



Critical properties of some aliphatic symmetrical ethers



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ABSTRACT

The critical temperatures T_c and the critical pressures p_c of dihexyl, dioctyl, and didecyl ethers have been measured. According to the measurements, the coordinates of the critical points are $T_c = (665 \pm 7) \text{ K}$, $p_c = (1.44 \pm 0.04) \text{ MPa}$ for dihexyl ether, $T_c = (723 \pm 7) \text{ K}$, $p_c = (1.19 \pm 0.04) \text{ MPa}$ for dioctyl ether, and $T_c = (768 \pm 8) \text{ K}$, $p_c = (1.03 \pm 0.03) \text{ MPa}$ for didecyl ether. All the ethers studied degrade chemically at near-critical temperatures. A pulse-heating method applicable to measuring the critical properties of thermally unstable compounds has been used. The times from the beginning of a heating pulse to the moment of reaching the critical temperature were from 0.06 to 0.46 ms. The short residence times provide little decomposition of the substances in the course of the experiments. The critical properties of the ethers investigated in this work have been discussed together with those of methyl to butyl ethers. The experimental critical constants of the ethers have been compared with those estimated by the group-contribution methods of Wilson and Jasperson and Marrero and Gani. The Wilson/Jasperson method provides a better estimation of the critical temperatures and pressures of simple aliphatic ethers in comparison with the Marrero/Gani method if reliable normal boiling temperatures are used in the method of Wilson and Jasperson.

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1. Introduction

Symmetrical or simple aliphatic ethers are an important class of organic compounds. For instance, dimethyl ether is well known to be used as a substitute for propane in liquefied petroleum gas, as a precursor to other organic compounds, as an aerosol spray propellant. Dimethyl ether is also a promising fuel in diesel and petrol engines and gas turbines; it is considered as a synthetic biofuel, which can be manufactured from forest products, agricultural by-products, organic waste and so forth [1]. Diethyl ether is used as a solvent in the production of cellulose plastics, as a starting fluid in combination with petroleum distillates for various engines, as a general anesthetic. Heavier simple ethers are in considerable use as solvents of fats, oils and resins. Linear dialkyl ethers with a chain length including the oxygen atom of 10 to 40 are employed as an additive to a diesel fuel based on ethanol. Such an additive provides burning of the fuel with small emissions of particles. Particularly suitable are dihexyl, dioctyl, and didecyl ethers [2].

Vapour+liquid critical properties are important characteristics of elements and compounds because they are input parameters for the estimation of many other physical properties by the application of the principle of corresponding states. It allowed Daubert to set the critical properties in the first place in his hierarchy of

thermophysical properties [3]. The critical constants of dimethyl and diethyl ethers have been measured by many researches. Kudchadker *et al.* [4] surveyed these data and gave the recommended values of the critical properties. Later Wu *et al.* [5] developed an equation of state for the thermodynamic properties of dimethyl ether. In particular, they fulfilled an analysis of the existing critical parameters and gave the recommended values. The recommended critical properties of dimethyl ether given by Kudchadker and co-authors and Wu and co-workers are close enough. There are experimental data on the critical constants of dimethyl and diethyl ethers that were not included into the papers by Kudchadker *et al.* and Wu *et al.* or published after the appearance of these reviews [6–8]. These data differ little from the recommended critical properties of dimethyl and diethyl ethers presented by Kudchadker *et al.* or Wu *et al.* The critical constants of dipropyl and dibutyl ethers [9–11] have been studied much worse than those of dimethyl and diethyl ethers. To our knowledge, the critical properties of simple aliphatic ethers heavier than dibutyl ether have never been measured.

Little is known about the thermal stability of simple ethers at their critical points. Polikhronidi *et al.* [8] observed the thermal decomposition of diethyl ether at near-critical temperatures. The magnitude of the decomposition effect depended on the temperature, pressure, and residence time in the measuring cell. For dipropyl ether, Ambrose *et al.* [9] noticed no dependence of the apparent critical temperature on the residence time, while Liang *et al.* [10] found that the apparent critical temperature rose from 533 to

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535 K as the residence time increased from 6 to 15 s. Toczylkin and Young write nothing about the thermal stability of dibutyl ether, the critical properties of which they experimentally determined [11]. In this work, we measured the critical constants of dihexyl, dioctyl, and didecyl ethers, the critical temperatures of which lie between about 700 and 770 K. It is reasonable to suggest that ethers with such high critical temperatures are unstable at their critical points; so the measurements were performed using the pulse-heating method applicable to thermally unstable compounds.

2. Experimental

2.1. Materials

The samples of symmetrical ethers were of commercial origin and used without any further purification. The Chemical Abstract Service Registry Numbers (CASRN), suppliers, and purities of the samples according to the suppliers' data are listed in table 1.

2.2. Method

The critical temperatures and the critical pressures of symmetrical ethers have been measured by the pulse-heating method that has been used by our team for many years. The physical basis, the details of the apparatus and the measurement procedure were described earlier [12–16]. The pulse-heating technique is based on the phenomenon of liquid superheat [17–19]. It is well known that liquid can be heated at a given pressure above the vapour+liquid equilibrium temperature and exist in superheated state. Under the conditions of rapid heating a metastable liquid will boil-up at the temperature of the attainable superheat (spontaneous boiling-up). The dependence of the temperature of the attainable superheat on pressure is called the line of the attainable superheat. This line ends at the critical point. Therefore, the critical pressure and the critical temperature can be determined by measuring the pressure dependence of the temperature of the attainable superheat.

The temperature of the attainable superheat at a given pressure was determined with the help of a platinum wire probe immersed into a liquid under study which was in a measuring chamber. The probe, 2×10^{-3} in diameter and (1–3) cm in length, served simultaneously as a heater and a resistance thermometer. The probe was heated by electric current pulses in such a way that by the end of a pulse the probe temperature reached the temperature of the attainable superheat and boiling-up took place. The time from the beginning of a pulse to the moment of boiling-up t^* was from 0.06 to 0.46 ms in various experiments. Such low heating times provided small decomposition of unstable compounds in the course of measuring the critical properties.

At the moment of boiling-up the conditions of heat transfer from the probe to the liquid changed and a temperature perturbation of the probe arose. The temperature perturbation is uniquely connected with a voltage perturbation on the probe. The voltage perturbation was observed on the screen of a digital oscilloscope. The temperature of the probe at the beginning of a temperature

perturbation, that is, at the beginning of boiling-up was determined from the resistance of the probe using a bridge circuit.

The dependence of the temperature of the attainable superheat on pressure was measured in the following way. At first the pressure in the chamber was established a little above the atmospheric pressure, and then the pressure was increased step by step. The probe temperature perturbation may be negative or positive in the initial stage of boiling-up. The sign of the perturbation is determined by the competition of two effects: heat consumption for vapour formation and screening of the wire surface by the vapour bubbles growing on the wire. For low-molar-mass compounds (nonpolymers) the temperature perturbation is negative at near-critical pressures. When the pressure approaches the critical pressure, the properties of the liquid and vapour phases come closer and the amplitude of the temperature perturbation drops. The pressure in the chamber was increased until the negative temperature perturbation decreased to the level of the apparatus sensitivity (1×10^{-3} K). This pressure and the temperature of the attainable superheat at this pressure were taken as the measured values of the critical pressure p_c^m and the critical temperature T_c^m .

The numerous pulse-heating experiments show that the values of p_c^m and T_c^m are a bit lesser than the true critical properties. For stable compounds, the true critical pressure p_c and temperature T_c are calculated by the following equations:

$$p_c = p_c^m / \pi_0, \quad T_c = T_c^m / \tau_0, \quad (1)$$

where $1/\pi_0$ and $1/\tau_0$ are correction factors. The quantities π_0 and τ_0 are the reduced pressure and the reduced temperature at which the theoretical value of the negative temperature perturbation drops to the level of the apparatus sensitivity. A formula for the calculation of the amplitude of the temperature perturbation was given in our previous papers [12,16]. The properties of a compound under study near the critical point which this formula contains are calculated by the principle of corresponding states [20] using the similarity parameter A suggested by Filippov [21]:

$$A = 100 \frac{p_{vp}(T/T_c = 0.625)}{p_c}. \quad (2)$$

Here p_{vp} is the vapour pressure at a reduced temperature equal to 0.625.

The critical temperatures and pressures and the Filippov parameters of a compound under study were calculated by an iteration method. The measured values of the critical properties, p_c^m and T_c^m , were employed as the critical constants for the first iteration. The vapour pressure at a reduced temperature $T/T_c = 0.625$ was estimated using an equation suggested by Filippov [21]:

$$\log_{10} \frac{P^*}{p_{vp}} = 3.9726 \log_{10} \frac{T^*}{T} + \left(\frac{T^*}{T} - 1 \right) \left(0.3252 + 0.40529 \frac{T^*}{T} \right). \quad (3)$$

Here P^* and T^* are the characteristic pressure and temperature. Equation (3) makes it possible to calculate the vapour pressure p_{vp} at any temperature T for a given compound if vapour pressures are known at two temperatures. For these two points, p_c^m and T_c^m and the boiling temperature at atmospheric or a reduced pressure were used. For dihexyl and dioctyl ethers, the normal boiling temperature was taken from the NIST Chemistry WebBook [22] (see table 2). For didecyl ether, the reduced boiling temperature $T_b = 196^\circ\text{C}/15.5 \text{ mmHg}$ [23] was employed. One can find in the literature the normal boiling temperature of didecyl ether [24], however, we preferred using the reduced boiling temperature as more reliable to estimate the Filippov parameter. After the estimation of the vapour pressure, the Filippov parameters, the correction factors, and the critical properties were calculated; then these val-

TABLE 1
Mole-fraction x purities of compounds used in critical point measurement (GC).

Compound	CASRN ^a	Supplier	$10^2 \cdot x$
Dihexyl ether (1,1'-oxybis-hexane)	112-58-3	Alfa Aesar, England	99.3
Dioctyl ether (1,1'-oxybis-octane)	629-82-3	Aldrich, USA	99.2
Didecyl ether (1,1'-oxybis-decane)	2456-28-2	Alfa Aesar, England	98.7

^a Chemical abstracts service registry number.

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