



Low pressure vapor–liquid equilibria modeling of biodiesel related systems with the Cubic–Plus–Association (CPA) equation of state



Mariana B. Oliveira^{a,*}, Luis A. Follegatti–Romero^b, Marcelo Lanza^c, Fabio R.M. Batista^b, Eduardo A.C. Batista^b, Antonio J.A. Meirelles^b

^a CICECO, Chemistry Department, University of Aveiro, 3810–193 Aveiro, Portugal

^b ExTrAE, Laboratory of Extraction, Applied Thermodynamics and Equilibrium, Department of Food Engineering, Faculty of Food Engineering, University of Campinas – UNICAMP, 13083–862 Campinas, SP, Brazil

^c EQA/CTC, Chemical and Food Engineering Department, Federal University of Santa Catarina–UFSC, 88040–900 Florianópolis, SC, Brazil

HIGHLIGHTS

- CPA was applied to predict VLE of 8 binary systems composed of FAEs and tetradecane.
- No binary interaction parameters were used for the binary systems.
- CPA was further evaluated in the prediction of real biodiesel + alcohol systems VLE.
- Biodiesel systems were predicted using parameters regressed from binary VLE data.

ARTICLE INFO

Article history:

Received 21 October 2013

Received in revised form 30 April 2014

Accepted 8 May 2014

Available online 22 May 2014

Keywords:

Biodiesels

Alcohols

VLE

Reduced pressures

CPA EoS

ABSTRACT

Fatty acid esters have a wide range of applications in various chemical industries, such as pharmaceutical, cosmetic, food and, most recently, in the biodiesel production. Being able to predict the phase equilibria at reduced pressures of systems composed either only of fatty acid esters as well as also of their mixtures with alcohols, is of major relevance for the design, optimization and operation of industrial facilities producing these compounds, or their use as fuels.

In the present work, the Cubic–Plus–Association Equation of State (CPA EoS) was applied to predict the isobaric vapor–liquid equilibria of six binary systems composed of ethyl/methyl fatty acid esters from laurate to linoleate in the pressure range 0.5–13.3 kPa, and the isothermal phase equilibria of the binary systems tetradecane + ethyl caproate/ethyl myristate at temperatures from 373.15 to 453.15 K.

The predictive ability of the CPA EoS was further evaluated in the description of multicomponent biodiesel systems with associating compounds. Using binary interaction parameters computed from fatty acid ester carbon number correlations previously established the equation was able to provide excellent predictions for the low pressure vapor–liquid equilibria of the systems soybean methylic biodiesel + methanol, soybean ethylic biodiesel + ethanol, *Jatropha curcas* methylic biodiesel + methanol, *Jatropha curcas* ethylic biodiesel + ethanol, in the pressure range 6.7–66.7 kPa.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Fatty acid esters are broadly available in nature and have been widely used as high-value fine chemicals in the food [1], cosmetic [2], pharmaceutical [3] and rubber [4] industries.

Recently, due to environmental and economical problems related to the use of conventional fuels, fatty acid esters (biodiesel) are being considered as reliable alternatives to fossil fuels [5].

Biodiesel is manufactured from naturally occurring fats and oils through the transesterification of the refined triglycerides with methanol or ethanol in presence of a catalyst [5]. Depending on the alcohol used, the obtained product can be a mixture of fatty acid methyl esters (FAMES) or fatty acid ethyl esters (FAEEs) [6].

The knowledge of the phase equilibria of the different systems formed during the biodiesel production process is essential for an adequate design, optimization and operation of the different units present in the industrial process. Processes under reduced pressure are gaining increasing importance in chemical industries, including the ones dealing with fatty acid ester systems, as it avoids the use

* Corresponding author. Tel.: +351 234 370 958; fax: +351 234 370 084.

E-mail address: mbelo@ua.pt (M.B. Oliveira).

Nomenclature

Abbreviations

AAD	global average deviation
CPA	Cubic–Plus–Association
EoS	equation of state
FAEE	fatty acid ethyl ester
FAME	fatty acid methyl ester
NRTL	non-random two liquid model
SAFT	statistical associating fluid theory
SRK	Soave–Redlich–Kwong
UNIQUAC	universal quasi-chemical activity coefficient model
VLE	vapor–liquid equilibria

List of Symbols

a	energy parameter in the physical term of the CPA EoS ($\text{J m}^3 \text{mol}^{-2}$)
a_0	parameter for calculating a ($\text{J m}^3 \text{mol}^{-2}$)
A_i	site A in molecule i
b	co-volume parameter in the physical term of the CPA EoS ($\text{m}^3 \text{mol}^{-1}$)
g	radial distribution function
k_{ij}	binary interaction parameter
P	vapor pressure (Pa)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	temperature (K)

x	mole fraction
X_{Ai}	fraction of molecule i not bonded at site A
w	mass fraction
Z	compressibility factor

Greek Symbols

β	association volume in the association part of the CPA EoS
Δ^{AiBj}	association strength between site A in molecule i and site B in molecule j in the association part of the CPA EoS ($\text{m}^3 \text{mol}^{-1}$)
ε	association energy in the association part of the CPA EoS (J mol^{-1})
η	reduced fluid density

Subscripts

c	critical
i, j	pure component indexes
r	reduced

Superscripts

<i>assoc.</i>	association
<i>phys.</i>	physical
<i>exptl</i>	experimental
<i>calcd</i>	calculated

of high temperatures thus reducing the energy consumption and high temperature degradation reactions [7]. Since the efficiency of these processes decreases with increasing fatty acid esters molecular weight, as pointed by Sahidi and Wanasundara [8], knowledge about the vapor–liquid equilibria of fatty acid ester containing systems is of major importance to correctly design and operate low pressure operating units.

Only recently researchers have published experimental data on the vapor–liquid behavior for systems containing fatty acid esters, and most use the conventional activity coefficient models to describe these data. Rose and Supina [9] conducted vapor–liquid equilibria experiments for binary mixtures composed of fatty acid methyl esters with 6–18 carbon atoms in the pressure range between 3999.7 and 13332.2 Pa and described the data with the Raoult's and Dalton's Law for ideal behavior. Lately, Silva et al. [10] presented vapor–liquid equilibria (VLE) data for the binaries between ethyl palmitate and ethyl stearate/oleate/linoleate at 5332.9 and 9332.6 Pa and correlated the data with the Wilson, the NRTL and the UNIQUAC models. More recently, Tang et al. [11] measured the vapor–liquid equilibria of the system ethyl myristate + ethyl palmitate at 0.5, 1.0 and 1.5 kPa and applied the NRTL and two UNIFAC based models to describe the experimental data. Benziane et al. [12] also used this last model to describe the vapor–liquid equilibria of tetradecane + fatty acid esters systems, for application in the formulation and use of biodiesel/diesel blends.

Considering real biodiesel systems, Veneral et al. [13,14] have lately measured, for the first time, the low pressure vapor–liquid equilibria of the methyl and ethyl biodiesels from soybean and *Jatropha curcas* oils and their mixtures with methanol and ethanol, in the pressure range 6.7–66.7 kPa. In this case, the UNIQUAC model was the activity coefficient based thermodynamic model chosen to represent the experimental data.

An alternative to the use of activity coefficient models to describe phase equilibria is the use of equations of state. Previous

works by Oliveira et al. [15–19] have shown the excellent predictive capability of the Cubic–Plus–Association equation of state (CPA EoS) when applied to the description of different phase equilibria of several biodiesel related systems. Considering the vapor–liquid equilibria of fatty acid esters containing systems, very good results using the CPA EoS were obtained by Oliveira et al. [16,19] for the vapor–liquid equilibria of several alcohol + fatty acid ester systems at atmospheric pressure and at near and supercritical conditions. The same Authors also applied this association equation of state to describe the VLE of several CO_2 + fatty acid ester systems in broad ranges of temperatures and pressures [15].

In the present work, the CPA EoS is applied, as an alternative approach to the commonly used activity coefficient models, to the description of the low pressure vapor–liquid equilibria of fatty acid systems of relevance to the biodiesel production, not only systems composed solely of fatty acid esters but as well in mixtures with paraffins. The equation will be used in a total predictive way, without using binary interaction parameters, to describe the isobaric vapor–liquid equilibria of six binary systems composed of ethyl/methyl fatty acid esters from laurate to linoleate in the pressure range 0.5–13.3 kPa, and the isothermal phase equilibria of the binary systems tetradecane + ethyl caproate/ethyl myristate at temperatures from 373.15 to 453.15 K. A final and stringent test to the predictive ability of the CPA EoS will be carried out through the description of the low pressure vapor–liquid equilibria of real biodiesels + alcohol systems, i.e. multicomponent systems with associating compounds, using temperature and pressure independent binary interaction parameters proposed for the vapor–liquid equilibria of binary systems at atmospheric pressure.

2. Model

The Cubic–Plus–Association (CPA) equation of state [20–22] combines a physical contribution from a cubic equation of state,

in this work the Soave–Redlich–Kwong (SRK), with an association term accounting for intermolecular hydrogen bonding and solvation effects [23,24], originally proposed by Wertheim and used in other association equations of state such as SAFT [25].

It can be expressed in terms of the compressibility factor as:

$$Z = Z^{phys.} + Z^{assoc.}$$

$$= \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i + \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

where a is the energy parameter, b the co-volume parameter, ρ is the molar density, g a simplified hard-sphere radial distribution function, X_{A_i} the mole fraction of pure component i not bonded at site A , and x_i is the mole fraction of component i .

The pure component energy parameter, a , is obtained from a Soave-type temperature dependency:

$$a(T) = a_0 \left[1 + c_1 (1 - \sqrt{T_r}) \right]^2 \quad (2)$$

When CPA is extended to mixtures, the energy and co-volume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (3)$$

and

$$b = \sum_i x_i b_i \quad (4)$$

X_{A_i} is related to the association strength $\Delta^{A_i B_j}$ between sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (5)$$

where

$$\Delta^{A_i B_j} = g(\rho) \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (6)$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and the association volume, respectively. For a binary mixture composed solely of non-associating compounds, as it is the case of the systems here considered, the binary interaction parameter, k_{ij} (Eq. (3)), is the only adjustable parameter.

The simplified radial distribution function, $g(\rho)$, is given by [26]:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad \text{where} \quad \eta = \frac{1}{4} b\rho \quad (7)$$

For non-associating components, such as esters and alkanes, the association term disappears and the CPA EoS is reduced to the SRK EoS, with only three pure component parameters (a_0 , c_1 and b). For associating components, like alcohols, the association term is introduced resulting in five pure compounds parameters (a_0 , c_1 , b , ε , β). In both cases, these are optimized simultaneously from vapor pressure and liquid density data. The objective function to be minimized is the following:

$$OF = \sum_i^{NP} \left(\frac{P_i^{\text{exptl}} - P_i^{\text{calcd}}}{P_i^{\text{exptl}}} \right)^2 + \sum_i^{NP} \left(\frac{\rho_i^{\text{exptl}} - \rho_i^{\text{calcd}}}{\rho_i^{\text{exptl}}} \right)^2 \quad (8)$$

For mixtures containing a self-associating and a non-associating compound, no combining rules are required for the association term and thus, the k_{ij} binary interaction parameter in the physical term is the only adjustable parameter.

On the other hand, when CPA is employed to mixtures containing cross-associating molecules, combining rules for the association energy and volume parameters are required. A particular case of this situation is found when systems are constituted by a self-associating compound and an inert compound that can solvate with the associating component. For that kind of systems, a different procedure is required to obtain the cross-associating energy and volume. As proposed by Folas et al. [27], the cross-association energy between the ester and the alcohol is considered to be half the alcohol association energy and the cross association volume is left as an adjustable parameter, to be fitted from equilibrium data. The referred approach was already successfully applied to model the water solubility in fatty acid esters and biodiesels [17,28], the atmospheric pressure and the near and supercritical vapor–liquid equilibria of fatty acid esters + alcohol systems [16,19] and the liquid–liquid equilibria of ternary systems composed of fatty acid esters, alcohols and water or glycerol [29–32].

The association term depends on the type and number of association sites. For alcohols, either the two-site (2B) or the three-site (3B) association schemes may be used. Following the results from Huang and Radosz [33] and from Kontogeorgis et al. [21] the 2B association scheme will be used in this work.

For the ester compounds, as shown before [16,17,19,28–32], a single association site is considered, that can cross-associate with the alcohol.

3. Results and discussion

3.1. Correlation of the CPA pure compound parameters

The CPA pure compound parameters values for tetradecane, methanol and ethanol were already previously established and applied in this work [34].

The FAEs and FAMEs studied here are all non-self-associating compounds and so only the three CPA pure compound parameters of the physical term (a_0 , c_1 and b) are needed to be estimated for each fatty acid ester. With the recent appearance of more experimental information for fatty acid methyl and ethyl esters vapor pressures and liquid densities it is now possible to regress the three CPA pure compound parameters for the majority of the esters appearing in common biodiesels composition. Parameters values were previously established for the compounds ethyl palmitate [32], ethyl oleate [32], ethyl linoleate [32], methyl laurate [35], methyl myristate [35] and methyl palmitate [35]. Using vapor pressure data measured for ethyl myristate by Tang et al. [11] and for ethyl hexanoate by Benziane et al. [36] along with the density data proposed by Pratas et al. [37] it was possible to determine in this work the three CPA pure compound parameters for these two compounds not yet studied within the CPA EoS framework, with global average deviations inferior to 2% for densities and to 6% for vapor pressures.

The pure compound parameters for all the compounds here studied, along with their critical temperatures, are reported in Table 1.

3.2. Correlation of the vapor–liquid equilibria

Having estimated the pure compound parameters, it was then possible to describe the experimental vapor–liquid equilibria data of selected binary systems composed of fatty acid esters with the CPA EoS. The CPA EoS is here used in a purely predictive way with the binary interaction parameters, k_{ij} , set to zero.

The first systems studied were ethyl palmitate + ethyl stearate/ethyl linoleate at 5332.9 and 9332.6 Pa, respectively. The CPA EoS is able to provide very good predictions for the vapor–liquid

Table 1

CPA pure compound parameters and critical temperatures for the compounds studied.

Compound	T_c (K)	a_0 ($\text{J m}^3 \text{mol}^{-2}$)	c_1	$b \times 10^5$ ($\text{m}^3 \text{mol}^{-1}$)	ε (J mol^{-1})	β
Methanol [34]	512.7	0.43	0.75	3.22	20859	0.034
Ethanol [34]	514.7	0.68	0.94	4.75	21336	0.019
Tetradecane [34]	693	7.63	1.32	25.18		
Ethyl caprate ^{this work}	615.2	3.85	1.23	14.92		
Ethyl myristate ^{this work}	744.27	9.20	1.61	29.42		
Ethyl palmitate [32]	766.41	9.82	2.12	33.80		
Ethyl stearate [32]	786.12	8.85	3.15	37.80		
Ethyl oleate [32]	771.07	14.36	1.34	37.64		
Ethyl linoleate [32]	785.19	11.99	1.82	36.13		
Methyl laurate [35]	710.41	6.71	1.53	23.01		
Methyl myristate [35]	740.97	8.03	1.61	26.36		
Methyl palmitate [35]	765.92	7.42	2.29	29.75		
Methyl stearate [35]	788.63	10.13	1.92	33.11		
Methyl oleate [35]	772.34	10.51	1.82	32.49		
Methyl linoleate [35]	786.37	8.99	2.16	31.71		
Methyl linolenate [35]	797.26	8.67	2.17	30.95		

equilibria of these systems, as presented in Figs. 1 and 2, respectively. Global average deviations inferior to 0.2% and to 3.6% were obtained for these systems, respectively for bubble temperatures and for vapor compositions, as reported in Table 2.

Fig. 3 shows the vapor–liquid equilibria prediction results for the ethyl palmitate + ethyl oleate system at 5332.9 and 9332.6 Pa. At the higher pressures, global average deviations of

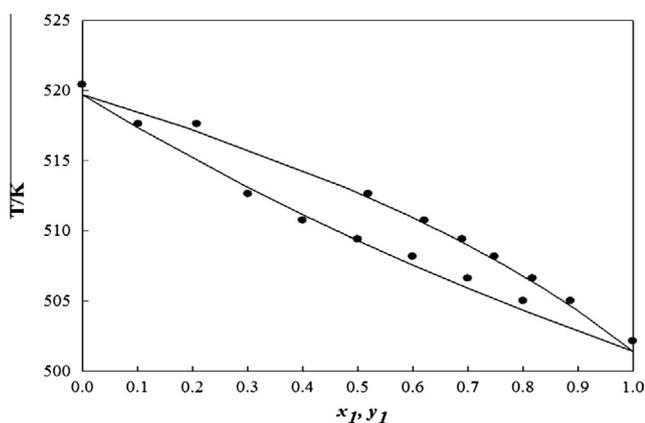


Fig. 1. Liquid–vapor equilibrium for the ethyl palmitate (1) + ethyl stearate (2) system at 5332.9 Pa. Experimental [10] (●) and CPA results (–).

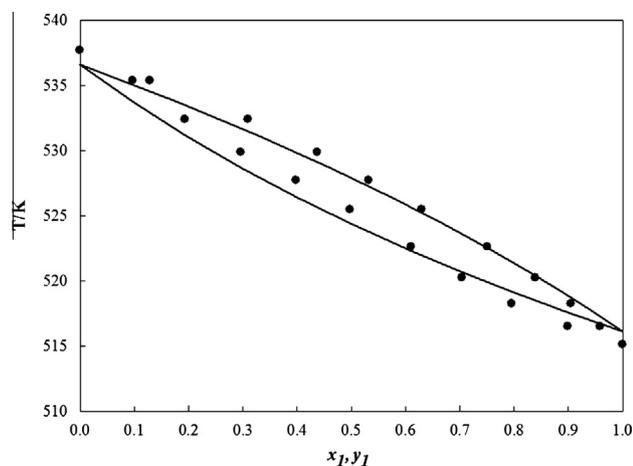


Fig. 2. Liquid–vapor equilibrium for the ethyl palmitate (1) + ethyl linoleate (2) system at 9332.6 Pa. Experimental [10] (●) and CPA results (–).

Table 2

Modeling results for the binary fatty acid systems.

System	Pressure (Pa)	% AAD T_b	% AAD y_i
Ethyl palmitate + ethyl stearate	5332.9	0.10	3.55
Ethyl palmitate + ethyl linoleate	9332.6	0.19	2.70
Ethyl palmitate + ethyl oleate	5332.9	0.23	4.99
Ethyl palmitate + ethyl oleate	9332.6	0.19	4.15
Methyl laurate + methyl myristate	3999.7	0.59	1.27
Methyl laurate + methyl myristate	5332.89	0.67	2.07
Methyl laurate + methyl myristate	6666.1	0.79	3.40
Methyl laurate + methyl myristate	13332.23	0.94	0.72
Methyl myristate + methyl palmitate	3999.7	0.53	3.31
Methyl myristate + methyl palmitate	5332.89	0.48	1.36
Methyl myristate + methyl palmitate	6666.1	0.56	4.22
Methyl myristate + methyl palmitate	13332.23	0.70	2.01
Global AAD %		0.50	2.81

only 0.19% and 4.15% were obtained for bubble temperatures and vapor compositions, respectively, as presented in Table 2. The larger deviations observed for this system at 5332.9 Pa are surely related to the uncertainty of the experimental data at this pressure, since a good prediction with the CPA EoS was observed at 9332.6 Pa.

Finally a last system composed solely of fatty acid ethyl esters was successfully described with the CPA EoS, as seen in Fig. 4. The bubble point data of the ethyl myristate + ethyl palmitate binary system is predicted with the CPA EoS at three different pressures, from 0.5 to 1.5 kPa, with global average deviations inferior to 0.5% as seen in Table 3.

The vapor–liquid equilibria of systems composed only of FAMES found in literature were also predicted in this work with the CPA EoS. Data were available for the methyl laurate + methyl myristate and methyl myristate + methyl palmitate systems at 3999.7, 5332.9, 6666.1 and 13332.2 Pa. Good prediction results for the vapor–liquid equilibria were obtained for all systems at all the studied pressures, as the deviations reported in Table 2 show. However, a degradation of the predictions with increasing pressure was observed, as shown in Figs. 5 and 6, which can be justified by the increasing scatter of the experimental data at higher pressures. Considering all binary systems containing FAMES, average absolute deviations inferior to 0.66% were obtained for bubble temperatures and inferior to 2.30% for vapor compositions.

The last binary systems considered in this work were those composed of a fatty acid ester and tetradecane, representative of the blends biodiesel/fuel. As seen in Tables 4 and 5 and in Figs. 7 and 8, for the systems composed of ethyl caproate and ethyl myristate, the CPA EoS is able to properly describe, without the need of

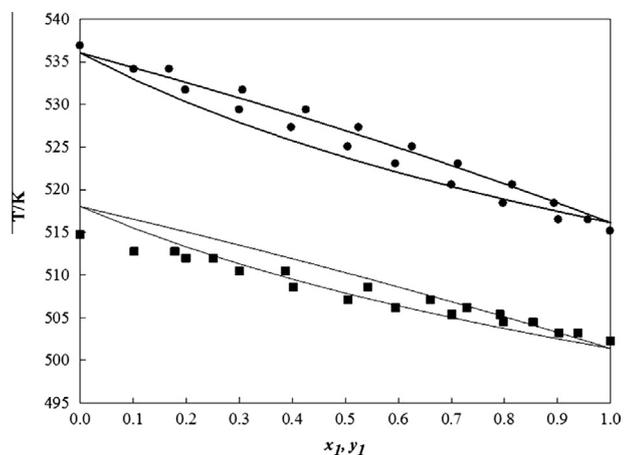


Fig. 3. Liquid–vapor equilibrium for the ethyl palmitate (1) + ethyl oleate (2) system. Experimental [10] (at 5332.9 Pa (■) and at 9332.6 Pa (●)) and CPA results (—).

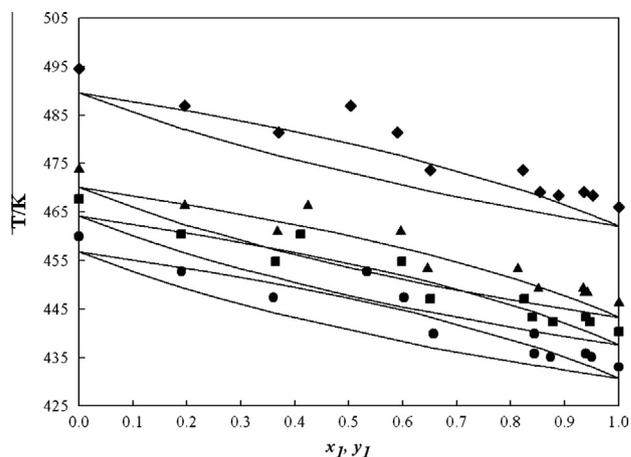


Fig. 5. Liquid–vapor equilibrium for the methyl laurate (1) + methyl myristate (2) system. Experimental [9] (at 3999.7 Pa (●), at 5332.89 Pa (■), at 6666.1 Pa (▲) and at 13332.23 Pa (◆)) and CPA results (—).

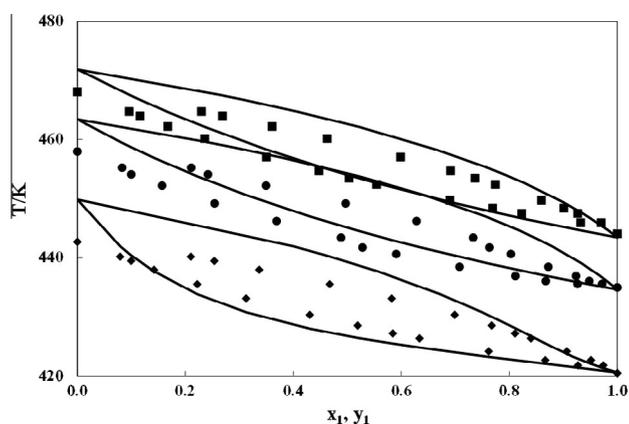


Fig. 4. Liquid–vapor equilibrium for the ethyl myristate (1) + ethyl palmitate (2) system. Experimental [11] (at 0.5 kPa (◆), at 1 kPa (●) and at 1.5 kPa (■)) and CPA results (—).

Table 3

Modeling results for the binary system ethyl myristate (1) + ethyl palmitate (2).

Pressure (Pa)	% AAD T_b	% AAD y_1
500	0.39	29.14
1000	0.70	5.88
1500	0.31	8.52
Global AAD %	0.47	14.51

binary interaction parameters, their vapor–liquid equilibria at nine different temperatures with global average deviations inferior to 15% in the phase compositions.

The Authors reporting the experimental data [10–12] also used the Wilson, NRTL and UNIQUAC activity coefficient models to describe the data. Although good results are obtained, these are achieved with the expense of using at least two binary interaction parameters, regressed from the experimental data and temperature or pressure dependent, on the contrary of what happens in this work with the CPA EoS which is able to properly describe the VLE of the different systems without using binary interaction parameters.

As a final and delicate test to the ability of the CPA EoS to be applied as a simple but yet powerful prediction tool in the biodiesel production process, the low pressure vapor–liquid equilibria of systems composed by methanol/ethanol and the methylic/ethylic

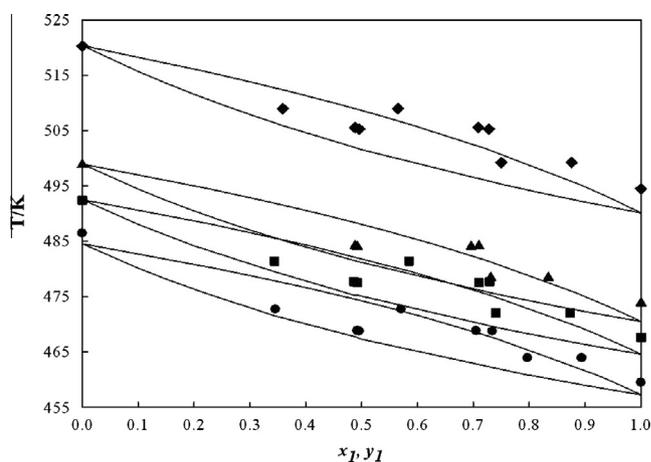


Fig. 6. Liquid–vapor equilibrium for the methyl myristate (1) + methyl palmitate (2) system. Experimental [9] (at 3999.7 Pa (●), at 5332.89 Pa (■), at 6666.1 Pa (▲) and at 13332.23 Pa (◆)) and CPA results (—).

Table 4

Modeling results for the binary system ethyl hexanoate (1) + tetradecane (2).

Temperature (K)	% AAD x_1	% AAD y_1
373.15	16.00	0.86
383.15	12.80	0.87
393.15	9.93	0.85
403.15	7.88	0.83
413.15	6.13	0.80
423.15	4.65	0.79
433.15	3.90	0.82
443.15	3.63	0.87
453.15	4.61	0.97
Global AAD %	7.73	0.86

biodiesels produced from two different oils, soybean and *Jatropha curcas*, were described with the selected model. The mixtures were treated as multicomponent systems. The biodiesels fatty acid esters compositions presented at the works from where the experimental low pressure vapor–liquid equilibria data were taken were here considered [13,14], i.e. soybean and *Jatropha* biodiesels are mainly composed by the esters of the fatty acids $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ [38,39]. The correspondent CPA pure compound parameters, previously determined [32,35] are depicted along with the critical temperatures values in Table 1. Since there is still no

Table 5
Modeling results for the binary system ethyl hexadecanoate (1) + tetradecane (2).

Temperature (K)	% AAD x_1	% AAD y_1
373.15	8.72	7.65
383.15	9.70	5.16
393.15	9.14	4.70
403.15	14.78	16.65
413.15	14.20	20.31
423.15	13.96	24.03
433.15	9.57	13.64
453.15	14.99	33.04
Global AAD %	11.88	15.65

data for the vapor pressures of ethyl linolenate the same set of CPA parameters values proposed for ethyl linoleate was used for that compound.

As explained in the Model Section, even if esters are non-self-associating compounds they are able to solvate with associating compounds like alcohols. In this special case, association is explicitly considered by the CPA EoS by simultaneously regressing the cross-association volume, τ , along with the k_{ij} . In a previous work [16], where the atmospheric pressure vapor–liquid equilibria of fatty acid ester + alcohols systems were studied with the CPA EoS, it was observed that, for the methanol and the ethanol

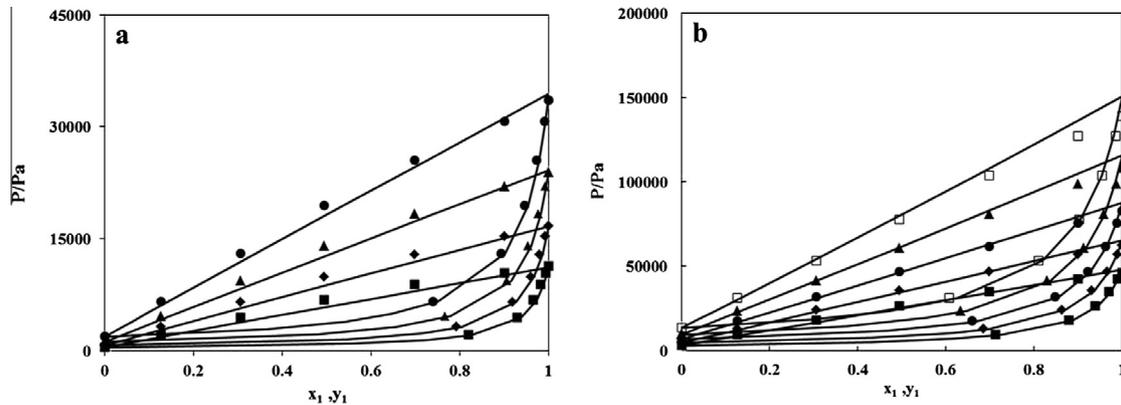


Fig. 7. Liquid–vapor equilibrium for the ethyl hexadecanoate (1) + tetradecane (2) system. Experimental [12] (a: at 373.15 K (■), at 383.15 K (◆), at 393.15 K (▲) and at 493.15 K (●); b: at 413.15 K (■), at 423.15 K (◆), at 433.15 K (●), at 443.15 K (▲), and at 453.15 K (□)) and CPA results (–).

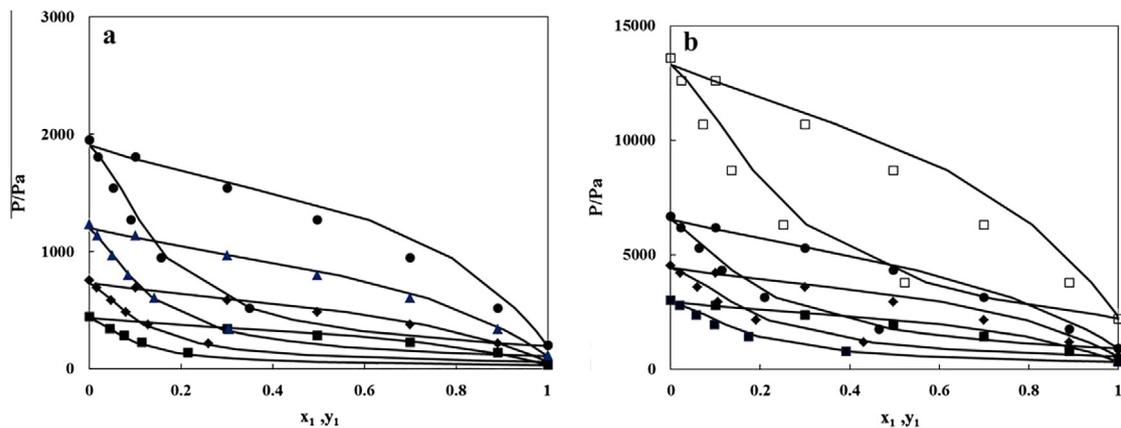


Fig. 8. Liquid–vapor equilibrium for the ethyl hexadecanoate (1) + tetradecane (2) system. Experimental [12] (a: at 373.15 K (■), at 383.15 K (◆), at 393.15 K (▲) and at 403.15 K (●); b: at 413.15 K (■), at 423.15 K (◆), at 433.15 K (●) and at 453.15 K (□)) and CPA results (–).

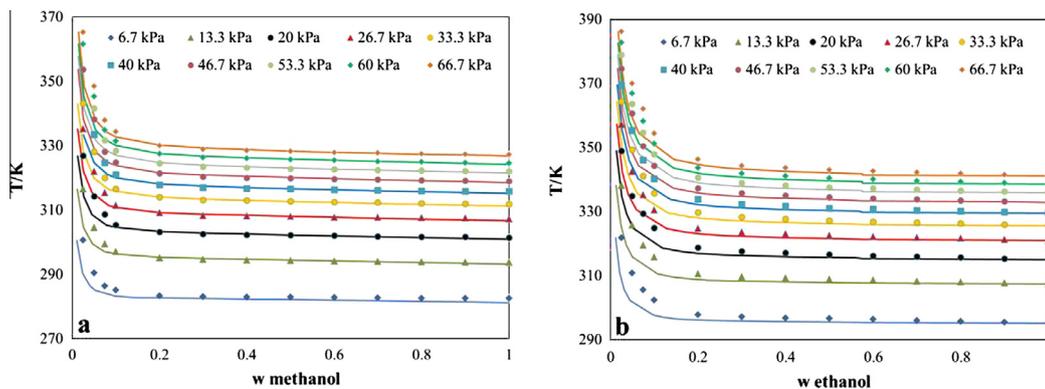


Fig. 9. Liquid–vapor equilibrium for a: the soybean methylic biodiesel + methanol; b: the soybean ethylic biodiesel + ethanol. Points are experimental data [14] and lines the CPA results.

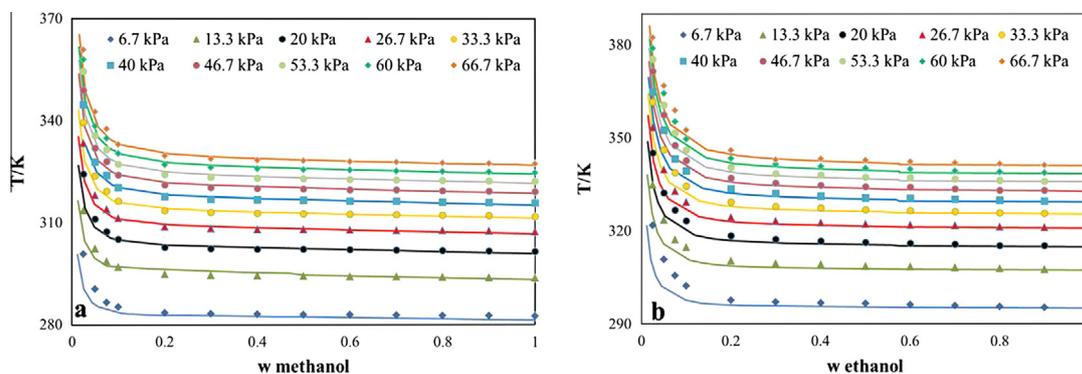


Fig. 10. Liquid–vapor equilibrium for a: the *Jatropa curcas* methylic biodiesel + methanol; b: the *Jatropa curcas* ethylic biodiesel + ethanol. Points are experimental data [13] and lines the CPA results.

systems, the k_{ij} 's followed linear correlations with the ester carbon number and it was possible to use a constant value for the cross-association volume. These binary parameters values were already used to successfully predict the near and supercritical vapor–liquid equilibria of fatty acid ester + alcohol systems [19]. Similarly, the same k_{ij} fatty acid ester carbon number correlation and the constant value for the cross-association volume established for the atmospheric pressure binary systems vapor–liquid equilibria were here used to predict the low vapor–liquid equilibria of the multicomponent systems soybean methylic biodiesel + methanol, soybean ethylic biodiesel + ethanol, *Jatropa curcas* methylic biodiesel + methanol and *Jatropa curcas* ethylic biodiesel + ethanol. Excellent prediction results were obtained as shown in Figs. 9 and 10 for 10 different pressures, being the model able to describe the drastic bubble temperature decrease with the addition of small amount of alcohol observed experimentally.

The UNIQUAC model was also previously applied to satisfactorily describe these low pressure vapor–liquid equilibria data [13,14]. Nevertheless, the biodiesels were considered as pseudo-components resulting in the description of a binary mixture instead of a multicomponent one as it is with the CPA EoS. In addition, and in contrary of what occurs with the CPA EoS, no information from binary systems ester–alcohol is considered for obtaining the interaction parameters between the biodiesels and the alcohols, being them regressed from the experimental data.

4. Conclusions

In this work, the Cubic–Plus–Association (CPA) equation of state was successfully applied to predict the reduced pressure vapor–liquid equilibria data of eight binary systems composed of fatty acid esters and tetradecane. The low pressure vapor–liquid equilibria of multicomponent and associating compounds containing systems were also here addressed. Soybean/*Jatropa curcas* methylic and ethylic biodiesels + methanol/ethanol systems were successfully predicted using interaction parameters regressed from binary systems atmospheric pressure vapor–liquid equilibria.

The results clearly show that the CPA equation of state is a predictive tool that can be applied in the design and operation of production facilities of fatty acid esters at the biodiesel industry.

Acknowledgments

The authors wish to acknowledge FAPESP (08/56258–8), CNPq (304495/2010–7 and 483340/2012–0), CAPES/PEC–PG, CAPES and CAPES/PNPD for their financial support and scholarships. Financial support was provided to LSRE by FEDER/POCI/2010. CICECO is

being funded by Fundação para a Ciência e a Tecnologia through Pest-C/CTM/LA0011/2013. Mariana B. Oliveira acknowledges Fundação para a Ciência e a Tecnologia for her Post-doctoral grant (SFRH/BPD/71200/2010).

References

- [1] Kim J, Altretreuer D, Clark D, Dordick J. Rapid synthesis of fatty acid esters for use as potential food flavors. *J Am Oil Chem Soc* 1998;75:1109–13.
- [2] Keng PS, Basri M, Zakaria MRS, Rahman MBA, Ariff AB, Rahman RNZA, et al. Newly synthesized palm esters for cosmetics industry. *Ind Crops Prod* 2009;29:37–44.
- [3] Pérez-Feás C, Barciela-Alonso M, Sedes-Díaz A, Bermejo-Barrera P. Phthalates determination in pharmaceutical formulae used in parenteral nutrition by LC-ES-MS: importance in public health. *Anal Bioanal Chem* 2010;397:529–35.
- [4] Vermeulen R, Jönsson BG, Lindh C, Kromhout H. Biological monitoring of carbon disulphide and phthalate exposure in the contemporary rubber industry. *Int Arch Occup Environ Health* 2005;78:663–9.
- [5] Ma F, Hanna MA. Biodiesel production: a review 1. *Bioresour Technol* 1999;70:1–15.
- [6] Van Gerpen J. Biodiesel processing and production. *Fuel Process Technol* 2005;86:1097–107.
- [7] Wanasundara UN, Wanasundara PKJPD, Shahidi F. Novel separation techniques for isolation and purification of fatty acids and oil by-products. *Bailey's Ind. Oil Fat Prod.*, John Wiley & Sons, Inc.; 2005.
- [8] Shahidi F, Wanasundara UN. Omega-3 fatty acid concentrates: nutritional aspects and production technologies. *Trends Food Sci Technol* 1998;9:230–40.
- [9] Rose A, Supina WR. Vapor pressure and vapor–liquid equilibrium data for methyl esters of the common saturated normal fatty acids. *J Chem Eng Data* 1961;6:173–9.
- [10] Silva LYA, Falleiro RMM, Meirelles AJA, Krähennühl MA. Vapor–liquid equilibrium of fatty acid ethyl esters determined using (DSC). *Thermochim Acta* 2011;512:178–82.
- [11] Tang G, Ding H, Hou J, Xu S. Isobaric vapor–liquid equilibrium for binary system of ethyl myristate+ethyl palmitate at 0.5, 1.0 and 1.5 kPa. *Fluid Phase Equilib* 2013;347:8–14.
- [12] Benziane M, Khimeche K, Mokbel I, Dahmani A, Jose J. Isothermal vapor–liquid equilibria of n-tetradecane + ethyl hexanoate, ethyl decanoate, and ethyl tetradecanoate. *J Chem Eng Data* 2013;58:492–8.
- [13] Venerai JG, Junior DLR, Mazutti MA, Voll FAP, Cardozo-Filho L, Corazza ML, et al. Thermophysical properties of biodiesel and related systems: low-pressure vapour–liquid equilibrium of methyl/ethyl *Jatropa curcas* biodiesel. *J Chem Thermodyn* 2013;60:46–51.
- [14] Venerai JG, Junior DLR, Mazutti MA, Voll FAP, Cardozo-Filho L, Corazza ML, et al. Thermophysical properties of biodiesel and related systems: low-pressure vapor–liquid equilibrium of methyl/ethyl soybean biodiesel. *J Chem Thermodyn* 2013;64:65–70.
- [15] Oliveira MB, Queimada AJ, Kontogeorgis GM, Coutinho JAP. Evaluation of the CO₂ behavior in binary mixtures with alkanes, alcohols, acids and esters using the Cubic–Plus–Association equation of state. *J Supercrit Fluids* 2011;55:876–92.
- [16] Oliveira MB, Miguel SI, Queimada AJ, Coutinho JAP. Phase equilibria of ester + alcohol systems and their description with the Cubic–Plus–Association equation of state. *Ind Eng Chem Res* 2010;49:3452–8.
- [17] Oliveira MB, Varanda FR, Marrucho IM, Queimada AJ, Coutinho JAP. Prediction of water solubility in biodiesel with the CPA equation of state. *Ind Eng Chem Res* 2008;47:4278–85.
- [18] Oliveira MB, Barbedo S, Soletti JI, Carvalho SHV, Queimada AJ, Coutinho JAP. Liquid–liquid equilibria for the canola oil biodiesel+ethanol+glycerol system. *Fuel* 2011;90:2738–45.

- [19] Oliveira MB, Queimada AJ, Coutinho JAP. Prediction of near and supercritical fatty acid ester+alcohol systems with the CPA EoS. *J Supercrit Fluids* 2010;52:241–8.
- [20] Kontogeorgis GM, Michelsen ML, Folas GK, Derawi S, von Solms N, Stenby EH. Ten years with the CPA (Cubic–Plus–Association) equation of state. Part 1. Pure compounds and self-associating systems. *Ind Eng Chem Res* 2006;45:4855–68.
- [21] Kontogeorgis GM, Michelsen ML, Folas GK, Derawi S, von Solms N, Stenby EH. Ten years with the CPA (Cubic–Plus–Association) equation of state. Part 2. Cross-associating and multicomponent systems. *Ind Eng Chem Res* 2006;45:4869–78.
- [22] Oliveira MB, Coutinho JAP, Queimada AJ. Mutual solubilities of hydrocarbons and water with the CPA EoS. *Fluid Phase Equilib* 2007;258:58–66.
- [23] Michelsen ML, Hendriks EM. Physical properties from association models. *Fluid Phase Equilib* 2001;180:165–74.
- [24] Wu J, Prausnitz JM. Phase equilibria for systems containing hydrocarbons, water, and salt: an extended Peng–Robinson equation of state. *Ind Eng Chem Res* 1998;37:1634–43.
- [25] Müller EA, Gubbins KE. Molecular-based equations of state for associating fluids: a review of SAFT and related approaches. *Ind Eng Chem Res* 2001;40:2193–211.
- [26] Kontogeorgis GM, Yakoumis IV, Meijer H, Hendriks E, Moorwood T. Multicomponent phase equilibrium calculations for water–methanol–alkane mixtures. *Fluid Phase Equilib* 1999;158–160:201–9.
- [27] Folas GK, Kontogeorgis GM, Michelsen ML, Stenby EH. Application of the Cubic–Plus–Association (CPA) equation of state to complex mixtures with aromatic hydrocarbons. *Ind Eng Chem Res* 2006;45:1527–38.
- [28] Oliveira MB, Pratas MJ, Queimada AJ, Coutinho JAP. Another look at the water solubility in biodiesels: further experimental measurements and prediction with the CPA EoS. *Fuel* 2012;97:843–7.
- [29] Oliveira MB, Barbedo S, Soletti JI, Carvalho SHV, Queimada AJ, Coutinho JAP. Liquid–liquid equilibria for the canola oil biodiesel + ethanol + glycerol system. *Fuel* 2011;90:2738–45.
- [30] Oliveira MB, Queimada AJ, Coutinho JAP. Modeling of biodiesel multicomponent systems with the Cubic–Plus–Association (CPA) equation of state. *Ind Eng Chem Res* 2010;49:1419–27.
- [31] Follegatti-Romero LA, Lanza M, Batista FRM, Batista EAC, Oliveira MB, Coutinho JAP, et al. Liquid–liquid equilibrium for ternary systems containing ethyl esters, anhydrous ethanol and water at 298.15, 313.15, and 333.15 K. *Ind Eng Chem Res* 2010;49:12613–9.
- [32] Follegatti-Romero LA, Oliveira MB, Batista FRM, Batista EAC, Coutinho JAP, Meirelles AJA. Liquid–liquid equilibria for ternary systems containing ethyl esters, ethanol and glycerol at 323.15 and 353.15 K. *Fuel* 2012;94:386–94.
- [33] Huang SH, Radosz M. Equation of state for small, large, polydisperse, and associating molecules. *Ind Eng Chem Res* 1990;29:2284–94.
- [34] Oliveira MB, Marrucho IM, Coutinho JAP, Queimada AJ. Surface tension of chain molecules through a combination of the gradient theory with the CPA EoS. *Fluid Phase Equilib* 2008;267:83–91.
- [35] Pratas MJ, Oliveira MB, Pastoriza-Gallego MJ, Queimada AJ, Piñeiro MM, Coutinho JAP. High-pressure biodiesel density: experimental measurements, correlation, and Cubic–Plus–Association equation of state (CPA EoS) modeling. *Energy Fuels* 2011;25:3806–14.
- [36] Benziane M, Khimeche K, Mokbel I, Sawaya T, Dahmani A, Jose J. Experimental vapor pressures of five saturated fatty acid ethyl ester (FAEE) components of biodiesel. *J Chem Eng Data* 2011;56:4736–40.
- [37] Pratas MJ, Freitas S, Oliveira MB, Monteiro SC, Lima AS, Coutinho JAP. Densities and viscosities of fatty acid methyl and ethyl esters. *J Chem Eng Data* 2013;55:3983–90.
- [38] Mazutti MA, Voll FAP, Cardozo-Filho L, Corazza ML, Lanza M, Priamo WL, et al. Thermophysical properties of biodiesel and related systems: Liquid–liquid equilibrium data for soybean biodiesel. *J Chem Thermodyn* 2013;58:83–94.
- [39] Tiwari AK, Kumar A, Raheman H. Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: an optimized process. *Biomass Bioenergy* 2007;31:569–75.