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Calibration of a low temperature calorimeter and application in the determination of isobaric heat capacity of 2-propanol

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ABSTRACT

Nowadays, the experimental thermodynamic characterization of solvents in an extended range of temperatures and pressures is essential for the development of a wide variety of industrial applications (refrigeration, reactors, pumping, etc.). Moreover, accurate experimental data are also the key for the successful development and subsequent benchmarking of thermodynamic theoretical models. In the particular case of isobaric heat capacities, there are quite a lot of reported experimental high temperature data but, on the other hand, low temperature data are practically inexistent for most compounds. Bearing this limitation in mind, the present work is focused on the development of a new calibration methodology for calorimetric determination of isobaric heat capacities in liquid state at low temperatures. For this purpose, a Calvet calorimeter, SETARAM BT 2.15 has been used. By means of the calibration procedure explained below, this calorimeter allows to determine phase transitions and thermodynamic properties in a wide range of temperature (233.15–473.15 K) and pressure (0.1–100 MPa).

1. Introduction

Accurate thermophysical properties are required in many scientific and industrial applications. Indeed, in Chemical Engineering the knowledge of such quantities is central for the design of unit operations, including for instance pumping, heating or cooling systems. From a theoretical point of view, experimental data are necessary to test and develop rigorous and reliable thermodynamic models. Among the set of experimentally accessible thermodynamic properties, isothermal compressibility κ_T, isobaric thermal expansion α_P or isobaric heat capacity C_P, have received considerable attention due to their definition from Gibbs free energy, G:

$$C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P \tag{1}$$

$$\alpha_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{\partial^2 G}{\partial T \partial P}\right)_P \tag{2}$$

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(\frac{\partial^2 G}{\partial P^2}\right)_T \tag{3}$$

where T, P and v are temperature, pressure and molar volume, respectively.

These thermodynamic relationships lead to a direct access to the second-order derivatives of this thermodynamic potential, and then provide useful information on the microscopic structure of fluids. Thus, second-order thermodynamic properties, and specially isobaric heat capacity, which is very sensitive to microscopic effects as for instance association between alcohol molecules [1–4], may be regarded as response functions of the involved fluids [5]. This means that their experimental macroscopic behaviour may be linked to the molecular level structure and interactions assumed to model or describe a given fluid, using for instance the analysis of energy and volume fluctuations within the framework of molecular simulation.

As detailed by Fulem et al. [6], two different types of heat capacities in the liquid phase, namely the isobaric C_P and the saturation C_{sat} heat capacities, are measurable and usually determined in experimental studies, and both of them are measured with the same accuracy. A survey of literature sources is given in the monograph by Zábranský et al. [7] for more than 1600 pure liquids, in a wide range of temperatures but only at atmospheric pressure. A detailed examination of these recommended values shows that, at this pressure, different trends versus temperature may appear [8]. Furthermore, many experiments have been carried out to determine the pressure dependence of C_P for several series of substances [9–16], but very few direct isobaric heat capacity measurements

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combining sub-ambient temperatures and high pressures have been performed [17–20].

Therefore, the aim of this work is to develop a new calibration methodology in order to provide comprehensive and accurate sets of C_P data covering an extended temperature range (233.15–473.15 K) at pressures up to 100 MPa.

In this context, a low temperature SETARAM BT 2.15 calorimeter was used, equipped with customized calorimetric cells allowing high-pressure operation. The experimental procedure is based on measurements of a differential heat-flow combined with a calibration technique, developed to determine with the highest feasible accuracy the isobaric heat capacity.

The work is organised as follows. In the first section, a complete description of the apparatus is given, underlining the details of the calibration procedure and the estimated data accuracy. In Section 2, novel experimental results are provided for a pure substance, isopropanol (2-propanol), which stands as the first step of an ongoing program to characterize the *P*–*T* behaviour of pure associated fluids and their mixtures.

2. Experimental set-up

A SETARAM BT 2.15 calorimeter was adapted to measure the isobaric heat capacity, C_P, of liquids up to 100 MPa. High-pressure calorimetric vessels were specifically designed to this aim. With the objective to incorporate the pressure as a thermodynamic variable a Calpresdat automated high pressure pump (250 cm^3 cylinder) was adapted to the device. In such a configuration, the BT 2.15 can operate as a temperature or pressure scanning calorimeter [21–22]. The pressure is measured with Viatran 245 transducers (precision ≤0.1% FSO). It's worthwhile to mention that the whole system is filled with the investigated liquid. A general view of the experimental set-up is presented schematically in Fig. 1.

Isobaric heat capacity measurements were performed using the temperature-scanning mode [23]. The temperature is increasing under isobaric conditions and the calorimetric response is recorded. The Calpresdat pump allows controlling isobaric conditions while the temperature is increasing. Under these conditions, in the case of an open-mass calorimetric vessel, the isobaric heat capacity is obtained on the basis of the following relation [24]:

$$C_P = \frac{P_{diff}(x) - P_{diff}(bl)}{\rho V_E (dT/dt)} \tag{4}$$

where $P_{diff}(x)$ is a differential calorimetric power signal obtained with the calorimetric measuring vessel filled with the studied fluid, and the reference one filled with helium at 0.1 MPa, $P_{diff}(bl)$ is a similar signal, but obtained with both vessels filled with helium at the same pressure of 0.1 MPa, ρ is the density of the studied fluid, V_E is the active volume (volume taken into account by the thermopiles), and t is the time. The use of helium in the reference vessel allows to avoid any condensation phenomenon under 273 K.

The differential calorimetric power signal is proportional to the differential calorimetric detector thermopile signal E via the static calibration constant k, as mentioned above.

Thus, Eq. (4) can be rewritten as

$$\frac{k}{V_E} = \frac{\rho C_P (dT/dt)}{E(x) - E(bl)} \tag{5}$$

This way, taking a fluid whose isobaric heat capacity and density are accurately known as a function of temperature at several pressures, calibration experiments can be performed, and the calibration ratio k/V_E can be determined.

3. Chemicals

n-Hexane (purity, 99%) and *n*-heptane (purity, 99%) were supplied by Fluka, and 2-propanol (purity, 99.9%) was supplied by Aldrich, and used without further purification.

4. Calibration results

The refrigeration of the BT 2.15 calorimeter was modified following the technique proposed by Hykrda et al. [17]. Instead of cooling the calorimeter by vaporization of nitrogen, the system was connected to an external cryothermostat, containing ethanol, with a temperature stability of ±0.01 K. This modification made it easier to control the temperature of the calorimeter block, keeping at the same time the operation costs remarkably low.

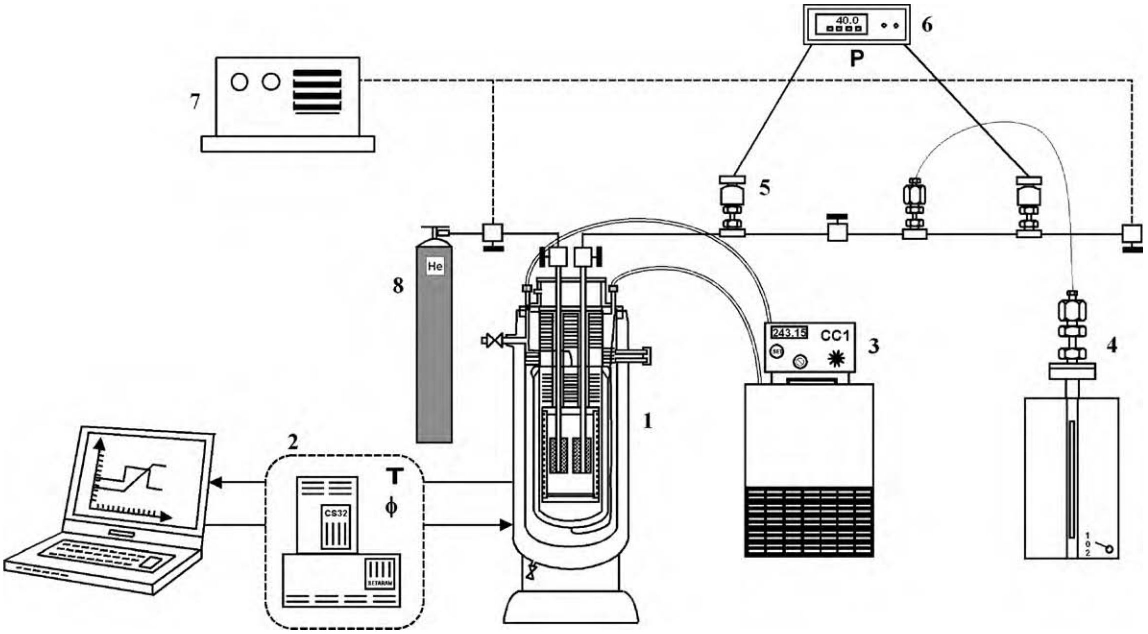

Fig. 1. Schematic diagram of the experimental set-up: (1) BT 2.15 calorimeter, (2) calorimeter controller, (3) cryothermostat, (4) Calpresdat automated high pressure pump, (5) Viatran 245 pressure transducers, (6) pressure controller, (7) vacuum pump and (8) gas tank.

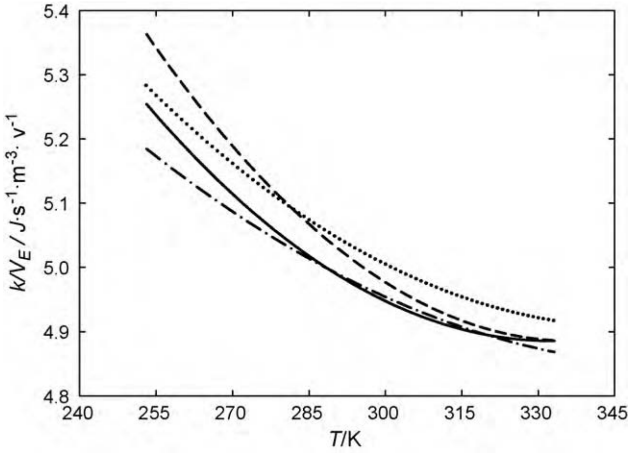

Fig. 2. Calibration constant k/V_E calculated at 0.1 MPa (- - - -), 10 MPa (– · – · –), 20 MPa (—), and 40 MPa (· · · ·).

The determination of the calibration ratio k/V_E by the isobaric heat capacity method was performed in the temperature range (253.15–333.15 K), at various pressures, with two calibrating substances. First, the results for the experiments with *n*-hexane [7,25] are illustrated in Fig. 2. The temperature scans were performed at a rate of 0.1 K/min.

In view of these results, we can firstly conclude that there is an insignificant dependence of k/V_E parameter with pressure, the average absolute deviation (AAD) being 1.5% with a maximum deviation at the lowest temperatures of 3%. Besides, the difference in the trend for the four isobars clearly indicates that k/V_E is not a systematic function of pressure. These two remarks allow us to neglect the effect of pressure in these temperature–pressure ranges, and consider only the dependence in temperature of the calibration constant. Then, a second substance was used, *n*-heptane, whose isobaric heat capacity is known with great accuracy (0.1%) only at atmospheric pressure [7]. This last step considering *n*-heptane data led to the determination of the following equation for the temperature dependence of the calibration constant:

$$\frac{k}{V_E} = 7.512 - 1.138 \times 10^{-2} T/\mathrm{K} + 1.053 \times 10^{-5} (T/\mathrm{K})^2 \tag{6}$$

This equation is in total accordance with the results obtained from *n*-hexane experiments.

5. Application to the experimental determination of C_P of 2-propanol

This experimental procedure was tested through the determination of the isobaric heat capacity of isopropanol in the temperature range (253.15–323.15 K) and from atmospheric pressure up to 40 MPa. Additional values of density, needed in C_P procedure in the same (P,T) range were measured with an Anton-Paar vibrating tube densimeter [26] previously calibrated with *n*-heptane and vacuum.

The expected uncertainty in the C_P determination with this technique is around 2%. The estimation of this value is based mainly on the estimated uncertainties in the calibration constant, ±1.5%, and the calorimetric signal reproducibility ±0.3%.

Table 1
Isobaric heat capacity C_P of isopropanol at various pressures.

T (K)	C_P (J mol^{-1} K^{-1})		
	P = 0.1 MPa	P = 20 MPa	P = 40 MPa
253.15	129.4	126.1	125.8
258.15	130.6	128.3	127.3
263.15	132.6	130.7	129.2
268.15	135.0	133.4	131.5
273.15	138.0	136.3	134.0
278.15	141.4	139.4	136.8
283.15	145.1	142.6	140.0
288.15	148.9	146.0	143.3
293.15	152.9	149.6	146.9
298.15	157.0	153.3	150.7
303.15	161.1	157.1	154.7
308.15	165.0	161.1	159.0
313.15	168.6	165.0	163.3
318.15	171.9	169.1	167.8
323.15	174.9	173.2	172.4

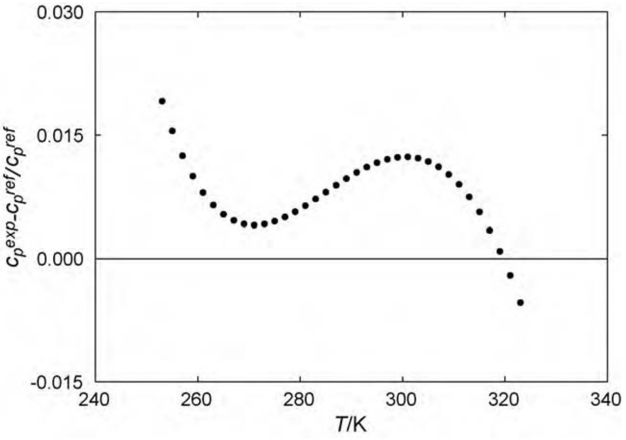

Fig. 3. Comparison of experimental isobaric heat capacity C_P of isopropanol, and the reference values [7] at atmospheric pressure.

The experimental isobaric heat capacities of isopropanol are presented in Table 1 with a temperature step of 5 K. These experimental data have been fitted to the following equation:

$$C_P(T/\mathrm{K}) = a_0 + a_1 T/\mathrm{K} + a_2 (T/\mathrm{K})^2 + a_3 (T/\mathrm{K})^3 \tag{7}$$

Fitting parameters, a_0, a_1, and a_2 are given in Table 2. The average absolute deviation, AAD = $(|R_{cor} - R_{exp}|/R_{exp} \times 100)$, for all pressures is less than 0.6%.

The experimental isobaric heat capacities of isopropanol at atmospheric pressure are plotted in Fig. 3 compared with literature values [6], showing a very good agreement between both sets of values (the average percent deviation is 0.8%), which certifies the reliability of the presented apparatus and calibration technique.

In order to further ensure the reliability of this work, another comparison has been made with unpublished experimental data from our laboratory [27] obtained with a previously developed C-80 SETARAM calorimeter [22,24] using the temperature-scanning mode in a temperature range of 301.15–401.15 K at the same studied pressures. Fig. 4 shows both sets of values. A very good agreement was also achieved by this way. The macroscopic

Table 2
Parameters of C_P correlation Eq. (7) and average absolute deviations.

	a_0	a_1	a_2	a_3	AAD (%)
P = 0.1 MPa	2.972E + 03	−3.022E + 01	1.050E−01	−1.184E−04	0.55
P = 20 MPa	7.109E + 02	−6.438E + 00	2.185E−02	−2.190E−05	0.36
P = 40 MPa	9.327E + 02	−8.248E + 00	2.631E−02	−2.496E−05	0.49

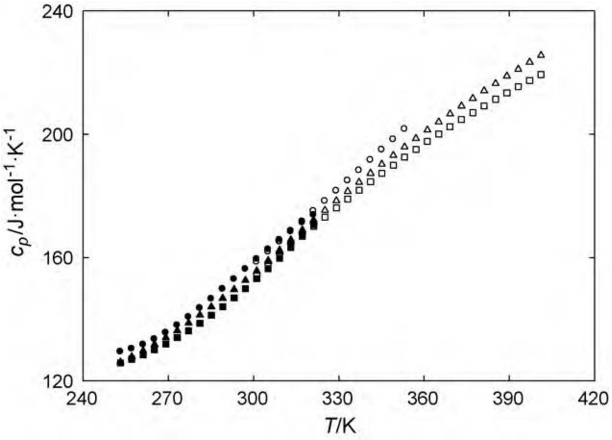

Fig. 4. Comparison of experimental isobaric heat capacity C_P of isopropanol from this work (●, 0.1 MPa; ■, 20 MPa; ▲, 40 MPa), and data from Ref. [27] (○, 0.1 MPa; □, 20 MPa; △, 40 MPa).

behaviour of the isobaric heat capacity displaying a convex to concave curvature versus temperature, which can be analyzed as an unambiguous manifestation of the association phenomenon represent an original information in order to test thermodynamic model.

6. Conclusion

A new calibration methodology developed to provide comprehensive and accurate sets of C_P data at low temperatures using a BT 2.15 calorimeter was developed. Calibration was performed in the temperature range (253.15–333.15 K) at pressures up to 40 MPa using *n*-hexane and *n*-heptane. Experimental data allowed determining the independence of k/V_E with pressure and its trend with temperature. This experimental calibration procedure was tested by determining the isobaric heat capacity of isopropanol in the temperature range (253.15–323.15 K) and from the atmospheric pressure to 40 MPa. Experimental results were compared with values from literature and unpublished experimental data from our laboratory. A remarkably good accuracy was achieved in both cases.

This work has then shown that it is possible to measure C_P of pure liquids at low temperatures by applying the proposed method to an estimated uncertainty of 0.5%, extending the temperature range usually explored in literature for the measurement of this thermodynamic magnitude, provided that experimental density data are available for the fluid under study in the same temperature and pressure conditions.

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