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Phase Equilibrium of Ethanol + CO_2 and Acetone + CO_2 at Elevated Pressures

Chany-Yih Day,[†] Chiehming J. Chang,*[‡] and Chiu-Yang Chen[†]

Departments of Environmental Engineering and Chemical Engineering, National Chung-Hsing University, #250, KuoKuang Road, Taichung, Taiwan 402, R.O.C.

Vapor−Liquid equilibria for two binary mixtures at elevated pressures were determined by a novel technique of density measurement. In this investigation using two high-pressure densitometers, phase diagrams for carbon dioxide + ethanol and carbon dioxide + acetone mixtures were established at five temperatures and pressures up to 14.39 MPa. Solubilities of carbon dioxide in both ethanol and acetone were found to increase with applied pressure but decreased with increasing temperature. The solubility for carbon dioxide in acetone was found to be greater than that of carbon dioxide in ethanol.

Introduction

Most ethanol is currently obtained by acid-catalyzed hydration of ethylene (Peters, 1993). One commercial process of acetone manufacture involves dehydrogenation of 2-propanol (McMurry, 1992). Vapor−liquid equilibria of carbon dioxide with hydrocarbons at elevated pressures are commonly used in the design and operation of separation equipment in the petroleum industry. However, limited data are available for carbon dioxide + alcohol mixtures at elevated pressures (Chang and Huang, 1994).

Panagiotopoulos and Reid (1987), Shibata and Sandler (1989), and Kato et al. (1991) recently measured the density of a high-pressure system using the vibrating-tube density meters with circulation in their vapor−liquid equilibrium apparatus. Panagiotopoulos and Reid studied the phase behavior of carbon dioxide + ethanol at different temperatures. Kato and Tanaka (1995) used the new density apparatus to measure high-pressure phase compositions of a carbon dioxide + ethanol mixture at 308.15 K. The authors (Chang, 1992; Chang et al., 1995) recently proposed volume expansion coefficients and activity coefficients of carbon dioxide + organic liquids at 298 K, and the solubilities of carbon dioxide and nitrous oxide in three liquid solvents were measured under phase equilibria at several temperatures at elevated pressures.

Experimental Section

Ethanol (Merck, 99.8+%), acetone (Merck, 99.5+%), carbon dioxide (Air Product local branch, 99.5+%), and nitrogen (Air Product local branch, 99.5+%) were purchased without further purification. Liquid and vapor densities were individually measured by using a system containing two vibrating tube densitometers (Anton Parr, DMA 512 and 512P and DMA60); pressure-related constants of two densitometers were determined from the period of vibrations of deionized water and nitrogen of accurately known densities, the information could be found elsewhere in the earliest study of Chang (1992).

The experimental system is illustrated schematically in Figure 1. At the beginning of an experiment, the residual solvent was evacuated from the equilibrium system. After degassing and evacuation of the whole system, carbon dioxide gas from a high-pressure cylinder was bubbled to an equilibrium cell up to the desired pressure and the circulation started. Recirculation was continued until reaching a stable density reading. The required time to attain equilibrium ranged from approximately 15 min at lower pressure to 30 min at higher pressure. The vapor and liquid compositions (y and x) at fixed temperature and pressure can be evaluated by combining a set of data, based on overall mass balances and the phase rule, which were used in the studies of Chang (1992), Chang et al. (1995), Kato et al. (1991), and Kato and Tanaka (1995). The sensitivity and absolute reliability of the equilibrium compositions appeared to be 0.0005 mole fraction, based on the accuracy of the density measurement. The absolute standard deviation of the temperature was within 0.015 K.

Results and Discussion

Figures 2 and 3 show the $P-x-y$ diagrams of CO_2 + ethanol at 308.11 K and 313.14 K. Compared with the data of Kato and Tanaka (1995) and Panagiotopoulos and Reid (1987), the differences of the vapor and liquid compositions were found to be within 2%. The $P-x-y$ diagrams at 291.15, 298.17, and 303.12 K are shown in Figure 4. At low pressures, the solubility of carbon dioxide (x_1) was relatively low and increased linearly with pressure, obeying Henry's law closely. At high pressures, x_1 could be up to 0.8 and decreased with temperature. Figures 5 and 6 represent the $P-x-y$ diagrams for CO_2 + acetone at 298.16 K and 313.13 K. The differences of x and y were found to be within 2%, when compared with data in the literature (Kato et al., 1991; Katayama et al., 1975; Panagiotopoulos, 1987). Figure 7 shows three $P-x-y$ diagrams at 291.15, 303.13, and 308.15 K. The solubility of CO_2 in acetone is similar to that of CO_2 + ethanol at low pressure, but larger than that of the CO_2 + ethanol system at high pressure. Tables 1 and 2 show the experimental results of coexisting phase compositions at every temperature, respectively. The difference of vapor and liquid densities between this study and Kato and Tanaka (1995) is 3% and 11%, respectively. Figures 8 and 9, respectively, show that the equilibrium constant of CO_2 + ethanol and CO_2 + acetone systems increases with temperature and decreases with pressure. The K value of carbon dioxide converged to 1 at each temperature, indicating that these two binary mixtures approached the critical state of carbon dioxide at high pressure. As the pressure approached the vicinity of the critical pressure of the mixture, the expansion of the liquid phase increased dramatically as a result of a nonlinear

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* To whom correspondence should be addressed.

[†] Department of Environmental Engineering.

[‡] Department of Chemical Engineering.

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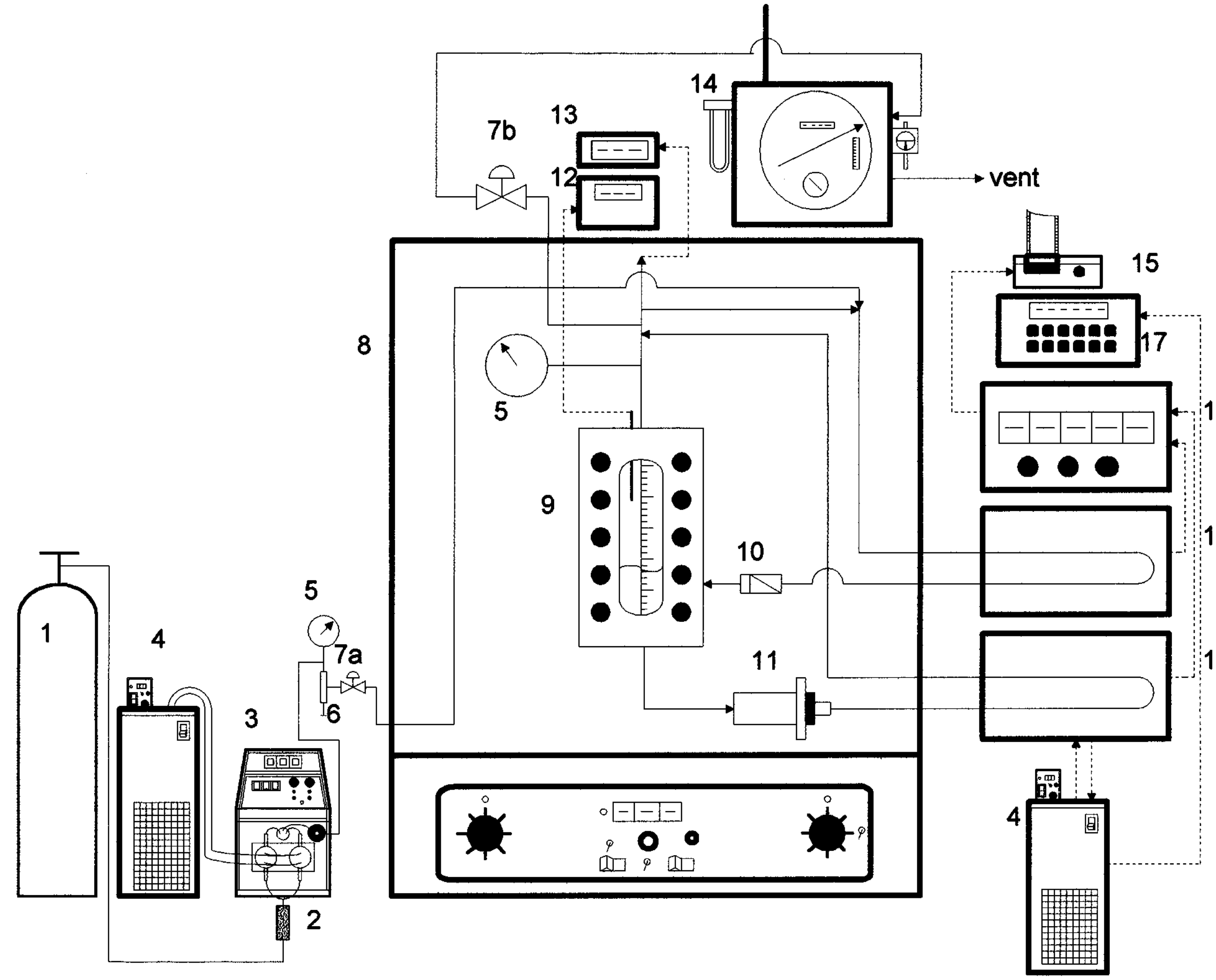

Figure 1. Experimental apparatus of V−L composition measurement for CO_2 + ethanol and CO_2 + acetone: (1) gas cylinder; (2) filter; (3) metering pump; (4) refrigerator; (5) pressure gauge; (6) relief valve; (7a,7b) needle valve; (8) air bath; (9) equilibrium cell; (10) check valve; (11) circulation pump; (12) digital thermometer; (13) digital pressure transducer; (14) wet gas meter; (15) line printer; (16) densitometer [a, DMA60; b, DMA512; c, DMA512P]; (17) high-precision thermometer.

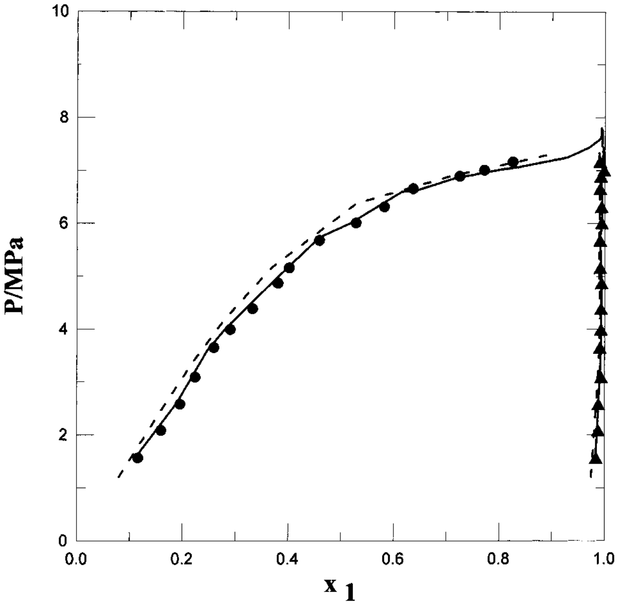

Figure 2. Vapor−liquid equilibria for carbon dioxide (1) + ethanol (2) at 308.11 K: (●) liquid; (▲) vapor; (—) Kato and Tanaka (1995); (- - -) Panagiotopoulos and Reid (1987).

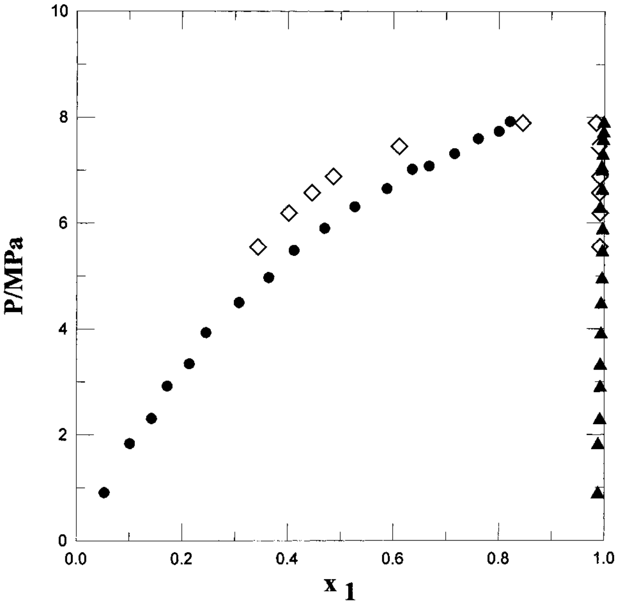

Figure 3. Vapor−liquid equilibria for carbon dioxide (1) + ethanol (2) at 313.14 K: (●) liquid; (▲) vapor; (◇) Jennings et al. (1991) at 314.5 K.

increase of the solubility of carbon dioxide. The equilibrium constant is represented as a function of relative volatility, which provides a measure of the chemical affinity of the gas to the liquid for comparison. In this study, carbon dioxide was found to have a larger affinity to acetone than ethanol.

Table 1. Experimental Data for Carbon Dioxide (1) + Ethanol (2) at Various Temperatures

P/MPa	x_1	y_1	ρ^V/kg·m^{-3}	ρ^L/kg·m^{-3}	P/MPa	x_1	y_1	ρ^V/kg·m^{-3}	ρ^L/kg·m^{-3}
T = 291.15 K									
0.87	0.1593	0.9893	12.2	683.6	3.45	0.4963	0.9950	68.9	711.4
1.25	0.2138	0.9889	19.1	687.8	3.84	0.5587	0.9932	79.9	713.6
1.73	0.2560	0.9888	28.7	692.2	4.36	0.6315	0.9966	96.7	720.2
2.14	0.2985	0.9925	37.4	697.0	4.97	0.7405	0.9957	121.8	728.2
2.41	0.3463	0.9940	43.7	700.8	5.30	0.7981	0.9916	137.0	733.3
2.81	0.3923	0.9940	52.9	703.7	5.45	0.8301	0.9952	147.6	739.0
3.10	0.4423	0.9948	59.8	707.4					
T = 298.17 K									
0.88	0.1296	0.9850	30.4	678.4	4.34	0.5139	0.9969	109.7	704.4
1.62	0.1865	0.9872	44.6	684.3	5.39	0.6357	0.9976	147.0	715.4
2.28	0.2622	0.9910	58.1	688.6	5.82	0.7400	0.9983	168.0	720.9
2.96	0.3268	0.9933	73.0	692.2	6.13	0.8302	0.9994	285.0	724.9
3.65	0.4095	0.9953	90.5	697.3					
T = 303.12 K									
0.86	0.0978	0.9754	11.9	668.6	4.95	0.4940	0.9941	106.9	693.9
1.64	0.1412	0.9880	26.1	672.6	5.58	0.5810	0.9945	129.5	697.5
2.34	0.2077	0.9930	41.4	676.3	5.93	0.6355	0.9919	144.1	703.5
2.82	0.2753	0.9921	51.8	685.4	6.27	0.7173	0.9907	161.6	707.4
3.89	0.3644	0.9939	75.6	687.8	6.48	0.7700	0.9916	173.6	710.6
4.25	0.4179	0.9934	85.6	691.2	6.63	0.8280	0.9916	183.9	712.4
T = 308.11 K									
1.57	0.1160	0.9838	18.8	670.6	5.16	0.4017	0.9919	123.5	697.7
2.09	0.1591	0.9882	30.0	675.1	5.68	0.4589	0.9914	140.5	699.5
2.58	0.1957	0.9884	42.7	678.6	6.01	0.5287	0.9947	153.2	732.3
3.09	0.2239	0.9936	62.5	684.1	6.31	0.5819	0.9939	166.2	703.9
3.65	0.2593	0.9913	82.2	687	6.66	0.6370	0.9913	183.3	706.4
4.00	0.2904	0.9932	90.8	689.5	6.89	0.7249	0.9926	196.9	707.7
4.39	0.3324	0.9932	101.3	692.3	7.01	0.7713	0.9989	204.7	708.7
4.87	0.3808	0.9941	114.7	694.4	7.17	0.8257	0.9909	216.1	708.8
T = 313.14 K									
0.91	0.0529	0.9878	8.40	657.8	5.90	0.4697	0.9969	122.8	685.7
1.84	0.1009	0.9883	24.9	663.6	6.31	0.5268	0.9925	137.2	688.6
2.31	0.1418	0.9917	33.7	666.1	6.65	0.5881	0.9965	150.7	690.5
2.92	0.1718	0.9925	45.8	668.8	7.02	0.6356	0.9962	167.3	693.1
3.34	0.2135	0.9928	54.9	672.8	7.08	0.6678	0.9954	170.1	694.7
3.93	0.2450	0.9941	68.1	676.0	7.31	0.7155	0.9972	182.2	695.5
4.50	0.3074	0.9939	82.2	678.1	7.60	0.7607	0.9977	198.5	696.2
4.97	0.3636	0.9960	94.4	680.1	7.73	0.7999	0.9985	207.8	696.6
5.49	0.4117	0.9963	109.5	682.7	7.92	0.8208	0.9989	221.4	697.2

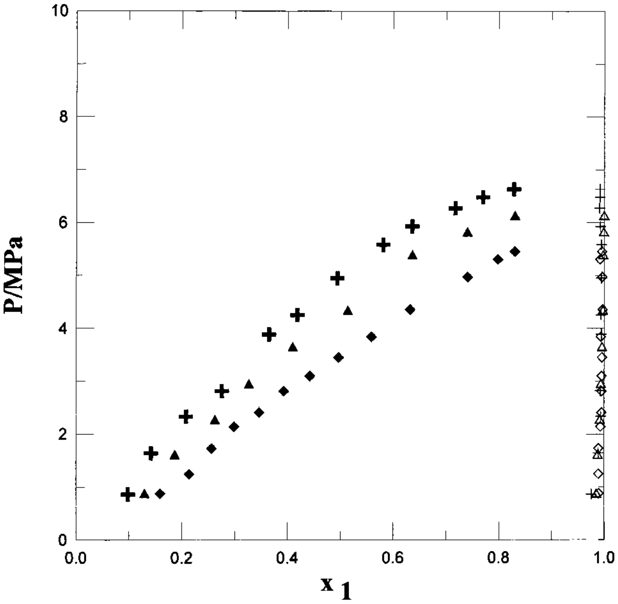

Figure 4. Vapor−liquid equilibria for carbon dioxide (1) + ethanol (2) at different temperatures: (+) liquid/(+) vapor at 303.12 K; (▲) liquid/(△) vapor at 298.17 K; (◆) liquid/(◇) vapor at 291.15 K.

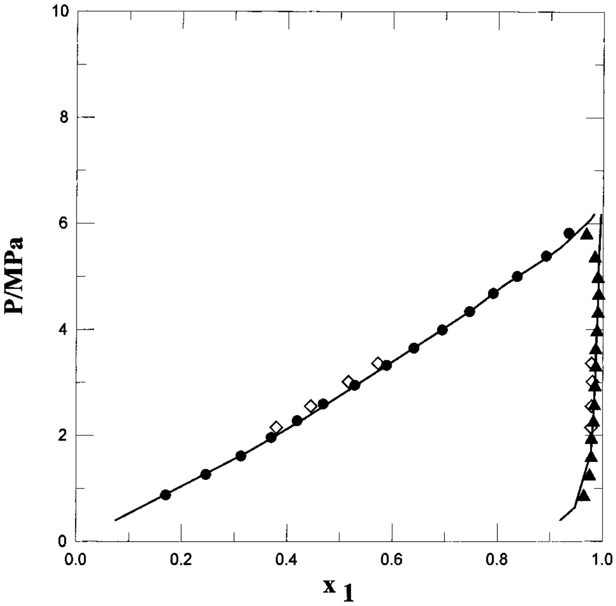

Figure 5. Vapor−liquid equilibria for carbon dioxide (1) + acetone (2) at 298.16 K: (●) liquid; (▲) vapor; (◇) Kato et al. (1991); (−) Katayama et al. (1975).

Conclusions

Two densitometers were used for the determination of high-pressure phase equilibria for mixtures of CO_2 + ethanol and CO_2 + acetone at five temperatures and pressures up to 14.39 MPa. A recirculation device for the liquid phase proved to be efficient for phase equilibrium studies. The result of this investigation showed that the mole fraction of carbon dioxide in the liquid phase is high

Table 2. Experimental Data for Carbon Dioxide (1) + Acetone (2) at Various Temperatures

P/MPa	x_1	y_1	ρ^V/kg·m^{-3}	ρ^L/kg·m^{-3}	P/MPa	x_1	y_1	ρ^V/kg·m^{-3}	ρ^L/kg·m^{-3}
				T = 291.15 K					
0.87	0.2150	0.9528	11.4	687.9	3.45	0.7119	0.9847	68.5	717.2
1.18	0.2885	0.9655	17.2	692.8	3.84	0.7670	0.9888	79.7	720.3
1.73	0.4027	0.9729	28.1	698.7	4.34	0.8177	0.9902	95.9	723.4
2.41	0.5208	0.9789	42.8	703.3	4.94	0.8662	0.9869	119.7	725.9
2.81	0.5940	0.9815	52.1	707.4	5.27	0.9100	0.9866	136.1	727.7
3.10	0.6545	0.9839	59.5	713.1					
				T = 298.16 K					
0.88	0.1699	0.9646	11.0	673.9	3.65	0.6409	0.9869	70.6	721.9
1.27	0.2460	0.9751	18.2	684.0	4.00	0.6945	0.9891	85.0	728.5
1.62	0.3125	0.9782	25.0	688.9	4.34	0.7465	0.9909	95.3	730.7
1.96	0.3701	0.9791	31.8	695.7	4.69	0.7912	0.9918	106.3	732.9
2.28	0.4190	0.9826	38.2	699.7	5.00	0.8368	0.9906	119.6	734.9
2.60	0.4687	0.9842	45.2	703.6	5.39	0.8917	0.9850	137.6	737.0
2.96	0.5291	0.9855	53.5	710.4	5.82	0.9350	0.9687	157.4	739.3
3.33	0.5890	0.9868	62.0	716.6					
				T = 303.13 K					
0.87	0.1655	0.9751	9.6	669.5	4.25	0.6886	0.9891	83.2	712.4
1.31	0.2360	0.9782	17.4	676.0	4.56	0.7314	0.9909	92.6	715.1
1.65	0.2927	0.9791	23.6	682.4	4.95	0.7738	0.9918	104.7	719.4
2.01	0.3482	0.9826	30.5	687.2	5.31	0.8167	0.9906	116.9	723.4
2.43	0.4191	0.9842	38.8	691.5	5.58	0.8502	0.9850	127.4	725.6
2.91	0.4823	0.9855	49.1	697.1	5.93	0.8870	0.9687	142.2	727.0
3.42	0.5695	0.9868	61.3	703.4	6.27	0.9197	0.9767	159.1	728.4
3.89	0.6330	0.9869	73.2	709.1					
				T = 308.15 K					
0.82	0.1620	0.9317	4.0	664.0	4.87	0.7026	0.9894	96.6	705.1
1.32	0.2252	0.9467	13.3	668.5	5.16	0.7497	0.9892	105.5	706.9
1.57	0.2649	0.9651	18.4	675.6	5.68	0.8017	0.9904	122.8	709.7
2.09	0.3349	0.9723	29.4	679.8	6.01	0.8319	0.9902	135.2	742.7
2.58	0.4080	0.9790	40.2	683.4	6.31	0.8630	0.9900	148.0	713.4
3.13	0.4787	0.9824	52.1	693.2	6.66	0.8920	0.9826	164.7	714.9
3.65	0.5476	0.9846	64.2	695.0	7.01	0.9256	0.9748	184.4	716.2
4.00	0.6006	0.9845	72.9	697.2	7.17	0.9336	0.9734	195.4	716.8
4.39	0.6516	0.9854	83.1	701.1					
				T = 313.13 K					
0.78	0.1428	0.9109	7.0	655.4	4.60	0.6368	0.9880	85.0	695.3
1.18	0.1882	0.9259	13.7	664.1	5.17	0.7022	0.9872	100.4	698.9
1.56	0.2468	0.9571	20.5	667.8	5.48	0.7471	0.9891	109.7	700.3
2.03	0.3078	0.9692	29.0	671.5	5.91	0.7964	0.9912	123.7	701.7
2.47	0.3634	0.9713	37.4	675.8	6.2	0.8153	0.9915	133.5	702.6
2.80	0.4068	0.9789	43.8	679.3	6.44	0.8464	0.9907	142.8	702.6
3.24	0.4663	0.9749	53.0	683.5	6.90	0.8670	0.9754	161.8	702.8
3.59	0.5369	0.9837	61.1	687.5	7.12	0.8920	0.9830	172.3	702.3
4.06	0.5762	0.9721	71.6	691.4	7.39	0.9083	0.9867	186.8	701.6

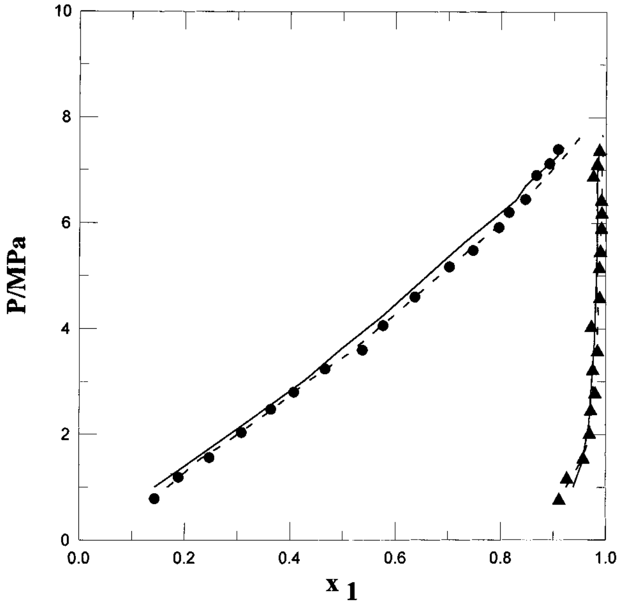

Figure 6. Vapor−liquid equilibria for carbon dioxide (1) + acetone (2) at 313.13 K: (●) liquid; (▲) vapor; (—) Katayama et al. (1975); (- - -) Panagiotopoulos and Reid (1987).

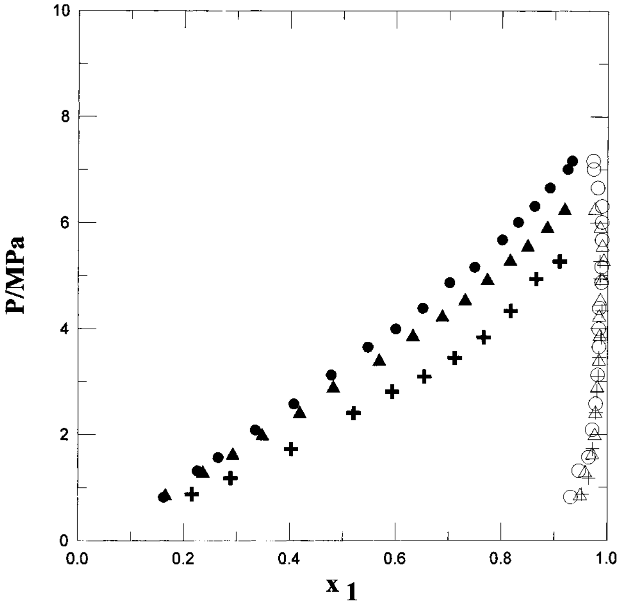

Figure 7. Vapor−liquid equilibria for carbon dioxide (1) + acetone (2) at different temperatures: (+) liquid/(+) vapor at 291.15 K; (▲) liquid/(△) vapor at 303.13 K; (●) liquid/(○) vapor at 308.15 K.

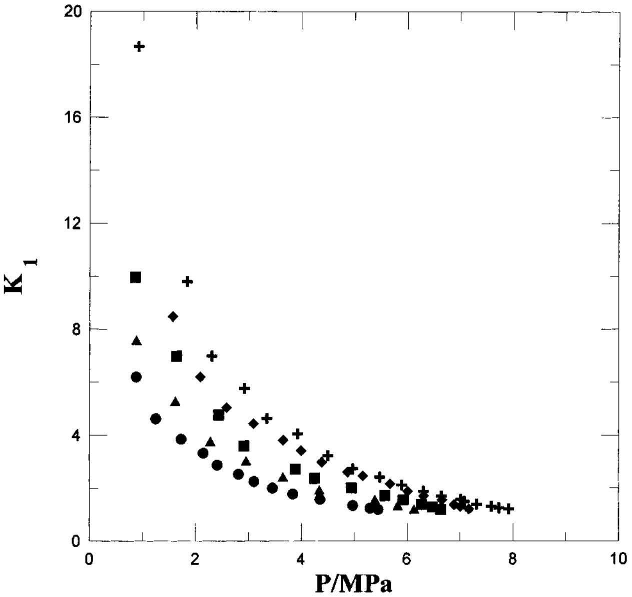

Figure 8. Equilibrium constants of carbon dioxide for ethanol CO₂ (1) at different temperatures: (●) 291.15 K; (▲) 298.17 ■) 303.12 K; (◆) 308.11 K; (+) 313.14 K.

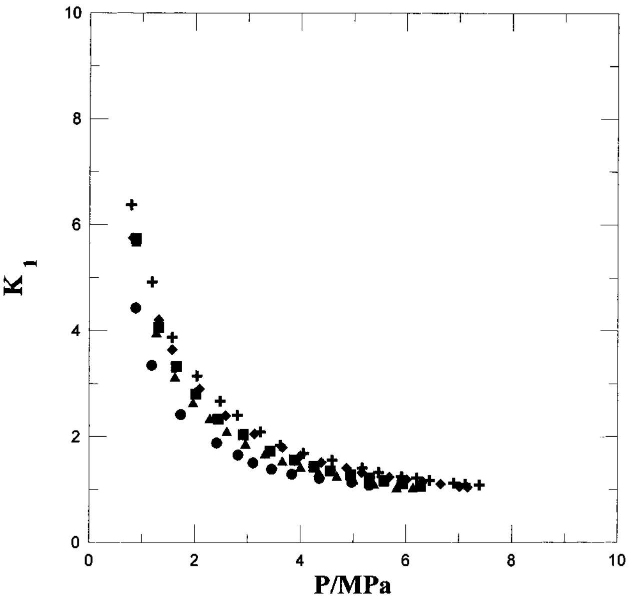

Figure 9. Equilibrium constants of carbon dioxide for acetone (2) + CO_2 (1) at different temperatures: (●) 291.15 K; (▲) 298.16 K; (■) 303.13 K; (◆) 308.15 K; (+) 313.13 K.

even at moderate pressure. The solubility of CO_2 in acetone is larger than that of CO_2 in ethanol, because ethanol is polar and is also self-associated, while acetone is polar but not associated. The use of equilibrium values provides computational convenience in material balance calculations and also indicates the critical point of these two binary mixtures. It is evident that the asymmetric binary mixture approaches the critical state of carbon dioxide when the system pressure is high enough.

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