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

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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.

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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.

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 trough 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

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

assoc.	association
phys.	physical
exptl	experimental
calcd	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 methylic and ethylic 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,