



Heat capacities of selected cycloalcohols



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ARTICLE INFO

Article history:

Received 28 July 2014

Received in revised form 29 September 2014

Accepted 1 October 2014

Available online 7 October 2014

Keywords:

Alcohols

Heat capacity

In liquid phase

Temperature correlation

IR spectroscopy

ABSTRACT

Isobaric heat capacities of selected cycloalcohols (cyclobutanol, CAS RN: 2919-23-5; cyclopentanol, CAS RN: 96-41-3; cyclohexanol, CAS RN: 108-93-0; cycloheptanol, CAS RN: 502-41-0; cyclooctanol CAS RN: 696-71-9) were measured with a highly sensitive Tian–Calvet calorimeter in the temperature range from 254 K to 352 K. Experimental heat capacity data were correlated as a function of temperature. The phase behavior was investigated with a differential scanning calorimeter. Calorimetric measurements were complemented by FTIR spectroscopy for less volatile compounds (cyclohexanol, cycloheptanol, cyclooctanol). The main aim of this work was to fill the gap in reliable heat capacity data for these compounds and to extend the knowledge base required for a better understanding of alcohols self-association.

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1. Introduction

Heat capacities belong among the fundamental thermophysical properties which are indispensable for evaluation of the variation of thermodynamic properties with temperature. Heat capacity data have a wide field of application in chemical engineering for establishing energy balances, in thermochemistry for calculating changes in reaction enthalpies as well as in evaluation of molecular and supramolecular interactions and structural changes of materials. Liquid heat capacities also serve as one of input data for reliable extrapolation of vapor pressure down to the triple point [1]. Extensive collection of critically assessed heat capacity data was published [2–4] and estimation methods based on this collection were developed [5,6]. The present paper is a continuation of our effort [7] to establish reliable heat capacity data for alcohols as they often exhibit a complex temperature dependence of liquid heat capacity, including inflection points [8], plateau or even maxima [9–13], which is not captured by the existing estimation methods and which leads to biased estimates with higher uncertainties when compared to other classes of compounds. For a better understanding of H-bonding, the stretching mode of O–H bond of cyclohexanol, cycloheptanol, and cyclooctanol was studied as a function of temperature. The phase behavior of cyclooctanol and

cyclobutanol was studied by DSC as previously published values were ambiguous.

2. Experimental

2.1. Samples description

The studied alcohols were of commercial origin and were used as received except drying over 0.4 nm molecular sieves since their purity, as checked by gas–liquid chromatography, was found satisfactory. The samples purity and water content are reported in Table 1.

2.2. Heat capacity measurements

A highly sensitive Tian–Calvet calorimeter (Setaram μ DSC IIIa) was used for the measurement of heat capacities using either the incremental temperature (step) or continuous method [14]. The two methods should yield identical results assuming that the calorimeter base-line changes linearly with temperature. This was confirmed for the Setaram μ DSC IIIa calorimeter and the temperature range from 258 K to 355 K used in this study [15]. The combined expanded uncertainty of the heat capacity measurements is estimated to be $U_c(C_p) = 0.01 C_p$. A detailed description of the calorimeter and its calibration can be found in a paper by Straka et al. [16]; the measuring procedure was described in detail previously [15,17].

For the correlation of heat capacity data, a polynomial equation was used:

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Table 1
Sample description table.

Compound	CAS number	Supplier	Mole fraction purity ^a	Water mass fraction w_{H_2O} ^b
Cyclobutanol	2919-23-5	Aldrich	0.9982	2.8×10^{-4}
Cyclopentanol	96-41-3	Aldrich	0.9993	1.2×10^{-5}
Cyclohexanol	108-93-0	Aldrich	0.9996	4.0×10^{-5}
Cycloheptanol	502-41-0	Aldrich	0.9937	1.5×10^{-5}
Cyclooctanol	696-71-9	Fluka	0.9925	1.0×10^{-5}

^a Gas–liquid chromatography analysis by Hewlett-Packard 6890 gas chromatograph equipped with column HP5 cross-linked 5% PHME siloxane, length 30 m, film thickness 0.25 μm , i.d. 0.32 mm, and FID detector.

^b Carl–Fischer analysis by Metrohm 831.

$$\frac{C_p}{R} = \sum_{i=0}^n A_{i+1} \left(\frac{T}{100} \right)^i \quad (1)$$

where R is the molar gas constant ($R = 8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$ [18]). Cyclohexanol, cycloheptanol, and cyclooctanol exhibit the solid–liquid phase transition inside the measured temperature range and therefore the heat capacity of solid samples was also determined, albeit in a rather short temperature range.

2.3. Phase behavior

The phase behavior of selected alcohols was investigated in the temperature range from 183 K to 303 K using a differential scanning calorimeter TA Q1000 (TA Instruments, USA). The measurements were carried out using continuous method [14] with a heating rate of 2 K min^{-1} . Temperature and enthalpy calibration of the device was performed using water, gallium, naphthalene, indium, and tin. The samples were enclosed in the so-called hermetic aluminum pans. Measurements at higher temperatures (up to normal boiling point temperature in order to see qualitatively the shape of heat capacity curve) were attempted after finishing the phase behavior studies. Relatively few experiments were successful and will be reported below.

2.4. FTIR spectroscopy

ATR FTIR spectra were collected using a Nicolet 6700 spectrometer equipped with deuterated triglycine sulfate (DTGS) detector, KBr beam splitter, and horizontal micro-ATR Golden Gate unit (SPECAC) with diamond crystal. The thin layers of liquid samples of alcohols were closed between diamond crystal surface and a glass plate separated by teflon spacer of thickness ca $50 \mu\text{m}$. The samples were first investigated at room temperature, and then gradually heated from 313 K to 473 K in steps of 20 K. 64 scans with spectral resolution 4 cm^{-1} were coadded at each temperature to achieve a good signal-to-noise ratio. Contribution from residual water vapor present in air to spectra was subtracted using OMNICTM software.

To locate the position of O–H stretching bands in spectra corresponding to free and hydrogen-bonded OH groups, 1% (v/v) solution of cyclooctanol in dry CCl_4 at 293 K was also measured. This measurement was performed in a cell for liquids closed with ZnSe windows separated by a silicon spacer of thickness of 0.88 mm.

3. Results and discussion

3.1. Heat capacities

Experimental heat capacities are listed in Table 2. A summary of performed experiments is presented in Table 3 along with the literature data. Selected data sets given in bold in Table 3 were correlated by Eq. (1) whose parameters are given in Table 4. Data selection was generally based on time of publishing (old data were not considered), purity and water content of samples, and

technique used (the uncertainty of results obtained by adiabatic calorimetry is usually lowest). The smoothed values (e.g. [19,20]) as well as the measurements at single temperature were not considered. The residuals of all data points from the present work from Eq. (1) are smaller than 1% (see Table 2). Note that the parameters in Table 4 represent the recommendation for the liquid phase heat capacities, while for the solid phase heat capacities they serve as a guide for the estimation of uncertainty of heat capacity measurements of cyclooctanol (by comparison of the data for solid cyclohexanol and cycloheptanol with accurate adiabatic measurements [21,22], as described below).

In the case of cyclobutanol, the only measurement of heat capacity was reported in a graphical form by McGregor et al. [23]. The comparison with data of this work is therefore not possible. Fig. 1 shows relative deviations of experimental data from Eq. (1) for cyclopentanol. The agreement of the present data with values published by Kabo et al. [24] is very good and also the data from other sources [19,25,26] are in a reasonable agreement. A single data point reported by Conti et al. [27] exhibit deviation higher than 1% for cyclopentanol as well as for cyclohexanol and cycloheptanol.

The agreement of our data for liquid cyclohexanol (Fig. 2) and liquid cycloheptanol (Fig. 3) with the data published by Adachi et al. [21,22] is very good in the liquid phase but less satisfactory in the crystal I phase (though within combined uncertainties of the two datasets). A possible explanation can be a different thermal history of the samples. While our samples were cooled from room temperature to 255 K using a cooling rate gradually decreasing from 0.3 K min^{-1} to 0.05 K min^{-1} (for details see Supporting information), the Adachi's samples were cooled to very low temperatures (well below 100 K) prior measurements of crystal I phase. Steele et al. [10] measured the heat capacity of two-phase system at constant volume C_V^I of cyclohexanol by a power-compensated DSC up to the critical temperature and converted the data to the heat capacity along saturation curve C_{sat} , which were almost constant over the temperature range from 440 K to 560 K, with a maximum value at 480 K, i.e. well above the normal boiling temperature 433.94 K [10]. Though C_{sat} can be in principle converted to C_p [2,28] using

$$C_p = C_{\text{sat}} + T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_{\text{sat}} \quad (2)$$

the variation of volume with temperature at constant pressure $(\partial V / \partial T)_p$ required for such recalculation is not available in the case of cyclohexanol. At temperatures well below the normal boiling point temperature the C_p and C_{sat} are however identical within the experimental uncertainty. Therefore, the values reported by Steele et al. [10] can be directly compared with the data of this work in the overlapping temperature range. The data agree within 1% with our C_p , however their scatter (caused by publishing rounded C_{sat} values in [10]) would somewhat distort the final fit. Note also a short extrapolation used when producing C_{sat} at 300 K in [10] (C_V^I were measured from 310 K to 590 K).

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