

Multiphase Behavior in Ternary Mixtures of Elevated Pressures

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INTRODUCTION

Separations using supercritical or near-critical fluids as solvents are frequently carried out in the presence of water. Extraction of products from fermentation broths, tertiary oil recovery by CO₂ flooding, and supercritical-fluid (SCF) chromatography are examples of separations in which water can be present. Such systems will often exhibit phase behavior in which several coexisting fluid phases are present at equilibrium. For example, extensive regions of liquid-liquid-gas equilibrium have been observed for water-alcohol-SCF mixtures (1-3), and even four coexisting phases (liquid-liquid-liquid-gas) have been observed for n-propanol-water-CO₂ mixtures (4).

There are several practical implications of three-phase, liquid-liquid-gas equilibrium. For conventional extraction processes, it is desirable to avoid such regimes, or in the case of CO₂ flooding of oil reservoirs, to accurately account for multiple phases in determining extraction efficiency. Alternatively, the formation of two liquid phases in the presence of a compressed gas can be exploited to achieve a desired separation.

In this paper, we present the results of an investigation of fluid phase equilibria at elevated pressures for the system isopropanol-water-CO₂. These results include measured equilibrium compositions for two, three, and four coexisting fluid phases over a range of temperatures and pressures in the vicinity of the critical point of CO₂. A computer simulation of the phase equilibria for this three-component system is also presented. The simulation, which is based on the Peng-Robinson equation of state (7) and the experimental results, demonstrates the complexity of phase behavior that can be obtained for aqueous solutions in the presence of SCF solvents. This phase behavior must be understood for correct interpretation of SCF extraction experiments, and for design of separation processes using supercritical or near-critical solvents at elevated pressures.

EXPERIMENTAL SECTION

Phase compositions (tie lines) for liquid-gas equilibrium were measured using a flow technique for mixing and for continuous sampling of the phases. Equilibrium compositions for three and four coexisting phases were obtained using a static technique with a variable-volume view cell. This technique

involved calculating phase compositions from component material balances and measured phase volumes at known cell loadings; no sampling of the individual phases is required. Both experimental techniques are described in detail elsewhere(5,6).

Phase compositions for liquid-gas and liquid-liquid-gas equilibria were measured as a function of pressure at several constant temperatures. Figure 1 shows these results for 60°C in the form of triangular phase diagrams corresponding to different pressures. The two-phase regions which bound the three-phase triangles at the intermediate pressures have been omitted for clarity. At lower temperatures, four equilibrium phases were observed, and Figure 2 gives the measured compositions of these phases at 40°C and 1110 psia.

EQUILIBRIUM PHASE BEHAVIOR

The phase behavior depicted in Figure 1 shows a dramatic shift in the tie lines for liquid-gas equilibrium as pressure is changed from 1500 psia to 2000 psia. At the lower pressure, the solubilities of water and isopropanol in supercritical CO₂ are low, although the selectivity for the alcohol is high. At 2000 psia, high solubilities are obtained with lower alcohol selectivities. A continuous shifting of the tie lines between these two pressures can not be obtained, however, as three coexisting phases emerge at intermediate pressures. With increasing pressure, the water-rich liquid phase splits into two liquid phases at a pressure between 1500 and 1600 psia (a critical endpoint). As pressure is increased further, the composition of the liquid phase of intermediate density, L₂, approaches that of the carbon dioxide-rich gas phase, and the alcohol concentration initially increases and then decreases. Eventually the L₂ phase and the gas phase merge to form a single fluid phase (another critical endpoint) at a pressure just below 2000 psia.

One practical implication of this phase behavior is that the solvent properties of CO₂ can be changed significantly over a relatively small pressure range. Thus solvent/extract separation can be easily achieved, and an optimal ratio of solvent capacity to selectivity can potentially be selected, depending on whether three coexisting phases can be avoided in the separation process. It is also possible to use the two liquid phases to separate other components that would be present in dilute aqueous solution by distributing these components between the L₁ and L₂ phases. The advantage of such a separation would include (1) moderate operating temperatures and pressures, (2) the ability to control the composition of the intermediate phase with pressure, (3) the complete reversibility of the phase splitting, and (4) the ability to form two liquid phases with components that are similar in molecular nature.

The four-phase equilibrium illustrated in Figure 2 suggests that the phase behavior for this ternary mixture can be quite complex at conditions near the critical point of CO₂. In order to describe global phase equilibria for this system, the Peng-Robinson equation of state was fit to the

experimental results and then used to predict phase behavior over an extended region of temperatures and pressures. Details of these calculations are given elsewhere(6). The calculated pressure-temperature projection for isopropanol-water-CO₂ is given in Figure 3. This projection depicts the four-phase (LLLG) line for the ternary mixture, the three-phase (LLG) line for the binary water-CO₂ system, the vapor pressure curve for carbon dioxide (CO₂ VP), and the liquid-gas and liquid-liquid critical lines (dashed lines) which bound the three-phase regions for the ternary mixture.

Two important aspects of the phase behavior are evident from this projection. First, the three-phase region extends to relatively high temperatures and pressures; that is, the multiphase behavior is not limited to conditions close to the critical point of CO₂. Second, at temperatures and pressures near this critical point, the phase behavior can be quite complex. Four different three-phase regions bound the four-phase line, and there are five different two-phase regions which bound these three-phase regions. Obviously, simple screening experiments on this three-component system to obtain "representative" alcohol/water solubilities in compressed CO₂ could give dramatically different results depending on the temperature, pressure, and mixture composition examined. At temperatures below 20°C, even more complex behavior is possible since a solid hydrate phase can also be obtained.

In conclusion, our experimental results and model calculations demonstrate that complex multiphase behavior can occur for mixtures containing water and supercritical or near-critical fluids at elevated pressures. The ability to predict such behavior is an important factor in interpreting solubility behavior for SCF solvent extractions and for the design of separation processes using dense fluids at elevated pressures. The ability to form two liquid phases in the presence of a compressed gas can also be exploited to achieve a desired separation of nonvolatile components in dilute aqueous solutions where it is not possible to dissolve these components in a dense fluid such as compressed CO₂.

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FIGURE 1.

Experimental Two-Phase
and Three-Phase Equilibria at 60°C



