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Bubble and Dew Point Measurements of the Ternary System Carbon Dioxide + Methanol + Hydrogen at 313.2 K

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Gas-expanded liquids offer many advantages as superior solvents for asymmetric hydrogenation reactions. To implement such applications, knowledge of the phase behavior of hydrogen with these tunable solvents is imperative. Phase boundary data are reported for the ternary system of carbon dioxide, methanol, and hydrogen at 313.2 K and pressures up to 21.7 MPa. The data were measured in a variable-volume windowed vessel by visual observation of one- to two-phase transitions.

Introduction

Gas-expanded liquids (GXLs) are highly tunable mixtures of organic solvents with a gas, where both the solvent power and the transport properties change significantly with concentration (pressure). CO_2 is generally the gas used because high concentrations require only modest pressures and it is inexpensive, nontoxic, and nonflammable. GXLs offer advantages for reactions[1−4] and separations.[5−7] Compared to regular solvents, GXLs afford increased solubility of gases, enhanced mass transfer, a measure of tunability of solvent strength, and the additional safety provided by a nonflammable solvent. Compared to supercritical or liquid CO_2, GXLs afford higher solubility of reactants and catalysts at significantly lower pressures. GXLs are especially attractive for homogeneously catalyzed multiphase reactions between reactants in the gas phase and those in the liquid phase because gases tend to have higher solubilities than liquids. Such reactions might include hydrogenation with H_2, oxidation with O_2, and hydroformylation with CO. Because many of these reactions are carried out under pressure anyway, the capital investment for the high-pressure equipment related to CO_2 is less of an issue.

Many properties of CO_2-expanded liquids have been reported, such as viscosity,[8,9] diffusion coefficients,[8,10,11] solubility,[12,13] and solvatochromic shift.[14,15] For ternary systems of GXLs that include two gaseous species, some critical and phase boundary data[16−19] are available. Although abundant vapor−liquid equilibrium data are available for the CO_2 + methanol, H_2 + methanol, and H_2 + CO_2 binary systems,[20] there are few phase equilibrium data available for the ternary system of CO_2 + methanol + H_2. Previous measurements at (278, 288, and 298) K have been reported by Bezanehtak et al.[21] Because hydrogenation reactions are being carried out in CO_2-expanded methanol in our laboratories and others,[1,22] we report the phase boundaries of the ternary system containing hydrogen, carbon dioxide, and methanol at 313.2 K measured synthetically in a variable-volume windowed vessel.

Experimental Section

Chemicals. Methanol (Aldrich, 99.93% HPLC grade, anhydrous) was used as received. Carbon dioxide (Matheson, SFC grade) and hydrogen (Air Products, ultrahigh purity) were passed through gas purifiers.

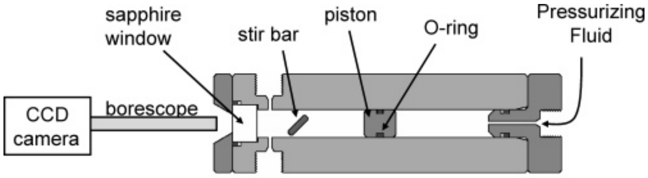

Figure 1. Variable-volume windowed pressure vessel.

Apparatus. Phase transitions were observed in a McHugh-type variable-volume windowed pressure vessel (Figure 1) reported previously.[23,24] The working volume of the pressure vessel could be varied from 5 mL to 20 mL with a piston, moved by an aqueous dye solution on the backside, connected to a syringe pump (ISCO model 260 D). The blue color of the aqueous dye solution is easily detectable through the window of the vessel should the O-ring on the piston fail. The entire cell was placed in a thermostated air bath (modified Varian 3400 gas chromatograph) with temperature control better than ±0.2 °C. The temperature was measured with a handheld readout (HH-22 Omega) and thermocouple (Omega Type K) inserted into the center of the phase equilibrium vessel. The thermocouple response time was on the order of seconds. The combination of thermocouple and readout was accurate to ±0.2 °C and calibrated for each experiment against a platinum RTD (Omega PRP-4) with a DP251 Precision RTD benchtop thermometer (DP251 Omega) accurate to ±0.025 °C and traceable to NIST. Back pressure was applied to the piston with a syringe pump (ISCO 100D) operated at constant pressure.

Methanol was introduced into the windowed pressure vessel with a six-port valve and injection loops (Valco) of known calibrated volumes. Another syringe pump (ISCO model 260 D) filled with compressed CO_2 was connected to one port of the six-port valve to meter CO_2 into the vessel. Methanol was injected through the injection loop with a gastight syringe (VWR) while the CO_2 flowed directly through to the vessel. As the valve was switched to position 2, the sample contained in the loop was displaced by CO_2 and carried into the vessel.

The temperatures in the windowed pressure vessel, the transfer vessel for H_2 (discussed below), and the syringe

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pump for CO_2 were measured to ±0.1 °C with type K thermocouples (Omega), which were previously calibrated in a hot point cell (Omega) and connected to digital temperature indicators (HH-22 Omega). The pressures in the windowed pressure vessel, the transfer vessel for H_2, and the syringe pump for CO_2 were measured to ±0.07 bar with pressure transducers (Druck Limited, DPI 260 readout PDCR-3040 transducer), which were calibrated against a hydraulic dead weight tester (Ruska). The vessel contents were mixed with a magnetic stir bar coupled with an external magnet. The phase behavior in the vessel was observed through the sapphire window with a borescope camera (Olympus F100-024-000-55), placed through the wall of the GC oven.

Procedure. The oven was controlled to 40 °C, and the backside volume was filled with the aqueous dye solution, taking care to avoid air bubbles. The vessel was mounted on the rack inside the GC oven and then connected to a syringe pump used to control pressure and to monitor volume changes.

Before each experiment, the air from the system was purged by pressurizing the system to 10 bar with CO_2 and then depressurizing, twice repeated. When the CO_2 purging process was completed, the piston in the variable-volume vessel was at its full range of travel. The volume reading on the controller of the backside syringe pump was recorded, and from the change of this volume reading, the volume of the $H_2 + CO_2 +$ MeOH ternary system in the vessel was calculated.

The vessel was filled with a known volume of methanol through the six-port valve with an injection loop of known volume; the uncertainty of added methanol is ±0.001 mol or, for the smallest loading, an error of ±2% in moles added. The injection loop was first filled with anhydrous methanol using a gastight syringe, and the methanol was carried into the vessel by CO_2 when the valve was switched. CO_2 and H_2 were subsequently added to the vessel.

CO_2 was loaded from the syringe pump set to a constant volumetric flow rate between 0.01 and 1.00 mL/min. Before loading, the volume and pressure readings on the pump controller and the temperature reading on the digital temperature indicator were recorded. During and after the loading, the temperature of CO_2 in the pump may change. After the temperature was stable, the volume, temperature, and pressure readings were recorded. The CO_2 density at specified temperature and pressure was calculated with the Span−Wagner equation of state.[25] The amount of CO_2 added to the vessel was calculated from the volume readings and the CO_2 densities before and after loading with an uncertainty of ±0.001 mol or, for the smallest loading, an error of ±1.5% in moles added.

H_2 was introduced into the vessel from a transfer vessel of known volume and temperature by pressure difference. Before and after loading, the stable temperatures and the pressures of the H_2 transfer vessel were recorded. The H_2 density at the specified temperature and pressure was calculated from the truncated virial expression and second virial coefficient from DIPPR[26] with an uncertainty of ±0.0015 mol or, for the smallest loading, an error of ±20% in moles added.

Visual observation of phase separation was used to measure the phase boundary of the $H_2{-}CO_2{-}$MeOH ternary system. In a typical run, the volume of the $H_2 + CO_2 +$ MeOH ternary system was decreased by increasing the pressure until the $H_2 + CO_2 +$ MeOH ternary system made the transition from two phases to one homogeneous phase. During this process, the liquid level increased until there was only one transparent liquid phase. After the temperature in the vessel was stable, the volume of the $H_2{-}CO_2{-}$MeOH ternary system was increased slowly by decreasing the pressure slightly until the cloud point was observed where the emergence of uniform bubbles in the liquid scatter light and cause a "black out" on the monitor. The last pressure when the liquid phase was still transparent was recorded, and the $H_2 + CO_2 +$ MeOH ternary system was pressurized back to this pressure. Smaller steps were used for further depressurization, and the pressurizing−depressurizing process was repeated at least three times for accuracy. The pressure and temperature in the vessel and the volume reading on the controller of the syringe pump for the aqueous dye solution were recorded. The process was repeated at least three times to verify the repeatability of the data point, and the average value was taken with the standard deviation for all points less than 0.4 bar. Additional H_2 or CO_2 was then added to the vessel for another measurement. When the pressure in the vessel exceeded 250 bar with the piston at the maximum volume position, the vessel was depressurized and cleaned to prepare for another series of experiments.

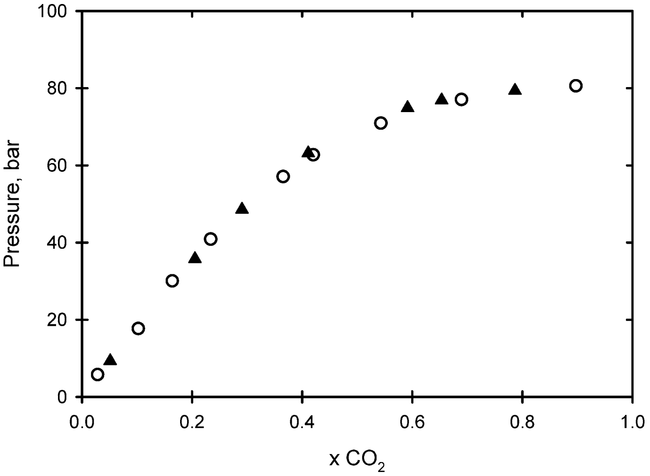

Figure 2. Bubble point data for the CO_2 + methanol binary system at 313.2 K: ○, Ohgaki and Katayama;[27] ▲, this work.

Table 1. Bubble Point Data for the CO_2 (1) + Methanol (2) Binary System at 313.2 K

phase boundary pressure P/bar	CO_2 mole fraction x_1
9.3	0.051
35.7	0.205
48.5	0.291
63.1	0.411
74.9	0.591
76.8	0.653
79.3	0.786

Results and Discussion

CO_2 + Methanol System. The bubble points for the binary CO_2 + methanol system measured at 313.2 K are listed in Table 1. These data are in good agreement with those reported by Ohgaki and Katayama[27] as shown in Figure 2.

CO_2 + Methanol + H_2 System. Phase boundary data for the ternary CO_2 + methanol + H_2 system obtained at 313.2 K are listed in Table 2. The solubility of H_2 in methanol + CO_2 mixtures, as shown in Figure 3, is linear with pressure, and the slope decreases with increasing CO_2 concentration. We were surprised that Henry's law was obeyed to concentrations as high as 0.2 mol fraction of H_2.

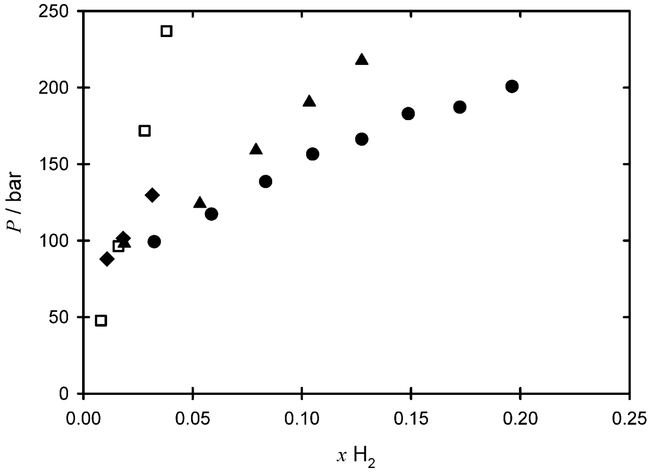

Figure 3. Hydrogen mole fraction in CO_2 (1) + methanol (2) at 313.2 K as a function of pressure and solute-free composition: □, $x_1 = 0$, Brunner et al.;[32] ◆, $x_1 = 0.415$; ▲, $x_1 = 0.776$; ●, $x_1 = 0.902$, this work.

Table 2. Phase Boundary Data for the CO_2 (1) + Hydrogen (2) + Methanol (3) Ternary System at 313.2 K

phase boundary pressure *P*/bar	CO_2 mole fraction x_1	H_2 mole fraction x_2	MeOH mole fraction x_3	x_1/x_3	x_2/x_3	
87.9	0.410	0.011	0.579	0.71		BP
101.5	0.408	0.018	0.574	0.71		BP
129.6	0.402	0.032	0.566	0.71		BP
98.0	0.754	0.019	0.217	3.47		BP
124.0	0.735	0.053	0.212	3.47		BP
158.8	0.715	0.079	0.206	3.47		BP
190.3	0.696	0.103	0.201	3.47		BP
217.6	0.677	0.129	0.195	3.47		BP
99.2	0.872	0.032	0.095	9.17		BP
117.3	0.849	0.059	0.093	9.17		BP
138.4	0.827	0.083	0.090	9.17		BP
156.4	0.807	0.105	0.088	9.17		BP
166.2	0.787	0.127	0.086	9.17		BP
182.8	0.768	0.149	0.084	9.17		BP
187.1	0.746	0.172	0.081	9.17		BP
200.7	0.725	0.196	0.079	9.17		BP
199.7	0.699	0.236	0.064		3.67	DP
171.8	0.742	0.203	0.055		3.67	DP
146.5	0.777	0.176	0.048		3.67	DP
129.3	0.807	0.152	0.041		3.67	DP
120.0	0.824	0.139	0.038		3.67	DP

We attempted to predict the Henry's law constants from the correlation of previously measured binary vapor−liquid equilibria using the Peng−Robsinon equation of state. The α value for methanol was changed to that recommended by Stryjek and Vera.[28] The methanol + CO_2 vapor−liquid equilibria, which is a severe test of thermodynamic models,[29] was not satisfactorily correlated using the quadratic mixing rules; therefore, we examined the Huron−Vidal mixing rule[30] with the NRTL model [31] as our expression for G^E at infinite pressure. Our initial regression of the three binary pairs of interaction parameters gave a poor prediction of our experimental Henry's constants. We found that the methanol + H_2 interaction parameters were quite correlated. This is expected because we were regressing two parameters and the experimental range of our independent variable, H_2 mole fraction, varied only between 0 and 0.04. Using both the ternary and binary data, we were able to fit acceptable parameters for methanol + H_2, although as seen in Figure 4 the model does not give as sharp a drop in the Henry's constant as measured.

Conclusions

For the ternary CO_2 + H_2 + methanol system 313.2 K, the two-phase envelope contracts with increasing pressure. The solubility of H_2 can be increased in the liquid phase with the addition of CO_2 to give a higher concentrations of H_2 at the same total pressure.

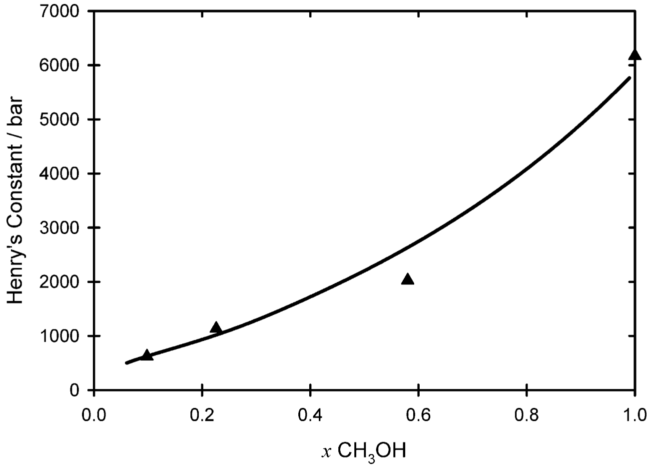

Figure 4. Henry's constant of hydrogen in the CO_2−expanded methanol mixture at 313.2 K. The curve is a prediction of Peng−Robinson with Huron−Vidal mixing rules.

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