



Vapor–liquid critical properties of components of biodiesel. 2. Ethyl esters of *n*-alkanoic acids



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HIGHLIGHTS

- Critical properties of five *n*-alkanoic acid ethyl esters were measured.
- These compounds are components of biodiesel.
- Equations for the estimation of the critical properties of esters were obtained.

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ABSTRACT

The critical temperatures and the critical pressures of *n*-alkanoic acid ethyl esters $C_nH_{2n-1}O_2C_2H_5$ with $n = 10, 11, 12, 14, 16$ have been measured by the pulse-heating technique. These esters are components of biodiesel. Equations for the calculation of the critical temperatures and pressures of ethyl esters of *n*-alkanoic acids have been obtained. Experimental critical properties have been compared with estimations made by these equations and by the group-contribution methods of Wilson and Jasperson, Constantinou and Gani, Cunico, Hukkerikar, Cerani, Sarupc, and Gani, and Nannoolal, Rarey, and Ramjugernath. The equations suggested in this study provide the best accuracy for the estimation of the critical properties of *n*-alkanoic acid ethyl esters with n from 5 to 16; these equations can be used for the calculation of the critical constants of heavier esters. The acentric factors of *n*-alkanoic acid ethyl esters have been estimated.

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1. Introduction

This work is part of an ongoing investigation of the critical properties of the components of biodiesel fuel. Biodiesel is a mixture of alkyl esters of fatty acids both saturated and unsaturated ones [1,2]. The vapor–liquid critical properties of pure components are of great importance; they are used in many corresponding states correlations for thermodynamic, volumetric and transport properties of gases and liquids [3,4]. In addition, a knowledge of the critical constants allows building an equation of state, extrapolating vapor pressure data to the critical point. In our previous paper [5], we considered the critical temperatures and pressures of methyl esters of *n*-alkanoic acids that are saturated acids with straight alkyl chains. In this paper, which is its direct continuation, we will discuss the critical parameters of *n*-alkanoic acid ethyl esters. The critical temperatures T_c and the critical pressures

p_c of *n*-alkanoic acid ethyl esters $C_nH_{2n-1}O_2C_2H_5$ have been measured for $n = 1-9$ and $n = 1-8$, respectively. The recommended values of the critical properties of these esters were given by Kudchadker et al. in their review of 2001 [6]. After publishing this review the critical constants of *n*-alkanoic acid ethyl esters were measured by Hu et al. [7], Nazmutdinov et al. [8] and Juntarachat et al. [9]. In this paper, we report the experimental critical temperatures and pressures of five ethyl esters of *n*-alkanoic acids: ethyl decanoate (ethyl caprate), Chemical Abstracts Service Registry Number [110-38-3], ethyl undecanoate ([627-90-7]), ethyl dodecanoate (ethyl laurate [106-33-2]), ethyl tetradecanoate (ethyl myristate [124-06-1]), and ethyl hexadecanoate (ethyl palmitate [628-97-7]).

Similar to many other homologous series, in particular, the series of *n*-alkanoic acid methyl esters, initial members of the series of ethyl esters of *n*-alkanoic acid are stable at their critical points but heavier esters are unstable. Ethyl ethanoate is stable at its critical point [10] while ethyl octanoate slightly decomposes at near-critical temperatures [11]. To minimize the thermal degradation of the compounds under study in the course of measuring the

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critical properties, we used in this work the pulse-heating method applicable to thermally unstable compounds [12–16].

2. Experimental

2.1. Materials

The samples of *n*-alkanoic acid ethyl esters were supplied by Alfa Aesar, a Johnson Matthew Company. The Chemical Abstracts Service Registry Numbers (CASRN's) and purities of the samples according to the suppliers' data are given in Table 1. The samples were used with no further purification.

2.2. Method

As noted above, this paper is a continuation of our previous paper [5] in which the critical temperatures and pressures of some methyl esters of *n*-alkanoic acids were measured, so that in this work we used the same method and procedure. Briefly, the technique we employed is called the pulse-heating method and based on the possibility of superheating a liquid above the liquid–vapor 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 pulse-heating experiments, the pressure dependence of the temperature of the attainable superheat is determined. With increasing pressure, the temperature of the attainable superheat tends to the critical temperature. The dependence of the temperature of the attainable superheat on pressure is measured with the help of a thin platinum wire probe heated by electric current pulses. The time from the start of a pulse to the moment of boiling-up was from (0.03 to 1.00) ms in various experiments. The short heating times provide the little decomposition of the compounds under study.

At the moment of boiling-up the conditions of heat transfer from the probe to the liquid sharply change, it gives rise to a probe temperature perturbation, which may be both positive and negative. When the pressure tends to the critical pressure, the thermophysical properties of the liquid and vapor approach closely and the amplitude of the temperature perturbation decreases. The pressure in the liquid increased until the negative temperature perturbation fell to the level of the apparatus sensitivity (1×10^{-3} K). This pressure was assumed to be the measured value of the critical pressure p_c^m , and the temperature of the attainable superheat at this pressure was taken as the measured value of 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:

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

where $1/\pi_0$ and $1/\tau_0$ are correction factors. The method of the calculation of the correction factors is given in our previous publica-

tions [16,17]. In this method, the thermophysical properties of the liquid and vapor phases at near-critical temperatures and pressures required for the calculation of the correction factors are estimated by the law of corresponding states using the similarity parameter A suggested by Filippov [4,18]:

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

where p_{vp} is the vapor pressure, $T_r = T/T_c$ is the reduced temperature. The well-known Pitzer acentric factor [19] is connected with the Filippov parameter by the following equation [18]:

$$\omega = 0.401 - 0.664 \log_{10} A. \quad (3)$$

To calculate the Filippov parameters and the critical temperatures and pressures of *n*-alkanoic acid ethyl esters an iteration method was employed. For the first iteration, the measured values of the critical properties, p_c^m and T_c^m , were used as the critical constants. The vapor pressure of ethyl esters of *n*-alkanoic acids at a reduced temperature $T_r = 0.625$ was estimated using the Antoine equation with parameters given by Benzianne et al. [20] for ethyl decanoate and by Silva et al. [21] for ethyl dodecanoate, ethyl tetradecanoate, and ethyl hexadecanoate. For ethyl undecanoate, in the literature, there are only scarce data on vapor pressure [22–26]. The Wagner equation based on these data was built by us in the following form [27]:

$$\ln p_{vpr} = (a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5)/T_r. \quad (4)$$

Here $p_{vpr} = p_{vp}/p_c$ is the reduced vapor pressure, $\tau = 1 - T_r$. The coefficients of Eq. (4) together with the standard errors obtained by us after two iterations are $a = -11.08718 \pm 250.3$, $b = 7.29265 \pm 730.0$, $c = -12.30493 \pm 945.0$, $d = 12.02461 \pm 1109.8$. Eq. (4) has four coefficients while the experimental data [22–26] contain only six data points, so that the errors of the calculation of these coefficients are very great and Eq. (4) should be used for estimating the vapor pressure of ethyl undecanoate with care, but it gives for $T_r = 0.625$ a reasonable value of the vapor pressure. After the estimation of the vapor pressure, the Filippov parameters, the correction factors, and the critical properties were calculated; then these values were used in the second iteration. Two iterations were enough because the correction factors depend only slightly on the Filippov parameter. The values of the correction factors are given in Tables 2 and 3.

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 the heating pulse. The durations of the heating pulses were 0.035, 0.060, 0.110, 0.220, and 0.460 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 constants measured by the pulse-heating method were discussed in detail in our previous papers [5,15,16,28]. It has been shown that for “usual” low-molar-mass compounds the uncertainties are $\delta p_c = 0.03 p_c$, $\delta T_c = 0.01 T_c$; for compounds with strong hydrogen bonding or with high acentric factors ($\omega \geq 1$) the uncertainties are $\delta p_c = 0.04 p_c$, $\delta T_c = 0.015 T_c$. Here T_c is the absolute temperature. The ethyl esters of alkanolic acids studied in this work have no hydrogen bonds and, according to our estimation, the acentric

Table 1

Purities of compounds used in critical point measurement (Alfa Aesar, GC, suppliers' data).

Compound	CASRN ^a	Purity (mol.%)
Ethyl decanoate	110-38-3	99.7
Ethyl undecanoate	627-90-7	98.6
Ethyl dodecanoate	106-33-2	99.8
Ethyl tetradecanoate	124-06-1	99.4
Ethyl hexadecanoate	628-97-7	98.5

^a Chemical abstracts service registry number.

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