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Speed of Sound, Density, and Derivative Properties of Ethyl Myristate, Methyl Myristate, and Methyl Palmitate under High Pressure

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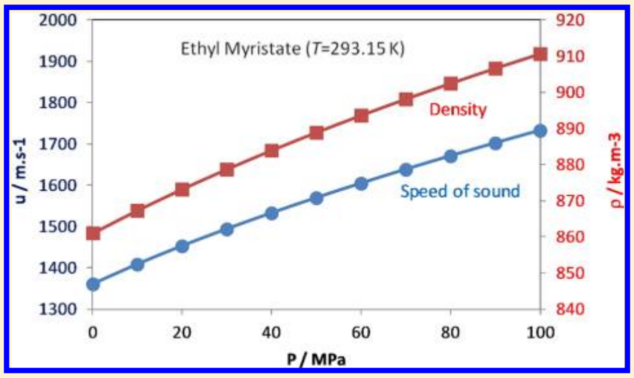
Supporting Information

ABSTRACT: Speeds of sound have been measured in ethyl myristate ($C_{16}H_{32}O_2$), methyl myristate ($C_{15}H_{30}O_2$), and methyl palmitate ($C_{17}H_{34}O_2$) at pressures up to 100 MPa along isotherms ranging from (293.15 to 403.15) K. The measurements were carried out using a pulse echo technique operating at 3 MHz. Additional compressed liquid density measurements were performed from (293.15 to 393.15) K with pressures from (0.1 to 100) MPa in order to evaluate isentropic compressibility using speed of sound measurements. An equation of state that represents both the density and the speed of sound temperature reported experimental data within their estimated uncertainties is given to evaluate the volume as well as its derivatives of these components.



■ INTRODUCTION

Extensive use of fossil fuels either for electricity generation in power plants or for transportation has led to an important decrease in the crude oil resources and also to a drastic increase of environmental degradations due to the emission of greenhouse gases (CO_2, NO_x, etc.). Alternatives to conventional energy sources have to be developed in order to meet future energy consumption while reducing greenhouse gas emissions. Solar power, geothermal energy, and waste heat represent possible alternative sources for power plants, whereas biomass appears as the main resources to substitute to fossil fuels in the transport sector. Actually, biomass can be converted into liquid biofuels that can be directly used in internal combustion engines unlike energy from other natural resources. Biodiesels along with bioalcohol appear as the most relevant types of biofuels. Biodiesels can be blended (typically (2 to 20) %) with conventional diesel fuel in order to reduce particulate and harmful gas emissions or used pure as a totally renewable energy for diesel engines. Biodiesels are produced by a transesterification reaction where vegetable oils or animal fats are combined with an alcohol such as methanol or ethanol to form fatty acid methyl (or ethyl) esters. Fatty acids coming from various sources have different chain lengths. Most vegetable oils used in biodiesel production (palm, soybean, rapeseed, and sunflower) contains fatty acids with 16 and 18 carbons, whereas chains of 20 and 22 carbon atoms appear in significant quantities only in some rape species and animals fats. Finally fatty acids with shorter chain lengths (10 to 14) can be found in coconut oils and palm kernel. Fatty acids differ in the degree of unsaturation as well. Consequently, the composition of fatty acid methyl esters may change a lot from one biodiesel to another as a function of the raw materials and their origin.[1] These differences in composition affect the physical properties of biodiesels and influence the engine efficiency as well as the harmful gas emissions.[2] Optimization of biodiesel formulation and diesel engine needs the knowledge of biodiesel thermophysical properties with accuracy.[3] These properties can be evaluated from pure compounds properties by using mixing rules when data concerning these components are available. Among all of the thermophysical properties, density and isentropic compressibility under pressure have a strong influence in the engine design and especially in the injection process. Actually, these properties directly affect the mass flow rate and the total amount of fuel injected in the cylinder. Density influences the conversion of volume flow rate into mass flow rate,[4] while compressibility affects the fuel injection

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timing.[5] Therefore reliable data of such thermophysical properties under pressure are required for pure fatty acid methyl esters.

This paper, which is a part of a wider project[6−10] to measure and correlate density and speed of sound in several fatty acids methyl and ethyl esters, presents measurements carried out in ethyl myristate, methyl myristate, and methyl palmitate over extended ranges of pressure and temperature. These measurements are here used to compute indirectly derivatives properties, that is, isentropic compressibility and isothermal compressibility of these components.

■ EXPERIMENTAL SECTION

Materials. Table 1 shows the sample descriptions of ethyl myristate (tetradecanoic acid, ethyl ester, CAS No.: 124-06-1, molar mass: 256.42 g·mol^{-1}), methyl myristate (tetradecanoic acid, methyl ester, CAS No.: 124-10-7, molar mass: 242.40 g·mol^{-1}), and methyl palmitate (hexadecanoic acid, methyl ester, CAS: 112-39-0, molar mass: 270.45 g·mol^{-1}) used in the present work.

Table 1. Sample Description

chemical name	source	initial mole fraction purity	purification method
ethyl myristate	Sigma-Aldrich	0.99	none
methyl myristate	Sigma-Aldrich	0.99	none
methyl palmitate	Sigma-Aldrich	0.99	none

Speed of Sound Measurement. The speed of sound was measured using a pulse-echo technique working in transmission mode because this method is *truly adapted* to the liquid state. The apparatus, which has been described previously in detail,[6] is essentially made up of an acoustic sensor composed of two piezoelectric disks (12 mm in diameter) whose resonant frequency is 3 MHz. These transducers are arranged facing each other at both ends of a stainless steel cylindrical support (30 mm in length). One of them generates the ultrasonic wave that travels into the fluid sample while the other is used to receive different echoes. The speed of sound is determined from the measurement of the time interval between two successive echoes received by the receiver using the base time of an oscilloscope.[11] The path length needed for calculating speed of sound was determined at different temperatures and pressures by measuring the time-of-flight of the wave into a liquid of known speed of sound. Water[12,13] and heptane[14] were used for this calibration. This calibration leads to an uncertainty in the speed of sound of about 0.06 %. The entire acoustic sensor is located within a stainless-steel high-pressure vessel closed at

Table 2. Experimental Values of Speed of Sound *c* at Temperatures *T* and Pressures *P* for the Liquid Ethyl Myristate, Methyl Myristate, and Methyl Palmitate[a]

P	T	c	T	c	T	c	T	c	T	c	T	c	T	c
MPa	K	m·s^{-1}	K	m·s^{-1}	K	m·s^{-1}	K	m·s^{-1}	K	m·s^{-1}	K	m·s^{-1}	K	m·s^{-1}
Ethyl Myristate														
0.1	293.15	1360.6	303.15	1321.8	323.15	1251.8	343.15	1184.7	363.15	1120.0	383.15	1056.9	403.15	996.1
10	293.15	1408.0	303.15	1370.9	323.15	1304.5	343.15	1241.3	363.15	1181.8	383.15	1122.3	403.15	1067.2
20	293.15	1453.3	303.15	1416.8	323.15	1353.4	343.15	1293.0	363.15	1236.4	383.15	1181.7	403.15	1130.3
30	293.15	1494.5	303.15	1460.6	323.15	1398.6	343.15	1341.9	363.15	1287.1	383.15	1235.6	403.15	1186.1
40	293.15	1533.5	303.15	1500.8	323.15	1441.1	343.15	1386.7	363.15	1334.2	383.15	1284.7	403.15	1237.3
50	293.15	1568.2	303.15	1539.9	323.15	1482.4	343.15	1428.8	363.15	1377.5	383.15	1330.3	403.15	1284.9
60					323.15	1519.7	343.15	1468.1	363.15	1418.8	383.15	1372.3	403.15	1327.9
70					323.15	1555.8	343.15	1506.4	363.15	1457.6	383.15	1412.6	403.15	1370.0
80					323.15	1590.8	343.15	1541.9	363.15	1495.5	383.15	1450.4	403.15	1409.7
90					323.15	1624.6	343.15	1576.2	363.15	1531.0	383.15	1486.9	403.15	1447.5
100					323.15	1655.7	343.15	1609.1	363.15	1564.6	383.15	1521.7	403.15	1483.2
Methyl Myristate														
0.1			303.15	1335.8	323.15	1264.0	343.15	1195.7	363.15	1130.9	383.15	1066.7	393.15	1036.2
10			303.15	1382.9	323.15	1316.4	343.15	1251.2	363.15	1190.4	383.15	1131.3	393.15	1103.6
20			303.15	1426.9	323.15	1364.8	343.15	1302.9	363.15	1245.2	383.15	1189.6	393.15	1163.5
30			303.15	1468.1	323.15	1409.6	343.15	1350.8	363.15	1295.9	383.15	1242.9	393.15	1217.8
40			303.15	1507.6	323.15	1451.9	343.15	1396.0	363.15	1342.5	383.15	1291.7	393.15	1267.7
50			303.15	1544.9	323.15	1492.5	343.15	1437.4	363.15	1385.7	383.15	1338.0	393.15	1314.4
60			303.15	1580.2	323.15	1530.5	343.15	1477.5	363.15	1426.7	383.15	1380.3	393.15	1357.8
70			303.15	1614.2	323.15	1566.8	343.15	1515.0	363.15	1465.5	383.15	1420.4	393.15	1397.8
80					323.15	1601.2	343.15	1550.8	363.15	1502.6	383.15	1457.6	393.15	1436.8
Methyl Palmitate														
0.1			313.15	1317.2	323.15	1283.4	343.15	1215.3	363.15	1150.1	383.15	1087.2	393.15	1056.9
10			313.15	1365.4	323.15	1333.7	343.15	1270.1	363.15	1208.9	383.15	1150.3	393.15	1121.2
20			313.15	1411.5	323.15	1381.1	343.15	1319.7	363.15	1262.5	383.15	1207.5	393.15	1180.4
30			313.15	1454.4	323.15	1425.2	343.15	1366.8	363.15	1311.1	383.15	1259.3	393.15	1234.2
40			313.15	1494.8	323.15	1467.4	343.15	1410.5	363.15	1355.7	383.15	1310.8	393.15	1284.7
50					323.15	1506.9	343.15	1450.6	363.15	1400.9	383.15	1358.3	393.15	1334.0

[a]Standard uncertainties u are $u(T)$ = 0.1 K and $u(P)$ = 0.01 MPa, and the combined expanded uncertainty U_c (level of confidence = 0.95) is $U_c(c)$ = 0.002c.

Table 3. Values of Densities ρ at Temperatures T and Pressures P Measured in Liquid Ethyl Myristate, Methyl Myristate, and Methyl Palmitate[a]

P / MPa	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}
						Ethyl Myristate						
0.1013	293.15	861.0	303.15	853.3	313.15	845.6	323.15	838.5	333.15	830.6	343.15	823.2
10	293.15	867.5	303.15	860.2	313.15	852.7	323.15	845.4	333.15	838.0	343.15	831.1
20	293.15	873.2	303.15	866.2	313.15	859.0	323.15	852.0	333.15	844.9	343.15	838.6
30	293.15	878.7	303.15	871.9	313.15	864.9	323.15	858.2	333.15	851.3	343.15	845.2
40	293.15	883.8	303.15	877.3	313.15	870.5	323.15	863.9	333.15	857.2	343.15	851.3
50	293.15	888.7	303.15	882.2	313.15	875.7	323.15	869.2	333.15	862.9	343.15	857.1
60	293.15	893.6	303.15	887.0	313.15	880.8	323.15	874.7	333.15	868.2	343.15	862.5
70			303.15	891.7	313.15	885.5	323.15	879.8	333.15	874.0	343.15	867.7
80			303.15	896.0	313.15	890.8	323.15	884.5	333.15	878.0	343.15	872.8
90			303.15	900.3	313.15	894.9	323.15	888.9	333.15	883.4	343.15	877.5
100			303.15	904.4	313.15	899.1	323.15	893.1	333.15	888.0	343.15	882.1
0.1013	353.15	815.6	363.15	808.4	373.15	800.1	383.15	792.1	393.15	784.5		
10	353.15	823.9	363.15	816.6	373.15	809.9	383.15	802.1	393.15	794.6		
20	353.15	831.8	363.15	824.6	373.15	817.9	383.15	810.7	393.15	803.7		
30	353.15	838.7	363.15	831.8	373.15	825.5	383.15	818.5	393.15	812.0		
40	353.15	845.0	363.15	838.6	373.15	832.4	383.15	825.9	393.15	819.5		
50	353.15	850.8	363.15	845.0	373.15	838.8	383.15	832.5	393.15	826.4		
60	353.15	856.4	363.15	850.6	373.15	844.9	383.15	838.9	393.15	832.9		
70	353.15	861.8	363.15	856.1	373.15	850.6	383.15	845.0	393.15	839.8		
80	353.15	866.9	363.15	861.3	373.15	856.2	383.15	850.5	393.15	845.6		
90	353.15	871.8	363.15	866.3	373.15	861.3	383.15	855.9	393.15	851.0		
100	353.15	876.4	363.15	871.1	373.15	866.1	383.15	861.0	393.15	855.6		
						Methyl Myristate						
0.1013	303.15	859.7	313.15	851.6	323.15	843.3	333.15	835.2	343.15	827.9	353.15	820.2
10	303.15	866.3	313.15	858.2	323.15	850.5	333.15	843.0	343.15	835.7	353.15	828.5
20	303.15	872.4	313.15	864.7	323.15	857.2	333.15	850.1	343.15	843.1	353.15	836.1
30	303.15	878.2	313.15	870.7	323.15	863.5	333.15	856.6	343.15	849.8	353.15	843.2
40	303.15	883.7	313.15	876.4	323.15	869.4	333.15	862.7	343.15	856.2	353.15	849.8
50	303.15	888.9	313.15	881.7	323.15	874.9	333.15	868.4	343.15	862.1	353.15	855.9
60	303.15	893.8	313.15	886.8	323.15	880.2	333.15	873.8	343.15	867.7	353.15	861.6
70	303.15	898.5	313.15	891.7	323.15	885.2	333.15	879.0	343.15	873.0	353.15	867.1
80			313.15	896.3	323.15	889.9	333.15	883.9	343.15	878.0	353.15	872.3
0.1013	363.15	812.6	373.15	804.6	383.15	796.4	393.15	788.5				
10	363.15	821.2	373.15	813.9	383.15	806.3	393.15	798.6				
20	363.15	829.2	373.15	822.2	383.15	815.1	393.15	807.7				
30	363.15	836.6	373.15	829.9	383.15	823.0	393.15	815.9				
40	363.15	843.4	373.15	836.9	383.15	830.3	393.15	823.5				
50	363.15	849.7	373.15	843.5	383.15	837.1	393.15	830.5				
60	363.15	855.6	373.15	849.6	383.15	843.4	393.15	837.0				
70	363.15	861.2	373.15	855.3	383.15	849.3	393.15	843.1				
80	363.15	866.6	373.15	860.8	383.15	854.9	393.15	848.8				
						Methyl Palmitate						
0.1013	313.15	849.9	323.15	842.5	333.15	835.2	343.15	827.8	353.15	820.4	363.15	812.8
10	313.15	856.3	323.15	849.0	333.15	842.0	343.15	835.1	353.15	827.7	363.15	820.3
20	313.15	861.8	323.15	855.5	333.15	848.7	343.15	842.0	353.15	835.1	363.15	828.0
30	313.15	867.9	323.15	861.4	333.15	854.9	343.15	848.5	353.15	841.7	363.15	835.0
40	313.15	872.1	323.15	866.8	333.15	860.4	343.15	854.4	353.15	847.9	363.15	843.8
50	313.15	878.4	323.15	871.8	333.15	866.7	343.15	859.6	353.15	853.8	363.15	848.6
0.1013	373.15	804.6	383.15	797.4								
10	373.15	813.8	383.15	806.8								
20	373.15	821.7	383.15	815.1								
30	373.15	829.0	383.15	822.7								
40	373.15	835.7	383.15	829.6								
50	373.15	841.9	383.15	836.5								

[a]Standard uncertainties u are $u(T)$ = 0.1 K and $u(P)$ = 0.01 MPa, and the combined expanded uncertainty U_c (level of confidence = 0.95) is $U_c(\rho)$ = 0.5 kg·m^{-3}.

one end by a plug in which three electric connections were machined. The pressure is raised into the cell by the liquid itself thanks to a high pressure volumetric pump. It is measured by using a pressure gauge (HBM) fixed on the circuit linking the pump to the measurement cell. To ensure satisfactory thermal uniformity within the fluid, the cell is fully immersed in a thermo-regulated bath of stability 0.02 K in the temperature range (283 to 403) K. The temperature is measured with an uncertainty of ± 0.1 K directly into the studied liquid by using a Pt 100 sensor housed in a metal finger (1.2 mm diameter) in order to isolate it from the effect of pressure. The error of the measuring chain consists of the error in the time-of-flight measurement, the acoustic path length, and the additional contribution due to pressure and temperature errors. Consequently the combined uncertainty in the reported speed of sound values is estimated to be 0.2 % in the pressure range investigated. Furthermore, beside these physical contributions, chemical impurities add uncertainty in the measurements linked to the degree of purity of the samples.

Density Measurement. An Anton-Paar densimeter connected to a high-pressure cell (DMA HPM) was used for measurements of compressed liquid up to 100 MPa. The apparatus consists in a U-shape tube densimeter related to a high pressure volumetric pump. The instrument was calibrated with vacuum and both water[15] and decane[16] according to the method proposed by Comuñas et al.[17] The temperature inside the densimeter is regulated by an external circulating fluid, and it is measured with a Pt100 with an uncertainty of ± 0.1 K. The pressure is measured thanks to a HBM pressure gauge (0.1 % of uncertainty) fixed on the circuit linking the pump to the U-tube cell. Taking into account the uncertainty of the temperature, the pressure, the density of the reference fluid as well as the error in the measurements of the period of oscillation for the vacuum and for both the reference and the studied liquid, the overall experimental uncertainty in the reported density values is estimated to be ± 0.5 kg·m^{-3} (0.06 %) between (0.1 and 100) MPa.

■ RESULTS AND DISCUSSION

The speed of sound of ethyl myristate was measured along isotherms spaced at 20 K intervals in the temperature range (293 to 403) K, whereas methyl myristate was investigated between (303 and 393) K. Finally, methyl palmitate was studied in the limited temperature range from (313 to 393) K due to a higher melting temperature. The measurements of speed of sound were carried out in 10 MPa steps from atmospheric pressure up to 100 MPa. However for both methyl myristate and methyl palmitate, measurements were limited in pressure to (80 and 50) MPa respectively by the appearance of solid in the liquid contained into the pressure gauge whose working temperature is limited to 310 K. Density was investigated in the same temperature and pressure ranges but with a temperature step of 10 K in order to have a representation of the influence of temperature sufficiently accurate to evaluate its derivative. The results are given in Tables 2 and 3 for speed of sound and density, respectively.

Densities in ethyl and methyl myristate as well as and methyl palmitate were measured previously at atmospheric pressure by several authors.[18−22] Some references provide only one or two data points whereas Pratas et al.[22] reported measurements performed at several temperature ranging from (293.15 to 363.15) K. A comparison between the present measurements and the data report by these authors shows a good agreement with an absolute average deviation of 0.014 % for ethyl myristate, 0.12 % for methyl myristate, and 0.07 % for methyl palmitate. Density data under pressure were only reported by Pratas et al.[23] for methyl myristate in a moderate pressure range (0.1 45 MPa) and for temperatures ranging from (293.15 to 333.15) K. The present measurements deviate from these data by 0.12 % on average (value of the absolute average deviation). As for speed of sound, no literature values are available under pressure, but few measurements were reported at atmospheric conditions. Gouw and Vlugter[24] report measurements in methyl myristate and methyl palmitate for two temperatures, (293 and 413) K. Ott et al.,[21] Paredes et al.,[10] and Daridon et al.[7] measured speed of sound in methyl palmitate as a function of temperature between (308 and 343) K. Measurement in methyl myristate and ethyl myristate were carried out by Freitas et al.[8,9] and Daridon et al.[7] for a few temperatures. A comparison (Table 4) of these data with our measurement shows good agreement with a deviation less than the estimated error.

Table 4. Literature Data and Deviations with the Reported Speed of Sound Measurements at Atmospheric Pressure

	c/m·s^{-1} (deviation %)		
T/K	ethyl myristate	methyl myristate	methyl palmitate
293.15	1360.5^d (0.008); 1361.1^f (−0.04)		
303.15	1323.9^d (−0.16); 1324.3^f (−0.03)	1334.9^c (0.06); 1335.4^d (0.03)	
313.15			1318^a (−0.06); 1320^b (−0.21); 1317.8^d (−0.05); 1319.4^e (−0.17)
323.15	1252.7^d (−0.07); 1253.1^f (−0.03)	1263.5^c (0.03); 1265.7^d (−0.14)	1285^b (−0.13); 1281.2^d (0.17); 1284.3^e (−0.07)
343.15	1183.3^d (0.12); 1184.7^f (−0.12)	1194.3^c (0.12); 1196.3^d (−0.05)	1214.2^d (0.09); 1215.8^e (−0.04)
363.15	1118.2^d (0.16)	1131.1^d (−0.02)	1147.5 (0.20)

^{a}Gouw and Vlugter.[10] ^{b}Ott et al.[11] ^{c}Freitas et al.[11] ^{d}Daridon et al.[12] ^{e}Paredes et al.[13] ^{f}Freitas et al.[14]

Simultaneous knowledge in the same P,T conditions of volume v (per unit of mass) and speed of sound u makes possible to evaluate isentropic compressibility with an uncertainty of 0.5 % according to the following equation:

$$\kappa_S = \frac{v}{u^2} \qquad (1)$$

The values obtained in this way are listed in Table 5. Ultimately, the knowledge of both density and speed of sound allows designing reliable equations of state that can calculate accurately both the volume and its derivatives with respect to temperature and pressure. This consistent procedure of adjustment of a PVT equation[25,26] rests on the so-called Newton−Laplace relationship that relates the isothermal compressibility κ_T to the isentropic compressibility κ_S:

$$\kappa_T = \kappa_S + \frac{Tv\alpha_P^2}{c_p} \qquad (2)$$

where α_P represents the isobaric thermal expansion and c_p the isobaric heat capacity. The combination of this relation with eq 1 leads to a key relation that connects the speed of sound to the thermodynamic properties:

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Table 5. Values of Isentropic Compressibility κ_S at Temperatures T and Pressures P^a

P	T	κ_S	T	κ_S	T	κ_S	T	κ_S	T	κ_S	T	κ_S
MPa	K	GPa^{-1}	K	GPa^{-1}	K	GPa^{-1}	K	GPa^{-1}	K	GPa^{-1}	K	GPa^{-1}
						Ethyl Myristate						
0.1	293.15	0.627	303.15	0.671	323.15	0.761	343.15	0.865	363.15	0.986	383.15	1.130
10	293.15	0.581	303.15	0.619	323.15	0.695	343.15	0.781	363.15	0.877	383.15	0.990
20	293.15	0.542	303.15	0.575	323.15	0.641	343.15	0.713	363.15	0.793	383.15	0.883
30	293.15	0.510	303.15	0.538	323.15	0.596	343.15	0.657	363.15	0.726	383.15	0.800
40	293.15	0.481	303.15	0.506	323.15	0.557	343.15	0.611	363.15	0.670	383.15	0.734
50	293.15	0.458	303.15	0.478	323.15	0.524	343.15	0.572	363.15	0.624	383.15	0.679
60					323.15	0.495	343.15	0.538	363.15	0.584	383.15	0.633
70					323.15	0.470	343.15	0.508	363.15	0.550	383.15	0.593
80					323.15	0.447	343.15	0.482	363.15	0.519	383.15	0.559
90					323.15	0.426	343.15	0.459	363.15	0.492	383.15	0.528
100					323.15	0.408	343.15	0.438	363.15	0.469	383.15	0.502
						Methyl Myristate						
0.1	303.15	0.652	323.15	0.742	343.15	0.845	363.15	0.962	383.15	1.104	393.15	1.181
10	303.15	0.604	323.15	0.679	343.15	0.764	363.15	0.860	383.15	0.969	393.15	1.028
20	303.15	0.564	323.15	0.627	343.15	0.699	363.15	0.778	383.15	0.867	393.15	0.915
30	303.15	0.529	323.15	0.584	343.15	0.645	363.15	0.712	383.15	0.787	393.15	0.826
40	303.15	0.499	323.15	0.547	343.15	0.600	363.15	0.658	383.15	0.722	393.15	0.756
50	303.15	0.473	323.15	0.514	343.15	0.562	363.15	0.613	383.15	0.667	393.15	0.697
60	303.15	0.447	323.15	0.486	343.15	0.528	363.15	0.574	383.15	0.622	393.15	0.648
70	303.15	0.426	323.15	0.460	343.15	0.499	363.15	0.541	383.15	0.584	393.15	0.607
80			323.15	0.438	343.15	0.474	363.15	0.511	383.15	0.550	393.15	0.570
						Methyl Palmitate						
0.1	313.15	0.678	323.15	0.721	343.15	0.818	363.15	0.930	383.15	1.061		
10	313.15	0.626	323.15	0.662	343.15	0.742	363.15	0.834	383.15	0.937		
20	313.15	0.582	323.15	0.613	343.15	0.682	363.15	0.758	383.15	0.841		
30	313.15	0.545	323.15	0.572	343.15	0.631	363.15	0.697	383.15	0.767		
40	313.15	0.513	323.15	0.536	343.15	0.588	363.15	0.645	383.15	0.702		
50			323.15	0.505	343.15	0.553	363.15	0.600	383.15	0.648		

[a]Standard uncertainties u are $u(T)$ = 0.1 K and $u(P)$ = 0.01 MPa, and the combined expanded uncertainty U_c (level of confidence = 0.95) is $U_c(\kappa_S)$ = 0.005 κ_S.

$$\frac{v^2}{u^2} = v\kappa_T - \frac{Tv^2\alpha_P^2}{c_p} \quad (3)$$

Heat capacity can be estimated by integration of the following thermodynamic relationship when values are known at reference pressure:[27]

$$\left(\frac{\partial c_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P \quad (4)$$

In this work, the values of $c_{P,\mathrm{ref}}$ were taken at atmospheric pressure from measurements of van Bommel et al.[28] and Kouakou et al.[29] and were expressed as a cubic function of temperature in the range investigated:

$$c_{P,\mathrm{ref}}(\mathrm{EeC14{:}0})/\mathrm{J\cdot K^{-1}\cdot kg^{-1}} = 2.369\cdot 10^3 + 1.510T + 2.613\cdot 10^{-3}T^2 \quad (5)$$

$$c_{P,\mathrm{ref}}(\mathrm{MeC14{:}0})/\mathrm{J\cdot K^{-1}\cdot kg^{-1}} = 1.369\cdot 10^3 + 1.748T + 1.678\cdot 10^{-3}T^2 \quad (6)$$

$$c_{P,\mathrm{ref}}(\mathrm{MeC16{:}0})/\mathrm{J\cdot K^{-1}\cdot kg^{-1}} = 1.369\cdot 10^3 + 2.331T + 2.122\cdot 10^{-3}T^2 \quad (7)$$

By straightforward transformation of eq 3, one can relate the square of the ratio of both properties measured to the derivatives of the volume with respect to temperature and pressure.

$$\left(\frac{v}{u}\right)^2 = -\left(\frac{\partial v}{\partial P}\right)_T - \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p^2 \quad (8)$$

with

$$c_P(T) = c_{P,\mathrm{ref}}(T) - T\frac{\partial^2}{\partial T^2}\int_{P_{\mathrm{ref}}}^{P} v\,\mathrm{d}P \quad (9)$$

As all the terms of the right-hand side of this expression can be expended from a PVT equation of state, the square of the ratio of the volume to the speed of sound was used to adjust an equation of state define by both the volume at atmospheric pressure (P_{ref} = 0.1013 MPa):

$$v_{\mathrm{ref}} = v_0 + v_1T + v_2T^2 + v_3T^3 \quad (10)$$

and the change in volume with respect to pressure. For this, we have considered a rational equation that usually leads to a fair representation of the inverse of the square of sound speed and therefore leads to an accurate calculation of the compressibility. However, in order to keep a form close to Tait-like equations, the following equation was used:

$$\left(\frac{\partial v}{\partial P}\right)_T = -\frac{A + CP}{B + P} \quad (11)$$

It simplifies to Tait equation when parameter C is assigned to zero. In this equation C is constant, whereas A and B are expressed as a function of temperature by considering a third- and second-order polynomial form, respectively:

$$A = A_0 + A_1T + A_2T^2 + A_3T^3 \quad (12)$$

$$B = B_0 + B_1T + B_2T^2 \quad (13)$$

Integration and or derivation of this equation allows calculating the volume and its derivatives and consequently all of the thermophysical properties, that is, the density, isobaric expansion, isothermal compressibility, heat capacity, and therefore isentropic compressibility and speed of sound. All of the details concerning the various stages in the calculations of these properties are given in the Supporting Information.

The procedure used to adjust this equation of state consists in first evaluating the parameter of v_{ref} from atmospheric density data and then to estimate the coefficient A, B, and C by minimizing the following objective function:

$$\mathrm{OF} = \sum_{i}^{N_{exp}} \left(-\left(\frac{\partial v}{\partial P}\right)_T^{cal} - \frac{T}{c_P^{cal}}\left(\frac{\partial v}{\partial T}\right)_p^{2,cal} - \left(\frac{v_i^{exp}}{u_i^{exp}}\right)^2 \right)^2 \quad (14)$$

The values of the height coefficients determined in this way are given in Table 6 along with the average deviation, the average absolute deviation, and the maximum deviation with experimental data for both the density and the speed of sound. It can be observed that in the worst case, the maximum deviation observed between the experimental and calculated density data is about 0.3 %. This deviation shows that the function provides a very good representation of density in the range of pressure and temperature investigated. Moreover, by comparing the average and absolute average deviations for each compound, it is found that the equation does not introduce any systematic error regarding the calculation of density. As for the speed of sound, the comparison of the experimental data with the values calculated from eqs 10 to 14 using the derivatives reported on the Supporting Information reveals an absolute average deviation in the order of 0.08 % and maximum deviation less than 0.3 %. Moreover, the values of the average deviation reveal that deviations are random. Finally, it can be noted from Figure 1, showing the density and speed of sound of methyl myristate at a given temperature, that the deviations do not increase systematically with pressure. This is a striking result taking into account the complex relation between sound speed and volumetric properties. It reveals that the approach here used is consistent for predicting all the volumetric properties and no systematic degradation appears when one moves from the volume calculation to its derivatives. Thus this equation can be used to derive the isothermal compressibility as well as the isobaric expansion.

Table 6. Parameters of eqs 10 to 14 and Deviations from Sound Speed and Density

parameters[a]	ethyl myristate	methyl myristate	methyl palmitate
v_0	$6.58794 \cdot 10^{-4}$	$4.11612 \cdot 10^{-5}$	$1.09970 \cdot 10^{-3}$
v_1	$3.10641 \cdot 10^{-6}$	$8.21687 \cdot 10^{-6}$	$-6.80870 \cdot 10^{-7}$
v_2	$-7.18680 \cdot 10^{-9}$	$-2.14170 \cdot 10^{-8}$	$3.53996 \cdot 10^{-9}$
v_3	$8.32116 \cdot 10^{-12}$	$2.15095 \cdot 10^{-11}$	$-1.85320 \cdot 10^{-12}$
A_0	$-6.71050 \cdot 10^{-5}$	$1.39436 \cdot 10^{-4}$	$-1.12580 \cdot 10^{-5}$
A_1	$1.31059 \cdot 10^{-6}$	$5.97453 \cdot 10^{-7}$	$4.75154 \cdot 10^{-7}$
A_2	$-3.87090 \cdot 10^{-9}$	$-4.48510 \cdot 10^{-9}$	$-4.77550 \cdot 10^{-10}$
A_3	$4.11792 \cdot 10^{-12}$	$6.86027 \cdot 10^{-12}$	0
B_0	$3.43403 \cdot 10^{2}$	$5.70490 \cdot 10^{2}$	$3.29059 \cdot 10^{2}$
B_1	-1.11381	-2.29631	$-9.74564 \cdot 10^{-1}$
B_2	$9.64222 \cdot 10^{-4}$	$2.49945 \cdot 10^{-3}$	$7.35998 \cdot 10^{-4}$
C	$6.89379 \cdot 10^{-8}$	$7.95407 \cdot 10^{-8}$	$4.60558 \cdot 10^{-8}$
range			
T/K	293 to 393	303 to 393	313 to 383
P/MPa	0.1 to 100	0.1 to 80	0.1 to 500
deviations			
AD% for ρ	$3.1 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$4.1 \cdot 10^{-2}$
AAD% for ρ	$3.7 \cdot 10^{-2}$	$3.6 \cdot 10^{-2}$	$5.2 \cdot 10^{-2}$
MD% for ρ	$9.7 \cdot 10^{-2}$	$1.9 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$
AD% for u	$-9.2 \cdot 10^{-3}$	$-7.3 \cdot 10^{-3}$	$-5.8 \cdot 10^{-2}$
AAD% for u	$5.9 \cdot 10^{-2}$	$8.5 \cdot 10^{-2}$	$8.8 \cdot 10^{-2}$
MD% for u	$2.7 \cdot 10^{-1}$	$3.0 \cdot 10^{-01}$	$2.8 \cdot 10^{-1}$

[a] AD = average deviation; AAD = absolute average deviation; MD = maximum deviation.

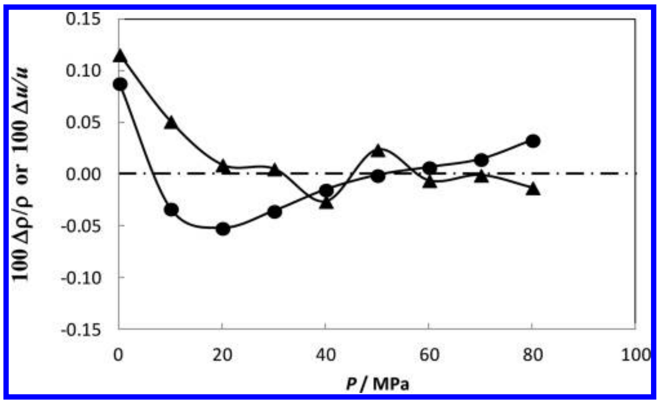

Figure 1. Relative deviations between measurements and calculation for the methyl myristate at 343.15 K. ▲ density deviation: $\Delta\rho/\rho = \{\rho(\exp) - \rho(\mathrm{cal})\}/\rho(\exp)$; ● speed of sound deviation: $\Delta u/u = \{u(\exp) - u(\mathrm{cal})\}/u(\exp)$.

CONCLUSIONS

Speeds of sound were measured for ethyl myristate, methyl myristate, and methyl methyl palmitate as a function of both pressure and temperature. Density was also measured for the same compounds by using a U-tube densimeter up to 100 MPa. These measurements were used to evaluate the isentropic compressibility. A single correlation was proposed to describe the density and speed of sound data. The very good agreement observed between the calculated and experimental data for both properties in this pressure range investigated as well as the absence of systematic deviations indicates the consistency between the two set of thermophysical properties and confirm the reliability of the experimental measurements. Finally, the evaluation through both speed of sound and density measurements of an equation of state provides a predictive tool to determine isothermal compressibility and isobaric coefficients whose direct measurement is not a common undertaking.

ASSOCIATED CONTENT

Supporting Information

Summary of equations for calculating volume and derivative properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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