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Phase Behavior of 4-Methoxyphenyl Acetic Acid in Carbon Dioxide

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Experimental data are presented on the high-pressure phase behavior of 4-methoxyphenylacetic acid (4MPA) with carbon dioxide. High-pressure portions of vapor−liquid, pressure−composition ($P-x$) isotherms were measured at 68.2, 80.2, and 94.8 °C and portions of two solid−fluid isotherms were measured at 35.3 and 52.0 °C. The 4MPA + CO_2 phase behavior is modeled with the Peng−Robinson equation of state with two mixture parameters fitted to the 80.2 °C $P-x$ isotherm. A reasonable fit of the data is obtained if k_{ij}, the parameter that accounts for specific interactions, is permitted to decrease with decreasing temperature.

Introduction

There is continuing interest in determining whether supercritical fluid solvent, especially CO_2, can be used effectively to separate isomers.[1−10] The studies cited here utilize binary isomer−CO_2 data to determine that the para isomers generally exhibit lower solubility in supercritical CO_2 as compared to the isomers likely due to enhanced *p*-isomer self-interactions that result from effective packing of these isomers. However, predicting the effectiveness of an isomer separation scheme becomes more complicated because of the cosolvent effect one isomer has on another isomer when both of these isomers are present in the CO_2-rich phase.[7]

The purpose of the short study reported here is to present solubility data for one particular nonvolatile solid isomer, 4-methoxyphenylacetic acid (4MPA), in CO_2. These solubility data complement those obtained by Lee et al.[4] who determined a limited amount of solid solubility data for methoxy phenyl acetic acid isomers, including 4MPA, at 35 °C. 4MPA is a para isomer that is expected to exhibit strong self-interactions because of its structural symmetry which facilitates polar interactions from the methoxy group at the α position of the aromatic ring and hydrogen bond dimmer formation from the carboxylic acid group at the para position. It has been demonstrated that CO_2 readily dissolves low molecular weight acids;[10−12] thus, it should be possible to dissolve 4MPA, especially at temperatures greater than the melting point. Table 1 lists the physicochemical characteristics of CO_2 and 4MPA. The large property differences between 4MPA and CO_2 leads to the class of phase behavior depicted in Figure 1.[13] The critical-mixture (L = V) curve is intersected in two locations by the solid−liquid−vapor (SLV) line: the upper (UCEP) and lower (LCEP) critical end points. The SLV line in Figure 1 is the pressure−temperature ($P-T$) trace of the melting point depression that occurs as low molecular weight, supercritical fluid (SCF) solvent dissolves in the solute-rich liquid that is present when the solid melts. Solid−fluid phase behavior occurs in the $P-T$ region between the two branches of the SLV line regardless of the system pressure. In the study reported here several pressure−composition ($P-x$) isotherms were obtained at temperatures in the liquid−vapor region of the phase diagram, and a small amount of solid solubility data were obtained at

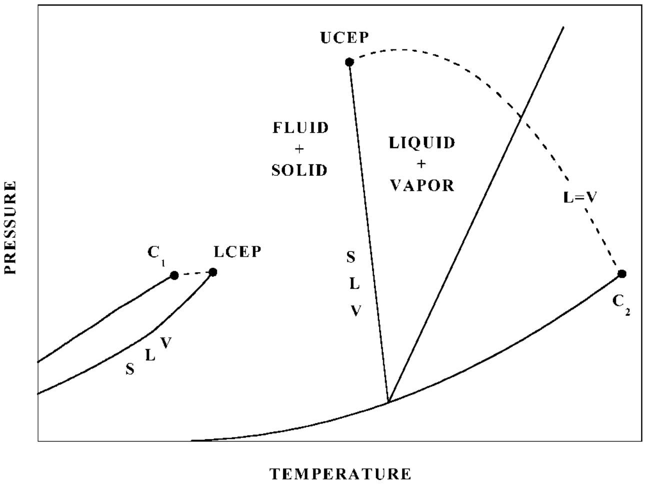

Figure 1. Schematic, pressure−temperature diagram for a mixture consisting of a heavy, nonvolatile solid and a low molecular weight solvent;[13] the lower (LCEP) and upper critical end points (UCEP) occur at the intersections of the critical mixture curve, designated L = V, and the solid−liquid−vapor (SLV) line; at the LCEP and UCEP there is a vapor−liquid critical point in the presence of excess solid; the two critical points are designated C_1 and C_2.

Table 1. Physical Properties of CO_2 Obtained from Reid, Prausnitz, and Poling[15] and 4-Methoxyphenylacetic Acid (4MPA) Reported by Lee et al.[4]

	4MPA	CO_2
molecular mass (g mol^{-1})	166.2	44.0
melting point (°C)	86	10
molar volume (cm^3 mol^{-1})	123.8	84.2
t_c (°C)	515.0	31.4
P_c (bar)	32.5	73.9
acentric factor (ω)	0.80	0.239

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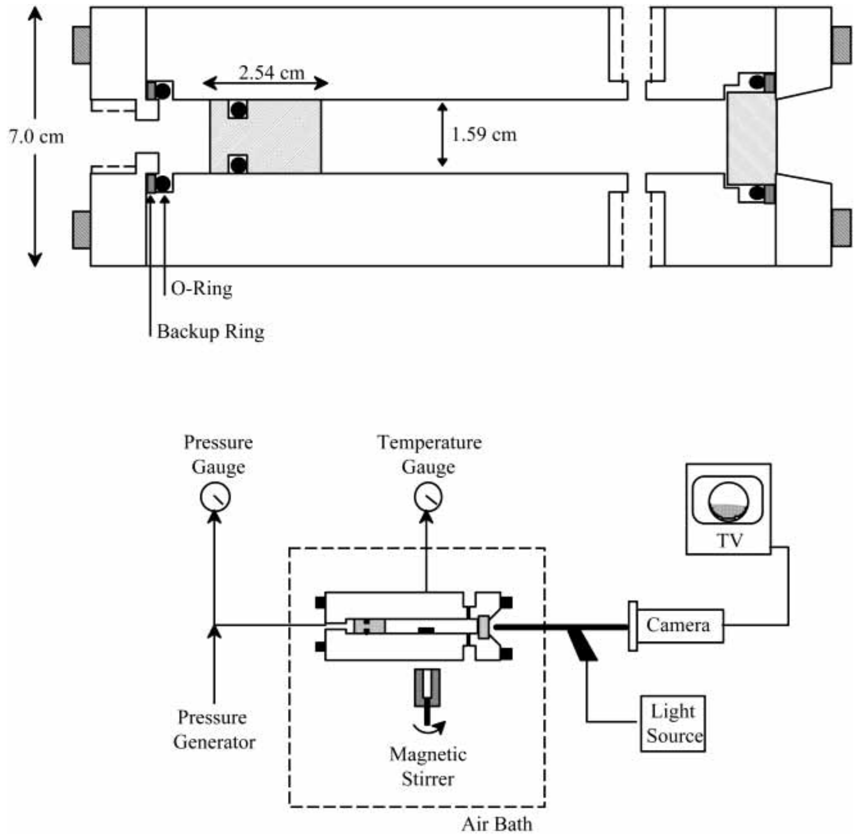

Figure 2. Schematic diagram of the view cell and experimental apparatus used in this study.

temperatures near the critical temperature of pure CO_2. No attempt was made in this work to measure the SLV line for 4MPA + CO_2 mixtures.

Experimental Section

Apparatus and Procedures. Figure 2 shows a schematic diagram of the experimental apparatus used in this study. The main component is a high-pressure, variable-volume cell constructed of a high-nickel-content austenitic steel (Nitronic 50, 5.7-cm o.d., 1.6-cm i.d. fitted with a 1.3-cm-thick sapphire window) capable of operating to pressures of 2000 bar. After 4MPA was loaded into the cell, to within ±0.002 g, the cell was purged several times with CO_2 at <5 bar pressure and room temperature to remove traces of air. Negligible losses of 4MPA were expected during the purging since 4MPA is a solid at room temperature and CO_2 is not expected to dissolve any 4MPA at these extremely low pressures. CO_2 was then added to the cell to within ±0.002 g from a high-pressure bomb. The mixture in the cell was stirred with a magnetic stir bar controlled by a magnet located beneath the cell. The contents of the cell were projected onto a video monitor using a camera coupled to a boroscope (Olympus Corp., model F100-024-000-55) placed directly against the sapphire window.

The solution was compressed to the desired pressure by moving a piston located within the cell using water pressurized by a high-pressure generator (HIP Inc., model 37-5.75-60). Because the pressure was measured on the water side of the piston, a small correction (0.7 bar) was added to account for the pressure required to move the piston. Pressures greater than 1000 bar were measured with a Heise gauge accurate to ±2.8 bar and pressures less than 1000 bar were measured with a different Heise gauge accurate to ±1.4 bar. The system temperature, maintained to within ±0.1 °C, was measured with a platinum-resistance device, placed in a thermowell on the surface of the cell, which is accurate to ±0.2 °C (Thermometrics Corp., Class A).

To reach thermal equilibrium, the cell remained at the temperature of interest for at least 30 min. The mixture in the cell was compressed to a single phase and the pressure was then slowly decreased until a second phase appeared. A bubble point was obtained if small bubbles appear in the cell, a dew point was obtained if a fine mist appears in the cell, and a solid solubility point was obtained if small crystals appear. In all three cases the composition of the predominant phase equals the overall mixture composition since the mass present in the second phase is negligible. Once the data point was obtained, a known mass of CO_2 was added to the cell and the procedure was repeated at this new concentration. Mixture-critical points were obtained if opalescence was observed together with equal liquid and vapor volumes when the second phase settled. Each data point was reproduced at least four times in a given experiment and the data for a given isotherm were obtained from several independent loadings of the apparatus.

Materials. The 4-methoxy phenyl acetic acid was obtained from Aldrich Inc. (99% purity). Carbon dioxide (bone dry grade, 99% purity) was obtained from Linde Corp.. These materials were used without further purification.

Results

Listed in Table 2 and shown in Figure 3 are the high-pressure portions of 4MPA + CO_2 isotherms at 94.8, 80.2, and 68.3 °C. As the temperature increases, the maximum pressure of these isotherms decreases. The amount of hydrogen bonding between 4MPA molecules is expected to decrease with increasing temperature, which makes it

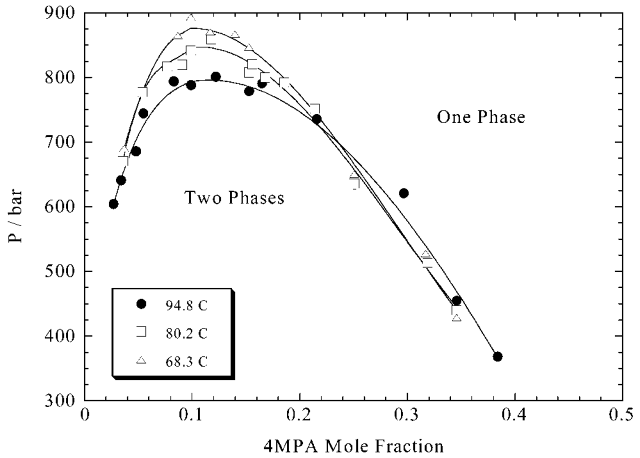

Figure 3. Experimental and calculated pressure–composition isotherms for 4MPA in CO_2 at 94.8, 80.2, and 68.3 °C.

Table 2. Pressure–Composition Data for 4-Methoxyphenylacetic Acid (4MPA) in Supercritical Carbon Dioxide Obtained in This Study at 94.8, 80.2, and 68.3 °C

P (bar)	4MPA (mole fraction)	transition
	T = 94.8 °C	
368.2	0.384	bubble point
454.7	0.346	bubble point
621.2	0.297	bubble point
625.0	0.251	bubble point
735.7	0.216	bubble point
778.7	0.153	bubble point
790.8	0.165	bubble point
801.2	0.122	bubble point
604.7	0.027	dew point
641.2	0.034	dew point
685.7	0.048	dew point
744.3	0.055	dew point
788.3	0.099	dew point
794.3	0.083	dew point
	T = 80.2 °C	
439.5	0.346	bubble point
513.3	0.319	bubble point
636.0	0.251	bubble point
751.2	0.214	bubble point
791.9	0.186	bubble point
799.4	0.168	bubble point
807.7	0.153	bubble point
820.1	0.156	bubble point
858.7	0.118	bubble point
670.2	0.036	dew point
777.0	0.054	dew point
816.7	0.077	dew point
819.4	0.091	dew point
841.1	0.099	dew point
	T = 68.3 °C	
428.5	0.346	bubble point
527.1	0.317	bubble point
650.5	0.251	bubble point
846.7	0.153	bubble point
866.7	0.140	bubble point
870.1	0.117	bubble point
690.2	0.037	dew point
864.9	0.087	dew point
892.8	0.099	dew point

easier to dissolve 4MPA in CO_2. The critical-mixture composition for these three isotherms shifts to a slightly higher 4MPA concentration because the temperature range is modest and the size difference between 4MPA and CO_2 is fairly large.

Table 3. Solid Solubility of 4-Methoxyphenylacetic Acid (4MPA) in Supercritical Carbon Dioxide Obtained in This Study at 52.0 and 35.3 °C

P (bar)	4MPA (mole fraction)	*P* (bar)	4MPA (mole fraction)
		T = 52.0 °C	
134.1	0.0011	358.2	0.0058
173.7	0.0020	428.8	0.0084
212.7	0.0031	490.9	0.0095
270.3	0.0041	618.5	0.0117
		T = 35.3 °C	
184.1	0.0019	328.9	0.0043
246.1	0.0027	430.9	0.0051
293.0	0.0038		

Listed in Table 3 and shown in Figure 4 are solubility data for solid 4MPA in CO_2 at 35.3 and 52.0 °C. Although only a limited amount of data was obtained at these two temperatures, it is apparent that the solubility of solid 4MPA in CO_2 is quite low. At 52.0 °C the solubility of 4MPA remains less than 1 mol % even at 600 bar. The solubility presented in this study, obtained by the synthetic method at 35 °C, is 3–5 times greater than that reported by Lee et al.[4] who used a dynamic flow technique with a chromatographic analysis of the sample. Once this discrepancy was discovered, additional solid-solubility experiments were performed with the same result that the solubilities obtained in the present study are higher than those reported by Lee et al.[4] The reason for the large difference in these two data sets could be a result of several factors. Because Lee et al.[4] used a dynamic flow technique to obtain solubility data, it was possible that either the flow rates were too high to obtain true equilibrium data or channeling of CO_2 through the packed column could have occurred, which reduced the effective rate of mass transfer from the solid to the CO_2-rich phase. These two potential limitations are eliminated with the well-mixed, static technique used in the present study. In addition, Lee et al.[4] used chromatography to analyze samples whereas in the present study the saturation of CO_2 was determined by visual observation, therefore eliminating the need to obtain a sample and to calibrate analytical instrumentation.

Modeling

The data obtained in this study were modeled with the Peng–Robinson (PR)[14] equation of state with the following mixing rules:

$$a_{\text{mix}} = \Sigma_i \Sigma_j x_i x_j a_{ij} \tag{1}$$

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \tag{2}$$

$$b_{\text{mix}} = \Sigma_i \Sigma_j x_i x_j b_{ij} \tag{3}$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})(1 - \eta_{ij})] \tag{4}$$

where k_{ij} and η_{ij} are mixture parameters that are determined by fitting pressure–composition data and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson.[14] The expression for the fugacity coefficient using these mixing rules is given elsewhere[13] and is not reproduced here. Table 1 lists the critical temperature, critical pressure, and the acentric factors for CO_2 obtained from Reid et al.[15] and 4MPA obtained from Lee et al.[4] who estimated these properties.

Values of the two mixture parameters, $k_{ij} = 0.060$ and $\eta_{ij} = -0.020$, were obtained by fitting the 4MPA–CO_2 80.2 °C isotherm. Both parameters are needed to obtain a good fit of this isotherm. However, the fit of the 94.8 and 68.3 °C isotherms is not nearly as good with these values of k_{ij} and η_{ij}. With η_{ij} held constant at -0.020, it is possible to obtain a much better fit of the 94.8 °C one if k_{ij} is adjusted

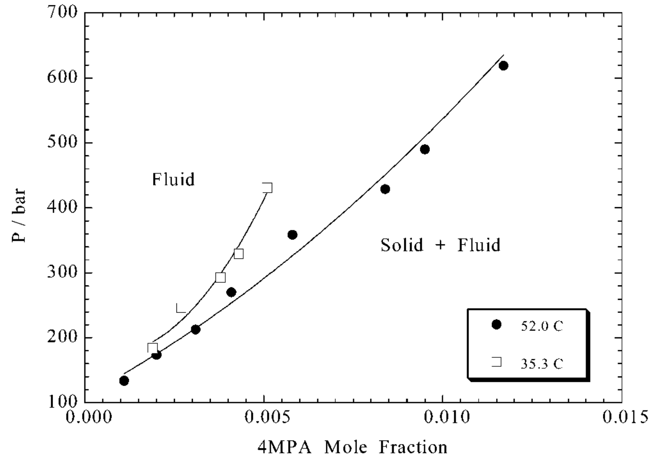

Figure 4. Solid solubility isotherms for 4MPA in CO_2 at 35.3 and 52.0 °C obtained in this study.

Table 4. Interaction Parameters and AARD Values for the 4-Methoxyphenylacetic Acid (4MPA) + Carbon Dioxide Systems

t (°C)	k_{12}	AARD[a] (%)
68.3	0.0585	9.0
80.2	0.0600	8.6
94.8	0.0605	13.1

[a] AARD $= 1/N\sum[|y_{\mathrm{corr}} - y_{\mathrm{exp}}|/y_{\mathrm{exp}}]$, where y_{corr} and y_{exp} are the correlated and experimental solubility values, respectively, and N is the number of data points.

slightly to 0.0605 and a better fit of the 68.3 °C isotherm is obtained with k_{ij} equal to 0.0585. Table 4 lists average absolute relative deviation (AARD) values of the three isotherm data. Although k_{ij} is typically treated as a correction to the geometric mixing rule for a_{ij} to correct for cross interactions, the structure of eq 2 suggests that k_{ij} can also be considered a correction for the pure component parameter $a_{\mathrm{4MPA-4MPA}}$. Hence, the decrease in k_{ij} with decreasing temperature is more than likely a correction for the enhanced self-association of pure 4MPA rather than a correction for enhanced cross interactions with CO_2 because the PR equation does not explicitly account for polar interactions and hydrogen bonding. It should also be noted that the value of k_{ij} used here is less than one-half the value used by Lee et al.[4] who fit solid solubility data at 35 °C. However, the calculations by Lee et al.[4] were not performed correctly because they used an estimate for the vapor pressure of 4MPA rather than an estimate of the sublimation pressure. No attempt was made to model solid solubility data because information on the sublimation pressure of 4MPA is not available.

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Literature Cited

(1) Chang, H.; Morrell, D. G. Solubilities of Methoxy-1-tetralone and Methyl Nitrobenzoate Isomers and Their Mixtures in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1985**, *30*, 74−78.
(2) Krukonis, V. J.; Kurnik, R. T. Solubility of Solid Aromatic Isomers in Carbon Dioxide. *J. Chem. Eng. Data* **1985**, *30*, 247−249.
(3) Dobbs, J. M.; Wong, J. M.; Lahiere, R. J.; Johnston, K. P. Modification of Supercritical Fluid Phase Behavior. *Ind. Eng. Chem. Res.* **1987**, *26*, 56−65.
(4) Lee, H.-K.; Kim, C.-H.; Kim, S.; Choi, C.-S. Solid Solubilities of Methoxyphenylacetic Acid Isomer Compounds in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1994**, *39*, 163−165.
(5) Iwai, Y.; Mori, Y.; Hosotani, N.; Higashi, H.; Furuya, T.; Arai, Y.; Yamamoto, K.; Mito, Y. Solubilities of 2,6-Dimethylnaphthalene and 2,7-Dimethylnaphthalene in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1993**, *38*, 509−511.
(6) Chen, J. W.; Tsai, F. N. Solubilities of methoxybenzoic acid isomers in supercritical carbon dioxide. *Fluid Phase Equilib.* **1995**, *107*, 189−200.
(7) Lucien, F. P.; Foster, N. R. Influence of Matrix Composition on the Solubility of Hydrobenzoic Acid Isomers in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1996**, *35*, 4686−4699.
(8) Lucien, F. P.; Foster, N. R. Solubilities of Mixed Hydrobenzoic Acid Isomers in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1998**, *43*, 726−731.
(9) Pfohl, O.; Pagel, A.; Brunner, G. Phase equilibria in systems containing *o*-cresol, *p*-cresol, carbon dioxide, and ethanol at 323.15−473.15 K and 10−35 MPa. *Fluid Phase Equilib.* **1999**, *157*, 53−79.
(10) Lucien, F. P.; Foster, N. R. Solubilities of solid mixtures in supercritical carbon dioxide: a review. *J. Supercrit. Fluids* **2000**, *17*, 111−134.
(11) Byun, H.-S.; Hasch, B. M.; M^{c}Hugh, M. A. Phase behavior and modeling of the systems CO_2−acetonitrile and CO_2−acrylic acid. *Fluid Phase Equilib.* **1996**, *115*, 179−192.
(12) Byun, H.-S.; Kim, K.; M^{c}Hugh, M. A. Phase Behavior and Modeling of Supercritical Carbon Dioxide-Organic Acid Mixtures. *Ind. Eng. Chem. Res.* **2000**, *39*, 4580−4587.
(13) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth: Stoneham, MA, 1994; p 49.
(14) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.
(15) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987; p 656.

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