



# Vapor-liquid critical temperatures and pressures of dicarboxylic acid diethyl esters



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## ABSTRACT

The critical temperatures and pressures of diethyl esters of straight-chain saturated dicarboxylic acids  $C_2H_5OOC(CH_2)_{n-2}COOC_2H_5$  with  $n = 5, 8, 10$  have been measured. The data of this work and the results of the previous measurements have been analyzed and the recommended critical temperatures and pressures of diethyl esters from diethyl ethanedioate to diethyl decanedioate have been given. The internal consistency of the experimental data has been tested by considering the plot  $(M/p_c)^{1/2}$  versus  $n$ , where  $M$  is the molar mass,  $p_c$  is the critical pressure. The acentric factors of dicarboxylic acid diethyl esters have been calculated.

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## 1. Introduction

We recently measured the critical temperatures  $T_c$  and pressures  $p_c$  of diethyl esters of straight-chain saturated dicarboxylic acids  $C_2H_5OOC(CH_2)_{n-2}COOC_2H_5$  with  $n = 3, 4, 6$  and gave the recommended values of  $T_c$  and  $p_c$  for esters with  $n$  from 3 to 6 [1]. In this paper, we present the results of measurement of the critical temperatures and pressures of esters with  $n = 5, 8, 10$ . This work should be considered as a direct continuation of our paper [1], so we are going to describe only briefly our approach to the study of critical properties of dicarboxylic acid diethyl esters because all the details were given in Ref. [1]. Taking into account the new experimental data, we reconsidered the recommended values of the critical temperatures and pressures of dicarboxylic acid diethyl esters. All the dicarboxylic acid diethyl esters decompose quite rapidly at their critical points, so that both in our previous paper [1] and in this work we used the pulse-heating method applicable to thermally unstable compounds to measure the critical temperature and pressure.

## 2. Experimental

### 2.1. Materials

Samples of dicarboxylic acid diethyl esters were purchased from Alfa Aesar and Sigma-Aldrich and used without any addi-

tional purification. The Chemical Abstract Service Registry Numbers (CASRN's) of the compounds studied and the purities of the samples according to the suppliers' certificates of analysis are given in Table 1.

### 2.2. Measurement of the critical properties by the pulse-heating method

The pulse-heating method used for the measurement of the critical temperatures and pressures of dicarboxylic acid diethyl esters was discussed in detail in previous papers [2–6]. It is important that the times of heating of a compound under study to the critical temperature are from 0.03 to 1.0 ms in the pulse-heating technique. It provides small decomposition of a compound under study in the course of measuring the critical properties. An inherent feature of the pulse-heating method is that the measured values of the critical temperature  $T_c^m$  and critical pressure  $p_c^m$  are a bit lesser than the true critical constants. For stable compounds, the true critical pressure  $p_c$  and temperature  $T_c$  are calculated by the following equations:

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

Here  $1/\pi_0$  and  $1/\tau_0$  are correction factors, the procedure of calculation of which were discussed in detail in previous papers [6,7]. The formulae for the calculation of the correction factors contain the similarity parameter of a compound under study suggested by Filippov [8]:

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

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**Table 1**

Purities of dicarboxylic acid diethyl esters used in critical point measurements (GC, suppliers' certificates of analysis).

Compound	CASRN <sup>a</sup>	Supplier	Purity (mol. fraction)
Diethyl pentanedioate (glutarate)	818-38-2	Alfa Aesar	0.996
Diethyl octanedioate (suberate)	2050-23-9	Alfa Aesar	0.995
Diethyl decanedioate (sebacate)	110-40-7	Sigma-Aldrich	0.997

<sup>a</sup> Chemical abstracts service registry number.

where  $p_{vp}$  is the vapor pressure,  $T_r = T/T_c$  is the reduced temperature.

An iteration method was used to calculate the Filippov parameters, the correction factors, and the critical properties of dicarboxylic acid diethyl esters. The measured values of the critical constants  $p_c^m$  and  $T_c^m$  were employed as the critical constants for the first iteration. The vapor pressure at a reduced temperature  $T_r = 0.625$  for diethyl pentanedioate was estimated using the Antoine equation taken from NIST Chemistry WebBook [9]. For diethyl octanedioate and diethyl decanedioate, these pressures were calculated by an equation suggested by Filippov [8]:

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

Here  $P^*$  and  $T^*$  are some constants for a given compound. The values of  $P^*$  and  $T^*$  were calculated from  $p_c^m$ ,  $T_c^m$ , and the experimental data by Vogel on the vapor pressures of diethyl octanedioate and diethyl decanedioate [10]. Then the Filippov parameters, the correction factors and the critical constants were calculated; these values were used in the second iteration. The iterative procedure was ended at the second iteration since the correction factors weakly depend on the Filippov parameter. Thermophysical properties of the esters studied in this work are close enough and it is not surprising that the values of the correction factors for these compounds are the same:  $1/\pi_0 = 1.05$  and  $1/\tau_0 = 1.005$ , so that using the correction factors increases the critical pressures and temperatures of the diethyl esters of dicarboxylic acids studied by about 5% and 0.5%, respectively.

The degradation of an unstable compound in the course of a pulse-heating experiment may cause the dependence of the apparent critical pressure and temperature on the duration of a heating pulse. In the experiments with dicarboxylic acid diethyl esters, the durations of heating pulses were 0.06, 0.11, 0.22, 0.46, and 0.85 ms and 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, and 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 vapor-liquid critical properties measured by the pulse-heating method are discussed in detail elsewhere [5,6,11]. It has been shown that for low-molar-mass compounds with low acentric factors ( $\omega < 1$ ) and without strong hydrogen bonding the uncertainties are  $\delta p_c = 0.03 p_c$ ,  $\delta T_c = 0.01 T_c$ , where  $T_c$  is the absolute temperature. The dicarboxylic acid diethyl esters studied are compounds of this type. Here the uncertainties are the combined expanded uncertainty at 95% level of confidence.

### 3. Results and discussion

All the experimental data on the critical temperatures and pressures of the dicarboxylic acid diethyl esters we found in the literature together with the results of this work are listed in Table 2 and shown in Fig. 1. For the esters for which there are more than one experimental value of the critical constants, we give the recommended values in Table 2. The new experimental data obtained in this work allowed us to reconsider the recommended values of dicarboxylic acid diethyl esters in comparison with those given in our previous work [1]. The internal consistency of the experimental critical pressures was checked by considering the plot  $(M/p_c)^{1/2}$  versus  $n$ , where  $M$  is the molar mass and  $n$  is the number of carbons in a molecule of the parent acid. According to the Lydersen method of the estimation of the critical properties, the quantity  $(M/p_c)^{1/2}$  should be a linear function of  $n$  [12]. This plot is shown in Fig. 2. Usually, to test the consistency of experimental critical temperatures, the plot  $T_c/T_{nb}$  versus  $n$  is considered, where  $T_{nb}$  is the normal boiling temperature. However, we failed to find in the literature any data on the normal boiling points of diethyl octanedioate and diethyl decanedioate.

The critical properties of diethyl ethanedioate were measured by Steele et al. [13] and VonNiederhausern et al. [14]. Steele and co-workers determined the critical temperature and the critical density of diethyl ethanedioate using differential scanning calorimetric heat-capacity measurements but they failed to measure the critical temperature of diethyl butanedioate by this method because of the rapid decomposition of this compound. They also measured the vapor pressure of diethyl ethanedioate and diethyl butanedioate and estimated the critical pressure of diethyl ethanedioate by a simultaneous non-linear least-squares fit of the vapor 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 vapor-pressure measurements. VonNiederhausern et al. [14] measured

**Table 2**

Critical temperatures  $T_c$ , critical pressures  $p_c$  and acentric factors  $\omega$  of dicarboxylic acid diethyl esters.

Ester	$T_c/K$	$p_c/MPa$	$\omega$
Diethyl ethanedioate	618 <sup>a</sup> 645.8 ± 2 <sup>b</sup>	2.140 <sup>a</sup> 3.06 ± 0.064 <sup>b</sup>	0.578
Recommended values	<b>646 ± 2</b>	<b>3.1 ± 0.1</b>	
Diethyl propanedioate	652 ± 7 <sup>c</sup> 651 ± 7 <sup>d</sup>	2.67 ± 0.08 <sup>c</sup> 2.70 ± 0.08 <sup>d</sup>	0.624
Recommended values	<b>652 ± 7</b>	<b>2.70 ± 0.1</b>	
Diethyl butanedioate	663 <sup>e</sup> 665 <sup>f</sup> 665 ± 7 <sup>c</sup> 666 ± 7 <sup>d</sup>	2.260 <sup>f</sup> 2.20 ± 0.07 <sup>c</sup> 2.29 ± 0.07 <sup>d</sup>	0.644
Recommended values	<b>666 ± 7</b>	<b>2.3 ± 0.1</b>	0.699
Diethyl pentanedioate	683 ± 7 <sup>c</sup> 682 ± 7 <sup>g</sup>	2.11 ± 0.06 <sup>c</sup> 2.13 ± 0.06 <sup>g</sup>	0.713
Recommended values	<b>683 ± 7</b>	<b>2.13 ± 0.06</b>	
Diethyl hexanedioate	696 ± 7 <sup>c</sup> 697 ± 7 <sup>d</sup> <b>697 ± 7</b>	2.05 ± 0.06 <sup>c</sup> 1.99 ± 0.06 <sup>d</sup> <b>1.99 ± 0.1</b>	0.728
Diethyl octanedioate	723 ± 7 <sup>g</sup>	1.57 ± 0.05 <sup>g</sup>	0.818
Diethyl decanedioate	740 ± 7 <sup>g</sup>	1.37 ± 0.04 <sup>g</sup>	

<sup>a</sup> Data by Steele et al. [13].

<sup>b</sup> Data by VonNiederhausern et al. [14].

<sup>c</sup> Data by Nikitin et al. [18].

<sup>d</sup> Data by Nikitin et al. [1].

<sup>e</sup> data by Radice [19].

<sup>f</sup> Steele et al. [13] measured the vapor pressure at temperatures (378.025 to 533.746) K and fitted the results by the Wagner equation; they included both  $T_c$  and  $p_c$  in the variables of the fit.

<sup>g</sup> This work. The relative combined expanded uncertainties are  $U_r(T_c) = 0.01$  and  $U_r(p_c) = 0.03$  with 0.95 level of confidence.

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