors.

The melting points of the materials listed in Tables 1 and 2 were also measured as a part of this effort, and a summary is given in Table 3. The standard deviation of the melting point over the pressure range of the vaporization experiments ranged from 0.59 to 1.84 K. This variance has contributions from both pressure variations and inherent DSC system variations. The average melting temperature of the distilled naphthalene of this study was 352.21 ± 0.62 K (1 standard deviation), compared to the NPL Certificate value [6] of 353.37 K. Melting points for biphenyl, and *o*-terphenyl were 340.84 ± 0.59 K and 328.02 ± 1.84 K, respectively, over the pressure range of 50 kPa to 1.4 MPa. These compare to literature values [4] of 342.27 K and 329.35 K, respectively.

In conclusion, the DSC method and data regression techniques outlined in this paper, and also being rigorously developed by ASTM E37, provides an accurate means to measure saturated pressures and temperatures which can be used to calculate the heat of vaporization of fluids. This technique has been used successfully by the authors to predict and design space application high-temperature thermal management systems. The general methodologies could also be adapted for the characterization of low-temperature working fluids, and also for enthalpy of sorption associated with gas–solid adsorption and absorption systems.

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