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Vapor–liquid critical point measurements of fifteen compounds by the pulse-heating method

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ABSTRACT

The critical temperatures and pressures have been measured by the pulse-heating method for fifteen compounds: benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, benzaldehyde, 4-methylbenzaldehyde, phenylmethanol, (4-methylphenyl)methanol, 2-carboxybenzaldehyde, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, methyl tetradecanoate, methyl hexadecanoate, methyl octadecanoate, and (Z)-9-methyl octadecenoate. The experimental critical properties have been compared with those estimated by the Wilson/Jasperson and Marrero/Gani methods.

1. Introduction

Project 851 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers has sponsored this study to measure the critical properties of compounds of industrial interest. The work was done in 2004, 2008, 2009, and 2011. The critical temperatures and pressures of fifteen substances have been measured. These compounds are benzoic acid (CARN 65-85-0), benzaldehyde (CASRN 100-52-7), 4-methylbenzaldehyde (CASRN 104-87-0), phenylmethanol (CASRN 100-51-6), (4-methylphenyl)methanol (CASRN 589-18-4), 2-methylbenzoic acid (CASRN 118-90-1), 3-methylbenzoic acid (CASRN 99-04-7), 4-methylbenzoic acid (CASRN 99-94-5), 2-carboxybenzaldehyde (CASRN 119-67-5), 1,3-propanediol (CASRN 504-63-2), 2,2-dimethyl-1,3-propanediol (CASRN 126-30-7), methyl tetradecanoate (CASRN 124-10-7), methyl hexadecanoate (CASRN 112-39-0), methyl octadecanoate (CASRN 112-61-8), and (Z)-9-methyl octadecenoate (CASRN 112-62-9). Among the compounds selected by the sponsors of Project 851 in 2008 was 4-carboxybenzaldehyde (CASRN 619-66-9). However, we failed to measure the critical constants of 4-carboxybenzaldehyde because of its fast decomposition at temperatures slightly above the melting point.

The critical temperatures of the compounds studied in this work lie in the range (692–864 K). At such high critical temperatures, one may expect the compounds studied to be thermally unstable at their critical points. Really, Anselm and Teja [1] and Ambrose et al. [2,3] report about the decomposition of benzaldehyde and phenylmethanol at near-critical temperatures. According to the observations of VonNiederhausern et al. [4] 1,3-propanediol shows degradation at near-critical temperatures too. Benzoic acid decomposes at 673 K in the liquid phase [5,6]. The thermal decomposition of fatty acid methyl esters is mainly studied in supercritical methanol or ethanol in connection with the problem of biodiesel production. In particular, according to the data by Quesada-Medina and Olivares-Carrillo [7] methyl palmitate begins to decompose at 623 K/43 MPa in supercritical methanol, while methyl oleate is stable at these conditions. Saka and Kusdiana [8,9] point out that the degradation of saturated fatty acid methyl esters starts at temperatures higher than 673 K. To minimize the decomposition of the compounds under study in the course of the measurements of the critical properties, a pulse-heating method with ultralow residence times has been used.

2. Experimental

2.1. Materials

The samples of the compounds studied were of commercial origin and used without any further purification. The sources, purities, and Chemical Abstracts Service Registry Numbers (CASRN's) are given in Table 1. Before and after the measurement of the critical properties, the purities of the samples were determined by proton magnetic spectroscopy (Bruker Avance DRX 400). Table 1 shows

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List of symbols

A	Filippov's similarity parameter
J	rate of bubble nucleation
p	pressure
T	temperature
t^*	time from the beginning of a heating pulse to the moment of boiling-up

Greek symbols

$1/\pi_0$	correction factor for the critical pressure
$1/\tau_0$	correction factor for the critical temperature
ω	acentric factor

Subscripts

c	critical state
nb	normal boiling
vp	vapor

Superscript

m	measured value

that the purity of the samples was not changed or changed insignificantly in the course of measuring the critical properties except 2-carboxybenzaldehyde, for which the purity decreased from 97.4 to 93.5%. Benzaldehyde and 4-methylbenzaldehyde are known to interact easily with oxygen of air giving the appropriate acids, so all the manipulations with the samples of these compounds were carried out in the atmosphere of argon.

When using the pulse-heating method for measuring the critical properties (see Section 2.2) it is important that the electrical conductivity of a substance under study is sufficiently low. Otherwise, the resistance and the temperature of the wire probe are measured improperly and, in addition, electrolysis of the substance on the probe takes place. Of the compounds studied, benzoic, 2-methylbenzoic, 3-methylbenzoic, and 4-methylbenzoic acids can have a high electrical conductivity. The electrical conductivity of samples of these substances was measured by Dr. Sergey Shkerin from the Institute of High-Temperature Electrochemistry (Ekaterinburg) using the Impedance Measurement Unit IM-6 produced by ZAHNER-Electrik. The measurements were performed at frequencies of electric current from 2 to 8×10^5 Hz. No evident dependence of the electrical conductivity on frequency was revealed. The temperature of the samples was about 20 K higher than the melting point, which corresponds to the conditions of measuring the critical constants. The electrical conductivity was found to be equal to 5×10^{-6} to $1 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$. Estimations showed that the electrical conductivity did not interfere with the measurement of the critical constants.

2.2. Method

The critical temperatures and the critical pressures were measured by the pulse-heating method discussed in detail in many previous publications [10–14]. The method is based on the phenomenon of liquid superheat [15–17]. It is well known that a liquid can be heated at a given pressure above the vapor–liquid equilibrium temperature and exist in a 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 critical point is not only the end point on the vapor–liquid equilibrium line, but the end point on the line of the attainable superheat as well. Therefore, the critical pressure and the critical temperature can be determined by measuring the pressure dependence of the temperature of the attainable superheat. This dependence is measured in the pulse-heating method with the help of a wire probe heated by electric current pulses.

The only distinction between this work and previous ones was in using two kinds of measuring chamber. Chamber 1 is schematically shown in Fig. 1. This chamber allows working with compounds with melting points up to 200 °C. A liquid under study filled a thin-walled (about 0.1 mm) Teflon cup. The pressure outside the cup was created by a press and measured by a dial gauge. The full-scale reading of the gauge was close to the critical pressure of the substance under study. The maximum uncertainty of the gauge was 0.15% of the full-scale reading. Special experiments showed that the pressure drop on the cup walls did not exceed 0.02 MPa. The second kind of measuring chamber (chamber 2) is given in Fig. 2. This chamber makes possible measuring the critical properties of compounds with melting temperatures up to 300 °C. Here a liquid under study filled the upper part of the chamber. The lower part of chamber 2 was filled with a confining fluid. As the confining fluid we used a mixture of gallium and indium (about 20 mass%). This alloy is liquid at room temperature. Mercury is generally used for this purpose; however, the normal boiling temperature of mercury is too low, about 357 °C. The pressure outside the confining fluid was created with a press and measured with a dial gauge like it was done with

Table 1
Sources and purities of materials used in critical point measurements.

Compound	CASRN[a]	Supplier	Purity (mol%)[b]	
			Before measuring the critical constants	After measuring the critical constants
Benzoic acid	65-85-0	Fluka	99.4	99.3
2-Methylbenzoic acid	118-90-1	Aldrich	99.9	99.9
3-Methylbenzoic acid	99-04-7	Aldrich	99.9	99.9
4-Methylbenzoic acid	99-94-5	Fluka	99.8	99.8
Phenylmethanol	100-51-6	Fluka	99.9	99.9
4-(Methylphenyl)methanol	589-18-4	Lancaster	99.9	99.9
Benzaldehyde	100-52-7	Aldrich	99.9	99.8
4-Methylbenzaldehyde	104-87-0	Lancaster	98.8	98.6
2-Carboxybenzaldehyde	119-67-5	Alfa Aesar	97.4	93.5
2,2-Dimethyl-1,3-propanediol	126-30-7	Aldrich	99.9	99.9
1,3-Propanediol	504-63-2	Aldrich	99.9	99.9
Methyl tetradecanoate (methyl myristate)	124-10-7	Alfa Aesar	99.4	99.4
Methyl hexadecanoate (methyl palmitate)	112-39-0	Sigma	99.9	99.9
Methyl octadecanoate (methyl stearate)	112-61-8	Alfa Aesar	98.7	98.7
(Z)-9-Methyl octadecenoate (methyl oleate)	112-62-9	Aldrich	99.8	99.6

[a] Chemical Abstracts Service Registry Number.
[b] According to proton magnetic spectroscopy (Bruker DRX 400).