Phase-Equilibrium Modeling in the Hydrogenation of Vegetable Oils and Derivatives

Selva Pereda*, Laura Rovetto, Susana B. Bottini, and Esteban A. Brignole

Planta Piloto de Ingeniería Química (PLAPIQUI), Universidad Nacional del Sur,
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), 8000 Bahía Blanca, Argentina

ABSTRACT: The main tool needed to carry out phase-equilibrium engineering of a given process is an adequate thermodynamic model adjusted to the range of process operating conditions of the working system. In the present work the Group Contribution with Association Equation of State (GCA-EoS) is used to model the phase behavior of reacting mixtures typical of the hydrogenation of vegetable oils and derivatives at supercritical or high-pressure conditions.

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Two important gas–liquid catalytic hydrogenation processes in the oleochemical industry are the manufacture of margarine and shortenings from vegetable oils and the production of fatty alcohols from alkyl esters, such as methyl esters:

$$RCOOCH_3 + 2\,H_2 \rightleftarrows RCH_2OH + CH_3OH \qquad [1]$$

These reactions can be carried out under homogeneous fluid conditions by the addition of an appropriate supercritical solvent such as propane, leading to improved processes with higher reaction rates and selectivities (1–3). A suitable thermodynamic model, capable of predicting the phase boundaries and fluid phase behavior of the working mixtures, is a critical tool for process design and optimization.

Group contribution methods are an efficient way to model the phase-equilibrium properties of mixtures including gases, TG, and derivatives, because a large number of systems can be represented by a limited number of functional groups. For example, besides hydrogen, the mixtures relevant to the hydrogenation of vegetable oils and fatty esters contain only five different functional groups: alkyl (CH_3 and CH_2), olefin (CH=CH), TG [$(CH_2COO)_2CHCOO$], ester (CH_2COO), and alcohol (CH_2OH). The Group Contribution Equation of State (GC-EoS) (4), extended to fatty oils (5) and associated compounds (6–8), i.e., the Group Contribution with Association Equation of State (GCA-EoS), is applied in the present work to model these reaction mixtures. Recent experimental data obtained by Rovetto *et al*. for propane + hydrogen + tripalmitin (9) and propane + hydrogen + alcohols/fatty esters (10,11) are used to tune the parameters of the model and to test its predictive capacity. The modeling results are essential for the phase-equilibrium engineering of reactors for the supercritical or high-pressure hydrogenation of oils and derivatives.

The parameters involved in each term of the GCA-EoS are presented in Table 1. The table also reports which parameters should be estimated in each case. The hard sphere critical diameter (d_c) is related to the molecular size of each component. In general, this parameter is obtained from critical properties and vapor pressure data of pure compounds. However, this type of information is not always available for low-volatility molecules such as TG. Bottini *et al*. (5) presented a correlation for the computation of d_c, obtained from values of infinite dilution activity coefficient of alkanes in high-M.W. paraffins and TG. Table 2 shows the d_c values and the critical temperatures T_c of the different components studied in this work.

RESULTS AND DISCUSSION

Phase-equilibrium modeling in the hydrogenation of vegetable oils. Skjold-Jørgensen (4) originally determined the interaction parameters between hydrogen and the paraffin group on the basis of experimental data on hydrogen solubility in alkanes containing up to 16 carbon atoms. These parameters had to be revised to obtain a good correlation of hydrogen solubility in molecules with more than 40 carbon atoms. The large number of paraffin groups in the TG molecule is the origin of large differences in the predictions with small changes in the H_2–CH_2 interaction parameter.

New binary interaction parameters for hydrogen–paraffin and hydrogen–TG were estimated on the basis of the new experimental data from Rovetto *et al.* (9). Table 3 reports the new set of binary interaction parameters obtained by fitting $n = 63$ data points with an SDV of 1.263% in the calculated hydrogen liquid molar fractions. The GCA-EoS correlation of hydrogen solubility in tripalmitin is very good, as shown in Figure 1.

For reactions carried out under supercritical propane, the behavior of mixtures containing this solvent must be studied. The phase equilibrium of TG + propane binary mixtures is type IV in the classification of van Konynenburg and Scott (12). In this type of phase behavior a region of liquid immiscibility is observed in the near-critical region of propane (T_c = 369.8 K). For example, Coorens *et al*. (13) report values of 349 and 370 K

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*To whom correspondence should be addressed at PLAPIQUI—Universidad Nacional del Sur, CONICET, Camino La Carrindanga, Km 7, C.C. 717, 8000 Bahía Blanca, Argentina.
E-mail: spereda@plapiqui.edu.ar

TABLE 1
Group Contribution with Association Equation of State (GCA-EoS) Model Parameters[a]

Term	Type		Parameter	
Repulsive	Molecular		Hard sphere diameter: d_c	Estimated
Attractive	Group	Single Group	Reference temperature: T^*	Constant
			Surface area: q_i	Constant
			Energy: g_{ii}, g_{ii}', g_{ii}''	Estimated
		Binaries	Interaction: k_{ij}^*, k_{ij}'	Estimated
			Nonrandom: α_{ij}, α_{ji}	Estimated
Associative	Group		Association energy: ε_i	Constant
			Association volume: κ_i	Constant

[a]Nomenclature as presented in the original paper (7).

for the lower and upper critical end points, respectively, of the propane + tripalmitin system. Espinosa *et al.* (14) fitted the model parameters to describe correctly the phase equilibria of mixtures of propane with TG.

Figure 2 shows GCA-EoS phase boundary predictions for the system hydrogen + propane + tripalmitin at 360 K and 4 MPa. Under these conditions, the model predicts phase immiscibility in the three binaries. The TG concentration in the l_2 liquid phase is negligible; therefore, the saturation line l_2 is almost coincident with the hydrogen + propane binary axis. At higher hydrogen concentrations a vapor phase is found and a three-phase equilibrium region l_1l_2g is obtained. For the same reason, the line l_2g lies virtually over the H_2–propane axis. A region of complete miscibility for this ternary system can be obtained by increasing the temperature above the T_c of propane and selecting a pressure above 100 bar. Thereby, a region suitable for single-phase hydrogenation can be reached (2).

TABLE 2
Pure Component Properties

Compound	d_c (cm mol^{-1})	T_c (K)
Hydrogen	2.672	33.2
Propane	4.017	369.8
n-Butane	4.362	425.18
Methanol	3.61	512.6
Methyl palmitate	7.695	735.9
n-Hexadecanol	7.376	770.
Tripalmitin[a]	11.44	1020.

[a]d_c obtained from Bottini *et al.* (5) correlation.

Predictions for the ternary H_2 + propane + tripalmitin mixture are compared with experimental data in Figures 3 and 4. The

TABLE 3
GCA-EoS Binary Interaction Parameters

Group *i*	Group *j*	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}	*N*	SDV%[a]	Ref.
H_2	CH_2/CH_3	1.0	0.0	11.846	11.846	63	1.263	9
H_2	TG	1.0	0.0	−10.144	−10.144			

[a]$SDV\% = 100 \sqrt{\sum((x_{calc}-x_{exp})/x_{exp})^2/N}$, where x = liquid phase composition. For other abbreviations see Table 1.

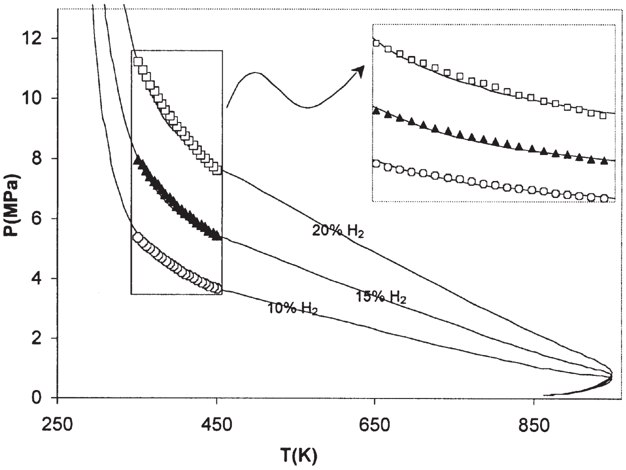

FIG. 1. Phase diagram of the binary system hydrogen + tripalmitin (PPP). ○, ▲, and □: experimental data (9). Solid line (—): Group Contribution with Association Equation of State (GCA-EoS) correlation.

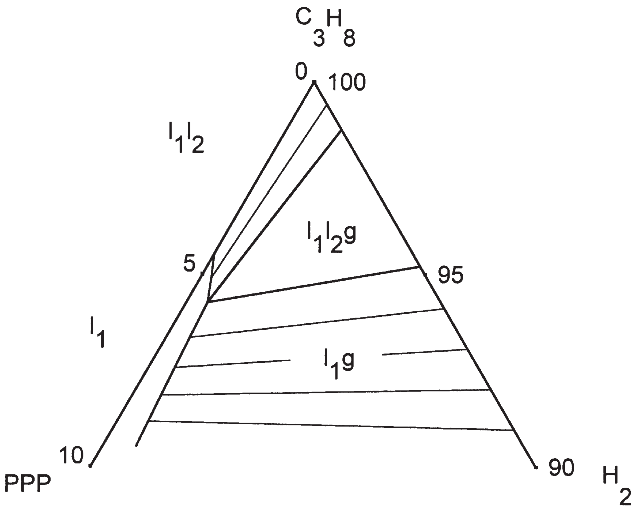

FIG. 2. Immiscibility region for the ternary system hydrogen + PPP + propane at 360 K and 4 MPa. For abbreviation see Figure 1.

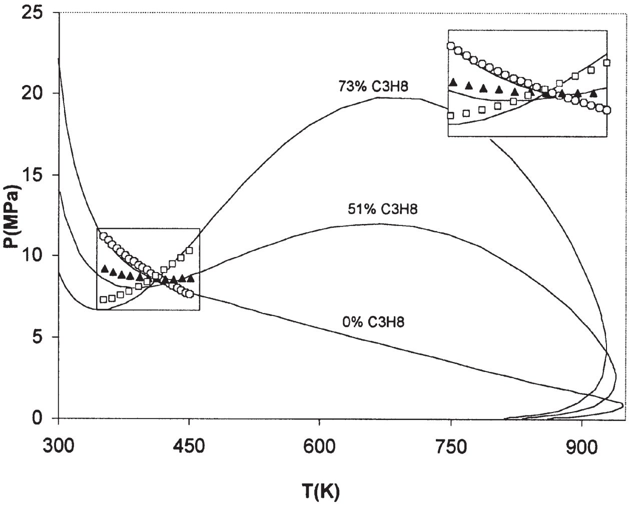

FIG. 3. Phase diagram of the ternary system hydrogen + propane + PPP at a constant molar ratio $x(PPP)/x(H_2) = 4.15$. (—) GCA-EoS predictions. ○, ▲, and □: experimental data (9). For abbreviations see Figure 1.

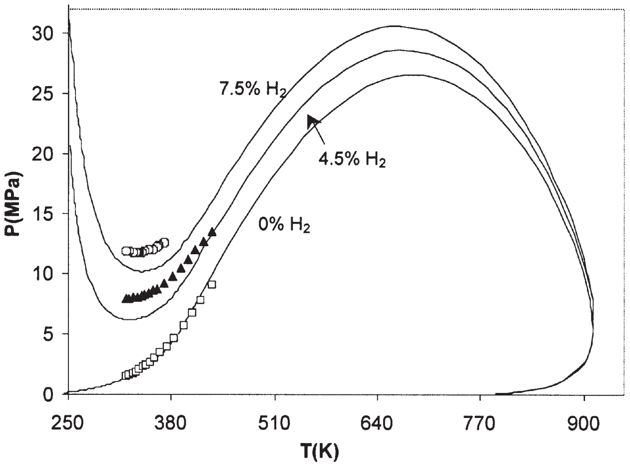

FIG. 4. Phase diagram of the ternary system hydrogen + propane + PPP at a constant molar ratio $x(C_3H_8)/x(PPP) = 7$. ○, ▲, and □: experimental data (9). Solid line (—): GCA-EoS predictions. For abbreviations see Figure 1.

agreement with the experimental data is quite good. Figure 3 shows how the slope of the pressure vs. temperature phase diagrams changes with the propane concentration. At low propane concentrations, the saturation pressure decreases with temperature, following the typical behavior of mixtures of hydrogen + liquid substrates. At higher propane concentrations, the saturation pressure increases with temperature, in agreement with the expected behavior of mixtures of propane with liquid substrates.

The correlations and predictions shown in this section were performed by using the parameters reported in Table 3 for the interactions H_2/CH_2 and H_2/TG and those given by Skjold-Jørgensen (4) for H_2/C_3H_8 and by Espinosa *et al.* (14) for CH_2/TG. This last paper also reported the binary interaction parameters between CH=CH and TG, which are required to predict the phase behavior of mixtures containing unsaturated TG.

Phase-equilibrium modeling in the hydrogenolysis of FAME. Following a similar procedure, the GCA-EoS model was extended to cover the phase-equilibrium engineering needs for the hydrogenolysis of methyl palmitate to hexadecanol. In this case, the number of components present in the mixture is greater and there is a significant change in the chemical nature of the mixture as the reaction proceeds from the fatty ester to the fatty alcohol + methanol products. The d_c and T_c of pure components are reported in Table 2. The required binary interaction parameters were obtained by fitting experimental data for binary mixtures of hydrogen, propane, and butane with either methyl palmitate or hexadecanol (9,11,15). Low-pressure data for mixtures of esters and alcohols (16,17) were also used. Again, the amount of experimental information is very limited, making it difficult to verify the predicting capability of the model. For this reason, only a fraction of the binary vapor–liquid equilibrium isopleths were applied in the estimation of parameters. The rest of the binary and ternary experimental data were used to validate the GCA-EoS phase-equilibrium predictions. The dashed lines in Figures 5 to 11 represent data correlations, and the solid lines are predictions.

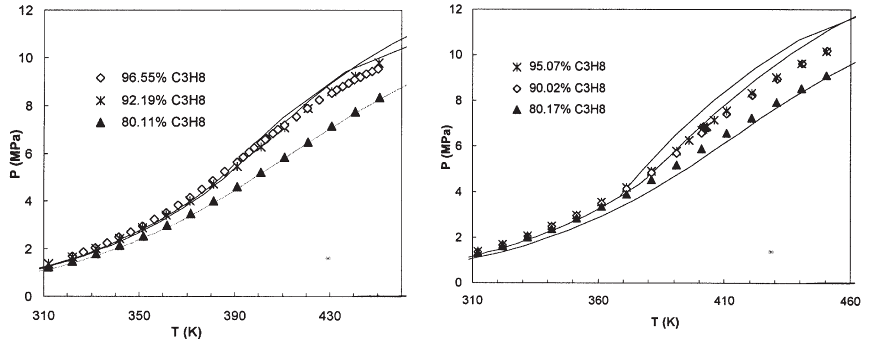

FIG. 5. (a) Phase diagram of the binary system methyl palmitate (MP) + propane. (b) Phase diagram of the binary system hexadecanol (HD) + propane. ▲, ✳, and ◇: experimental data (10,11). Dashed line (- - -): GCA-EoS correlation. Solid line (—): GCA-EoS predictions. For abbreviations see Figure 1.

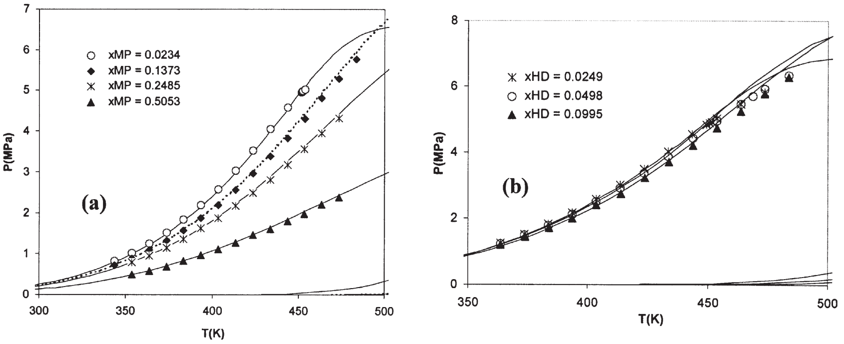

FIG. 6. (a) Phase diagram of the binary system MP + butane. (b) Phase diagram of the binary system HD + butane. ▲, ✳, ◆, and ○: experimental data (15). Dashed line (- - -): GCA-EoS correlation. Solid line (—): GCA-EoS predictions. For abbreviations see Figures 1 and 5.

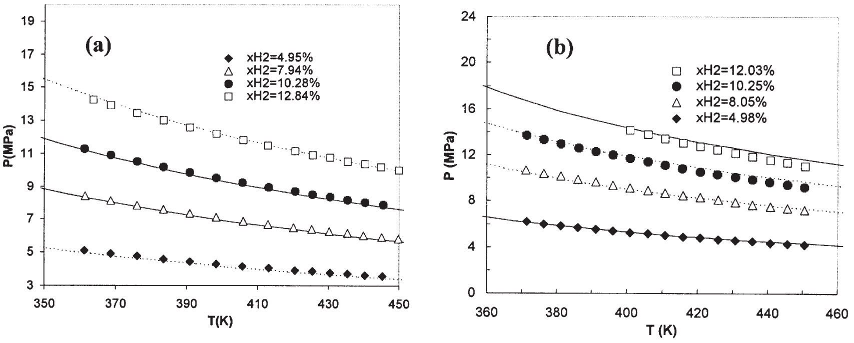

FIG. 7. (a) Bubble points of the binary system MP + hydrogen; (b) bubble points of the binary system HD + hydrogen. ◆, △, ●, and □: experimental data (10,11). Dashed line (- - -) GCA-EoS correlations. Solid line (—) GCA-EoS predictions. For abbreviations see Figures 1 and 5.

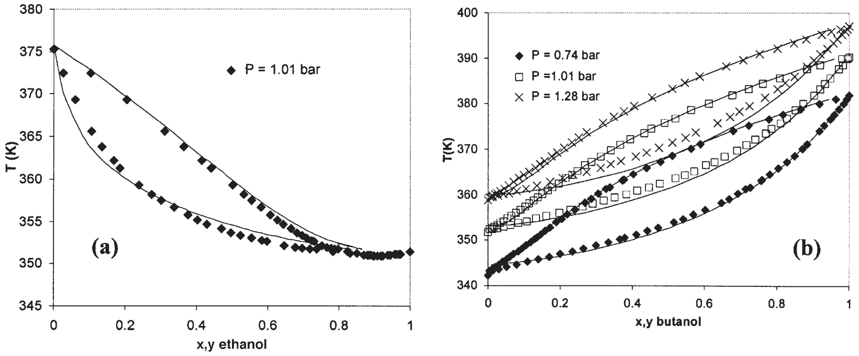

FIG. 8. (a) Vapor-liquid equilibria of the binary system ethanol + methylbutanoate. (b) Vapor-liquid equilibria of the binary system butanol + methylpropanoate. ◆, □, and X: experimental data (20,21). Solid line (—): GCA-EoS predictions. For abbreviation see Figure 1.

Table 4 reports the binary interaction parameters estimated in the present work. The remaining parameters required for phase-equilibrium correlation and prediction in these systems were obtained from Skjold-Jørgensen (4) for the H_2-alkyl group interactions and from Gros *et al.* (18) for the CH_2OH-alkyl group interactions.

(i) Binary systems: hydrogen with methyl palmitate and n-hexadecanol. Figure 7 shows the bubble pressures of the systems H_2 + methyl palmitate and H_2 + hexadecanol. By comparing the bubble pressures of each system for isopleths with similar hydrogen compositions, one may observe that the bubble pressures of hexadecanol are higher than those of methyl palmitate. This indicates that hydrogen is less soluble in the fatty alcohol. This phenomenon was also observed by van den Hark (1), who found problems of phase separation in the course of the hydrogenolysis process due to decreased hy-

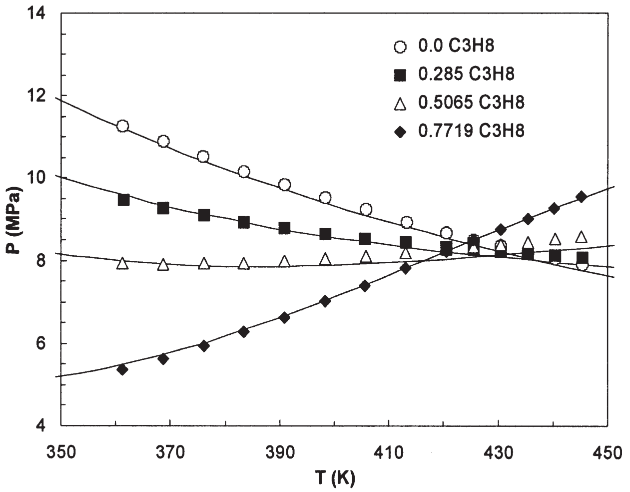

FIG. 9. Bubble pressure of the ternary system MP + hydrogen + propane (x_{MP}/x_{H2} = 8.7). ◆, △, ■, and ○: experimental data (10). Solid line (—): GCA-EoS predictions. For abbreviations see Figures 1 and 5.

drogen solubility as the reaction proceeds to the formation of fatty alcohol.

(ii) Binary systems: propane and butane with methyl palmitate and n-hexadecanol. Figure 5 shows the correlation and prediction of phase equilibria for the binary systems propane + methyl palmitate and propane + hexadecanol, together with experimental data (10,11). In general, very good agreement was obtained. However, greater deviations were found in the prediction of dew points. This is due to the great sensitivity of dew points to the fugacity computation of heavy compounds. Equations of state in general have difficulties in predicting the solubility of heavy compounds in a high-pressure vapor phase.

Figure 6 shows the correlation and predictions of binary phase equilibria for butane + methyl palmitate and butane + hexadecanol. The agreement with experimental data (15) for both systems is very good.

(iii) Binary systems: alcohol with esters. The interaction parameters between the ester (CH_2COO) and alcohol (CH_2OH) groups were determined by fitting the low-pressure isothermal

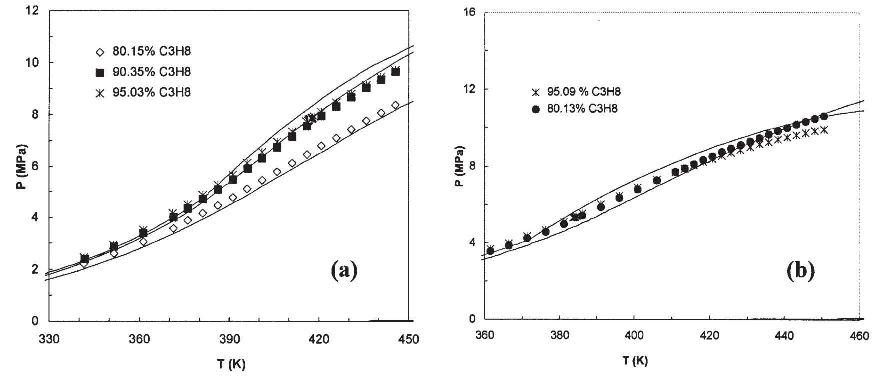

FIG. 10. (a) Bubble points of the ternary system MP + HD + hydrogen (x_{HD}/x_{MP} = 1). (b) Bubble points of the ternary system HD + methanol + hydrogen ($x_{HD}/x_{Methanol}$ = 1). ◇, ■, ●, and ✳: experimental data (11). Solid line (—): GCA-EoS predictions. For abbreviations see Figures 1 and 5.

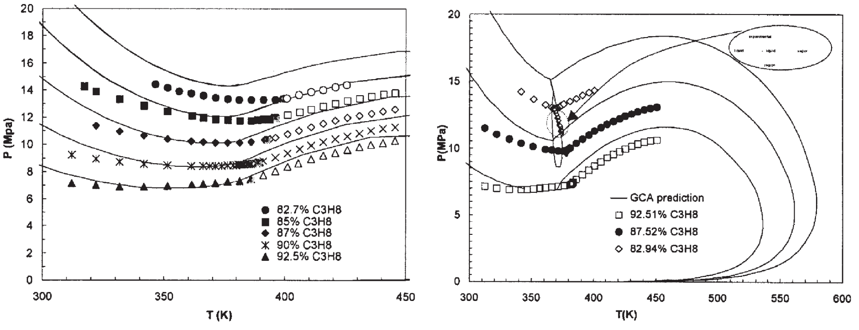

FIG. 11. (a) Phase diagram of the ternary system MP + propane + hydrogen (x_{H2}/x_{MP} = 4). (b) Bubble points of the ternary system HD + propane + hydrogen (x_{H2}/x_{HD} = 4). ▲, △, ✳, X, ◆, ◇, ■, □, ●, and ○: experimental data (10,11). Solid line (—): GCA-EoS predictions. For abbreviations see Figures 1 and 5.

TABLE 4
GCA-EoS Binary Interaction Parameters

Group *j*	Group *i*	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}	Ref.
CH_2/CH_3	CH_2COO	0.8794	0.05024	4.045	−16.601	10[a], 15[b]
H_2	CH_2COO	1.0	0.0	0.879	0.879	10[c]
H_2	CH_2OH	0.9481	0.1138	−2.9583	−2.9583	11[d]
CH_2COO	CH_2OH	1.1649	0.0	−2.8298	−2.8298	16,17

[a] From Rovetto *et al.* (10): C_3H_8 + methyl palmitate [isopleth: $x(C_3H_8) = 0.8011$].
[b] From Brands (15): C_4H_{10} + methyl palmitate [isopleth: $x(C_4H_{10}) = 0.8627$].
[c] From Rovetto *et al.* (10): H_2 + methyl palmitate [isopleths: $x(H_2) = 0.0495$ and 0.1284].
[d] From Rovetto *et al.* (11): H_2 + 1-hexadecanol [isopleths: $x(H_2) = 0.0805$ and 0.1025].

TABLE 5
Systems Used for Parameter Estimation Between the CH_2COO and CH_2OH Groups

System	*T* (K)	*N*	$\Delta P\%$[a]	$\Delta y\%$[a]
1-Propanol + methylpropanoate	328.15–348.15	40	3.65	6.07
1-Propanol + methylbutanoate	333.15–353.15	48	2.93	2.52
1-Butanol + methylpropanoate	348.15	20	3.09	6.80
1-Butanol + methylbutanoate	348.15–368.19	39	2.80	3.48

[a] $\Delta P\% = 100\sqrt{\sum_N ((P_{calc}-P_{exp})/P_{exp})^2/N}$, and $\Delta y\% = 100\sqrt{\sum_N ((y_{calc}-y_{exp})/y_{exp})^2/N}$.

data reported by Fernández *et al.* (16,17). Table 5 gives the number of data points and the temperature range of each system, together with the average errors in pressure and vapor-phase compositions. These deviations between predicted and experimental data were obtained from bubble pressure calculations at a given temperature and liquid composition.

The predictive capability of the model was verified by comparison with isobaric data measured by Susial and Ortega (19,20) and by Ortega *et al.* (21) for the system ethanol + methylbutanoate and butanol + methypropanoate (Fig. 8).

Predictions for ternary systems. Rovetto *et al.* (10,11) reported equilibrium data for ternary systems of interest in the hydrogenolysis of methyl palmitate. The effect of propane concentration on the phase behavior of the system hydrogen + propane + methyl palmitate was determined at a constant ester/hydrogen molar ratio of 8.7, for propane molar fractions in the range 0–77%. Figure 9 shows the experimental and predicted bubble pressures of this system. At low propane concentration, the isopleths have a negative slope, typical of hydrogen solubility behavior (i.e., solubility increases with temperature). At higher propane concentrations, the system presents the standard behavior of increased pressure with increased temperature. It is interesting to note that there is a propane concentration range where the system pressure is almost independent of temperature. The model predicts very closely this behavior and the composition at which the change in slope takes place.

The results reported by van den Hark (1) and the phase-equilibrium engineering carried out by Pereda *et al.* (2) for this system indicate that high propane concentrations are required to perform the reaction in a homogeneous fluid medium. The predictions for ternary mixtures of propane + methyl palmitate + *n*-hexadecanol and propane + hexadecanol + methanol at high propane concentrations are shown in Figures 10a and 10b, respectively.

Finally, the phase-equilibrium predictions for the ternaries hydrogen + methyl palmitate + propane and for hydrogen + *n*-hexadecanol + propane are represented in Figures 11a and 11b, respectively. In both cases, the hydrogen/substrate molar ratio was kept constant at 4. All isopleths depict a minimum in pressure, close to the mixture critical point. The model qualitatively predicts this unusual behavior. The system hydrogen + *n*-hexadecanol + propane also exhibits a region of liquid–liquid–vapor equilibrium that is qualitatively predicted by the model. Peters (22) showed that binary mixtures of *n*-alkanols with propane exhibit partial liquid miscibility starting with carbon number 18. However, the addition of hydrogen to the system has an antisolvent effect, and liquid–liquid–vapor behavior is observed for *n*-hexadecanol. Again, the model gives a correct qualitative description of the three-phase region. It is interesting to note that the narrow range of liquid–liquid–vapor behavior was found experimentally by studying the three phase conditions predicted by the thermodynamic model.

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