# Critical temperatures and pressures of some dicarboxylic acid diethyl esters

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ABSTRACT

The critical temperatures and pressures of diethyl esters of dicarboxylic acids $C_2H_5OOC(CH_2)_{n-2}COOC_2H_5$ with straight alkyl chains and $n = 3, 4, 6$ have been measured. These data and the results of the previous measurements have been analyzed and the recommended critical properties of dicarboxylic acid diethyl esters from diethyl ethanoate to diethyl hexanoate have been determined. The experimental critical constants of dicarboxylic acid diethyl esters have also been compared with those calculated using the group-contribution methods of Wilson and Jasperson, Marrero and Gani, and Nannoolal, Rarey, and Ramjugernath. The acentric factors of dicarboxylic acid diethyl esters have been calculated.

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## 1. Introduction

Diethyl esters of straight-chain saturated dicarboxylic acids $C_2H_5OOC(CH_2)_{n-2}COOC_2H_5$ where $n$ is the number of carbons in the parent acid are an important family of organic compounds. Lower-chain esters are used as solvents and coupling agents, plasticizers and flavoring base materials. Higher-chain compounds are employed as lubricants, detergents, emulsifiers, surfactants, wetting agents textile treatments and so forth. These esters are also used as intermediates for the manufacture of a variety of compounds.

Information about the thermal stability of diethyl esters of dicarboxylic acids is scanty. Radice [1] reported that diethyl butanedioate decomposed during measuring the critical temperature. Probably, all the dicarbolylic acid diethyl esters are unstable at their critical points, so that lately only techniques applicable to thermally unstable compounds are used to measure the critical properties of these esters. Steele et al. [2] used differential scanning calorimetric heat-capacity measurements to determine the critical temperature and the critical density of ethyl ethanoate. To reduce the sample decomposition, they employed a single continuous heat at a heating rate of 0.333 $K \cdot s^{-1}$, but they could not determine the critical temperature of diethyl butanedioate because of the decomposition of this compound. They also measured the vapour pressure of both compounds and estimated the critical pressure of diethyl ethanedioate by a simultaneous non-linear least-squares fit of the vapour pressures and the two-phase heat capacities. For diethyl butanedioate, both the critical temperature and the critical pressure were obtained by including them in the variables of a fit to the vapour-pressure measurements. VonNiederhausern et al. [3] measured the critical temperature and pressure of diethyl ethanedioate using a low residence time flow method. We experimentally determined the critical temperatures and pressures of diethyl esters of propanedioic, butanedioic, pentanedioic, and hexanedioic acids by the pulse-heating method with residence times from $(0.01-1)$ ms [4]. In these experiments, we used samples of the esters synthesized and purified by Dr. Krasnykh at the Samara State Technical University. Now we report the critical temperatures and pressures of diethyl esters of propanedioic, butanedioic, and hexanedioic acids; the samples of the esters were purchased from Sigma−Aldrich.

## 2. Experimental

### 2.1. Materials

The samples of diethyl esters were of commercial origin

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(Sigma–Aldrich) and used without any additional purification. The Chemical Abstract Service Registry Numbers (CASRN's) of the compounds studied and the purities of the samples according to the suppliers' data are given in Table 1.

## 2.2. Method

The pulse-heating method used for the measurement of the critical temperatures and pressures of dicarboxylic acid diethyl esters has been discussed in detail in previous papers [5–9]. Briefly, the method is based on the phenomenon of liquid superheat [10–12]. It is well known that a liquid can be heated above the liquid–vapour equilibrium temperature at a given pressure. Under conditions of rapid heating, a superheated liquid boils up at the temperature of the attainable superheat (spontaneous boiling-up). In the course of the experiments, the pressure dependence of the temperature of the attainable superheat is measured. 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. Thus, when the pressure in the liquid approaches the critical pressure, the temperature of the attainable superheat approaches the critical temperature.

The temperature of the attainable superheat at a given pressure is measured with the help of a wire probe heated by electric current pulses. The probe is made of platinum, has a diameter of $2 \times 10^{-3}$ cm and a length of 1–3 cm. The probe serves simultaneously as a heater and a resistance thermometer. The probe is heated by electric pulses in such a way that the probe temperature reaches the temperature of spontaneous boiling-up by the end of a pulse. The time from the beginning of a pulse to the moment of boiling-up $t*$ in various experiments is from 0.03 to 1.0 ms. At the moment of boiling-up a probe temperature perturbation takes place because the conditions of heat transfer from the probe to the liquid change sharply. The temperature perturbation is uniquely connected with a voltage perturbation on the probe. The voltage perturbation is observed on the screen of a digital oscilloscope or a personal computer. The temperature of the probe at the beginning of the temperature perturbation, that is, at the beginning of boiling-up is determined from the resistance of the probe.

The probe temperature perturbation may be negative or positive. The sign of the perturbation depends on the thermophysical properties of a substance under study and the time $t*$. For comparatively low-molar-mass compounds (nonpolymers) at near-critical pressures the temperature perturbation is negative. When the pressure approaches the critical pressure, the properties of the liquid and vapor phases come closer and the amplitude of the temperature perturbation drops. The pressure in the chamber with a substance under investigation increases step by step until the negative temperature perturbation decreases to the level of the apparatus sensitivity ($1 \times 10^{-3}$ K). This pressure and the temperature of boiling-up at this pressure are considered as the measured values of the critical pressure $p_c^m$ and the critical temperature $T_c^m$.

An inherent feature of the pulse-heating technique is that the values of $p_c^m$ and $T_c^m$ are slightly lesser than the true critical parameters. For stable compounds, the true critical pressure $p_c$ and

temperature $T_c$ are calculated by the following equations:

$$p_c = p_c^m / \pi_0, \quad T_c = T_c^m / \tau_0, \tag{1}$$

where $1/\pi_0$ and $1/\tau_0$ are correction factors [5,9,13]. For the estimation of the correction factors some properties of a compound under investigation at near-critical states are required. These properties are as follows: density, thermal conductivity, heat capacity of the liquid phase, density of the vapour phase, enthalpy of vaporization, boiling temperature, and the temperature of the attainable superheat. The properties are calculated using the formulas [9,13] obtained by the principle of corresponding states. The formulas contain the similarity parameter of the compound under study suggested by Filippov [14]:

$$A = 100 \frac{p_{vp}(T_r = 0.625)}{p_c}, \tag{2}$$

where $p_{vp}$ is the vapour pressure, $T_r = T/T_c$ is the reduced temperature. The sense of the Filippov parameter is close to that of the well-known Pitzer acentric factor [15]. The relation between the Filippov parameter and the acentric factor can be established with the help of an equation for the dependence of the vapour pressure on the temperature. Filippov, using the equation by Riedel [16], obtained the following formula:

$$\omega = 0.401 - 0.664 \log_{10} A. \tag{3}$$

The Filippov parameters and the critical properties were calculated in this work by an iteration method. The measured values of the critical parameters, $p_c^m$ and $T_c^m$, were employed as the critical constants for the first iteration. The vapour pressures at a reduced temperature $T_r = 0.625$ for diethyl propanedioate and diethyl hexanedioate were estimated using the Antoine equation with the parameters given in the NIST Chemistry WebBook [17]. The vapour pressure of diethyl butanedioate was calculated by the Wagner–Ambrose equation with the parameters determined by Steele et al. [2]. Then the Filippov parameters, the correction factors and the critical constants were calculated; these values were used in the second iteration. Two iterations were enough because the correction factors depend only slightly on the variations of Filippov's parameter.

For the calculation of the correction factors two other quantities are needed: the factor $G_T \equiv \partial \ln J / \partial T$, where $J$ is the rate of bubble nucleation in a superheated liquid, and the ideal gas heat capacity of the compound under investigation. The factor $G_T$ was measured in one experiment with the measurement of the critical constants as described previously [5,9] and estimated at 8 K$^{-1}$. The ideal gas heat capacity was estimated using the atomic contribution method by Rihani and Doraiswamy as given by Reid et al. [18].

The decomposition of unstable compounds in the course of pulse-heating experiments may cause the dependence of the apparent critical pressures and temperatures on the duration of a heating pulse. The durations of heating pulses were 0.06, 0.11, 0.22, 0.46, and 0.85 ms; the probe lengths were 1, 2, and 3 cm. Two or three samples of each compound were used. No obvious dependence of the apparent critical parameters on the durations of the heating pulses was found for the investigated esters, so that the measured values of the critical temperature $T_c^m$ and pressure $p_c^m$ were determined by averaging over all the heating times, lengths, and samples.

## 2.3. Uncertainties

The uncertainties of the critical properties measured by the pulse-heating method are discussed in detail elsewhere [8,9,19]. It

**Table 1**
Purities of compounds used in critical point measurement (Sigma–Aldrich, GC, suppliers' data).

| Compound | CASRN[a] | Purity (mol. %) |
|---|---|---|
| Diethyl propanedioate (malonate) | 105-53-3 | 99.8 |
| Diethyl butanedioate (succinate) | 123-25-1 | 99.8 |
| Diethyl hexanedioate (adipate) | 141-28-6 | >99.9 |

[a] Chemical abstracts service registry number.