Registry No. ONP, 88-75-5; OAP, 95-55-6; H_2, 1333-74-0; methanol, 67-56-1; water, 7732-18-5.

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Gas-Liquid Equilibrium for Ethanol-Water-Carbon Dioxide Mixtures at Elevated Pressures

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Phase compositions for gas-liquid equilibrium have been measured for ternary ethanol-water-CO_2 mixtures at temperatures of 35, 50, and 65 °C and pressures of 10.2, 13.6, and 17.0 MPa. The experimental results can be used to characterize the solvent properties of dense CO_2 in the extraction of ethanol from aqueous solutions.

Introduction

Supercritical or near-critical fluids can be used as solvents for the extraction of organic compounds from aqueous solutions (*1*). One potential application for this solvent extraction technique would be to recover products from fermentation broths. Conventional recovery methods can be prohibitively expensive in these applications since product concentrations are typically quite low. Furthermore, the chemical nature of the products may preclude the use of separations involving distillation or extraction with organic solvents.

In this paper, we present the results of an experimental study of gas-liquid equilibrium at elevated pressures for the ternary system ethanol-water-carbon dioxide. Our results consist of equilibrium phase compositions for the two coexisting fluid phases as a function of temperature and pressure in the vicinity of the critical point of CO_2.

Studies on different aspects of fluid-phase equilibria for ethanol-water-CO_2 mixtures at elevated pressures have been reported previously in the literature. The triangular composition diagram for this ternary mixture at 25 °C and 6.5 MPa has been reported by Francis (*2*). Baker and Anderson (*3*) measured the phase boundary for gas-liquid equilibrium at temperatures from 10 to 50 °C and pressures up to 20 MPa. Although phase boundaries were determined with only moderate accuracy, the extent of the two-phase region on triangular composition diagrams was observed to initially decrease and then increase with increasing temperature at constant pressure. Their results also show that ethanol extraction with compressed CO_2 as the solvent will not give alcohol concentrations greater than that corresponding to the ethanol-water azeotrope. Efremova and Shvarts (*4*, *5*) measured gas-liquid and liquid-liquid critical end points which bound three-phase, gas-liquid-liquid equilibrium. They observed a tricritical point at 47.4 °C and 9.17 MPa where the gas-liquid and liquid-liquid critical end-point curves intersect. Kuk and Montagna (*6*) measured both CO_2 solubilities in ethanol-water mixtures and ethanol-water solubilities in compressed CO_2 at 40 and 60 °C, elevated pressures, and various ethanol concentrations. The reported results can be used to construct the phase boundary for gas-liquid equilibrium, but cannot be used to generate equilibrium tie-line compositions for this ternary system.

Experimental Section

A schematic diagram of the experimental apparatus is presented in Figure 1. A flow technique is used to facilitate mixing and subsequent sampling of the two fluid phases at elevated pressures. Liquid CO_2 and the ethanol-water solution are compressed to the desired operating pressure and delivered by separate high-pressure, liquid feed pumps (Milton Roy Model 396-89). These pumps are rated to 40 MPa and can operate over a range of flow rates from 46 to 460 mL/h. Typical flow rates for both pumps were on the order of 5 g/min.

After exiting the feed pumps, the two streams are combined and heated to the desired operating temperature in the crimped preheat line within the constant temperature bath. The equilibrated mixture then enters the view cell (Jerguson sight gauge, Model 17-T-40) where the two equilibrium phases separate. The more dense, liquid phase flows out the bottom of the view cell and is flashed to atmospheric pressure across the back pressure regulator (Grove Model 5-91 XW). The condensed portion of this sample is trapped in a dry ice-acetone bath while the CO_2 volume is measured by passing the gas through a wet-test meter (Precision Scientific Co.). The trapped condensate is subsequently weighed and analyzed by standard gas chromatographic techniques. The less dense fluid phase flows out the top of the view cell and is flashed across the heated micrometering valve (Whitey Co.). This two-phase sample is then analyzed by the same procedure described above for the dense, liquid phase.

The operating pressure of the system is set and maintained with the back pressure regulator, while the liquid level in the view cell is controlled by visually monitoring the gas-liquid meniscus and adjusting the micrometering valve to maintain two phases within the cell. System pressure is measured with a Bourdon-type Heise gauge (Gregory Model CM, 0-5000 psi range) accurate to ±0.05 MPa. Pressure variations due to pumping were found to be less than ±0.167 MPa over the entire pressure range studied, and were typically less than ±0.10 MPa. System temperature is controlled to within ±0.15 °C with a Sargent-Welch Thermonitor, and is measured to

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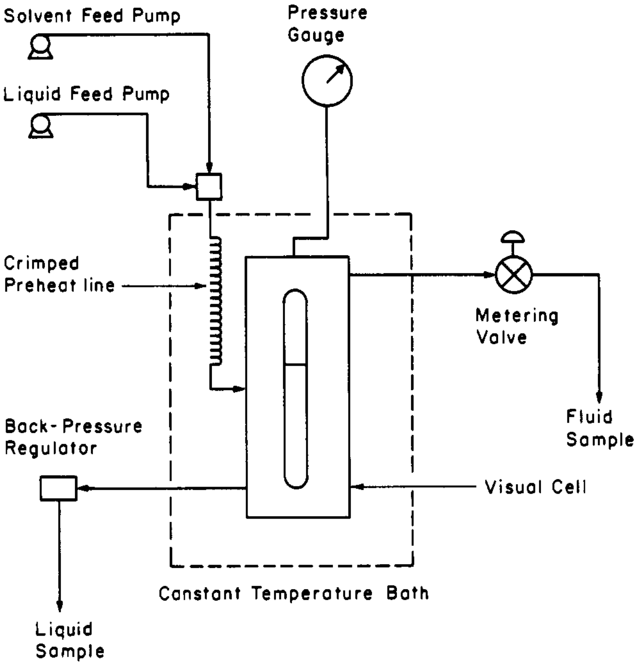

Figure 1. Schematic diagram of the experimental apparatus.

Table I. Measured Equilibrium Tie-Line Compositions (in Mole Fractions) for Ethanol-Water-CO_2 Mixtures at 35 °C

fluid phase			liquid phase		
H_2O	ETOH	CO_2	H_2O	ETOH	CO_2
P = 10.2 MPa					
0.004	0.005	0.991	0.944	0.032	0.024
0.015	0.060	0.925	0.510	0.339	0.151
0.018	0.065	0.917	0.421	0.370	0.210
0.030	0.101	0.869	0.242	0.377	0.381
0.012	0.044	0.944	0.678	0.249	0.073
0.007	0.021	0.972	0.852	0.118	0.030
P = 13.6 MPa					
0.004	0.005	0.991	0.943	0.032	0.025
0.027	0.087	0.886	0.415	0.362	0.223
0.060	0.160	0.780	0.220	0.350	0.430
0.044	0.132	0.824	0.248	0.362	0.390
0.015	0.054	0.931	0.691	0.238	0.071
0.007	0.020	0.973	0.850	0.120	0.030
P = 17.0 MPa					
0.004	0.005	0.991	0.942	0.032	0.026
0.034	0.102	0.864	0.408	0.358	0.234
0.059	0.152	0.792	0.254	0.351	0.395
0.016	0.055	0.929	0.696	0.234	0.070
0.008	0.022	0.970	0.856	0.113	0.031

Table II. Estimated Plait Points for Ethanol-Water-CO_2 Mixtures at 35 °C

	plait point compositions[a]		
press., MPa	ethanol	water	CO_2
10.2	0.163	0.062	0.775
13.6	0.194	0.082	0.724
17.0	0.212	0.102	0.686

[a] In mole fractions.

within 1 °C with a calibrated copper-constantan thermocouple.

Linde "bone dry" grade (99.8% purity) carbon dioxide, reagent grade ethanol (U.S. Industrial Chemical Co.) and distilled/deionized water were used without further purification.

Results and Discussion

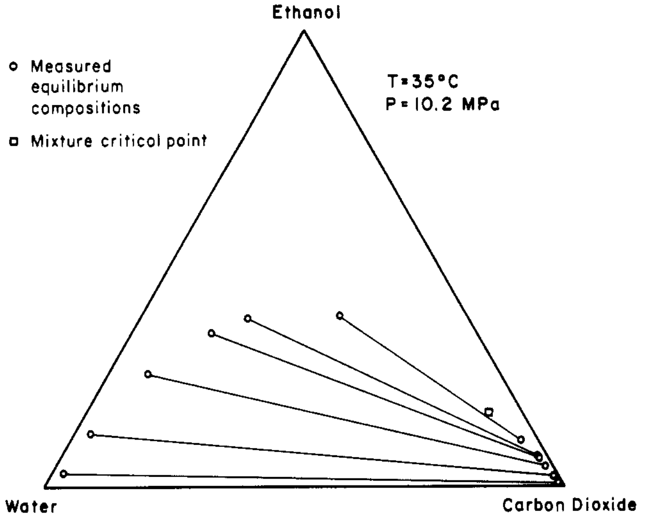

Figure 2. Measured equilibrium tie-line compositions in mole fractions for ethanol-water-CO_2 mixtures at 35 °C and 10.2 MPa.

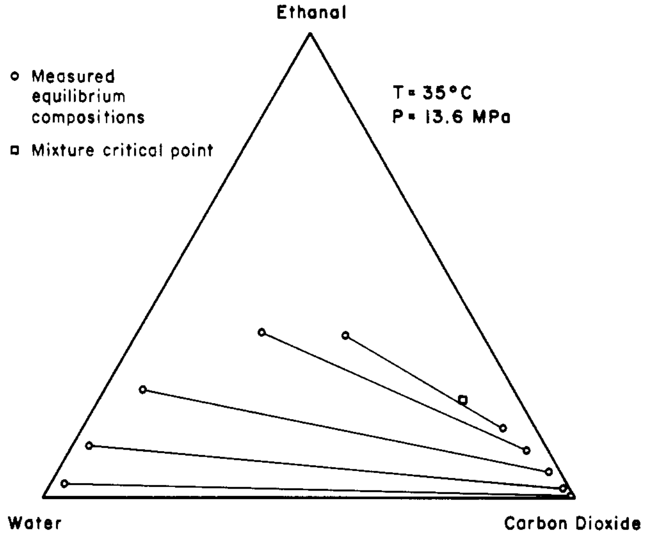

Figure 3. Measured equilibrium tie-line compositions in mole fractions for ethanol-water-CO_2 mixtures at 35 °C and 13.6 MPa.

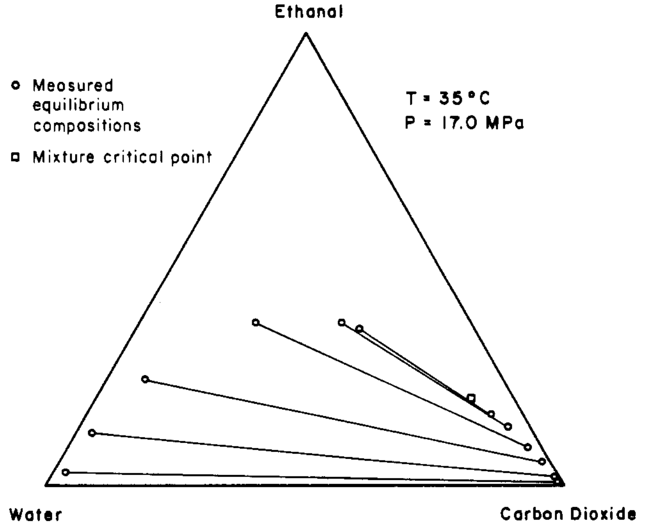

Figure 4. Measured equilibrium tie-line compositions in mole fractions for ethanol-water-CO_2 mixtures at 35 °C and 17.0 MPa.

Measured equilibrium tie-line compositions at 35 °C and pressures of 10.2, 13.6, 17.0 MPa are given in Table I and on triangular composition diagrams in Figures 2, 3, and 4, respectively. The reported compositions represent average values obtained from duplicate samples which were reproducible to within 0.5 mol %. The experimental uncertainties in these compositions have been estimated to be less than 1%

Table III. Measured Equilibrium Tie-Line Compositions (in Mole Fractions) for Ethanol-Water-CO_2 Mixtures at 50 and 60 °C

fluid phase			liquid phase		
H_2O	ETOH	CO_2	H_2O	ETOH	CO_2
T = 50 °C, P = 10.2 MPa					
0.004	0.004	0.992	0.946	0.032	0.022
0.012	0.048	0.940	0.410	0.371	0.219
T = 50 °C, P = 13.6 MPa					
0.006	0.005	0.989	0.945	0.031	0.023
0.027	0.083	0.890	0.408	0.356	0.236
T = 50 °C, P = 17.0 MPa					
0.006	0.006	0.988	0.945	0.031	0.024
0.037	0.104	0.859	0.401	0.346	0.253
T = 65 °C, P = 10.2 MPa					
0.005	0.005	0.990	0.948	0.031	0.021
0.007	0.020	0.973	0.417	0.389	0.194
T = 65 °C, P = 13.6 MPa					
0.006	0.006	0.988	0.948	0.030	0.022
0.019	0.060	0.921	0.400	0.355	0.245
T = 65 °C, P = 17.0 MPa					
0.006	0.007	0.987	0.946	0.030	0.024
0.042	0.106	0.852	0.390	0.340	0.270

of the measured value or 0.1 mol % whichever is greater. Mixture critical points or plait points have also been estimated from the experimental data by using a graphical method (*7*), and are included in these figures. These estimated plait points are listed in Table II. Equilibrium tie-line compositions measured at the same three pressures but higher temperatures, 50 and 65 °C, are presented in Table III.

The experimental results can be used to characterize the solvent properties of dense CO_2 in the extraction of ethanol from aqueous solutions. At all conditions studied, fluid-phase ethanol solubilities are appreciably higher than water solubilities, which indicates that compressed CO_2 at moderate temperatures and pressures would be a reasonably selective solvent for the extraction of ethanol from aqueous solutions. However, the results also show that ethanol concentrations greater than that corresponding to the ethanol-water azeotrope would not be obtained by extraction with CO_2 at the temperatures and pressures studied. This finding is in agreement with the experimental observations of Baker and Anderson (*3*).

The effect of solvent density on the solvent properties of CO_2 is also evident from the effect of pressure on plait point compositions at 35 °C (Table II). Ethanol mole fractions at the plait point increase from 0.163 to 0.212 as pressure is increased from 10.2 to 17.0 MPa. Water mole fractions also increase from 0.062 to 0.102 over the same pressure range. The higher solubilities correspond to greater solvent capacities at higher CO_2 densities. However, reduced ethanol selectivities are also obtained with greater solvent capacities. A similar effect can be found by examining ethanol-water solubilities in the fluid phase as a function of isobaric temperature changes.

Although the observed changes in solvent properties of CO_2 are appreciable for this ternary mixture, much more dramatic changes have been observed for 2-propanol-water-CO_2 mixtures (*8*). The phase behavior for this latter ternary mixture in the vicinity of the critical point of CO_2 is also much more complex. This suggests that the solvent properties of supercritical CO_2 cannot be correlated with CO_2 density alone; the phase behavior for the ternary mixture is an important factor. This phase behavior is the subject of a subsequent paper (*9*).

Registry No. CO_2, 124-38-9; ethanol, 64-17-5.

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Experimental Study of Excess Enthalpies for the Binary Gaseous System Methane-Ethylene by Flow Calorimetry

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Excess enthalpies for the binary system methane-ethylene were measured in an isothermal flow calorimeter. The experimental study has been made at three temperatures, 293.15, 305.15, and 313.15 K, and pressures of 1.114, 1.520, and 3.445 MPa (11, 15, and 34 atm). The experimental results were compared with those predicted from Redlich-Kwong and Benedict-Webb-Rubin equations of state. The binary interaction coefficient, k_{ij}, has been determined from experimental data by an optimization procedure. A single value independent of temperature and pressure was sufficient to represent all the network of data.

Introduction

Excess enthalpies are very important for solving engineering problems. They are very useful in equipment design, heat of solution calculations, and energy balances. Excess enthalpies are also particularly important from a scientific point of view since they are useful to verify prediction of thermodynamic properties of mixtures by equations of state. These predictive equations are usually based upon theories of molecular interaction.

The excess enthalpy of a mixture at constant temperature and pressure is defined as

$$H^E_{T,P} = \Delta H_m - \Delta H_m^{id} = [H_m - \sum x_i H_i]_{T,P} \qquad (1)$$

For an ideal solution, the heat of mixing is zero ($\Delta H_m^{id} = 0$), so either of the terms excess enthalpy or heat of mixing can be used, since these two quantities are numerically equal ($H^E_{T,P} = \Delta H_m$).

Although many experimental studies of excess enthalpies for liquids are reported in literature, few data for gas mixtures are

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