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Experimental Vapor Pressures of Five Saturated Fatty Acid Ethyl Ester (FAEE) Components of Biodiesel

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ABSTRACT: Vapor pressures of five saturated fatty acid ethyl esters (FAEEs), ethyl hexanoate (or ethyl caproate), ethyl octanoate (or ethyl caprylate), ethyl decanoate (or ethyl caprate), ethyl dodecanoate (or ethyl laurate), and ethyl tetradecanoate (or ethyl myristate), were measured at pressures from 1 Pa to 180 kPa and temperatures from (253.15 to 463.15) K using a static apparatus. These esters are a light fraction present in biodiesel derived from palmist oil and copra oil (Ballerini and Alazard-Toux, *Les biocarburants*; IFP Publications: Paris, 2006). The experimental data ($P-T$) were smoothed using the Antoine equation and compared with the available literature values. The molar enthalpies of vaporization at the mean temperature of the experimental range were derived from the Clausius–Clapeyron equation. From these results the standard enthalpies of vaporization at T = 298.15 K were calculated.

INTRODUCTION

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal, and natural gas). However, these sources are limited and will be exhausted. Vegetable oil is used for the production of biodiesel which is a promising substitute for petroleum-based fuels. It is biodegradable, is produced from renewable energy sources (vegetable oils and animal fats), is nontoxic, and may decrease the emission levels of some pollutant gases. The most widely used method to produce biodiesel is transesterification as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple.

One possible mode to use vegetable oils is by direct chemical synthesis of alkyl esters (methyl or ethyl). Methanol is the prevalent alcohol, globally, for the production of fatty acid esters for use as biodiesel, thus fatty acid methyl esters (FAMEs) are widely employed. The reason for this choice is that methanol is by far the least expensive of alcohols. In some regions, most notably Brazil, the raw material and technology available allow economical production of ethanol by fermentation, resulting in a product that is less expensive than methanol. It should however be noted that the methanol remains more toxic than ethanol.

Vapor pressure is an essential physicochemical property for fuels, because it reflects the volatility, stability, and security of the fuel, besides being important in the development of separation processes. In the present study, vapor pressure measurements of five fatty acid esters existing in the light fraction of biodiesel resulting from palm and copra oil,[1] namely, ethyl caproate, ethyl caprylate, ethyl caprate, ethyl laurate, and ethyl myristate, are reported. A thorough literature search revealed that only few data are available on the vapor pressure of fatty acid ethyl esters (FAEEs) especially in the low vapor pressure range which prompted us to undertake this experimental study. From the temperature dependence of the vapor pressures, enthalpies of vaporization ($\Delta_{vap}H$) of the FAEE were deduced and compared with the available literature data.

Table 1. Source and Purity of Compounds

chemical name	synonym	CAS no.	source	purity/mol %
ethyl hexanoate	ethyl caproate	123-66-0	Sigma Aldrich	≥ 98
ethyl octanoate	ethyl caprylate	106-32-1	Sigma Aldrich	≥ 98
ethyl decanoate	ethyl caprate	110-38-3	Aldrich Chem	≥ 99
ethyl dodecanoate	ethyl laurate	106-33-2	Sigma Aldrich	≥ 98
ethyl tetradecanoate	ethyl myristate	124-06-1	Aldrich Chem	≥ 99

EXPERIMENTAL SECTION

Chemicals. The suppliers and the purities of the five saturated FAEEs are reported in Table 1. These compounds were used without any further purification.

Apparatus. Vapor pressures were measured using a static apparatus. The description of the apparatus and the experimental procedure can be found elsewhere;[2−4] hence we only highlight the main points. The apparatus is equipped with a differential pressure gauge from MKS, type 670, model 616A. The pressure

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measurement consisted of applying the vapor pressure of the sample on the measurement side of the sensor, while its reference side is permanently submitted to a dynamic pumping. The residual pressure was held at 0.0001 Pa and therefore can be neglected. Temperature measurements were carried out using a copper−constantan thermocouple calibrated against a 25 Ω platinum resistance standard thermometer (accuracy of ± 0.001 K claimed by the manufacturer on the IPTS 90) with a Leeds and Northrup bridge (± 0.0001 Ω). As the uncertainty of the voltmeter for the thermocouple reading is 0.1 mV, the precision of the temperature readings is about 0.02 K.

Uncertainty on the Vapor Pressures and System Temperature. The uncertainty of the measurements is estimated to be: $\sigma(P) = 0.1$ Pa + $0.03(P/\text{Pa})$ for pressures lower than 600 Pa, $\sigma(P) = 0.01(P/\text{Pa})$ for P in the range (600 to 1300) Pa, $\sigma(P) = 0.003(P/\text{Pa})$ for pressures over 1300 Pa, and $\sigma(T) = 0.02$ K for the temperature range $253.15 \leq T/\text{K} \leq 463.15$.

RESULTS AND DISCUSSION

Comparison of Experimental Vapor Pressures with Literature Data. The experimental T and P values of the different FAEE are reported in Table 2. The data were fitted using the Antoine equation:

$$\log_{10} P/\text{mmHg} = A - \frac{B}{C + t/°\text{C}} \tag{1}$$

where P is the pressure, t is the temperature, and A, B, and C are the Antoine equation constants determined from least-squares fitting, as in Table 3. The minimized objective function S is as follows:

$$S = \sum_{i=1}^{n} \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2 \tag{2}$$

The experimental values of vapor pressure at different temperatures for the five FAEEs are represented in Figure 1.

Several authors have studied ethyl hexanoate, as in Figure 2. Verevkin and Heintz[5] determined vapor pressures in a narrow temperature range, from (280 to 310) K, by the transpiration method. Covarrubias-Cervantes et al.[6] studied ethyl hexanoate from (250 to 300) K using the static method. The values published by Plyasunov et al.[7] are compiled data. As shown in Figure 2, our experimental vapor pressures are in good agreement with Verevkin et al.[5] data (mean relative deviation less than 3 %) except at 280 K (relative deviation of 11 %). As for Covarrubias-Cervantes et al.[6] values, the relative deviation increases from (5 to 35) % when the pressure decreases from 200 Pa down to 4 Pa. On the other hand the vapor pressures of the present study are in very good agreement with Plyasunov et al.[7] data in the whole pressure range (from 66 Pa to 17.5 kPa), with a mean relative deviation of 2 %.

Table 2. Experimental Vapor Pressures of the Five FAEEs

T/K	P/Pa	% $\Delta P/P^a$	T/K	P/Pa	% $\Delta P/P^a$
	Ethyl Hexanoate			Ethyl Octanoate	
253.41	3.43	−3.50	273.26	2.19	−2.40
263.26	10.55	2.30	283.08	6.26	3.10
283.06	66.30	3.50	293.05	15.55	2.30
293.05	144.14	2.00	303.09	34.96	−0.79
303.03	290.84	0.26	313.20	75.69	−1.00
313.15	561.55	−0.57	323.31	152.67	−1.90
323.18	1018.22	−1.70	351.90	867.90	−0.90
333.11	1780.926	−0.97	362.10	1487.096	−0.22
343.09	2977.779	−0.89	372.06	2432.075	0.54
351.97	4553.223	−0.85	382.13	3872.262	1.40
362.10	7183.509	−0.44	392.19	5904.255	0.80
372.13	10932.835	−0.06	402.13	8723.039	0.19
382.15	16065.471	−0.37	412.13	12674.240	0.06
392.23	23186.752	−0.20	422.12	18044.334	0.12
402.19	32560.435	−0.09	432.22	25218.952	−0.04
412.21	44896.242	0.05	442.26	34490.672	−0.35
422.19	60617.662	0.07	452.30	46421.210	−0.55
432.28	80756.486	0.16			
442.29	105573.394	0.17			
452.34	136730.021	0.58			
462.43	174600.839	0.85			
	Ethyl Decanoate			Ethyl Dodecanoate	
303.10	4.46	1.10	313.10	1.83	1.40
313.16	10.53	0.12	351.88	34.62	−2.10
333.23	47.80	−2.00	362.10	67.38	−1.90
343.20	95.19	−1.10	372.12	124.18	−2.20
353.16	181.48	0.26	382.17	228.72	1.10
363.12	328.47	0.72	392.24	398.97	1.90
412.15	3649.802	1.30	402.20	669.22	2.50
422.13	5471.540	0.99	422.15	1695.019	0.98
432.24	8069.930	0.80	432.26	2646.682	1.30
442.23	11548.264	0.16	442.27	3985.610	0.61
452.28	16280.889	−0.31	452.31	5803.883	−1.60
462.37	22350.173	−1.80	462.43	8489.696	−1.70
	Ethyl Tetradecanoate				
333.22	1.47	−1.60			
343.19	3.60	2.30			
353.15	7.75	−0.50			
363.09	16.33	0.30			
371.72	30.18	1.70			
382.03	57.21	−1.50			
391.87	105.43	−0.47			
401.89	186.93	−0.64			
411.93	321.79	−0.47			
421.97	539.03	0.12			
432.22	886.99	0.81			
442.39	1393.754	0.01			
452.25	2126.849	0.03			
462.30	3199.695	0.03			

[a] $\% \Delta P/P = 100 \cdot (P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}$.

Concerning ethyl octanoate, our results are in a good agreement with those given by Plyasunov et al.[7] with a mean relative deviation of 2 %, as in Figure 3. The deviation increases reaching a value of 7 % when pressures decrease (between 34 and 152 Pa). In the case of ethyl decanoate, one reference was found for comparison: Zaitsau et al.[8] who used a Knudsen effusion method in a narrowed temperature range from (303.68 to 323.24) K. A mean relative deviation of 7 % is observed with the present study in the mentioned experimental range, as in Figure 4. In a recent study, Akisawa Silva et al.[9] measured ethyl dodecanoate and ethyl tetradecanoate using differential scanning calorimetry (DSC), which is an indirect vapor pressure determination. For ethyl

Table 3. Antoine Equation Parameters A, B, and C and Mean Relative Deviation d

		parameters of the Antoine equation			
FAEE	T/K	A (σ_A)	B (σ_B)	C (σ_C)	100 d[a]
ethyl hexanoate	253.41 to 462.44	9.106 (0.028)	1476 (14)	192.2 (1.2)	0.9
ethyl octanoate	283.8 to 462.31	9.385 (0.046)	1766 (25)	195.4 (1.8)	1.0
ethyl decanoate	303.1 to 462.37	9.850 (0.065)	2169 (42)	205.7 (2.9)	0.9
ethyl dodecanoate	313.1 to 462.43	10.738(0.142)	2894 (98)	236.2 (5.7)	1.7
ethyl tetradecanoate	333.22 to 462.3	10.153 (0.096)	2571 (61)	197.6 (3.7)	0.75

[a] $d = (1/n)\Sigma\,(|P_{\text{exp}} - P_{\text{cal}}|)/(P_{\text{exp}})$.

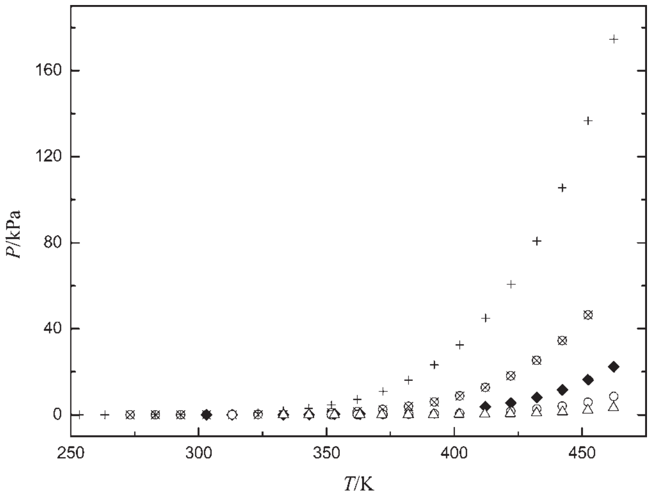

Figure 1. Experimental vapor pressures versus temperature T/K for the five FAEEs: +, ethyl hexanoate; ⊗, ethyl octanoate; ◆, ethyl decanoate; ○, ethyl dodecanoate; △, ethyl tetradecanoate.

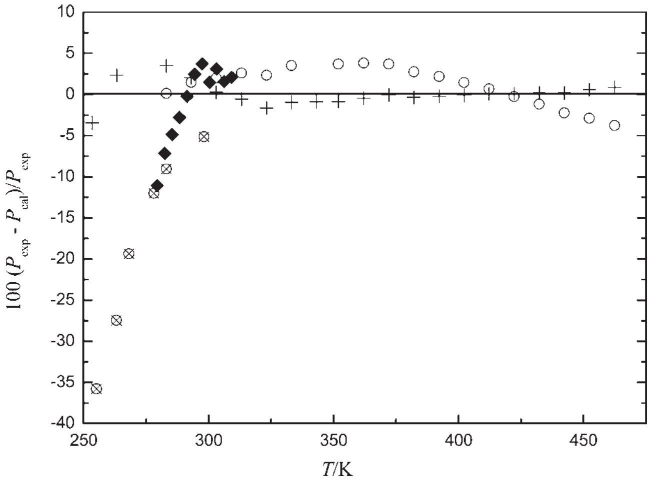

Figure 2. Relative deviation of the experimental vapor pressures of Ethyl Hexanoate from values obtained with Antoine equation as a function of temperature T/K: +, this work; ⊗, Covarrubias-Cervantes et al.;[7] ◆, Verevkin et al.;[6] ○, Plyasunov et al.[8]

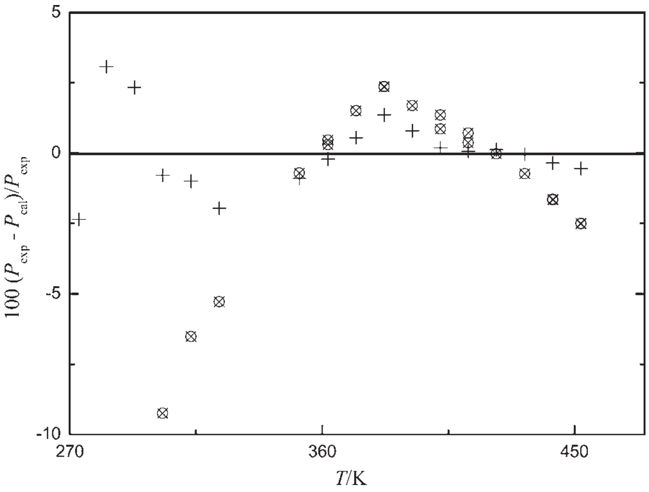

Figure 3. Relative deviation of the experimental vapor pressures of ethyl octanoate from values obtained with the Antoine equation as a function of temperature T/K: +, this work; ⊗, Plyasunov et al.[8]

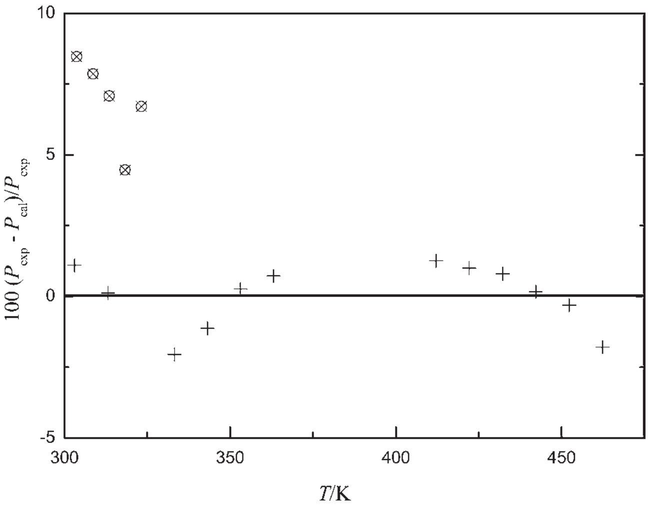

Figure 4. Relative deviation of the experimental vapor pressures of ethyl decanoate from values obtained with the Antoine equation as a function of temperature T/K: +, this work; ⊗, Zaitsau et al.[9]

dodecanoate, our experimental data are in a good agreement with cited literature values (mean deviation of 3.1 %) except at 420 K where the relative deviation of pressure reaches 12 %, Figure 5. For ethyl tetradecanoate, three experimental points were performed by the latter authors: the relative deviation is of 8 % at (460.03 and 470.26) K, and it reaches 20 % at 450 K, as in Figure 6.

Comparison of Enthalpies of Vaporization and Boiling Points with Literature Data. From the Clausius−Clapeyron fit, the enthalpy of vaporization at mean temperature, T_m, of the ethyl esters $\Delta_{\text{vap}}H_{\text{m}}$ (T_{m}), was determined and presented in Table 4:

$$\ln(P/\text{Pa}) = A' - \frac{B'}{T/\text{K}} \tag{3}$$

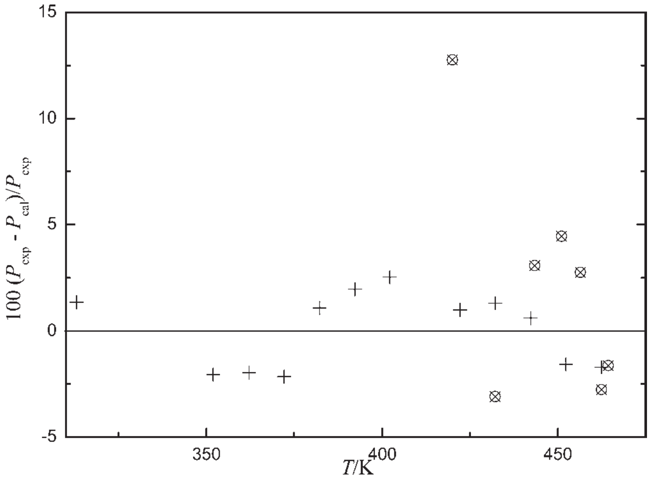

Figure 5. Relative deviation of the experimental vapor pressures of ethyl dodecanoate from values obtained with the Antoine equation as a function of temperature T/K: +, this work; ⊗, Akisawa Silva et al.[10]

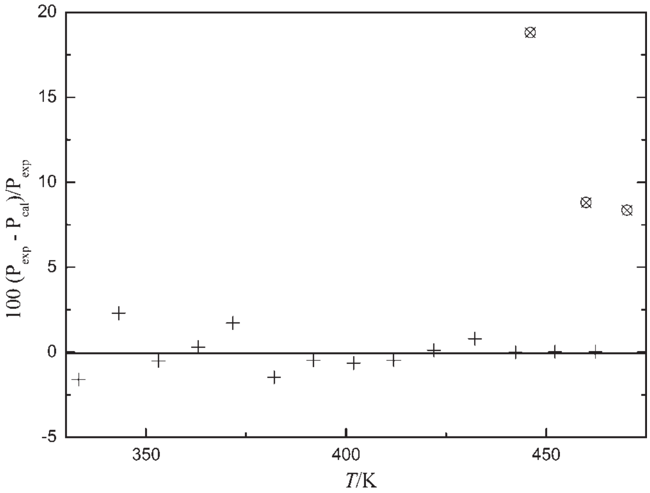

Figure 6. Relative deviation of the experimental vapor pressures of ethyl tetradecanoate from values obtained with the Antoine equation as a function of temperature T/K: +, this work; ⊗, Akisawa Silva et al.[10]

where $B' = (\Delta_{\text{vap}}H_{\text{m}}T_{(\text{m})})/R$ and $R = 8.314\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Vaporization enthalpies at the temperature 298.15 K were derived from the vaporization enthalpies calculated at the mean temperature, T_{m}, of the experiments using the Chickos et al.[10] equation:

$$\Delta_{\text{vap}}H_{\text{m}}(298.15) = \Delta_{\text{vap}}H_{\text{m}}(T_{\text{m}}) - 54.4\cdot(298.15 - T_{\text{m}})/(\text{J}\cdot\text{mol}^{-1}) \tag{4}$$

The values of $\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K) deduced from the present study and reported in Table 4 demonstrate discrepancies of (2 to 4) $\text{kJ}\cdot\text{mol}^{-1}$ which are acceptable.[11−14]

Consistency of the Experimental Results. The correlation of enthalpies of vaporization with the number of C-atoms in the series of homologues is a valuable test to check the internal consistency of the experimental results. In Figure 7 the plot of $\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K) versus the number of C-atoms in the linear aliphatic chain of the esters (eq 5) is represented. The obtained linear equation (with $R^2 = 0.997$) shows the consistency of the measurements and would allow the determination of $\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K) for other homologues esters with $n_{\text{C}} < 6$ or $n_{\text{C}} > 14$.

$$\Delta_{\text{vap}}H_{\text{m}}(n_{\text{C}})(298.15\text{K}) = 4.47n_{\text{C}} + 26.7 \tag{5}$$

n_{C} is the number of C-atoms in the linear aliphatic chain of the esters.

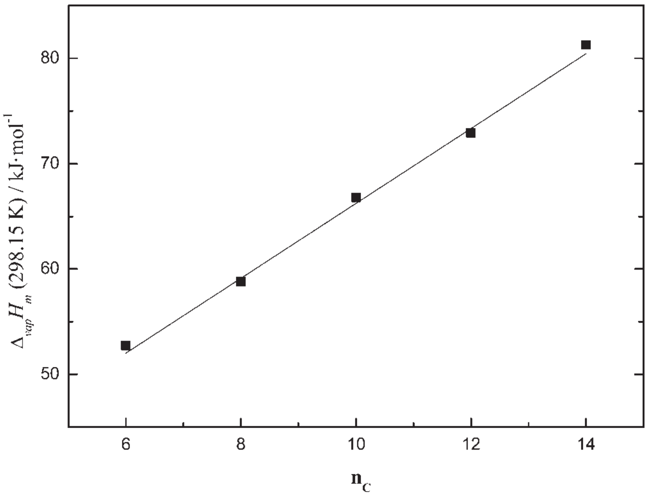

Figure 7. Enthalpy of vaporization of ethyl esters (FAEEs) versus of the number of carbons n_{C}.

Table 4. Enthalpy of Vaporization Calculated at T_{mean}, 298.15 K, and Comparison with the Literature

	T	T_{mean}	$\Delta_{\text{vap}}H_{\text{m}}^{\text{cal}}(T_{\text{m}})$	$\Delta_{\text{vap}}H_{\text{m}}^{\text{cal}}$ (298.15 K)	$\Delta_{\text{vap}}H_{\text{m}}^{\text{lit}}$ (298.15 K)	$\Delta_{\Delta\text{vap}H}$[a]
FAEE	K	K	$\text{kJ}\cdot\text{mol}^{-1}(\sigma)$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
ethyl hexanoate	253.41 to 462.44	357.93	49.5 ± 0.5	54.1 ± 0.5	51.6 ± 1.6[b]	−2.5
					51.72 ± 0.10[c]	−2.4
					50.55 ± 0.37[d]	−3.5
ethyl octanoate	283.80 to 462.31	373.06	55.0 ± 0.6	62.0 ± 0.6	59.5 ± 0.3[b]	−2.5
ethyl decanoate	303.10 to 462.37	382.74	62.2 ± 0.8	71.4 ± 0.8	67.3 ± 0.3[b]	−4.1
ethyl dodecanoate	313.10 to 462.43	387.77	68.0 ± 0.9	79.3 ± 0.9	77.2[e]	−2.1
ethyl tetradecanoate	333.22 to 462.30	397.76	75.9 ± 0.4	90.1 ± 0.4	87.0[e]	−3.1

[a] $\Delta_{\Delta\text{vap}H} = \Delta_{\text{vap}}H_{\text{m}}^{\text{lit}}(298.15\ \text{K}) - \Delta_{\text{vap}}H_{\text{m}}^{\text{cal}}(298.15\ \text{K})$. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 14.

CONCLUSION

In this work, we presented vapor pressures of five FAEEs in a large pressure range (1 Pa to 180 000 Pa) determined by a static apparatus, by setting the temperature and measuring the pressure at equilibrium. Except for ethyl hexanoate, we increased the pressure range of the remaining ethyl esters where no literature exists. The obtained results are consistent and in good agreement with the available literature data. From the experimental $T-P$ values, enthalpies of vaporization $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) were deduced. The comparison of the latter parameter with the literature values confirmed the consistency and the reliability of the present study.

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