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Vapour liquid equilibria of monocaprylin plus palmitic acid or methyl stearate at P = (1.20 and 2.50) kPa by using DSC technique

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ABSTRACT

The Differential Scanning Calorimetry (DSC) technique is used for measuring isobaric (vapour + liquid) equilibria for two binary mixtures: {monocaprylin + palmitic acid (system 1) or methyl stearate (system 2)} at two different pressures P = (1.20 and 2.50) kPa. The obtained PTx data are correlated by Wilson, NRTL and UNIQUAC models. The original UNIFAC group contribution method is also considered and new binary interaction parameters for the main groups CH$_2$, CCOO, OH and COOH are regressed, to account for the non-idealities found in these lipid systems. Established thermodynamic consistency tests are applied and attest the quality of the measured data. In terms of relevance of the selected components, system 1 can be found in the purification and deodorization steps during the production of edible oils, while, system 2 can be found in the purification steps of biodiesel. It should be noted that no such data could be found in the open literature, not only for the specific components selected but also for the combination of the classes of components considered; that is, acylglycerol plus fatty acid or fatty ester.

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1. Introduction

From 1990 to 2008, the average energy use per person increased by 10%, and the world population increased by 27%, with fossil fuels supplying 86% of the world's energy consumption [1]. In this context, biodiesel has emerged as an important alternative to replace fossil fuels, due to its renewability, non-toxicity and biodegradability. Also in the scenario of lipid technology, the growth in the production of vegetable oils [2] challenges the lipid processing industry to (re)design and to develop better-quality processes.

Modelling, simulation and design of unit operations involved in the production of edible oils/fats and biodiesel, require knowledge of phase equilibria in (vapour + liquid) (VLE), (liquid + liquid) (LLE) as well as (solid + liquid) (SLE). Refining of oils/fats involves a crucial stripping step named steam deacidification/deodorization during which undesirable components, such as free fatty acids and odors (aldehydes, hydrocarbons and ketones) are removed on the basis of the differences in their volatilities in relation to

triacylglycerols. In conjunction with this targeted removal, there is also an undesirable loss of neutral oil (triacylglycerols, and partial acylglycerols, as mono- and diacylglycerols) due to volatilisation [3,4]. In the purification steps of biodiesel and bioglycerin, partial acylglycerols formed in the transesterification reaction are removed from a mixture of fatty esters or glycerol. Knowledge of the (vapour + liquid) equilibria involved in these steps is therefore fundamental for understanding the behaviour of these chemicals under the processing conditions [5]. Our previous works [6–8] indicated a lack of experimental data of thermophysical properties of pure fatty components and their mixtures. VLE data involving monoacylglycerols or diacylglycerols are not available in the open literature [6]. In fact, before the work of Damaceno et al. [5] in which vapour pressure data were measured as a function of temperature, P = (1.10 to 13.20) kPa, for four short-chain partial acylglycerols by using DSC technique, the available data were restricted to only six values of boiling points for six different monoacylglycerols at 0.13 kPa. It seems that the major bottleneck that has led to this scenario is the very high costs of high purity components involved in lipid technology.

Recently, Matricarde Falleiro et al. [9,10], Akisawa Silva et al. [11] and Damaceno et al. [5] measured vapour pressures/boiling temperatures of pure fatty components and binary fatty systems

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using the DSC technique. The use of DSC technique for measuring thermophysical properties of fatty systems is increasing due to certain advantages in comparison with ebulliometry, namely, it is cost-effective because it uses very small amounts of samples (4 to 5) mg, it provides the results in a shorter operation time, avoiding thereby, thermal degradation of components prior to the vaporisation process, and it does not require chemical analysis for obtaining the composition of the phases in equilibrium (vapour and liquid phases, in the case of PTxy data).

DSC technique is a promising alternative method for measuring VLE and vapour pressure data [5,9–12] and together with the static cell and the infinite-dilution ebulliometry, provide valuable PTx data [13]. As pointed out by Sandler [13], these data can be used in the regression of binary parameters of activity coefficient models from excess Gibbs energy. These parameters can then be used in the calculation of the absent vapour phase composition and the complete PTxy diagram can be depicted. The recent literature [9,11,14–27] reports some PTx data for a variety of lipid technology components, such as fatty esters [11,14–17], biodiesel [18–22], glycerol [16,23–25], fatty acids [9], vegetable oils [26] and short-chain triacylglycerols [27].

Recent papers have been published in the literature [6–8,26] pointing out that there is a gap of experimental data on thermophysical properties involving pure components and mixtures related to lipid technology. Computer-aided tools are at hand for oil/fat/biodiesel industry for developing process design, simulation and optimisation. But, the reliability of their predictive capacity depends on the quality of their built-in models and methods. In this scenario, the release of novel phase equilibrium data in the open literature involving fatty systems becomes relevant. In particular, lipid technology involves a great variety of components with similar molecular structures, and its fatty mixtures are essentially multicomponent [27]. So, group contribution methods are very suitable for estimating the behaviour of these mixtures under different processing conditions. In order to check the effect of group binary interaction parameters of group contribution methods, such as UNIFAC, it is mandatory to have phase equilibrium data for fatty mixtures involving different sets of main groups, distributed if possible in different molecular structures. For describing the main composition of oils/fats and biodiesel with UNIFAC, in terms of tri-, di-, monoacylglycerols, fatty acids, and fatty esters, it would be necessary to consider only five main groups, i.e., CH_2, $C = C$, CCOO, OH and COOH, and the subgroups CH_3, CH_2, CH, CH = CH, CH_3COO, CH_2COO, OH, and COOH. So, for testing the predictive capacity of this method, it would be interesting, for example, to have mixtures combining these main groups and subgroups in different ways.

As a contribution to fulfil this gap, the DSC technique is used in this work for measuring boiling points of two binary fatty mixtures composed of a monoacylglycerol (monocaprylin) and a fatty acid (palmitic acid – system 1) or a fatty methyl ester (methyl stearate – system 2) at two sub-atmospheric pressures (1.20 and 2.50) kPa. Two thermodynamic consistency tests are applied to verify the quality of the measured data. The pure component consistency test ($Q_{test,5}$ of the TDE program from NIST) [28] is used to test the consistencies of the pure component end-points of the VLE data, and a variation of the Van Ness test [29] ($Q_{test,1}$ of program TDE from NIST) [28] that checks the consistency of the measured data as represented by a flexible thermodynamic trial function. The measured data are correlated by the Wilson [30], NRTL [31] and UNIQUAC [32] models. The original UNIFAC [33] model parameters are first checked for their predictive capability and then fine-tuned in terms of new regressed binary interaction parameters for the main groups found in the chemical systems studied. The performances of the original and modified UNIFAC models are also compared.

2. Experimental

2.1. Materials

Table 1 lists the reagents used in this work (CAS Registry numbers, purities in mass fraction, IUPAC names, and suppliers). All chemicals were used without any further purification steps. The samples are placed in aluminium crucibles (pans + lids) purchased from TA Instruments. Following the procedure described by Matricarde Falleiro et al. [9,10] and Damaceno et al. [5], a pinhole of diameter of 800 μm is made on each lid using a system consisting of a fixation assembly, mandrel and drills. A small tungsten carbide ball with a diameter of 1000 μm is obtained from the disassembly of a ballpoint pen, and placed over the pinhole [5].

2.2. Sample preparation

Each of the two fatty systems considered in this work are prepared by mixing known amounts (in grams) of the pure components in an analytical balance (Model AS220 – Radwag) to obtain approximately 0.2 g of the binary mixture. In total, nine binary mixtures with mole fraction (x_1) ranging from 0.1 to 0.9 of the more volatile component (monocaprylin) are produced in intervals of 0.1 mol fraction to cover the entire range of compositions in an isobaric Tx diagram. The pure component data, that is, mole fraction of the more volatile component equal to 0 ($x_1 = 0$) and equal to 1 ($x_1 = 1$) are also considered. In the case of system 1, an additional binary mixture with a mole fraction of the more volatile component equal to 0.0554 is produced, giving thereby, ten binary mixtures. Microsamples (4 to 5) mg are obtained from each binary mixture with micropipets of (5×10^{-10} to 10×10^{-10}) m³ (Model Research – Eppendorf), and then weighted in a microanalytical balance (Model C-33 – Thermo Scientific).

2.3. Apparatus

A schematic diagram of the experimental apparatus is given by Matricarde Falleiro et al. [10]. A Differential Scanning Calorimetry (DSC) Model Q20P – TA Instruments is connected to a vacuum system, which consists of a trap to pressurise the vacuum line, a ballast tank to avoid pressure oscillations, a micrometer valve to adjust the pressure, a digital pressure gauge Model Rücken RMD with 0.25% full scale accuracy, and a vacuum pump Model RV5 – Edwards [5]. N-tetradecane is used to calibrate the pressure gauge. A computer is used to run the DSC and record data from each experiment. A press (Model SN6205 – TA Instruments) is used to seal the crucibles (pans + lids) [5].

TABLE 1
Provenance and mass fraction of the materials studieds.

Compound	IUPAC name	CAS registry No.	Supplier	Purity (mass fraction)[a]
n-Tetradecane	Tetradecane	629-59-4	Sigma–Aldrich	>0.99
Monocaprylin[b]	2,3-Dihydroxypropyl octanoate	502-54-5	Nu-Chek Prep, Inc.	>0.99
Palmitic acid	Hexadecanoic acid	57-10-3	Nu-Chek Prep, Inc.	>0.99
Methyl stearate	Methyl octadecanoate	112-61-8	Nu-Chek Prep, Inc.	>0.99

[a] CG – gas liquid chromatography.
[b] Thin layer chromatography showed only the monoacylglycerol moiety present according to the certificate of analysis provided by Nu-Chek Prep, Inc.

2.4. Calibration

The baseline, cell constant and temperature are calibrated according to the standard methods and ASTM E1782-08 guidelines [33]. For temperature calibration, indium and zinc standards purchased from TA instruments are used, following a run with a heating rate of 25 K · min^{-1} at atmospheric pressure, and the melting point obtained are $T = 431.62$ K (indium) and $T = 692.37$ K (zinc), respectively, which are in accordance with the International Practical Temperature Scale [34].

2.5. Experimental procedure

The employed experimental procedure follows the ASTM E1782-08 guidelines [33], with adjustments suggested by Matricarde Falleiro et al. [9,10], and followed by Damaceno et al. [5]. A Differential Scanning Calorimetry (Model Q20P – TA Instruments) with a pressure cell (PDSC) and connected to a vacuum system is used to measure boiling points of the binary mixtures and of the pure components at selected pressures [5,9,10]. In each run, a pair of hermetically sealed crucibles with a pinhole on the lid, and a tungsten carbide ball over it is placed in the pressure cell. One of them is kept empty (as a reference) and the other is filled with a microsample (4 to 5) mg. The pressure cell is then subjected to a heating rate of 25 K · min^{-1}, raising the temperature from (300 to 700) K at constant absolute pressure. As the heating time is ended, the pressure cell is restored to ambient conditions. For each pressure selected in this work (1.20 and 2.50) kPa, the boiling points of different mole fraction of each binary mixture are determined from the extrapolated onset temperature obtained from the thermal curves generated by the DSC software [5,9,10].

2.6. Thermodynamic consistency tests

For VLE systems, many thermodynamic consistency tests derived or not from the Gibbs–Duhem equation have been proposed [35]. A detailed description and application of the thermodynamic consistency tests available for VLE systems are given by Kang et al. [36]. However, few of the available thermodynamic consistency tests can be applied to PTx data. The analysis of the available thermodynamic tests for systems with lipids has been presented in our previous works [6,7]. One test that can be performed for PTx or PTy data set is the pure component consistency test ($Q_{test,5}$ of TDE program from NIST) [28]. In this test, quality factors associated with the consistencies of the end-points ($x_1 = 0$ and $x_1 = 1$) of the VLE data, are determined by comparing these values with their pure component vapour pressures.

The quality factor for this pure component consistency test is calculated as [36],

$$Q_{test5} = \frac{2}{100(\Delta p_1^0 + \Delta p_2^0)}, \quad \text{for} \quad \Delta p_1^0 \text{ and } \Delta p_2^0 \geqslant 1, \tag{1}$$

where Δp_1^0 and Δp_2^0 are the relative deviations between the measured vapour pressure at the boiling point and the known vapour pressure values from the literature at the same temperature. Values of Δp_1^0 and Δp_2^0 are calculated when the mole fraction of component 1 equals 0 ($x_1 = 0$) and 1 ($x_1 = 1$), respectively.

The other test considered in this work, which is a variation of the Van Ness test ($Q_{test,1}$ of TDE program from NIST) [28] is applied for analysing the intermediate points of the measured PTx data. It is also able to check if the measured data are smooth and without any "exceptions". It should be noted that this variation of the Van Ness test is not on the basis of the Gibbs–Duhem equation, for which PTxy data are necessary. Pressure and vapour phase compositions are calculated using a thermodynamic model (for

example, Wilson, NRTL, UNIQUAC, etc.) within a bubble-point calculation.

The quality factor for this variation of the Van Ness test utilises the values of the measured boiling temperature instead of measured pressure or vapour mole fraction:

$$Q_{test1} = \frac{1}{1 + ARD \ (\%)}, \tag{2}$$

where ARD (%) is the average relative deviation between the measured boiling temperature and the estimated boiling temperature by the thermodynamic model (Wilson, NRTL and UNIQUAC), calculated using equation (3).

$$ARD \ (\%) = 100 \frac{1}{NC} \sum_i^{NC} \frac{|T_i^{work} - T_i^{calc}|}{T_i^{work}}, \tag{3}$$

where T_i^{work} is the experimental boiling temperature, T_i^{calc} is the calculated boiling temperature, and NC is the number of the data points considered.

2.7. Property modelling

For the regression of parameters of the thermodynamic models considered in this work (Wilson, NRTL, UNIQUAC), the following objective function is used in the bubble-point calculations:

$$F_{VLE} = \sqrt{\sum_i^{NC} \frac{\left(T_i^{work} - T_i^{calc}\right)^2}{NC}} \quad \text{for} \quad i = 1, NC. \tag{4}$$

A global set of parameters for each model is obtained for each binary system considering measured data at each pressure separately. For comparison purposes, the original UNIFAC model is used for predicting the boiling temperatures. The average relative deviations (ARD) between calculated and measured boiling points were calculated with equation (3).

## 3. Results and discussion

3.1. Binary systems

Table 2 lists the measured boiling points for different mole fraction of the more volatile component of system 1 (monocaprylin + palmitic acid) and of system 2 (monocaprylin + methyl stearate) at (1.20 and 2.50) kPa together with the expected standard uncertainties, which were equal to the positive square root of the estimated variance. Figures 1 and 2 show plots of measured isobaric vapour liquid equilibria for systems 1 and 2 at (1.20 and 2.50) kPa, respectively.

For system 1, a non-ideal behaviour is observed at both pressures, and the boiling points of the binary mixtures richer in the heavier component (palmitic acid) change substantially, that is, for the concentration range of monocaprylin between (0.0 and 0.5). For system 2, non-ideality is even more pronounced at both pressures, and the boiling points of the binary mixtures richer in the heavier component (methyl stearate) decrease substantially, that is, for the concentration range of monocaprylin between (0.0 and 0.4). Outside this range, the boiling points remain almost unchanged (less than $T = 2.0$ K of difference among the measured values). It can be noted that both systems form minimum boiling azeotropes, that is, the boiling temperatures of the binary mixtures are lower than the values for the pure components. Non-idealities as the ones observed in this work have also been found by Coelho et al. [18] and Veneral et al. [24], for binary mixtures of ethanol and glycerol or ethyl esters, and for mixtures of biodiesel and methanol or ethanol. All of them have shown negative deviations from

TABLE 2
Experimental values for boiling points T/K with standard uncertainty u (T)/K for systems 1 and 2.

System 1 monocaprylin (1) + palmitic acid (2)					System 2 monocaprylin (1) + methyl stearate (2)				
Pressure[a]	1.20 kPa		2.50 kPa		Pressure[a]	1.20 kPa		2.50 kPa	
Mole fraction (x_1) [a]	T/K	u (T)/K	T/K	u (T)/K	Mole fraction (x_1) [a]	T/K	u (T)/K	T/K	u (T)/K
0.0000	483.15	0.54	498.35	0.16	0.0000	475.97	0.46	493.38	0.46
0.0554	478.11	0.31	494.10	0.37	0.1018	472.10	0.36	491.26	0.46
0.0991	475.96	0.36	491.78	0.31	0.1993	469.50	0.31	487.88	0.53
0.1938	472.16	0.42	488.90	0.51	0.3099	465.48	0.34	483.97	0.50
0.3035	468.14	0.75	486.66	0.16	0.4007	462.15	0.45	480.07	0.41
0.4065	466.36	0.43	485.43	0.51	0.5005	461.78	0.49	479.07	0.21
0.4991	464.66	0.43	483.40	0.06	0.6018	461.29	0.45	478.60	0.35
0.6033	464.24	0.32	482.02	0.43	0.7022	461.24	0.12	478.66	0.08
0.7016	463.47	0.40	480.97	0.44	0.7970	461.65	0.11	478.97	0.44
0.7852	463.08	0.55	480.35	0.37	0.8938	462.10	0.46	479.4	0.25
0.9031	462.67	0.40	480.07	0.34	1.0000	462.94	0.10	480.41	0.42
1.0000	462.94	0.10	480.41	0.42					

[a] Standard uncertainties are u (p) = 0.05 kPa and u (x_1) = 0.0004.
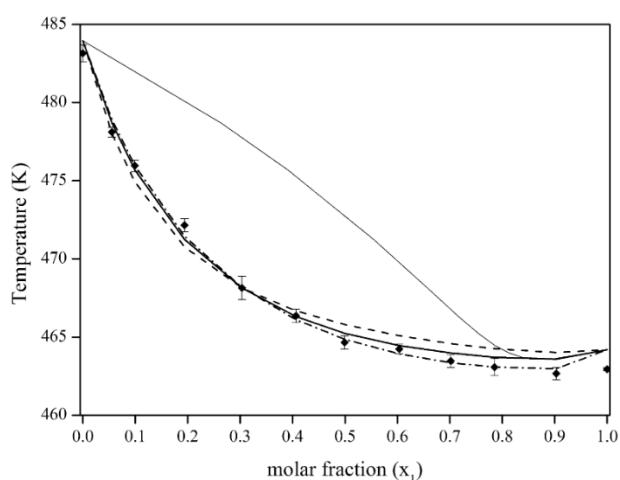
FIGURE 1A. Vapour liquid equilibrium for the system 1 {monocaprylin (1) + palmitic acid (2)} at 1.20 kPa. ♦ Experimental values (this work); –– NRTL (with vapour phase calculated by the model); - - - UNIQUAC; -.-.- Wilson.
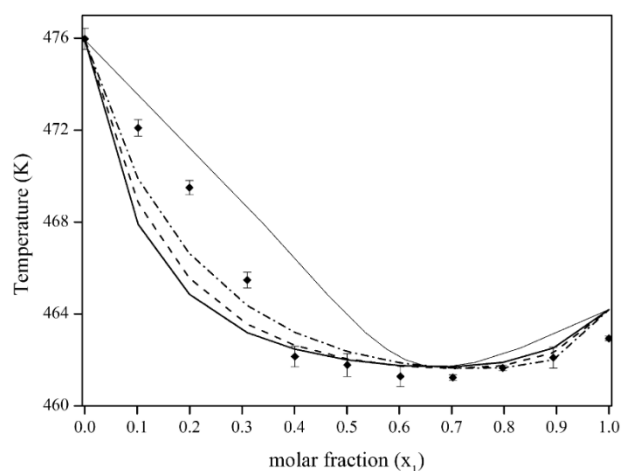
ideality. One should note that for the DSC technique, deviations lower than T = 1.3 K among replicates of measured boiling points are considered adequate.
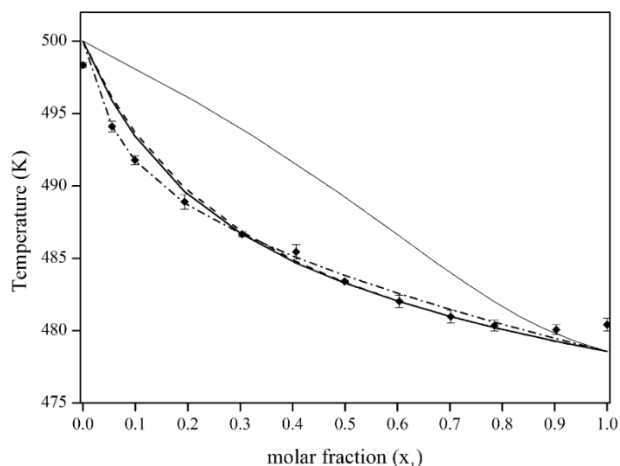
The results found for the thermodynamic consistency tests applied for measured VLE data in this work are given in tables 3 and 4 for the variation of the Van Ness test ($Q_{test,1}$ of TDE program from NIST) [28], and for the pure component consistency test ($Q_{test,5}$ of TDE program from NIST) [28], respectively. For calculating the vapour pressures, Antoine equations are used (table 5). For the variation of the Van Ness test, only the NRTL model is reported, since the Wilson, NRTL and UNIQUAC models gave very similar results for boiling point calculations (see tables 7 and 8). For comparison purposes, table 4 also brings some measured values (T/K *versus* P/kPa) provided by open literature for monocaprylin [5], palmitic acid [37–39] and methyl stearate [40]. As one can see, a good agreement was found for all pure compounds in the pressure range considered in this work.

It can be noted from table 3 that the values of the quality factors ($Q_{test,1}$) are higher than 0.77, which is an indicative of satisfactory quality for the measured values. Regarding the pure component test (see table 4), for both systems at the two pressures considered, the quality factors ($Q_{test,5}$) are equal to 1, indicating that the end-points of the binary mixtures analysed are in agreement with the expected values of the pure component data.

The regressed parameters for Wilson, NRTL and UNIQUAC models are also given in table 6. The parameters for the Wilson model are λ_{12} and λ_{21} in K^{-1}. The values of the molar volumes required by the Wilson model are calculated using the Marrero and Gani group

FIGURE 1B. Vapour liquid equilibrium for system 1 {monocaprylin (1) + palmitic acid (2)} at 2.50 kPa. ♦ Experimental values (this work); –– NRTL (with vapour phase calculated by the model); - - - UNIQUAC; -.-.- Wilson.

FIGURE 2A. Vapour liquid equilibrium for system 2 {monocaprylin (1) + methyl stearate (2)} at 1.20 kPa. ♦ Experimental data (this work); –– NRTL (with vapour phase calculated by the model); - - - UNIQUAC; -.-.- Wilson.
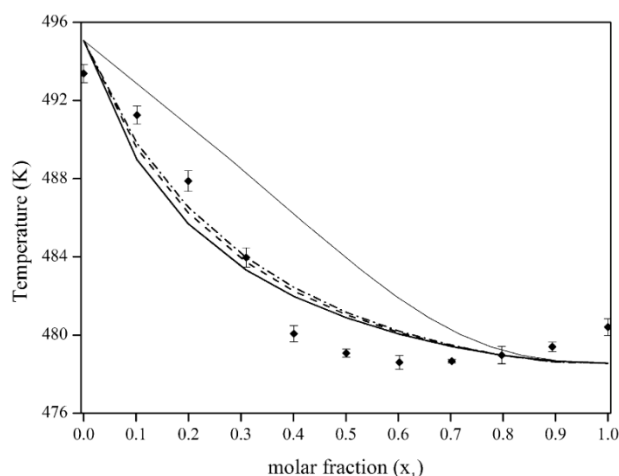
FIGURE 2B. Vapour liquid equilibrium for system 2 {monocaprylin (1) + methyl stearate (2)} at 2.50 kPa. ♦ Experimental values (this work); –– NRTL (with vapour phase calculated by the model); - - - UNIQUAC; -.-.- Wilson.

TABLE 3
Experimental data sets and the quality factors calculated for the variation of the Van Ness consistency test.

Experimental data sets	Pressure/ kPa	Quality factor $(Q_{test,1})$
Monocaprylin (1) + palmitic acid (2)	1.20	0.893
	2.50	0.861
Monocaprylin (1) + methyl stearate (2)	1.20	0.785
	2.50	0.776

contribution method [42], to be 213.32 cm$^3 \cdot$ mol^{-1} for monocaprylin, 295.63 cm$^3 \cdot$ mol^{-1} for palmitic acid, and 348.35 cm$^3 \cdot$ mol^{-1} for methyl stearate. The parameters for the NRTL model are Δg_{12} and Δg_{21} in J $\cdot$ mol^{-1}, and α_{12}. The parameters for the UNIQUAC model are Δu_{12} and Δu_{21} in J $\cdot$ mol^{-1}. Tables 7 and 8 bring the estimated values for boiling points using Wilson, NRTL and UNIQUAC models for systems 1 and 2, respectively, and also the values of the average relative deviations. The performance of Wilson model is more suitable for both systems.

The vapour phase fugacity coefficients are calculated using the "chemical theory" for predicting the second virial coefficient [43]. Taking into account the classes of the components in the binary mixtures (carboxylic acids and acylglycerols, for example), the association of the components via stable hydrogen bonds could

TABLE 5
Parameters for the Antoine equations for vapour pressure of components.[a]

Component	A	B	C
Monocaprylin	24.808	−11522.0	3.692
Palmitic acid	23.372	−11385.9	7.032
Methyl stearate	20.002	−9873.2	22.208

[a] $\ln P^{sat}/kPa = A + B/\{(T/K) + C\}$.

lead to large deviations from the ideal behaviour. Nevertheless, the values found for the fugacity coefficients are close to unity, indicating ideal behaviour for vapour phase, which can be explained by the effect of the long carbon chain of the carboxylic acid that makes its dimerization weak or absent [44,45]. Perhaps most importantly, the observed behaviour is a consequence of the low pressure considered (ideal gas). The same behaviour has been observed by Matricarde Falleiro *et al.* [9,10] for binary mixtures of fatty acids.

Figures 1 and 2 also show the performances for selected models for systems 1 and 2, respectively. It can be noted that a good representation of experimental results is obtained at both pressures for the selected thermodynamic models (Wilson, NRTL, and UNIQUAC) with ARD lower than 0.3%.

3.2. Modified UNIFAC

In general, the original UNIFAC model parameters [33] do not give good predictions for both systems, and it predicts a phase split for system 2. For system 1 and 2, ARD values are found to be 0.37% and 1.47% (Unstable), respectively, considering both pressures (see tables 7 and 8 for predicted boiling point values and ARD on each pressure). Considering that lipid systems may not have been considered in the databank of original UNIFAC, a possible way to improve its performance is to fine-tune the group interaction parameters using the lipid datasets. Thus, in this work, new interaction parameters are regressed for functional groups with chain groups, such as the main group COOH for fatty acids with the main group CH$_2$. More details about the main groups of the Original UNIFAC utilised in this work for representing lipids are given in our previous work [7]. Main groups used in system 1 are: CH$_2$, CCOO, OH and COOH. In system 2, the same main groups are used except COOH. Since a larger number of interaction parameters are necessary for VLE calculations in comparison with the measured data, an objective function that employs a regularisation term F_R [46] is considered:

$$F_{UNIFAC} = F_{VLE} + F_R, \qquad (5)$$

TABLE 4
Experimental data points ($x_1 = 0$ and $x_1 = 1$) and the calculated variables necessary for the quality factor calculations of the pure component consistency test.

Component	Temperature/K	Measured values	Pressure/kPa	From literature	Pressure/kPa	Δp_1^0/kPa
Monocaprylin	462.94	$x_1 = 1$	1.20	CAPEC_LIPIDS_Database[a]	1.12	0.07
	480.41		2.50	CAPEC_LIPIDS_Database[a]	2.74	0.10
	462.66			[5]	1.10	
	479.02			[5]	2.50	
Palmitic acid	483.15	$x_1 = 0$	1.20	CAPEC_LIPIDS_Database[a]	1.15	0.04
	498.35		2.50	CAPEC_LIPIDS_Database[a]	2.32	0.07
	478.15			[37]	1.00	
	483.85			[38]	1.33	
	494.65			[39,40]	2.13	
	499.85			[38]	2.67	
Methyl stearate	475.97	$x_1 = 0$	1.20	CAPEC_LIPIDS_Database[a]	1.20	0.00
	493.38		2.50	CAPEC_LIPIDS_Database[a]	2.35	0.06
	477.25			[41]	1.30	
	495.45			[41]	2.50	

[a] Calculated considering estimated values for the boiling points (see table 5 for equation and parameters).

TABLE 6
Binary interaction parameters for Wilson, NRTL and UNIQUAC models and the experimental data sets.

System	Pressure/kPa	Temperature range/K	Wilson parameters		NRTL parameters		UNIQUAC parameters		
			λ_{12}/K	λ_{21}/K	Δg_{12}/J mol^{-1}	Δg_{21}/J mol^{-1}	α_{12}	Δu_{12}/J mol^{-1}	Δu_{21}/J mol^{-1}
Monocaprylin (1) + palmitic acid (2)	1.20	462.94 to 483.15	130.6	891.74	6304.11	−409.72	0.3	219.83	219.50
	2.50	480.41 to 498.35	943.54	−341.7	1245.42	1261.41	0.3	101.73	103.01
Monocaprylin (1) + methyl stearate (2)	1.20	462.94 to 475.97	252.88	562.58	2723.7	2720.51	0.3	218.61	233.56
	2.50	480.41 to 493.38	202.06	132.4	1345.67	1339.91	0.3	102.32	101.84

TABLE 7
Estimated boiling points for system 1 {monocaprylin (1) + palmitic acid (2)} using the Wilson, NRTL and UNIQUAC models, the original and modified UNIFAC model.

Pressure[a]	1.20 kPa					2.50 kPa				
Mole fraction (x_1)[a]	Correlated models			UNIFAC		Correlated models			UNIFAC	
	Wilson	NRTL	UNIQUAC	Original	Modified	Wilson	NRTL	UNIQUAC	Original	Modified
0.0000	483.95	483.95	483.95	483.96	483.96	500.00	500.00	500.00	500.01	500.01
0.0554	478.92	478.70	478.01	477.24	479.93	494.10	495.90	496.10	492.80	495.70
0.0991	475.96	475.70	474.92	474.08	477.55	491.76	493.44	493.70	489.41	493.15
0.1938	471.46	471.25	470.77	470.18	473.89	488.81	489.60	489.86	485.19	489.21
0.3035	468.17	468.14	468.14	467.88	471.15	486.66	486.66	486.83	482.70	486.25
0.4065	466.12	466.31	466.68	466.62	469.35	485.06	484.67	484.77	481.33	484.28
0.4991	464.86	465.24	465.80	465.84	468.11	483.81	483.28	483.33	480.48	482.93
0.6033	463.92	464.46	465.09	465.18	466.99	482.55	482.00	482.01	479.75	481.71
0.7016	463.36	463.98	464.58	464.68	466.12	481.45	480.97	480.97	479.19	480.74
0.7852	463.08	463.71	464.26	464.35	465.48	480.58	480.21	480.20	478.82	480.03
0.9031	462.98	463.59	464.01	464.09	464.71	479.44	479.25	479.24	478.51	479.16
1.0000	464.19	464.19	464.19	464.19	464.19	478.56	478.56	478.56	478.57	478.57
ARD (%)	0.085	0.120	0.187	0.237	0.472	0.107	0.162	0.175	0.497	0.181

[a] Standard uncertainties are u (p) = 0.05 kPa and u (x_1) = 0.0004.

TABLE 8
Estimated boiling points for system 2 {monocaprylin (1) + methyl stearate (2)} using the Wilson, NRTL and UNIQUAC models, the original and modified UNIFAC model.

Pressure[a]	1.20 kPa					2.50 kPa				
Mole fraction (x_1)[a]	Correlated models			UNIFAC		Correlated models			UNIFAC	
	Wilsonodel	NRTL	UNIQUAC	Original	Modified	Wilson	NRTL	UNIQUAC	Original	Modified
0.0000	475.92	475.92	475.92	Unstable[b]	475.94	495.07	495.07	495.07	Unstable[b]	495.10
0.1018	469.88	467.91	468.83		471.03	489.80	488.97	489.54		488.66
0.1993	466.64	464.86	465.56		468.36	486.54	485.69	486.26		485.23
0.3099	464.37	463.19	463.56		466.47	483.97	483.32	483.73		482.78
0.4007	463.20	462.47	462.64		465.44	482.44	481.97	482.25		481.43
0.5005	462.37	462.00	462.05		464.65	481.16	480.88	481.04		480.36
0.6018	461.87	461.75	461.73		464.12	480.19	480.04	480.12		479.57
0.7022	461.64	461.70	461.63		463.78	479.47	479.41	479.44		479.00
0.7970	461.65	461.89	461.75		463.65	478.96	478.97	478.96		478.64
0.8938	462.01	462.52	462.32		463.73	478.63	478.67	478.64		478.46
1.0000	464.19	464.19	464.19		464.19	478.56	478.56	478.56		478.57
ARD (%)	0.190	0.274	0.232	1.288	0.376	0.265	0.289	0.271	1.655	0.267

[a] Standard uncertainties are u (p) = 0.05 kPa and u (x_1) = 0.0004.
[b] Phase-split.

$$F_R = \frac{1}{\beta}\sum_m \sum_n \left(a_{mn} - a_{mn}^0\right)^2. \tag{6}$$

This has also been employed by Balslev and Abildskov [47]. Considering this objective function, equation (5), only the most sensitive parameters are allowed to deviate from their nominal values, a_{mn}^0. The value of β in equation (6) is empirical. It is determined from several minimizations, monitoring the parameter norm, F_R, and the residual norm, F_{VLE}. When β is small, that is 10^3, the residual norm is great. Then, by increasing β the parameter norm increases, while, the residual norm decreases up to some optimal value of β (typically 10^4 or 10^5), after which the residual norm no longer decreases, but the parameter norm continues to increase. In this work, the optimal β of 10^4 is used, and a_{mn}^0 are equal to the original UNIFAC

values. The current and the revised binary interaction parameters for the UNIFAC model are given in table 9. Perhaps not unexpectedly, the greatest changes have been found for the hydrocarbon – alcohol interaction parameters. For systems 1 and 2, ARD values are found to be 0.33% for modified UNIFAC. In comparison with original UNIFAC, a more substantial difference in ARD values was achieved for system 2 (table 8). Notably, no phase split is found for it with modified UNIFAC. Figure 3 shows a comparison of measured isobaric vapour liquid equilibria for systems 1 (figure 3A) and 2 (figures 3B) at (1.20 and 2.50) kPa, respectively. Also shown are the predicted values given by original and modified UNIFAC for system 1, and modified UNIFAC for system 2. It is important to note that the obtained parameters should be used only for systems covered by the measured values.

TABLE 9
Binary interaction parameters for the original and modified UNIFAC model.

Main group	CH_2	OH	CCOO	COOH
	Current UNIFAC matrix			
CH_2	0	986.5	232.1	663.5
OH	156.4	0	101.1	199
CCOO	114.8	245.4	0	660.2
COOH	315.3	−151.0	−256.3	0
	Revised UNIFAC matrix			
CH_2	0	391.23	284.80	624.17
OH	−91.60	0	19.80	337.67
CCOO	153.89	180.88	0	691.69
COOH	267.97	−28.04	−160.89	0
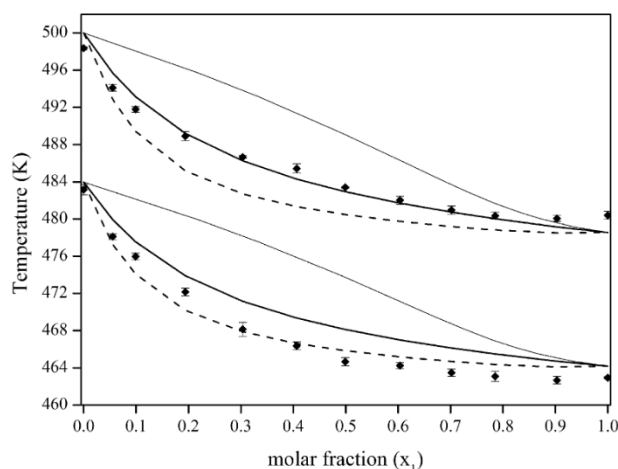
FIGURE 3A. Vapour liquid equilibrium for system 1 {monocaprylin (1) + palmitic acid (2)} at (1.20 and 2.50) kPa. ♦ Experimental values (this work); –– modified UNIFAC (with the vapour phase calculated by the method); - - - original UNIFAC.
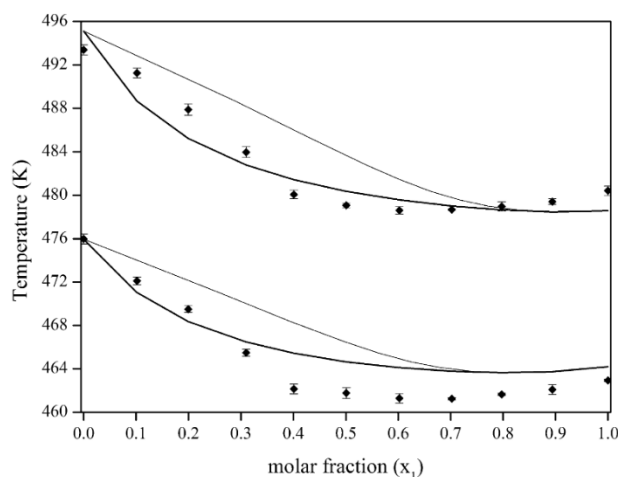

FIGURE 3B. Vapour liquid equilibrium for system 2 {monocaprylin (1) + methyl stearate (2)} at (1.20 and 2.50) kPa. ♦ Experimental values (this work); –– modified UNIFAC (with the vapour phase calculated by the method).

4. Conclusions

A novel DSC technique to measure VLE data for monocaprylin with palmitic acid, and monocaprylin with methyl stearate has been employed. The DSC technique is considered suitable for the two binary mixtures studied in this work mainly because of the low amounts of mass used in each sample. Satisfactory results have been obtained from the employed thermodynamic consistency tests, indicating the acceptable quality of the measured VLE data. The model parameters for the Wilson, NRTL and UNIQUAC models have been regressed with the measured data, with average relative deviations lower than 0.3% for all cases. Also, the UNIFAC model with regressed parameters and employing regularisation in the objective function, gave satisfactory representation of the VLE data for the two binary systems.

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