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High-Pressure Phase Equilibria of Carbon Dioxide + 1-Butanol, and Carbon Dioxide + Water + 1-Butanol Systems

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Phase equilibria data for CO_2 + 1-butanol and CO_2 + water + 1-butanol systems have been measured in the pressure range from 50 bar to 130 bar at 333.15, 343.15, and 353.15 K. A novel phase behavior apparatus was used for the measurements. For the CO_2 + 1-butanol binary system, only vapor−liquid-phase equilibria were observed over the whole range. For the CO_2 + water + 1-butanol ternary system, experimental observations were made of three single-phase regions, one vapor−liquid−liquid equilibrium region, two vapor−liquid equilibrium regions, and one liquid−liquid equilibrium region.

Introduction

Supercritical fluids are of increasing interest because of their unique properties, such as liquidlike density, low viscosity, high diffusivity, and so forth.[1] In recent years, supercritical fluid technologies have been widely developed and applied in diverse fields, for example, particle-forming techniques,[1−4] pharmaceutical industries,[5−7] food and biomaterials,[8,9] material science,[1−4,10,11] and polymerization.[12,13] High-pressure phase equilibria data can provide mutual solubilities, compositions of coexisting phases, distribution coefficients, and separation factors, which are of fundamental importance in supercritical fluid applications. Therefore, phase equilibria data are required for basic calculations in practical designs of a supercritical process. However, very few data have been published concerning the phase equilibria measurements of complex systems at high pressures.

Butanol and butanol−water mixtures are commonly used for synthesizing particles via sol−gel processes.[3] By means of drying in supercritical carbon dioxide, fine particles with high porosity and large surface area can be obtained. Hence, the high-pressure phase equilibria data for CO_2 + butanol and CO_2 + water + butanol systems are necessary for the process design. Previous works on the CO_2 + 1-butanol system have been reported by King et al.[14] at 313.15 K, Jennings et al.[15] at 314.8, 325.3, and 337.2 K, Suzuki et al.[16] at 313.4 and 333.4 K, Chang[17] at 298.15 K, Jensen et al.[18] at 313.4 K, Ishihara et al.[19] at 313.15 K, Hiaki et al.[20] at 313.2 K, and, Silva-Oliver and Galicia-Luna[21] at 324.16, 333.58, 355.38, 392.72, and 426.95 K. Only a few VLE data[21] at temperatures above 337.2 K can be found. For the CO_2 + water + 1-butanol system, phase equilibria have been measured by Panagiotopoulos and Reid[22] at temperatures of 313.15 and 333.15 K and pressures ranging from 20 bar to 150 bar. However, no data were reported at temperatures higher than 333.15 K.

The main objective of this paper is to measure the equilibrium data for the CO_2 + 1-butanol and CO_2 + water + 1-butanol systems at 333.15, 343.15, and 353.15 K. To ensure the accuracy and reliability of the measured equilibrium data, the obtained binary equilibrium compositions at 333.15 K were compared with the reports by Jennings et al.[15] and Silva-Oliver and Galicia-Luna,[21] and the obtained ternary equilibrium compositions at 333.15 K and pressures of 60 bar and 80 bar were compared with the report by Panagiotopoulos and Reid.[22]

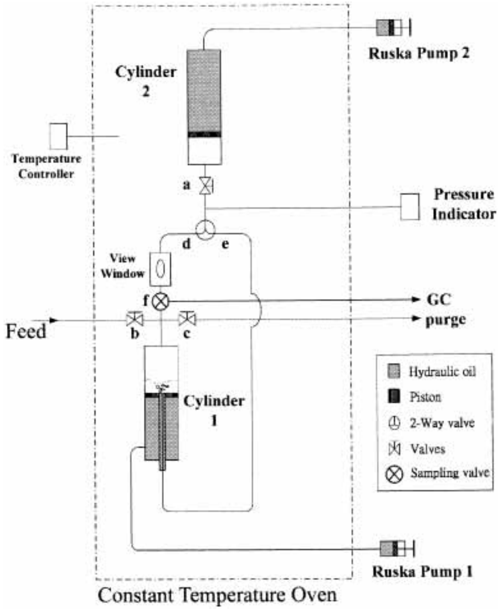

Figure 1. Schematic diagram of the high-pressure phase behavior apparatus.

Experimental Section

Materials. 1-Butanol (purity 99.8%) was purchased from Merck Co. Carbon dioxide (purity 99.99%) was supplied by San Fu Chemical Co., Taiwan, with a minimum purity of 99.99%. The deionized water used in this experiment was further purified by distillation.

Apparatus and Procedure. The apparatus is a static circulation type with a maximum temperature and pressure of 423 K and 40 MPa, respectively. The detailed experimental procedures for measuring the phase equilibrium data were described elsewhere.[23] As shown in Figure 1, the apparatus consists of five units: two high-pressure

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Table 1. Measured Compositions of Equilibrium Vapor (Y) and Liquid (X) Phases for the CO_2 + 1-Butanol System

		vapor phase	liquid phase
T/K	P/bar	Y_{CO_2}	X_{CO_2}
333.15	50.17	0.9963	0.2640
	55.00	0.9970	0.2860
	60.20	0.9970	0.3240
	70.03	0.9975	0.3720
	79.98	0.9974	0.4300
	89.98	0.9982	0.4960
	100.67	0.9855	0.5870
	115.08	0.9695	0.7637
	116.05	0.9603	0.7721
	117.99	0.9558	0.7992
	118.97	0.9345	0.8259
343.15	50.17	0.9979	0.2375
	60.02	0.9958	0.2890
	70.02	0.9970	0.3370
	79.98	0.9935	0.3791
	89.98	0.9927	0.4436
	100.67	0.9939	0.5050
	110.01	0.9853	0.5800
	120.24	0.9870	0.6375
353.15	50.17	0.9978	0.2185
	60.02	0.9947	0.2642
	70.02	0.9989	0.3084
	79.98	0.9965	0.3560
	89.98	0.9981	0.4010
	100.67	0.9951	0.4549
	110.01	0.9630	0.5042
	120.24	0.9733	0.5680

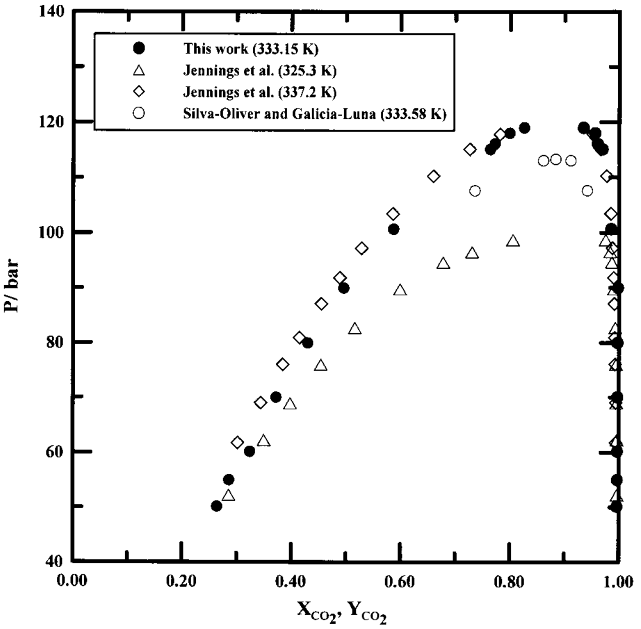


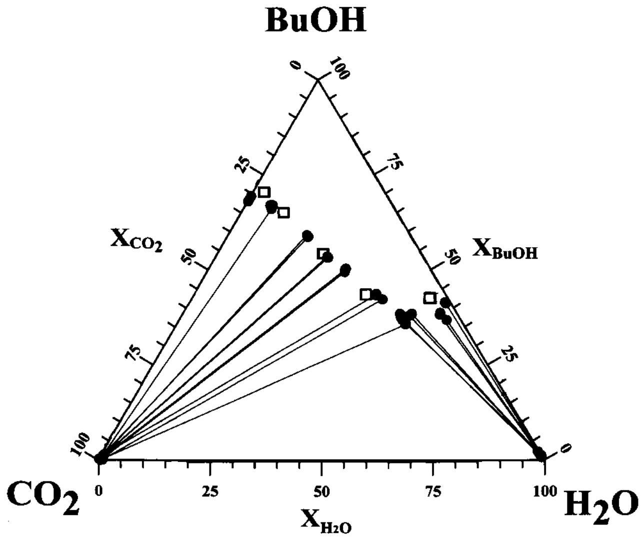
Figure 2. Phase diagram for the CO_2 + 1-butanol system at 333.15 K.

Table 2. Measured Compositions of the Equilibrium Vapor, Liquid I, and Liquid II Phases for the CO_2 + Water + 1-Butanol System

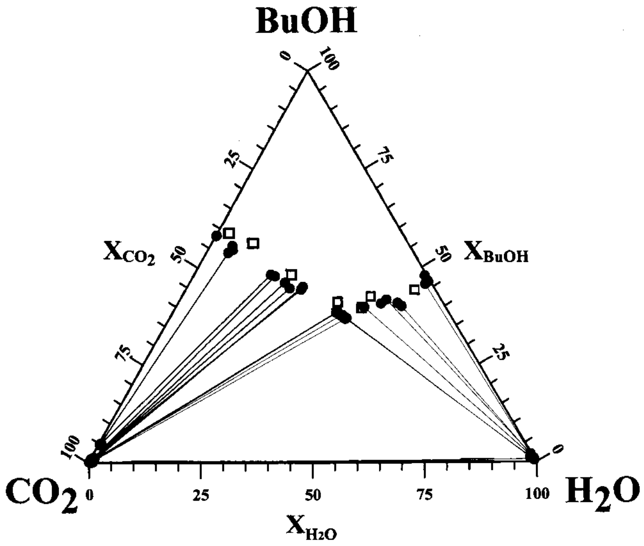
		vapor phase		liquid phase I		liquid phase II	
T/K	P/bar	Y_{CO_2}	Y_{BuOH}	X_{CO_2}	X_{BuOH}	X_{CO_2}	X_{BuOH}
333.15	60	0.9969	0.0030	0.3145	0.6854		
		0.9945	0.0022	0.2746	0.6663		
		0.9834	0.0119	0.2336	0.5875		
		0.9892	0.0058	0.2164	0.5332		
		0.9922	0.0006	0.1942	0.4992		
		0.9824	0.0135	0.1544	0.4313		
		0.9892	0.0288	0.1300	0.3682	0.0028	0.0119
				0.0127	0.4131	0.0033	0.0139
				0.0373	0.3788	0.0034	0.0124
				0.1060	0.3822	0.0033	0.0153
	80	0.9951	0.0048	0.4182	0.5817		
		0.9485	0.0481	0.4036	0.5464		
		0.9872	0.0091	0.3435	0.4805		
		0.9823	0.0129	0.3248	0.4545		
		0.9855	0.0069	0.2953	0.4478		
		0.9935	0.0025	0.2486	0.3864		
		0.9914	0.0024	0.2369	0.3743	0.0045	0.0076
				0.0089	0.4656	0.0037	0.0206
				0.1124	0.4084	0.0019	0.0098
				0.1811	0.3982	0.0019	0.0100
343.15	60	0.9951	0.0048	0.2874	0.7125		
		0.9928	0.0033	0.2388	0.6978		
		0.9728	0.0217	0.2265	0.6455		
		0.9777	0.0138	0.1882	0.5484		
		0.9929	0.0005	0.1746	0.4736		
		0.9813	0.0021	0.1257	0.4196		
		0.9766	0.0005	0.0913	0.3473	0.0023	0.0172
				0.0178	0.3503	0.0047	0.0523
				0.0346	0. 3513	0.0029	0.0138
	80	0.9936	0.0063	0.3791	0.6208		
		0.9829	0.0141	0.3541	0.5883		
		0.9723	0.0237	0.3134	0.5270		
		0.9823	0.0123	0.2772	0.4834		
		0.9930	0.0025	0.2589	0.4287		
		0.9855	0.0073	0.2107	0.3988		
		0.9709	0.0043	0.1663	0.3316	0.0031	0.0102
				0.0161	0.3368	0.0038	0.0235
				0.0415	0.3593	0.0030	0.0126
				0.0985	0.3328	0.0003	0.0028
353.15	60	0.9947	0.0052	0.2641	0.7358		
		0.9859	0.0094	0.2123	0.7147		
		0.9584	0.0346	0.2022	0.6578		
		0.9783	0.0137	0.1651	0.5667		
		0.9863	0.0041	0.1561	0.4803		
		0.9816	0.0077	0.1146	0.4269		
		0.9722	0.0006	0.0983	0.3800	0.0010	0.0147
				0.0084	0.3991	0.0034	0.0226
				0.0451	0.3963	0.0032	0.0170
	80	0.9965	0.0034	0.3563	0.6436		
		0.9753	0.0213	0.3225	0.6129		
		0.9658	0.0295	0.2991	0.5785		
		0.9755	0.0179	0.2481	0.5085		
		0.9890	0.0046	0.2354	0.4347		
		0.9724	0.0167	0.1879	0.4033		
		0.9760	0.0037	0.1629	0.3657	0.0027	0.0159
				0.0139	0.3633	0.0044	0.0408
				0.0812	0.3872	0.0030	0.0137

cylinders, a view window, a fluid sampling valve, and a two-way valve. The temperature of the oven was controlled and measured to within ±0.1 K. The pressure was measured within ±0.1 bar with a Validyne pressure transducer. The transducer was calibrated with a dead-weight tester before measurements.

Compositional Analysis. The equilibrium composition of each phase was analyzed using an on-line gas chromatograph (GC-14A, Shimadzu Co., Japan) equipped with a thermal conductivity detector. The gas and liquid samples were in-situ taken through a 10-μL sampling valve (Valco Instruments Inc., Houston, TX). The current used in the TCD was 140 mA. Helium flowing at a rate of 30 mL$\cdot$min^{-1} was employed as the carrier gas. The GC column used was 2 m long and was packed with Porapak Q. During analysis, the oven temperature was initially kept constant at 383.15 K for 10 min, then raised to 453.15 K with a heating rate of 35 K$\cdot$min^{-1}, and held for 23 min. Each sample was analyzed at least five times, and the reproducibility of the analyses was within 3%.

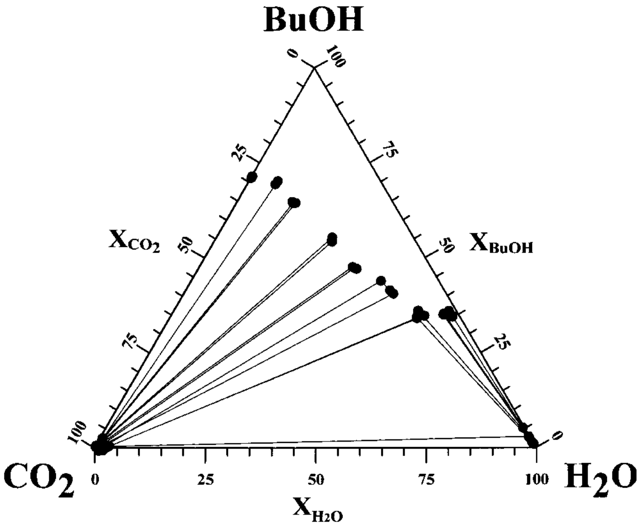


(a) 60 bar

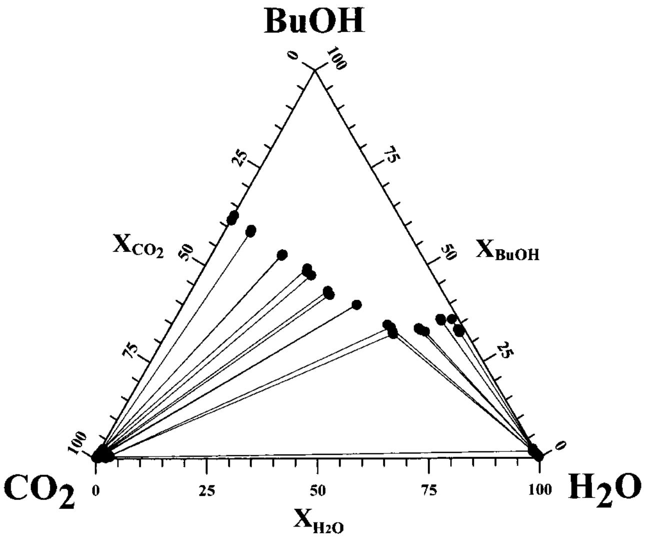


(b) 80 bar

Figure 3. (a) Phase diagrams for the CO_2 + 1-butanol + water system at 333.15 K and 60 bar: (●) experimental data; (□) Panagiotopoulos and Reid.[22] (b) Phase diagrams for the CO_2 + 1-butanol + water system at 333.15 K and 80 bar: (●) experimental data; (□) Panagiotopoulos and Reid.[22]



(a) 60 bar



(b) 80 bar

Figure 4. Phase diagrams for the CO_2 + 1-butanol + water system at 343.15 K: (a) 60 bar; (b) 80 bar.

Results and Discussion

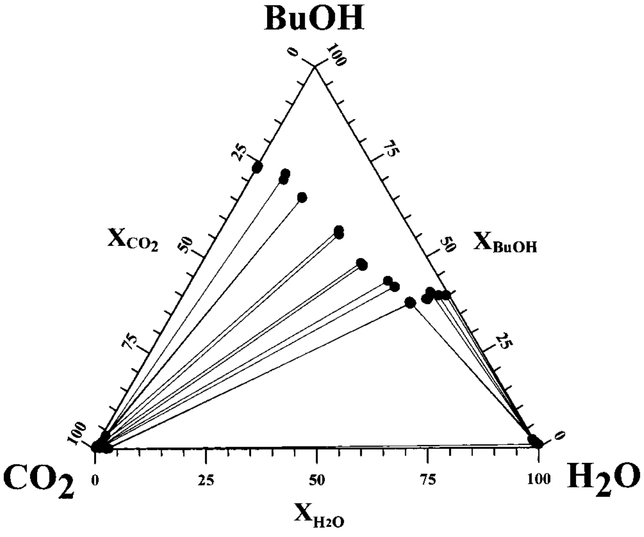
CO_2 + 1-Butanol System. Vapor–liquid equilibria data for the CO_2 + 1-butanol system at 333.15, 343.15, and 353.15 K are summarized in Table 1. Equilibrium $P-x-y$ data obtained at 333.15 K are used to confirm the accuracy of the measurement. This shows that the data are in good agreement with those reported by Jennings et al.,[15] and Silva-Oliver and Galicia-Luna,[21] as shown in Figure 2. Comparing the data of this work with those of Jennings, the average deviations of liquid-phase compositions were within 2.5% and those of vapor-phase compositions were within 0.5%.

As can be seen in Table 1, the solubility of CO_2 in 1-butanol decreases with increasing temperature, while it increases with increasing pressure. Moreover, the solubility of 1-butanol in CO_2 is relatively low and it shows no significant change with temperature and pressure, except in the vicinity of the critical point. When the pressure reaches the critical point, the mutual solubilities of the CO_2 + 1-butanol system rise dramatically. The critical pressures at 343.15 and 353.15 K, which are higher than that at 333.15 K, are beyond our experimental pressure range.

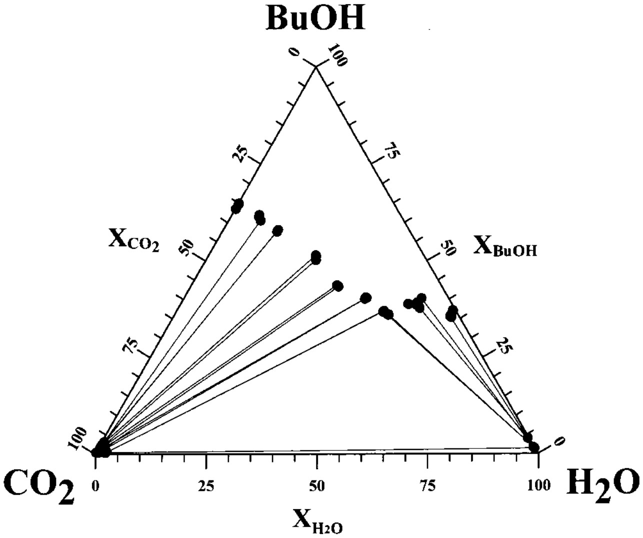
From the results, only vapor–liquid-phase equilibria exist over the whole range of experimental conditions. This behavior is consistent with the report by Lam et al.[24] that the liquid–liquid–vapor locus in the CO_2 + 1-butanol system terminates at an upper critical end point (UCEP) at 22.99 bar and 259.25 K.

CO_2 + Water + 1-Butanol System. The measured VLL equilibrium compositions for the CO_2 + water + 1-butanol system at 333.15, 343.15, and 353.15 K are listed in Table 2. Figure 3 illustrates the results obtained at pressures of 60 bar and 80 bar, respectively, at the temperature 333.15 K. It shows good agreement with those measured by Panagiotopoulos and Reid.[22]

Figures 4 and 5 demonstrate phase diagrams at 343.15 and 353.15 K, respectively. Except single phases at compositions near any apex of the triangular diagram, the



(a) 60 bar



(b) 80 bar

Figure 5. Phase diagrams for the CO_2 + water + 1-butanol system at 353.15 K: (a) 60 bar; (b) 80 bar.

ternary system exhibits one vapor–liquid–liquid equilibrium (VLLE) region, two vapor–liquid equilibrium (VLE) regions, and one liquid–liquid equilibrium (LLE) region. The effects of temperature and pressure on the phase behavior can also be observed from Figures 3–5. They illustrate that the solubility of CO_2 in 1-butanol decreases with increasing temperature at the same pressure. In contrast with this tendency, the solubility of 1-butanol in water increases with temperature. At a constant temperature, the solubility of CO_2 in 1-butanol increases as the pressure increases, but the liquid–liquid equilibrium region between 1-butanol and water is not significantly affected by the pressure. Moreover, at compositions near the apex of the VLLE region (1-butanol-rich phase) the composition moves toward enriching CO_2 as the pressure increases. Thus, the solubility of CO_2 in the 1-butanol-rich phase increases with an increase of pressure.

It is somewhat difficult to determine the CO_2–water equilibrium region exactly, because this VLE region is very narrow and close to the sideline of CO_2–water region. However, the immiscible region between the VLLE region and the sideline of the CO_2–water region cannot be neglected. This result is supported by Adrian et al.,[25] who showed that the immiscibility was a typical characteristic of the phase behavior for systems containing gas, water, and polar solvent.

Conclusions

In this work, phase equilibria data and the phase behavior for CO_2 + 1-butanol and CO_2 + water + 1-butanol systems were investigated. Under the experimental conditions, only a VLE region was observed for the CO_2 + 1-butanol system. On the other hand, the CO_2 + water + 1-butanol system exhibited three single-phase regions, one VLLE region, two VLE regions, and one LLE region. These equilibrium data will be helpful for process design for systems involving CO_2, water, and 1-butanol.

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