

AN UNCOMMON TYPE OF HIGH-PRESSURE FOUR PHASE EQUILIBRIA AND EFFECTS OF MULTIPHASE SPLIT ON SUPERCRITICAL FLUID EXTRACTION

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INTRODUCTION

High-pressure phase equilibria are of increasing interest due to the development of supercritical fluid technologies. The extension of the high-pressure phase equilibrium database has therefore received much attention in the last decades. The CO₂ + water + alcohol systems are of special interest in such areas as the design of solvent pairs for supercritical extraction, separation of alcohols from mixtures in which they are synthesized, and others. Several systematic investigations of ternaries CO₂ + water + alcohol have been carried out recently, e.g. [1-3], a review can be found in [4].

The present work addresses both thermodynamics of high-pressure multiphase equilibria and their influence on supercritical fluid extraction processes. The phase behavior of mixtures consisting of carbon dioxide, water and aliphatic alcohols (C1 to C8) was systematically studied based on new experimental data obtained in the present work with an analytic high-pressure view cell as well as literature data. The studies give a comprehensive picture of the multiphase behavior of these mixtures. In the system carbon dioxide + water + 1-hexanol, an uncommon type of four phase equilibrium was found. That type of four phase equilibrium was already predicted by J.W. Gibbs in the 19th century but has previously not been observed experimentally before. For modeling, the Redlich-Kwong-Soave equation of state with Huron-Vidal mixing rules was used. The simulations were performed using different algorithms, in particular the Interval-Newton Method.

I - EXPERIMENTAL SECTION

The measurements were carried out in a high-pressure optical cell (volume about 50 cm³; material: stainless steel). The cell is placed in an air bath to keep the temperature constant. The temperature was measured with a calibrated Pt100 resistance thermometer placed inside the cell with an accuracy of ± 0.1 K. The pressure was measured with a pressure transducer. The transducer was calibrated against a high-precision pressure gauge. The accuracy of the pressure measurements is ± 0.015 MPa.

To charge the cell, alkanol and water were pumped from storage vessels into the cell. Next, CO₂ was added by a compressor to adjust the desired pressure. The cell has two external loops in which samples from two different phases (heavy, light) are re-circulated

through stainless steel tubing with an inner diameter of 0.03 inches driven by HPLC pumps. It was assumed that equilibrium was reached in the cell, when the pressure and temperature were constant for at least 2 h.

Samples of the equilibrated phases were taken from the loops through two sampling valves (volume of 5 μl for the light phases and 1 μl for the heavy phases) and analyzed by gas chromatography. The tubing between the sampling valves and the gas chromatograph was heated in order to avoid condensation of the heavy components. Each sample was analyzed at least five times. The relative error of the analysis is about 4 %.

Critical points were determined by visual observation of the critical opalescence. For more details see [5].

II - HIGH-PRESSURE FOUR PHASE EQUILIBRIA

The phase behavior of the systems carbon dioxide + water + alkanol was studied in the region of the anticipated four-phase equilibrium. According to the Gibbs phase rule the number of degrees of freedom for a ternary mixture in a four-phase equilibrium is equal to one. Thus, the representation of the four-phase equilibrium in the p - T diagram of a ternary system is a curve, similar to the vapor-pressure curve of pure substances. The location of the four-phase equilibrium line is a central feature of the topology of phase diagrams of ternary systems and therefore significant for their classification.

A well-known type of phase behavior with four phase equilibria is observed in the system carbon dioxide + water + 1-butanol. For this system, Fig. 1 shows a prism consisting of isobaric-isothermal Gibbs phase diagrams for different pressures at 303.15 K. The information given in Fig. 1 is based on the experimental data of Winkler and Stephan [1]. The representation of concentrations however, has only qualitative character, because some of the phase regions are extremely small so that they were magnified for better visibility.

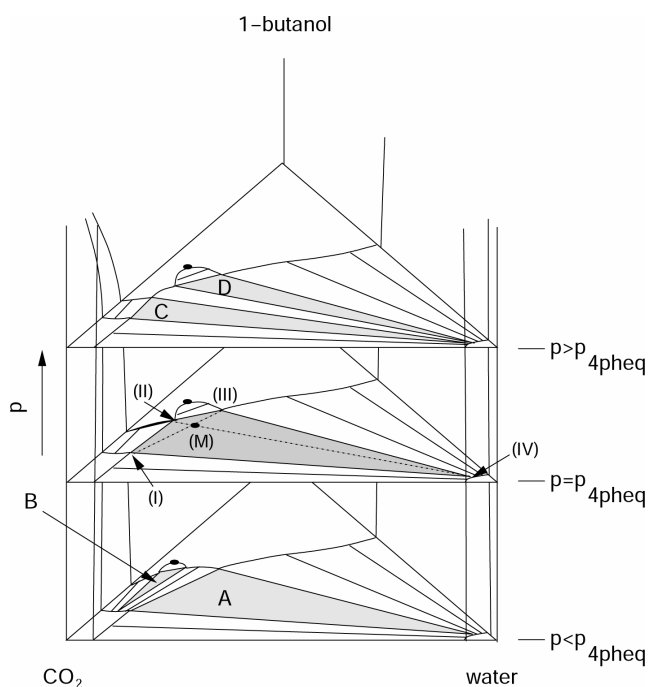


Figure 1. Phase behavior of mixtures of carbon dioxide + water + 1-butanol at 303.15 K ($p_{4pheq} = 6.74$ MPa);

At the highest pressure shown in Fig. 1, there exist two triangles representing two different three-phase equilibria (indicated by C and D). On all sides of the two three phase equilibria, there are two-phase regions, which either end in a binary systems or with a critical point. With decreasing pressure the three-phase equilibria C and D approach each other and finally merge along a common side forming a tetragonal four-phase equilibrium region.

If substance is removed from the equilibrium cell in which a four-phase equilibrium is established, e.g. by opening a shut-off valve, the pressure will not decrease, provided the temperature is constant. The change will only affect the mass ratios of the co-existing phases in the cell. This is another aspect of the similarity between the four-phase equilibria in ternary systems and the two-phase equilibria in binary systems.

The mechanism of the formation and splitting of four phase equilibria described above for the system carbon dioxide + water + 1-butanol is well known and has been observed in several other systems, e.g. in carbon dioxide + water + isopropanol [6]. Such behavior was predicted for the first time by J.W. Gibbs at the beginning of the last century [7]. It is noteworthy to mention that in the same work Gibbs anticipated another type of phase diagram, which, however, has not been observed so far.

Fig. 2 qualitatively represents experimental results obtained in the present work for the phase behavior of the system carbon dioxide + water +1-hexanol at 303.15 K. The main difference compared to Fig. 1 is the type of four-phase equilibrium. For carbon dioxide + water +1-hexanol at 303.15 K, the fourth phase lies inside the triangle formed by the other three phases. Lowering the pressure results in a disappearance of that fourth phase. Increasing the pressure results in a split of the four-phase region into three different three-phase regions (B, C, D in Fig. 2, upper diagram), which are connected by three two-phase regions that encircle a homogeneous region.

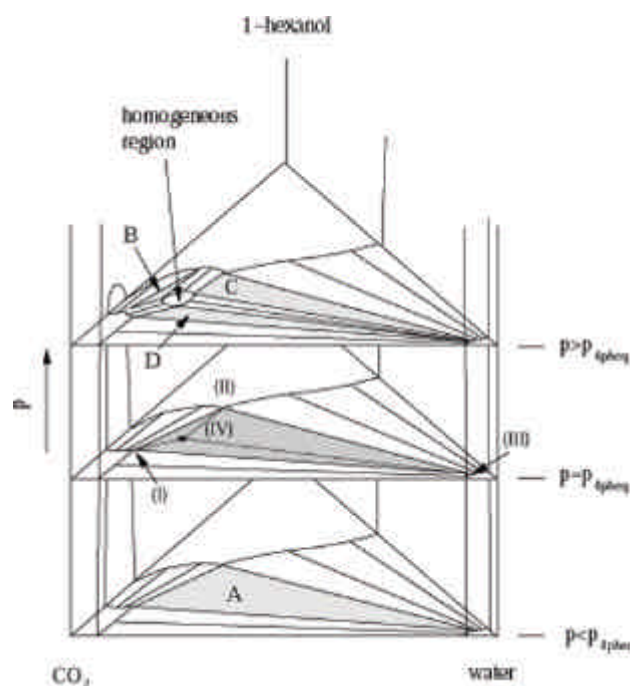


Figure2. Phase behavior of mixtures of carbon dioxide + water + 1-hexanol at 303.15 K ($p_{4pheq} = 6.91$ MPa);

In the experiments of the present work, the type of four-phase equilibrium described above was directly observed as well as two of the three three-phase equilibria (C and D). The three-phase region B is very small, so that it is hard to investigate it directly (Fig. 2 is only qualitative and region B is strongly magnified). Also the three-phase equilibrium A at low pressures was observed in the experiments.

III - MODELING

The phase equilibrium calculations carried out in the present work are based on the Redlich-Kwong-Soave equation of state with the energy-parameter calculated using the method of Sandarusi [8]. The mixing-rules of Huron and Vidal were used in their original form based on the NRTL-model for the G^E -term [9]. This model has three parameters for each of the pure components, which were fitted to the vapor-pressure curve, and three binary parameters for each binary mixture that were determined from experimental data for binary systems (mainly vapor-liquid equilibria).

The calculations of multiphase equilibria in ternary mixtures were initialized using two-phase equilibria in binary sub-mixtures as starting points. The binodal curves in the ternary mixture were found by increasing the concentration of the third component in the course of the calculations. Using a stability algorithm based on tangent-plane criterion [10] in combination with visual control of loops along the binodal curves, unstable states were identified. Then these states were chosen as initial values for finding compositions of three- and four-phase equilibria.

In the entire region of states of interest in the present work, the calculations are in qualitative agreement with the phase behavior observed experimentally. In particular, they confirm the new type of the four-phase equilibrium observed in the system carbon dioxide + water + 1-hexanol.

IV - EFFECTS OF MULTIPHASE SPLIT ON SUPERCRITICAL FLUID EXTRACTION

In addition to these fundamental thermodynamic studies, experiments with a laboratory high-pressure extraction column were carried out to examine the consequences of a multiphase-split on supercritical extraction processes. The extraction of acetone from aqueous solution with carbon dioxide, as a supercritical solvent at 313.15 K and 7.5 MPa, was chosen as an example, because the phase-behavior of this mixture is well investigated.

In contrast to most existing plants for SFE the extraction column offers the opportunity to watch the process via view glasses, which was important for current studies. The column was temperature and pressure-controlled so that one could establish isothermal and isobaric conditions, which is the common way to operate this process. Details on the experimental set-up are described in [5].

At the conditions studied here, the carbon dioxide + water + acetone system has a large three-phase equilibrium. The feeds to the extraction column were chosen so that during the extraction process a three-phase split had to occur (feed: mixture of about 10 mole % of acetone in water, solvent: pure carbon dioxide, solvent/feed ratios so that the overall mixing point was inside the three phase region). The process yields an extract rich in carbon dioxide and acetone and a raffinate rich in water with comparatively low acetone concentration. After expanding the extract, a mixture of acetone and water with a low water concentration is obtained.

The three phases, which can be found in the column, differ in their density. The water-rich phase (type L_1) has the highest density, the carbon dioxide-rich phase (type V) has the lowest density, and the density of the acetone-rich phase (type L_2) lies between the two other ones. In normal extraction processes, the continuous phase can be chosen deliberately. If the light phase is chosen, the disperse phase moves downward and vice versa. In the present case, in which a three-phase region has to be crossed, however, the choice is no longer deliberate. The dense phase (type L_1) has to be chosen as continuous one. Dispersing the light solvent CO_2 in this phase leads to gas-like bubbles (type V) enriching more and more with acetone in the lower part of the column (Fig. 3). When reaching the three-phase-equilibrium, bubbles with the concentration of the third phase (L_2) are formed that rise inside the continuous phase together with the lightest phase (V). After passing some height, the bubbles with the lower concentration of acetone (lightest phase V) disappear and a normal two phase extraction is observed again (disperse phase: type L_2 , continuous phase type L_1). This behavior has been proven experimentally by visual observation as well as analysis of the extract phase. A steady-state operation of the process could be reached despite the crossing the three-phase equilibrium.

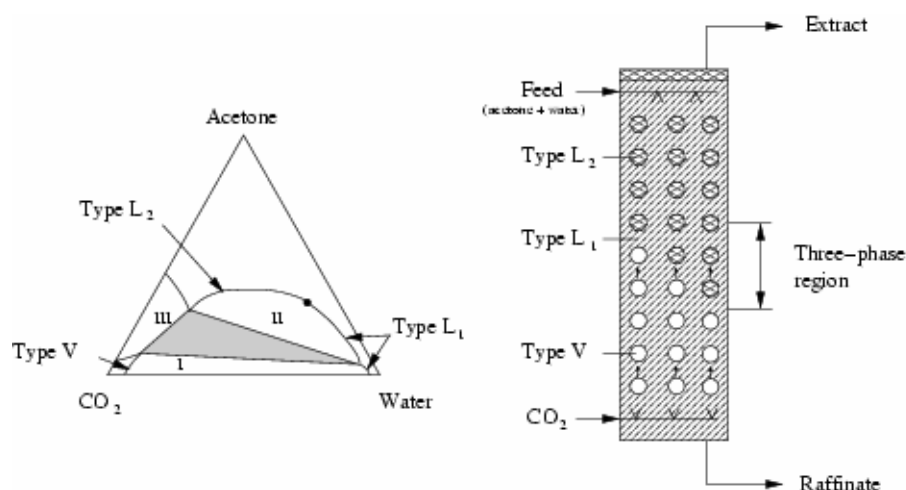


Figure 3. Supercritical fluid extraction process with three-phases: phase diagram of the system under investigation (left) and scheme of the extraction process (right).

It would be a wrong way to choose the lighter phase (Type V, Type L_2) as the continuous one. At the lower part of the column one begins with the lighter, CO_2 -rich continuous phase V and beginning at some point in the column, it should be replaced by a Type L_2 phase. As this phase is heavier than the phase V, it will fall to the bottom of the column and remix with the phase V. This means the process is stopped at this point of the column. The last point to be reached is the three-phase-equilibrium. This behavior was observed by a stable arrangement of layers inside the column and the analysis of the extract showing the concentration of the three-phase-equilibrium.

CONCLUSION

The phase behavior of the ternary system carbon dioxide + water + 1-hexanol was studied experimentally at 303.15 and 313.15 K. An uncommon type of four phase equilibria, which was already predicted by J.W. Gibbs in 19th century, but has previously not been observed experimentally, was found at 303.15 K. The phase behavior of the system carbon dioxide + water + 1-hexanol is qualitatively discussed and compared to a common type of phase behavior of ternary systems with four phase equilibria, using the system carbon dioxide + water + 1-butanol as an example. The experimental results are correlated with the Redlich-Kwong-Soave equation of state with Huron-Vidal mixing rules. With that simple model the complicated topology of the phase behavior of the studied system is successfully described, including the uncommon type of four-phase equilibria.

The study reveals the fundamental behavior of supercritical extraction processes under multiphase conditions. Extraction processes operated near states with multiphase-equilibria should be planned carefully with regard to the choice of the continuous phase.

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