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Single-Phase Limit for Mixtures of Tri-*n*-butyl Phosphate + CO_2 and Bis(2-ethylhexyl)phosphoric Acid + CO_2

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With a high-pressure variable-volume view cell, the single-phase limit for binary mixtures of tri-*n*-butyl phosphate (TBP) + CO_2 and bis(2-ethylhexyl)phosphoric acid (DEHPA) + CO_2 was determined at conditions applicable to supercritical fluid extraction of metal extractants (313.15−353.15 K, 4−30 MPa, 0−0.19 mole fraction of TBP, and 0−0.60 mole fraction of DEHPA). For each binary TBP + CO_2 and DEHPA + CO_2 system, the locus of the $P-T-x$ limit of the single-phase region was measured.

Introduction

Supercritical fluid extraction (SFE) using CO_2 with an organic chelating agent such as tri-*n*-butyl phosphate (TBP) and bis(2-ethylhexyl)phosphoric acid (DEHPA) has been recognized as a promising advanced method for separating metal ions from liquid-phase wastes in nuclear industry and hydrometallurgy. One of advantages of SFE is that extraction efficiency and selectivity can be enhanced by fine-tuning pressure and/or temperature (McHugh et al., 1994). Also, SFE can minimize the amount of solvent waste. Examples of SFE applications include a separation of metal ions from nitric acid solution by supercritical CO_2 solvent containing an organophosphorus extractant such as TBP or DEHPA. Hence, an increasing number of studies on the development of SFE of metals are available (Wai et al., 1997; Smart et al., 1997a). There have been studies on the solubility and/or phase behavior of organophosphorus compounds in supercritical CO_2 to establish extraction conditions for SFE and to design a new extractant feasible for SFE of metal ions (Smart et al., 1997b; Lin et al., 1995).

Besides solubility measurement, determination of phase behaviors such as the single-phase limit for binary mixtures of chelating agent and supercritical CO_2 over a wide range of temperatures and pressures is important to establish suitable conditions for SFE. There have been studies on the phase behavior of organophosphorus compounds in supercritical CO_2 (Page et al., 1993). However, their studies of phase behavior frequently were at a limited range of equilibrium conditions.

In the present study, the phase behavior of TBP and DEHPA in supercritical CO_2 was measured over a wide range of temperatures (313.15−353.15 K), pressures (4−30 MPa), and concentrations of chelating agents (0−0.19 mole fraction of TBP and 0−0.60 mole fraction of DEHPA). These results can be very valuable information for rational design and operation of SFE processes for the separation of metal ions from various types of liquids.

Experimental Section

Apparatus. A schematic diagram of a variable-volume view cell is shown in Figure 1. The internal volume of the cell is 33 cm^3. This apparatus was built to operate up to 35 MPa and up to 473.15 K. The valves are products from Autoclave Inc. (Erie, PA), and the syringe pump (ISCO 260DM, Lincoln, NE) was equipped to accurately charge CO_2 (±2.0%). A Fisher Hamilton tight syringe (Pittsburgh, PA) was used to charge organic modifiers into the cell. Pressure in the cell was generated via pressurization with a pressure generator (Model No. 550.0202.1, NOVA, Swiss). The equilibrium pressure in the cell is measured with a DP cell (ISI 0163-5 OCB, Winchester, MA) to within ±0.05 MPa. The temperature in the cell was maintained with a PID regulator (Hanyoung Co., Seoul, Korea) in an air bath (Jeio Tech. FO-600M, Seoul, Korea) to within ±0.1 K. The temperature was measured with a standard thermometer (Witeg, Germany) and a Pt-100Ω thermocouple to within ±0.1 K. A sapphire window was attached at the front end of the cell, and phase equilibrium behavior was observed with a CCD (charge coupled device) with a halogen light source, a camera (Toshiba IK-C41MF, Japan), and a real time frame grabber (Data Translation Co., MASH Series DT3155, MA). A magnetic stirrer is used for mixing the fluid mixture in the cell.

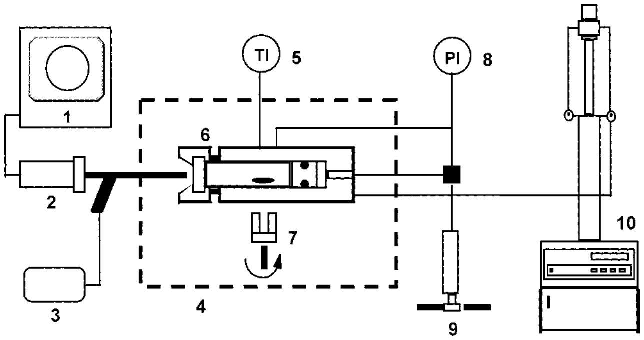

Figure 1. Schematic of the high-pressure variable-volume view cell: 1, monitor; 2, CCD camera; 3, halogen light source; 4, air oven; 5, temperature indicator; 6, variable volume view cell; 7, magnetic stirrer; 8, pressure indicator; 9, pressure generator; 10, syringe pump.

Experiment. High-purity TBP (>99%) was from Aldrich Co. (Milwaukee, WI), and DEHPA (>99%) was from Merck & Co., Inc. (Whitehouse Station, NJ). CO_2 (>99.9%) was purchased from Seoul Gas Co. (Seoul, Korea). For each run, the whole line of the apparatus was evacuated with a

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Table 1. $P-T-x$ Surface for Single-Phase Limit of TBP/CO_2 System

	P/MPa						
T/K	$x_{TBP} = 0.037$	$x_{TBP} = 0.055$	$x_{TBP} = 0.073$	$x_{TBP} = 0.078$	$x_{TBP} = 0.098$	$x_{TBP} = 0.137$	$x_{TBP} = 0.189$
313.15	8.9	8.9	9.8	8.8	8.8	8.6	8.2
318.15	10.0	10.1	9.8	9.7	9.4	8.8	8.5
323.15	11.1	11.3	11.1	11.0	10.6	10.0	9.1
328.15	12.5	12.6	12.4	12.4	11.8	11.1	10.1
333.15	13.5	13.8	13.6	13.5	13.0	12.1	10.8
343.15	14.7	15.0	14.8	14.9	14.3	12.8	11.6
353.15	15.8	16.1	16.0	15.9	15.4	13.9	12.2

Table 2. $P-T-x$ Surface for Single-Phase Limit of DEHPA/CO_2 System

	P/MPa							
T/K	$x_{DEHPA} = 0.031$	$x_{DEHPA} = 0.049$	$x_{DEHPA} = 0.089$	$x_{DEHPA} = 0.199$	$x_{DEHPA} = 0.268$	$x_{DEHPA} = 0.336$	$x_{DEHPA} = 0.450$	$x_{DEHPA} = 0.594$
313.15	21.3	23.7	21.9	9.5	7.9	7.0	4.9	3.6
318.15	22.3	24.2	22.6	10.5	8.4	7.6	5.4	3.8
323.15	23.1	25.0	23.5	11.3	9.1	8.2	5.7	4.0
328.15	24.2	25.9	24.5	12.4	9.5	8.5	6.0	4.2
333.15	25.1	26.7	25.6	13.6	10.0	9.0	6.3	4.5
343.15	27.8	28.0	27.5	15.6	11.1	10.1	7.0	4.8
353.15	29.1	29.3	29.2	17.1	12.4	11.2	8.3	5.4

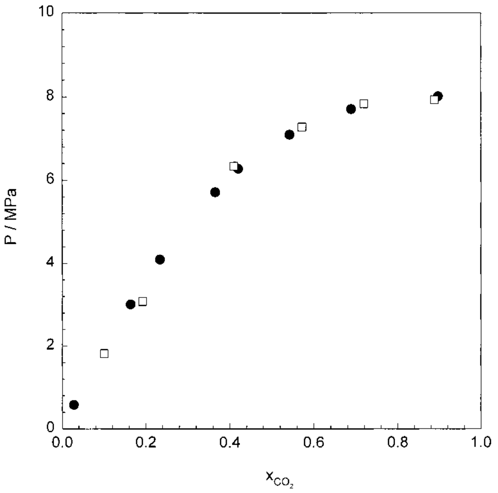

Figure 2. Phase behavior of the methanol/CO_2 system at 313.15 K: (□) data obtained in this work; (●) data reported by Ohgaki et al. (1976).

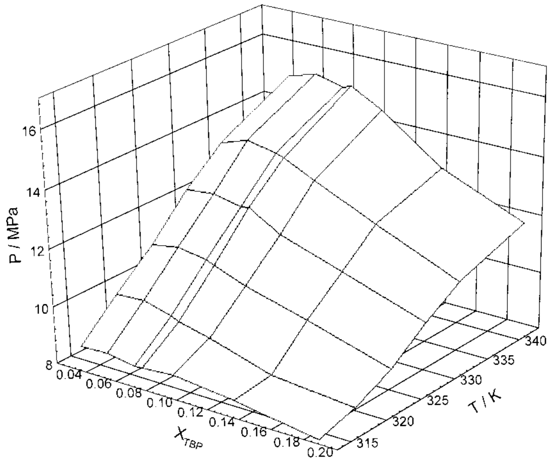

Figure 3. Single-phase limit in $P-T-x$ space for the TBP/CO_2 system.

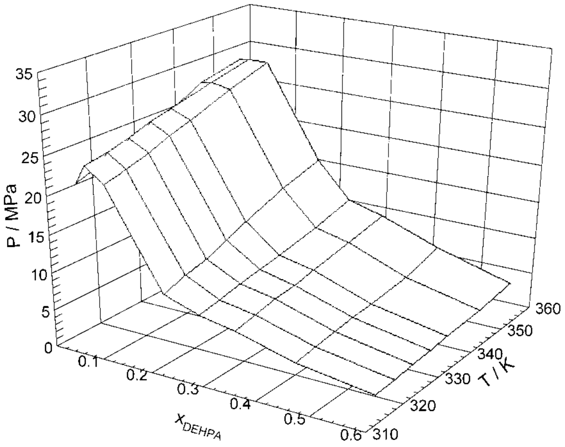

Figure 4. Single-phase limit in $P-T-x$ space for the DEHPA/CO_2 system.

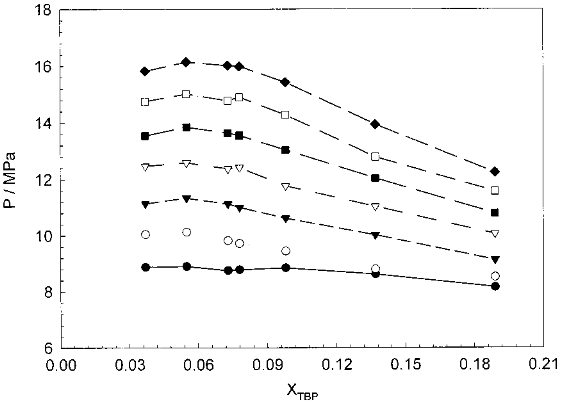

Figure 5. Locus of transition pressures versus TBP mole fraction in the TBP/CO_2 system: (●) 313.15 K; (○) 318.15 K; (▼) 323.15 K; (▽) 328.15 K; (■) 333.15 K; (□) 343.15 K; (◆) 353.15 K.

vacuum pump. While the cell was kept evacuated, a known amount of TBP or DEHPA was charged into the cell with the gastight syringe. A known volume of liquid CO_2 at 313.15 K and 20 MPa was charged into the cell with the ISCO syringe pump and well mixed for 1 h. While the isothermal conditions of the cell were maintained, the mixture of TBP or DEHPA with CO_2 was pressurized to a high pressure to make the mixture a homogeneous single phase. By adjusting the intensity of the halogen light source, the phase behavior in the cell was observed on the computer monitor. The mixture in the cell was well mixed for several hours, and the phase state was checked repeatedly. After it was confirmed whether the fluid mixture was a single-phase equilibrium or not, the pressure in the cell was slowly lowered with the pressure generator. Then the

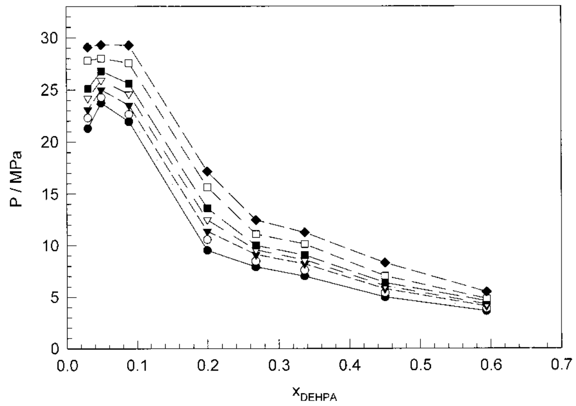

Figure 6. Locus of transition pressures versus DEHPA mole fraction in DEHPA/CO_2 system: (●) 313.15 K; (○) 318.15 K; (▼) 323.15 K; (▽) 328.15 K; (■) 333.15 K; (□) 343.15 K; (◆) 353.15 K.

transition pressure (pressure at which the two-phase to one-phase transition takes place) was measured. For each mixture, measurement of the phase behavior was repeated three times.

Phase Behavior of TBP + CO_2 and DEHPA + CO_2

To check the reliability of the apparatus, transition pressures were measured for the methanol + CO_2 system at 313.15 K over an entire range of concentrations of methanol. The results were compared with existing reliable data (Ohgaki et al., 1976) in Figure 2. After the confirmation, the phase behaviors of TBP + CO_2 and DEHPA + CO_2 were measured. Phase behavior data for the TBP + CO_2 system measured at various conditions (313.15−353.15 K, 0.037−0.189 mole fraction of TBP) and results were summarized in Table 1. Similar data for the DEHPA + CO_2 system at various equilibrium conditions (313.15−353.15 K and 0.031−0.594 mole fraction of DEHPA) were summarized in Table 2. The standard deviation of the transition pressures measured in the present work was within ±0.01−0.20 MPa.

The data for the TBP + CO_2 system obtained in the present study were well in agreement with the data reported by Page et al. (1993). However, the results obtained in this work cover a wider range of conditions than the results reported by the previous investigators. On the basis of data in Table 1 and Table 2, the $P-T-x$ surface for the single-phase limit was shown in a 3-D diagram in Figure 3 for the TBP + CO_2 system and in Figure 4 for the DEHPA + CO_2 system. In these figures, the upper part is the single-phase region and the lower part is the two-phase region.

With increasing the concentration of TBP in the TBP + CO_2 system at isothermal conditions and 0.073 mole fraction of TBP, there exists a maximum point of the locus of the transition pressure, as shown in Figure 5. In Figure 5 the upper part is the single-phase region. However, the phase behavior of the DEHPA + CO_2 system is significantly different from that of the TBP + CO_2 system, as shown in Figure 6. On increasing the concentration of DEHPA at a constant temperature, the transition pressure is lowered in the DEHPA + CO_2 system. Especially in the low DEHPA concentration region (0.031−0.089 mole fraction), the transition pressure was elevated significantly. The critical opalescence was observed for the DEHPA + CO_2 system in the mole fraction range from 0.031 to 0.049 in Figure 6. This means that there exists a pseudocritical point of this mixture. Also, for these TBP + CO_2 and DEHPA + CO_2 systems, transition pressures at constant concentrations were elevated with increasing equilibrium temperature.

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