PHASE EQUILIBRIA IN MIXTURES OF HYDROGEN, PROPANE AND FATTY OIL DERIVATIVES AT SUPERCRITICAL CONDITIONS

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Abstract

The most common industrial process to obtain natural fatty alcohols is by catalytic hydrogenation of fatty acid methyl esters. The addition of supercritical propane to the reactive mixture can bring the organic substrate and hydrogen into a homogeneous phase, increasing reaction rate and selectivity.

Knowledge of the phase behavior of these mixtures is a prerequisite in order to select adequate process conditions. In the present work experimental phase equilibrium data on selected binary and ternary mixtures, typical of the supercritical hydrogenation of fatty acid methyl esters, are reported. From earlier work it became apparent that GCA-EoS is capable to model the vapor–liquid (VLE) and liquid–liquid equilibria (LLE) related to these systems. Therefore, this equation was chosen to model the fluid phase behavior of the system.

INTRODUCTION

The production of a variety of fatty alcohols, used as lubricants and surfactants, are carried out by hydrogenation of fatty acids and their methyl esters (FAME)[1]. These processes require large excess of hydrogen, high recirculation, long reaction time, and excessive use of catalyst. [2, 3]. These are three-phase processes, where mass-transfer of hydrogen from the gas into the liquid has been recognized as the rate-controlling step [4]. Transport limitation has a strong influence not only in the reaction rate, but also on the selectivity.

Supercritical hydrogenation of FAME has been investigated as an alternative technology using propane as a supercritical solvent [5, 6]. Reaction rates 500 times higher than those obtained in the traditional two-phase process have been reported [7]. The solubility problem is overcome by having the reactive mixture in a *homogeneous single phase*. The single-phase condition can be achieved by the addition of a supercritical solvent to the reactive mixture. This allows much higher concentrations of hydrogen (H_2) in the reaction mixture than the conventional process.

Homogenous hydrogenation offers significant advantages over conventional methods. In order to explore the feasibility of this process it is necessary to know the phase behavior of the reactive system in the region of interest in terms of pressure, temperature, composition, and degree of conversion. Experimental data on the phase behavior of mixtures of interest for these hydrogenation processes are very scarce in the open literature.

For design, simulation and optimization proposes it is essential to have available a suitable thermodynamic model, able to predict multi-phase equilibrium conditions and to give

a good representation of experimental data. The group contribution equation of state GC-EoS [8] and its upgraded version with association GCA-EoS [9] have shown to give a realistic description of the high-pressure phase behavior of multi-component asymmetric mixtures [10, 11].

This work presents the correlation and prediction of phase equilibria of binary and multicomponent reaction mixtures, on the basis of recent experimental data

Depending on its concentration, hydrogen may have an anti-solvent effect, reducing the solubility of reactants and products in the supercritical fluid. The solubility of hydrogen in fatty alcohols is lower than that in the corresponding methyl esters; hence, in the hydrogenolysis process the limits of the one-phase region depend on the extent of reaction. Regions of partial liquid miscibility have been predicted by the GCA-EoS model [12] and experimentally verified.

EXPERIMENTAL

All measurements were carried out in a Cailletet apparatus, which operates according to the synthetic method. A sample of known overall composition is studied and the phase transitions are determined visually.

Pressure measurements are as accurate as 0.03% of the reading. The temperature is measured within $\pm$ 0.02 K. The experimental work was performed in the temperature region 300<T/K<450 (maximum operating temperature of the apparatus), while pressures up to 15 MPa have been applied. A detailed description of the experimental facility, the operating procedure and sample preparation are given by Raeissi and Peters[13].

Aldrich supplied methyl palmitate (purity better than 99 %); 1-hexadecanol (purity approximately of 99%) was purchased from Fluka. Scott Specialty Gases supplied propane (purity better than 99.95% molar), and Hoek Loos hydrogen (purity of 99.999% molar). All components were used without further purification.

THERMODYNAMIC MODELING

Even though natural products are complex multi-component mixtures, their components can in general be represented by molecular structures having just a few functional groups. This feature supports the selection of a group contribution procedure to predict and correlate phase equilibria in mixtures containing natural oils and derivatives.

The GCA-EoS model is a group contribution equation of state based on a three-term residual Helmholtz energy with a free volume, attractive and associative contributions. A complete description of the model is presented by Gros *et al.*[9]. The attractive term contains four binary interaction parameters: the symmetrical binary parameters k_{ij}* and k_{ij}' and the asymmetrical non-randomness parameters α_{ij} and α_{ji}. Table 1 reports the values of the binary interaction parameters obtained in this work for some non-available group-interactions. The table also includes the reference to the experimental data used to fit the parameters.

The values of the remaining group interaction parameters not included in Table 1 were taken from Skjold-Jorgensen[8], Gros et al.[9] and Espinosa et al.[14].

Only some isopleths of each binary system were used to fit the parameters. The rest of the available experimental data were used to test the predictive capacity of the model. The figures in the results section show the GCA-EoS correlations with dash lines, and the GCA-EoS predictions with full lines.

Table 1. GCA-EoS binary interaction parameters.

Group j	Group i	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}	Ref.
CH2/CH3	CH2COO	0.8794	0.05024	4.045	-16.601	(a), [15]
H2	CH2COO	1.0	0.0	0.879	0.879	(b)
H2	CH_2OH	0.9481	0.1138	-2.9583	-2.9583	(c)
CH_2COO	CH_2OH	1.1649	0.0	-2.8298	-2.8298	[16, 17]

(a) This work: binary C_3H_8 + methyl palmitate (isopleth: $x(C_3H_8) = 0.8011$)
[15] Brands: binary C_4H_{10} + methyl palmitate (isopleth: $x(C_4H_{10}) = 0.8627$)
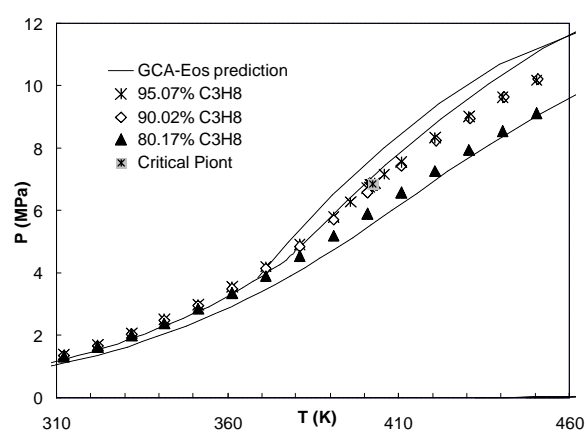(b) This work: binary H_2 + methyl palmitate (isopleths: $x(H_2) = 0.0495, 0.1284$)
(c) This work: binary H_2 + 1-hexadecanol (isopleths: $x(H_2) = 0.0805, 0.1025$)

RESULTS AND DISCUSION

This paper reports some experimental results on the phase behavior of the binary systems methyl palmitate (MP) + C_3H_8, 1-hexadecanol (HD)+ C_3H_8, MP+H_2 and HD+H_2, as well as some data on ternary mixtures between these components. The results of the GCA-EoS correlation and predictions are also shown.

Binary Systems with C_3H_8

To the best of our knowledge no phase equilibrium data has been reported in the literature for the systems MP + C_3H_8 or HD + C_3H_8. The fluid phase equilibria of these binary mixtures was studied in the temperature range between 310 K (close to the appearance of a solid phase) and 450 K. For isopleths with more than 95molar % of propane, not only bubble points were determined, but also critical and dew points as well. Figure 1 and Figure 2 show some experimental data, together with the results of the GCA-EoS correlation and predictions for these binary mixtures. It can be observed that the higher errors are in the prediction of dew points. This is in accordance with the difficulties found with the GCA-EoS model in quantitatively predicting the low solubility of high molecular weight compounds in supercritical solvents [18].
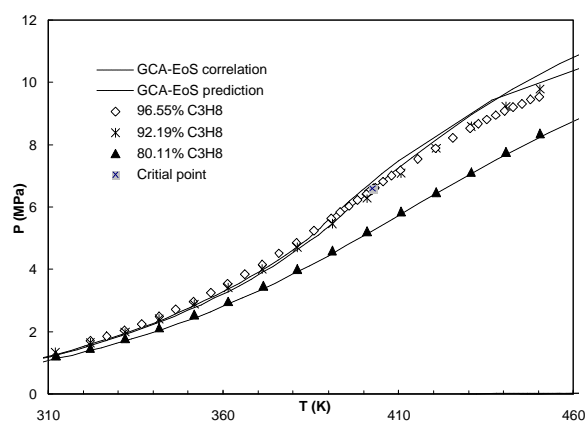
Figure 1: VLE of the binary MP+ C_3H_8 Figure 2: VLE of the binary HD+C_3H_8

Binary Systems with H_2

The low solubility of H_2 in the liquid phase produces a large increase in the bubble pressure of the mixture with a small increase in the hydrogen overall mole fraction. This is illustrated in Figure 3 and Figure 4.

A comparison between the equilibrium pressures of both systems for the isopleths with the same H_2 composition exhibit lower solubility of H_2 in hexadecanol than in methyl palmitate. This explains the fact observed by van der Hark et al [19], that the reaction mixture becomes less soluble as the hydrogenolysis reaction proceeds and the alcohol concentration in the reactor increases.
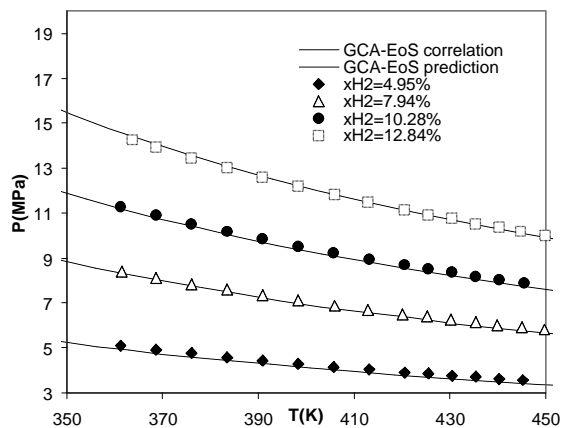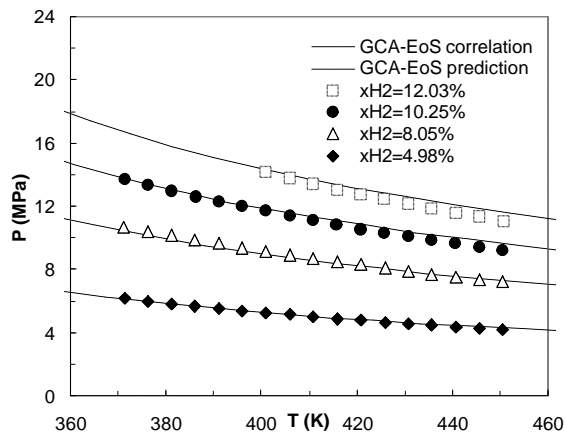

Figure 3:Bubble points of the binary MP+H_2

Figure 4:Bubble points of the binary HD+H_2

Ternary Systems

In order to see the effect of propane in the phase behavior of the reactive mixture, ternary isopleths on the MP + H_2 + C_3H_8 system were measured, increasing the amount of propane in the mixture from 0 to 77 mole % and keeping the substrate / H_2 ratio fixed at 8.7. The measured bubble pressures of different isopleths are depicted in Figure 5. This figure show that isopleths with low concentration of C_3H_8 in the liquid phase have a negative slope in a pressure vs. temperature diagram (hydrogen-like behavior); this is the typical of gas solubility behavior at very high reduce temperatures. On the other hand, at higher C_3H_8 concentrations the slope of the isopleths change sign and become positive (propane-like behavior). From Figure 5 it can also be observed that at propane concentrations close to 50 % molar, the influence of the temperature on the equilibrium pressure becomes almost negligible. The GCA-EoS model describes very well this behavior; i.e. it is able to predict the change of the slope with high precision.
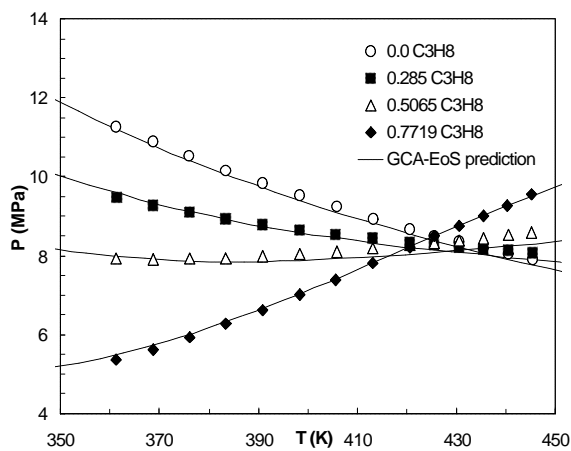

Figure 5: Ternary system MP + H_2 + C_3H_8
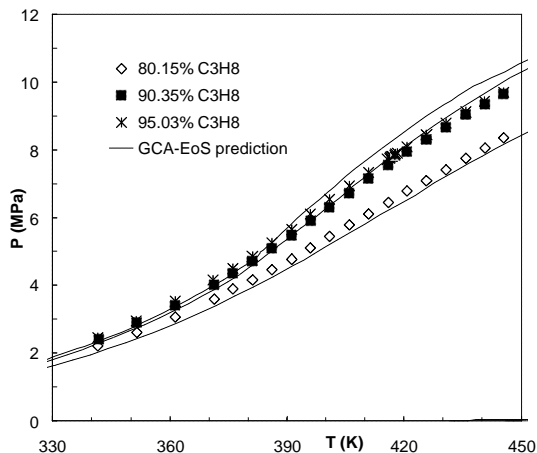(x(MP) : x(H_2) = 8.7)

Figure 6: Ternary system MP + HD + C_3H_8
(x(HD) : x(MP) = 1)

4

Previous experimental studies by Van den Hark and Härröd [6] and by Macher [7], and phase equilibrium predictions by Pereda et al. [12], suggest that high propane concentrations are needed to achieve single-phase conditions at the required ratio of the reaction components. Three different isopleths of the ternary system MP + HD + C_3H_8, having propane concentrations grater than 75 % molar and a stoichiometric ratio between the heavy components equal to 1, were measured. The experimental data and the GCA-EoS predictions are shown in Figure 6

In general, increasing the concentration of H_2 in ternary mixtures of the nature H_2 + (MP or HD) + C_3H_8 will lead to an increase in the equilibrium pressure. Furthermore, it is known that, depending on its concentration, H_2 may act as an anti-solvent. The latter phenomenon may reduce the solubility of both, methyl palmitate (reactive) or hexadecanol (reaction product) in the supercritical media. Measurements have been carried out in the ternary system H_2 + MP + C_3H_8 for mixtures having a fixed ratio of H_2 to MP equal to 4. Comparisons between experimental data and GCA-EoS predictions are shown in Figure 7. All experimental isopleths present a minimum pressure near the critical point of the mixture. This unusual behavior is also qualitatively well described by the GCA-EoS model.

Figure 8 presents some results for ternary mixtures of H_2 + HD + C_3H_8 having a fixed ratio of H_2 to HD equal to 4. This system shows a three-phase liquid-liquid-vapor region. Binary systems of n-alcanols and propane show three-phase behavior beyond C_{18} [17]. It becomes apparent that the addition of H_2 moves the system into the three-phase region. Within the range of compositions measured in this work, the liquid-liquid-vapor region became smaller at higher propane concentrations and for some of the isopleths it was not possible to determine the limits of that region. The GCA-EoS model is able to predict the existence of this three-phase split. For the isopleth containing 82.9 mole % of propane, Figure 8 shows the liquid-liquid-vapor region predicted by the GCA-EoS equation, and the experimental data at which this phenomena was observed. Once again there is a good agreement between experimental evidence and GCA-EoS predictions.
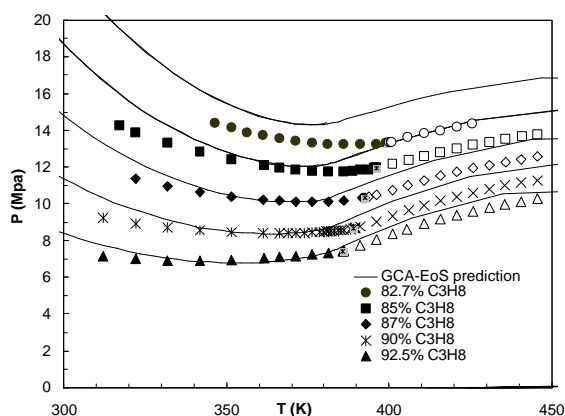

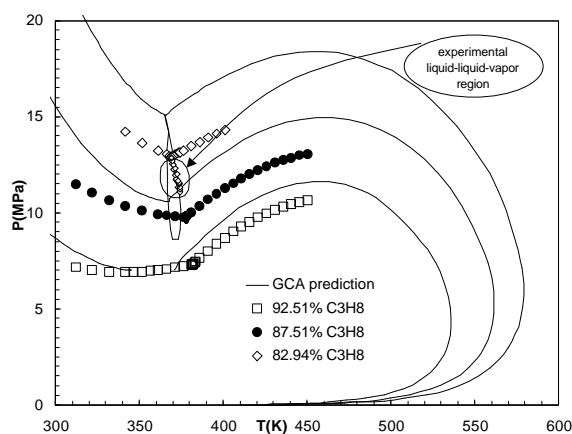Figure 7: Ternary system H_2 + MP + C_3H_8
(x(H_2) : x(MP) = 4)

Figure 8: Ternary system H_2 + HD + C_3H_8
(x(H_2) : x(HD) = 4)

CONCLUSIONS

In this work, the phase equilibrium behavior of mixtures related to the hydrogenolysis of fatty acid methyl esters under supercritical propane was studied. The GCA-EoS model is able to give a good representation of the experimental data and to predict vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibria using the same set of parameters. Therefore, the GCA-EoS model appears to be a useful tool to predict the phase behavior of the reactive mixtures and to determine the region of feasible operating conditions that will ensure a one-phase supercritical hydrogenation process.

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