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# Vapor Pressure Data of Soybean Oil, Castor Oil, and Their Fatty Acid Ethyl Ester Derivatives

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This work reports new vapor pressure data of soybean oil, castor oil, and their fatty acid ethyl ester mixtures (FAEE) obtained from an enzyme-catalyzed reaction. Vapor pressure measurements were carried out in a temperature range of (290 to 355 K) using a static method having a differential pressure transducer with a precision of 5 Pa. Degassing was performed inside the equilibrium cell by freezing and thawing the samples under moderate vacuum (about 50 kPa). For vegetable oils, vapor pressure values varied in the range of (0.19 to 2.16) kPa, whereas for FAEE mixtures a maximum value of 4.85 kPa was found. Experimental vapor pressure data were correlated by the Antoine equation with good agreement between experiment and the model.

## Introduction

In recent decades, there has been growing interest in the transformation of vegetable oils and fats into high-grade, high-value-added products with potential use in the pharmaceutical, food, and chemical industries. Enzyme-catalyzed reactions between a vegetable oil and ethanol (transesterification) produce a mixture of fatty acid ethyl esters (FAEE) known as biodiesel, a much less polluting fuel obtained from a renewable resource. Modeling and simulation of the reaction course, especially those conducted in a near-critical or supercritical solvent, require a knowledge of physicochemical properties such as the vapor pressure of substrates and products present in the reaction medium. For example, vapor pressure data are needed for the estimation of pure-component parameters of the SAFT equation of state.[1,2] These data can also be used to provide important information on other thermodynamic properties such as the heat of vaporization by means of the Clausius−Clapeyron equation. For vegetable oils and their FAEE derivatives, experimental information on these thermodynamic properties is very scarce in the literature. Vapor pressures for these compounds are usually very low, and thus measurements must be performed using an accurate technique. As pointed out by Abdi and Meisen[3] and by Lemmon and Goodwin,[4] numerous techniques for determining the vapor pressure can be found in the literature. However, not all methods provide precise and accurate data. Some methods provide useful data for a particular temperature range, whereas other methods fail in the same operating interval. The United States Environmental Protection Agency[5] provides a comprehensive review of the experimental techniques for vapor pressure measurements including recommendations for the temperature and pressure operation ranges for each method.

Vapor pressure data of some pure triglycerides, mixed triglycerides, and natural fats have been reported in the literature by Perry et al.[6] Measurements were accomplished indirectly using a pendulum tensimeter according to the Hickman and Weyerts technique[7] in the temperature range from (373 to 674) K. In all cases investigated by the authors, the original oil was first distilled into equal fractions, the two middle fractions having been molecularly distilled, a 25% strip cut was removed, and then the succeeding 50% was collected for examination in the tensimeter. A serious limitation of this procedure relies on the fact that only the heavy fraction of natural fats is analyzed and thus the obtained data does not correspond to those of the real product. Additionally, Perry et al.[6] reported an abnormal behavior when castor oil was used, where poor data reproducibility was observed. This fact shows clearly the necessity of a more conclusive investigation of the vapor pressure of these substances using a reliable experimental technique. In this sense, the aim of this work is to provide new vapor pressure data for commercial refined soybean oil, pharmaceutical castor oil, and their respective FAEE products obtained from an enzyme-catalyzed reaction using the static method.

## Experimental Section

***Materials.*** In this work, commercial refined soybean oil and pharmaceutical castor oil (Importadora Química Delaware LTDA, Brazil) were used as purchased without any pretreatment. The chemical composition of castor oil was determined using a gas chromatograph (HP 5890) with a flame ionization detector using a modified poly(ethylene glycol) column (FFAP2 − 25 m × 0.20 mm i.d. × 0.30 $\mu$m film), a split ratio of 1:50, and an injection volume of 0.2 $\mu$L. The column temperature was programmed from (453 to 483) K at 2 K·min$^{-1}$. Hydrogen was the carrier gas, and the injection and detector temperatures were 523 K and 553 K, respectively. For soybean oil, a gas chromatograph (Agilent 6850 series GC system) was employed using a capillary column (DB-23 Agilent, 50% cyanopropyl-methylpolysiloxane, 60 m × 0.25 mm i.d. × 0.25 $\mu$m film), a split ratio of 1:50, and an injection volume of 1.0 $\mu$L. The column temperature was programmed from 448 K (held for 5 min)

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**Table 1. Chemical Composition of Vegetable Oils Used in This Work**

| triglyceride | composition/wt %<br>soybean oil | <br>castor oil |
|---|---|---|
| triestearin | 3.48 ± 0.03 | 0.9 ± 0.2 |
| tripalmitin | 11.30 ± 0.01 | 1.4 ± 0.2 |
| triolein | 23.63 ± 0.11 | 3.5 ± 0.2 |
| trilinolein | 54.71 ± 0.07 | 4.9 ± 0.2 |
| trilinolenin | 6.88 ± 0.01 | 0.3 ± 0.1 |
| triricinolein |  | 88.9 ± 1.4 |

to 488 K (held for 37 min) at 5 K·min$^{-1}$. Helium was the carrier gas, and the injection and detector temperatures were 523 K and 553 K, respectively. The chemical composition of the oils is presented in Table 1.

The FAEE derivatives were obtained by an enzyme-catalyzed reaction in the presence of ethanol according to the experimental procedure reported by Oliveira and Oliveira[8] and Oliveira et al.[9] The enzyme-catalyzed reactions were performed in *n*-hexane as the solvent medium using immobilized lipases. This procedure allows the production of high-grade FAEE because the catalyst can be easily recuperated. There is no alteration in the acid number compared to that of the original oil. Metallic residues (compared to the alkaline-catalyzed reaction) and soaps are not produced during the reaction, which in turn facilitates the separation of FAEE after achieving complete reaction conversion. This quality of FAEE is, of course, requested for reliable vapor pressure measurements using the static method. The complete conversion of the enzyme-catalyzed reaction was confirmed by chromatographic analysis.

Fatty acid ethyl ester samples from castor oil were analyzed through a GC/MSD (Shimadzu QP5050A) using a PE-5 capillary column (20 m × 0.18 mm i.d. × 0.25 $\mu$m film), split mode (split ratio 1:20), and an injection volume of 0.5 $\mu$L. The column temperature was programmed from 333 K (held for 3 min) to 573 K at 3 K·min$^{-1}$ and from this temperature to 673 K at 5 K·min$^{-1}$. Helium was the carrier gas, and the injection and detector temperatures were 553 K and 593 K, respectively. The identification and quantification of the compounds were accomplished through the injection of ethyl ricinoleate (Sigma, 25 mg·mL$^{-1}$) as an internal standard. For the case of FAEE from soybean oil, the same equipment and experimental conditions were employed, but using a capillary column DB-5 (30 m × 0.25 mm i.d. × 0.25 $\mu$m film). The identification and quantification of the compounds were accomplished through the injection of authentic standards (Sigma) and squalene (Sigma) as an internal standard by comparing the mass spectra and GC retention time. All analyses were replicated at least three times.

***Apparatus and Experimental Procedure.*** The equipment used to obtain the vapor pressure of the compounds investigated in this work is shown schematically in Figure 1 and is very similar to that used by Oliveira and Uller[10,11] and by Dariva et al.[12] The equilibrium cell is made of Pyrex glass and has a conical shape having a total capacity of approximately 30 mL. The differential pressure transducer is an LD301 Smar model calibrated in the operation range of (0.125 to 5) kPa and has a precision of 5 Pa. Lines connected to the two sockets of the pressure transducer are separated by a Nupro bellow valve. A high-performance vacuum pump (Edwards model C56) was used to sample degassing and gas removed from the equilibrium system. The vacuum pump is connected to the process lines by a Swagelok quick connection. All process lines are $^1/_4$ in. o.d. stainless steel tubing.

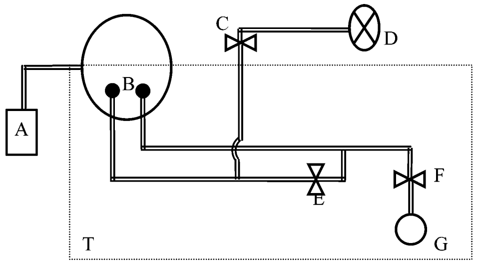

**Figure 1.** Schematic diagram of the experimental apparatus: A, portable programmer for pressure data acquisition; B, differential pressure transducer; C, Swagelok quick connection; D, vacuum pump; E, bellow valve; F, ball valve; G, equilibrium cell; T, water bath.

**Table 2. Comparison of Measured and Literature Vapor Pressure Data of Water**

| $T \pm 0.1$/K | $p$/kPa<br>this work | <br>literature[13] |
|---|---|---|
| 283.1 | 1.252 | 1.228 |
| 288.4 | 1.738 | 1.738 |
| 293.6 | 2.391 | 2.411 |
| 298.1 | 3.187 | 3.167 |
| 303.6 | 4.331 | 4.366 |

In the static method used in this work, the equilibrium vapor pressures at defined temperatures are determined using a diaphragm capacitance manometer. At thermodynamic equilibrium, the vapor pressure established in a closed system is determined at a specified temperature. This method is suitable for one-component as well as for multicomponent solid or liquid systems. According to the United States Environmental Protection Agency, the recommended range for the static technique is from 10 up to $10^5$ Pa in pressure and from 273 K up to 373 K in temperature.

Before each measurement, all parts of the apparatus were thoroughly evacuated. After being filled with around 10 mL of the desired substance, the equilibrium cell was connected to the Whitey ball valve (a constant-volume valve) using a Cajon Ultra-Torr glass−metal connection. Degassing was performed by freezing the cell content with liquid nitrogen and melting it at room temperature under moderate vacuum (about 50 kPa). This procedure was repeated (at least 10 times) until no gas bubbles were observed during the melting step. Because the substances used in this work are in fact mixtures, the degassing process must be carried out carefully to avoid sample fractionation. After degassing was completed, the content inside the cell was weighed, and no significant mass losses (in all cases lower than 0.005 g) compared to the mass of the original sample were found. After that, the cell was reconnected to the apparatus, and the process lines were evacuated with the bellow valve opened. To minimize the thermal transpiration effect, which means a significant pressure difference between the two ends of a pipe due to a large temperature difference, all of the process lines, including the equilibrium cell and sockets of the differential pressure transducer, were submersed in a water bath (manufactured by Menoncim, Brazil, with an approximate volume of 100 L) (as shown in Figure 1). The temperature was monitored continuously by two PT100 thermo sensors, one placed beside the equilibrium cell and the other one placed near the pressure transducer chamber. With this arrangement, the temperature precision was better than 0.1 K. Once the bath temperature was stabilized, measurements were performed by opening the ball valve of the equilibrium cell. The pressure change observed in the

**Table 3. Experimental Vapor Pressure Data for Soybean Oil, Castor Oil, and Their FAEE Derivatives**

| soybean oil | | | castor oil | | | FAEE from soybean oil | | | FAEE from castor oil | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $p$/kPa | | | $p$/kPa | | | $p$/kPa | | | $p$/kPa | |
| $T$/K | measured | $\sigma$ | $T$/K | measured | $\sigma$ | $T$/K | measured | $\sigma$ | $T$/K | measured | $\sigma$ |
| 294.1 | 0.354 | 0.019 | 299.1 | 0.192 | 0.023 | 290.4 | 0.437 | 0.035 | 290.7 | 0.259 | 0.006 |
| 299.5 | 0.453 | 0.015 | 304.2 | 0.258 | 0.009 | 294.6 | 0.549 | 0.018 | 293.7 | 0.323 | 0.017 |
| 304.0 | 0.543 | 0.043 | 308.9 | 0.328 | 0.003 | 299.5 | 0.718 | 0.014 | 298.0 | 0.427 | 0.053 |
| 309.3 | 0.661 | 0.075 | 313.6 | 0.416 | 0.021 | 304.7 | 0.916 | 0.033 | 303.8 | 0.577 | 0.084 |
| 313.8 | 0.753 | 0.083 | 319.1 | 0.529 | 0.032 | 309.0 | 1.144 | 0.077 | 308.9 | 0.753 | 0.126 |
| 318.8 | 0.892 | 0.114 | 323.5 | 0.647 | 0.049 | 314.5 | 1.447 | 0.086 | 313.7 | 0.951 | 0.167 |
| 323.5 | 1.033 | 0.140 | 329.2 | 0.806 | 0.048 | 319.5 | 1.781 | 0.086 | 318.5 | 1.198 | 0.214 |
| 328.7 | 1.195 | 0.151 | 334.0 | 0.979 | 0.053 | 324.3 | 2.196 | 0.104 | 323.4 | 1.505 | 0.267 |
| 333.9 | 1.364 | 0.146 | 339.2 | 1.182 | 0.031 | 328.9 | 2.652 | 0.091 | 328.0 | 1.857 | 0.315 |
| 338.7 | 1.513 | 0.111 | 344.2 | 1.402 | 0.020 | 334.4 | 3.228 | 0.025 | 333.2 | 2.301 | 0.337 |
| 344.0 | 1.717 | 0.073 | 348.2 | 1.648 | 0.031 | 338.9 | 3.958 | 0.014 | 338.6 | 2.806 | 0.273 |
| 348.9 | 1.962 | 0.063 | 354.0 | 1.950 | 0.185 | 344.3 | 4.658 | 0.165 | 343.5 | 3.415 | 0.224 |
| 353.2 | 2.155 | 0.006 | | | | | | | 348.5 | 4.000 | 0.044 |
| | | | | | | | | | 354.6 | 4.848 | 0.540 |

**Table 4. Constants for the Antoine Equation**

| substance | $A$ | $B$ | $C$ | $R^a$ |
|---|---|---|---|---|
| soybean oil | 11.4785 | −708.72 | −167.48 | 0.999 |
| castor oil | 14.1201 | −1377.17 | −143.56 | 0.999 |
| FAEE from soybean oil | 17.5872 | −2390.66 | −82.58 | 0.999 |
| FAEE from castor oil | 15.5076 | −1523.20 | −137.32 | 0.999 |

[a] Correlation coefficient.

portable programmer represents the vapor pressure of the substance contained in the equilibrium cell. Measurements were started at the minimum temperature, and after the procedure at one temperature was completed, the bath temperature was increased to the new desired value keeping valve C closed and valve F open. Triplicate runs were accomplished for all reported temperatures leading to good reproducibility of the vapor pressure measurements.

## Results and Discussion

To check the accuracy of the experimental procedure, vapor pressure measurements of deionized water were performed, and the results were compared with those obtained from the literature,[13] as shown in Table 2. Owing to the limited operation range of the pressure transducer (up to 5 kPa), only measurements at temperatures lower than 305 K were accomplished for the case of water.

Table 3 presents the experimental vapor pressure data and the related experimental standard deviation ($\sigma$) for soybean oil, castor oil, FAEE from soybean oil, and FAEE from castor oil. For vegetable oils, relatively low values but higher than those reported by Perry et al.[6] were observed. This trend may be explained by different experimental techniques and, more importantly, by the purification procedure used by Perry et al.,[6] where only the heavy fraction of oil was analyzed.

In addition to vapor pressure experimental data, the Antoine equation was employed to correlate the measured values

$$\ln(p/\mathrm{Pa}) = A + \frac{B}{C + (T/\mathrm{K})} \tag{1}$$

where $p$ is the saturation pressure at temperature $T$ and $A$, $B$, and $C$ are adjustable parameters (values given in Table 4). In this Table, we also report the correlation coefficient $R$ obtained by fitting eq 1 to the experimental data through the minimization of the following objective function OF

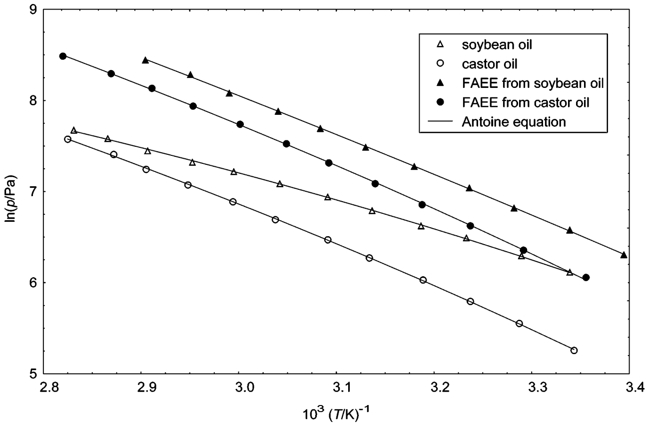

**Figure 2.** Vapor pressure vs temperature diagram for soybean oil, castor oil, and their FAEE derivatives.

$$\mathrm{OF} = \sum_i [\ln(p^{\mathrm{exptl}}/\mathrm{Pa}) - \ln(p^{\mathrm{calcd}}/\mathrm{Pa})]_i^2 \tag{2}$$

where subscripts exptl and calcd denote, respectively, experimental and calculated values.

Figure 2 shows the behavior of vapor pressure versus temperature for all substances used in this work. Points are experimental values, and solid lines represent correlation results from eq 1. One can see from this Figure that a good smooth representation of the measured values is possible with eq 1. The experimental data corroborate the fact that FAEE vapor pressures are higher than the values observed for the corresponding oils. The values observed for castor oil and its FAEE mixture are, respectively, lower than those verified for soybean oil and its FAEE mixture, which is due probably to the hydroxyl group in triricinolein and ethyl ricinoleate.

## Conclusions

New vapor pressure data for vegetable oils and their fatty acid ethyl ester derivatives were presented in this report. Measurements were carried out using an accurate experimental procedure that led to good reproducibility of the experimental data. All data reported here were correlated using the Antoine equation. It is believed that the vapor pressure data reported here can be useful for the design and operation of industrial processes containing soybean oil, castor oil, and their fatty acid ethyl esters.

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