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Vapour–liquid critical properties of components of biodiesel. 3. Methyl esters of linoleic, linolenic, and erucic acids

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HIGHLIGHTS

- Critical properties of some unsaturated fatty acid methyl esters were measured.
- These compounds are components of biodiesel.
- Pulse-heating method with ultralow residence times was used.

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ABSTRACT

The critical temperatures and the critical pressures of methyl esters of linoleic, linolenic, and erucic acids have been measured by the pulse-heating technique. Triglycerides of these acids are a considerable fraction of many vegetable oils. The critical temperatures of methyl esters of acids from stearic (C18:0) to linolenic (C18:3) remain almost equal, which correlates well with the fact that the normal boiling temperatures of these esters are practically equal too. The critical pressure monotonically increases in this series. Experimental critical properties have been compared with estimations made by the group-contribution methods of Wilson and Jasperson (WJ), Marrero and Gani (MG), Nannoolal, Rarey, and Ramjugernath (NRR). All the group contribution methods considered in this study predict the critical temperatures of the esters investigated well enough. For the critical pressures, the NRR method gives the best estimation, next are the WJ and MC methods. The acentric factors of the esters studied have been estimated.

1. Introduction

This work is part of an ongoing investigation of the critical properties of the components of biodiesel which has been conducted at the Institute of Thermal Physics of RAS. Previously, we have measured the critical temperatures and pressures of methyl oleate and some methyl and ethyl esters of *n*-alkanoic acids [1–3]. In this paper, we report experimental critical temperatures and pressures of methyl ester of (Z,Z)-9,12-octadecanoic acid (methyl linoleate, Chemical Abstracts Service Registry Number [112-63-0]), methyl ester of (Z,Z,Z)-9,12,15-octadecadienoic acid (methyl linolenate [301-00-8]), and methyl ester of (Z)-13-docosenoic acid (methyl erucate [1120-34-9]). Triglycerides of linoleic, linolenic, and erucic acids are a considerable fraction of many vegetable oils [4,5].

Methyl esters of *n*-alkanoic acids heavier than methyl heptanoate decompose at their critical points [6,7]. One might expect that the esters studied in this work degrade at their critical temperatures too. To diminish the thermal decomposition of the compounds under study in the course of measuring the critical properties, we used in this work the pulse-heating method applicable to thermally unstable compounds [8–12].

2. Experimental

2.1. Materials

The samples of esters were purchased from Sigma–Aldrich; 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 without any further purification.

2.2. Method

To measure the critical temperatures and pressures, we employed in this work the same method and procedure as in the previous papers [1–3]. Briefly, the technique we used is called

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Table 1

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

Compound	CASRN[a]	Purity (mol.%)
(Z,Z)-9,12-octadecadienoic acid methyl ester (methyl linoleate)	112-63-0	99
(Z,Z,Z)-9,12,15-octadecatrienoic acid methyl ester (methyl linolenate)	301-00-8	99.4
(Z)-13-docosenoic acid methyl ester (methyl erucate)	1120-34-9	99.4

[a] Chemical abstracts service registry number.

the pulse-heating method [8–12] and based on the phenomenon of liquid superheat [13–15]. 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 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.

The conditions of heat transfer from the probe to the liquid sharply change at the moment of boiling-up, and it causes 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 vapour 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 less 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. The method of calculating the correction factors is given in our previous publications [12,16]. In this method, the thermophysical properties of the liquid and vapour 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 proposed by Filippov [17,18]:

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

where p_{vp} is the vapour pressure, $T_r = T/T_c$ is the reduced temperature. The Filippov parameter has a sense which is close to that of the well-known Pitzer acentric factor [19]. The Filippov and Pitzer parameters are connected by the following equation [17]:

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

An iteration method was employed to calculate the Filippov parameters and the critical temperatures and pressures of the compounds under study. In the first iteration, the measured values of the critical properties, p_c^m and T_c^m, were used as the critical constants. The vapour pressure of methyl esters of fatty acids at a reduced temperature $T_r = 0.625$ was estimated using an equation suggested by Filippov [17]:

$$\log_{10}\frac{P^*}{p_{vp}} = 3.9726\log_{10}\frac{T^*}{T} + \left(\frac{T^*}{T} - 1\right)\left(0.3252 + 0.40529\frac{T^*}{T}\right) \tag{4}$$

This equation gives the dependence of the vapour pressure on temperature from the triple to the critical point. Filippov calls P^* and T^* the «pseudocritical» parameters of a compound because, if these parameters instead of the critical constants are used to determine the reduced quantities, the reduced vapour pressure

Table 2

Normal boiling temperatures T_{nb}, correction factors $1/\tau_0$, and critical temperatures T_c of methyl esters of fatty acids: experimental values[a] and comparison with predictive methods.

Ester	T_{nb} (K)[b]	$1/\tau_0$	T_k (K)			
			Exptl	WJ[f]	MG[g]	NRR[h]
Methyl stearate (C18:0)	620.15		785 ± 8[c]	768.50	782.24	776.62
Methyl oleate (C18:1)	619.15		777 ± 8[c]	769.79	785.83	781.40
Methyl linoleate (C18:2)	619.15	1.003	778 ± 8[d]	772.37	789.37	787.68
Methyl linolenate (C18:3)	620.15	1.006	779 ± 8[d]	776.25	792.85	795.53
Methyl behenoate (C22:0)	666.15		815.55[e]	800.66	820.71	807.60
Methyl erucate (C22:1)	666.15	1.006	817 ± 8[d]	802.93	823.75	813.03
AAPE/%[i]				1.17	1.11	1.10
MAPE/%[j]				2.10	1.78	2.12

[a] The uncertainties of the critical temperatures measured in this work are the combined expanded uncertainty at the 95% level of confidence.

[b] Krop et al. [21].

[c] Nikitin and Popov [1].

[d] This work.

[e] Estimated by Nikitin and Popov [2]; this value was not taken into account when calculating AAPE and MAPE.

[f] The method of Wilson and Jasperson as presented by Poling et al. [26].

[g] The method of Marrero and Gani [27].

[h] The method of Nannoolal et al. [28].

[i] $\mathrm{AAPE} = (100/N)\left(\sum|Y_c^{\mathrm{exp}} - Y_c^{\mathrm{calc}}|\right)/Y_c^{\mathrm{exp}}$), where N is the number of experimental data points, Y_c^{exp} is the experimental value of the critical property, and Y_c^{calc} is the calculated value of the critical property.

[j] $\mathrm{MAPE} = 100 \cdot |Y_c^{\mathrm{exp}} - Y_c^{\mathrm{calc}}|_{\mathrm{max}}/Y_c^{\mathrm{exp}}$.