Vapor−Liquid Equilibria of the Binary Carbon Dioxide−Tetrahydrofuran Mixture System

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Binary vapor liquid equilibrium data were measured for the carbon dioxide + tetrahydrofuran system at five temperatures from (311.01 to 331.33) K. A circulating type apparatus with on-line gas chromatography was used in this study. The measured data were correlated well by the Peng−Robinson equation of state with van der Waals one fluid mixing rules.

Introduction

Recently, many research groups have made particles with the supercritical antisolvent (SAS) process to use in various fields of polymer, biopolymer, and pharmaceutical industries and so forth. The SAS process is a promising technique to produce micronized particles. CO_2 is generally used as an antisolvent because not only is it miscible with various solvents but it also has a low critical temperature. Moreover, it is nontoxic, nonflammable, and inexpensive. The SAS process is based on the following principle. When the solution is injected into antisolvent (CO_2), which is miscible with the solvent but cannot dissolve the solute, the solute is supersaturated and precipitated. At this stage, the formation of micronized particles is known to occur.[1−3] Thus, the choice of the solvent is the most important thing considered in the SAS process. They must be completely miscible with each other at operating conditions, and the antisolvent must not dissolve the solute. To choose a good solvent for the CO_2, vapor−liquid equilibrium data for CO_2 and solvents are required. Phase equilibrium data are also used to predict the phase behavior of CO_2 + solvent systems to find the optimum operating conditions to control the particle size, but the data are scarce. THF is often used in the polymer industry, because various polymers such as polystyrene, poly(methyl methacrylate) (PMMA), polycarbonate, and so forth are soluble in the solvent. Thus, THF is expected to work as a solvent in the SAS process. Therefore, we measured binary vapor−liquid equilibria of CO_2 + tetrahydrofuran (THF) at temperatures from (311.01 to 331.33) K. The measured data were correlated with the Peng−Robinson equation of state (EOS) and the van der Waals one fluid mixing rules.

Experimental Section

Chemicals. CO_2 with a 99.99% purity was supplied by Korean Industrial Gases. THF with a minimum 99.9% (HPLC grade) purity was supplied by J. T. Baker. Both components were used without further purification in these experiments.

Apparatus. Figure 1 shows the schematic diagram of the experimental apparatus. We used an apparatus, which was described previously,[4,5] with a few modifications. In this work, we used two magnetic pumps used to circulate the vapor and liquid phases separately, and we also used two sampling loops. By circulating the vapor and liquid phases with two magnetic pumps, the equilibrium state was quickly attained. An equilibrium cell was made of type 316 stainless steel with an internal volume of approximately 320 mL. In the first step, CO_2 and a solvent were introduced into this cell and allowed to reach vapor−liquid equilibrium. The cell had two reinforced glass windows of 19 mm thickness on both sides of the cell, through which the phase boundary could be observed. We used a gas booster pump to charge CO_2 into the cell and a liquid pump to charge a solvent. The equilibrium temperature of the system was monitored with a 100 Ω platinum resistance thermometer (PRT) (model 5627, Hart Scientific Co.) with an accuracy of 0.05 °C and a 1502A digital indicator (Hart Scientific). The PRT was calibrated by comparison to a standard platinum resistance thermometer (SPRT). That has been calibrated on the ITS-90 scale and is traceable to the National Institute of Standards and Technology (NIST). A model Super TJE (<103 bar) pressure transducer (Sensotec Co.) connected to a model L20010WM1 digital indicator (Laurel) was used to measure the pressure of the system. The estimated accuracy of the digital pressure gauge is 0.05%. An on-line gas chromatograph with a thermal conductivity detector (TCD) was used to analyze the vapor- and liquid-phase compositions. A Rheodyne 7413 valve with a 0.5 μL sampling loop and a Rheodyne 7010 with a 10 μL sampling loop were used to trap liquid and vapor samples separately. A packed column with OV17 packing material (length 6 m, mesh size 80/100, 1/8 in. stainless steel, from Restek) was used with helium as a carrier gas. To calibrate THF and CO_2, a Hamilton microliter syringe with a volume of 0.5 μL and a Hamilton gastight syringe (500 μL) were used, respectively.

Experimental Procedure. After the cell was evacuated, a solvent was injected into the cell, and then CO_2 was charged. Two magnetic pumps were started, and vapor and liquid phases were circulated. When an equilibrium condition was reached, the vapor and liquid samples were sent to the gas chromatograph to measure vapor and liquid composition.

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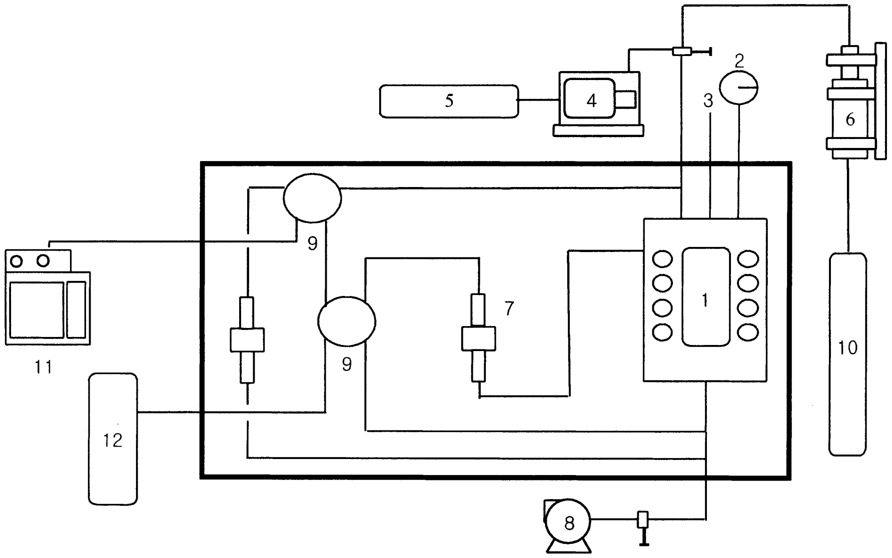

Figure 1. Experimental apparatus: 1, cell; 2, pressure gauge; 3, thermometer; 4, liquid pump; 5, sample cylinder; 6, booster pump; 7, magnetic pump; 8, vacuum pump; 9, sampling valve; 10, CO_2 tank; 11, GC; 12, carrier gas.

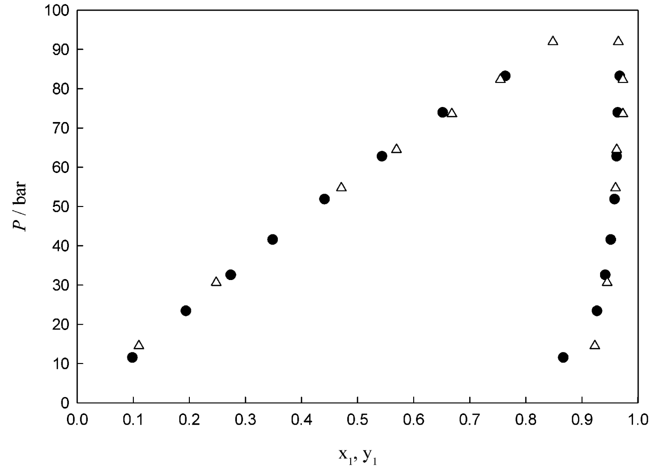

Figure 2. Comparison of the experimental data for the CO_2 (1) + chloroform (2) system with literature data: ●, this work, 333.32 K; △, Scurto et al., 333.15 K.

Results and Discussion

We chose the CO_2 + chloroform binary system at 333.15 K by Scurto et al.[6] to test the validity of our modified experimental apparatus. Good results were obtained. Figure 2 compares the CO_2 + chloroform vapor liquid equilibrium data of Scurto et al. at 333.15 K and our data at nearly the same temperature, 333.32 K. As Figure 2 shows, the experimental data agree well with the compared data. Vapor liquid equilibrium data were measured for CO_2 + THF at (311.01, 316.05, 321.05, 326.23, and 331.33) K. The data are presented in Table 1. Experimental data were correlated with the Peng–Robinson equation of state[7] (PR-EOS) using the van der Waals one fluid mixing rules.

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

$$a(T) = 0.45724\frac{R^2T_c^{\ 2}}{P_c}\alpha(T_r,\omega) \tag{2}$$

$$\alpha(T_r,\omega) = (1+\kappa(1-T_r^{\ 1/2}))^2 \tag{3}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4}$$

Table 1. Vapor–Liquid Equilibrium Data of the CO_2 + THF System

P/bar	x_1	y_1	P/bar	x_1	y_1
		T = 311.01 K			
9.73	0.1507	0.9320	48.01	0.6718	0.9838
17.67	0.2684	0.9608	55.37	0.7581	0.9846
27.03	0.3965	0.9727	64.19	0.8573	0.9869
33.89	0.4978	0.9785	71.07	0.9190	0.9880
41.34	0.5929	0.9817			
		T = 316.05 K			
8.26	0.1168	0.9048	51.28	0.6581	0.9811
16.28	0.2288	0.9505	59.92	0.7567	0.9826
24.06	0.3318	0.9654	70.09	0.8530	0.9840
31.88	0.4382	0.9733	77.51	0.9209	0.9846
41.48	0.5492	0.9780			
		T = 321.05 K			
8.13	0.1052	0.8992	52.82	0.6326	0.9778
18.12	0.2338	0.9499	61.03	0.7146	0.9795
27.09	0.3459	0.9642	70.92	0.8102	0.9804
35.22	0.4460	0.9713	78.36	0.8835	0.9815
42.87	0.5279	0.9752			
		T = 326.23 K			
12.37	0.1459	0.9215	49.51	0.5516	0.9754
20.72	0.2435	0.9537	61.01	0.6637	0.9770
30.49	0.3531	0.9676	71.85	0.7667	0.9771
38.89	0.4475	0.9720	80.20	0.8387	0.9772
		T = 331.33 K			
10.86	0.1187	0.9120	48.14	0.5045	0.9707
21.03	0.2288	0.9473	57.09	0.5855	0.9722
29.11	0.3255	0.9591	67.88	0.6813	0.9730
40.20	0.4332	0.9676	81.38	0.7998	

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{5}$$

$$a_m = \sum_i\sum_j x_i x_j a_{ij} \tag{6}$$

$$b_m = \sum_i x_i b_i \tag{7}$$

where

$$a_{ij} = (1-k_{ij})a_i^{1/2}a_j^{1/2} \tag{8}$$

The physical properties of each component are listed in Table 2. The binary interaction parameter, k_{ij}, was obtained

Table 2. Physical Properties

	CO_2	C_4H_8O
T_c/K	304.12[a]	540.20[a]
P_c/bar	73.74[a]	51.90[a]
ω	0.225[a]	0.217[b]

[a] Reference 8. [b] Reference 9.

Table 3. Interaction Parameter and AAD/(%) for the CO_2 + THF Systems

T/K	k_{12}	AAD [a]/%
311.01	−0.0025	1.08
316.05	−0.0024	1.03
321.05	−0.0032	1.43
326.23	0.0008	1.32
331.33	−0.0042	1.14
overall	−0.0027	1.25

[a] $AAD = (100/N)\sum_i^N |P_{exp} - P_{cal}|/P_{exp}$.

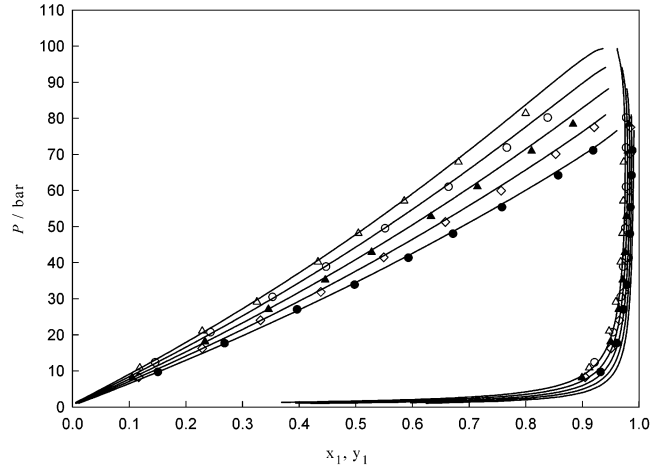

Figure 3. Vapor−liquid equilibria of the CO_2 (1) + THF (2) system: △, 331.33 K; ○, 326.23 K; ▲, 321.05 K; ◇, 316.05 K; ●, 311.01 K; —, Peng−Robinson EOS with $k_{ij} = -0.0027$.

by fitting the experimental vapor−liquid equilibrium data, to minimize the objective function (OF). We used the Marquardt algorithm to minimize the objective function,

$$OF = \sum_i^N \left|\frac{P_{exp} - P_{cal}}{P_{exp}}\right| \qquad (9)$$

where N is the number of experimental data points and P_{exp} and P_{cal} are the experimental and calculated pressures, respectively. Table 3 shows the binary interaction parameters for the CO_2 + THF system. The agreement is satisfactory with an absolute average deviation of less than 1.3% for CO_2 + THF. Vapor−liquid equilibrium data for the CO_2 + THF system are shown and compared with the calculated values with $k_{ij} = -0.0027$ in Figure 3. We also chose the experimental critical points of the CO_2 + THF system reported by Ziegler et al.[10] to compare with our calculated results. Figure 4 compares the critical points of Ziegler et al. and our calculated values. Our calculated results agree quite well with the experimental critical points, although the PR-EOS overestimates the pressure at higher temperature.

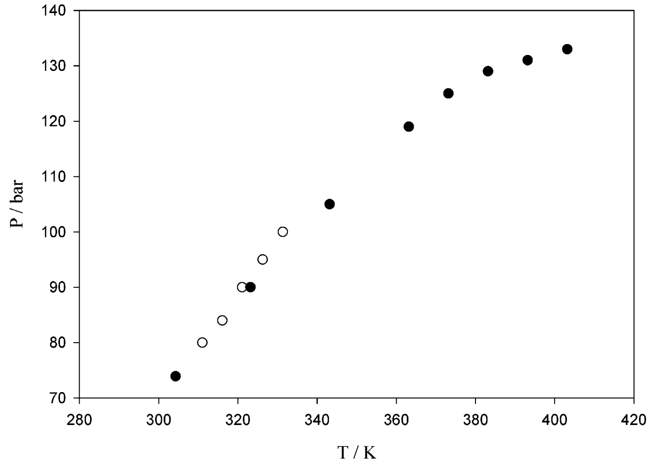

Figure 4. Comparison of the calculated critical points for the CO_2 + THF system with the experimental data of ref 10: ○, this work; ●, Ziegler et al.

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