J. Chem. Eng. Data **2003,** *48,* 1407−1412

High-Pressure Vapor−Liquid Equilibria for CO_2 + 2-Butanol, CO_2 + Isobutanol, and CO_2 + *tert*-Butanol Systems

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In this study, the vapor−liquid equilibrium data of CO_2 + isobutanol, CO_2 + 2-butanol, and CO_2 + *tert*-butanol systems were measured with an improved static-type phase equilibrium apparatus at temperatures of (331.9, 341.6, and 351.3) K and pressures from (50 to 120) bar. To ensure the accuracy and reliability of these measurements, the experimental data were compared with literature values, and these were found to be in quite good agreement. The mutual solubilities of CO_2 + isomeric butanol systems decreased in the following order: CO_2 + *tert*-butanol, CO_2 + 2-butanol, and CO_2 + isobutanol. The temperature and pressure effects on mutual solubilities between CO_2 and isomeric butanols were also demonstrated and discussed.

Introduction

Recently, supercritical carbon dioxide has been utilized widely in biochemistry,[1,2] material cleaning,[3,4] food processing,[5,6] material preparation,[7] supercritical chromatography,[1] and so forth. For the rapid developments of supercritical technology, accurate phase equilibrium measurements for CO_2-containing systems are of great importance in the process design.

Among numerous CO_2-containing systems, CO_2 + alcohol systems have received much attention over the past years.[8−10] Especially, short-chain alcohols extensively served as model substances to study the phase behavior of supercritical fluid + polar substance systems. Butyl alcohols can be solvents, entrainers, modifiers, and simulators for supercritical fluid extraction, supercritical fluid chromatography, biomaterials, and so forth. Also, they are commonly used in synthesizing high-porosity materials via sol−gel processes and in supercritical drying processes. As a result, the further understanding of phase behavior for CO_2 + butyl alcohols greatly contributes to the developments of supercritical fluid technologies. Over the past years, many investigations were done on the high-pressure phase equilibrium of the CO_2 + *n*-butanol binary system,[8,11−22] but fewer studies were on the CO_2 + 2-butanol,[14,15,21,22] CO_2 + isobutanol,[23,24] and CO_2 + *tert*-butanol[25,26] systems. For the CO_2 + 2-butanol system, Hiaki et al.[14] measured the vapor−liquid equilibrium (VLE) data at 313.2 K and in the pressure range from (40 to 70) bar. Stevens et al.[15,22] investigated the VLE at near critical point conditions and the vapor−liquid−liquid equilibrium (VLLE) at lower temperatures. For the CO_2 + isobutanol system, most studies[23,24] were carried out at normal atmosphere. Yet, high-pressure phase equilibrium data have never been reported in the literature. For the CO_2 + *tert*-butanol system, Heo et al.[25] have measured the VLE data via a nonanalytical method. Kim et al.[26] also measured the VLE for the CO_2 + *tert*-butanol system at temperatures of (323.2 and 343.2) K and pressures from (60 to 120) bar. However, little attention was paid to CO_2 + isomeric butanol systems, especially the CO_2 + 2-butanol, CO_2 + isobutanol, and CO_2 + *tert*-butanol binary systems. In this study, new VLE data of CO_2 + 2-butanol, CO_2 + isobutanol, and CO_2 + *tert*-butanol systems were measured at (331.9, 341.6, and 351.3) K and at pressures from (50 to 120) bar. The phase behaviors for the CO_2 + isomeric butanol binary systems were also compared and discussed.

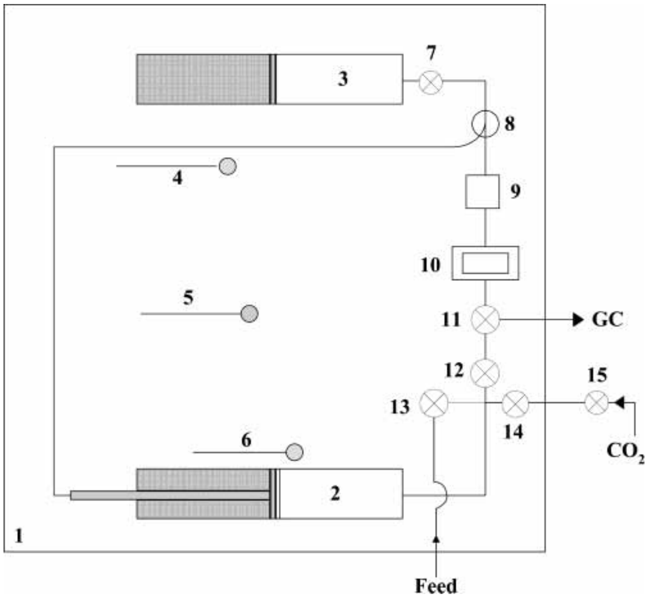

Figure 1. Schematic diagram of the improved static phase equilibrium apparatus: 1, air-bath oven; 2 and 3, equilibrium cell; 4−6, thermocouple; 7 and 11−15, valve; 8, two-way valve; 9, pressure indicator; 10, view window; 11, sampling valve.

Experimental Section

Materials. Carbon dioxide was supplied by San Fu Chemical Co., Taiwan, with a minimum purity of 99.99%. 2-Butanol (purity, 99.8% by mass) was purchased from Fluka Co. Isobutanol and *tert*-butanol were purchased from Riedel-deHaën Co., both with purity of 99.5% by mass.

Apparatus and Procedure. The improved static-type phase equilibrium apparatus as illustrated in Figure 1 was employed to measure the VLE data in this work. This

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10.1021/je020214r CCC: $25.00

apparatus consists of five units: two high-pressure equilibrium cells, a view window, a fluid sampling valve, and a two-way valve. During a phase behavior experiment, vapor is in equilibrium cell 3, liquid is in equilibrium cell 2, and the vapor−liquid interface can be seen in the view window. Mixing of vapor and liquid was accomplished by circulating vapor between the two equilibrium cells. The vapor was driven into the porous disk of equilibrium cell 2 and bubbles through the liquid.[27] When the piston of one equilibrium cell was advanced, the piston of the other equilibrium cell was retracted to maintain a constant operating pressure. The mixing step was repeated until there was no change in the total volume of the fluid. The vapor (or liquid) phase samples were taken by pumping vapor (or liquid) phase through the sampling valve and sent for analysis of the composition. The oven temperature was measured within ±0.1 K, and the temperature uniformity in the oven was controlled within ±0.6 K. The pressure was measured within ±0.1 bar with a Validyne pressure transducer. The transducer was calibrated with a deadweight tester yearly.

Compositional Analysis. The equilibrium compositions of the phases were determined by using an on-line gas chromatograph (GC-14A, Shimadzu Co., Japan) equipped with a thermal conductivity detector (TCD). A 10 μL sampling loop (Valco Instruments Inc., Houston, TX) was equipped on-line to take samples from the vapor and liquid phases for analysis. Each sample was analyzed at least five times, and the reproducibility of the analysis was within 3%. Helium was chosen as the carrier gas at a flow rate of 23.5 mL·min^{-1}. The length of the separation column was 2 m, and it was packed with Porapak Q. The temperature of injection and the column temperature were kept at 473.15 K, and the TCD and detector were at a constant temperature of 493.15 K.

Results

CO_2 + 2-Butanol System. The reliability and accuracy of our measurements have been checked by the VLE data for the CO_2 + *n*-butanol binary system which was published previously.[12] For that system, in comparison of our results with those reported by Jennings et al.,[20] the average deviations of liquid-phase compositions were within 2.5% and those of vapor phase compositions were within 0.5%.

Hiaki et al.[14] measured the phase equilibrium data for the CO_2 + 2-butanol system at 313.2 K. Stevens et al.[15,22] also measured the VLE data with a Calletet apparatus[28] in the near-critical region, the critical curve, and the VLLE at temperatures of (250.95 and 251.15) K. Silva-Oliver and Galicia-Luna[21] measured the VLE data for this system at (335.14, 348.77, 374.10, 402.47, and 431.73) K in the near-critical region.

The vapor−liquid phase equilibrium data obtained in this work at (331.9, 341.6, and 351.3) K are summarized in Table 1 and illustrated in Figure 2. The results of Silva-Oliver and Galicia-Luna[21] at (335.14 and 348.77) K are also shown in Figure 2 for comparison. Our data at (331.9 and 341.6) K exhibited a tendency similar to those reported by Silva-Oliver and Galicia-Luna,[21] in both the vapor and liquid phases near the critical state.

Moreover, as can be seen from Figure 2, the mutual solubility of CO_2 + 2-butanol is increased with increasing pressure. Furthermore, the solubility of CO_2 in the 2-butanol-rich phase (liquid phase) is decreased with increasing temperature, but just a slight increase is found for the solubility of 2-butanol in the CO_2-rich phase (vapor phase) under moderate pressures. However, this temperature effect becomes considerable as the pressure is higher. In addition, only vapor−liquid phase equilibrium can be found over the whole experimental region.

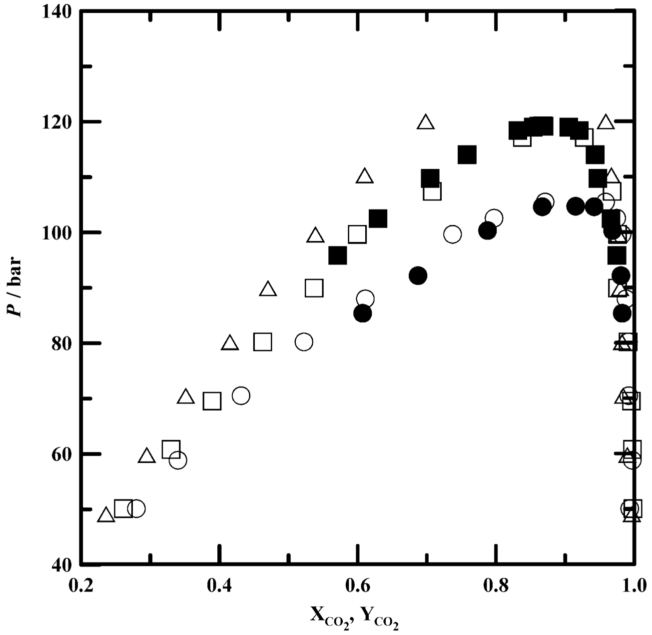

Figure 2. Vapor−liquid phase equilibrium diagram for the CO_2 + 2-butanol system at different temperatures. This work: ○, 331.9 K; □, 341.6 K; △, 351.3 K. Silva-Oliver and Galicia-Luna (ref 21): ●, 335.14 K; ■, 348.77 K.

Table 1. Equilibrium Compositions for the CO_2 + 2-Butanol System

T/K	*P*/bar	vapor phase, y_{CO_2}	liquid phase, x_{CO_2}
331.9	50.1	0.9935	0.2799
	58.9	0.9972	0.3400
	70.5	0.9921	0.4313
	80.2	0.9915	0.5223
	88.0	0.9881	0.6111
	99.7	0.9824	0.7373
	102.6	0.9746	0.7972
	105.5	0.9585	0.8711
341.6	50.1	0.9981	0.2611
	60.8	0.9974	0.3300
	69.6	0.9959	0.3894
	80.2	0.9910	0.4627
	89.9	0.9758	0.5369
	99.7	0.9758	0.5994
	107.4	0.9679	0.7078
	117.2	0.9277	0.8380
351.3	49.2	0.9966	0.2362
	59.8	0.9900	0.2949
	70.5	0.9840	0.3514
	80.2	0.9824	0.4152
	89.9	0.9796	0.4703
	99.7	0.9770	0.5390
	110.4	0.9669	0.6101
	120.1	0.9589	0.6984

CO_2 + Isobutanol System. Battino et al.[23] and Takahashi et al.[24] measured the phase equilibrium data at normal atmosphere. But for the high-pressure region, it seems no VLE data for this system have been reported. In this work, the VLE data for this system were measured at temperatures of (331.9, 341.6, and 351.3) K and pressures from (50 to 120) bar. The experimental data are listed in Table 2, and the vapor−liquid phase equilibrium diagram is shown in Figure 3. This figure shows that the effects of pressure and temperature on the phase behavior of the CO_2 + isobutanol system are similar to those of the CO_2 + 2-butanol system. Only vapor−liquid phase equilibrium can be observed under the experimental conditions.

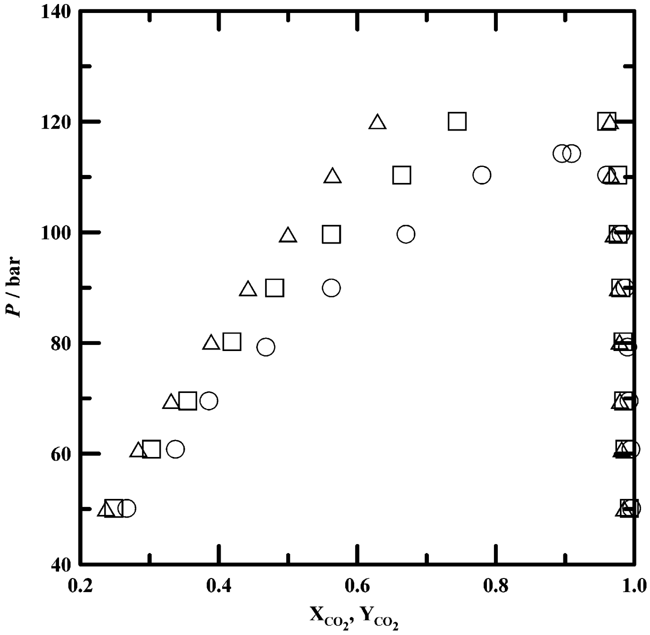

Figure 3. Vapor−liquid phase equilibrium diagram for the CO_2 + isobutanol system at different temperatures: ○, 331.9 K; □, 341.6 K; △, 351.3 K.

Table 2. Equilibrium Compositions for the CO_2 + Isobutanol System

T/K	P/bar	vapor phase, y_{CO_2}	liquid phase, x_{CO_2}
331.9	50.1	0.9961	0.2670
	60.8	0.9951	0.3372
	69.6	0.9924	0.3855
	79.3	0.9902	0.4678
	89.9	0.9866	0.5625
	99.7	0.9809	0.6702
	110.4	0.9601	0.7799
	114.2	0.9095	0.8956
341.6	50.1	0.9929	0.2481
	60.8	0.9862	0.3027
	69.6	0.9844	0.3551
	80.2	0.9839	0.4189
	89.9	0.9806	0.4805
	99.7	0.9767	0.5625
	110.4	0.9763	0.6640
	120.1	0.9602	0.7443
351.3	50.1	0.9853	0.2369
	60.8	0.9818	0.2838
	69.6	0.9793	0.3310
	80.2	0.9787	0.3888
	89.9	0.9764	0.4421
	99.7	0.9703	0.4997
	110.4	0.9658	0.5642
	120.1	0.9650	0.6290

CO_2 + tert-Butanol System. Heo et al.[25] measured the bubble pressure (in the liquid phase) of the CO_2 + *tert*-butanol system at (333.15, 343.15, and 353.15) K. Only the liquid phase equilibrium data were obtained in their work. Kim et al.[26] also reported the VLE phase equilibrium data for this system merely at 343.2 K. In this work, the VLE data at (331.9, 341.6, and 351.3) K are listed in Table 3 and shown in Figure 4. The phase behavior of the CO_2 + *tert*-butanol system is similar to that of the CO_2 + 2-butanol and CO_2 + isobutanol systems; only vapor−liquid phase equilibria can be observed experimentally. The mutual solubility of CO_2 + *tert*-butanol is increased when the pressure is raised. Moreover, when the temperature is increased, the solubility of CO_2 in the *tert*-butanol-rich phase is decreased.

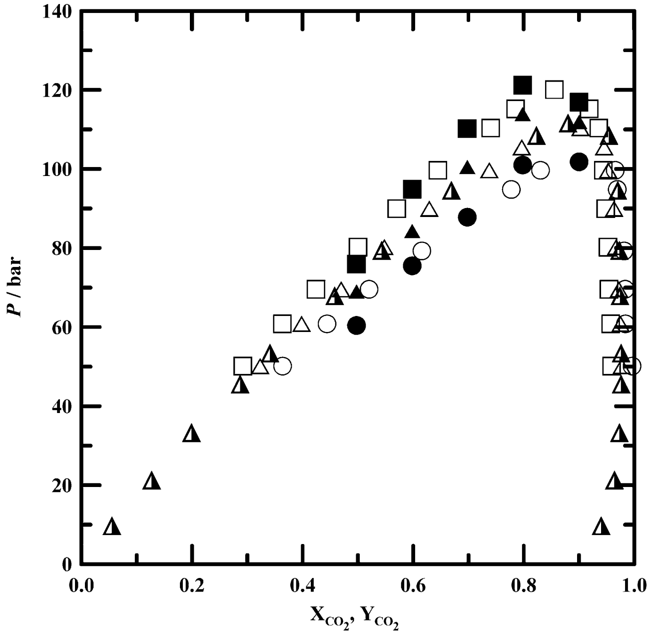

Figure 4. Vapor−liquid phase equilibrium diagram for the CO_2 + *tert*-butanol system at different temperatures. This work: ○, 331.9 K; □, 341.6 K; △, 351.3 K. Heo et al. (ref 25): ●, 333.15 K; ▲, 343.15 K; ■, 353.15 K. Kim et al. (ref 26): ◭, 343.2 K.

Table 3. Equilibrium Compositions for the CO_2 + *tert*-Butanol System

T/K	P/bar	vapor phase, y_{CO_2}	liquid phase, x_{CO_2}
331.9	50.1	0.9959	0.3638
	60.8	0.9839	0.4441
	69.6	0.9834	0.5202
	79.3	0.9814	0.6157
	94.8	0.9691	0.7774
	99.7	0.9654	0.8303
341.6	50.1	0.9771	0.3232
	60.8	0.9751	0.3981
	69.6	0.9722	0.4696
	80.2	0.9671	0.5479
	89.9	0.9633	0.6291
	99.7	0.9526	0.7377
	105.5	0.9454	0.7963
	110.4	0.9027	0.9027
351.3	50.1	0.9588	0.2918
	60.8	0.9573	0.3633
	69.6	0.9541	0.4241
	80.2	0.9524	0.5003
	89.9	0.9482	0.5701
	99.7	0.9439	0.6448
	110.4	0.9356	0.7402
	115.2	0.9182	0.7851
	120.1	0.8554	0.8554

Discussion

Effect of Temperature and Pressure on Phase Behavior. At vapor−liquid equilibrium, the mutual solubility of CO_2 + solute (butanol) is strongly related to the vapor pressure of the solute and the density of the solvent (CO_2).[29] In this work, the operating conditions with pressures of (50 to 120) bar and temperatures of (331.9 to 351.3) K are located in the sub- and supercritical regions of CO_2 (T_c = 304.15 K, P_c = 73.8 bar). Therefore, the density of CO_2 increases consistently with increasing pressure,[29] which results in an enhancement of the solubility of CO_2 in the liquid phase. On the other hand, the solubilities of butanols in the vapor phase depend on the pressure condition.[29] Under extremely low pressure conditions, the solubility of an organic solute decreases with increasing pressure due to the vapor pressure effect. As the pressure rises, the

Table 4. Physical Properties of Isomeric Butanols[a]

Substance	n-butanol	iso-butanol	2-butanol	tert-butanol
Formula	CH3-CH2-CH2-CH2-OH	CH3 | CH3-CH-CH2-OH	OH | CH3-CH2-CH-CH3	CH3 | CH3-C-CH3 | OH
M.P./K	183.35	165.2	158.5	298.55
B.P./K	390.88	381.04	372.66	355.49
T_c/K	563.05	547.78	536.05	506.21
P_c/bar	44.23	43.00	41.79	39.73
Dipole/debye	1.8	1.7	1.7	1.7
Vapor pressure/bar at 298.15 K	0.013	0.016	0.022	0.055

[a] References 32 and 33.

solubility increases slightly. However, it increases dramatically with pressure crossing the critical region, because the density effect is stronger than the pressure effect. Herein, the operating conditions are over the sub- and supercritical regions of CO_2. Therefore, at lower pressures, the solubility of butanols in the vapor phase exhibits only a small increase with increasing pressure, whereas at a pressure near the critical point, it increases significantly with an increase of pressure. This common phenomenon has also been reported elsewhere.[29−31] As the temperature increases, because the density of CO_2 decreases, the solubility of CO_2 in the liquid phase also decreases. On the contrary, the solubilities of butanols in the vapor phase increase with increasing temperatures due to an increase of the vapor pressures of butanols.

Comparison of CO_2 + Isomeric Butanol Systems. The phase equilibrium data of the CO_2 + *n*-butanol system[12] at (333.15, 343.15, and 353.15) K are compared with those of three CO_2 + butanol systems in this work. Figures 5−7 show the comparisons of the phase diagrams of four CO_2 + isomeric butanol systems at about (331.9, 341.6, and 351.3) K, respectively. Although the experimental temperatures for the CO_2 + *n*-butanol system[12] (333.15, 343.15, and 353.15) K do not exactly coincide with the conditions (331.9, 341.6, and 351.3) K of this work, the comparisons should still be helpful to realize the phase behavior of CO_2 + isomeric butanol systems. As shown in Figures 5−7, the mutual solubilities for CO_2 + isomeric butanol systems decrease in the following order: CO_2 + *tert*-butanol; CO_2 + 2-butanol; CO_2 + isobutanol; and CO_2 + *n*-butanol, both in the vapor and liquid phases.

The physical properties of four isomeric butanols[32,33] are summarized in Table 4. Since carbon dioxide is nonpolar and there are no significant differences in the polarities of the four butanols, the mutual solubility of CO_2 + butanol is predominantly determined by the nature of the butanols. The critical temperatures and critical pressures of the four butanols decrease in the following order: *n*-butanol; isobutanol; 2-butanol; and *tert*-butanol. This reveals that the intermolecular forces also decrease in this order. Moreover, Rytting et al.[34] reported the effect of chain branching on the vapor pressures of isomeric butanols in a nonpolar solvent. Also, they proposed a self-association number that is based on the molecular stereostructure. However, as the butanol with the largest number of branched chains, *tert*-butanol exhibits the highest tendency for evaporating into the vapor phase. On the contrary, *n*-butanol, which is not branched, exhibits the highest activity when dissolved in the liquid phase. Therefore, it is understandable that the mutual solubilities for CO_2 + isomeric butanol systems decrease in the following sequence: CO_2 + *tert*-butanol > CO_2 + 2-butanol > CO_2 + isobutanol > CO_2 + *n*-butanol.

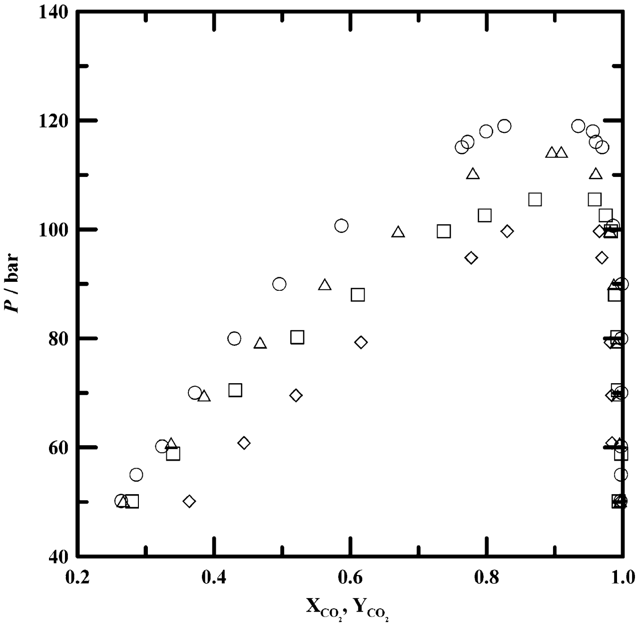

Figure 5. Comparison of the phase equilibrium diagrams for four CO_2 + isomeric butanol systems at 331.9 K: ○, *n*-butanol; △, isobutanol; □, 2-butanol; ◇, *tert*-butanol.

Conclusion

The vapor−liquid phase equilibrium data of CO_2 + isobutanol, CO_2 + 2-butanol, and CO_2 + *tert*-butanol systems were measured at (331.9, 341.6, and 351.3) K and pressures from (50 to 120) bar. The measurements exhibit high accuracy. When the phase equilibrium data for the

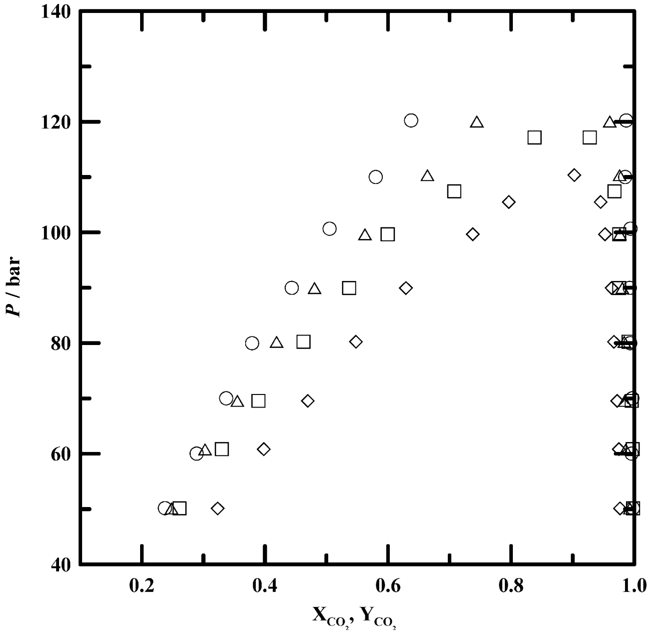

Figure 6. Comparison of the phase equilibrium diagrams for four CO_2 + isomeric butanol systems at 341.6 K: ○, *n*-butanol; △, isobutanol; □, 2-butanol; ◇, *tert*-butanol.

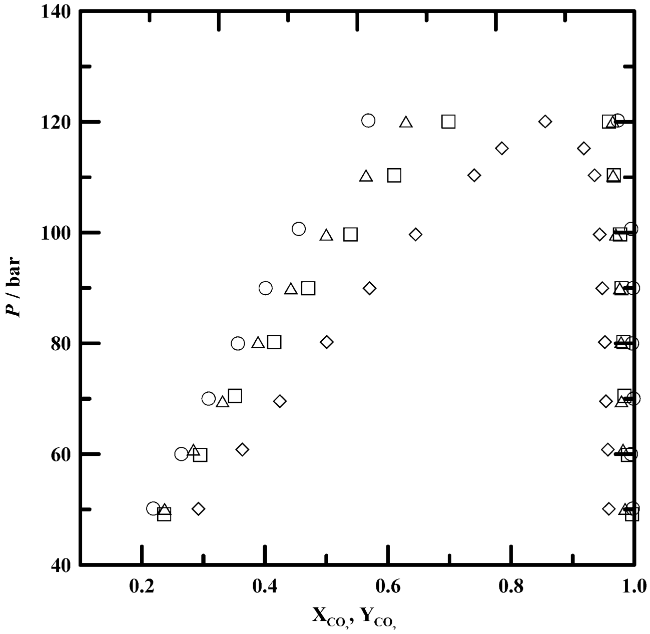

Figure 7. Comparison of the phase equilibrium diagrams for four CO_2 + isomeric butanol systems at 351.3 K: ○, *n*-butanol; △, isobutanol; □, 2-butanol; ◇, *tert*-butanol.

CO_2 + isobutanol, CO_2 + 2-butanol, and CO_2 + *tert*-butanol systems were compared with those of the CO_2 + *n*-butanol system, it was found that the phase behaviors for these four binary systems are similar. The mutual solubility of CO_2 + butanol decreased with increasing temperatures, while it increased with increasing pressures. Nothing but vapor−liquid phase equilibria was observed in the experimental regions. In addition, the mutual solubilities for these binary systems are in the following order: CO_2 + *tert*-butanol > CO_2 + 2-butanol > CO_2 + isobutanol > CO_2 + *n*-butanol.

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Received for review November 25, 2002. Accepted August 15, 2003.

JE020214R