



Heat capacities of 2-propenol and selected cyclohexylalcohols



Martin Straka, Květoslav Růžička*, Michal Fulem

Department of Physical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

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ABSTRACT

Isobaric heat capacities of four selected alcohols, cyclohexanemethanol (CAS RN: 100-49-2), cyclohexaneethanol (CAS RN: 4442-79-9), cyclohexanepropanol (CAS RN: 1124-63-6), and 2-propenol (CAS RN: 107-18-6), were measured with a sensitive Tian–Calvet calorimeter in the temperature range from 254 K to 352 K. The phase behaviour was investigated with a differential scanning calorimeter. Experimental heat capacity data were correlated as a function of temperature. 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 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 are also used as one of the input data for reliable extrapolation of vapor pressures down to the triple point [1]. An extensive collection of critically assessed heat capacity data was published [2–4] and estimation methods based on this data set were developed [5–7]. The present paper is a continuation of our effort [8–11] to establish reliable heat capacity data for alcohols as they often exhibit a complex temperature dependence of liquid heat capacity, including inflection points [12] and even maxima [8,13–15], 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. New heat capacity measurements of alcohols are therefore desirable. Cyclohexylalcohols selected for this work were supplemented with 2-propenol, which appears on the list of compounds with missing or limited heat capacity data [16].

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. The samples purity and water content are reported in Table 1.

2.2. Heat capacity measurements

The μ DSC IIIa calorimeter (Setaram, France) was used for the heat capacity determination in the temperature range from 254 K to 352 K. The incremental temperature mode (step method) was used [17]. Each 5 K step included a heating rate of 0.3 K min^{-1} followed by an isothermal delay of 2400 s. The mass of the samples, as determined by an analytical balance with a readability of 0.01 mg, ranged from 0.60 g to 0.73 g (see Table 2). The combined expanded uncertainty (0.95 level of confidence) of the heat capacity measurements is estimated to be $U_c(C_p) = 0.01 \cdot C_p$. 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 by Fulem et al. [19].

Experimental heat capacity data were correlated using a polynomial equation:

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

where R is the molar gas constant ($R = 8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$ [20]).

* Corresponding author. Tel.: +420 220 444 116.

E-mail address: kvetoslav.ruzicka@vscht.cz (K. Růžička).

Table 1
Sample description table.

Compound	CAS number	Supplier	Mole fraction purity ^a	Water mass fraction ^b
Cyclohexanemethanol	100-49-2	Aldrich	0.9982	1.6×10^{-4}
Cyclohexaneethanol	4442-79-9	Aldrich	0.9993	1.2×10^{-5}
Cyclohexanepropanol	1124-63-6	Aldrich	0.9920	3.3×10^{-5}
2-Propenol	107-18-6	Aldrich	0.9978	8.8×10^{-4}

^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.

2.3. Phase behaviour

The phase behaviour of all 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 [17] with a heating rate of 2 K min^{-1} . The temperature and enthalpy calibration was performed using water, gallium, naphthalene, indium and tin.

3. Results and discussion

3.1. Heat capacities

Experimental heat capacities listed in Table 2 were correlated by Eq. (1) whose parameters are given in Table 3. No literature

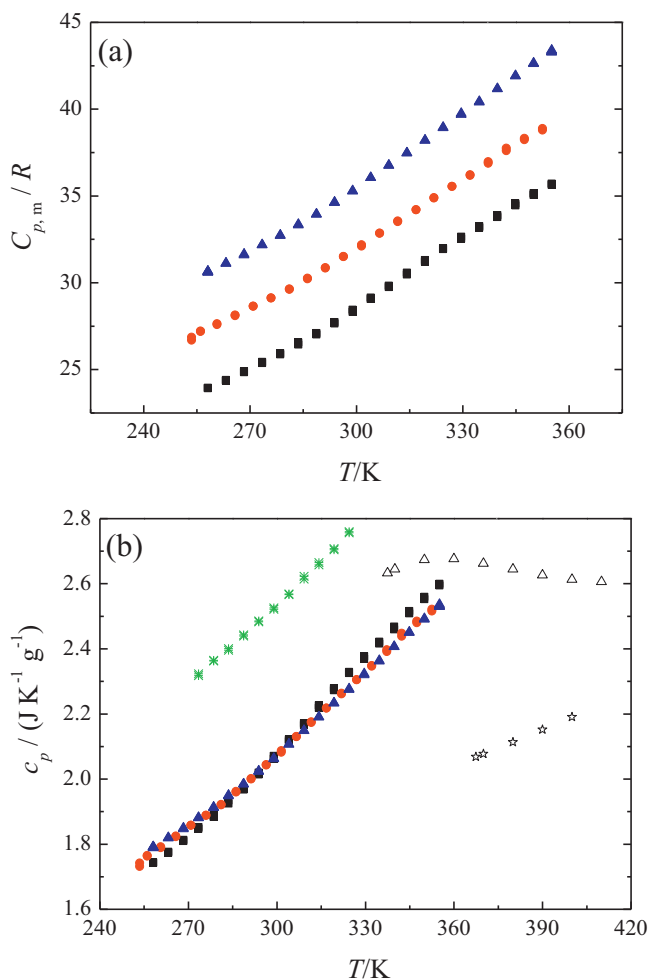


Fig. 1. Molar (a) and specific (b) heat capacities of studied alcohols. This work: (■) cyclohexylmethanol, (●) cyclohexylethanol, (▲) cyclohexylpropanol, (✱) 2-propenol. Literature values [15]: (Δ) dicyclohexylmethanol, (☆) tricyclohexylmethanol.

data were found for any of the studied alcohols. The residuals of all experimental data points from Eq. (1) are less than 1%.

The heat capacity of 2-propenol was measured only up to 324 K due to its high volatility, which would require application of correction for evaporation according to Hoge [2,21,22]; the data required for evaluation of this correction (vapor pressure and its derivatives with respect to temperature, density of liquid and gaseous phases) are not available. Moreover, due to technical problems with the thermostat, the measurements below 273 K could not have been performed for this compound.

3.2. Phase behaviour

The TA Q1000 differential scanning calorimeter was used in the temperature range 183 K–303 K, but enthalpy and temperature of fusion was not detected in this temperature range. Note that alcohols easily undercool, especially in the case of very small samples, therefore it cannot be ruled out that the fusion takes place in the studied temperature range.

3.3. General trends in liquid heat capacities of studied alcohols

Fig. 1 shows a comparison of the heat capacities of cyclohexanemethanol, cyclohexaneethanol, and cyclohexanepropanol. It can be seen that the molar liquid heat capacity increases with the molar mass as expected (Fig. 1a). While the data for cyclohexaneethanol and cyclohexanepropanol seem to perfectly fall onto the same curve when expressed as the specific heat capacity c_p (Fig. 1b), the data for cyclohexylmethanol differs by slightly more than a combined uncertainty of the measurements

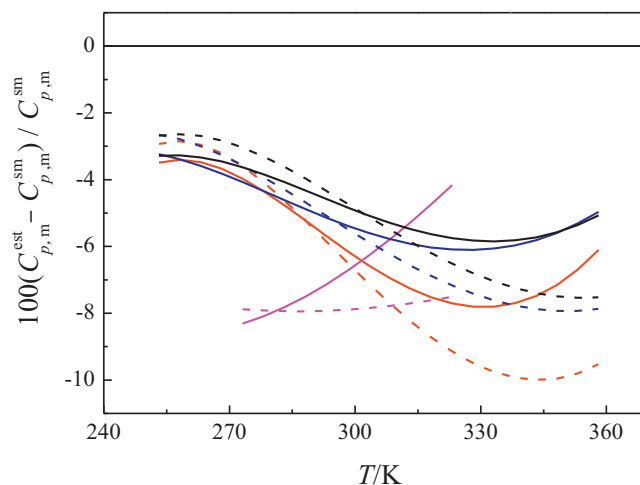


Fig. 2. Relative deviations of the heat capacity estimated by the methods of Zábanský and Růžička [6] and of Kolská et al. [7] from the smoothed data of this work (calculated by Eq. (1) with the parameters from Table 3). (—) cyclohexylmethanol [6], (---) cyclohexylmethanol [7], (—) cyclohexylethanol [6], (---) cyclohexylethanol [7], (—) cyclohexylpropanol [6], (---) cyclohexylpropanol [7], (—) 2-propenol [6], (---) 2-propenol [7].

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