Phase Equilibria Modeling of the Ternary and Quaternary Systems Containing Carbon Dioxide, Alcohol, Water and Glucose

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Phase equilibria for the quaternary system CO_2 + isopropanol + water + glucose has been predicted by using the Group Contribution Associating Equation of State (GCA-EoS). According with experimental data, the model can predict the coexistence of three phases in the pressure range of 9 to 12 MPa, while increasing pressure the middle liquid phase and the vapor phase merge and the system exhibit two phase vapor-liquid equilibria.

Besides the capability of the GCA-EoS model to differentiate the vapor-liquid-liquid and vapor-liquid equilibria regions using a unique set of parameters, adequate phase compositions are predicted when representing glucose solubility in the supercritical phase and glucose distribution between the two liquid phases. Thus, the model has been employed to predict the carbohydrate solubility in the supercritical phase when different alcohols are present in the mixture.

INTRODUCTION

Oligosaccharides can be obtained by means of enzymatic reactions. A mixture of components with different ring numbers is generally formed, following a costly purification stage in order to achieve the desired products. Liquid chromatography is used for that purpose at present, but new alternatives such as supercritical fluid extraction (SFE) is receiving considerably attention.

The use of supercritical carbon dioxide (SC-CO_2) to extract polar substances is generally accomplished by the addition of small amounts of co-solvents, which increase the solubility of the polar compound in the supercritical phase. However, addition of components to the supercritical solvent increase the complexity of the mixture phases equilibrium behavior. Particularly, mixtures containing CO_2, alcohol, water and carbohydrates exhibit a phase behavior transition from vapor-liquid-liquid (VLLE) to vapor-liquid equilibria (VLE) when increasing pressure, in the typical pressure range of supercritical fluid processes. Thus, both experimental phase equilibrium data and reliable thermodynamic models are necessary to support extraction experiments and process design.

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In this work the capability of a group contribution model, the GCA-EoS, to represent phase equilibrium behavior of mixtures containing CO_2, isopropanol, water and glucose is explored on the basis of the experimental data available in the literature. The group contribution approach allows a straight application of the thermodynamic model to systems containing different type of alcohols and carbohydrates, since the representation of the CO_2 + alcohol + water + carbohydrate mixture can be achieve with a reduced number of functional groups. The study is presented as a first step to model the extraction behavior of a mixture of carbohydrates in supercritical CO_2 with alcohol and water as modifiers.

I – THE GCA-EoS MODEL

The Group Contribution Associating Equation of State (GCA-EoS) [1] is an upgraded version of the GC-EoS developed by Skjold-Jørgensen [2]. The GCA-EoS model includes three contributions to the system residual Helmholtz energy: a repulsive free volume term, a contribution which accounts for dispersive attractive group interactions and a contribution from group association effects. For a detailed description of the model the reader is referred to Skjold-Jørgensen [2] and Gros et al. [1].

Espinosa et al. [3, 4] demonstrated that the model can represent vapor-liquid (VLE), liquid-liquid (LLE) and vapor-liquid-liquid (VLLE) equilibria, using a unique set of parameters, in mixtures of supercritical fluids with natural oils and derivatives. Additionally, Gros et al. [1] extended the application of the model to alcohols, water, gases and their mixtures by using a single self-associative hydroxyl (OH) group.

The extensive GCA-EoS parameter table reported in the literature [1, 2, 4-8] is based on the regression of a large set of binary phase equilibrium data, and is used in this work to explore the capability of the model to represent the phase equilibrium behavior of systems containing CO_2, isopropanol, water and glucose as a model carbohydrate. Association effects -which play a major role in this type of systems-, are taking into account by considering a single hydroxyl (OH) associative group, with the same associative strength in the water (H-OH), isopropanol (CH-OH) and glucose (AC-OH) molecules.

II – PHASE EQUILIBRIUM MODELING AND SOLUBILITY PREDICTIONS

In order to explore the capability of the GCA-EoS model to represent high pressure phase equilibria of mixtures containing CO_2, alcohol, water and carbohydrates, the ternary CO_2 + isopropanol + water system was analyzed first. Figure 1 shows a comparison between the experimental [9] VLE two-phase region (at 333 K and 20 MPa) and the phase envelope predicted by using the GCA-EoS model. Slopes of calculated tie lines are in good agreement with experimental data. Additionally, a comparison between experimental and calculated vapor/liquid phase compositions is depicted in detail in Figure 2. The two-phase vapor-liquid region calculated with the GCA-EoS model is in accordance with the experimental pressure range explored, i.e. between 13.8 and 30 MPa. Decreasing pressure up to 11.5 MPa the existence of a second liquid phase is predicted by the model, following the reported experimental data [10] for pressures below 12 MPa.
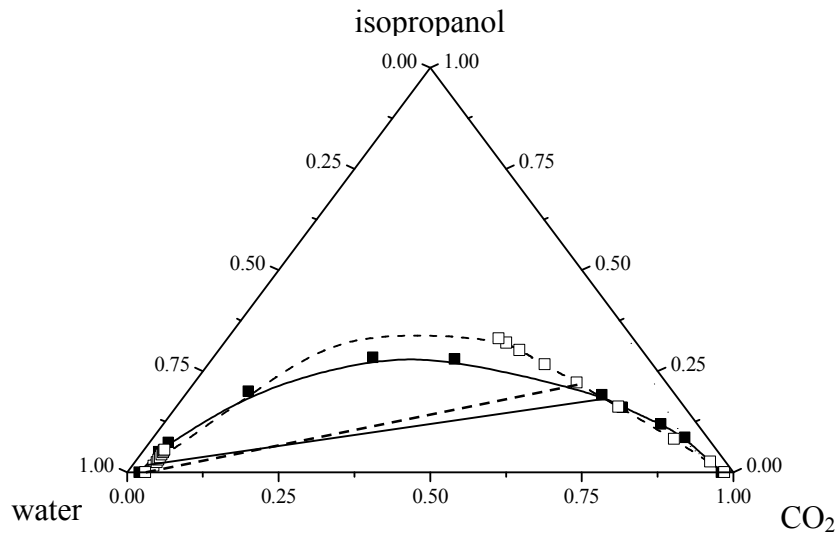
Figure 1.- Triangular diagram of the ternary CO_2 – isopropanol – water system at 333 K and 20 MPa. Solid lines and full symbols represent experimental data [9]; dotted lines and empty symbols represent GCA-EoS predictions.
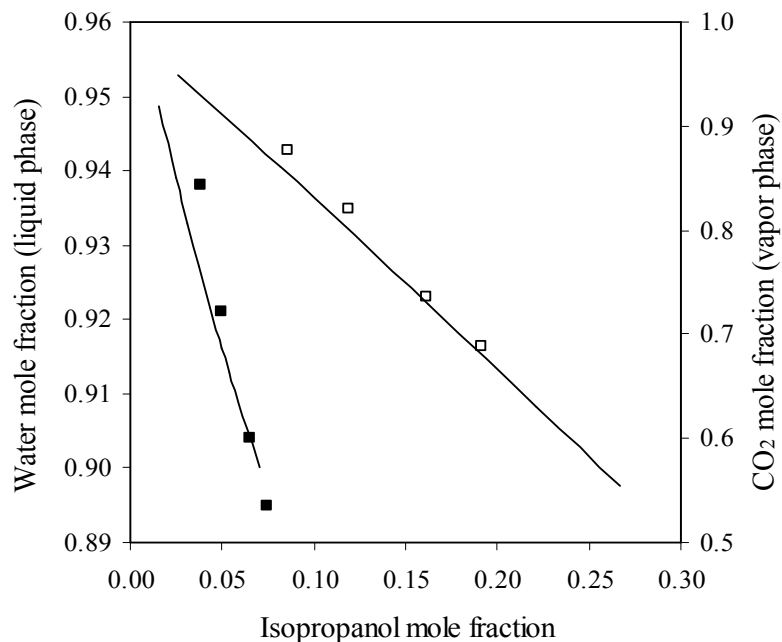

Figure 2.- Comparison between experimental liquid (■) and vapor (□) phase compositions with the GCA-EoS predictions for the ternary system CO_2 – isopropanol – water system at 333 K and 20 MPa.

The experimental phase equilibria reported for the quaternary CO_2 + isopropanol + water + glucose system [9, 10] also exhibits a VLLE region at low pressures, while increasing pressure at constant temperature the composition of the low-density liquid phase becomes more similar to the composition of the gas phase, and finally the two phases merge and VLE is attained. A comparison between the experimental CO_2 + isopropanol + water + glucose VLLE data and the GCA-EoS predictions is analyzed in Figures 3 and 4. The mole fractions of water and carbon dioxide in the vapor phase (V) divided by their mole fractions in the middle liquid phase (L2) at 333.15 K, are shown in Figure 3 as a function of pressure. Extrapolation of experimental data indicate that the L2 and V phases merge to one vapor phase at around 12 MPa, while the model prediction is 13.4 MPa. The glucose partition coefficient between the middle (L2) and lower liquid phase (L1) are satisfactory predicted, except at pressures very close to the L2-V merging point (see Figure 4).
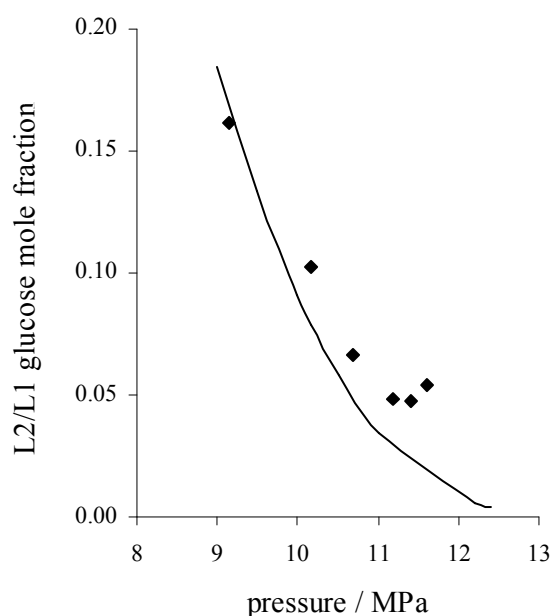

Figure 3.- Glucose mole fraction in de middle phase (L2) divided the glucose mole fraction in the lower phase (L1) at 333.15 K and different pressures. (◆): experimental data [10]; (———) GCA-EoS prediction.
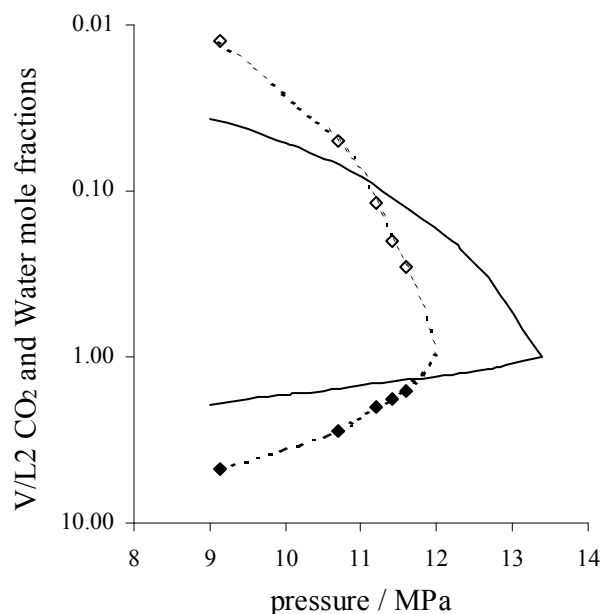
Figure 4.- Mole fraction of water (◇) and carbon dioxide (◆) in the vapor phase (V) divided by their mole fractions in the middle phase (L2) at 333.15 K and different pressures. (– –) extrapolation of experimental data [10]; (——) GCA-EoS prediction.

For the quaternary system, at 333.15 K and pressures above 13.4 MPa, the GCA-EoS model predicts VLE behavior. The experimental glucose solubility in the supercritical phase is compared with those calculated by the model in Figure 5, as a function of the sum of water and isopropanol vapor phase mole fractions. The glucose solubility mainly depend on the vapor phase loading with water and isopropanol, and increase exponentially with increasing

concentration of water + isopropanol [9]. The glucose mole fractions calculated with the GCA-EoS model are in quite good agreement with experimental data, although the model predicts a higher effect of pressure on glucose solubility than the experimentally observed.

Figure 6 shows the variation of glucose solubility in the supercritical phase, as predicted by the GCA-EoS model in the VLE calculation of mixtures with the same global molar composition but different type of alcohol (ethanol, isopropanol and 1-propanol). According to these results, when the same water + alcohol loading can be achieved in the vapor phase, higher glucose solubilities are obtained with ethanol.
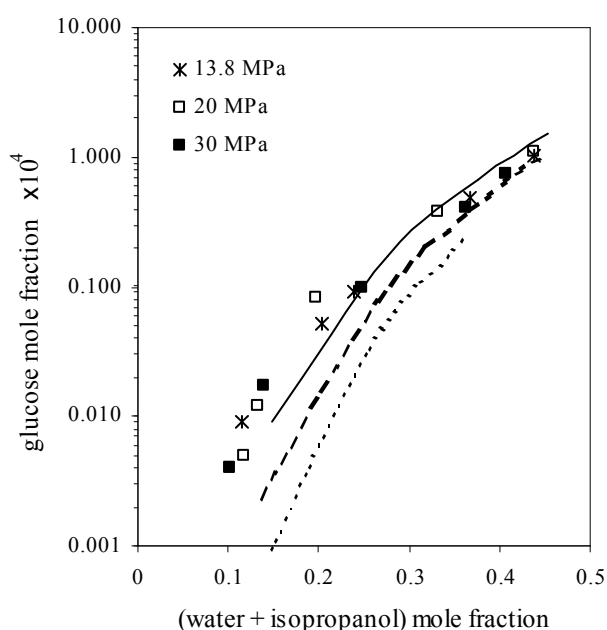
Figure 5.- Glucose solubility in the vapor phase vs. the sum of water and isopropanol mole fractions in the vapor phase at 333.15 K for the quaternary system CO_2 + isopropanol + water + glucose [9]. GCA-EoS predictions: $(\cdot\cdot\cdot)$13.8 MPa, $(- -)$ 20 MPa and $(—)$ 30 MPa.
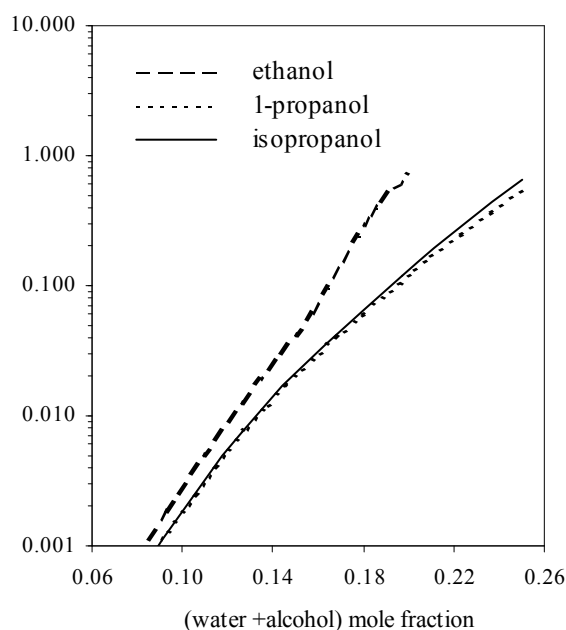
Figure 6.- Glucose solubility in the vapor phase vs. the sum of water and alcohol mole fractions in the vapor phase at 333.15 K and 20 MPa for the quaternary system CO_2 + alcohol + water + glucose.

CONCLUSIONS

The capability of the GCA-EoS model to represent high pressure phase equilibria of the CO_2 + isopropanol + water ternary system and CO_2 + isopropanol + water + glucose quaternary system has been explored in this work. Using a unique set of parameters, the model can predict the phase behavior transition from vapor-liquid-liquid to vapor-liquid

equilibria when increasing pressure. Furthermore, phase compositions are in quite good agreement with experimental data reported in the literature. These preliminary results encourage the fine-tuning of the GCA-EoS model to analyze the extraction and fractionation of carbohydrates by using SC-CO$_2$ and water + alcohol mixtures as co-solvents. At present, experiments are being conducted in our laboratory to selectively fractionate a group of carbohydrates using a mixture of SC-CO$_2$ + water + alcohol; experimental data obtained will be used to tune the GCA-EoS model.

ACKNOWLEDGEMENT

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