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Vapor–liquid equilibrium of fatty acid ethyl esters determined using DSC

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ABSTRACT

The vapor–liquid equilibrium data for the systems: ethyl palmitate + ethyl stearate at 5332.9 Pa, ethyl palmitate + ethyl oleate at 5332.9 Pa and 9332.6 Pa and ethyl palmitate + ethyl linoleate at 9332.6 Pa were determined by differential scanning calorimetry (DSC). The esters used in this study are the major components of biodiesel obtained from the transesterification of soybean oil with ethanol. According to the results, DSC is appropriate for determining the vapor–liquid equilibrium of binary systems. The binary interaction parameters of the models Wilson, NRTL and UNIQUAC were fitted to the experimental data obtained in this study.

1. Introduction

Biodiesel is a biodegradable, renewable fuel showing properties similar to those of petrodiesel, but with lower greenhouse gas emissions. It consists of the alkyl esters of fatty acids, obtained by the transesterification of fats and oils with a short chain alcohol such as methanol or ethanol.

The use of ethanol in the production of biodiesel is still restricted, due to problems in the glycerol separation step. In countries like Brazil, where ethanol is widely produced, this alcohol has great potential for use as one of the raw materials in the production of biodiesel.

The thermophysical properties and phase equilibrium data involving the fatty esters are very important in the design, modeling, simulation and optimization of the production of biodiesel. Due to the scarcity of vapor–liquid equilibrium data for the ethyl esters and their importance to the biodiesel industry, the aim of the present study was to determine the vapor–liquid equilibrium data of the following systems: ethyl palmitate + ethyl stearate at 5332.9 Pa, ethyl palmitate + ethyl oleate at 5332.9 Pa and 9332.6 Pa and ethyl palmitate + ethyl linoleate at 9332.6 Pa, using differential scanning calorimetry (DSC).

DSC using the "boiling point" method [1] has been successfully employed to determine the vapor pressure of pure organic compounds [2–4], but is still little used for the determination of the vapor–liquid equilibrium data. Matricarde Falleiro et al. [5] successfully determined the vapor–liquid equilibrium data of fatty acid binary mixtures using DSC.

The operating conditions used in this study were established in a former study by the same investigators and were: a sample size of 2–5 mg, heating rate of 25 °C min^{-1} and a pinhole of 0.25 mm in diameter. The data measured by DSC were used to fit the binary interaction parameters of the models Wilson, NRTL and UNIQUAC.

2. Experimental

2.1. Chemicals

Ethyl palmitate (CAS no 628-97-7), ethyl stearate (CAS no 111-61-5) and ethyl linoleate (CAS no 544-35-4) with a purity of 99% molar, and ethyl oleate (CAS no 111-62-6) with a purity of 98% molar, were purchased from Sigma–Aldrich from the USA. Methyl myristate (CAS no 124-10-7) and methyl palmitate (CAS no 112-39-0) were obtained from Nu-Check Prep. Inc. (USA), with a purity of 99% molar. The chemicals were used without further purification.

2.2. Equipment

A model 2920 heat flux DSC from TA Instruments (1), equipped with a pressure cell (2) was used in the vapor–liquid equilibrium measurements. The system was evacuated using a high vacuum pump (Edwards – E2M5) (3) and the pressure was adjusted using a

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Nomenclature

P	pressure in mmHg
T	temperature in °C
FO	objective function

Subscripts

exp	experimental
calc	calculated
i	component
n	experimental data

needle valve (4). The absolute pressure inside the cell was measured with a U-shaped mercury manometer (5) with precision of ±0.5 mmHg, and the ballast tank (6) was used to stabilize the pressure system. Fig. 1 presents a scheme of the experimental apparatus.

2.3. Calibration

The calorimeter was calibrated using standards of indium (melting point = 156.6 °C) and zinc (melting point = 419.5 °C). The calibration was carried out at atmospheric pressure, since the pressure has little effect on the melting point [4,6].

2.4. Sample preparation

Samples of ethyl ester binary mixtures were prepared covering the entire range of composition from 0 to 100% of ethyl palmitate. A suitable mass of each ester, calculated to obtain the desired mole fraction, was weighed on an analytical balance (Tecnal) with a precision of ±0.0001 g, and the esters then melted in a heating mantle to ensure the homogeneity of the mixture. The samples were maintained refrigerated until analyzed in the DSC. The samples presented an accuracy of 0.02% in the molar fraction.

2.5. Experimental

A mass of 2–5 mg of sample was weighed using a microanalytical balance (Perkin Elmer, AD6) with a precision of ±0.01 mg and placed in a hermetic aluminum pan (TA Instruments).

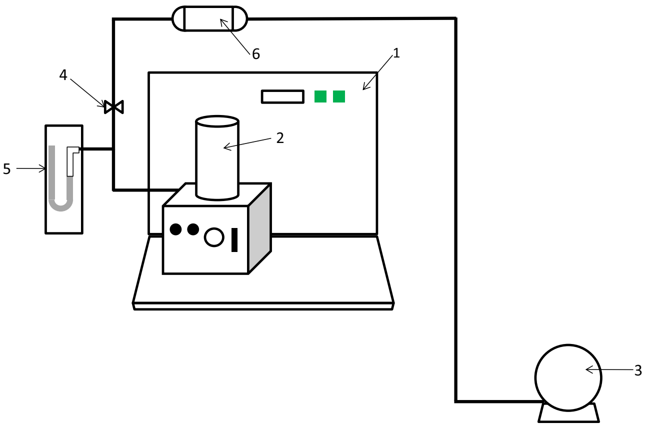

Fig. 1. Scheme of the experimental apparatus.

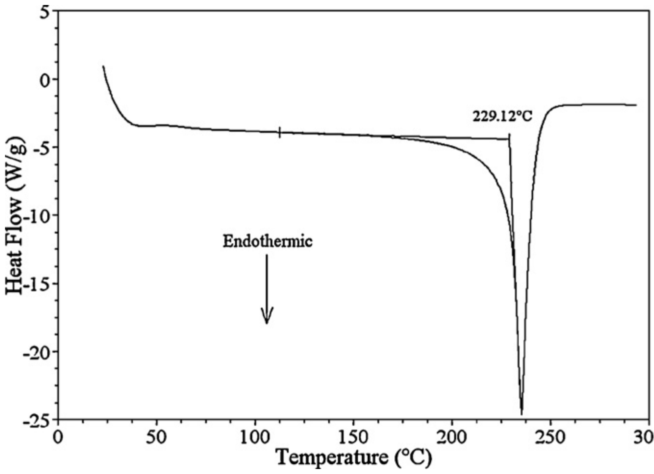

Fig. 2. Thermogram of pure ethyl palmitate at 5332.9 Pa. Onset temperature = 229.12 °C.

A common problem in determining the boiling points by DSC is the pre vaporization of the substance before the condition of isothermal boiling is reached [2,3,7,8]. This problem can be overcome using a pan lid with a small hole ("pinhole") that allows the sample to assume the same pressure as the equipment without any substantial loss of liquid before boiling. In the present work, a pinhole with a diameter of 0.25 mm was used.

The system was evacuated to the desired pressure, and once the pressure had stabilized, heating of the sample was begun from room temperature up to the point of complete boiling, at a rate of 25 °C min^{-1}.

3. Results and discussion

The boiling temperature of the binary mixture was determined from the extrapolated onset temperature. The extrapolated onset temperature was defined from the intersection of the tangents to the endothermic curve, as can be seen in Fig. 2. The deviation in temperature was 0.37 °C.

The performance of DSC in determining the vapor–liquid equilibrium data of binary mixtures of fatty esters was evaluated by comparing the equilibrium data of the system methyl myristate (1) + methyl palmitate at 3999.67 Pa obtained in the present study with that determined by Rose and Supina [9] using ebulliometry, as shown in Fig. 3. Table 1 shows the comparison between the data determined by Rose and Supina [9] and the temperature obtained by cubic spline interpolation of the data determined in the present

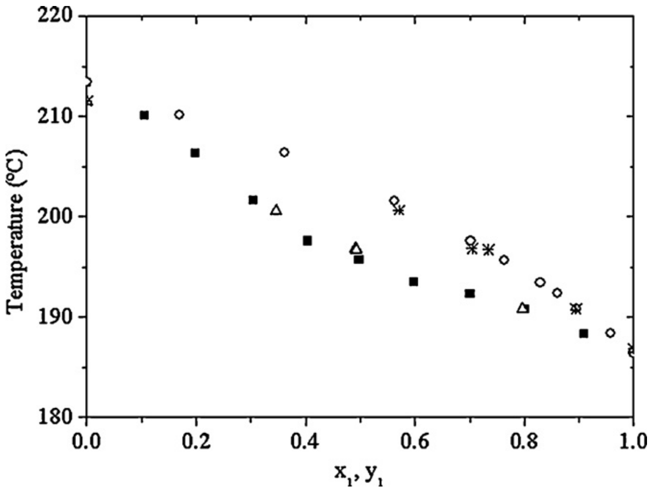

Fig. 3. Vapor–liquid equilibrium of the system methyl myristate (1) + methyl palmitate (2) at 3999.7 Pa. ■, liquid phase (present study); △, liquid phase (Rose and Supina [9]); ○, vapor phase (present study); *, vapor phase (Rose and Supina [9]).

Table 1
Vapor–liquid equilibrium data of the system methyl myristate (1) + methyl palmitate (2) at 3999.7 Pa.

x_1	T (°C) Rose and Supina [9]	T (°C) the present study	Absolute deviation
0	211.5	213.42	1.92
0.346	200.6	199.69	0.91
0.492	196.8	195.82	0.98
0.496	196.7	195.74	0.96
0.797	190.8	190.91	0.11
1	186.8	186.47	0.35

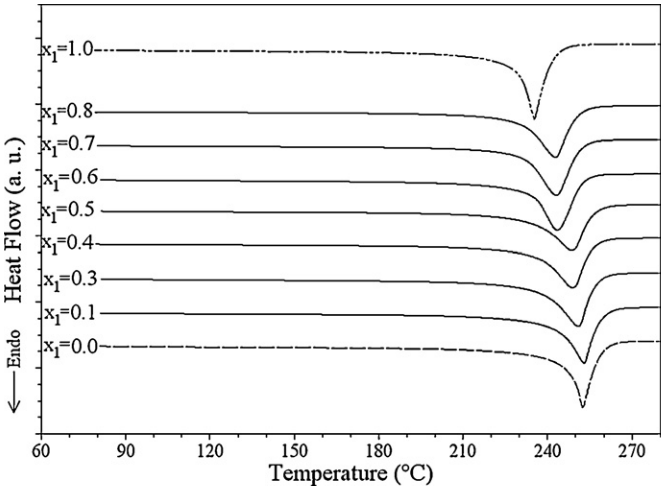

Fig. 4. Endothermic boiling curves of the system ethyl palmitate (1) + ethyl stearate (2) at 5332.9 Pa.

study. According to Table 1 there was good agreement between the data obtained by DSC and that found in the literature, showing that DSC is a suitable technique for the determination of vapor–liquid equilibrium data.

Figs. 4–7 show the endothermic curves obtained in the determination of the vapor–liquid equilibrium of the systems: ethyl palmitate + ethyl stearate at 5332.9 Pa, ethyl palmitate + ethyl oleate at 5332.9 Pa and 9332.6 Pa and ethyl palmitate + ethyl linoleate at 9332.6 Pa. Tables 2–5 show the P–T–x vapor–liquid equilibrium data determined by DSC. The mole fraction of the vapor phase, y, was calculated using the coexistence equation [10].

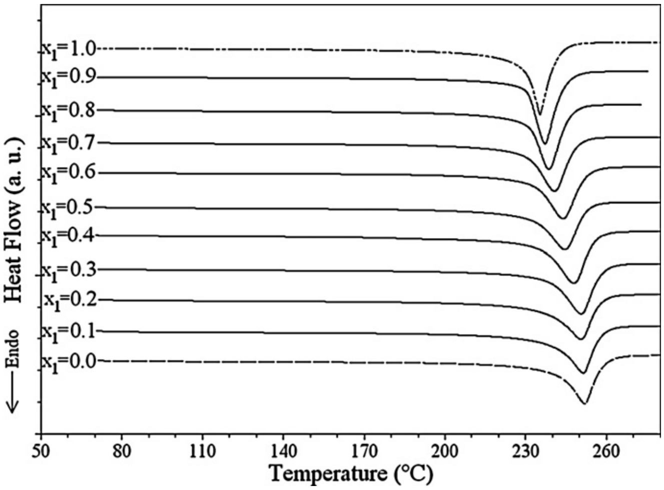

Fig. 5. Endothermic boiling curves of the system ethyl palmitate (1) + ethyl oleate (2) at 5332.9 Pa.

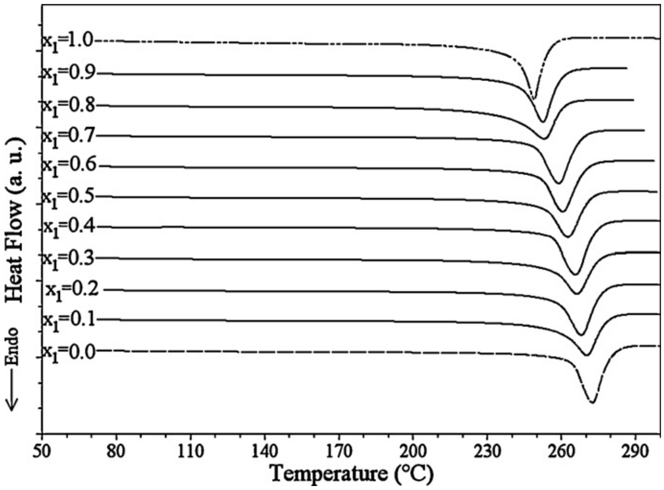

Fig. 6. Endothermic boiling curves of the system ethyl palmitate (1) + ethyl oleate (2) at 9332.6 Pa.

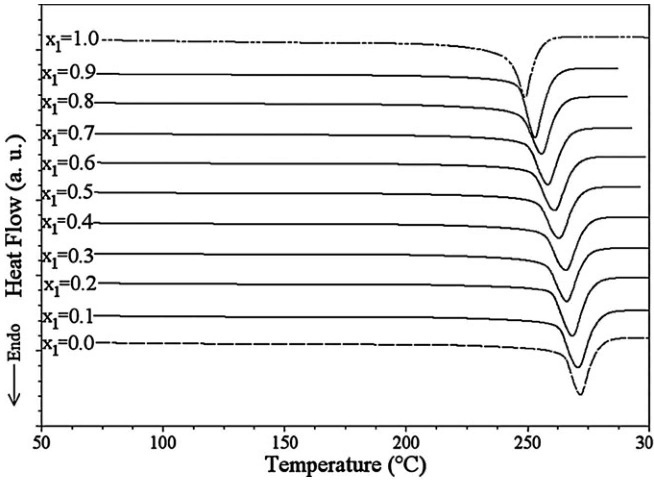

Fig. 7. Endothermic boiling curves of the system ethyl palmitate (1) + ethyl linoleate (2) at 9332.6 Pa.

From the experimental data, the binary interaction parameters of the G^E models, Wilson, NRTL and UNIQUAC [11] were determined by minimizing the following objective function:

$$\mathrm{FO} = \sum_{n}\sum_{i}\left(\frac{\gamma_{\mathrm{exp}} - \gamma_{\mathrm{calc}}}{\gamma_{\mathrm{exp}}}\right)_{i,n} \tag{1}$$

The minimization method used was the simplex method as modified by Nelder and Mead [12].

Table 6 shows the binary interaction parameters for each model and the standard deviation of the temperature.

Table 2
Vapor–liquid equilibrium data of the system ethyl palmitate (1) + ethyl stearate (2) at 5332.9 Pa.

x_1	y_1	T (°C)
0	0	247.41
0.1017	0.2084	244.61
0.3012	0.5198	239.61
0.4004	0.6215	237.72
0.5003	0.6901	236.39
0.5998	0.7485	235.15
0.7001	0.8179	233.60
0.8010	0.8869	231.99
1	1	229.12

Table 3
Vapor–liquid equilibrium data of the system ethyl palmitate (1) + ethyl oleate (2) at 5332.9 Pa.

x_1	y_1	T (°C)
0	0	241.46
0.1017	0.1782	239.63
0.1990	0.2503	238.82
0.3002	0.3866	237.34
0.4021	0.5425	235.49
0.5051	0.6608	233.93
0.5950	0.7294	233.05
0.7007	0.7911	232.24
0.7979	0.8540	231.32
0.9024	0.9384	230.08
1	1	229.12

Table 4
Vapor–liquid equilibrium data of the system ethyl palmitate (1) + ethyl oleate (2) at 9332.6 Pa.

x_1	y_1	T (°C)
0	0	263.68
0.1017	0.1684	260.94
0.1990	0.3067	258.49
0.3002	0.4264	256.18
0.3985	0.5257	254.09
0.5051	0.6265	251.84
0.5950	0.7134	249.85
0.7007	0.8154	247.39
0.7979	0.8945	245.23
0.9024	0.9582	243.30
1	1	241.98

Table 5
Vapor–liquid equilibrium data of the system ethyl palmitate (1) + ethyl linoleate (2) at 9332.6 Pa.

x_1	y_1	T (°C)
0	0	264.54
0.0974	0.1291	262.21
0.1935	0.3097	259.25
0.2965	0.4377	256.72
0.3984	0.5325	254.58
0.4977	0.6300	252.33
0.6105	0.7509	249.47
0.7042	0.8394	247.10
0.7958	0.9051	245.10
0.8992	0.9586	243.36
1	1	241.98

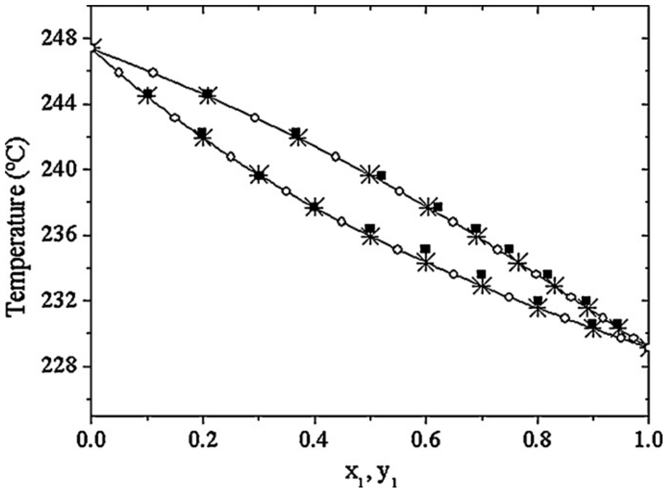

Fig. 8. Vapor–liquid equilibrium of the system ethyl palmitate (1) + ethyl stearate (2) at 5332.9 Pa. ■, present study; —, Wilson; *, NRTL; ○, UNIQUAC.

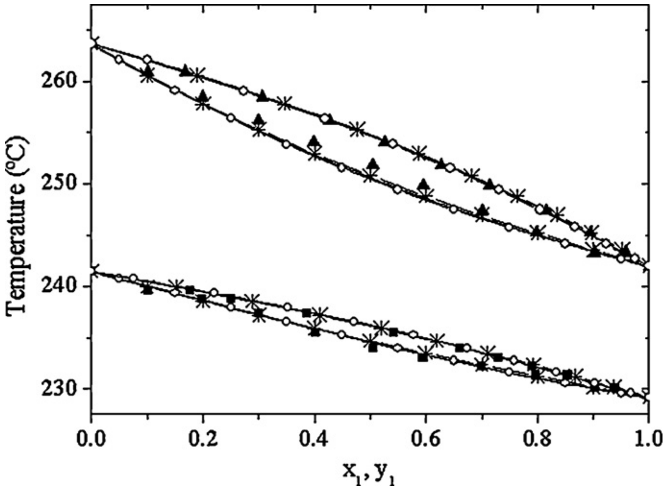

Fig. 9. Vapor–liquid equilibrium of the system ethyl palmitate (1) + ethyl oleate (2) at 5332.9 Pa and 9332.6 Pa. ■, present study; —, Wilson; *, NRTL; ○, UNIQUAC.

Figs. 8–10 and the values for the standard deviation of the temperature presented in Table 6, show that the models Wilson, NRTL and UNIQUAC represent the vapor–liquid equilibrium of the systems studied equally well. Table 7 shows the parameters r, q, and q'

Table 6
Binary interaction parameters of the models Wilson, NRTL and UNIQUAC.

Ethyl palmitate (1) + ethyl stearate (2) at 5332.9 Pa

Model	A_{12} (cal mol^{-1})	A_{21} (cal mol^{-1})	α	Standard deviation of T
Wilson	−260.0597	530.9586	–	0.47
NRTL	595.6012	−303.8005	0.3055	0.48
UNIQUAC	162.1036	−130.8214	–	0.48

Ethyl palmitate (1) + ethyl oleate (2) at 5332.9 Pa and 9332.6 Pa

Model	A_{12} (cal mol^{-1})	A_{21} (cal mol^{-1})	α	Standard deviation of T (5332.9 Pa)	Standard deviation of T (9332.6 Pa)
Wilson	−616.3624	1029.6194	–	0.33	0.93
NRTL	32.4059	−20.998	0.3046	0.35	0.82
UNIQUAC	456.6957	−370.3745	–	0.33	1.05

Ethyl palmitate (1) + ethyl linoleate (2) at 9332.6 Pa

Model	A_{12} (cal mol^{-1})	A_{21} (cal mol^{-1})	α	Standard deviation of T
Wilson	−329.7993	318.9022	–	0.42
NRTL	372.4063	−405.5694	0.3145	0.40
UNIQUAC	90.1500	−92.9405	–	0.39

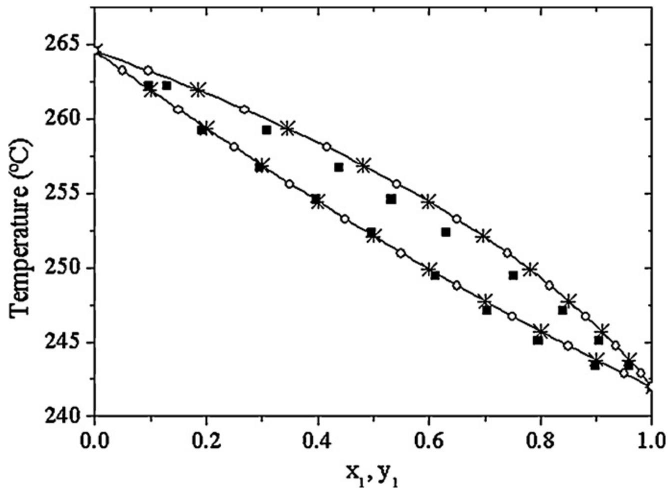

Fig. 10. Vapor–liquid equilibrium of the system ethyl palmitate (1) + ethyl linoleate (2) at 9332.6 Pa. ■, present study; —, Wilson; *, NRTL; ○, UNIQUAC.

Table 7
Parameters *r*, *q*, and *q*′ of UNIQUAC model.

Ester	*r*	*q*	*q*′
Ethyl palmitate	12.92020	10.67600	10.67600
Ethyl stearate	14.26900	11.75600	11.75600
Ethyl oleate	14.03690	11.54300	11.54300
Ethyl linoleate	13.80480	11.33000	11.33000

Table 8
Molar volume of ethyl esters.

Ester	Molar volume ($cm^3 mol^{-1}$)
Ethyl palmitate	331.95
Ethyl stearate	295.68
Ethyl oleate	356.92
Ethyl linoleate	352.17

of UNIQUAC model. The values of molar volume used in the Wilson model are presented in Table 8.

4. Conclusions

The vapor–liquid equilibrium data involving fatty esters of great importance to the biodiesel industry were determined by differential scanning calorimetry. The technique was shown to be feasible for the determination of the vapor–liquid equilibrium data of binary mixtures containing fatty esters, and in addition presented the advantages of using a small sample size and being a speedy analytical method.

The binary interaction parameters of the G^E models, Wilson, NRTL and UNIQUAC were determined, and it was shown that these three models were suitable to represent the vapor–liquid equilibrium of the systems studied.

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