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Thermochimica Acta 347 (2000) 37–44

thermochimica
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Highly precise determination of the heat capacity of liquids by DSC: calibration and measurement

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Received 5 August 1999; accepted 27 August 1999

Abstract

The heat capacities of various liquids were determined with a high precision using differential scanning calorimetry. The calibration and measurement procedures, as implemented on a Setaram Micro DSC II calorimeter based on Calvet's differential detection of the heat flow rate in the measuring and reference vessels are analysed and discussed. An experimental procedure for determining heat capacities based on the scanning method is proposed. Calibration is done with liquids of known heat capacity. The proposed method was checked against various standard liquids. The results of ensuing scanning method are compared with those obtained by using the isothermal step method. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heat capacity; Organic liquids; DSC; Calibration; Measurement

1. Introduction

Heat capacity is a macroscopic quantity related to microscopic properties of substances; knowledge of the heat capacity of liquids over a wide temperature range is of thermodynamic interest, and it provides information about molecular structure in the liquid state. The experimental measure of this quantity is the isobaric heat capacity, C_p. Measuring this quantity in a precise manner is highly desirable with a view, for example, to determining the excess heat capacity of a binary liquid mixture. As a rule, experimental measurements of C_p in liquids are subject to a number of problems largely derived from their volatility. Such problems are even worse when measurements are to be made near the boiling point of the liquid concerned. Some calorimeters typically used to determine C_p in liquids (e.g., the Picker flow calorimeters) must operate at near room temperature and are thus, scarcely flexible as regards temperature adjustment; Picker flow calorimeters and other ones (e.g., adiabatic calorimeters) can only operate at a single temperature in each experiment, so determining the temperature dependence of the heat capacity $C_p(T)$ is labour-intensive and time-consuming. Although differential scanning calorimetry is not a standard technique for determining liquid heat capacities, it is the most suitable choice when measurements at a variable temperature are required. However, most differential scanning calorimeters lack the resolution needed for the precise determination of liquid C_p values.

Setaram Micro DSC instruments afford the highly precise measurement of liquid heat capacities over a

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PII: S0040-6031(99)00414-1

wide temperature range. These calorimeters are designed in such a way that they minimise most of the problems encountered in the experimental determination of C_p in liquids. In this work, a technique for measuring C_p based on the scanning method (the best choice for determining $C_p(T)$) with a Micro DSCII was developed. The underlying study was focused on calibration of the calorimetric signal. Although this is usually based on the Joule effect, calibration with liquids of known heat capacity was chosen; in that sense, the recommendations of the GEFTA working group 'Calibration of Scanning Calorimeters' [1–4] were followed. The general measurement procedure is described, with emphasis on the different factors affecting measurements (viz. thermal lag, scanning rate, interpolated baseline).

The isothermal step method is the recommended and most widely used choice with this type of calorimeter on account of its precision. Its foundation is well documented [5–7], so only a brief description is provided here as an introduction to the scanning method. The proposed method was validated by measuring the heat capacity of pure liquids and liquid mixtures, and also by comparing the results with those provided by the isothermal step method and with reported values.

2. Micro DSC II calorimeter

This instrument is described in detail in the literature [5–9]. Basically, it consists of two differentially assembled vessels (reference and measuring) accommodated in a calorimetric block immersed in a thermostating liquid (undecane) the temperature of which is controlled via the Peltier effect. This ensures a highly uniform temperature and very low thermal inertia, and allows operation in the scanning mode. The assembly is placed in an inert atmosphere of dry nitrogen. The temperature is measured near the vessels, inside the calorimetric block. The reproducibility is ±0.01 K and the operating range is 253.15–373.15 K. The calorimeter operation is based on Calvet's principle: the calorimetric signal is the differential heat flow rate, which is measured by one thermopile around each vessel. The detection limit of the heat flow rate ranges from 0.2 to 2 μW, depending on the particular conditions. This calorimeter combines the power of differential scanning calorimetry and the precision of Calvet calorimetry, so it is suitable for the precise determination of heat capacities over a wide temperature range.

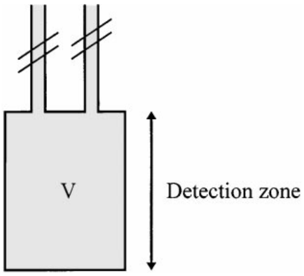

Fig. 1. Scheme of a Setaram liquid heat capacity vessel.

Most of the vessels used in conventional calorimeters are designed in such a way that a vapour phase is always present; this calls for measurement corrections. Setaram liquid heat capacity vessels circumvent this shortcoming by avoiding the presence of the vapour phase over the liquid (see Fig. 1). Thus, the calorimeter detection zone is in contact with a small, constant volume V of about 1 cm^3 filled with liquid phase and no vapour phase correction is needed. The calorimetric signal is proportional to the heat capacity per unit volume C_pV^{-1} of the unknown liquid; determining this quantity per unit mass obviously entails using density data which, in this work, were measured by means of an Anton–Paar vibrating tube densimeter. One of the major advantages of the calorimetric vessels used is that they do not need to be removed for cleaning (usually by flushing with an organic solvent); this allows the system geometry to be preserved between measurements and calibrations to hold over long periods.

3. Calibration and measurement

The use of liquids of known heat capacity is the most suitable choice for calibration in both the isothermal step and the scanning method. The heat capacity of the sample was obtained in three experiments: in the first (I), both vessels were filled with heptane (reference sample); in the second (II) and third (III), heptane was replaced with a reference material and the sample, respectively, in the measuring vessel. Experiments I and II, which constituted the actual calibration procedure, were performed in triplicate under identical conditions. Experiment I defined the asymmetry of the measuring system; although this step is usually performed with two empty vessels, we chose to fill both with heptane in order to determine the asymmetry in both the vessels and the effect of the volume difference between them when filled with liquid. In addition, the reference vessel held the same liquid in the three experiments. The reference material used in experiment II, butan-1-ol, was chosen on account of its well-known heat capacity and of the fact that C_pV^{-1} for most liquids is between those of heptane and butan-1-ol (see Table 1), so the calibration spanned the range of interest; data for both heptane and butan-1-ol were taken from literature [11,12]. In each experiment, the temperature T and the differential heat flow rate dH/dt were recorded against time t.

3.1. Isothermal step method

In this method, a temperature increment of 1 K centred at the measurement temperature was applied at a constant rate of 0.2 K min^{-1}. In order to minimise the effect of convection currents due to the liquid phase outside the thermostated zone, a positive and a negative temperature increment were programmed in each experiment. The heat capacity of the sample was computed from the peak areas $S_{\mathrm{A,B}}$ obtained in I, II, and III. The peaks were integrated with respect to a linear baseline joining the isothermal starting and end lines, using software from Setaram. The isobaric molar heat capacity $C_{\mathrm{p,m}}$ of the sample was calculated from

$$(C_{\mathrm{p,m}})_{\mathrm{S}} = M_{\mathrm{S}}\left[\frac{\rho_{\mathrm{RM}}((C_{\mathrm{p,m}})_{\mathrm{RM}}/M_{\mathrm{RM}}) - \rho_{\mathrm{R}}((C_{\mathrm{p,m}})_{\mathrm{R}}/M_{\mathrm{R}})}{\rho_{\mathrm{S}}} \times \frac{S_{\mathrm{S,R}} - S_{\mathrm{R,R}}}{S_{\mathrm{RM,R}} - S_{\mathrm{R,R}}} + \frac{\rho_{\mathrm{R}}(C_{\mathrm{p,m}})_{\mathrm{R}}}{\rho_{\mathrm{S}}M_{\mathrm{R}}}\right], \qquad (1)$$

where ρ denotes the density; M molecular weight; and subscripts S, RM and R properties of the sample, reference material and reference sample, respectively.

Table 1

Heat capacity per unit volume C_pV^{-1} of various liquids at 298.15 K

Liquid	$(C_pV^{-1})^{\mathrm{a}}$ (J K^{-1} cm^{-3})
Toluene	1.472
Hexane	1.485
Benzene	1.518
Heptane	1.526
Octane	1.554
Decane	1.606
Propyl ether	1.609
Methyl acetate	1.802
Propyl formate	1.825
Ethanol	1.914
Propan-1-ol	1.914
Butan-1-ol	1.925
2-Methyl, propan-1-ol	1.948
Nitromethane	1.964
Propan-2-ol	2.010
Butan-2-ol	2.125

[a] Calculated from literature data [10].

3.2. Scanning method

In this method, the temperature was changed at a constant rate by heating and cooling in order to minimise the effect of convection currents. $C_{\mathrm{p,m}}$ at the temperature T was calculated from

$$(C_{\mathrm{p,m}})_{\mathrm{S}} = M_{\mathrm{S}}\left[\frac{\rho_{\mathrm{RM}}((C_{\mathrm{p,m}})_{\mathrm{RM}}/M_{\mathrm{RM}}) - \rho_{\mathrm{R}}((C_{\mathrm{p,m}})_{\mathrm{R}}/M_{\mathrm{R}})}{\rho_{\mathrm{S}}} \times \frac{((\mathrm{d}H/\mathrm{d}t)_{\mathrm{S,R}}/\beta_{\mathrm{S,R}}) - ((\mathrm{d}H/\mathrm{d}t)_{\mathrm{R,R}}/\beta_{\mathrm{R,R}})}{((\mathrm{d}H/\mathrm{d}t)_{\mathrm{RM,R}}/\beta_{\mathrm{RM,R}}) - ((\mathrm{d}H/\mathrm{d}t)_{\mathrm{R,R}}/\beta_{\mathrm{R,R}})} \times + \frac{\rho_{\mathrm{R}}}{\rho_{\mathrm{S}}}\frac{(C_{\mathrm{p,m}})_{\mathrm{R}}}{M_{\mathrm{R}}}\right] \qquad (2)$$

Again, subscripts S, RM and R denote properties of the sample, reference material and reference sample, respectively; $\beta = \mathrm{d}T/\mathrm{d}t$ is the scanning rate.

Fig. 2 shows the curves obtained in experiments (I–III); data are valid within the range where quasi-stationary conditions hold, viz. after a time greater than 10 times the calorimeter's time constant ($\tau = 60$ s), has elapsed. As it can be seen, the isothermal starting and end lines coincided in both experiments, so the heat flow rates of Eq. (2) were always referred to the same baseline.

We examined the difference between the preset scanning rate, β_{pre}, and the true scanning rate, β_{true}. Sarge et al. [3,4] found calculating β from pairs of consecutive T and t values to be a more accurate approach to β_{true} than was using the preset rate. Fig. 3 shows the variation of β_{true} in the course of an experiment. As it can be seen, the calculated and

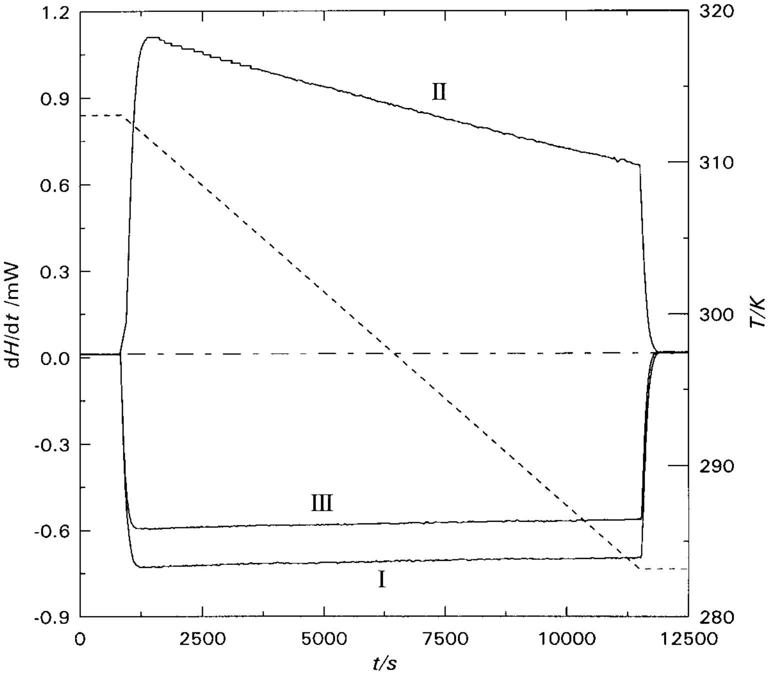

Fig. 2. (—) Differential heat flow rate d*H*/d*t* against time *t* in experiments (I–III); I sample – reference sample, II reference material – reference sample, III reference sample – reference sample, (- - -) temperature program (temperature *T* against *t*), (– – –) interpolated baseline.

preset values were quite similar, which allows one to use β_{pre} in Eq. (2).

The scanning rate chosen was neither too low so as to avoid unduly long experiments nor too high in order to avoid an excessive thermal lag between the recorded and real temperatures. Although no significant differences are observed using scanning rates over the range (0.05–0.80) K min^{-1}, an operating scanning rate β=0.15 K min^{-1} was chosen. At such a rate, the thermal lag was about 0.5 K; although this resulted in no appreciable error in $C_{\mathrm{p,m}}$ for pure liquids, the temperature was calibrated to introduce an appropriate correction.

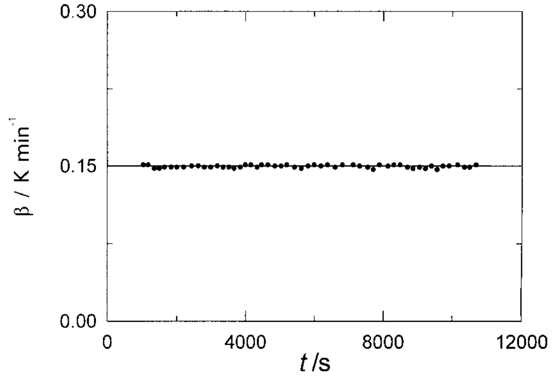

Fig. 3. Scanning rate β against time *t*. (●) True values; (—) preset value.

4. Results and discussion

Existing uses of Micro DSC calorimeters for measuring $C_{\mathrm{p,m}}$ in pure liquids and excess molar heat capacities $C^{\mathrm{E}}_{\mathrm{p,m}}$ in liquid mixtures all rely on the isothermal step method [5–7,13–17]. We used the scanning method to determine the heat capacities of seven pure liquids over the temperature range 288.15–308.15 K; the results were fitted to the following equation:

$$C_{\mathrm{p,m}} = A_0 + A_1T + A_2T^2 \tag{3}$$

Table 2 gives the values of the A_i coefficients and the standard deviations σ; it also contains sources and purities of the chemicals used; the purities were

Table 2
Coefficients A_i of Eq. (3) and standard deviations σ for the isobaric molar heat capacity-temperature relationship of the liquids of this work in the temperature range (288.15–308.15) K

Liquid	Source	Purity in %	A_0	A_1	A_2	σ
Toluene	Fluka	>99.8	174.37	−0.37529	0.0010689	0.0012
Hexane	Fluka	>99.5	202.64	−0.38554	0.0012147	0.0004
Octane	Fluka	>99.5	187.89	0.031196	−0.00064275	0.0007
Decane	Aldrich	>99.5	252.03	−0.073802	−0.00094751	0.003
Nitromethane	Fluka	>99.0	−67.534	1.0488	−0.0015667	0.005
Butan-2-ol	Aldrich	>99.8	–283.66	2.0814	−0.0015822	0.003
2-Methyl, propan-1-ol	Aldrich	>99.5	74.018	−0.20924	0.0019028	0.00012

determined by g. c. analysis in our laboratory. Fig. 4 compares $C_{p,m}(T)$ curves obtained for hexane, decane and toluene with literature data [12,18,19]. As can be seen, the results are quite consistent as regards both magnitude and variation with temperature; the average relative deviation from the experimental values is about 0.23%.

Table 3 gives the $C_{p,m}$ values for pure liquids as obtained with both methods (isothermal step and scanning), in addition to literature values [6,10,20–24].

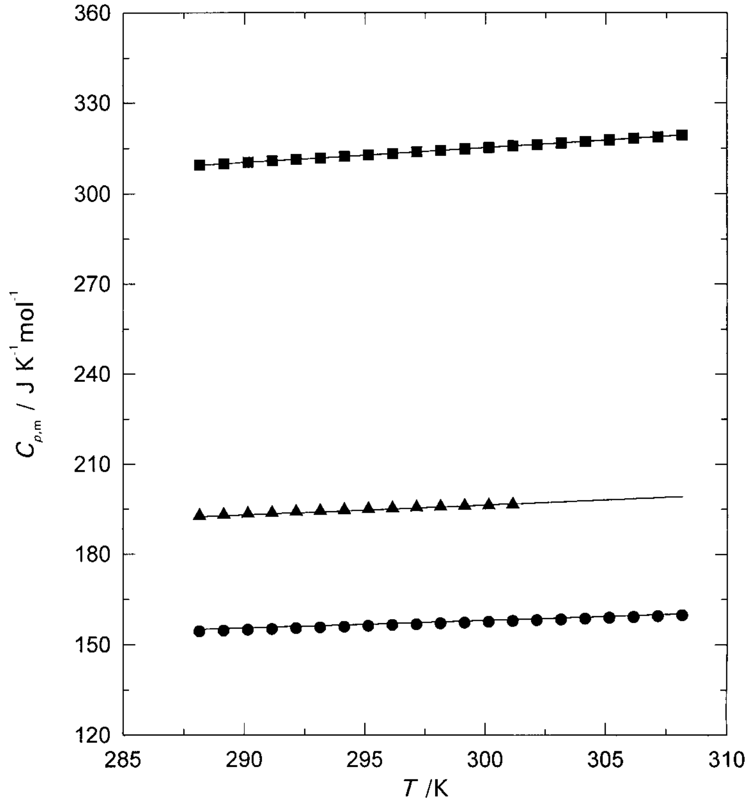

Fig. 4. Isobaric molar heat capacities $C_{p,m}$ against temperature T. Literature data: (●) toluene [18], (▲) hexane [19], (■) decane [12]. (—) Values of this work using the scanning method.

Table 3
Isobaric molar heat capacities $C_{p,m}$ of the liquids of this work at the temperature T

Liquid	T (K)	$C_{p,m}$ (J K mol^{-1})		
		Scanning method	Isothermal step method	Literature
Hexane	298.15	195.66		195.48 [10], 195.76 [20], 195.80 [21]
Octane	298.15	254.33		254.15 [10]
Decane	298.15	314.26	314.14	314.54 [10]
Toluene	298.15	157.49		157.29 [10], 156.88 [6], 157.026 [22]
Nitromethane	288.15	104.58	104.54	
	293.15	105.29	105.32	
	298.15	105.90	105.90	
	308.15	106.89	106.88	107.03 [10]
Butan-2-ol	288.15	184.72	184.65	
	293.15	190.52	190.46	
	298.15	196.26	196.21	196.67 [23]
	308.15	207.47	207.41	
2-Methyl, propan-1-ol	288.15	171.72	171.71	
	293.15	176.20	176.20	
	298.15	180.78	180.77	181.00 [10], 181.05 [24]
	308.15	190.22	190.25	

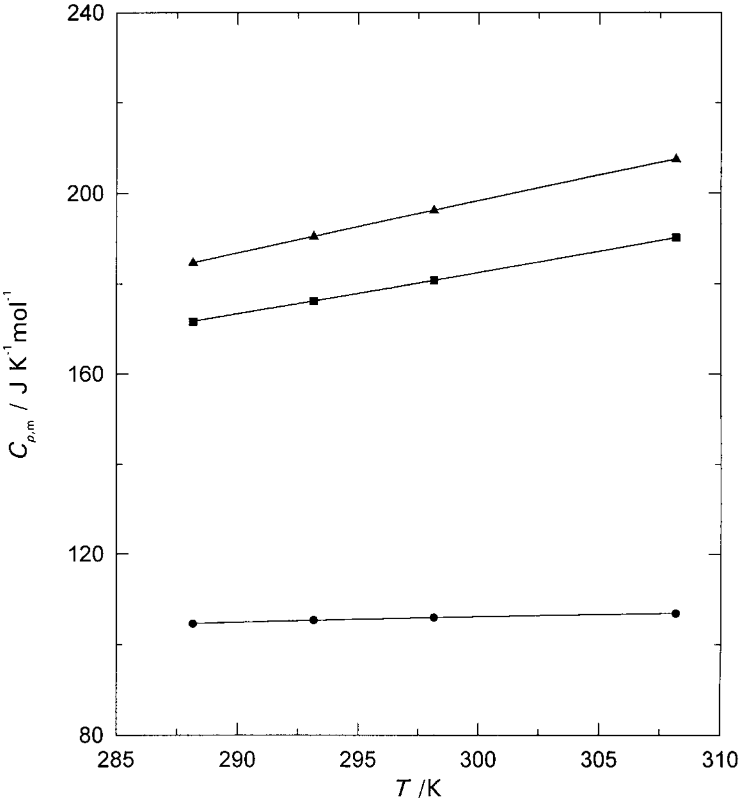

Fig. 5. Isobaric molar heat capacities $C_{p,m}$ against temperature T. Isothermal step method: (●) nitromethane, (▲) butan-2-ol, (■) 2-methyl, propan-1-ol. (—) Scanning method.

Table 4
Excess isobaric molar heat capacities $C^E_{p,m}$ for x nitromethane+(1−x)butan-1-ol

x	T (K)	$C^E_{p,m}$ (J K^{-1} mol^{-1})	
		Scanning method	Isothermal step method
0.05763	288.15	3.34	3.44
	293.15	3.38	3.52
	298.15	3.39	3.50
	308.15	3.32	3.37
0.10652	288.15	5.72	5.72
	293.15	5.78	5.80
	298.15	5.78	5.77
	308.15	5.59	5.52
0.94641	288.15	1.22	1.32
	293.15	0.96	1.13
	298.15	0.71	0.88
	308.15	0.23	0.39

Results from both methods agree closely with literature values. The average relative deviation between the results of both methods was about 0.02%; therefore, both lead to very similar results (see also Fig. 5).

One appropriate test for validating the scanning method was to determine the $C^E_{p,m}$ of binary liquid mixtures. Table 4 shows the results obtained for three different mixtures and those provided by the isothermal step method. As can be seen, the data are quite consistent, so the scanning method is precise enough for the reliable determination of $C^E_{p,m}$ values (see Fig. 6). Based on these results, the precision of the scanning method is essentially identical with that of the isothermal step method.

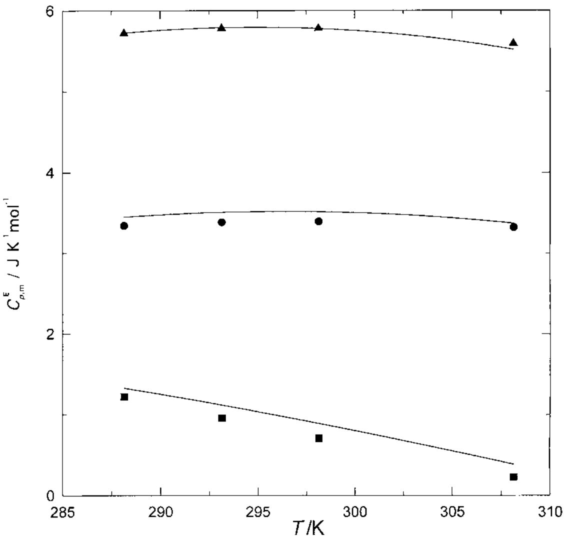

Fig. 6. Excess isobaric molar heat capacities $C^E_{p,m}$ for x nitromethane+(1−x)butan-1-ol against temperature T. Isothermal step method: (●) x=0.05763, (▲) x=0.10652, (■) x=0.94641, (—) scanning method.

5. Conclusions

As shown in this work, Micro DSC calorimeters are suitable for the precise determination of liquid heat capacities with the advantage over other alternatives (e.g., Picker flow calorimeters) that they afford convenient operation over wide temperature ranges in a simple manner. Also, a small amount of sample is required in contrast to the large amounts in adiabatic calorimetry. The precision of the scanning method is identical to that of the isothermal step method, which is much more time-consuming.

In future work, the scanning method will be applied over a broader temperature range. In addition, attempts will be made at improving both temperature and heat flow rate calibrations by using a more comprehensive set of standard reference substances.

Acknowledgements

This work is part of Research Project XUGA 38305B97. The authors are indebted to the Dirección

Xeral de Ordenación Universitaria e Política Científica (Xunta de Galicia) for financial support.

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