

Vapor pressure measurements on saturated biodiesel fuel esters by the concatenated gas saturation method[☆]

Jason A. Widegren, Thomas J. Bruno^{*}

Thermophysical Properties Division, National Institute of Standards and Technology (NIST), 325 Broadway, Boulder, CO 80305, USA

ARTICLE INFO

Article history:

Received 26 August 2010

Received in revised form 18 November 2010

Accepted 26 November 2010

Available online 9 December 2010

Keywords:

Biodiesel fuel

Vapor pressure

Saturated ester

Concatenated gas saturation method

Transpiration method

ABSTRACT

The purpose of this work was to determine vapor pressures for saturated biodiesel esters at the low-temperature end of their liquid range. A “concatenated” gas saturation apparatus capable of simultaneous measurements on 18 samples was used for measurements on methyl palmitate, ethyl palmitate, methyl stearate, ethyl stearate, and eicosane (C₂₀H₄₂) over the temperature range 323.15 K–343.15 K. Eicosane, a linear alkane with a well known vapor pressure curve (in the same range as the biodiesel esters), was included as a control compound. Importantly, the measured vapor pressures for eicosane are in excellent agreement with reference values, which is good evidence of the low uncertainty of the measurements on the biodiesel esters. Over this temperature range, the measured vapor pressure ranges were 0.145 Pa–1.11 Pa for methyl palmitate, 0.0687 Pa–0.616 Pa for ethyl palmitate, 0.0159 Pa–0.183 Pa for methyl stearate, and 0.00704 Pa–0.0912 Pa for ethyl stearate. The combined standard uncertainty in the vapor pressure measurements ranged from 8% to 15%.

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1. Introduction

This work is part of a larger effort at NIST to provide thermophysical data and models for biodiesel fuel and its components [1–10]. Such work is meant to enhance design and operational specifications for these fluids, and to facilitate refining and new applications. The thermophysical properties that are being measured include equilibrium properties (such as the vapor pressure, density, and heat capacity) and transport properties (such as viscosity and thermal conductivity).

Biodiesel fuel is composed of alkyl esters of fatty acids. Currently, the methyl esters (i.e., FAMES) dominate biodiesel fuel production because of low cost [11], but there is interest in other esters (such as ethyl or *iso*-propyl esters) because of potential improvements in fuel properties [12]. Most of the available thermophysical property data are for the methyl esters. However, even for these, important property data are often lacking, as illustrated by a continuing reliance on predicted values for vapor–liquid equilibrium and vapor pressure [13–15].

In this work, we use a gas saturation method to measure vapor pressures for four saturated biodiesel esters: methyl palmitate (C16:0M), ethyl palmitate (C16:0E), methyl stearate (C18:0M),

and ethyl stearate (C18:0E). For our initial study of biodiesel esters, we chose to measure only saturated compounds because their resistance to oxidation [12,16] makes them easier to handle and removes a potential source of measurement error. Additionally, even for these relatively stable compounds, the extant data tend to be limited or in poor agreement. For both C16:0M and C18:0M, there are two reported vapor pressure studies that cover the low-temperature end of their liquid ranges [17,18]. For both compounds, the two extant sets of data are in poor agreement. Similarly, there are two sets of data available for C18:0E at the low-temperature end of its liquid range [17,19]; the temperature ranges do not overlap, but the two data sets appear to be in poor agreement. There is only one reported vapor pressure study for C16:0E at the low-temperature end of its liquid range [19], so a confirmatory set of data would be useful. Our goal for this work is to provide data with well-understood uncertainties for the low-temperature end of the vapor pressure curves for all four of these compounds.

A variety of “indirect” methods are capable of measuring the vapor pressures of low-volatility compounds [20–22]; however, the gas saturation method and the effusion method (when high-purity samples are available) are generally considered to be the most accurate of these methods for low vapor pressures [22]. The gas saturation method, also called the transpiration method, is a simple technique that involves the saturation of a carrier gas stream with the vapor of a condensed phase of the compound of interest [20–28]. The most common approach is to strip the vapor from a measured volume of the saturated carrier gas using an adsorber or cold trap, and then measure the recovered mass with an appro-

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^{*} Corresponding author. Tel.: +1 303 497 5158; fax: +1 303 497 6682.

E-mail addresses: jason.widegren@nist.gov (J.A. Widegren), thomas.bruno@nist.gov, bruno@boulder.nist.gov (T.J. Bruno).

appropriate analytical method. The vapor pressure is then calculated with the ideal gas equation,

$$P_{\text{sat}} = (m \cdot R \cdot T) / (V \cdot M), \quad (1)$$

where P_{sat} is the vapor pressure, m is the recovered mass of the vapor, R is the gas constant, T is the absolute temperature of the saturator, V is the volume of carrier gas at the temperature and pressure of the saturator, and M is the molar mass of the compound.

The gas saturation method has several key advantages [21,22,25–28]. The most important advantage is that impurities have a relatively small effect on the measured vapor pressures, assuming that a separation technique such as gas chromatography is used to determine the quantity of vapor, so samples of limited purity (or limited stability) can be used. Small sample quantities are needed for a measurement (typically tens of milligrams or less), assuming that a sensitive analytical method is used to determine the amount of vapor. The method does not require calibration; however, measurements on control compounds are important (see below). Finally, such an apparatus is simple and inexpensive to build and operate. On the other hand, gas saturation methods have two potential drawbacks. First, the method is susceptible to certain types of systematic errors (e.g., leaks) that can be difficult to detect. Second, measurement periods can be quite long if a large volume of carrier gas is needed in order to collect a sufficient amount of vapor for analysis.

The “concatenated” gas saturation (CGS) method [21,29,30] was developed in order to compensate for the drawbacks mentioned above. In this type of apparatus, several saturator–adsorber pairs are linked in series, so that multiple measurements can be made simultaneously with the same carrier gas stream. An important advantage of this approach is that it allows for strategies that ensure data quality. For example, a control compound with a well known vapor pressure can be measured simultaneously with the sample compounds. If the control measurements yield the expected vapor pressure for the control compound, one has a high level of confidence in the other measurements that were made simultaneously. The CGS method also speeds data collection and saves labor (e.g., only one determination of V is needed for each set of samples).

2. Materials and methods

2.1. Materials

Reagent-grade acetone was obtained from a commercial source and used as received. It has a stated purity of 99.5%, which is consistent with our own routine analyses of such solvents by gas chromatography [31]. Sulfur hexafluoride (SF_6) was obtained from a commercial source with a stated purity of 99.9%. Before use, the SF_6 was transferred into an aluminum cylinder to facilitate mass determinations. Eicosane was obtained from a commercial source with a stated purity of 99.8% and was used as received. The biodiesel esters were also obtained from commercial sources and used as received. Their molar masses, melting temperatures [32], and purities are given in Table 1 along with useful identifiers.

2.2. Concatenated gas saturation apparatus

The apparatus used for these measurements was designed and constructed at NIST. A detailed description of the apparatus is published in a recent paper [30], so only an overview of the principal components is given here. This apparatus is similar to an earlier apparatus for which a detailed description has also been published [21]. The principal components of the apparatus are illustrated schematically in Fig. 1. The carrier gas supply includes an aluminum gas cylinder, pressure regulator, and flow controller. Carrier

gas from the flow controller first passes through an adsorbent column packed with the porous polymer adsorbent poly(2,6-diphenyl-1,4-phenylene oxide) [31,33]. The gas then flows through the 18 saturator–adsorber pairs that are linked in one continuous series. The saturators are located inside a forced-air, temperature-controlled chamber (capable of temperatures from -35°C to 177°C) and consist of PTFE tubes (1 m in length with an inside diameter of 0.48 cm) filled with glass beads with a diameter of 0.3 cm. The adsorbers, which are removable, are located on a manifold above the chamber (at room temperature, approximately 21°C) and consist of stainless-steel tubes packed with poly(2,6-diphenyl-1,4-phenylene oxide). A stainless-steel capillary tube attached to the inlet end of each adsorber penetrates through the wall of the temperature-controlled chamber and into the end of the saturator, which prevents the loss of vapor as the carrier gas flows from the temperature-controlled saturator to the room temperature adsorber. Between each saturator–adsorber pair, a Bourdon tube pressure gauge displays the pressure. At the end of the saturator–adsorber series, the carrier gas exits the apparatus at ambient pressure (approximately 83.5 kPa in Boulder, CO).

2.3. Vapor pressure measurements

First, each saturator was coated with one of the biodiesel esters or with eicosane. This was done by wetting the saturator with a 10% solution of one of the compounds in acetone, and then removing the acetone by gently flowing helium through the adsorber at room temperature for 0.5 h. Approximately 2 mL of solution was used to wet each saturator, which means that approximately 0.2 g of the compound was deposited. Given the surface area of the saturator (approximately 0.024 m^2), we estimate that the average thickness of the coating was $8\text{ }\mu\text{m}$. The saturators were then installed in the temperature-controlled chamber of the apparatus. The saturators had to be coated only once for all of the vapor pressure measurements because no more than 2 mg of any compound evaporated from a saturator during a measurement.

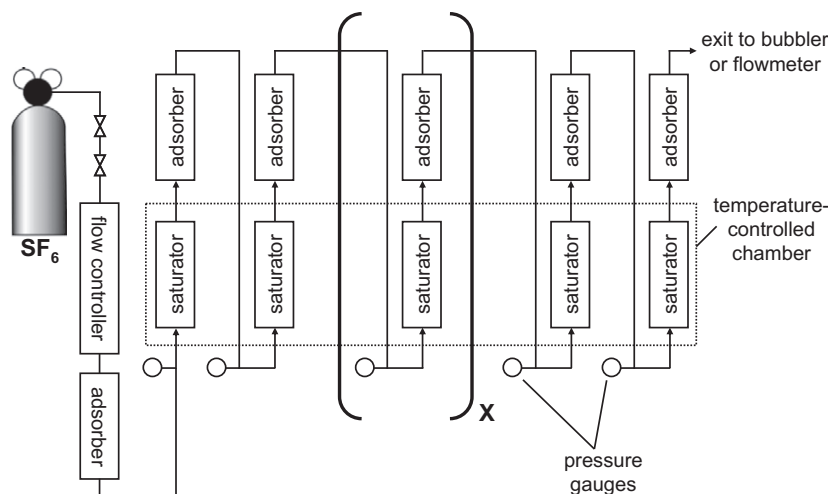
Before starting a measurement, the SF_6 supply cylinder was weighed on a 25 kg two-pan balance with a sensitivity of 2.5 mg. In order to eliminate a buoyancy correction, an evacuated ballast cylinder was placed on the other balance pan (along with class S standard weights). After weighing, the SF_6 cylinder was connected to the gas saturation apparatus and the adsorbers were also installed. The temperature was set and, after thermal equilibration, the flow of SF_6 was initiated. The flow rate of carrier gas was between 0.6 L and 0.8 L per day, which means that the residence time of the carrier gas in a saturator was approximately 0.25 h. Flow times ranged from 7 days (at 343.15 K) to 34 days (at 323.15 K).

Upon passage of a sufficient quantity of carrier gas, the flow of SF_6 was stopped and the cylinder weighed again. One-by-one, the adsorbers were removed from the apparatus. As this was done, the saturators were immediately capped in order to exclude moisture and oxygen. Then the adsorbers were eluted with acetone by use of a syringe pump set to deliver acetone at a rate of 0.25 mL/min. The first 0.75 mL of eluent from each adsorber was collected into a pre-weighed autosampler vial, which was immediately capped. The next 0.75 mL of eluent from each adsorber was collected into a second pre-weighed autosampler vial, which was immediately capped. Finally, the adsorber was flushed with 6 mL of acetone at a flow rate of 1 mL/min. Typically, the first eluent fraction contained all of the detectable solute, even for the most concentrated samples. This method of analyzing multiple eluent fractions ensures that all detectable solute has been stripped from the adsorber. After elution, the adsorbers were dried with a flow of warm helium before using them for the next vapor pressure measurement.

The eluent fractions were analyzed by gas chromatography with flame ionization detection (GC–FID). Research-grade nitrogen

Table 1The abbreviation, CAS Registry Number (CASRN), molar mass (MW), melting temperature (T_m) and purity of each biodiesel ester.

Compound	Abbreviation	CASRN	MW/g · mol ⁻¹	T (°C)	Purity (%)
Methyl palmitate	C16:0M	112-39-0 ^a	270.45	29.5–30.5	>99
Ethyl palmitate	C16:0E	628-97-7 ^b	284.48	23.2–24.8	>99
Methyl stearate	C18:0M	112-61-8 ^c	298.50	37.9–39.1	>99
Ethyl stearate	C18:0E	111-61-5 ^d	312.53	31.0–33.5	>99

^a IUPAC Standard InChI = IS/C17H34O2/cl-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17(18)19-2/h3-16H2,1-2H3.^b IUPAC Standard InChI = IS/C18H36O2/cl-3-5-6-7-8-9-10-11-12-13-14-15-16-17-18(19)20-4-2/h3-17H2,1-2H3.^c IUPAC Standard InChI = IS/C19H38O2/cl-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/h3-18H2,1-2H3.^d IUPAC Standard InChI = IS/C20H40O2/cl-3-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19-20(21)22-4-2/h3-19H2,1-2H3.**Fig. 1.** A concatenated gas saturation apparatus with 18 saturator–adsorber pairs linked in one continuous series ($x = 14$).

was used as the carrier and makeup gas. The split/splitless injection inlet was used in the splitless mode and maintained at 250 °C. The samples were separated on a 30 m capillary column coated with a 0.1 μm film of (5%-phenyl)-methylpolysiloxane. The temperature program was 1 min at 50 °C, followed by a 100 °C/min gradient to 75 °C, followed by a 20 °C/min gradient to 210 °C, and then holding at 210 °C for 7 min. The FID was maintained at 275 °C.

The mass change of the supply cylinder was used to calculate the amount of SF_6 used for each measurement. The volume of carrier gas, V in Eq. (1), at the experimental temperature and ambient pressure, was then calculated by use of an equation of state for SF_6 that is explicit in Helmholtz energy [34], as implemented in REFPROP [35]. The mass of vapor collected in the adsorber, m in Eq. (1), was determined by calibrated gas chromatography, as described above.

2.4. Ensuring data quality

With the gas saturation technique there are several potential pitfalls that can cause systematic errors in measurements of p_{sat} . For the concatenated apparatus used herein, which has a large number of connections along the carrier gas stream, one potential source of error is a leak of the carrier gas, which would result in low values of p_{sat} downstream from the leak. Some other possible sources of systematic error are inefficient trapping of the sample vapor in the adsorbers, incomplete elution of a sample from the adsorbers, insufficient analytical sensitivity when determining the amount of sample in the eluent, a carrier gas flow rate that is too fast (insufficient equilibration time in the saturator) or too slow (mass transport by diffusion can become significant), and decomposition of a sample during the measurement.

Our primary strategy for ensuring the quality of the data for the biodiesel esters was to make simultaneous measurements on a control compound with a vapor pressure curve in the same pressure range as the vapor pressure curves for the biodiesel esters. In this work, the successful measurements on eicosane provide direct evidence against several of the potential problems mentioned above, including leaks. Another strategy that we routinely employ is to measure each compound in triplicate, and space these measurements along the apparatus in a particular way. Specifically, C16:0M was measured in the 5th, 11th, and 17th saturator–adsorber pairs. C16:0E was measured in the 4th, 10th, and 16th saturator–adsorber pairs. 18:0M was measured with the 3rd, 9th, and 15th saturator–adsorber pairs. 18:0E was measured with the 2nd, 8th, and 14th saturator–adsorber pairs. Eicosane was measured with the 6th, 12th, and 18th saturator–adsorber pairs. (The 1st, 7th, and 13th saturator–adsorber pairs were used to measure a compound unrelated to this work.) With this type of spacing, comparisons of p_{sat} measured in different parts of the apparatus can be used to detect (and even pinpoint) leaks or other problems that could occur within the saturator–adsorber chain. Eicosane was measured using the 6th, 12th and 18th (i.e., last) saturator–adsorber pairs so that any “upstream” problems would affect at least one of these control measurements. Spacing the samples in this way also allows us to detect inefficient vapor trapping by carry-over to the next adsorber (something that was not observed during these measurements). The elution procedure described in Section 2.3 is specifically designed to ensure that all detectable solute has been stripped from the adsorber. Calibration curves show that GC–FID is sufficiently sensitive in the range of these experiments. No decomposition products were apparent in the GC–FID analysis of eluent fractions from the adsorbers.

2.5. Estimating the uncertainty of the vapor pressure measurements

There are several sources of uncertainty in the measurement of vapor pressure with the concatenated gas saturation apparatus. One of the most important sources of uncertainty is in the temperature control of the saturators. By use of an ITS-90 calibrated platinum resistance thermometer with an uncertainty of 0.01 K, we estimate an uncertainty of 0.5 K in the temperature control, which results in a relative standard uncertainty of between 5.2% and 6.6% in the measured vapor pressures of these samples. Another important source of uncertainty is in the analysis of the mass of recovered vapor by GC–FID. This determination has a relative standard uncertainty of between 4% and 13%, depending on the sample. The pressure in the saturators is not directly controlled, which results in a relative standard uncertainty of 3% in the measured vapor pressures (which is due to a pressure drop across the apparatus and barometric variability). The relative standard uncertainty for saturator efficiency is estimated to be 1% [21]. The relative standard uncertainty estimated for the elution efficiency is $\leq 1\%$. The determination of carrier gas volume, by weighing the SF₆ cylinder and using an equation of state, results in a relative standard uncertainty of $<0.1\%$ in the measured vapor pressures. The adsorber efficiency is not detectably less than 1, and is, therefore, not assigned an uncertainty. There are also uncertainties caused by impurities in the sample compounds and by the use of the ideal gas law [21]. In an ideal-mixture approximation, the partial pressure of the major component of a sample is equal to the product of its mole fraction and its vapor pressure. The mass fraction purities of the biodiesel esters and the eicosane are at least 0.99 (Section 2.1). It is likely that the average molar mass of the impurities is similar to the molar mass of the sample compound; in that case, the mole fraction purity of the sample compound is also 0.99, which would result in a 1% decrease in the measured vapor pressures. In a similar way, solubility of the carrier gas in the condensed phase can cause a shift in the measured vapor pressures. Based on the trends for SF₆ solubility in linear alkanes at 298.15 K [36], the mole fraction solubility of SF₆ in eicosane is expected to be $<<0.01$ at the conditions of the vapor pressure measurements; hence, the expected shift in p_{sat} is also $<<1\%$. The solubility of SF₆ in the biodiesel esters is not known; for the purposes of our uncertainty analysis, we assume that the magnitude of the effect is $<<1\%$ for these compounds also. The Poynting correction to the pure-liquid fugacity is approximately 1%. Any nonideality of saturated solute vapor is expected to be negligible because the pressures are low, and there is no reason to suspect an effect like gas-phase dimerization. Interaction of the solute vapor with the carrier gas could significantly change the measured vapor pressure [21], but the interaction virial coefficients are not known for these systems, so they are assumed to be negligible. Instead of trying to correct for these effects, we treat them all as uncertainties in the measurement. Hence, the quadrature sum of relative standard uncertainties associated with the method, the sample purity, and the ideal gas approximation is 8%

for eicosane, 12% for C16:0M, 15% for C16:0E, 14% for C18:0M, and 14% for C18:0E.

3. Results and discussion

The vapor pressures (p_{sat}) of C16:0M, C16:0E, C18:0M, C18:0E, and eicosane were determined at temperatures of 323.15 K, 333.15 K, and 343.15 K. In this temperature range, all of these compounds are in the liquid phase (at ambient pressure). Three simultaneous measurements of p_{sat} were made for each compound at each temperature, and the mean values and standard deviations are given in the tables.

3.1. Vapor pressure measurements on the control compound, eicosane

The gas saturation method does not require calibration; however, as discussed in Section 2.4, there are some potential problems that must be guarded against. Our primary strategy for ensuring the quality of the data for the biodiesel esters was to make simultaneous measurements on a control compound with a similar vapor pressure. This strategy helps (1) to validate the analytical methodology used to determine the amount of trapped vapor, (2) to ensure sufficient equilibration time (i.e., proper carrier gas flow rate), and (3) to detect a variety of other potential problems (poor temperature control, leaks, etc.). As in the past [29,30], we chose a linear alkane as the control compound for a variety of reasons: the vapor pressure curves are well known for this class of compounds [37,38]; it is possible to choose a linear alkane with a vapor pressure that is close to the other samples being measured; alkanes are stable and unreactive; and they are available commercially at low cost and with an acceptable purity. For this work, we used eicosane as the control compound because, in the temperature range studied, its vapor pressure curve is right in the middle of those for the biodiesel esters.

Reference values of p_{sat} for eicosane were taken from the NIST ThermoData Engine (TDE) [39]. The reference values are shown in Table 2 along with their combined standard uncertainty (u_c), as determined by TDE. For comparison, the values of p_{sat} for eicosane that were measured in the concatenated gas saturation apparatus also are shown in Table 2. The difference between the TDE reference values and our measured values is less than the combined standard uncertainty of our measurements, Table 2. Because the measured values of p_{sat} for eicosane are the same as the reference values, we have confidence in the other values of p_{sat} that were measured simultaneously. Also, the standard deviations (s) of replicate vapor pressure measurements for eicosane (see Table 2) are about the same as the estimated combined standard uncertainty for the measurement (see Section 2.5), which is evidence that our uncertainty estimates are reasonable.

3.2. Vapor pressure measurements on the biodiesel esters

Table 3 shows the mean values of p_{sat} for the four biodiesel esters that were measured in the concatenated gas saturation apparatus. The standard deviations of replicate vapor pressure measurements and the estimated combined standard uncertainty for the measurements (see Section 2.5) are also in Table 3. In this temperature range, the vapor pressure of each methyl ester is about twice the vapor pressure of the corresponding ethyl ester. Also, the vapor pressure of each palmitate ester is almost an order of magnitude higher than the vapor pressure of the corresponding stearate ester. For C16:0M, C16:0E and C18:0M, the values of s are about the same as, or smaller than, the values of u_c , as expected. However, for C18:0E, the values of s are significantly larger than the values of u_c . The reason for this is not clear; it could be the re-

Table 2
Comparison of reference values and measured values for eicosane vapor pressure (p_{sat}).

T (K) ^a	TDE reference values		Gas saturation measurements		
	p_{sat} (Pa)	u_c (Pa) ^b	p_{sat} (Pa) ^c	s (Pa) ^d	u_c (Pa) ^b
323.15	0.047	0.004	0.044	0.003	0.004
333.15	0.139	0.010	0.139	0.012	0.011
343.15	0.381	0.025	0.391	0.027	0.031

^a Eicosane is a liquid in this temperature range.

^b u_c is the combined standard uncertainty of p_{sat} .

^c Each value is the mean of three replicate measurements.

^d s is the standard deviation of the p_{sat} measurements.

Table 3

Vapor pressures (p_{sat}) of biodiesel esters determined by the concatenated gas saturation method.

Ester ^a	T (K)	p_{sat} (Pa) ^b	s (Pa) ^c	u_c (Pa) ^d
C16:0M ^e	323.15	0.145	0.009	0.017
C16:0M	333.15	0.404	0.036	0.049
C16:0M	343.15	1.109	0.109	0.133
C16:0E ^f	323.15	0.069	0.008	0.010
C16:0E	333.15	0.206	0.024	0.031
C16:0E	343.15	0.616	0.079	0.092
C18:0M ^g	323.15	0.016	0.002	0.002
C18:0M	333.15	0.050	0.010	0.007
C18:0M	343.15	0.183	0.025	0.026
C18:0E ^h	323.15	0.0070	0.0014	0.0010
C18:0E	333.15	0.0233	0.0054	0.0033
C18:0E	343.15	0.0912	0.0177	0.0128

^a All of the esters are liquids in this temperature range.

^b Each value is the mean of three replicate measurements.

^c s is the standard deviation of the p_{sat} measurements.

^d u_c is the combined standard uncertainty of p_{sat} .

^e C16:0M is methyl palmitate, CAS Number 112-39-0.

^f C16:0E is ethyl palmitate, CAS Number 628-97-7.

^g C18:0M is methyl stearate, CAS Number 112-61-8.

^h C18:0E is ethyl stearate, CAS Number 111-61-5.

sult of the small sample size that was used to determine s , or it could be that we have underestimated u_c for C18:0E.

As discussed in the Introduction, few vapor pressure data exist for biodiesel esters at the low-temperature end of their liquid ranges. There are only two papers that report p_{sat} for liquid C16:0M below 378 K [17,18]. Spizzichino used a static method to measure p_{sat} of C16:0M over the temperature range 308.99 K–374.87 K [17]. More recently, van Genderen et al. used three different methods to measure p_{sat} of C16:0M from 303.46 K to 361.21 K [17]. Our values of p_{sat} for C16:0M are in excellent agreement with the data reported by van Genderen et al., as demonstrated by a deviation plot, Fig. 2. Their data are about 7% higher than the Clausius–Clapeyron fit to our own data (represented by the zero line in Fig. 2), which is less than the standard uncertainty in our data. On the other hand, the data from Spizzichino are as much as 43% lower than the fit line in this temperature range, and show considerably more scatter than the other data.

The situation for C18:0M is similar to C16:0M. There are only two papers that report p_{sat} for liquid C18:0M below 383 K [17,18]. Spizzichino

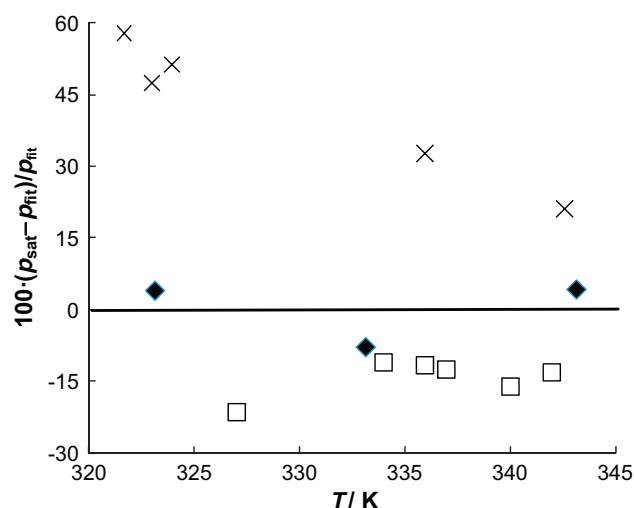


Fig. 3. Deviation plot of vapor pressure data for C18:0M: x, van Genderen et al.; ♦, this work; □, Spizzichino; —, fit to the data from this work.

reports p_{sat} for C18:0M over the temperature range 326.99 K–393.07 K [17]. More recently, van Genderen et al. used two different methods to measure p_{sat} of C18:0M from 316.04 K to 359.12 K [18]. Fig. 3 shows a deviation plot of all of the data in the temperature range that we measured. The zero line in Fig. 3 represents a Clausius–Clapeyron fit to our own data. Our values of p_{sat} again fall in the middle of the previously reported data, but in this case are closer to those of Spizzichino.

Omar [19] is the only source of p_{sat} data for C16:0E below 400 K. In that work, the Knudsen effusion method was used to measure p_{sat} in the temperature range 298.15 K–318.15 K, and a correlation to the measurements is reported [19]. Although that temperature range does not quite overlap the temperature range that we measured, an extrapolation of the Clausius–Clapeyron fit of our data was within 8% of Omar's correlated data, which is less than the standard uncertainty in our data.

Omar [19] and Spizzichino [17] also report vapor pressures at the low-temperature end of the liquid range for C18:0E. Omar reports a correlation to p_{sat} measurements between 310.15 K and

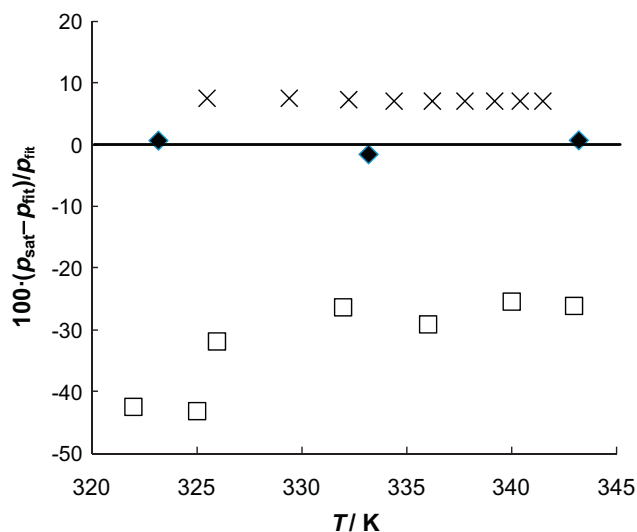


Fig. 2. Deviation plot of vapor pressure data for C16:0M: x, van Genderen et al.; ♦, this work; □, Spizzichino; —, fit to the data from this work.

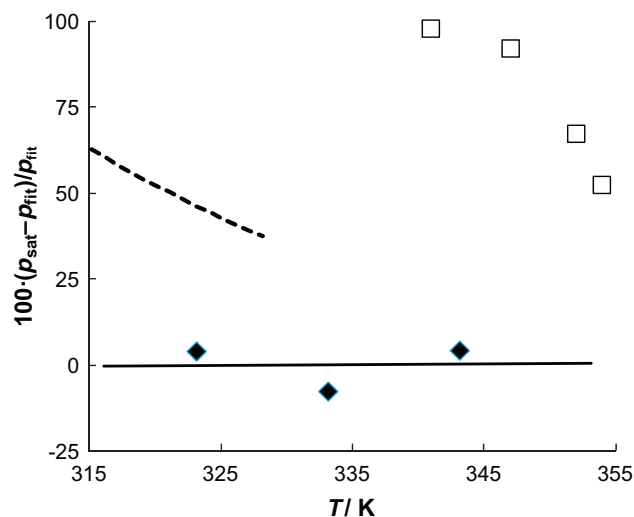


Fig. 4. Deviation plot of vapor pressure data for C18:0E: ---, Omar; ♦, this work; □, Spizzichino; —, fit to the data from this work.

328.15 K, which just overlaps the temperature range that we measured. Spizzichino reports p_{sat} measurements between 340.98 K and 398.07 K, which also just overlaps the temperature range that we measured. Fig. 4 shows a deviation plot of all of the data in the temperature range that we measured. The zero line in Fig. 4 represents a Clausius–Clapeyron fit to our own data. The agreement between the sets of data is not good. Spizzichino's data point at 340.98 K is 98% higher than the Clausius–Clapeyron fit to our data. Omar's correlation is 46% higher than the Clausius–Clapeyron fit to our data at 323.15 K.

We can also compare our measurements with a group contribution model for FAME vapor pressures [14,15]. The model was developed by correlating a limited set of extant vapor pressure data for fatty compounds [15]. The data used to develop the model were generally at much higher pressures than the measurements reported herein; therefore, it is interesting to see how well the model performs at low pressures. For C16:0M, the group contribution model predicts vapor pressures that are about 20% lower than the fit to our data (i.e., the zero line in Fig. 2). For C18:0M, the group contribution model predicts vapor pressures that are about 25% lower than the fit to our data (i.e., the zero line in Fig. 3).

4. Conclusion

An important advantage of the CGS method is that it allows for several strategies that ensure data quality, as described in Section 2.4. Most importantly, a control compound with a well known vapor pressure can be measured simultaneously with the sample compounds. In this case, measurements on eicosane yielded vapor pressures that were within experimental uncertainty of reference values. We believe that this lends a great deal of confidence to the measurements on the biodiesel esters.

For C16:0M, C18:0M, and C18:0E previously reported sets of low-temperature data are in poor agreement with one another. For C16:0M and C18:0M our vapor pressure data falls in between previously reported sets of data. For C18:0E our vapor pressure data were substantially lower than either of the previously reported sets of data. For C16:0E there was good agreement between our data and the one previously reported set of data near room temperature. Our data C16:0M and C18:0M show reasonable agreement with a previously reported group contribution model for FAME vapor pressures.

In the future we plan to make measurements on other biodiesel esters. In particular, we believe that there is a need for reliable vapor pressure data for unsaturated esters. These compounds are less stable and, therefore, more difficult to measure accurately. We believe that the CGS method is suitable for such measurements because of the various quality control measures that it allows.

Acknowledgement

We thank Dr. Allan H. Harvey (NIST) for insightful comments about the ideal gas approximation.

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