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Phase Behavior of Diethyl Methylphosphonate and 2-Chloroethyl Methyl Sulfide in Supercritical Carbon Dioxide

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Pressure−composition isotherms are reported for diethyl methylphosphonate and 2-chloroethyl methyl sulfide in carbon dioxide at 35, 55, and 75 °C. These two CO_2−polar solute systems do not exhibit three-phase equilibria in the vicinity of the critical point of CO_2. Pressures less than ≈140 bar are needed to obtain a single phase for both binary mixtures at temperatures up to 75 °C.

Introduction

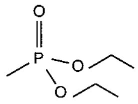
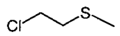
There is heightened interest in eliminating or safely deactivating large United States stockpiles of chemical warfare agents (CWAs). Alternatives to incineration are desirable for the reduction of the stockpiles of these dangerous agents without the concomitant production of noxious byproducts.[1] In addition, there is a concern that CWAs exhibit a long lifetime in soil,[2] which has led to the development of selective extraction techniques for contaminated soils to detect low concentrations of these toxic compounds.[3,4] Supercritical carbon dioxide is an especially attractive solvent for processing CWAs because CO_2 is a nontoxic environmentally acceptable solvent.[5] Fundamental phase equilibrium data are needed for CWA + CO_2 mixtures to ascertain whether supercritical fluid technology can be used to process sulfide-based and phosphorus-based compounds.

In this paper, we present the phase behavior for diethyl methylphosphonate and 2-chloroethyl methyl sulfide in CO_2 at temperatures from 35 to 75 °C. Diethyl methylphosphonate (DEMP), whose structure is shown in Table 1, is a simulant for the type of precursors used as nerve agents.[4] The chloroethyl methyl sulfide (CEMS), whose structure is also shown in Table 1, has a chemical structure close to that of mustard gas, which is bis(2-chloroethyl) sulfide.[2] The phase behavior data for DEMP and CEMS in supercritical CO_2 provides insight into the pressures needed to dissolve or extract them at low to moderate temperatures. A limited number of experiments were also performed at temperatures of approximately 7 °C below the critical temperature of CO_2 ($T_c = 31.0$ °C) to search for a three-phase region.[6]

Experimental Section

The experimental apparatus and techniques used in this study are described in detail elsewhere[7] and are briefly described here. The synthetic method is used to obtain dew, bubble, and critical points. The main component of the experimental apparatus is a high-pressure, variable-volume cell (Nitronic 50, 7.0-cm o.d. × 1.6-cm i.d., ≈30-cm^3 working volume). Initially, the cell is loaded with a measured amount of DEMP or CEMS to within ±0.002 g. The cell is then flushed very slowly with CO_2, at pressures <3 bar, to remove entrapped air. CO_2 is then transferred into the cell gravimetrically to within ±0.02 g using a high-pressure bomb. The mixture in the cell is viewed with a borescope (Olympus Corporation, model F100-024-000-55) placed against a sapphire window secured at one end of the cell. A stir bar actuated by a magnet located below the cell mixes the contents of the cell.

Table 1. Structure of Diethyl Methylphosphonate and 2-Chloroethyl Methyl Sulfide

Diethyl Methylphosphonate ($C_5H_{13}O_3P$)	2-Chloroethyl Methylsulfide (C_3H_7ClS)
	

The solution can be compressed to the desired operating pressure by a movable piston fitted within the cell. System pressure is measured with a Heise gauge accurate to within ±0.7 bar. Because the pressure is measured on the water side of the piston, the pressure needed to move the piston (0.7 bar) is added to gauge pressure to obtain the absolute pressure. The system temperature, measured to within ±0.1 °C with a type K thermocouple, is maintained to within ±0.2 °C.

Dew, bubble, and mixture-critical points are detected visually in the following manner. At a fixed temperature the mixture in the cell is compressed to a single phase. The pressure is then slowly decreased until a second phase appears. If a fine mist appears, a dew point is obtained; however, if a small vapor bubble is observed, a bubble point is obtained. In either case, the composition of the major phase present is equal to the composition of the overall solution because the small amount of mass in the precipitated phase can be neglected. The transition is a mixture-critical point if a reddish-orange critical opalescence is observed during the transition process and if two phases

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Table 2. Pressure−Composition Data for the Carbon Dioxide + Diethyl Methylphosphonate (DEMP) System Obtained in This Study; BP Is a Bubble Point and DP Is a Dew Point

t = 35.0 °C			*t* = 55.0 °C			*t* = 75.0 °C		
mole fraction DEMP	*P* (bar)	transition	mole fraction DEMP	*P* (bar)	transition	mole fraction DEMP	*P* (bar)	transition
0.794	14.1	BP	0.714	30.0	BP	0.245	101.0	BP
0.549	29.7	BP	0.417	56.9	BP	0.189	114.8	BP
0.465	37.8	BP	0.251	75.2	BP	0.112	124.8	BP
0.324	48.6	BP	0.168	85.0	BP	0.112	123.1	BP
0.261	53.8	BP	0.168	85.9	BP	0.082	129.7	BP
0.221	56.9	BP	0.112	94.5	BP	0.037	131.2	DP
0.173	60.0	BP	0.083	97.2	BP	0.037	131.7	DP
0.123	62.8	BP	0.069	97.9	BP	0.023	127.9	DP
0.113	66.6	BP	0.036	101.7	BP	0.017	125.2	DP
0.069	67.6	BP	0.023	102.1	BP			
0.040	71.7	BP	0.017	101.6	BP			
0.028	75.9	BP						
0.016	75.9	BP						
0.006	75.9	BP						

Table 3. Pressure−Composition Data for the Carbon Dioxide + 2-Chloroethyl Methyl Sulfide (CEMS) System Obtained in This Study; BP Is a Bubble Point and DP Is a Dew Point

t = 35.0 °C			*t* = 55.0 °C			*t* = 75.0 °C		
mole fraction CEMS	*P* (bar)	transition	mole fraction CEMS	*P* (bar)	transition	mole fraction CEMS	*P* (bar)	transition
0.845	19.9	BP	0.845	23.8	BP	0.845	29.3	BP
0.585	40.3	BP	0.585	54.3	BP	0.585	70.8	BP
0.415	50.0	BP	0.415	68.6	BP	0.415	88.6	BP
0.280	59.0	BP	0.280	83.1	BP	0.280	110.0	BP
0.161	65.9	BP	0.161	94.5	BP	0.161	127.9	BP
0.105	67.9	BP	0.105	98.3	BP	0.105	133.4	BP
0.078	70.7	BP	0.078	101.0	BP	0.078	135.5	BP
0.066	70.7	BP	0.066	101.7	BP	0.066	134.8	BP
0.028	72.8	BP	0.028	102.1	BP	0.028	125.2	DP
0.023	74.1	BP	0.023	99.7	DP	0.023	119.9	DP

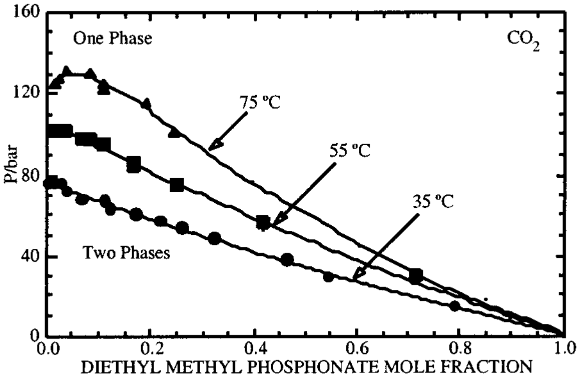

Figure 1. Pressure composition isotherms for diethyl methyl phosphonate in CO_2 at 35, 55, and 75 °C.

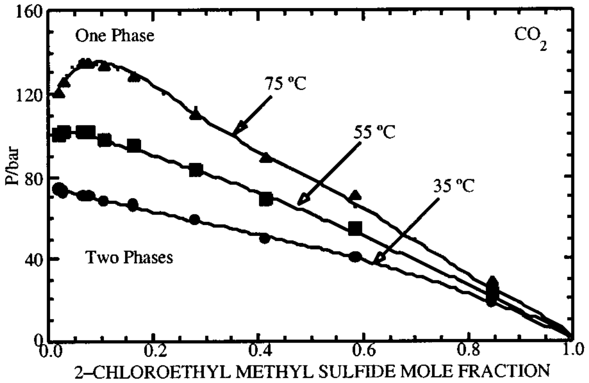

Figure 2. Pressure composition isotherms for 2-chloroethyl methyl sulfide in CO_2 at 35, 55, and 75 °C.

of equal volume are present when the mixture phase-separates.

Materials. Carbon dioxide was obtained from Roberts Oxygen (99.8% minimum purity) and was used as received. The diethyl methylphosphonate and 2-chloroethyl methyl sulfide were obtained from Aldrich Chemical Co. (97% purity) and used as received. Aldrich Chemical Co. reports a boiling point of 194 °C for DEMP and 55 °C for CEMS.

Results and Discussion

Experimental pressure−composition ($P-x$) data for the DEMP and CEMS systems are shown in Figures 1 and 2 and are listed in Tables 2 and 3. The mole fractions for the solubility isotherms at 35, 55, and 75 °C are averaged values of at least two independent data points. Although the experimental technique used to load the variable-volume cell with CO_2 and DEMP or CEMS results in an accumulated error of <1.0%, the purity of the DEMP and CEMS is only 97% so that the error in the reported mole fractions is expected to be slightly >3.0%. The pressures for each bubble, dew, and critical point are reproducible to within ±0.34 bar. Three phases were not detected at any of the temperatures investigated in this study nor were they observed for the limited number of visual experiments performed at approximately 24 to 35 °C and pressures near 70 bar. Hence, it is assumed that each of these two binary mixtures exhibit a continuous critical-mixture curve, which is a characteristic of type I phase behavior.[5,6]

Figure 1 shows the $P-x$ isotherms at 35, 55, and 75 °C for the DEMP−CO_2 system. Each solubility isotherm exhibits a maximum in pressure, which is a characteristic of type I systems.[5,6] The maximum pressure of the 35 °C isotherm is very close to the critical pressure of pure CO_2, which indicates that DEMP is very soluble in supercritical CO_2. Figure 2 shows the $P-x$ isotherms at 35, 55, and 75 °C for the CEMS + CO_2 system. Again, each solubility isotherm exhibits a maximum in pressure, which is a characteristic of type I systems. Because the pressures needed to obtain a single phase for these two compounds are quite modest, even at 75 °C, CO_2 can be considered a good candidate SCF solvent for dissolving or extracting this compound from a contaminated mixture.

It is interesting that the DEMP and CEMS solubility isotherms shown in Figures 1 and 2 exhibit virtually the same mixture critical pressures at similar temperatures, even though these two compounds are from very different chemical families. Both DEMP and CEMS are liquids at room temperature; however, the normal boiling point is 194 °C for DEMP and 55 °C for CEMS, which implies that the cohesive energy density of DEMP is much higher than that of CEMS. The mixture critical points for the DEMP + CO_2 and CEMS + CO_2 systems increase in pressure and solute concentration as the temperature increases from 35 to 75 °C, which suggests that the critical mixture curve for both mixtures exhibits a maximum in pressure−temperature space between the critical point of pure CO_2 and critical point of the heavy solute. Unfortunately, to the best of our knowledge, there are no critical point or vapor pressure data reported in the literature for either compound. Hence, no attempt is made to use an equation of state to model the data reported here.

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