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**DOI: 10.1016/j.jct.2016.04.023**

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# Improving a variation of the DSC technique for measuring the boiling points of pure compounds at low pressures



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## ARTICLE INFO

### Article history:

Received 17 February 2016  
Received in revised form 15 April 2016  
Accepted 30 April 2016  
Available online 2 May 2016

### Keywords:

Differential scanning calorimetry  
Ballpoint pen ball  
Boiling point  
Heating rate  
Sample size

## ABSTRACT

This study aims to improve a variation of the differential scanning calorimetry (DSC) technique for measuring boiling points of pure compounds at low pressures. Using a well-known *n*-paraffin (*n*-hexadecane), experimental boiling points at a pressure of 3.47 kPa with  $u(P) = 0.07$  kPa were obtained by using a variation of the DSC technique, which consists of placing samples inside hermetically sealed aluminum crucibles, with a pinhole (diameter of 0.8 mm) made on the lid and a tungsten carbide ball with a diameter of 1.0 mm over it. Experiments were configured at nine different combinations of heating rates ( $\text{K}\cdot\text{min}^{-1}$ ) and sample sizes (mg) following a full factorial design ( $2^2$  trials plus a star configuration and three central points). Individual and combined effects of these two independent variables on the difference between experimental and estimated boiling points (NIST Thermo Data Engine v. 5.0 – Aspen Plus v. 8.4) were investigated. The results obtained in this work reveal that although both factors affect individually the accuracy of this variation of the DSC technique, the effect of heating rate is the most important. An optimized region of combinations of heating rate and sample size for determining boiling points of pure compounds at low pressures was obtained using the response-surface methodology (RSM). Within this optimized region, a selected condition, combining a heating rate of  $24.52 \text{ K}\cdot\text{min}^{-1}$  and a sample size of  $(4.6 \pm 0.5) \text{ mg}$ , was tested for six different compounds ( $92.094\text{--}302.37 \text{ g mol}^{-1}$ ) comprising four fatty compounds (tributylin, monocaprylin, octanoic acid and 1-octadecanol), glycerol and *n*-octadecane, besides *n*-hexadecane. This condition was also successfully applied for obtaining boiling points of *n*-hexadecane at pressures up to 18.66 kPa with  $u(P) = 0.18$  kPa. The optimized region obtained in this work, in terms of heating rates and sample sizes, is specific for the crucible configuration tested.

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## 1. Introduction

Vapor pressure is one of the most important thermophysical properties for characterization of substances and is essential for modeling and simulation of separation processes, such as distillation and stripping. Among other methods, DSC technique has been studied for determining vapor pressures of a variety of compounds [1–7], as an alternative method with remarkable advantages for costly, low-volatile and/or heat-sensitive compounds in terms of sample size (mg) and/or operation time [8], respectively. Recently, Siitsman and Oja [7] summarized seventeen studies published in the literature since 1972 that applied the DSC technique for measuring vapor–liquid equilibria data and/or vapor pressure data of different classes of compounds. Two other studies, not listed by Siitsman and Oja [7], involving analysis of fatty compounds, were lately released [1,8]. As emphasized by Siitsman and Oja [7], the

standardized method has rarely been fully applied, and these previous works, besides providing valuable experimental data, were also concerned with the development of the technique itself, namely, the best combination of operational conditions that delivered reliable results for a chosen application. In fact, a number of factors related to the accuracy of the DSC technique for measuring vapor pressures of pure compounds are identified in the literature [3,5–7,9–11], *i.e.*, sample size, heating rate, sample purity, pressure range, crucible configuration and pinhole size. The standard test method for determining vapor pressure of pure compounds by thermal analysis at 0.2–2000 kPa of the American Society for Testing and Materials (ASTM E1782-14) [12] suggests a sample size of (1–5) mg, a heating rate of  $5 \text{ K}\cdot\text{min}^{-1}$  and a pinhole size up to 0.350 mm. Brozena [6] successfully measured vapor pressures of 1-octanol using pinhole sizes up to 0.350 mm while keeping the heating rate at  $5 \text{ K}\cdot\text{min}^{-1}$  at 0.197 kPa up to atmospheric pressure. Despite these recommendations, Matricarde Falleiro et al. [3] and Damaceno et al. [1] determined boiling points of fatty compounds and tocopherols by applying a combination of a higher heating rate

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(25 K·min<sup>-1</sup>) and the use of a small tungsten carbide sphere (1 mm of diameter) acting as a relief valve placed over a pinhole larger than the recommended value (0.8 mm of diameter). The first use of a ballpoint pen ball over the pinhole in a DSC crucible was described by Farritor and Tao [13]. Heating rates higher than the recommended value of 5 K·min<sup>-1</sup> were also tested by Contreras et al. [10]. The authors investigated the variation of boiling points of isopropyl palmitate (298.5 g·mol<sup>-1</sup>) given by the DSC technique at pressures below 5 kPa configured with three different heating rates (5, 10 and 15 K·min<sup>-1</sup>) while fixing sample size (5.0 ± 0.5) mg and pinhole size (0.4 mm of diameter). Siitsman et al. [5] found out that sample size has a great influence on the accuracy of the DSC technique, especially around 15 kPa and over 250 kPa, while working with tobacco related materials with fixed pinhole size (0.5 mm) and heating rate (5 K·min<sup>-1</sup>).

In this context, this work presents a systematic study of the influence of two selected factors, sample size (mg) and heating rate (K·min<sup>-1</sup>), in the accuracy of a variation of the DSC technique for measuring boiling points of pure compounds at low pressures. *n*-Hexadecane, an *n*-paraffin of sixteen carbons with a molar mass of 226.45 g·mol<sup>-1</sup> was selected for this investigation. Experiments were configured following a full factorial design (2<sup>2</sup> trials plus a star configuration and three central points). Individual and combined effects of these two independent variables on the difference between experimental and estimated boiling points for the pure compound (NIST Thermo Data Engine v. 5.0 – Aspen Plus v. 8.4) were investigated while fixing other two measurement conditions: (1) samples were placed inside hermetically sealed aluminum crucibles, with a fixed pinhole diameter (0.8 mm) on the lid and a tungsten carbide ball with a diameter of 1.0 mm over it, following our previous works [1,3,8], and (2) pressure set at 3.47 kPa with  $u(P) = 0.07$  kPa. Surfaces and contour plots were sketched using the quadratic models for the statistically significant variables according to response surface methodology. The ranges of the independent variables investigated were (3.5–5.0) mg for sample size and (5–30) K·min<sup>-1</sup> for heating rates. For further analysis, six different compounds (92.094–302.37 g·mol<sup>-1</sup>) comprising four fatty compounds (tributyryn, monocaprylin, octanoic acid and 1-octadecanol), glycerol and *n*-octadecane were selected for testing the reliability of the optimized conditions. Complementarily, the selected condition within the optimized region was tested for *n*-hexadecane at four different pressures: 10.37 kPa with  $u(P) = 0.19$  kPa, 15.17 kPa with  $u(P) = 0.19$  kPa, 18.66 kPa with  $u(P) = 0.18$  kPa, and 22.39 kPa with  $u(P) = 0.23$  kPa.

## 2. Experimental

### 2.1. Material

Table 1 lists the reagents used in this work together with CAS Registry numbers, IUPAC names, purities in mass fraction, molar

mass (MW), normal boiling points, and suppliers. All chemicals were used without any further purification steps.

Hermetic aluminum crucibles (pans + lids) for DSC (max 10 μL) were purchased from TA Instruments. A pinhole of a diameter of 0.8 mm was made on each lid using a system consisting of a fixation assembly, mandrel and drills. From the disassemble of a ballpoint pen, a small tungsten carbide ball with a diameter of 1.0 mm was obtained, and was placed over the pinhole, following guidelines of previous works [1,3,8,13].

### 2.2. Apparatus

The experimental apparatus used in this work is detailed by Matricarde Falleiro et al. [3]. It consists of a differential scanning calorimeter (DSC) model Q20P – TA Instruments with a pressure cell (PDSC) connected to a vacuum system, which is an arrangement of a trap for pressurizing the vacuum line, a ballast tank for avoiding pressures oscillations, a micrometer valve for adjusting the pressure, a digital pressure gauge Model Ruchen RMD with 0.25% full scale accuracy, and a vacuum pump Model RV5 – Edwards. The digital pressure gauge was calibrated with *n*-tetradecane. A personal computer (PC) allows running the DSC and recording data from each experimental trial. A microanalytical balance (Model C-33 – Thermo Scientific) and micropipettes of (0.5–10) μL (Model Research – Eppendorf) were used for microsample preparation. Crucibles (pan + lids) were sealed with a press (Model SN6205 – TA Instruments).

### 2.3. Experimental design

Experiments were carried out using a full factorial design (2<sup>2</sup> trials plus a star configuration and three central points). In this way, nine different combinations of the two independent variables selected, sample size (mg) and heating rate (K·min<sup>-1</sup>), were tested in eleven trials (Table 2). Each trial was repeated in triplicate.

For each run, a sealed crucible with a sample of *n*-hexadecane with its size in mg established by the factorial design (Table 2) was placed together with an empty crucible (as a reference) in the pressure cell. The absolute pressure of 3.47 kPa with  $u(P) = 0.07$  kPa was set using the referred vacuum system at ambient temperature. After 30 min of stabilization of the system pressure [5], the heating ramp started at a heating rate in K·min<sup>-1</sup> defined by the factorial design for that specific trial (Table 2), raising the temperature up to 600 K. After the heating time, the pressure cell was restored to ambient conditions.

From a recorded endotherm generated by the DSC software for each run (heat flow in W·g<sup>-1</sup> versus *T* in K), boiling point can be determined as the extrapolated onset temperature, which is defined as the intersection of the tangents to the baseline and to the thermal event peak (Fig. 1). In order to determine the extrapolated onset temperature, five different points along the baseline were subjectively selected for setting its tangent. Table 3 examples

**Table 1**  
List of reagents.

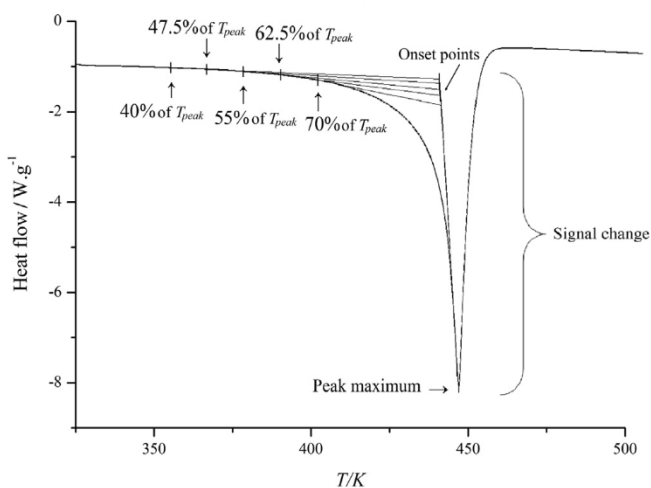
Compound	IUPAC name	CAS number	Purity (mass fraction)	Supplier	MW (g·mol <sup>-1</sup> )	<i>T</i> <sub>nb</sub> (K) <sup>a</sup>
Glycerol	Propane-1,2,3-triol	56-81-5	≥0.995	Sigma-Aldrich	92.094	563.06 ± 4.26
Octanoic acid	Octanoic acid	124-07-2	≥0.99	Sigma-Aldrich	144.21	512.601 ± 0.406
Monocaprylin	2,3-Dihydroxypropyl octanoate	502-54-5	≥0.99	Nu Chek Prep.	218.29	591.39 <sup>b</sup>
<i>n</i> -Hexadecane	Hexadecane	544-76-3	>0.99	Sigma-Aldrich	226.45	560.045 ± 0.626
<i>n</i> -Octadecane	Octadecane	593-45-3	≥0.99	Vetec	254.50	589.58 ± 2.49
1-Octadecanol	Octadecan-1-ol	112-92-5	≥0.99	Sigma-Aldrich	270.49	523.74 ± 1.54
Tributyryn	1,3-Di(butanoyloxy)propan-2-yl butanoate	60-01-5	>0.99	Sigma-Aldrich	302.37	588.44 ± 8.95
<i>n</i> -Tetradecane	Tetradecane	629-59-4	≥0.99	Sigma-Aldrich	198.39	526.694 ± 0.150

<sup>a</sup> *T*<sub>nb</sub> (K) = Normal boiling point retrieved from NIST ThermoData Engine v. 5.0 – Aspen Plus v. 8.4.

<sup>b</sup> Calculated with Marrero and Gani [14] method, as referred in [1].

**Table 2**Full Factorial design for samples of *n*-hexadecane.

	Trial	$t_{CAL}^a/K\cdot min^{-1}$	Coded variables		Real variables		$T_b^{exp}^d/K$	(DIF/K) <sup>e</sup>	$u(T)/K$ <sup>f</sup>	Signal change/ $kW\ mol^{-1}$ <sup>g</sup>	$u(SC)/kW\ mol^{-1}$ <sup>h</sup>
			$X_1$	$X_2$	$t^b/K\cdot min^{-1}$	$m^c/mg$					
Factorial design	1	10	-1	-1	8.6	3.7	425.40	-19.33	1.06	0.65	0.02
	2		+1	-1	26.4	3.7	442.49	-2.24	0.70	2.4	0.1
	3		-1	+1	8.6	4.8	432.97	-11.76	0.78	0.74	0.02
	4		+1	+1	26.4	4.8	444.06	-0.67	0.32	2.43	0.07
Star points	5		-1.41	0	5.0	4.3	418.74	-25.99	0.34	0.377	0.005
	6		+1.41	0	30.0	4.3	445.86	+1.13	0.24	2.81	0.05
	7		0	-1.41	17.5	3.5	438.27	-6.46	0.17	1.51	0.02
	8		0	+1.41	17.5	5.0	441.51	-3.22	0.67	1.71	0.07
Central points	9		0	0	17.5	4.3	440.97	-3.76	0.50	1.69	0.04
	10		0	0	17.5	4.3	440.75	-3.98	0.57	1.70	0.06
	11		0	0	17.5	4.3	440.19	-4.54	0.71	1.67	0.07
Additional replicates	5	5	-1.41	0	5.0	4.3	417.61	-27.12	0.34	0.297	0.004
	6	5	+1.41	0	30.0	4.3	443.96	-0.77	0.63	2.50	0.09

<sup>a</sup> Heating rate in  $K\cdot min^{-1}$  used for performing DSC calibration.<sup>b</sup> Heating rate in  $K\cdot min^{-1}$  used for running the factorial design.<sup>c</sup> Sample size in mg.<sup>d</sup> Average experimental boiling point value of a triplicate in K.<sup>e</sup>  $DIF = (T_b^{exp} - T_b^{cal})$  in K.<sup>f</sup> Standard uncertainty  $u(T)$  in K.<sup>g</sup> Average experimental signal change value in  $kW\ mol^{-1}$  (calculated from the endothermic peak size in Fig. 1 in  $W\ g^{-1}$  converted to  $kW\ mol^{-1}$  using MW of *n*-hexadecane in  $g\cdot mol^{-1}$  given in Table 1).<sup>h</sup> Standard uncertainty  $u(SC)$  in  $kW\cdot mol^{-1}$ .**Fig. 1.** DSC endotherm recorded for a run of trial number 11 (Table 2) for *n*-hexadecane: onset points between 40% and 70% of the temperature of the peak maximum ( $T_{peak}/K$ ), peak maximum, and signal change (peak size in  $W\ g^{-1}$ ).**Table 3**Extrapolate onset temperatures ( $T_{onset}$ ) for samples of *n*-hexadecane obtained at five points at baseline for a run of trial number 11 (Table 2) according to Fig. 1.

$T_{peak}/K$	447.39
$T_{onset}/K$	
40% of $T_{peak}$	440.28
47.5% of $T_{peak}$	440.38
55% of $T_{peak}$	440.52
62.5% of $T_{peak}$	440.65
70% of $T_{peak}$	440.87
Average value	440.54
Standard deviation	0.21

the procedure, giving the extrapolated onset temperature values calculated for a run of trial number 11 (Table 2). The first point

was located at 40% of the value of the temperature of the peak maximum ( $T_{peak}/K$ ) of the endotherm and the last one at 70% of it, with three intermediate points at 47.5%, 55% and 62.5% of  $T_{peak}$ . The peak maximum temperature and the onset temperatures can be determined using the Thermal Analysis software from TA Instruments. This procedure was followed to account for the influence of mass loss due to pre-boiling vaporization on the onset temperature, and consequently, on the dependent variable DIF/K, given by the variation of the DSC technique under study. It is of note that Matricarde Falleiro et al. [2] highlighted that extrapolated onset temperatures obtained from tangents set at different points along the baseline can be slightly different (up to 0.8 K).

Other suitable endotherm characteristics pursued (Fig. 1) for correct determination of extrapolated onset temperature are peak size (signal change), peak broadness and its leading edge, and the inclination of the baseline prior to boiling. Peak size (signal change in  $W\cdot g^{-1}$ ) is used to calculate the maximum signal change value between two selected points. The signal change can also be determined using Thermal Analysis software, and it depends mostly on heating rate, but also on other factors, such as sample size, thermo-physical properties of compound, and its purity [15]. High baseline inclination (non-flat baseline) and reduced leading edge of the endothermic peak are indicative of the occurrence of pre-boiling vaporization [6]. These parameters can be related to the accuracy of the DSC technique.

Table 2 brings mean values and the standard deviations of signal change in  $kW\cdot mol^{-1}$  calculated for each trial (runs in triplicate) by converting the endothermic peak size in  $W\cdot g^{-1}$  to  $kW\cdot mol^{-1}$  using compound molar mass (MW of *n*-hexadecane, in this case) in  $g\cdot mol^{-1}$  given in Table 1.

The accuracy of the DSC technique was quantified as the difference between experimental ( $T_b^{exp}/K$ ) and estimated ( $T_b^{cal}/K$ ) boiling points for the pure compound. For each trial, the dependent variable of the factorial design (response of interest), DIF/K, given in Table 2, was calculated as the average value of three independent runs (triplicate). Boiling points ( $T_b^{cal}/K$ ) were estimated from Antoine equations (Eq. (1)), in which constants  $A$ ,  $B$  and  $C$  were obtained by regression of experimental values retrieved from NIST

Thermo Data Engine v. 5.0 – Aspen Plus v. 8.4. Table 4 gives regressed values for constants  $A$ ,  $B$  and  $C$ , together with temperature range (K) and pressure range (kPa) of experimental data, and the estimated value at 3.47 kPa. For monocaprylin, constants  $A$ ,  $B$  and  $C$  are provided by Damaceno et al. [1]. Refs. [1,16–27] and the supplementary references given in Table S1 (Supporting Information) were used for regressing Eq. (1).

$$\ln p = A + \left( \frac{B}{T + C} \right) \quad (1)$$

where  $p$  is the vapor pressure in kPa,  $T$  is the boiling point in K, and  $A$ ,  $B$  and  $C$  are regressed constants.

Experimental results (Table 2) were analyzed to establish the individual and combined effects of sample size (mg) and heating rate ( $\text{K}\cdot\text{min}^{-1}$ ) on the accuracy of a variation of the DSC technique for measuring boiling points of pure compounds at low pressures. Surface and contour plots were then built using the model for the statistically significant variables and an optimized region of possible combinations of these two independent variables was achieved.

For further analysis, a selected condition within the optimized region given by the response surface methodology was checked experimentally for  $n$ -hexadecane and other six compounds ( $92.094\text{--}302.37\text{ g}\cdot\text{mol}^{-1}$ ) comprising four fatty compounds (tributyrin, monocaprylin, octanoic acid and 1-octadecanol), glycerol and  $n$ -octadecane. Complementarily, this selected condition was tested at four different pressures for  $n$ -hexadecane: 10.37 kPa with  $u(P) = 0.19\text{ kPa}$ , 15.17 kPa with  $u(P) = 0.19\text{ kPa}$ , 18.66 kPa with  $u(P) = 0.18\text{ kPa}$ , and 22.39 kPa with  $u(P) = 0.23\text{ kPa}$ .

#### 2.4. DSC calibration

The calibration of the DSC was done according to the standard method ASTM E967-08 (14) [28] guidelines with indium and zinc as standard materials. For practical purposes, calibrations of the baseline, cell constant and temperature were done at atmospheric pressure with a fixed heating rate of  $10\text{ K}\cdot\text{min}^{-1}$  for all experiments of the full factorial design in Table 2. Therefore, the heating rate used in DSC calibration ( $t_{\text{CAL}}/\text{K}\cdot\text{min}^{-1}$ ) was different from all the five levels of heating rates ( $t/\text{K}\cdot\text{min}^{-1}$ ) used in the experimental trials. Additional replicates were done for trials 5 (heating rate of  $5\text{ K}\cdot\text{min}^{-1}$ ,  $X_1$  at  $-\alpha$ ) and 6 (heating rate of  $30\text{ K}\cdot\text{min}^{-1}$ ,  $X_1$  at  $+\alpha$ ) after performing the DSC calibration with heating rates of  $5\text{ K}\cdot\text{min}^{-1}$  and  $30\text{ K}\cdot\text{min}^{-1}$ . Mean values for  $T_b^{\text{exp}}/\text{K}$  and standard uncertainties  $u(T)$  of triplicates are given in Table 2. It was inferred from the  $t$ -test [29] that, for both trials, the differences between the results obtained for  $T_b^{\text{exp}}/\text{K}$  in runs done after performing the DSC calibration at heating rates of  $5\text{ K}\cdot\text{min}^{-1}$ ,  $10\text{ K}\cdot\text{min}^{-1}$  or  $30\text{ K}\cdot\text{min}^{-1}$  were not statistically significant at 95% of confidence. Then, it is reasonable to affirm that within the range of the heating rates used in this work ( $5\text{ K}\cdot\text{min}^{-1}$  to  $30\text{ K}\cdot\text{min}^{-1}$ ), the heating rate

used in DSC calibration did not influenced the result obtained for  $T_b^{\text{exp}}/\text{K}$  at 95% of confidence. Nevertheless, this effect is assessed by the statistical analysis within the full factorial design given in Table 2. In fact, the effect of the independent variable heating rate ( $X_1$ ) gathers all the interrelated effects caused by its variation, including the consequent difference between the heating rate used for performing runs of a specific trial and the one used for DSC calibration.

It should be emphasized that for experiments conducted using the selected condition, in terms of heating rate and sample size, within the optimized region, for tributyrin, monocaprylin, octanoic acid, 1-octadecanol, glycerol,  $n$ -octadecane, and  $n$ -hexadecane, a heating rate of  $25\text{ K}\cdot\text{min}^{-1}$  was used for performing DSC calibration.

### 3. Results and discussion

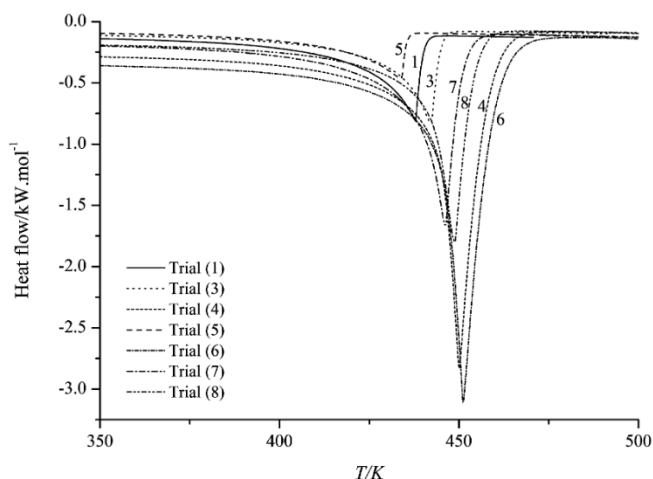
The experimental results shown in Table 2 reveal that the accuracy of the DSC technique (DIF/K) is a function of the two variables studied. It can be observed, in a comparison of trials 5 and 6 ( $X_1$  varying from  $-\alpha$  to  $+\alpha$ ), and trials 7 and 8 ( $X_2$  varying from  $-\alpha$  to  $+\alpha$ ), that the difference between the experimental and estimated boiling points for  $n$ -hexadecane at 3.47 kPa with  $u(P) = 0.07\text{ kPa}$  decreased with an increase in heating rate or an increase in sample size, respectively. Combined effects were also present. DIF values decreased 8.6 times between trials 1 and 2 ( $X_1$  varying from  $-1$  to  $+1$  while  $X_2$  was maintained at  $-1$ ) and 17.6 times between trials 3 and 4 ( $X_1$  varying from  $-1$  to  $+1$  while  $X_2$  was maintained at  $+1$ ). Trial 6 ( $X_1$  at  $+\alpha$  and  $X_2$  at 0) was the only one with a positive value of DIF. The lowest absolute value for DIF ( $+0.67\text{ K}$ ) was achieved at trial 4 ( $X_1$  at  $+1$  and  $X_2$  at  $+1$ ) and the highest value ( $+25.99\text{ K}$ ) at trial number 5 ( $X_1$  at  $-\alpha$  and  $X_2$  at 0) indicating the relevant effects of these two configuration variables of the DSC technique on its accuracy.

Fig. 2 shows selected endotherms obtained for runs of trials 1, 3–8. Looking at Table 2, one can see that the highest absolute values for DIF ( $+11.76\text{ K}$ ,  $+19.33\text{ K}$ , and  $+25.99\text{ K}$ , respectively) were obtained at trials 3 ( $X_1$  at  $-1$ ), 1 ( $X_1$  at  $-1$ ) and 5 ( $X_1$  at  $-\alpha$ ). Unsurprisingly, these trials were the ones that presented boiling endotherms increasingly broad, confirming the key influence of heating rate on the peak shape, and consequently, on the accuracy of the DSC technique. On the opposite, trial 4 ( $X_1$  at  $+1$  and DIF =  $-0.67\text{ K}$ ) has no peak shape deterioration. Corroborating with this findings, trials 1, 3 and 5 generated the lowest values of signal change (peak size), 0.65, 0.74 and  $0.377\text{ kW}\cdot\text{mol}^{-1}$ . By comparing endotherms obtained for runs of trials 5 and 6, ( $X_1$  varying from  $-\alpha$  to  $+\alpha$  while keeping  $X_2$  at 0), and trials 7 and 8 ( $X_2$  varying from  $-\alpha$  to  $+\alpha$  while keeping  $X_1$  at 0), it is possible to observe the individual effects of heating rate ( $X_1$ ) and sample size ( $X_2$ ) on endotherm characteristics, respectively. Sample size had a small

**Table 4**  
Constants  $A$ ,  $B$  and  $C$  for Eq. (1) with their respective temperature and pressure ranges,<sup>a</sup> coefficients of determination, and the estimated boiling points at 3.47 kPa ( $T_b^{\text{cal}}/\text{K}$ ).

Compounds	Constants			Temperature range/K	Pressure range/kPa	Number of points	$R^2$	$(T_b^{\text{cal}}/\text{K})$
	$A$	$B$	$C$					
Glycerol	14.574	-4070.6	-154.3	392.18–563.13	0.102–101.33	31	0.9996	459.68
Octanoic acid	15.426	-4233.1	-119.0	383.93–510.17	0.520–101.33	90	0.9992	417.49
Monocaprylin	24.554	-11083.3	-9.951	462.66–792.13	1.1–13.2	09	0.9990	485.43
$n$ -Hexadecane	15.58	-5237.79	-79.36	409.98–495.41	0.800–199.98	87	0.9994	444.73
$n$ -Octadecane	13.945	-4219.3	-137.3	434.39–590.04	0.800–101.33	60	0.9996	469.51
1-Octadecanol	13.907	-4291.3	-162.5	467.83–574.27	0.857–32.809	32	0.9999	501.38
Tributyrin	17.947	-7343.1	-38.5	468.65–589.30	2.3998–101	16	0.9991	478.13

<sup>a</sup> Experimental values were retrieved from the NIST ThermoData Engine v. 5.0 – Aspen Plus v. 8.4, including Refs. [1,16–27], and the supplementary references given in Table S1 (Supporting Information).



**Fig. 2.** DSC endotherms for runs of trials 1, 3–8 for *n*-hexadecane at 3.47 kPa with  $u(P) = 0.07$  kPa.

influence in peak shape within the studied range (3.5–5 mg). On the other hand, main effect of heating rate was in peak sharpness.

Clearly, independent of sample size (in the range of 3.5 mg to 5.0 mg), more suitable heating rates for the DSC technique considering a sealed aluminum crucible, with a pinhole (diameter of 0.8 mm) made on the lid and a tungsten carbide ball with a diameter of 1.0 mm over it, are much higher than the recommended value of 5 K·min<sup>-1</sup> [12]. This observation corroborates with previous works [1,2,11]. It is of note that the selected range of sample size (3.5–5 mg) avoided overflowing of liquid during crucible sealing with a press. However, it must be emphasized that larger sample sizes could compensate the pre-boiling vaporization at lower heating rates within the factorial design [7], generating deeper endotherms, and consequently lower values of DIF/K than the ones obtained in this work (see trials 1, 3 and 5 in Fig. 2).

The statistical analysis of the experimental results given in Table 2 allowed to formulate models as functions of the statistically significant variables for two responses of interest, viz. DIF/K and signal change (SC/kW·mol<sup>-1</sup>). Eqs. (2) and (3) represent DIF/K and SC/kW·mol<sup>-1</sup>, respectively. Table 5 shows the analysis of variance (ANOVA) for these two responses at 95.0% of confidence. Both responses presented high correlation coefficients ( $R^2$ ). In addition, the *F*-test showed that the models are predictive and reliable, since the *F* values obtained are at least 4 times greater than the tabulated values [30].

$$\text{DIF/K} = -4.402 + 8.328 \cdot X_1 + 1.722 \cdot X_2 - 4.054 \cdot X_1^2 - 1.498 \cdot X_1 \cdot X_2 \quad (2)$$

**Table 5**  
Analysis of variance (ANOVA) for full factorial design described in Table 2 for samples of *n*-hexadecane.

	Source of variation	SS <sup>a</sup>	DF <sup>b</sup>	MS <sup>c</sup>	<i>F</i> -test
DIF/K	Regression	686.45	4	171.61	61.5 <sup>d</sup>
	Residual	16.74	6	2.79	
	Total	703.19	10		
	$R^2$	0.976			
SC/kW mol <sup>-1</sup>	Regression	5.97	4	1.49	876.5 <sup>d</sup>
	Residual	0.01	6	0.0017	
	Total	5.98	10		
	$R^2$	0.998			

<sup>a</sup> Sum of squares.

<sup>b</sup> Degrees of freedom.

<sup>c</sup> Mean square.

<sup>d</sup>  $F_{0.95,4,6} = 4.53$ .

$$\text{SC/kW} \cdot \text{mol}^{-1} = 1.6865 + 1.7241 \cdot X_1 + 0.0984 \cdot X_2 - 0.1148 \cdot X_1^2 - 0.1032 \cdot X_2^2 \quad (3)$$

where  $X_1$  is the coded variable for heating rate (K·min<sup>-1</sup>) and  $X_2$  is the coded variable for sample size (mg).

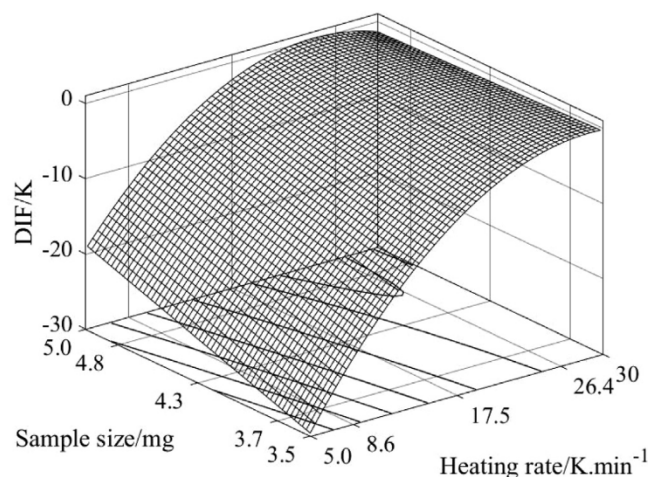
The statistical models revealed that the effect of heating rate was predominant for both responses. For DIF, the interaction between heating rate and sample size was also statistically significant at 95.0% of confidence.

From the quadratic models presented in Eqs. (2) and (3), it was possible to plot surfaces and contour plots that depicted the effects of heating rate and sample size in the responses of interest. As one can see, in Fig. 3, within the range of the independent variables studied, it was possible to get an optimized region for DIF/K, i.e., a combination of conditions of heating rate and sample size that maximized the accuracy of a variation of the DSC technique as considered in this work.

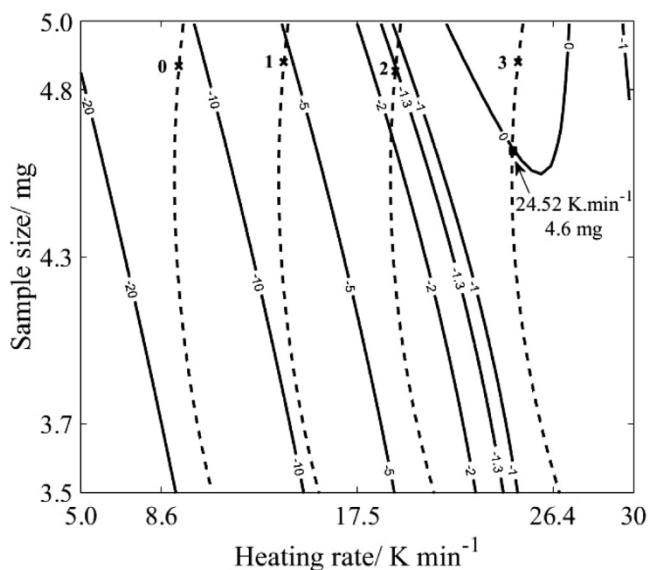
Fig. 4 shows the superposition of contour curves for DIF/K and SC/kW·mol<sup>-1</sup> as function of heating rate/K·min<sup>-1</sup> and sample size/mg. In the optimized region, in which the accuracy of a variation of the DSC technique is considered adequate ( $-1.3 < \text{DIF/K} < +1.3$ ), sample size did not show a relevant effect, and SC assumed values not lower than 2 kW·mol<sup>-1</sup>.

For further analysis, a selected condition in terms of heating rate (24.52 K·min<sup>-1</sup>) and sample size (4.6 ± 0.5) mg within the optimized region (Fig. 4), was applied for determining the boiling points of six different compounds, besides *n*-hexadecane, comprising four fatty compounds (tributyryn, monocaprylin, octanoic acid and 1-octadecanol), glycerol and *n*-octadecane at 3.47 kPa with  $u(P) = 0.07$  kPa. Mean values and standard uncertainties for  $T_b^{\text{exp}}/\text{K}$ , DIF/K and SC/kW·mol<sup>-1</sup> are given in Table 6. Fig. S1 (Supporting Information) shows linearized relations of vapor pressures as a function of temperature ( $\ln p/\text{kPa}$  versus  $T_b^{-1}/\text{K}^{-1}$ ) for the seven compounds described in Table 4, using literature data retrieved from NIST ThermoData Engine v. 5.0 – Aspen Plus v. 8.4. A supplementary list of references are included in Table S1 (Supporting Information). For comparison purposes, experimental data obtained in this work (Table 6) and lines corresponding to the adjusted equations (Eq. (1)) were also included in Fig. S1.

In general, experimental values obtained in this work for  $T_b^{\text{exp}}/\text{K}$  at 3.47 kPa with  $u(P) = 0.07$  kPa using the selected conditions within the optimized region (Table 6) are very reasonable in comparison with boiling points ( $T_b^{\text{lit}}/\text{K}$  at  $p/\text{kPa}$ ) from literature within the same pressure range. By comparing experimental values of  $T_b$



**Fig. 3.** Response surface and contour curves of DIF/K as a function of heating rate/K·min<sup>-1</sup> and sample size/mg for *n*-hexadecane.

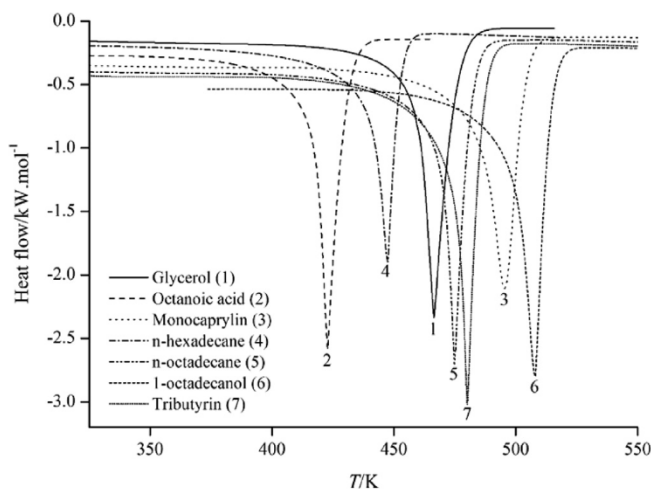


**Fig. 4.** Superposition of contour curves for DIF/K (solid lines) and SC/kW mol<sup>-1</sup> (dashed lines) as function of heating rate/K·min<sup>-1</sup> and sample size/mg for samples of *n*-hexadecane.

<sup>exp</sup>/K in Table 6 and  $T_b^{calc}$ /K reported in Table 4, very good results were achieved for all compounds selected, but 1-octadecanol (270.49 g·gmol<sup>-1</sup>) and tributyrin (302.37 g·gmol<sup>-1</sup>) for which DIF values were -2.41 K and -3.58 K. Still, relative to  $T_b^{exp}$ /K, the calculated deviations are lower than 0.8%. In the case of tributyrin, this higher value of DIF may be a consequence of a poor estimation of  $T_b^{cal}$ /K, considering that only sixteen experimental values for vapor pressure are available at NIST TDE database over a wide pressure range, i.e., (2.3998–101) kPa.

For illustration of the consistency of these results, Fig. 5 shows the endotherms obtained for runs at the selected conditions for compounds listed in Table 6. It is of note that SC is lower than 2 kW·mol<sup>-1</sup> only for monocaprylin.

Complementarily, the selected condition within the optimized region was also tested at four different pressures for *n*-hexadecane: 10.37 kPa with  $u(P)$  = 0.19 kPa, 15.17 kPa with  $u(P)$  = 0.19 kPa, 18.66 kPa with  $u(P)$  = 0.18 kPa, and 22.39 kPa with  $u(P)$  = 0.23 kPa. At these pressures, Eq. (1) gives 474.93 K,



**Fig. 5.** Endotherms obtained by the DSC technique configured with a heating rate of 24.52 K·min<sup>-1</sup> used for running the experiments, a heating rate of 25 K·min<sup>-1</sup> used for performing DSC calibration, and a sample size of (4.6 ± 0.5) mg for selected compounds.

486.63 K, 493.30 K and 499.34 K for  $T_b^{cal}$  for this *n*-paraffin. Experimental values of boiling points,  $T_b^{exp}$ , were 474.05 K with  $u(T)$  = 0.31 K, 486.81 K with  $u(T)$  = 0.16 K, 493.60 K with  $u(T)$  = 1.07 K and 496.42 K with  $u(T)$  = 0.90 K, respectively, and the calculated values for DIF were -0.88 K, +0.18 K, +0.30 K and -2.92 K, accordingly. From the literature,  $T_b^{lit}$ , were 475.7 K at 10.666 kPa [26], 488.16 K at 15.824 kPa [27], 493.13 K at 18.414 kPa [19], and 500.5 K at 22.8861 kPa [27], respectively. From the above results, one may realize that the optimized region for heating rate and sample size achieved in this work is still valid up to 18.66 kPa with  $u(P)$  = 0.18 kPa, despite the fact that no peak misshape or baseline deterioration were observed in any of the obtained endotherms. No further pressures were tested.

An important observation about the use of the selected condition within the optimized region, for different compounds and for *n*-hexadecane at different pressures, is that it is still valid despite the different heating rate used for performing DSC calibration. This result reaffirm the minor effect, of the difference between the heating rate used for performing runs and the one used for DSC calibration, in  $T_b^{exp}$ /K.

**Table 6**

Boiling points  $T_b^{exp}$ /K, DIF/K and signal change SC/kW·mol<sup>-1</sup> for selected compounds at 3.47 kPa with  $u(P)$  = 0.07 kPa using a heating rate<sup>a</sup> of 24.52 K·min<sup>-1</sup> and a sample size of (4.6 ± 0.5) mg, and experimental data from the literature ( $T_b$ /K at  $p$ /kPa).

Compound	$T_b^{exp}$ /K <sup>b</sup>	DIF/K <sup>c</sup>	$u(T)$ /K <sup>d</sup>	Signal change/kW·mol <sup>-1</sup> <sup>e</sup>	From literature <sup>f</sup> $T_b^{lit}$ /K - $p$ /kPa
Glycerol	459.28	-0.40	0.15	2.10 ± 0.08	452.64–2.747 [16], 463–3.850 [17]
Octanoic acid	417.19	-0.30	0.44	2.34 ± 0.09	417.15–3.433 [18]
Monocaprylin	485.05	-0.38	0.46	1.76 ± 0.05	485.63–3.60 [1]
<i>n</i> -hexadecane	444.06	-0.67	0.98	2.39 ± 0.05	443.08–3.273 [19], 443.99–3.620 [20]
<i>n</i> -octadecane	469.96	0.45	0.46	2.27 ± 0.02	467.13–3.015 [21], 473.13–3.870 [19]
1-Octadecanol	499.04	-2.41	0.43	2.21 ± 0.03	498.7–3.132 [22], 502.34–3.585 [23]
Tributyrin	474.55	-3.58	0.45	2.51 ± 0.11	468.65–2.3998 [24], 508.17–13.1989 [25]

<sup>a</sup> Heating rate in K·min<sup>-1</sup> used for running the experiments. Heating rate used for performing DSC calibration was 25 K·min<sup>-1</sup>.

<sup>b</sup> Average experimental boiling point value of a triplicate in K.

<sup>c</sup> DIF = ( $T_b^{exp}$  -  $T_b^{lit}$ ) in K.

<sup>d</sup> Standard uncertainty  $u(T)$  in K.

<sup>e</sup> Signal change in kW mol<sup>-1</sup> (endothermic peak size in Fig. 1).

<sup>f</sup> Data retrieved from NIST ThermoData Engine v. 5.0 - Aspen Plus v. 8.4.

#### 4. Conclusions

In this study, different configurations of a variation of the DSC technique in terms of heating rates and sample sizes were tested for determining boiling points of pure compounds at low pressures. An optimized region for the combination of these two variables was achieved at 3.47 kPa with  $u(P) = 0.07$  kPa, considering a sealed aluminum crucible, with a pinhole (diameter of 0.8 mm) made on the lid and a tungsten carbide ball with a diameter of 1.0 mm over it, and proved to be valid for other selected compounds. Within the range of the heating rates used in this work ( $5 \text{ K}\cdot\text{min}^{-1}$  to  $30 \text{ K}\cdot\text{min}^{-1}$ ), the heating rate used in DSC calibration did not influence the results obtained for  $T_b^{\text{exp}}/\text{K}$  at 95% of confidence. Complementarity, pressure was set at values up to 18.66 kPa with  $u(P) = 0.18$  kPa with no considerable effects on accuracy of the DSC technique. This work confirms that this technique is suitable for determining vapor pressures of pure compounds provided a proper configuration.

#### Acknowledgements

R. Ceriani acknowledges FAPESP (2013/12735-5) for the financial support and CNPq (304303/2013-5) for her individual grant. K.L. Troni and D.S. Damaceno acknowledge respectively, CAPES and CNPq for their individual grants.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2016.04.023>.

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