



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



Larissa P. Cunico^a, Daniela S. Damaceno^b, Rafael M. Matricarde Falleiro^c, Bent Sarup^d, Jens Abildskov^a, Roberta Ceriani^{b,*}, Rafiqul Gani^a

^a CAPEC, Dept. of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs Lyngby, Denmark

^b Faculty of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Cidade Universitária Zeferino Vaz, 13083-852 Campinas, SP, Brazil

^c Dept. of Exact and Earth Sciences, Federal University of São Paulo (UNIFESP), 09972-270 Diadema, SP, Brazil

^d Vegetable Oil Technology Business Unit, Alfa Laval Copenhagen A/S, Maskinevej 5, DK-2860 Soeborg, Denmark

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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 $P = (1.20 \text{ and } 2.50) \text{ kPa}$. 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, $P = (1.10 \text{ to } 13.20) \text{ kPa}$, 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

* Corresponding author. Tel.: +55 19 3521 3961; fax: +55 19 3521 3909.

E-mail address: rceriani@feq.unicamp.br (R. Ceriani).

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.*, CH₂, C=C, CCOO, OH and COOH, and the subgroups CH₃, CH₂, CH, CH=CH, CH₃COO, CH₂COO, 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 ($Q_{\text{test},5}$ 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] ($Q_{\text{test},1}$ 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 studied.

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.

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