



Calorimetric and FTIR study of selected aliphatic heptanols



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ABSTRACT

Isobaric liquid phase heat capacities of nine selected aliphatic heptanols (1-heptanol, CAS RN: 111-70-6; 3-heptanol, CAS RN: 589-82-2; 4-heptanol, CAS RN: 589-55-9; 2-methyl-2-hexanol, CAS RN: 625-23-0; 5-methyl-2-hexanol, CAS RN: 627-59-8; 2-methyl-3-hexanol, CAS RN: 617-29-8; 3-ethyl-3-pentanol, CAS RN: 597-49-9; 2,2-dimethyl-3-pentanol, CAS RN: 3970-62-5; 2,4-dimethyl-3-pentanol, CAS RN: 600-36-2) were measured with a highly sensitive Tian-Calvet calorimeter in the temperature range from 261 K to 382 K. Experimental heat capacity data were correlated as a function of temperature. For eight compounds, a maximum on temperature dependence of heat capacity was observed. The phase behavior was investigated with a differential scanning calorimeter. Calorimetric measurements were complemented by FTIR spectroscopy from room temperature to a maximum of 428 K. 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. Although extensive collection of critically assessed heat capacity data was published [1–3] and estimation methods based on this collection were developed [4,5], new measurements are necessary for alcohols. This group of compounds often exhibit a complex temperature dependence of liquid heat capacity, including inflection points [6], plateau or even maxima [7–12], 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. The present paper is a continuation of our effort [8,12–15] to establish reliable heat capacity data for alcohols. For a better understanding of H-bonding, the stretching mode of O–H bond of selected alcohols was studied as a function of temperature. The phase behavior was studied using differential scanning calorimetry (DSC) as no literature data were found for 2-methyl-2-hexanol, 5-methyl-2-hexanol, and 2-methyl-3-hexanol.

2. Experimental

2.1. Samples description

The studied alcohols were of commercial origin. Purification of 1-heptanol was described previously [8]. Remaining alcohols were used as received except drying over 0.4 nm molecular sieves since their purity, as checked by gas-liquid chromatography, was found satisfactory. For 5-methyl-2-hexanol, 2-methyl-3-hexanol, and 2,2-dimethyl-3-pentanol, a mass spectroscopy analysis was performed to identify the main impurities which allowed correcting the heat capacity data for these impurities. Sample loading into calorimetric vessels and pans was performed in a glovebox (MBraun LabStar) under dry nitrogen atmosphere. 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 [16]. 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 261 K to 382 K used in this study [17]. The

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Table 1
Sample description table.

Compound	CAS RN	Supplier	Mole fraction purity ^a	Mole fraction purity ^b	Water mass fraction $w_{\text{H}_2\text{O}}$ ^c
1-heptanol	111-70-6	Aldrich	0.980	0.9961	2.3×10^{-5}
3-heptanol	589-82-2	Aldrich	0.996	0.9980	4.2×10^{-5}
4-heptanol	589-55-9	TCI	0.992	0.9953	1.3×10^{-5}
2-methyl-2-hexanol	625-23-0	Aldrich	0.990	0.9919	– ^d
5-methyl-2-hexanol	627-59-8	Aldrich	0.990	0.9894 ^e	1.3×10^{-5}
2-methyl-3-hexanol	617-29-8	Aldrich	0.982	0.9725 ^f	– ^d
3-ethyl-3-pentanol	597-49-9	Aldrich	0.985	0.9919	– ^d
2,2-dimethyl-3-pentanol	3970-62-5	Aldrich	0.973	0.9732 ^g	– ^d
2,4-dimethyl-3-pentanol	600-36-2	Aldrich	0.993	0.9913	0.6×10^{-5}

^a Purity stated by the manufacturer.

^b Gas-liquid chromatography analysis performed 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.

^c Karl-Fischer analysis by Metrohm 831.

^d Below the detection limit of Karl-Fischer analysis.

^e The main impurities detected were 5-methyl-2-hexanone ($x = 0.0039$) and 2-heptanol ($x = 0.0025$).

^f The main impurity detected was 2-methyl-3-hexanone ($x = 0.0229$).

^g The main impurity detected was tertbutylpropyl ether ($x = 0.0225$).

combined expanded uncertainty (0.95 level of confidence) 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. [18]; the measuring procedure was described in detail previously [19,20].

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

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

where R is the molar gas constant ($R = 8.3144598 \text{ J K}^{-1} \text{ mol}^{-1}$ [21]).

2.3. Phase behavior

The phase behavior of selected alcohols was investigated in the temperature range from 183 K to 413 K (in the case of 5-methyl-2-hexanol until 437 K) using a differential scanning calorimeter TA Q1000 (TA Instruments, USA). The measurements were carried out using continuous method [16] with a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$; in the case of 4-heptanol, heating rate $0.5 \text{ K} \cdot \text{min}^{-1}$ was also used. 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.

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. Small amounts of liquid samples of alcohols were injected using a syringe into a space hermetically closed between diamond crystal surface and a copper plate separated by a ring spacer from silicone rubber. The samples were heated gradually from 303 K in steps of 10 K until a highest temperature below the sample boiling point was achieved. 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 OMNIC™ 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 selected alcohol in dry CCl_4 at 298 K was measured. This measurement was performed in transmission using a cell for liquids closed with ZnSe windows separated by a silicon rubber spacer

of thickness of 0.88 mm.

3. Results and discussion

3.1. Heat capacities

Experimental heat capacities obtained in this work with Setaram μDSC IIIa, are listed in Table 2 and shown in Fig. 1. For 5-methyl-2-hexanol, 2-methyl-3-hexanol, and 2,2-dimethyl-3-pentanol, the original experimental heat capacities were recalculated using the heat capacities of main impurities (see Table 1) and assuming that excess heat capacity can be neglected. Experimental heat capacities of impurities were not found (with the exception of a single point found for 2-methyl-3-hexanone [22], the impurity in 2-methyl-3-hexanol). Therefore, the estimation method by Kolská et al. [5] was used for calculation of C_p of impurities. Original uncorrected data are presented in the Supporting information (SI) in Table S1. The maximum correction amounted to 0.1%, 0.7% and 0.8% for 5-methyl-2-hexanol, 2-methyl-3-hexanol and 2,2-dimethyl-3-pentanol, respectively. Due to the uncertainty of this correction, the overall uncertainty of heat capacity for 5-methyl-2-hexanol, 2-methyl-3-hexanol, and 2,2-dimethyl-3-pentanol might be slightly higher than for the rest of the studied compounds. A summary of performed experiments is presented in Table 3 along with the literature data, which were available only for 1-heptanol, 4-heptanol, and 3-ethyl-3-pentanol.

In the case of 1-heptanol, the data obtained in this work agree within the stated uncertainty with the equation recommended by Zábanský et al. [26]. The recommendation [26] is based on ten datasets with a dominant influence of the dataset by Miltenburg et al. [15] (the lowest uncertainty 0.2% and the highest number of data points: 78 out of 210). As the uncertainty of recommended data is lower than that of this work, our data were not used for the development of parameters of Eq. (1) and are only compared to recommended data in Fig. 2. The agreement is well within stated uncertainty of our measurements.

For 4-heptanol, the heat capacity at single temperature 298.15 K was measured by Conti et al. [23] and by Verevkin and Schick [25] with the deviation from our data +1.4% and –2.1%, respectively. In case of 3-ethyl-3-pentanol, the recommendation by Zábanský et al. [26] is based on dataset by Cerdeirina et al. [9] obtained with a Tian-Calvet calorimeter Setaram μDSC IIa (and single datapoint from [24]). The measurements were repeated in the same laboratory in 2007 [10] with practically identical results. Moreover, the measurements were performed at higher temperatures using

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