Prediction of Water Solubility in Biodiesel with the CPA Equation of State

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The recent growing interest in biofuels is due to the continuous increase in crude oil prices, limited resources of fossil energies, and environmental concerns. In what concerns road transportation, biodiesel is being considered a good alternative to conventional diesels. It consists of a blend of fatty acid esters, and its production and formulation needs to be optimized to ensure that the fuel quality complies with the legal standards. Although in various aspects biodiesel is superior to conventional diesel, it also poses some problems such as its poor behavior at low temperatures and higher hygroscopicity than conventional diesel. Up to now, little information is available about the water solubility in fatty acid methyl and ethyl esters and commercial biodiesels. To overcome this lack of data, water solubility measurements were carried out for 11 pure esters and 6 biodiesels in the temperature range 288.15−323.15 K. This new experimental data was successfully modeled with the cubic-plus-association (CPA) equation of state with global average deviations inferior to 7% for the ester systems, and predictions with deviations of 16% for commercial biodiesels were achieved.

1. Introduction

Coal, petroleum, and natural gas are the most used energy sources to fulfill the current energy demand. The continuous increase in oil prices caused by limited oil reserves, concentrated in regions of the world with politic instability, the CO_2 emission limitations imposed by the Kyoto protocol, and simultaneously the increase in energy demand, due to the industrialization in countries such as India and China, lead to the need for new energy solutions.

Biofuels, liquid fuels from renewable sources for road transportation, are being considered to limit our dependency on fossil fuels and control CO_2 emissions. Among these, biodiesel is now seen as a good alternative to conventional diesel. Its price and properties are acceptably close to petroleum-based diesel, so that it is possible to mix it with regular diesel with no motor changes being required. Besides being produced from renewable sources, it is biodegradable, is nontoxic, and has lower emission profiles, thereby being more environmentally beneficial.[1]

Biodiesel consists normally of a blend of fatty acid methyl esters (FAMEs), although alternatively other alcohols may be used in the esterification process. The most commonly used method to produce biodiesel is the transesterification of vegetable oils and animals fats with monohydric alcohols using a homogeneous basic catalyst such as NaOH.

Initially, the biodiesel advantages were discredited by the poor quality of the fuel produced that originated engine problems and, consequently, a low acceptance among consumers. The European Committee for Standardization (CEN) developed quality standards specifying minimum requirements and test methods for biodiesel to be used in diesel engines and for heating purposes, to increase the biodiesel quality and its acceptance. One of these quality values is the water content, which the DIN EN 14214:2003 limits to the maximum value of 0.05% (w/w).

Water is introduced into biodiesel during the production process and may remain in it if the drying procedure is not efficient. It can also be absorbed during storage, since FAMEs are hygroscopic compounds, making the biodiesel much more hydrophilic than the regular diesel. The amount of water in biodiesel affects its calorific value and, above all, the shelf life of the fuel, since biodiesel with a high water content clearly has a lower oxidation stability. The lower the oxidation stability, the larger is the probability that oxidation products will be formed during long storage periods. These can cause engine problems particularly within the injection system (blocking due to deposits formed and also wearing of the zinc and chrome parts). The presence of water can also cause biological growth and can cause the esters to react, producing soaps and, consequently, modifying the biodiesel composition and lowering its quality.[2,3]

The capacity to describe the water solubility in fatty acid ester systems and biodiesels is, therefore, important to ensure the fuel quality during production. However, there is still a lack of experimental data of water solubility in fatty acid esters and biodiesels that hampers the development of models to describe this property. To overcome this limitation, measurements were carried our for 11 esters and 6 commercial biodiesels in the temperature range of 288.15−323.15 K.

Some previous approaches to the modeling of ester systems can be found in the literature. Quantitative structure–property relationships (QSPR) were developed using a genetic-algorithm-based variable-selection approach with quantum chemical descriptors, to efficiently describe the aqueous solubility of 71 sulfur-containing aromatic esters.[4] The UNIFAC model provided good predictions for the VLE of binary mixtures of propyl/methyl esters and alkan-1-ols and also for the liquid−liquid equilibrium (LLE) of ternary systems with water, acids, and esters.[5–7] The nonrandom two-liquid model (NRTL) was used to correlate the LLE of aqueous ternary mixtures containing esters, methanol,[8] or 2-propanol[9] and the vapor−liquid equilibrium (VLE) of binary mixtures with ethanol and methyl esters.[10]

Bureau et al.[11] applied several cubic equations of state to model the phase equilibria of methane + long ester systems. They found

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10.1021/ie800018x CCC: $40.75
Published on Web 05/17/2008

Table 1. Experimental Results for the Water Solubility in Alkyl Esters

T/K	($x_{H_2O} \pm \sigma^a$)	T/K	($x_{H_2O} \pm \sigma^a$)	T/K	($x_{H_2O} \pm \sigma^a$)
ethyl butanoate		propyl butanoate		methyl hexanoate	
288.2	0.0504 ± 0.0003	288.15	0.0445 ± 0.0002	288.2	0.0414 ± 0.0005
293.2	0.056 ± 0.001	293.15	0.045 ± 0.004	293.2	0.0452 ± 0.0008
298.2	0.060 ± 0.002	298.15	0.051 ± 0.002	298.2	0.0497 ± 0.0003
303.2	0.0644 ± 0.0004	303.15	0.05370 ± 0.00003	303.2	0.0531 ± 0.0003
308.2	0.0694 ± 0.0001	308.15	0.0581 ± 0.0003	308.2	0.0567 ± 0.0002
313.2	0.0741 ± 0.0004	313.15	0.0623 ± 0.0005	313.2	0.0597 ± 0.0003
318.2	0.0770 ± 0.0005	318.15	0.0654 ± 0.0006	318.2	0.0628 ± 0.0008
methyl heptanoate		methyl octanoate		ethyl decanoate	
288.2	0.035 ± 0.001	288.2	0.0313 ± 0.0001	288.2	0.0243 ± 0.0005
293.2	0.0379 ± 0.0004	293.2	0.0341 ± 0.0005	293.2	0.0270 ± 0.0011
298.2	0.0412 ± 0.0004	298.2	0.0381 ± 0.0002	298.2	0.0302 ± 0.0004
303.2	0.0446 ± 0.0001	303.2	0.0401 ± 0.0005	303.2	0.0327 ± 0.0004
308.2	0.0495 ± 0.0007	308.2	0.0446 ± 0.0004	308.2	0.0351 ± 0.0002
313.2	0.053 ± 0.001	313.2	0.0461 ± 0.0005	313.2	0.0370 ± 0.0008
318.2	0.0568 ± 0.0008	318.2	0.049 ± 0.001	318.2	0.0405 ± 0.0008
methyl dodecanoate		methyl tetradecanoate		methyl hexadecanoate	
288.2	0.0234 ± 0.0003				
293.2	0.02511 ± 0.0002	293.2	0.0223 ± 0.0002		
298.2	0.0289 ± 0.0002	298.2	0.0242 ± 0.0003		
303.2	0.0306 ± 0.0001	303.2	0.0270 ± 0.0002		
308.2	0.03351 ± 0.00003	308.2	0.0298 ± 0.0004	308.2	0.0295 ± 0.0002
313.2	0.0354 ± 0.0002	313.2	0.0324 ± 0.0003	313.2	0.0315 ± 0.0004
318.2	0.0382 ± 0.0005	318.2	0.0344 ± 0.0002	318.2	0.0322 ± 0.0002
323.2	0.0415 ± 0.0004	323.2	0.0367 ± 0.0004	323.2	0.0331 ± 0.0002
methyl octadecanoate		methyl oleate			
		288.2	0.0209 ± 0.0002		
		293.2	0.0207 ± 0.0001		
		298.2	0.0223 ± 0.0001		
		303.2	0.0246 ± 0.0001		
		308.2	0.0274 ± 0.0002		
313.2	0.0298 ± 0.0007	313.2	0.0304 ± 0.0001		
318.2	0.0325 ± 0.0005	318.2	0.0353 ± 0.0005		
323.2	0.035 ± 0.003	323.2	0.0390 ± 0.0006		

[a] Standard deviation.

Table 2. Experimental Results for the Water Solubility in Commercial Biodiesels

biodiesel A		biodiesel B		biodiesel C		biodiesel D	
T/K	($x_{H_2O} \pm \sigma^a$)	T/K	($x_{H_2O} \pm \sigma^a$)	T/K	($x_{H_2O} \pm \sigma^a$)	T/K	($x_{H_2O} \pm \sigma^a$)
288.2	0.0225 ± 0.0002	288.2	0.0220 ± 0.0006	288.2	0.0236 ± 0.0005	288.2	0.0217 ± 0.0006
293.2	0.0248 ± 0.0003	293.2	0.024 ± 0.002	293.2	0.026 ± 0.001	293.2	0.024 ± 0.001
298.2	0.0270 ± 0.0005	298.2	0.0262 ± 0.0001	298.2	0.0282 ± 0.0006	298.2	0.026 ± 0.005
303.2	0.030 ± 0.006	303.2	0.029 ± 0.002	303.2	0.032 ± 0.005	303.2	0.028 ± 0.001
308.2	0.034 ± 0.001	308.2	0.03217 ± 0.00001	308.2	0.0330 ± 0.0002	308.2	0.0323 ± 0.0005
313.2	0.038 ± 0.004	313.2	0.038 ± 0.005	313.2	0.0356 ± 0.0003	313.2	0.035 ± 0.005
318.2	0.043 ± 0.004	318.2	0.042 ± 0.005	318.2	0.039 ± 0.006	318.2	0.039 ± 0.002

biodiesel E		biodiesel F	
T/K	($x_{H_2O} \pm \sigma^a$)	T/K	($x_{H_2O} \pm \sigma^a$)
288.2	0.0223 ± 0.0004	288.2	0.0209 ± 0.0007
293.2	0.026 ± 0.003	293.2	0.023 ± 0.004
298.2	0.0274 ± 0.0002	298.2	0.025 ± 0.002
303.2	0.029 ± 0.002	303.2	0.02755 ± 0.00001
308.2	0.0325 ± 0.0002	308.2	0.0307 ± 0.0005
313.2	0.036 ± 0.002	313.2	0.033 ± 0.003
318.2	0.041 ± 0.005	318.2	0.037 ± 0.003

[a] Standard deviation.

that the coupling of the Soave−Redlich−Kwong (SRK) equation of state with the MHV2 and (UNIFAC) mixing rule gives very poor results while the Peng–Robinson (PR) equation of state using binary interaction parameters equal to zero gives the best results for low pressures but poor ones for high pressures. For these conditions, the Elliott−Suresh−Donohue equation of state (EoS) provided much better predictions. The Peng–Robinson and Soave−Redlich−Kwong equations of state with various types of mixing rules were used as well to satisfactorily correlate the VLE of mixtures of CO_2 with esters.[12–14]

Skjold-Jørgensen developed a GC-EoS through the combination of four equations and principles in phase equilibrium thermodynamics: the van der Waals equation of state, the Carnahan–Starling expression for hard spheres, the NRTL equation, and the group-contribution principle.[15] This model

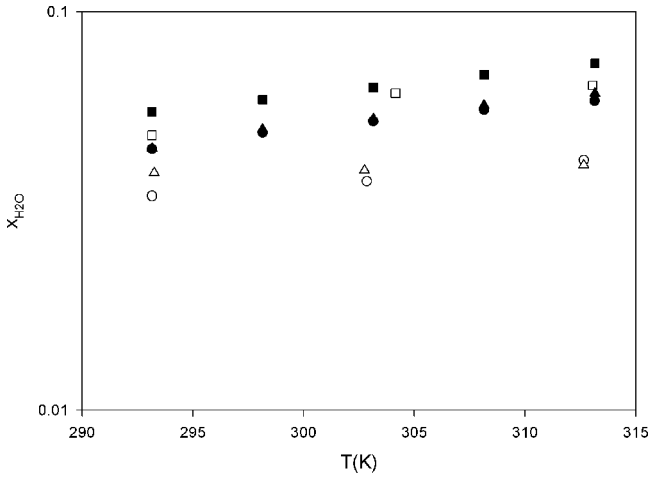

Figure 1. Experimental water solubility from this work (full symbols) and reported in the literature (empty symbols), in ethyl butanoate (■, □), in methyl hexanoate (•, o), and in propyl butanoate (▲, Δ).

was mainly applied to model high-pressure phase equilibria in mixtures of fatty oils and alkyl esters with supercritical fluids.[16]

Gros et al.[17] extended the GC-EoS model to associating systems by the inclusion of a group-contribution associating term and applied it to the modeling of mixtures of fatty oils and their derivatives (fatty acids, fatty acid esters, mono- and diglycerides) with supercritical solvents like carbon dioxide or propane.[18]

When water is involved, association equations of state are required for the description of the systems, since the general cubic equations of state such as the SRK and the PR EoS's are not able to take into account the association between two molecules of water or the solvation between glycols, aromatic hydrocarbons, esters, and water. Among these associating equations are the statistical associating fluid theory (SAFT)[19] and the cubic-plus-association (CPA) equations of state.[20,21] Recently, two versions of the GC-SAFT EoS based on the original SAFT and SAFT-VR were developed and applied to esters.[22]

A group-contribution version of the simplified PC-SAFT was also developed for several families of nonassociating compounds (alkanes, aromatics, esters, etc.) and used to successfully model the vapor–liquid phase equilibria of their mixtures.[23] None of these works deal, however, with the water solubility in fatty acid esters.

The cubic-plus-association equation of state (CPA EoS) combines the Soave−Redlich−Kwong (SRK) cubic contribution for describing the physical interactions with the association contribution proposed by Wertheim.[24] CPA was previously shown to be able to provide an accurate description of the mutual solubilities of binary mixtures of water and hydrocarbons.[25–27] It was also successfully applied to cross-association mixtures such as water−alcohol[28,29] and water−glycol,[30] and it can take into account the solvation phenomena occurring between water and aromatic hydrocarbons, olefinic hydrocarbons,[31] and aromatic perfluorocarbons.[32]

In this work, the ability of the CPA EoS to model the water solubility in several binary aqueous mixtures with methyl, ethyl, and propyl fatty acid esters will be investigated. A cross-association between the ester group and water was considered as was previously done for aromatic hydrocarbons,[32] and the k_{ij} values are shown to follow a linear trend with the carbon number. The water solubility in biodiesel can be adequately predicted using a correlation for the interaction parameters obtained from the binary mixtures studied.

2. Experimental Section

Materials. The water solubility was measured in the following esters: ethyl butanoate (Fluka, ≥98%), propyl butanoate (Fluka, ≥99%), methyl hexanoate (SAFC, ≥99%), methyl heptanoate (Fluka, ≥99%), methyl octanoate (Fluka, ≥99%), ethyl decanoate (Fluka, ≥99%), methyl dodecanoate (SAFC, >98%), methyl tetradecanoate (SAFC, >98%), methyl hexadecanoate (SAFC, 97%), methyl octadecanoate (Fluka, ≥99%), and methyl oleate (Aldrich, 99%). The water solubility in six commercial biodiesels provided by GALP was also measured.

Experimental Procedure. The water solubility measurements were carried out at temperatures from 288.15 to 323.15 K and at atmospheric pressure. The methodology adopted in this work has been previously used for other organic compounds at our laboratory.[33–35] The ester and the water phases were initially agitated vigorously and allowed to reach the saturation equilibrium by the separation of both phases in 20 mL glass vials for at least 48 h. This period proved to be the minimum time required to guarantee a complete separation of the two phases and that no further variations in mole fraction solubilities occurred.

The temperature was maintained by keeping the glass vials containing the phases in equilibrium inside an aluminum block specially designed for this purpose, which is placed in an isolated air bath capable of maintaining the temperature within (±0.01 K). The temperature control was achieved with a proportional−integral−derivative (PID) temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminum block. In order to reach temperatures below room temperature, a Julabo circulator, model F25-HD, was coupled to the overall oven system, allowing the passage of a thermostatized fluid flux around the aluminum block. The solubility of water in the ester rich phase was determined using a Metrohm 831 Karl Fischer (KF) coulometer.

The ester rich phase was sampled at each temperature from the equilibrium vials using glass syringes that were maintained dry and at the same temperature of the measurements. Samples of 0.1−0.2 g were taken and injected directly into the KF coulometric titrator. The water solubility results at each individual temperature are an average of at least five independent measurements.

3. Model

The CPA equation of state can be expressed as the sum of two contributions: one accounting for physical interactions, which in the current work is taken as the SRK EoS, and another accounting for association, the Wertheim association term,[24,26,36]

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

where a is the energy parameter, b is the covolume parameter, ρ is the density, g is the simplified radial distribution function,[28] X_{Ai} is 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 of CPA has a Soave-type temperature dependency,

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

Table 3. CPA Pure-Compound Parameters and Modelling Results

family	compound	a_0	c_1	b	AAD % P^σ	AAD % ρ
methyl esters	C_2COOC[41]	1.8506	0.9557	8.1288E-05	2.78	1.20
	C_3COOC[41]	2.3522	0.9759	9.8316E-05	1.65	1.02
	C_8COOC[43]	5.4452	1.2128	1.8451E-04	1.63	
	C_9COOC[41]	5.9540	1.3237	2.0425E-04	1.82	1.29
	$C_{10}COOC$[43]	6.8030	1.3220	2.2240E-04	3.64	
	$C_{11}COOC$[41]	7.4563	1.3712	2.4041E-04	0.80	1.31
	$C_{12}COOC$[42]	8.1607	1.4347	2.5988E-04	0.46	
	$C_{13}COOC$[42]	8.8395	1.5074	2.7951E-04	3.66	
	$C_{14}COOC$[42]	9.5184	1.5597	2.9818E-04	1.66	
	$C_{15}COOC$[42]	10.2544	1.5832	3.1389E-04	6.80	
	$C_{16}COOC$[42]	10.9475	1.6534	3.3230E-04	4.76	
	$C_{17}COOC$[42]	11.6406	1.7176	3.5070E-04	3.53	
ethyl esters	C_2COOC_2[41]	2.3480	0.9927	9.8182E-05	0.64	0.66
	C_3COOC_2[41]	2.9571	0.9033	1.1556E-04	0.91	1.18
propyl esters	C_2COOC_3[41]	2.8515	1.0123	1.1579E-04	1.48	1.26
	C_3COOC_3[41]	3.4243	1.0046	1.3226E-04	1.04	1.73
butyl esters	C_2COOC_4[41]	3.3900	1.1064	1.3314E-04	0.33	1.06
	C_3COOC_4[41]	4.0173	1.1260	1.5299E-04	3.66	2.02
	C_4COOC_4[41]	4.5473	1.2651	1.6876E-04	0.27	1.20
	C_8COOC_4[41]	7.5301	1.1118	2.4252E-04	3.78	2.17
formates	$HCOOC$[41]	1.0393	0.8190	4.9680E-05	1.95	1.62
	$HCOOC_2$[41]	1.4557	0.8405	6.6506E-05	0.37	0.59
	$HCOOC_3$[41]	1.8771	0.9468	8.2539E-05	3.05	0.73
	$HCOOC_4$[41]	2.3936	0.9648	9.9354E-05	0.2	0.62
	$HCOOC_5$[41]	3.0040	1.0185	1.1792E-04	1.69	1.70
	$HCOOC_6$[41]	3.4688	1.1202	1.3323E-04	0.4	0.65
	$HCOOC_7$[41]	4.2287	1.0560	1.5258E-04	2.81	1.44
	$HCOOC_8$[41]	5.0661	0.9747	1.6997E-04	2.27	2.04
	$HCOOC_9$[41]	5.4631	1.1793	1.8795E-04	2.89	1.72
	$HCOOC_{10}$[41]	6.1485	1.2265	2.0461E-04	3.35	1.97
acetates	$CCOOC$[41]	1.4581	0.8949	6.6792E-05	0.82	1.87
	$CCOOC_2$[41]	1.8790	0.9474	8.1881E-05	1.39	0.70
	$CCOOC_3$[41]	2.3361	1.0311	9.9573E-05	2.90	0.87
	$CCOOC_4$[41]	2.9069	1.0261	1.1629E-04	0.82	1.84
	$CCOOC_5$[41]	3.4448	1.0782	1.3365E-04	2.61	0.91
	$CCOOC_6$[41]	4.0822	1.1282	1.5166E-04	0.38	1.35
	$CCOOC_7$[41]	4.7416	1.1271	1.6603E-04	0.79	1.39
	$CCOOC_8$[41]	5.1500	1.2306	1.7953E-04	0.74	0.94
	$CCOOC_9$[41]	5.9716	1.2906	2.0493E-04	5.13	2.86
	$CCOOC_{10}$[41]	6.6576	1.3692	2.2240E-04	5.68	2.36
	$CCOOC_{12}$[46]	7.3148	1.5212	2.6012E-04	1.74	
	$CCOOC_{14}$[46]	8.7248	1.5407	2.9791E-04	1.20	
unsaturated esters	$C_6C{=}CC_7COOC$[47]	9.5316	1.7179	3.0300E-04	3.46	
	$C_8C{=}CC_7COOC$[41]	10.6962	1.8649	3.3387E-04	4.81	1.74
	$C_5C{=}CCC{=}CC_7COOC$[47]	10.5436	1.9079	3.3495E-04	4.78	
	$C_2C{=}CCC{=}CCC{=}CC_7COOC$[47]	10.50627	1.9561	3.3576E-04	5.06	
global AAD %					2.32	1.39

where a_0 and c_1 are regressed (simultaneously with b) from pure-component vapor-pressure and liquid-density data. When CPA is extended to mixtures, the energy and covolume parameters of the physical term are calculated by employing the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3}$$

and

$$b = \sum_i x_i b_i \tag{4}$$

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

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_iB_j}} \tag{5}$$

where

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

where $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are the association energy and the association volume, respectively. The simplified radial distribution function, $g(\rho)$, is given by[28]

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

For nonassociating components, such as *n*-alkanes and *n*-esters, CPA has three pure-component parameters (a_0, c_1, and b), while for associating components like *n*-alcohols, it has five (a_0, c_1, b, ε, β). In both cases, parameters are regressed simultaneously from vapor-pressure and liquid-density data. The objective function used is as follows:

$$\mathrm{OF} = \sum_i^{\mathrm{NP}} \left(\frac{P_i^{\mathrm{exp.}} - P_i^{\mathrm{calc.}}}{P_i^{\mathrm{exp.}}} \right)^2 + \sum_i^{\mathrm{NP}} \left(\frac{\rho_i^{\mathrm{exp.}} - \rho_i^{\mathrm{calc.}}}{\rho_i^{\mathrm{exp.}}} \right)^2 \tag{8}$$

This approach has advantages over the conventional approach of the SRK EoS based on critical properties, since no experi-

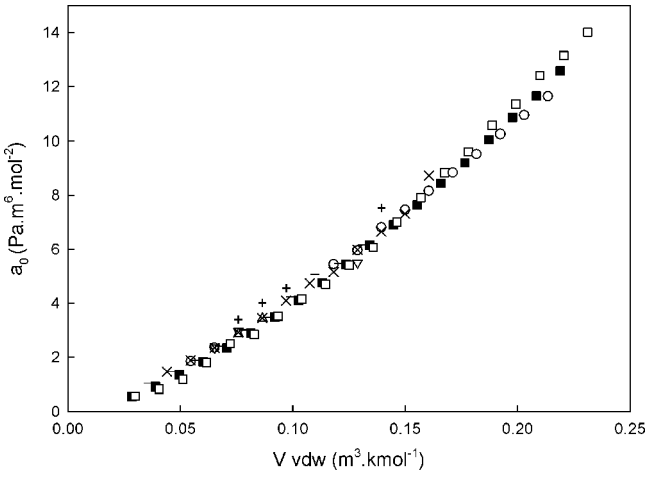

Figure 2. CPA pure-parameter a_0 trend with the van der Waals volume (■, *n*-alkanes; □, *n*-alcohols; o, methyl esters; ▽, ethyl esters; Δ, propyl esters; +, butyl esters; ×, acetates; −, formates).

mental critical properties are available for most fatty acid esters. For a binary mixture composed by a self-associating and a nonassociating compound, as, for example, the water + *n*-alkane systems, the binary interaction parameter k_{ij} is the only adjustable parameter.

When CPA is employed to mixtures containing cross-associating molecules, combining rules for the association energy and volume parameters are required.[29,31] In the particular case of the ester + water systems studied in this work, cross-association occurs even if the ester itself is not a self-associating molecule. This is different from the classical cross-associating examples where both components are self-associating.

Folas et al.[31] studied some of these binary mixtures such as water + aromatics, proposing that the cross-association energy ($\varepsilon^{A_iB_j}$) could be taken as half the water association energy and that the cross-association volume ($\beta^{A_iB_j}$) would be left as an adjustable parameter, fitted to equilibrium data. The same methodology was adopted in this work.

$$\varepsilon^{A_{ester}B_{H_2O}} = \frac{\varepsilon^{A_{H_2O}B_{H_2O}}}{2} \tag{9}$$

For estimating the k_{ij} and $\beta^{A_iB_j}$ parameters, the following objective function was employed,

$$\mathrm{OF} = \sum_{i}^{\mathrm{NP}} \left(\frac{x_i^{\mathrm{calc.}} - x_i^{\mathrm{exp.}}}{x_i^{\mathrm{exp.}}} \right)^2 \tag{10}$$

where single-phase or all-phase data can be selected during the parameter optimization. In this work, only the ester rich phase was studied.

Equation 5 shows that the association term depends on the number and type of association sites. For water, a four-site (4C) association scheme is adopted, considering that hydrogen bonding occurs between the two hydrogen atoms and the two lone pairs of electrons in the oxygen of the water molecule.[37] For alcohols, the two-site (2B) or the three-site (3B) association schemes may be applied. The results from Huang et al.[37] and from Kontogeorgis et al.[38] suggest the use of the 2B scheme for alcohols, which proposes that hydrogen bonding occurs between the hydroxyl hydrogen and one of the lone pairs of electrons from the oxygen atom in another alcohol molecule. For the ester family, a single association site is considered (the ester group), cross-associating with water.

4. Results and Discussion

The water solubility results in 11 esters and 6 commercial biodiesels in the temperature range 288.15−318.15 K are listed in Tables 1 and 2, as well as their respective standard deviations.

Data concerning the water solubility in esters is scarce but can still be found for the smaller esters.[39,40] The results presented in this work are in agreement with the available literature data, as seen in Figure 1, showing the ability of the experimental methodology used for measuring the water solubility in heavier esters and commercial biodiesels. The results show that the water solubility in fatty acid esters decreases with the decrease in polarity (thus, with increasing chain length) of the ester and increases with the ester insaturation.

Experimental measurements are time-consuming and often expensive, making it, therefore, useful to develop thermodynamics models able to predict that data. In this work, the CPA EoS will be used to model the water solubility in ester systems.

The *n*-alkanes are nonassociating compounds, and therefore, there are only three parameters of the physical part of EoS to be estimated. The *n*-alcohols are self-associating, and two more parameters are required: the association volume and the energy. In both cases, a simultaneous regression of the selected vapor-pressure and saturated liquid-density data is used for their estimation. In a previous work, results for the pure-compound parameters for these two families were presented as well as their overall deviations in the description of the vapor pressures and liquid densities.[41]

The compounds of the ester family studied in this work are all non-self-associating. In the DIPPR database,[42] vapor-pressure and saturated liquid-density data were available for 12 methyl esters, 2 ethyl esters, 2 propyl esters, and 4 butyl esters, as well as for 12 acetates and 10 formates, allowing us to study esters from 2 to 19 carbons atoms, covering the range of reduced temperatures from 0.45 to 0.85. An excellent description of the experimental vapor pressure and liquid densities is achieved with CPA, with global average deviations of 2.3% and 1.4%, respectively. The pure-compound parameters are reported in Table 3.

In a previous work,[41] it was shown that the a_0, c_1, and b CPA parameters of the *n*-alkanes and *n*-alcohols followed a trend within each homologous series, allowing the equation of state to be used as a predictive tool for these families of compounds in the absence of vapor-pressure and liquid-density data. Quadratic and linear correlations for the estimation of these parameters were then proposed. The same result was here observed for the esters studied, as seen in Figures 2, 3, and 4, where the pure-compound parameters are plotted against the van der Waals volume. For the a_0 and b parameters, similar trends to the ones for the *n*-alkane and *n*-alcohol families were observed.

It was also possible to see that esters with the same carbon number have very similar values for the pure-compound parameters, especially for a_0 and c_1, whether they were methyl, ethyl, propyl or butyl esters, acetates, or even formates.

Long-chain methyl esters and acetates were also evaluated. Vapor-pressure data was available for these heavier methyl esters[43,44] (C_{10}, C_{12}, and C_{14}−C_{19}), in temperature ranges between 271.4 and 430.0 K, and the set of regressed pure-compound parameters, which followed the trends of the lighter esters, are reported in Table 3. The critical temperatures were estimated through the Nikitin et al.[45] model that was previously assessed and found to be the most appropriate one for fatty acid esters.[46] The same approach was used for the long-chain acetates

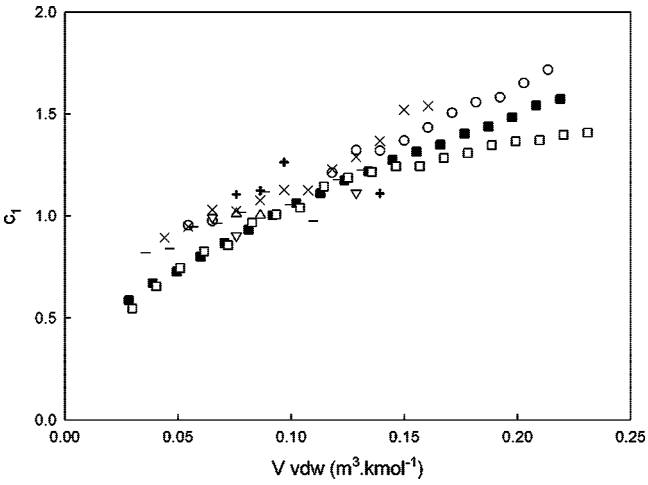

Figure 3. CPA pure-parameter c_1 trend with the van der Waals volume (■, *n*-alkanes; □, *n*-alcohols; o, methyl esters; ▽, ethyl esters; Δ, propyl esters; +, butyl esters; ×, acetates; −, formates).

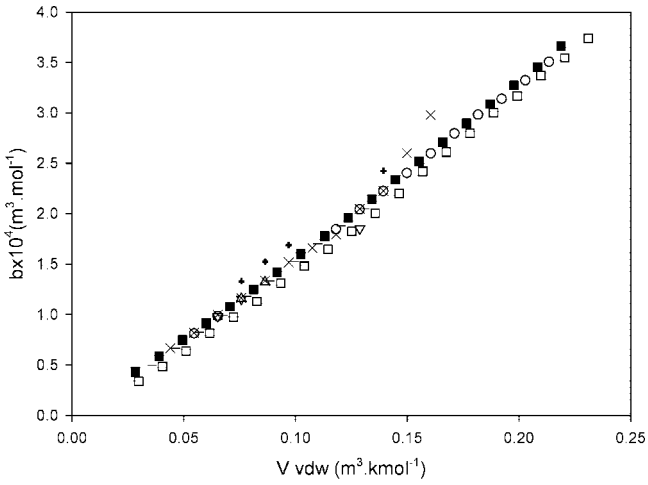

Figure 4. CPA pure-parameter *b* trend with the van der Waals volume (■, *n*-alkanes; □, *n*-alcohols; o, methyl esters; ▽, ethyl esters; Δ, propyl esters; +, butyl esters; ×, acetates; −, formates).

(C_{14} and C_{16}), where experimental data in the temperature range 288.9–320.3 K were available.[47]

Unsaturated esters that are commonly present in biodiesel blends were also studied. Following a previous work,[46] the best group-contribution model to critical temperatures was that proposed by Ambrose.[45] Vapor pressures were available in the 290–450 K range,[48] and once again, the set of pure-compound parameters that better described these data were obtained and are presented in Table 3.

After the pure-compound parameters were estimated, it was possible to model the presented experimental data for the water solubility in several methyl, ethyl, and propyl esters (ethyl butanoate, propyl butanoate, methyl hexanoate, methyl heptanoate, methyl octanoate, ethyl decanoate, methyl dodecanoate, methyl tetradecanoate, methyl hexadecanoate, and methyl octadecanoate). An aqueous mixture with the unsaturated ester methyl oleate was also studied. For methyl octanoate, methyl hexanoate, methyl heptanoate, and ethyl decanoate, no vapor-pressure and liquid-density data was available, and so their pure-compound parameters were considered to be equal to the ones of the ester with the same carbon number.

As mentioned above in the description of the model, the cross-association between the ester group and water was taken into account as previously done for aromatic hydrocarbons,[31] and

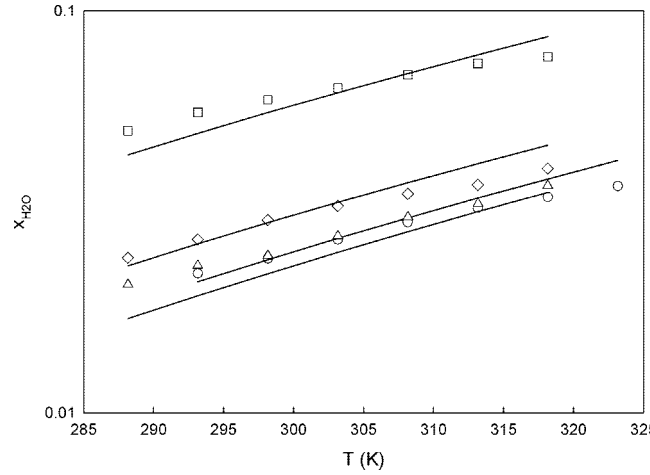

Figure 5. Water solubility in ethyl butanoate (□, experimental; (−), CPA regressed parameters), in methyl tetradecanoate (o, experimental; (−), CPA regressed parameters), in ethyl decanoate (◇, experimental; (−), CPA regressed parameters), and in Biodiesel F (Δ, experimental; (−), CPA regressed parameters).

Table 4. Deviations in the Mole Fraction Water Solubility from CPA and Respective Binary Interaction Parameters (with β_{ij} = 0.201)

no. carbons	compounds	k_{ij}	AAD %
6	ethyl butanoate	−0.254	7.42
7	propyl butanoate	−0.238	6.97
7	methyl hexanoate	−0.234	7.38
8	methyl heptanoate	−0.221	6.00
9	methyl octanoate	−0.210	7.52
12	ethyl decanoate	−0.166	6.40
13	methyl dodecanoate	−0.150	7.39
15	methyl tetradecanoate	−0.123	6.44
17	methyl hexadecanoate	−0.092	9.35
19	methyl octadecanoate	−0.075	3.10
19	methyl oleate	−0.100	4.27
	global AAD %		6.57

the solvation scheme involving combining rules for the cross-association energy and volume parameters was used. Using this approach, and in a first attempt, both the binary interaction k_{ij} and the cross-association β_{ij} parameters were fitted to the experimental water solubility data shown in Table 1. If the solvation phenomena is not considered, the water solubility is strongly underestimated.

As expected, since the cross-association between water and esters will always occur between water and the ester group, the majority of the regressed values for β_{ij} were close to 0.201. Therefore, this parameter was fixed to that value, and the k_{ij}'s were then refitted.

A generalized linear correlation for the k_{ij} binary interaction parameter was found with the chain length of the ester, C_n, described by eq 11. This linear dependency with the solvent chain length had been previously observed in studies involving the phase equilibria of water + *n*-alkane systems.[27]

$$k_{ij} = 0.0136 \times C_n - 0.3322 \tag{11}$$

With this single value of k_{ij} for each system, it was possible to describe the water solubility with a global average deviation less than 7.0%. Values for the binary interaction parameters and average deviations are presented in Table 4.Water solubility in the ethyl butanoate, ethyl decanoate, and methyl tetradecanoate rich phases is presented as an example in Figure 5.

For the methyl oleate system, the same value for β_{ij} was used, but the regressed k_{ij}'s do not fit in the linear dependency with the carbon number determined for the saturated methyl esters;

Table 5. Compositions of the Studied Biodiesels and Mole Fraction Water Solubility Deviations from CPA

compound	biodiesel A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	global AAD %
methyl hexadecanoate	1.90	10.90		9.80	6.37	6.07	
methyl linoleate	60.30	32.60	13.75	2.20	30.90	22.47	
methyl oleate	37.80	56.20	86.19	87.40	60.65	63.78	
methyl octadecanoate		0.30		0.10	2.07	1.30	
AAD x_{H_2O}%	18.59	15.84	18.36	13.33	16.89	9.83	15.47

however, this set of optimized binary parameters still provides a very good description of the water solubility, with global average deviations smaller than 5%, as shown in Table 4.

The new experimental data for the water solubility in six biodiesels, whose compositions were measured by GC-MS and are reported in Table 5, were predicted using the proposed approach to evaluate the model performance for these real systems. Only binary interaction parameters for ester + water were considered, with the k_{ij}'s for ester + ester being set to zero. The binary interaction parameter correlation and the constant cross-association volume here proposed were used. For the binary system linoleate + water, we used the same value for the k_{ij} as the one estimated for the oleate + water mixture. Good results were obtained with global average deviations of 15.5%, as presented in Table 5, thus showing the adequacy of the proposed model for the prediction of the water solubility in biodiesels. The water solubility in the biodiesel F rich phase is presented in Figure 5.

5. Conclusions

New experimental data for the water solubility in 11 fatty acid esters (ethyl butanoate, propyl butanoate, methyl hexanoate, methyl heptanoate, methyl octanoate, ethyl decanoate, methyl dodecanoate, methyl tetradecanoate, methyl hexadecanoate, methyl octadecanoate, and methyl oleate) and in 6 commercial biodiesels was presented in a wide temperate range.

This novel data was correlated with the cubic-plus-association equation of state (CPA EoS). A single, small, and temperature-independent binary interaction parameter was sufficient, and a constant value for the cross-association volume was adopted. A chain-length-dependent correlation for the binary interaction parameters is proposed, making the model predictive.

The CPA EoS can take into account the strong polar interactions between esters and water, describing the water solubility in binary ester systems, with global average deviations less than 7%, and predicting it in six different biodiesels with global deviations smaller than 16%.

The model used seems to be a promising tool for the biodiesel industry, and future work will focus in extending this approach to other systems of interest for biodiesel production and purification.

Acknowledgment

Financial support for this work was provided by the national research project POCI/EQU/58239/2004, "*Equilibrium and Interfacial Properties of Water + Oil Systems*", and by LSRE financing by FEDER/POCI/2010, for which the authors are thankful. M.B.O. acknowledges the financial support from *Fundação para a Ciência e a Tecnologia* through her Ph.D. (SFRH/BD/29062/2006) scholarship. A.J. Queimada acknowledges financial support from POCI/N010/2006. The authors also gratefully acknowledge Dr. Jorge Correia Ribeiro from GALP for providing the biodiesels samples used in this work.

Nomenclature

List of Abbreviations

AAD = average absolute deviation
CPA = cubic-plus-association
EoS = equation of state
FCs = fluorocarbons
G^E = excess molar Gibbs energy
LLE = liquid–liquid equilibria
MHV2 = second-order modified Huron−Vidal mixing rules
NRTL = nonrandom two liquid
PR = Peng–Robinson
SAFT = statistical associating fluid theory
SRK = Soave−Redlich−Kwong
UNIFAC = universal functional activity coefficient model

List of Symbols

a = energy parameter in the physical term
a_0, c_1 = parameters for calculating a
A_i = site A in molecule i
b = covolume
g = radial distribution function
k_{ij} = binary interaction parameters
P = vapor pressure
R = gas constant
T = temperature
x = mole fraction
X_A = fraction of molecule not bonded at site A
Z = compressibility factor

Greek Symbols

β = association volume
ε = association energy
η = reduced fluid density
ρ = mole density
Δ = association strength

Subscripts

i,j = pure-component indexes
liq. = liquid
r = reduce

Superscripts

assoc. = association
phys. = physical

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Received for review January 4, 2008
Revised manuscript received March 3, 2008
Accepted March 11, 2008

IE800018X