AIChE

Description of the Mutual Solubilities of Fatty Acids and Water With the CPA EoS

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DOI 10.1002/aic.11766

Data for the mutual solubilities of fatty acid + water mixtures are scarce and so measurements for seven fatty acid (C_5-C_{10}, C_{12}) + water systems were carried out. This new experimental data was successfully modelled with the cubic plus association EoS. Using data from C_6 to C_{10} and the Elliot's cross-associating combining rule a correlation for the k_{ij} binary interaction parameter, as a function of the acid chain length, is proposed. The mutual solubilities of water and fatty acids can be adequately described with average deviations inferior to 6% for the water rich phase and 30% for the acid rich phase. Furthermore, satisfactory predictions of solid-liquid equilibria of seven fatty acids (C_{12}-C_{18}) + water systems were achieved based only on the k_{ij} correlation obtained from liquid–liquid equilibria data. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1604–1613, 2009

Keywords: biodiesel, CPA EoS, fatty acids, mutual solubilities, water

Introduction

Fatty acids are important commodities with an increasing wide range of industrial applications.[1] Widespread use can be found in different products, such as: household and industrial cleaners, coatings and adhesives, paints, personal care products, pharmaceuticals, cosmetics, industrial lubricants, corrosion inhibitors, polymers, textiles, foods, paper, crayons, candles, and waxes. Particular applications of some specific fatty acids can be found elsewhere.[1] Fatty acids can also be used as raw materials for fatty alcohols and biodiesel production.[1,2]

Although the chain length limits used to define fatty acids are not strict, these are typically higher chain length aliphatic carboxylic acids with 6–24 carbon atoms. According to

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literature, the worldwide production capacity for fatty acids in 2001 was around 4×10^6 metric tons.[1]

Although shorter chain length carboxylic acids are usually produced synthetically, most of the fatty acids are obtained from natural oils and fats by hydrolysis (chemical or enzymatic). Hydrolysis converts the oil or fat (a triglyceride) into three fatty acid molecules and glycerol, usually at high temperature and high pressure conditions, using about 30–60% water in a fatty acid weight basis. In some cases, acid washing is performed before the hydrolysis reaction to remove impurities. After hydrolysis, different purification processes can be employed, among them crystallization (typically with methanol or acetone), solvent extraction (either liquid–liquid or supercritical fluid extraction) distillation and adsorption. Distillation removes colour and odour bodies,[3] low boiling unsaponifiable materials, polymerized materials, triglycerides and heavy decomposition products. Other separation processes include hydrophilization, panning and pressing and formation of solid urea complexes.[1]

Although fatty acids may be used for biodiesel production, transesterification is the most frequently used[4] method for producing biodiesel from vegetable oils, tallow or waste cooking oils.[5] It consists on the reaction of an oil or fat with an alcohol to form fatty esters with glycerol as a byproduct. A catalyst is necessary to increase reaction rate and yield and basic catalysts are preferred due to higher reaction rates and lower process temperatures.[6] Methanol and ethanol can be used as alcohols in the reaction, but methanol is preferred due to its low cost and physical and chemical advantages in the process.[4,7]

In the biodiesel production process the fatty esters rich current coming from the reactor is saturated with glycerol, alcohol, catalyst, and unreacted soaps. This current is washed in a liquid–liquid extractor in counter current with acidified water to neutralize the catalyst and to convert soaps to free fatty acids. The raffinate current is composed of water saturated biodiesel while the extract is a low pH aqueous solution containing the polar compounds.[8] The design and optimization of the purification of biodiesel with water requires a model that can describe this phase equilibria.

Despite the importance of the phase equilibria of fatty acid + water systems, there is a lack of experimental data for their mutual solubilities. To overcome this limitation, measurements were carried out for the water solubility in six fatty acids and the complete phase diagrams were established for pentanoic, hexanoic and dodecanoic acids.

Several models have been previously applied to systems containing fatty acids with different degrees of success. Carboxylic acids can form dimers in the vapor phase as well as dimers, trimers or even oligomers in the liquid phase, which make acid mixtures highly nonideal, requiring a model able to take into account these interactions, to correctly describe their phase equilibria.

One of those approaches is the UNIFAC model. Yet, this model does not perform well when dealing with polar compounds with association, such as the water + acid systems,[9–12] because it does not take explicitly into account the association interactions present in these systems. Moreover it does not take into account the dimerization in the vapor phase. Improvements with respect to the original UNIFAC model were achieved by the addition of an association term so as to take into account the association effects. The A-UNIFAC model was satisfactorily applied to predict vapor-liquid and liquid–liquid equilibria and to compute infinite dilution activity coefficients for mixtures containing alcohols, carboxylic acids, water, esters, aromatic hydrocarbons, and alkanes.[13] Applying the A-UNIFAC model to associating systems is quite demanding since it is necessary to analyze every UNIFAC functional group to recognize the presence of associating sites.

Another thermodynamic model proposed for acid systems is the group contribution equation of state, GC-EoS developed by Skjold-Jørgensen[14] that was extended by Gros et al.[15] to mixtures of fatty oils and their derivatives (fatty acids, fatty acid esters, mono- and di-glycerides) with supercritical solvents like carbon dioxide or propane. The association model proposed by Gros et al. provided results in better agreement with the experimental data than the GC-EoS.

The coupling of a cubic equation of state (SRK) with a model that expresses the dimerization of the acid molecules was also used to correlate experimental VLE for gases in acetic acid.[16,17]

The statistical associating fluid theory (SAFT) model was used to compute phase equilibria of formic, acetic and propanoic acid binary systems with aromatic hydrocarbons.[18] The same approach was followed by Fu and Sandler[19] and their results compared to those of the simplified SAFT EoS. These two models were also used, in the same work, to correlate cross-associating systems containing acids, alcohols and water. The original SAFT model performed better than the simplified one, but none of them was able to produce a good description of aqueous systems.

The cubic plus association (CPA) EoS was used to correlate VLE and liquid–liquid equilibria (LLE) for short chain acids + aliphatic hydrocarbons, in agreement with the experimental data.[20] The extension of the application of this model to binary aqueous mixtures was only made up to acetic acid systems, with satisfactory results.[21]

As a result of our ongoing effort to develop an equation of state model for the description of the phase equilibria, relevant for the biodiesel production, in a previous work, the CPA EoS was shown to be an accurate model to describe the water solubility in fatty acid esters and commercial biodiesels.[22]

In this subsequent study, whose scope is also of interest for the biodiesel industry, the CPA EoS is applied for the first time to carboxylic acids heavier than propanoic acid (up to C_{20} for pure component properties and up to C_{18} for mixtures), and to the description of LLE and SLE of their binary mixtures with water.

In the mentioned preceding article, the CPA EoS was applied to mixtures of fatty acid esters (nonself-associating compounds) and water, while in this article mixtures of acids (self-associating compounds) and water are studied. Systems with carboxylic acids are usually strongly nonideal and considerably more difficult to model than ester mixtures.

Two different associating combining rules are here evaluated on the basis of their ability to correlate these water + fatty acid systems.

It will be shown that short chain and long chain carboxylic acids have different behavior requiring different cross-associating combining rules and that the dissociation of the acids smaller than pentanoic acid will have a major impact on their mutual solubilities with water. To correlate the mutual solubilities of water and carboxylic acids studied in this work, only binary interaction parameters (k_{ij}) in the physical part of CPA were used, and these were found to be linearly dependent on the acid chain length.

Using this dependency for the interaction parameters, SLE predictions for seven fatty acids in water will also be presented in this work.

Experimental Section

Water solubility measurements were carried in: pentanoic acid (SIGMA, ≥99%), hexanoic acid (SIGMA, ≥99.5%), heptanoic acid (FLUKA, ≥99%), octanoic acid (SIGMA, ≥99%), nonanoic acid (SIGMA, ≥99.5%) and decanoic acid (SIGMA, ≥98%), at temperatures from 288.15 to 323.15 K and at atmospheric pressure. The methodology used in this work, has previously been successfully used for other organic compounds at our laboratory.[22–25] The acid and the water phases were initially agitated vigorously and allowed to reach equilibrium by separation of both phases in 20 mL glass vials for at least 48 h. This period proved to be the 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 aluminium 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 PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminium block. 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 aluminium block. The solubility of water in the acid rich phase was determined using a Metrohm 831 Karl Fischer (KF) coulometer.

The acid rich phase was sampled at each temperature from the equilibrium vials using glass syringes kept dry and at the same temperature of the measurements. Samples of 0.1 to 0.2 g were injected directly into the KF coulometric titrator.

For pentanoic, hexanoic, and dodecanoic (SIGMA, ≥99%) acids, measurements of the phase envelope for the two phase region were made by turbidimetry. Several samples covering the entire concentration range were prepared. The mixture was heated inside a closed glass tube in a thermostatic bath up to the one phase region. On slowly cooling, the phase separation temperature was registered. The temperature assigned to the phase envelope is an average of five measurements.

For heavier acids, melting temperatures are significantly higher, what therefore prevents the measurements of solubilities in a temperature range adequate to the experimental techniques used in this work.

Model

The CPA equation of state can be described as the sum of two contributions: one accounting for physical interactions, that in the current work is taken as the SRK EoS, and another accounting for association, the Wertheim association term.[26,27]

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

where a is the energy parameter, b the covolume parameter, ρ is the 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 of CPA has a Soave-type temperature dependency:

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

where a_0 and c_1 are regressed from pure component vapor pressure and liquid density data.

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:

$$X_{A_i} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{B_j}\Delta^{A_iB_j}} \qquad (3)$$

where

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j} \qquad (4)$$

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:

$$g(\rho) = \frac{1}{1-1.9\eta} \qquad \text{where} \qquad \eta = \frac{1}{4}b\rho \qquad (5)$$

For nonassociating components, such as n-alkanes, CPA has three pure component parameters (a_0, c_1, and b) while for associating components like organic acids it has five (a_0, c_1, b, ε, β). In both cases, these parameters are regressed simultaneously from pure component experimental data. The objective function used is:

$$\text{OF} = \sum_i^{\text{NP}}\left(\frac{P_i^{\text{exp.}} - P_i^{\text{calc.}}}{P_i^{\text{exp.}}}\right)^2 + \sum_i^{\text{NP}}\left(\frac{\rho_i^{\text{exp.}} - \rho_i^{\text{calc.}}}{\rho_i^{\text{exp.}}}\right)^2 \qquad (6)$$

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:

$$a = \sum_i\sum_j x_i x_j a_{ij} \qquad a_{ij} = \sqrt{a_i a_j}\left(1-k_{ij}\right) \qquad (7)$$

and

$$b = \sum_i x_i b_i \qquad (8)$$

For a binary mixture composed by a self-associating and a nonassociating compound, as for example water + n-alkane

Table 1. Water Solubility in Fatty Acids by Karl Fisher Coulometry

	Pentanoic Acid	Hexanoic Acid	Heptanoic Acid	Octanoic Acid	Nonanoic Acid	Decanoic Acid
T/K	($x_{H_2O} \pm \sigma$*)	($x_{H_2O} \pm \sigma$*)	($x_{H_2O} \pm \sigma$*)	($x_{H_2O} \pm \sigma$*)	($x_{H_2O} \pm \sigma$*)	($x_{H_2O} \pm \sigma$*)
288.15	0.4566 ± 0.0006	0.252 ± 0.001	0.171 ± 0.001		0.1008 ± 0.0004	
293.15	0.4791 ± 0.0008	0.268 ± 0.003	0.1863 ± 0.0003	0.136 ± 0.002	0.1111 ± 0.0004	
298.15	0.4995 ± 0.0006	0.284 ± 0.002	0.196 ± 0.001	0.151 ± 0.001	0.1205 ± 0.0005	
303.15	0.508 ± 0.004	0.307 ± 0.003	0.2132 ± 0.0007	0.167 ± 0.004	0.133 ± 0.002	
308.15	0.536 ± 0.003	0.338 ± 0.003	0.2470 ± 0.0003	0.1852 ± 0.0006	0.1502 ± 0.0003	0.123 ± 0.002
313.15	0.547± 0.006	0.342 ± 0.006	0.240 ± 0.002	0.199 ± 0.004	0.1546 ± 0.0007	0.138 ± 0.005
318.15	0.562 ± 0.002	0.364 ± 0.003	0.265 ± 0.005	0.210 ± 0.004	0.171 ± 0.006	0.154 ± 0.007
323.15	0.588 ± 0.005	0.389 ± 0.003		0.229 ± 0.017		0.1686 ± 0.004

*Standard deviation

systems, the binary interaction parameter k_{ij} is the only adjustable parameter.

For cross-associating systems, combining rules for the cross-association energy, ε_{ij}, and cross-association volume, β_{ij} (or the cross-association strength, $\Delta^{A_iB_j}$) are required. Different sets of combining rules have been proposed by several authors[19,28–30]:

(i)

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_i} + \varepsilon^{B_j}}{2}, \quad \beta^{A_iB_j} = \frac{\beta^{A_i} + \beta^{B_j}}{2}, \tag{9}$$

which is referred as the CR-1 set[30]

(ii)

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_i} + \varepsilon^{B_j}}{2}, \quad \beta^{A_iB_j} = \sqrt{\beta^{A_i} + \beta^{B_j}}, \tag{10}$$

which is referred as the CR-2 set[30]

(iii)

$$\varepsilon^{A_iB_j} = \sqrt{\varepsilon^{A_i} + \varepsilon^{B_j}}, \quad \beta^{A_iB_j} = \sqrt{\beta^{A_i} + \beta^{B_j}}, \tag{11}$$

which is referred as the CR-3 set[30]

(iv)

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}}, \tag{12}$$

which is referred as the CR-4 set (or Elliot rule)[30]

CR-2 and CR-4 are the most commonly used. Only these combining rules have been found to be successful in previous applications.[27,31] CR-2 provided very good results in the modelling of the VLE of glycol + water systems,[31] the LLE and VLE of water + heavy alcohol systems[30] and the LLE of the water + amine systems[32]; on the other hand, the CR-4 approach performed better in predicting the VLE and SLE of water + small alcohols systems,[30] the VLE of small acids + water or small acids + alcohol systems,[20] the VLE of amine + alcohol[32] systems and the SLE of the MEG + water systems.[33] In this work, the CR-2 and the CR-4 were evaluated on the basis of their ability to describe LLE and SLE of water and fatty acids binary mixtures.

For the estimation of the k_{ij} parameter the objective function employed was:

$$\mathrm{OF} = \sum_{i}^{\mathrm{NP}} \left(\frac{x_i^{\mathrm{calc.}} - x_i^{\mathrm{exp.}}}{x_i^{\mathrm{exp.}}} \right)^2 \tag{13}$$

where single phase or both phase data can be selected for the parameter optimization.

The association term depends on the number and type of association sites. For water a four-site (4C) association scheme was adopted,[34] and for acids the carboxylic group is treated as a single association site (1A).

Carboxylic acids can form dimers in the vapor phase as well as dimers, trimers or even oligomers in the liquid phase. Several previous works with the CPA EoS or with some variants of the SAFT EoS had already discussed the best association scheme for organic acids.[16–20] Several association schemes were evaluated for both the gas and liquid phases (1A, 2B, and 4C). It was showed that when using the CPA EoS, the 1A scheme performs globally better than the two-site (2B) model (VLE, LLE, second virial coefficients and equilibrium constants[20]). Huang and Radosz using SAFT[18] also used the one site model for carboxylic acids such as formic, acetic, and *n*-propanoic. The same associating scheme for carboxylic acids (1A) can also be found in the article of Fu and Sandler.[19] Therefore this association scheme was adopted in this work.

Results and Discussion

Experimental results

The data for the water solubility in six fatty acids, in the temperature range 288.15–323.15 K, are listed in Table 1 as well as their respective standard deviations. Results are presented at temperatures above the melting point of each compound. The water solubility results at each individual temperature are an average of at least five independent measurements.

The experimental liquid–liquid phase envelopes for pentanoic, hexanoic and dodecanoic acids, obtained by turbidimetry, are presented in Table 2.

The results show that the water solubilities increase with temperature and decrease with chain length. The differences in water solubility between consecutive chain length acids also tend to become smaller as the chain length increases.

Data concerning the water solubility in fatty acids are scarce but can still be found for the smaller pentanoic and hexanoic acids in the temperature range 293.15–343.15 K.[35] The data measured in this work are in good agreement with the few and old available literature data, as seen in Figure 1, showing the ability of the experimental methodology used for measuring the water solubility in heavier acids.

The two experimental techniques used in this work provided very similar results for the water solubility.

Table 2. LLE Data for Pentanoic Acid + Water, Hexanoic Acid + Water and Dodecanoic Acid + Water Determined by Turbidimetry

$x_{\text{pentanoic acid}}$	$(T \pm \sigma^*)$/K	$x_{\text{hexanoic acid}}$	$(T \pm \sigma^*)$/K	$x_{\text{dodecanoic acid}}$	$(T \pm \sigma^*)$/K
0.3025	352.13 ± 0.43	0.0091	425.04 ± 0.57	0.1613	336.93 ± 0.91
0.4019	323.33 ± 0.17	0.0190	439.31 ± 0.30	0.1770	344.64 ± 0.01
0.4756	304.44 ± 0.04	0.0415	440.12 ± 0.22	0.1848	349.09 ± 0.06
0.0452	385.49 ± 0.03	0.0724	439.70 ± 0.21	0.2960	380.46 ± 0.14
0.0693	385.62 ± 0.03	0.1059	438.77 ± 0.122	0.3960	409.24 ± 0.08
0.1426	382.87 ± 0.16	0.1498	435.96 ± 0.14	0.5717	434.55 ± 0.62
0.2787	358.22 ± 0.08	0.2143	426.94 ± 0.23	0.5141	444.85 ± 0.08
0.0202	380.27 ± 0.03	0.2965	410.61 ± 0.37		
0.0306	384.38 ± 0.08	0.4346	376.35 ± 0.65		
0.2113	372.91 ± 0.13	0.4952	357.49 ± 0.07		
		0.6108	327.15 ± 0.34		

*Standard deviation.

Correlation of the CPA pure compound parameters

The organic acids studied in this work are all self-associating and so the five CPA parameters must be estimated for each compound. This was done by a simultaneous regression of vapor pressure and saturated liquid density data, collected from the DIPPR database,[36] covering the range of reduced temperatures from 0.45 to 0.85, for linear saturated carboxylic acids from 1 up to 20 carbons atoms and the unsaturated oleic acid, an important natural product with 18 carbon atoms and a double bound at carbon 9, usually referred as 18:1. The reasonability of the application of DIPPR correlations in a broad temperature range is questionable when actual experimental data is missing, and extrapolation was required in some cases, as can be seen in Table 3, where the reduced temperature ranges for which experimental data for vapor pressures and liquid densities are available from DIPPR are presented for the organic acids studied. The results reported in Table 4, show that it is possible with CPA to achieve an excellent description of the experimental (correlated) vapor pressure and liquid densities for all the studied acids, with global average deviations of about 2% for both properties.

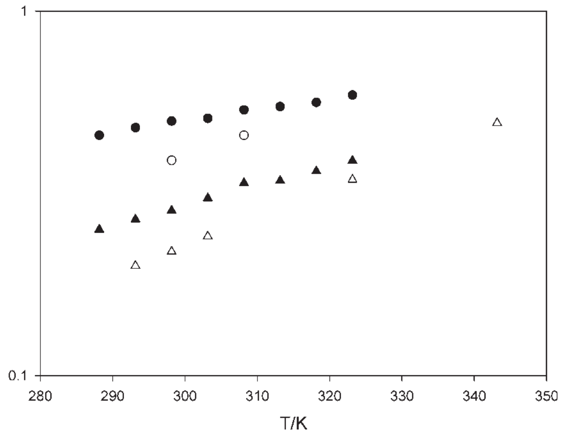

Figure 1. Experimental water solubility from this work (full symbols) and reported in the literature (empty symbols), in pentanoic acid (circles), and in hexanoic acid (triangles).

Once again, as was observed previously for several families of other compounds (*n*-alkanes, *n*-alcohols, n-FCs and esters),[22,38] the CPA pure component parameters for the acid series also seem to follow a smooth trend with the carbon number.

Having estimated the pure component parameters it was possible to model binary mixtures of water with several acids (pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, and decanoic acid). Although the solubility of these acids in water was available in the literature[39] between 298.15 and 373.15 K, little information was found for the water solubility on the acids[35] prompting the measurement of these data in this work.

Correlation of the mutual solubilities

To obtain a good description of the mutual solubilities of water and fatty acids the fitting of the binary interaction parameter k_{ij} of Eq. 7 is required. Data from both the organic

Table 3. Temperature Limits for the Experimental Data Available in DIPPR[36] for Vapor Pressures and Liquid Densities for the Organic Acids Studied

	P^{σ}		ρ	
No. of Carbons	T_r min	T_r max	T_r min	T_r max
1	0.45	0.75	0.47	0.96
2	0.46	1.00	0.46	1.00
3	0.46	0.99	0.38	1.01
4	0.47	1.00	0.44	1.01
5	0.46	0.89	0.36	0.83
6	0.43	0.81	0.41	0.84
7	0.44	0.77	0.40	0.52
8	0.52	0.78	0.42	0.83
9	0.42	0.79	0.41	0.50
10	0.55	0.79	0.42	0.77
11	0.42	0.80	0.40	0.48
12	0.51	0.81	0.39	0.63
13	0.54	0.81	0.39	0.56
14	0.43	0.84	0.38	0.75
15	0.42	0.83	0.38	0.55
16	0.43	0.84	0.37	0.73
17	0.42	0.84	0.37	0.52
18	0.43	0.99	0.36	0.71
18:01	0.37	1.00	0.37	0.58
19	0.63	0.86	0.36	0.42
20	0.44	0.86	0.35	0.45

Table 4. Critical Temperatures for Acids, CPA Pure Compounds Parameters and Average Absolute Deviations of Vapor Pressure and Liquid Densities from the CPA EoS. The "4C" Association Scheme is Considered for Water and for Acids the "1A" Scheme

							AAD%	
No. of Carbons	T_c (K)[36]	a_0 (J m^3 mol^{-2})	c_1	b × 10^5 (m^3 mol^{-1})	ε (J mol^{-1})	β	P^σ	ρ
1	605.9	0.6749	0.5466	3.24	20724.7	3.06E-01	0.47	0.97
2	594	0.8312	0.7101	4.69	33709.5	3.96E-02	2.06	1.17
3	606.9	1.4631	0.7913	6.33	30121.7	6.38E-03	0.76	0.47
4	625	2.3128	0.8554	8.50	31665.2	6.44E-04	1.05	1.6
5	645.8	2.8564	0.917	9.77	30738.5	5.58E-04	2.77	4.66
6	660.4	3.41	1.0001	11.50	37909	1.31E-04	2.56	3.02
7	677.9	4.0657	1.0333	13.40	39224.5	1.21E-04	3.52	3.00
8	693.5	4.8206	1.0883	15.30	41221.2	4.23E-05	1.42	1.68
9	708.6	5.55	1.1414	17.30	38553.3	7.71E-05	1.51	2.47
10	721.7	5.9482	1.1927	18.80	40685.3	1.34E-04	1.06	1.38
11	734.9	6.8717	1.2423	20.70	39467.1	6.97E-05	2.3	2.85
12	746	7.4908	1.2904	22.40	44385.4	3.77E-05	2.75	1.87
13	761	8.1444	1.3447	24.10	44431	3.77E-05	3.77	2.22
14	763.7	9.097	1.3822	26.00	43772.2	3.14E-05	2.57	1.95
15	778.3	9.8006	1.4419	27.80	45888.3	1.54E-05	3.78	2.29
16	788.3	10.9279	1.4689	30.70	44729.7	2.54E-05	1.98	2.04
17	801.5	11.4163	1.5105	31.50	44943.9	1.60E-05	1.30	2.70
18	808.3	12.336	1.5597	33.70	44506.6	1.99E-05	2.88	2.16
18:01	781	11.7378	1.2303	32.90	55646.4	4.71E-05	1.84	3.05
19	817.7	13.2612	1.5921	35.90	43926.7	2.54E-05	3.81	2.83
20	830	14.1516	1.6348	38.20	41738.4	4.51E-05	3.54	2.93
Water[37]	647.29	0.1228	0.6736	1.45	16655	6.92E-02	1.72	0.82
Global AAD %							2.27	2.25

$$\left(\%\mathrm{AAD} = \frac{1}{\mathrm{NP}} \sum_{i=1}^{\mathrm{NP}} \mathrm{ABS}\left[\frac{\exp_i - \mathrm{calc}_i}{\exp_i}\right] \times 100 \right)$$

and aqueous phases were used for the binary interaction parameter optimization. Values for the binary interaction parameters obtained using both combining rules under study are presented at Table 5.

To improve the predictive character of the CPA EoS, linear correlations for the k_{ij} values with the carbon number were previously proposed for alkanes + water[37] and ester + water[22] mixtures. For the heavier acids the trends of the k_{ij} values with the carbon number are also close to a linear tendency, as seen in Figure 2. The k_{ij} values for the smaller acids are somewhat off the linear tendency, particularly for pentanoic acid. Nevertheless, to increase the predictive character of the model, linear correlations of the k_{ij} with the chain length of the acid, C_n, for the two combining rules evaluated, were proposed, and described by Eqs. 14 and 15 for CR-2 and CR-4, respectively, to allow the applicability of the model for heavier acids when equilibria data are not available. The extrapolation of the linear correlation will further be shown to be successful for the description of fatty acids + water systems from C_{12} to C_{18}.

$$k_{ij} = -0.0140 \times C_n + 0.0070 \tag{14}$$

$$k_{ij} = -0.0142 \times C_n + 0.0020 \tag{15}$$

Results on the water rich phase are more dependent on the binary interaction parameter than the acid rich phase. Small variations in the k_{ij}*'s* values result in significant deviations in the description of the water rich phase with almost no

Table 5. CPA Modelling Results for the Mutual Solubilities and Binary Interaction Parameters

	CR-2			CR-4		
		AAD%			AAD%	
No. of Carbons	k_{ij}	Acid Rich Phase	Water Rich Phase	k_{ij}	Acid Rich Phase	Water Rich Phase
5	−0.0903	39.01	10.4	−0.0951	56.17	9.19
6	−0.0833	11.87	4.24	−0.0894	42.40	4.67
7	−0.0918	21.14	2.70	−0.0987	29.51	2.08
8	−0.0967	40.49	2.38	−0.1033	24.78	2.63
9	−0.1151	84.39	6.93	−0.1217	11.14	8.11
10	−0.1333	78.5	8.83	−0.1430	9.05	3.88
AAD global %		45.90	5.92		28.84	5.09

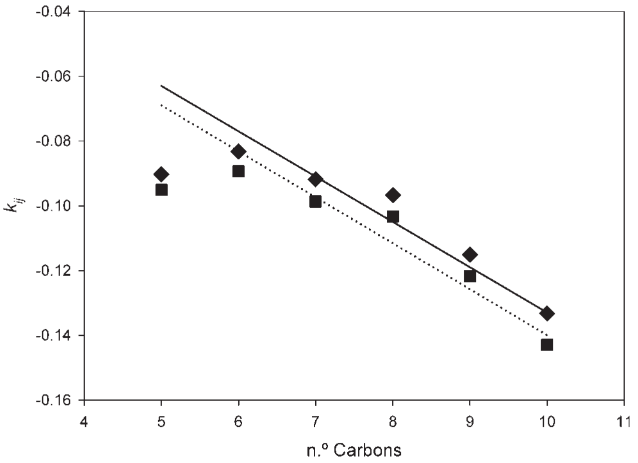

Figure 2. k_{ij} trend with the acid carbon number (◆, CR-2; ■, CR-4) and linear correlations (—, CR-2; ⋯, CR-4).

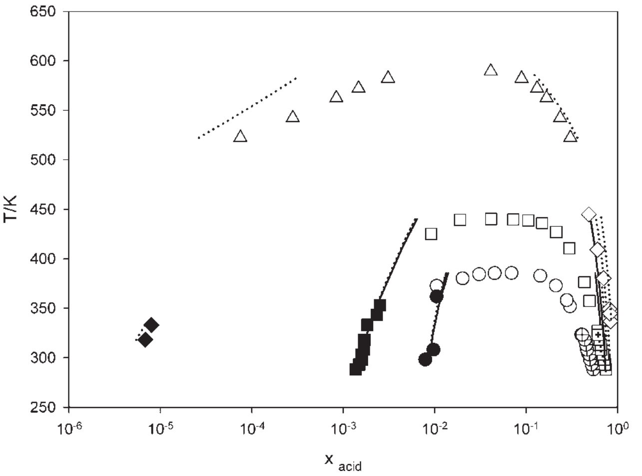

Figure 3. LLE for three water + acid systems: experimental values for pentanoic acid (○, turbidimetry; ⊕, Karl Fisher; ●, literature data), for hexanoic acid (□, turbidimetry; ☒, Karl Fisher; ■, literature data), for dodecanoic acid (◇, turbidimetry; ◆, literature data), and for oleic acid (△, literature data), and CPA results (—, CR-2; ⋯, CR-4).

impact in the acid rich phase. In fact, and for both association combining rules, the values for the k_{ij}'s optimized using both phases follow the same dependency as the k_{ij}'s evaluated solely from the water rich phase. The results obtained indicate that it is possible to predict the behavior of the acid rich phase from the binary interaction parameters optimized using only data from the water rich phase.

The estimated k_{ij}'s are small, indicating that the CPA EoS is able to take adequately into account the cross-association interactions that occur in water + fatty acid systems, with any of the combining rules studied.

As shown in Figure 2, for the pentanoic acid + water system, the k_{ij} value was considerably off the linear tendency observed for the other compounds, indicating that different interactions may be present on this system. This deviation of the pentanoic acid system from the behavior of the other acid systems may be due to a higher degree of dissociation of the pentanoic acid in water, that the CPA EoS does not take into account. This may also be related to the unexpected behavior of butanoic acid. From the analysis of the mutual solubilities of the higher acids, the phase envelopes of pentanoic and hexanoic acids, and the CPA predictions using the k_{ij} correlations, it would be expected that butanoic acid would only be partially miscible with water at room temperature. Yet, full miscibility of butanoic acid and water is observed under these conditions. The enhanced solubility of the lower acids in water results from new favourable interactions between the two compounds, not fully represented by the approached used in this work.

Evaluation of the combining rule

The two combining rules studied produce very different descriptions of the acid rich phase but have no impact on the water rich phase, showing very similar global average deviations.

As shown in Table 5 the CR-2 combining rule produces better results for smaller acids up to C_7. An increase in global average deviations with the chain length of the acid is observed for the heavier compounds of the homologous series. The opposite behavior was observed for the CR-4 rule, producing very good results for the heavier acids. The CR-4 combining rule performs globally better than the CR-2 with the advantage of increasing the calculation speed. With this combining rule, the water solubility in acids is described with a global average deviation below 30%. The acid solubility in water is estimated with a global average deviation below 6%, as reported in Table 5. Phase equilibria results for water + fatty acid systems are depicted in Figures 3 and 4.

The results clearly indicate that the CPA-EoS provides a good description of the phase equilibria for water-fatty acid

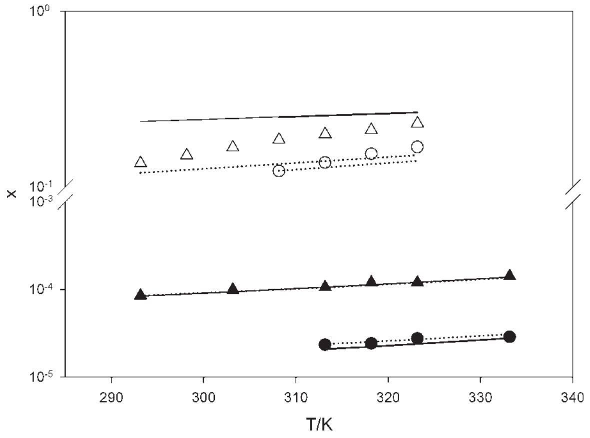

Figure 4. Mutual solubilities for two water + acid systems: experimental results for water + decanoic acid (▲, aqueous phase; △, acid phase), and for water + decanoic acid (●, aqueous phase; ○, acid phase) and CPA results using two different combining rules (—, CR-2; ⋯, CR-4).

Table 6. Values of T_m and $\Delta_{fus}H$ and CPA SLE Modelling Results

No. of Carbons	$\Delta_{fus}H$ (J mol^{-1})	T_m (K)	AAD%	
			CR-2	CR-4
12	36650	317.15	33.00	45.44
13	33729	314.65	28.51	47.81
14	45100	327.15	54.12	66.73
15	41520	325.68	30.05	48.62
16	54894	335.73	90.97	93.50
17	51342	334.25	55.13	66.53
18	61209	343.15	64.03	73.97
AAD global %			50.83	63.23

binary systems. The proposed model and the linear correlation for the binary interaction parameters can be used as a predictive tool to the description of systems of interest in industrial processes were organic and aqueous phases are present. For instance, for the oleic acid + water system, for which LLE data at higher temperatures and pressures were available in the literature.[40] The CR-4 combining rule and the k_{ij} predicted through the linear correlation were used. As seen in Figure 3 very good results were obtained for the water solubility with a global average deviation inferior to 6%. The same prediction was made for the dodecanoic acid + water system with global average deviations inferior to 22% for the water solubility.

Prediction of the solubility of solid fatty acids in water

Saturated fatty acids above decanoic acid are solid at room temperature and their solubilities in water are solid-liquid equilibria.

The CPA EoS has been previously applied to the description of the SLE of alcohol–alkanes, glycol–water, and alcohol–water[26] mixtures, but never to the SLE of fatty acids and water systems. The purpose here is to investigate the predictive performance of the CPA EoS with the interaction parameter correlations obtained from LLE data and for each combining rule selected.

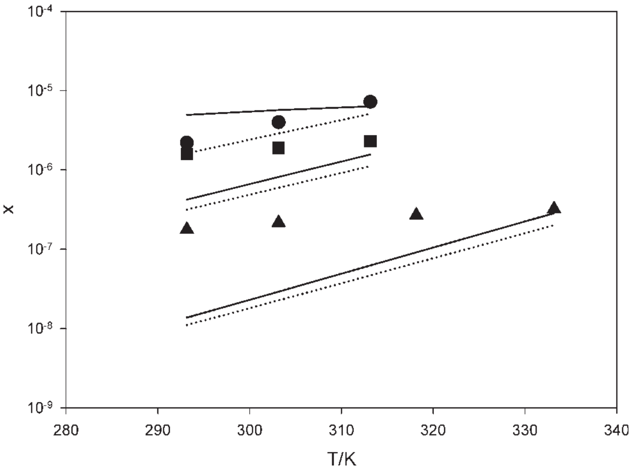

Figure 5. SLE prediction for three water + acid systems: experimental values for dodecanoic acid (●), for tetradecanoic acid (■) and for octadecanoic acid (▲), and CPA results (—, CR-2; ···, CR-4).

Equations to describe the SLE for binary systems are well established in the literature.[41]

Considering the formation of a pure solid phase and neglecting the effect of pressure, the solubility of a solute *s* can be calculated from the following generalized expression that relates the reference state fugacities:

$$\ln\frac{f_s^{liq}(T,P)}{f_s^{sol}(T,P)} = \frac{\Delta_{fus}H_s}{R}\left(\frac{1}{T}-\frac{1}{T_{m,s}}\right) - \frac{\Delta C_p}{R}\left[\frac{T_m}{T} - \ln\left(\frac{T_m}{T}\right) - 1\right] \quad (16)$$

where $\Delta_{fus}H$ is the enthalpy of fusion, T is the absolute temperature, T_m is the melting temperature, ΔC_p is the difference of the liquid and solid molar heat capacities and R the gas constant.

The heat capacity contribution can be neglected with respect to the enthalpic term, as already observed for fatty acid systems in the work from Costa et al[42] where the high pressure solid-liquid equilibria of fatty acids was studied. Complete immiscibility in the solid phase and absence of a solid-complex phase were also assumed.

The following expression for the solubility is considered,

$$x_s = \frac{\varphi_s^{L_0}}{\varphi_s^{L}} \exp\left[-\frac{\Delta_{fus}H_s}{R}\left(\frac{1}{T}-\frac{1}{T_{m,s}}\right)\right] \quad (17)$$

where φ is the fugacity coefficient and subscript 0 refer to pure component.

Few experimental SLE data are available in the literature and only for 7 fatty acids (from C_{12} to C_{18}).[38,40]

The values for the thermophysical properties needed to perform SLE calculations, melting temperature (T_m) and heat of fusion ($\Delta_{fus}H$), found in literature for the pure compounds (from C_{12} to C_{18})[36] are presented at Table 6.

These properties increase with the organic acid carbon number and a parity effect can be observed due to differences in the molecular packing of these compounds in the solid state.

The CR-2 combining rule performed better than CR-4 with global average deviations of 51% and 63%, respectively, as seen in Table 6 and Figure 5.

Part of these deviations may be attributed to the low accuracy of the experimental data available. However, very satisfactory SLE predictions were achieved with the proposed model and using a single interaction parameter correlated from LLE data.

Conclusions

Water solubilities in six fatty acids and LLE phase envelopes for three fatty acid + water systems were determined, using respectively Karl-Fisher coulometry and turbidimetry. The measured data are in good agreement with previously available measurements.

The CPA EoS was here extended to long chain carboxylic acids and their binary aqueous mixtures. Two different combining rules were tested.

A single, small, temperature independent and chain length dependent binary interaction parameter was enough to describe the mutual solubilities. A correlation for the binary interaction parameters was proposed.

For small acids, from C_5 to C_7, the CR-2 combining rule produced somewhat better results for the mutual solubilities, while the Elliot combining rule (CR-4) performed better for the heavier fatty acids up to C_{10}. Using the CPA EoS and the CR-4 combining rule, global average deviations lower than 30% were obtained for the water solubility and than 6% for the acid solubility.

The k_{ij} correlation was successfully extrapolated to model the LLE of the oleic acid + water and dodecanoic acid + water systems and to predict the SLE of binary aqueous mixtures with fatty acids from C_{12} to C_{18}, supporting the use of a linear correlation with the acid carbon number for the binary interaction parameters.

The good results obtained for the different types of equilibria of water + fatty acid mixtures and for the mutual solubilities of water + ester binary systems encourage the application of the CPA EoS for the design of extraction units for fatty acid and biodiesel production.

Acknowledgments

Financial support was provided by the national project POCI/EQU/58239/2004: "Equilibrium and Interfacial Properties of Water + Oil Systems", and by LSRE financing by FEDER/POCI/2010. Mariana B. Oliveira acknowledges Fundação para a Ciência e a Tecnologia through her PhD (SFRH/BD/29062/2006) scholarship. A. J. Queimada acknowledges support from POCI/N010/2006. The authors also gratefully acknowledge Dr. Ramesh Gardas for the help on the experimental measurements.

Notation

a = energy parameter in the physical term
a_0, c_1 = parameters for calculating a
A_i = site A in molecule i
b = covolume
C_p = heat capacity
g = simplified hard-sphere radial distribution function
H = enthalpy
k_{ij} = binary interaction parameter
P = vapor pressure
R = gas constant
s = solubility
T = temperature
x = mole fraction
X_{Ai} = fraction of molecule i not bonded at site A
Z = compressibility factor
AAD = average absolute deviation
CPA = cubic-plus-association
CR = combining rule
EoS = equation of state
LLE = liquid–liquid equilibria
VLE = vapor-liquid equilibria
SLE = solid-liquid equilibria
SAFT = statistical associating fluid theory
SRK = Soave-Redlich-Kwong

Greek letters

β = association volume
ε = association energy
η = reduced fluid density
ρ = mole density
Δ = association strength
Δ = variation
σ = vapor
γ = activity coefficient
φ = fugacity coefficient

Subscripts

c = critical
fus = fusion
i,j = pure component indexes
liq. = liquid
m = melting
r = reduced

Superscripts

assoc. = association
phys. = physical

Literature Cited

1. Kirk RE, Othmer DF. *Encyclopedia of Chemical Technology: Carboxylic Acids, Economic Aspects*, 4th ed. Boston: Wiley, 1997.
2. Aranda DAG, Santos RTP, Tapanes NCO, Ramos ALD, Antunes OAC. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. *Catal Lett*. 2008;122:20–25.
3. Prieto MM, Bada JC, Camacho ML, Constante EG. Deacidification and recovery of distillates in the physical refinig of edible oils. *Eur J Lipid Sci Technol*. 2008;110:101–110.
4. Ma FR, Hanna MA. Biodiesel production: a review. *Bioresour Technol*. 1999;70:1–15.
5. Encinar JM, Gonzalez JF, Rodriguez-Reinares A. Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. *Ind Eng Chem Res*. 2005;44:5491–5499.
6. Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. *J Am Soc Brew Chem*. 1986;63:1375–1380.
7. van Kasteren JMN, Nisworo AP. A process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification. *Resour Conserv Recycling*. 2007;50:442–458.
8. Haas MJ, McAloon AJ, Yee WC, Foglia TA. A process model to estimate biodiesel production costs. *Bioresour Technol*. 2006;97:671–678.
9. Ince E, Kirbaslar SI, Sahin S. Liquid-liquid equilibria for ternary systems of water plus formic acid plus dibasic esters. *J Chem Eng Data*. 2007;52:1889–1893.
10. Bilgin M, Kirbaslar SI, Ozcan O, Dramur U. Liquid plus liquid equilibria of water plus butyric acid plus isoamyl alcohol ternary system. *J Chem Thermodyn*. 2005;37:297–303.
11. Kirbaslar SI, Bilgin M, Batr D. Liquid plus liquid equilibria of (water plus butyric acid plus cyclohexyl acetate ternary system. *J Chem Thermodyn*. 2005;37:175–180.
12. Kirbaslar SI, Sahin S, Bilgin M. Liquid plus liquid equilibria of water plus butyric acid plus dibasic esters ternary systems. *J Chem Thermodyn*. 2007;39:284–290.
13. Ferreira O, Macedo EA, Bottini SB. Extension of the A-UNIFAC model to mixtures of cross- and self-associating compounds. *Fluid Phase Equilib*. 2005;227:165–176.
14. Skjoldjorgensen S. Group contribution equation of state (Gc-Eos)—a predictive method for phase-equilibrium computations over wide ranges of temperature and pressures up to 30 MPa. *Ind Eng Chem Res*. 1988;27:110–118.
15. Gros HP, Bottini S, Brignole EA. A group contribution equation of state for associating mixtures. *Fluid Phase Equilibria*. 1996;116:537–544.
16. Twu CH, Coon JE, Cunningham JR. An equation of state for carboxylic-acids. *Fluid Phase Equilib*. 1993;82:379–388.
17. Jonasson A, Persson O, Rasmussen P, Soave GS. Vapor-liquid equilibria of systems containing acetic acid and gaseous components. Measurements and calculations by a cubic equation of state. *Fluid Phase Equilib*. 1998;152:67–94.
18. Huang SH, Radosz M. Equation of state for small, large, polydisperse, and associating molecules—extension to fluid mixtures. *Ind Eng Chem Res*. 1991;30:1994–2005.

19. Fu YH, Sandler SI. A simplified saft equation of state for associating compounds and mixtures. *Ind Eng Chem Res*. 1995;34:1897–1909.
20. Derawi SO, Zeuthen J, Michelsen ML, Stenby EH, Kontogeorgis GM. Application of the CPA equation of state to organic acids. *Fluid Phase Equilib*. 2004;225:107–113.
21. Zeuthen J. Extension of the CPA EoS to systems containing organic acids, Master thesis, Center for Phase Equilibria and Separation Processes (IVC-SEP), Department of Chemical Engineering. 2003, DTU: Lyngby, Denmark. p. 120.
22. Oliveira MB, Varanda FR, Marrucho IM, Queimada AJ, Coutinho JAP. Prediction of water solubility in biodiesel with the CPA EoS. *Ind Eng Chem Res*. 2008;47:4278–4285.
23. Freire MG, Neves CMSS, Carvalho PJ, Gardas RL, Fernandes AM, Marrucho IM, Santos LMNBF, Coutinho JAP. Mutual solubilities of water and hydrophobic ionic liquids. *J Phys Chem B*. 2007;111: 13082–13089.
24. Freire MG, Santos LMNBF, Fernandes AM, Coutinho JAP, Marrucho IM. An overview of the mutual solubilities of water-imidazolium-based ionic liquids systems. *Fluid Phase Equilib*. 2007;261: 449–454.
25. Freire MG, Gomes L, Santos LMNBF, Marrucho IM, Coutinho JAP. Water solubility in linear fluoroalkanes used in blood substitute formulations. *J Phys Chem B*. 2006;110:22923–22929.
26. 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;45:4855–4868.
27. 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;45:4869–4878.
28. Suresh SJ, Elliott JR. Multiphase equilibrium-analysis via a generalized equation of state for associating mixtures. *Ind Eng Chem Res*. 1992;31:2783–2794.
29. Suresh J, Beckman EJ. Prediction of liquid-liquid equilibria in ternary mixtures from binary data. *Fluid Phase Equilib*. 1994;99:219–240.
30. Voutsas EC, Yakoumis IV, Tassios DP. Prediction of phase equilibria in water/alcohol/alkane systems. *Fluid Phase Equilib*. 1999;160: 151–163.
31. Folas GK, Gabrielsen J, Michelsen ML, Stenby EH, Kontogeorgis GM. Application of the cubic-plus-association (CPA) equation of state to cross-associating systems. *I Ind Eng Chem Res*. 2005;44: 3823–3833.
32. Kaarsholm M, Derawi SO, Michelsen ML, Kontogeorgis GM. Extension of the cubic-plus-association (CPA) equation of state to amines. *Ind Eng Chem Res*. 2005;44:4406–4413.
33. Folas GK, Derawi SO, Michelsen ML, Stenby EH, Kontogeorgis GM. Recent applications of the cubic-plus-association (CPA) equation of state to industrially important systems. *Fluid Phase Equilib*. 2005;228:121–126.
34. Huang SH, Radosz M. Equation of state for small, large, polydisperse, and associating molecules. *Ind Eng Chem Res*. 1990;29:2284–2294.
35. Sorensen JM, Arlt W. *Liquid-Liquid Equilibrium Data Collection*. Frankfurt: DECHEMA, 1980.
36. DIPPR, Thermophysical Properties Database, 1998.
37. Oliveira MB, Coutinho JAP, Queimada AJ. Mutual solubilities of hydrocarbons and water with the CPA EoS. *Fluid Phase Equilib*. 2007;258:58–66.
38. 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.
39. Yalkowsky SH, Yan H. *Handbook of Aqueous Solubility Data*. CRC Press, 2003.
40. Ralston AW, Hoerr CW. The solubilities of the normal saturated fatty acids. *J Org Chem*. 1942;7:546–555.
41. Prausnitz JM, Lichtenthaler RN, Azevedo EGD. *Molecular Thermodynamics and Fluid Phase Equilibria Prentice-Hall*, 1999.
42. Costa MC, Krahenbuhl MA, Meirelles AJA, Daridon JL, Pauly J, Coutinho JAP. High pressure solid-liquid equilibria of fatty acids. *Fluid Phase Equilib*. 2007;253:118–123.

Manuscript received May 9, 2008, and revision received Nov. 4, 2008.