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Vapor−Liquid Equilibrium for Binary Systems of Carbon Dioxide + Methanol, Hydrogen + Methanol, and Hydrogen + Carbon Dioxide at High Pressures

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Vapor−liquid equilibrium data and density of the liquid phase for binary systems of carbon dioxide + methanol, hydrogen + methanol, and carbon dioxide + hydrogen at high pressures were determined. A dynamic technique with liquid-phase recirculation and on-line gas chromatography was used in this study. The equilibrium data and density were measured at temperatures between 278.15 K and 308.15 K, and pressures between 15 bar and 192.53 bar. The isothermal volume expansion behavior for the carbon dioxide + methanol system at various temperatures was also determined.

Introduction

A recently reported application of dense gases is the utilization of expanded solvents as reaction media[1] and as antisolvents.[2] Such interest provided the incentive for the current investigation of the phase equilibria of systems containing hydrogen, carbon dioxide, and methanol.

Vapor−liquid equilibrium data for the CO_2 + MeOH (methanol), H_2 + MeOH, and H_2 + CO_2 binary systems have been published previously, as shown in Table 1. However, there is a considerable degree of inconsistency between the various data sets. To improve the reliability of the data, vapor−liquid equilibrium data for the CO_2 + MeOH, H_2 + MeOH, and H_2 + CO_2 binary systems were determined at temperatures from 278.15 K to 308.15 K and for pressures in the range 15 bar to 193 bar. The liquid-phase densities (ρ_L) of the CO_2 + MeOH, H_2 + MeOH, and H_2 + CO_2 binary systems were also measured for each of the experimental conditions investigated.

The validity of the experimental technique used was confirmed by comparing the results obtained in this work for the CO_2 + MeOH binary system with literature values at 298.15 K and 308.15 K.

Recently, binary systems consisting of CO_2 and MeOH have been utilized for crystallization, purification of solids, and reaction media. The expansion behavior of solvent with CO_2 is required for the design and optimization of these processes. While volume expansion (ΔV) data for a number of solvents have been reported by Kordikowski et al.,[30] no such data for MeOH have been published. Consequently, in this work the volumetric expansion of MeOH by CO_2 was measured at various temperatures.

Materials

Carbon dioxide (Industrial Grade, 99.5%), hydrogen (high purity, 99.98%), and argon (high purity, 99.997%) were supplied by BOC Gases Australia Ltd. Methanol (99.8 wt %, HPLC grade) and acetonitrile (99.8 wt %, HPLC grade) were purchased from Mallinckrodt, Australia Pty Ltd.

Table 1. Published Data for Binary Systems of Carbon Dioxide + Methanol, Hydrogen + Methanol, and Hydrogen + Carbon Dioxide

system	T/K	refs
CO_2 + MeOH	298.15	3
	313.15	4
	298.15 and 313.15	5
	230.00 to 330.00	6
	298.15 to 473.15	7
	233.10 to 298.15	8
	243.15 to 298.15	9
	313.15	10, 11
	333.15 to 393.15	12
	291.15 to 313.15	13
	100.00 to 298.15	14
	323.15 to 398.15	15
	323.15 to 477.55	16
H_2 + MeOH	297.55 to 372.45	17
	298.15 to 373.15	7
	296.25 and 413.45	18
	291.00	19
	298.15 to 333.15	20
	293.00 to 328.00	21
	213.15 to 298.15	22
	298.15	23
H_2 + CO_2	220.00 to 290.00	24
	244.90 to 289.90	25
	273.15	26
	281.15 and 288.15	27
	233.15 and 298.15	28
	298.20	29

Experimental Section

Apparatus. The dynamic-liquid recirculation apparatus that was used for the vapor−liquid equilibrium studies is shown in Figure 1. A Jerguson sight gauge (Series No. 32) with total volume 60 cm^3 was used as an equilibrium cell.

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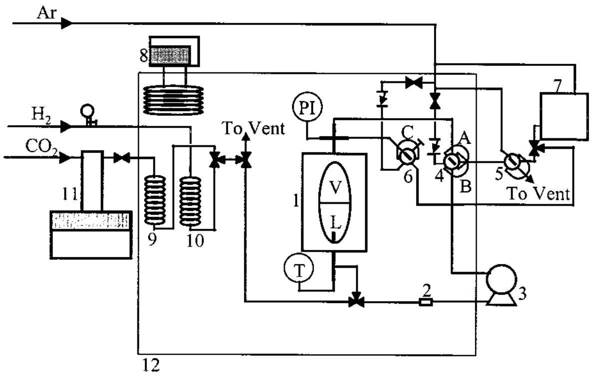


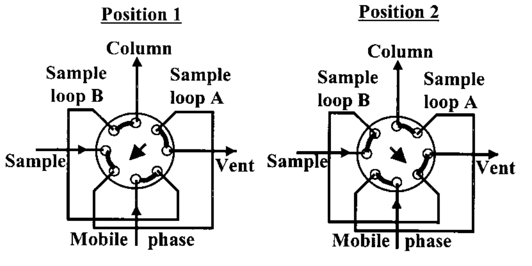
Figure 1. Schematic diagram of the vapor−liquid equilibrium apparatus: (1) equilibrium cell; (2) filter; (3) metering pump; (4) eight-port valve; (5 and 6) six-port valve; (7) gas chromatograph; (8) immersion heater or immersion cooler; (9 and 10) heating coil; (11) syringe pump; (12) water bath; (13) regulator.

The high-pressure cell allows the visual observation of the phase behavior and liquid level at various conditions. The temperature of the system was controlled with a Unistat 130 heater (Thermoline, Australia Pty Ltd) or a TIC2−581-T cooler (Thermoline, Australia Pty Ltd). The temperature of the equilibrium cell was monitored with a type T thermocouple (Pyrosales, Australia) which was calibrated against a precalibrated mercury thermometer and was connected to a digital temperature indicator (Pyrosales). The pressure of the system was measured with a pressure transducer (Druck Limited, PDCR610, 350 barg) which was previously calibrated against a hydraulic dead weight tester (Pressurements Ltd). The equilibrium was established in the system by recirculating liquid phase through the vapor phase using a metering pump (Eldex Laboratories, Inc.). Carbon dioxide was transferred to the system with a syringe pump (ISCO Model 260D), and H_2 was introduced directly into the system via a regulator (BOC Gases Australia Ltd, HPS4-3000-4F-4F).

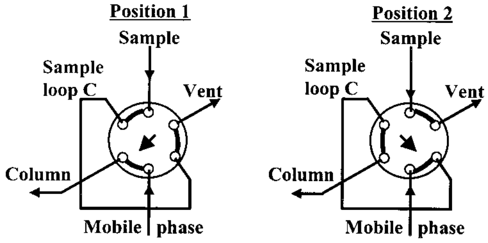
The sampling section consisted of two different valves. Eight- and six-port valves (Valco) were used for sampling liquid and vapor phases, respectively. The eight-port valve was located on the recirculation line after the metering pump. As shown in Figure 1, two sample loops, A and B, were located on the eight-port valve. In a dual configuration of the sample loop in the eight-port valve, as shown in Figure 2a, sample was injected in both positions. In position 1, loop A was loaded while the mobile phase passed through loop B. The loop A sample was then injected into the column by switching the valve from position 1 to position 2. At this stage another sample was loaded into loop B. Upon returning the valve to position 1, the loop B sample was injected into the column and loop A was reloaded. The six-port valve configuration is shown in Figure 2b. At position 1, sample flowed through the external loop (C) while the mobile phase flowed directly through to the chromatographic column. As the valve was switched to position 2, the sample contained in the loop was displaced by the mobile phase and carried into the column.

The volume expansion was visually monitored using an accurate cathetometer (Precision Tool & Instrument Co. Ltd).

Procedure. The equilibrium cell was filled with a known volume of MeOH and placed in a constant temperature water bath. The air from the system was purged by pressurizing the system to 10 bar with CO_2 and then depressurizing the equilibrium cell. The second component (CO_2 or H_2) was then added to the equilibrium cell very slowly. The experiment for the binary $H_2 + CO_2$ system was performed by adding H_2 into the system prior to CO_2. The system was isolated using a three-way valve at the bottom of the Jerguson sight gauge as the operating pressure in the system was approached. The system was left overnight at constant temperature and pressure. Equilibrium between the two phases was ensured by recirculating the liquid phase through the vapor phase for at least 2 h. The samples were withdrawn from each phase by manipulating the sampling valves and injecting the samples into the gas chromatograph.



a: Eight port valve



b: Six port valve

Figure 2. Configuration of sample loops on the eight-port (a) and six-port (b) valves.

At least three samples were withdrawn from each phase at each set of operating conditions with the relative standard deviation (RSD) of measured compositions being less than 4.4%. The equilibrium data for the CO_2 + MeOH binary system at 298.15 K and for pressures between 16.7 bar and 60.8 bar were compared with the result of Brunner et al.[7] in order to confirm the reliability of the experimental apparatus. An absolute average deviation (AAD%) of 4.6% was obtained.

The volumetric expansion of MeOH with CO_2 was determined by measuring the volume of the liquid phase at a given temperature and pressure. The expansion was calculated by the following equation:

$$\Delta V/\% = \frac{V_f - V_i}{V_i} \times 100 \qquad (1)$$

where V_f is the final equilibrium volume at a given temperature and pressure, and V_i is the initial volume of the liquid phase at atmospheric pressure.

The liquid-phase densities of all binary systems investigated were calculated at each equilibrium point by determining the number of moles of each component in a known volume of liquid mixture. The liquid-phase densities for the CO_2 + MeOH system were also calculated by measuring the volume expansions of the liquid phase at each equilibrium point and determining the number of moles of each component.

Analytical Techniques

Gas Chromatography Technique. The concentrations of all components in each phase were determined with an

Table 2. Isothermal Vapor–Liquid Equilibrium Data for a Binary System of CO_2 (1) + MeOH (2)

P/bar	x_1	y_1	ρ_L/kg·m^{-3}	ΔV/%	P/bar	x_1	y_1	ρ_L/kg·m^{-3}	ΔV/%
T = 278.15 K; RSD = 4.34					T = 298.15 K; RSD = 3.19				
15.00	0.1248	0.9948	795.4	20.48	15.00	0.1026	0.9899	792.2	10.21
25.00	0.2342	0.9975	724.5	35.10	29.46	0.2054	0.9959	837.4	25.52
30.86	0.3543	0.9982	716.0	45.83	40.80	0.2903	0.9944	833.3	40.83
35.00	0.4542	0.9975	723.1	106.93	47.10	0.3551	0.9949	876.6	61.25
36.85	0.5929	0.9976	740.9	182.88	54.10	0.4335	0.9921	848.1	110.01
38.25	0.6129	0.9974	716.8	252.64	56.00	0.5436	0.9912	861.7	121.66
38.75	0.7295	0.9972	695.7	409.59	59.14	0.6919	0.9935	843.6	–
39.30	0.8222	0.9965	697.0	960.50	59.54	0.7318	0.9908	811.5	484.14
					60.80	0.8821	0.9941	767.8	1133.80
T = 288.15 K; RSD = 2.78					T = 308.15 K; RSD = 2.92				
15.00	0.1118	0.9936	835.3	20.67	15.37	0.0903	0.9838	866.2	2.17
25.00	0.1964	0.9959	828.4	28.94	25.00	0.1467	0.9863	889.2	6.50
35.00	0.3095	0.9967	862.3	57.89	35.45	0.2074	0.9855	867.6	17.32
45.00	0.4307	0.9975	875.6	136.45	45.75	0.2742	0.9867	930.2	32.48
48.00	0.6131	0.9974	763.8	228.93	56.24	0.3622	0.9890	919.6	67.12
48.80	0.7937	0.9961	643.7	688.77	66.33	0.4904	0.9891	914.6	121.68
49.50	0.8384	0.9967	623.2	1032.55	69.73	0.5798	0.9890	896.5	192.87
					72.63	0.7799	0.9828	836.2	686.15
					74.33	0.8869	0.9575	784.2	1035.82

Table 3. Isothermal Vapor–Liquid Equilibrium Data for a Binary System of H_2 (1) + MeOH (2)

P/bar	x_1	y_1	ρ_L/kg·m^{-3}	P/bar	x_1	y_1	ρ_L/kg·m^{-3}
T = 278.15 K; RSD = 2.39; H = 5831.6 bar				T = 298.15 K; RSD = 3.41; H = 5341.3 bar			
20.26	0.0039	0.9838	811.2	20.00	0.0035	0.9942	855.4
30.00	0.0056	0.9864	807.1	30.00	0.0067	0.9628	806.4
49.75	0.0096	0.9953	809.1	50.14	0.0101	0.9836	823.8
70.00	0.0121	0.9983	836.3	69.93	0.0134	0.9915	840.4
90.00	0.0153	0.9985	840.1	90.00	0.0163	0.9955	938.2
110.00	0.0182	0.9986	827.6	110.10	0.0203	0.9902	823.3
T = 288.15 K; RSD = 3.33; H = 5666.7 bar				T = 308.15 K; RSD = 3.10; H = 5157.8 bar			
20.00	0.0034	0.9887	855.4	20.00	0.0037	0.9781	849.3
30.00	0.0057	0.9866	820.6	30.00	0.0067	0.9976	867.0
50.00	0.0098	0.9919	823.1	50.00	0.0100	0.9918	850.2
69.73	0.0126	0.9964	862.5	70.00	0.0135	0.9943	864.5
89.81	0.0152	0.9980	851.4	90.00	0.0173	0.9999	842.0
110.20	0.0192	0.9961	831.1	110.00	0.0211	0.9955	873.4

Table 4. Isothermal Vapor–Liquid Equilibrium Data for a Binary System of H_2 (1) + CO_2 (2)

P/bar	x_1	y_1	ρ_L/kg·m^{-3}	P/bar	x_1	y_1	ρ_L/kg·m^{-3}	P/bar	x_1	y_1	ρ_L/kg·m^{-3}
T = 278.15 K; RSD = 0.99				T = 290.15 K; RSD = 0.78				T = 278.15 K; RSD = 1.38			
48.05	0.0088	0.1139	598.4	61.74	0.0113	0.0495	566.6	71.93	0.0096	0.0425	555.6
58.64	0.0202	0.1842	611.3	71.00	0.0228	0.0979	567.1	80.20	0.0284	0.0743	558.8
69.33	0.0249	0.2533	599.8	83.92	0.0349	0.1556	499.8	85.92	0.0382	0.1006	531.6
77.22	0.0290	0.2789	498.2	92.30	0.0523	0.2056	499.0	90.61	0.0444	0.1333	540.6
86.71	0.0445	0.3037	521.1	93.10	0.0541	0.2189	520.1	95.70	0.0561	0.1609	529.3
99.61	0.0614	0.3411	527.3	97.90	0.0573	0.2389	518.8	110.90	0.0808	0.1938	511.4
108.6	0.0661	0.3581	544.8	99.30	0.0605		564.7	113.90	0.0878		499.9
114.00	0.0718	0.3762	529.1	103.70	0.0661		560.3	115.90	0.0890		507.9
117.70	0.0749	0.3818	546.3	109.30	0.0713		526.9				
126.00	0.0819	0.4102	524.3	116.20	0.0796	0.2735	522.7				
136.88	0.0912	0.4331	518.7	123.80	0.0897	0.2820	512.6				
144.87	0.0970	0.4507	526.0	132.90	0.1031	0.2918	515.5				
153.67	0.1026	0.4796	528.6	135.58	0.1037		527.5				
169.85	0.1179	0.5038	529.8	145.47	0.1139		525.2				
186.8	0.1291	0.5042	534.8	149.97	0.1215		512.7				
192.53	0.1307	0.5055	533.3	160.26	0.1364	0.3201	502.8				
				175.65	0.1545	0.3362	500.6				
				183.94	0.1571	0.3229	506.6				

on-line gas chromatographic technique. A thermal conductivity detector (TCD) gas chromatograph (Shimadzu GC-8A) connected to an integrator (Shimadzu Chromatopac C-R6A) was used for the analysis. The column (2.44 m by 3.17 mm) used for the analysis was packed with Porapak N (SGE, Australia). Argon was used as a carrier gas at a flow rate of 22 mL/min. The temperature of the column was kept at 343 K, and injector and detector temperatures were kept at 393 K.

The gas chromatograph was calibrated for each component (H_2, CO_2, and MeOH). Known volumes of each component were injected into the gas chromatograph, and the response factors were obtained.

Calibration of Sampling Loops. The volumes of the sampling loops used were measured according to the following procedure.

First, known volumes of MeOH were injected directly into the gas chromatograph with a 5 μL syringe (SGE,

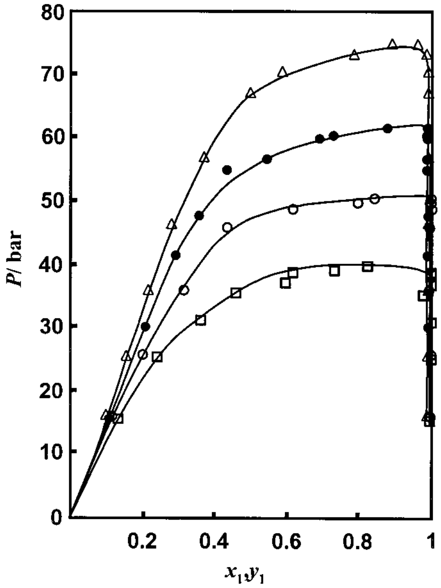


Figure 3. Vapor−liquid equilibrium for a CO_2 (**1**) + MeOH (**2**) binary system at various temperatures: △, 308.15 K; ●, 298.15 K; ○, 288.15 K; □, 278.15 K.

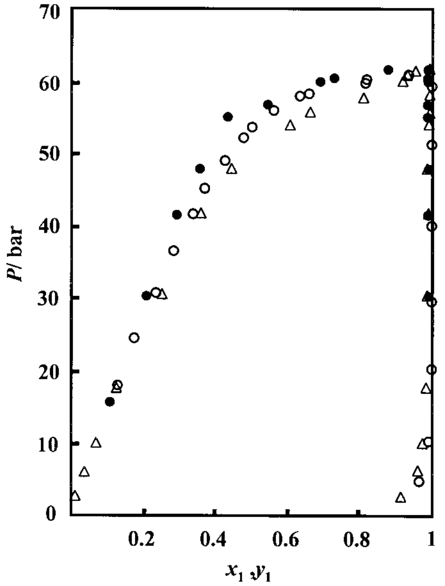


Figure 4. Vapor−liquid equilibrium for a CO_2 (**1**) + MeOH (**2**) binary system at the isotherm 298.15 K: ●, this work; △, Katayama and Ohgaki;[3] ○, Brunner et al.[7]

Australia). The response factors obtained were plotted against the volumes injected, and the gradient of the fitted line between the data points was calculated. Second, various concentrations of MeOH which were prepared by mixing different volume ratios of MeOH and acetonitrile (CH_3CN) were injected into the gas chromatograph via the sample loop. The response factors were again plotted as a function of the volumes of MeOH injected, and the gradient of the best fitted line was obtained. Finally, the volume of each sample loop was determined from the ratio of the two gradients. The calculated volumes of sample loops A, B, and C were 1.94 μL, 2.2 μL, and 2.05 μL, respectively.

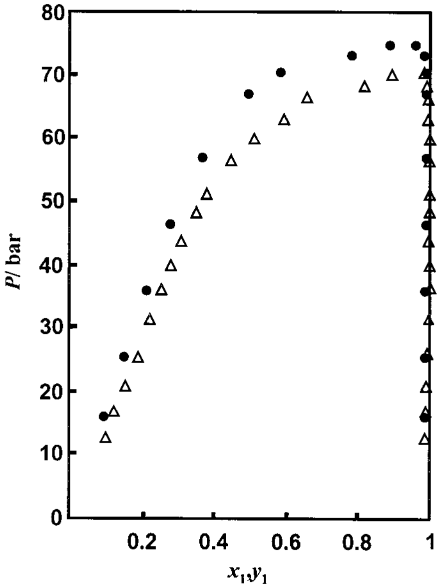


Figure 5. Vapor−liquid equilibrium for a CO_2 (**1**) + MeOH (**2**) binary system at 308.15 K: ●, this work; △, Chang et al.[13]

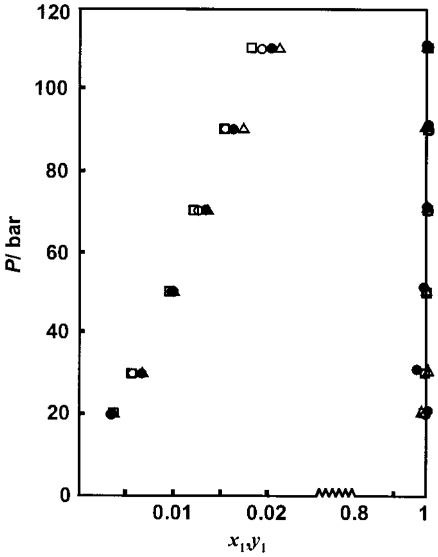


Figure 6. Vapor−liquid equilibrium for a H_2 (**1**) + MeOH (**2**) binary system at various temperatures: △, 308.15 K; ●, 298.15 K; ○, 288.15 K; □, 278.15 K.

Results and Discussion

CO_2 + MeOH System. The vapor−liquid equilibrium data for the CO_2 + MeOH system were measured at 278.15 K, 288.15 K, 298.15 K, and 308.15 K, and are presented in Table 2. As shown in Figure 3, the solubility of carbon dioxide in MeOH increased with increasing pressure and with decreasing temperature over the range of conditions studied. The binary phase envelopes contracted as the temperature of the system decreased.

Vapor−liquid equilibrium data for the CO_2 + MeOH system have been reported previously, as listed in Table 1. It is clear that considerable inconsistencies exist between studies. The results obtained at 298.15 K in the present study were compared with the data in the literature, as shown in Figure 4. At pressures below 50 bar, the results of this study were very close to the data reported by Brunner et al.[7] and Katayama and Ohgaki.[3] However, in the vicinity of the critical point, the data of Katayama and Ohgaki[3] deviated from the present work and those of Brunner et al.[7] The absolute average deviation between the data presented in this study and those of Brunner et al.[7] at 298.15 K was 4.6%, while the average deviation approached 9.6% when the comparison was with Katayama and Ohgaki[3] data. It is always difficult to measure data for systems containing methanol, due to water content.

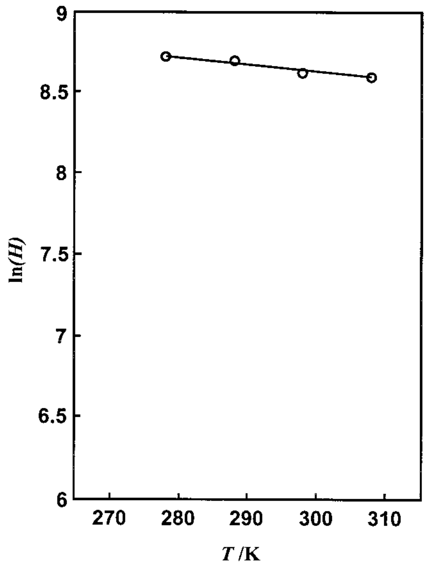


Figure 7. Henry's constants (bar) of H_2 in MeOH at various temperatures ($\ln(H) = 9.8642 - 0.0043T$).

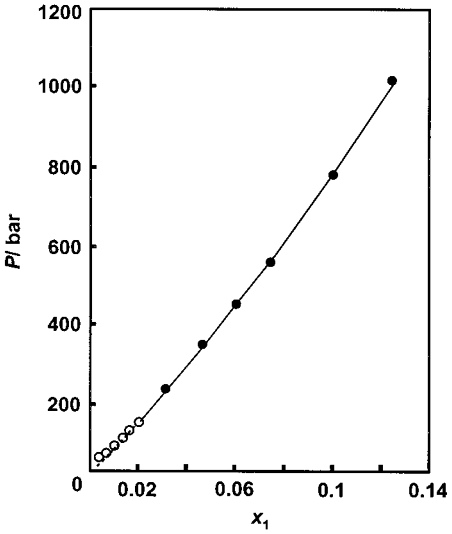


Figure 8. Vapor−Liquid equilibrium for a H_2 (**1**) + MeOH (**2**) binary system at $T = 298.15$ K: ●, Brunner et al.;[7] ○, this work.

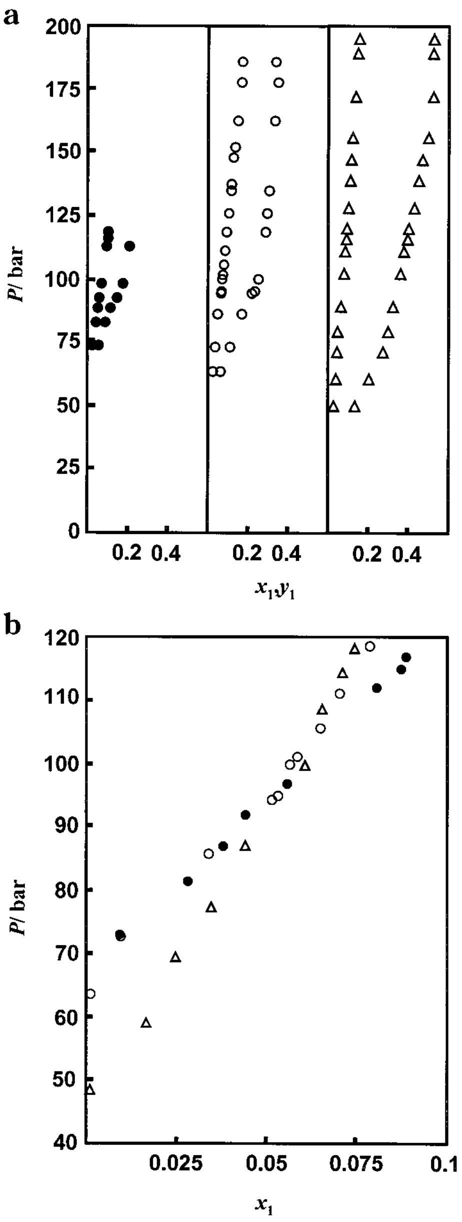


Figure 9. (a) Vapor−liquid equilibrium for a H_2 (**1**) + CO_2 (**2**) binary system at various temperatures: ●, 298.15 K; ○, 290.15 K; △, 278.15 K. (b) Vapor−liquid equilibrium data for a H_2 (**1**) + CO_2 (**2**) binary system at lower pressures and temperatures: ●, 298.15 K; ○, 290.15 K; △, 278.15 K.

The deviation observed between these three sets of data may be due to the impurity of the material.

The vapor−liquid equilibrium data obtained at 308.15 K in this study were also compared with the results of Chang et al.,[13] as illustrated in Figure 5. The average deviation was less than 9.4% even though different experimental techniques were used. Again, most of the deviation occurred in the near critical region.

H_2 + MeOH System. Vapor−liquid equilibrium data for the H_2 + MeOH system were obtained at 278.15 K, 288.15 K, 298.15 K, and 308.15 K, for pressures between 20 bar and 110 bar, and are listed in Table 3.

The data in Figure 6 demonstrate that at a given pressure the solubility of H_2 in the liquid phase increased with increasing temperature, as is typical for hydrogen in organic solvents. The solubility of H_2 in the liquid phase followed Henry's law over the range of pressure investigated. The Henry's law constants (H) for H_2 in MeOH were calculated at various temperatures and are shown in Figure 7.

Vapor−liquid equilibrium data for the H_2 + MeOH binary system have been reported previously at pressures above 105 bar (see Table 1). The trends obtained by Brunner et al.[7] at 298.15 K were extrapolated to lower pressures and compared with the results of this study. As shown in Figure 8, both data sets followed the same trend, indicating that pressure versus mole fraction possessed a linear behavior in a broad range of pressure.

H_2 + CO_2 System. High-pressure vapor−liquid equilibrium data were obtained for the H_2 + CO_2 binary system at 278.15 K, 290.15 K, and 298.15 K, and are presented in Table 4. The data were obtained below 200 bar at 278.15 K and 290.15 K, and below 120 bar at 298.15 K because of the limitation of the apparatus for visual observation of the vapor−liquid interface. At pressures below 90 bar, as shown in Figure 9, the solubility of H_2 in the liquid CO_2 decreased with increasing system temperature. Above 90 bar, however, the solubility of H_2 in the liquid CO_2 increased with increasing temperature. The hydrogen solubility in the liquid phase increased with increasing

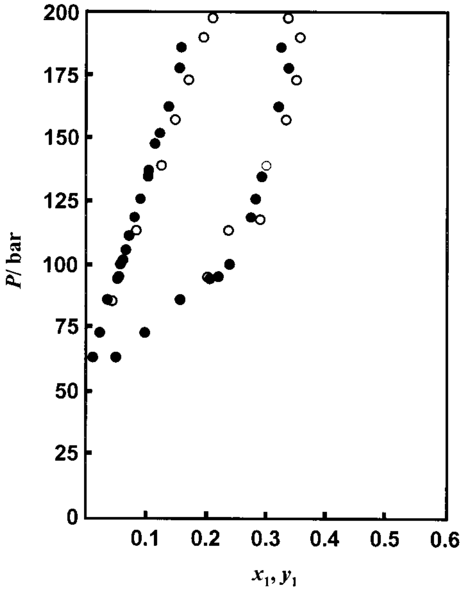


Figure 10. Vapor–liquid equilibrium for a H_2 (**1**) + CO_2 (**2**) binary system at $T = 290.15$ K: ○, Tsang and Streett;[24] ●, this work.

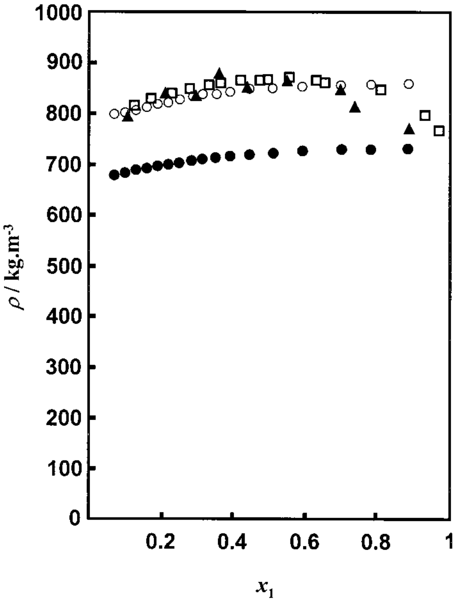


Figure 11. Density of the CO_2 (**1**) + MeOH (**2**) binary system at 298.15 K: ▲, this work; ○, Chang et al.;[31] □, Brunner et al.;[7] ●, Chang et al.[13]

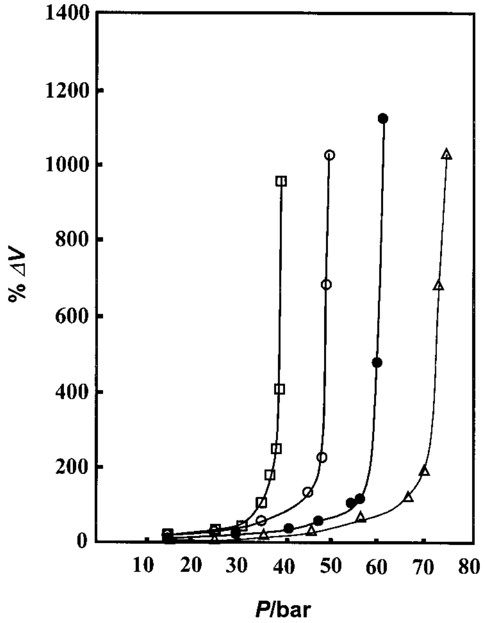


Figure 12. Percent volume expansion of MeOH as a function of pressure in a CO_2 + MeOH system at various temperatures: △, 308.15 K; ●, 298.15 K; ○, 288.15 K; □, 278.15 K.

pressure. Below the critical point of the mixture, the hydrogen composition in the vapor phase increased with increasing pressure for each isotherm. However, in the vicinity of the critical point, the hydrogen composition in the vapor phase decreased with increasing pressure for each isotherm.

As mentioned, the vapor–liquid equilibrium data for the $H_2 + CO_2$ binary system have been reported previously (see Table 1). The results obtained at 290.15 K in the present study were compared with data reported by Tsang and Streett,[24] as presented in Figure 10. Deviations for liquid and vapor phases were less than 7.1% and 9.4%, respectively. The larger deviations obtained are due to experimental difficulties in this system.

Density Measurements. In this study, the liquid-phase densities of CO_2 + MeOH, H_2 + MeOH, and $H_2 + CO_2$ binary mixtures were measured at temperatures between 278.15 K and 308.15 K and for various pressures. The results are presented in Tables 2–4.

The liquid-phase density of the CO_2 + MeOH system has been reported by Brunner et al.,[7] Chang et al.,[13] and Chang et al.[31] The average deviation between the data generated at 298.15 K by Brunner et al.[7] and Chang et al.[31] and the present study was found to be less than 2.5% (Figure 11). However, a large deviation (14.7%) was found between these sets of data and those obtained by Chang et al.,[13] even though the same experimental technique was used by Chang et al.[13] and Chang et al.[31]

The density–composition profiles for the CO_2 + MeOH system at 298.15 K obtained by Brunner et al.[7] and Chang et al.[31] and this study are shown in Figure 11. The density of the mixture ranged from 787 kg·m^{-3}, the density of pure methanol, to 713 kg·m^{-3}, the density of pure CO_2, passing through a maximum at 0.5 CO_2 mole fraction.

Volume Expansions. Volume expansion data for the CO_2 + MeOH system are presented in Figure 12 and Table 2. The volume expansion dependence on the mole fraction of CO_2 has also been plotted in Figure 13 for isotherms between 278.15 K and 308.15 K. The different expansion isotherms exhibit similar behavior with respect to the mole fraction of CO_2 and collapse to the same line. Therefore, the volume expansion was a function of CO_2 concentration in the expanded liquid phase. The data generated by Kordikowski et al.[30] for acetonitrile, ethyl acetate, 1,4-dioxane, DMF (*N*,*N*-dimethyl formamide), DMSO (dimethyl sulfoxide), and ethanol pressurized with CO_2 followed the same trend.

It was found that, in the H_2 + MeOH system, the volume of MeOH did not significantly change upon addition of H_2 into the system, even at elevated pressure, which is consistent with the very low solubility and negligible interaction of H_2 with MeOH.

Conclusion

The vapor–liquid equilibrium data were successfully determined for the CO_2 + MeOH, H_2 + MeOH, and $H_2 + CO_2$ binary systems.

It was shown that, in the CO_2 + MeOH system, the two-phase envelope expands with increasing temperature. The

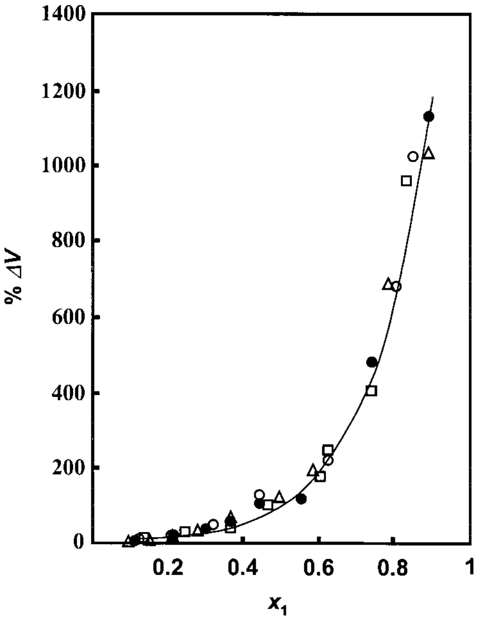


Figure 13. Percent volume expansion of MeOH as a function of mole fraction in a CO_2 (**1**) + MeOH (**2**) system at various temperatures: △, 308.15 K; ●, 298.15 K; ○, 288.15 K; □, 278.15 K.

solubility of MeOH in the vapor phase reached a maximum of 4.25% (74.33 bar and 308.15 K) over the range of conditions studied. The vapor−liquid equilibrium data obtained were consistent with the literature. The volume expansion of MeOH with CO_2 was shown to be a function of CO_2 concentration in the liquid phase.

Hydrogen solubility in the liquid phase of the H_2 + MeOH binary system was less than 2.11% (110 bar and 308.15 K), and was increased by increasing the pressure and temperature of the system. Henry's law was valid for correlating the H_2 solubility in MeOH, and the Henry's constant decreased with increasing temperature.

The H_2 + CO_2 system exhibited a crossover behavior for the solubility of H_2 in the liquid phase at a pressure around 90 bar. Hydrogen solubility increased with temperature above 90 bar and decreased with temperature below 90 bar down to the vapor pressure of CO_2. The H_2 + CO_2 system exhibited only a limited miscibility gap at the temperatures studied.

Literature Cited

(1) Combes, G. B.; Dehghani, F.; Lucien, F. P.; Dillow, A. K.; Foster, N. R. Asymmetric Catalytic Hydrogenation in CO_2 Expanded Methanol − An Application of Gas Anti-solvent Reactions (GASR). *React. Eng. Pollut. Prev.* **2000**, 173−181.

(2) Warwick, B.; Dehghani, F.; Foster, N. R.; Biffin, J. R.; Regtop, H. C. Synthesis, Purification and Micronisation of Pharmaceuticals Using the Gas Antisolvent Technique. *Ind. Eng. Chem. Res.* **2000**, *39*, 4571−4579.

(3) Katayama, T.; Ohgaki, K. Isothermal Vapour-Liquid Equilibria of Acetone-Carbon Dioxide and Methanol-Carbon Dioxide Systems at High Pressures. 2. *J. Chem. Eng. Jpn.* **1975**, *8*, 89−92.

(4) Yoon, J. H.; Lee, H. S.; Lee, H. High-Pressure Vapour-Liquid Equilibria for Carbon Dioxide + Methanol, Carbon Dioxide + Ethanol and Carbon Dioxide + Methanol + Ethanol. *J. Chem. Eng. Data* **1993**, *38*, 53−55.

(5) Ohgaki, K.; Katayama, T. Isothermal Vapor-Liquid Equilibrium Data for Binary Systems Containing Carbon Dioxide at High Pressures: Methanol-Carbon Dioxide, *n*-Hexane-Carbon Dioxide and Benzene-Carbon Dioxide. 1. *J. Chem. Eng. Data* **1976**, *21*, 53−55.

(6) Hong, J. H.; Kobayashi, R. Vapor-Liquid Equilibrium Studies for the Carbon Dioxide-Methanol System. *Fluid. Phase. Equilib.* **1988**, *41*, 269−276.

(7) Brunner, E.; Hultenschmidt, W.; Schlichtharle, G. Fluid Mixtures at High Pressures (IV. Isothermal Phase Equilibria in Binary Mixtures Consisting of (Methanol+Hydrogen or Nitrogen or Methane or Carbon Monoxide or Carbon Dioxide). *J. Chem. Thermodyn.* **1987**, 273−291.

(8) Weber, W.; Zeck, Z.; Knapp, H. Gas Solubilities in Liquid Solvents at High Pressures: Apparatus and Results for Binary and Ternary Systems of N_2, CO_2 and CH_3OH. *Fluid Phase Equilib.* **1984**, *18*, 253−278.

(9) Chang, T.; Rousseau, R. W. Solubilities of Carbon Dioxide in Methanol and Methanol-Water at High Pressures: Experimental Data and Modeling. *Fluid Phase Equilib.* **1985**, *23*, 243−258.

(10) Suzuki, K.; Sue, H.; Itou, M.; Smith, L. R.; Inomata, H.; Arai, K.; Saito S. Isothermal Vapor-Liquid Equilibrium Data for Binary Systems at High Pressures: Carbon Dioxide-Methanol, Carbon Dioxide-Ethanol, Carbon Dioxide-1-Propanol, Methane-Ethanol, Methane-1-Propanol, Ethane-Ethanol and Ethane-1-Propanol Systems. *J. Chem. Eng. Data* **1990**, *35*, 63−66.

(11) Suzuki, K.; Sue, H.; Itou, M.; Smith, L. R.; Inomata, H.; Arai, K.; Saito, S. High-Pressure Vapor-Liquid Equilibrium Data of the 10-Component System Hydrogen, Carbon Monoxide, Carbon Dioxide, Water, Methane, Propane, Methanol, Ethanol and 1-Propanol at 313.4 and 333.4 K. *J. Chem. Eng. Data* **1990**, *35*, 67−69.

(12) Page, S. H.; Goates, S. R.; Lee, M. L. Methanol/CO_2 Phase Behavior in Supercritical Fluid Chromatography and Extraction. *J. Supercrit. Fluids* **1991**, *4*, 109−117.

(13) Chang, C. J.; Day, C. Y.; Ko, C. M.; Chiu, K. L. Densities and P-x-y Diagrams for Carbon Dioxide Dissolution in Methanol, Ethanol and Acetone Mixtures. *Fluid Phase Equilib.* **1997**, *131*, 243−258.

(14) Reighard, T. S.; Lee, S. T.; Olesik, S. V. Determination of Methanol/CO_2 and Acetonitrile/CO_2 Vapor−Liquid-Phase Equilibria Using a Variable−Volume View Cell. *Fluid Phase Equilib.* **1996**, *123*, 215−230.

(15) Semenova, A. I.; Emel′yanova, E. A.; Tsimmerman, S. S.; Tsiklis, D. S. Phase Equilibria in the Methanol-Carbon Dioxide System. 10. *Russ. J. Phys. Chem.* **1979**, *53*, 1428−1433.

(16) Leu, A. D.; Chung, S. Y. K.; Robinson, D. B. The Equilibrium Phase Properties of (Carbon dioxide−Methanol). *J. Chem. Thermodyn.* **1991**, *23*, 979−985.

(17) Michels, A.; De Graaff, W.; Van Der Somme, J. Gas-Liquid-Phase Equilibrium in the System Methanol-Hydrogen. *Appl. Sci. Res. 4 (Section A)* 105−108.

(18) Liu, Q.; Takemura, F.; Yabe, A. Solubility of Hydrogen in Liquid Methanol and Methyl Formate at 20 °C to 140 °C. *J. Chem. Eng. Data* **1996**, *41*, 1141−1143.

(19) Wainwright, M. S.; Ahn, T.; Trimm, D. L. Solubility of Hydrogen in Alcohols and Esters. *J. Chem. Eng. Data* **1987**, *32*, 22−24.

(20) Radhakrishnan, K.; Ramachandran, P. A.; Brahme, P. H.; Chaudhari, R. V. Solubility of Hydrogen in Methanol, Nitrobenzene, and Their Mixtures. Experimental Data and Correlation. *J. Chem. Eng. Data* **1983**, *28*, 1−4.

(21) Choudhary, V. R.; Sane, M. G.; Vadgaonkar, H. G. Solubility of Hydrogen in Methanol Containing Reaction Species for Hydrogenation of *o*-Nitrophenol. *J. Chem. Eng. Data* **1986**, *31*, 294−296.

(22) Katayama, T.; Nitta, T. Solubilities of Hydrogen and Nitrogen in Alcohols and n-Hexane. 2. *J. Chem. Eng. Data* **1976**, *21*, 194−196.

(23) Frolich, P.; Tauch, E. J.; Hogan, J. J.; Peer, A. A. Solubilities of Gases in Liquids at High Pressure. 5. *Ind. Eng. Chem.* **1931**, *23*, 548−550.

(24) Tsang, C. Y.; Streett, W. B. Phase Equilibria in the H_2/CO_2 System at Temperatures From 220 to 290 K and Pressures to 172 MPa. *Chem. Eng. Sci.* **1981**, *36*, 993−1000.

(25) Spano, J. O.; Heck, C. K.; Barrick, P. L. Liquid-Vapor Equilibria of the Hydrogen-Carbon Dioxide System. 2. *J. Chem. Eng. Data* **1968**, *13*, 168−171.

(26) Yorizane, M.; Yoshimura, S.; Masuoka, K. Vapor Liquid Equilibrium at high Pressures. N_2−CO_2, H_2, CO_2 Systems. 9. *Kagaku Kogaku* **1970**, *34*, 953−957.

(27) Mills, J. R.; Miller, F. J. L. Liquefaction of Carbon Dioxide. *Can. Chem. Process Ind.* **1945**, *29*, 651−653.

(28) Kaminishi, G.; Toriumi, T. Gas−Liquid Equilibrium Under High-Pressure VI. Vapor-Liquid-Phase equilibrium in the CO_2−H_2, CO_2−N_2 and CO_2−O_2 Systems. 2. *Kogyo Kagaku Zasshi* **1966**, *69*, 175−178.

(29) Abdullaev, Y. A. Phase Behaviour in Mixture of Carbon Dioxide with Hydrogen, Nitrogen and Carbon Monoxide. *Zh. Fiz. Khim.* **1939**, *13*, 986−988.

(30) Kordikowski, A.; Schenk, A. P.; Van Neilen, R. M.; Peters, C. J. Volume Expansions and Vapor-Liquid Equilibria of Binary Mixtures of a Variety of Polar Solvents and Certain Near-Critical Solvents. *J. Supercrit. Fluids* **1995**, *8*, 205−216.

(31) Chang, C. J.; Chiu, K. L.; Day, C. Y. A New Apparatus for the Determination of P−x-y Diagrams and Henry's Constants in High-Pressure Alcohols with Critical Carbon Dioxide. *J. Supercrit. Fluids* **1998**, *12*, 223−237.

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