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Phase Behavior and Modeling of CO_2/Methanol/Tetramethylammonium Bicarbonate and CO_2/Methanol/Tetramethylammonium Bicarbonate/Water Mixtures at High Pressures

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High-pressure phase behavior has been measured for CO_2/methanol/tetramethylammonium bicarbonate (TMAB) and CO_2/methanol/TMAB/water systems at (25 and 70) °C and pressures up to 30 MPa. An increase in methanol concentration results in a decrease in the phase-transition pressure due to the higher miscibility of methanol and salt in CO_2. At higher methanol concentrations, single phase mixtures could be achieved at moderate pressures with up to 70 mol % CO_2. As expected, the addition of water sharply increases the phase transition pressure. The experimental results for the above systems were modeled using the Peng−Robinson equation of state; model predictions were found to be sensitive to adjustable parameters.

Introduction

Cleaning processes represent about 35% of the elementary production steps in advanced integrated circuit (IC) manufacturing, and photoresist stripping accounts for half of these (i.e., typically 50 of the 300 production steps).[1] As feature dimensions decrease and new materials are incorporated into device structures, photoresist stripping and etch residue removal face several challenges. Incomplete removal of the residues leads to defects and impurity incorporation into devices, resulting in reduced device yield and reliability.[2] Conventional stripping by plasmas[3,4] and wet processes[5−7] have serious drawbacks. Plasma cleaning can alter structure and properties of low-*k* dielectrics. Liquid strippers may lead to silicon and metal surface oxidation and have difficulty penetrating narrow trenches of modern devices (<100 nm). Even if entry into small vias and trenches is possible, transport of liquid and associated residues or contaminants out of the high aspect ratio features will be difficult. In addition, the use of liquid chemistries, which are based mostly on hazardous solvents, bases, and acids, has significant environmental impact. Moreover, large amounts of deionized water (DIW), and isopropanol alcohol (IPA) for drying, are required to complete the photoresist-stripping process.[8] Hence, an ideal alternative to the present methods would be a vapor-phase approach that minimizes hazardous materials usage.

An important additional advantage of using a gas- or fluid-based process is the elimination of any meniscus and the concomitant surface tension forces. Liquids tend to have rather large surface tensions. As features get smaller and smaller, the radius of curvature of the interface also gets smaller and generates relatively greater forces, which can cause feature collapse.[9,10]

To allow technology evolution and alleviate environmental concerns, conventional processes based on concentrated liquid chemicals should be replaced by alternative treatments. Supercritical CO_2 is currently being considered as an environmentally benign approach to photoresist and etch residue removal. In particular, CO_2 has been applied to precision cleaning (for metal surfaces)[11−13] and to wafer cleaning[14−16] and drying.[17−18] Because of its easily attainable critical temperature and pressure, nonflammability, ease of availability, and low cost, CO_2 presents a very attractive green solution for photoresist and residue removal. However, since SCF CO_2 has little solvating power for photoresist or inorganic materials, it requires the addition of modifiers or additives.[19−21] Recently we demonstrated that tetramethylammonium hydroxide (TMAH) is an efficient base additive in the cosolvent due its ability to attack the plasma-processed photoresist crust.[22−24] Because of the polar nature of TMAH, its solubility in CO_2 is expected to be small. Since methanol and other low molecular weight alcohols are completely miscible with CO_2, 25% TMAH in methanol solution was chosen as the cosolvent.

These results suggest that a knowledge of phase behavior may assist the optimization of additive concentrations to achieve improved cleaning performance. This was a strong incentive to investigate the phase behavior of these systems with and without the addition of water.

Vapor−liquid equilibrium data for the systems CO_2/methanol and CO_2/methanol/water have been widely studied.[25−27] However, an extensive literature search did not identify studies of vapor−liquid equilibria data for salt/methanol/CO_2 or salt/methanol/water/CO_2 systems at high CO_2 concentrations. Furthermore, few studies have been performed that describe the solubility and phase behavior of organic salts in CO_2 at elevated pressures.[29−31]

The main goal of this work is to obtain experimental data of the high-pressure phase behavior for the systems of CO_2/tetramethylammonium bicarbonate (TMAB)/methanol and CO_2/TMAB/methanol/water mixtures and to compare these data to predictions obtained from the Peng−Robinson (PR) equation of state.

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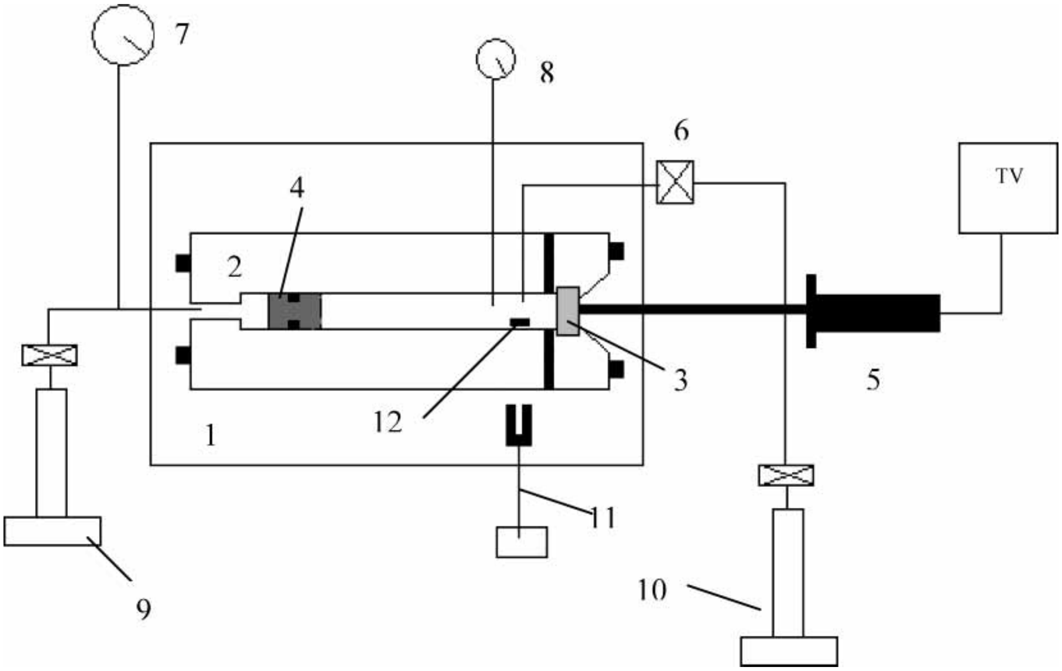

Figure 1. Schematic diagram of the view cell and experimental apparatus: (1) modified Varian 3400 gas chromatograph oven; (2) high-pressure cell (1.59 cm^3 i.d., 20 cm^3 maximum volume); (3) sapphire window; (4) variable volume piston; (5) CCD camera mounted on a boroscope; (6) six-port valve; (7) pressure gauge; (8) hand-held temperature readout; (9, 10) high-pressure pump; (11) external magnet connected to the motor; (12) stirrer bar.

Experimental Section

Apparatus and Procedure. Figure 1 shows a schematic of the experimental apparatus used in this work. Phase-behavior data were obtained by using a high-pressure cell (1.59 cm^3 i.d., 20 cm^3 maximum volume) similar to that used by McHugh (Figure 1 (part 2))[32] and described elsewhere.[33] A 1.27 cm thick sapphire (Figure 1 (part 3)) window was fitted in the cell to allow visual observation of the phase transition with a CCD camera (Sony) mounted on a 0.635-cm boroscope (Olympus) (Figure 1 (part 5)). The variable volume piston (part 4) and vessel window (part 3) were sealed with Buna N−O rings (McMaster Carr) that were resistant to water and organics at elevated pressures (up to 27.58 MPa) and moderate temperatures (up to 100 °C). The O rings were replaced after each experiment. The mixtures were stirred with a Teflon-coated stir bar coupled to an external magnet (parts 11 and 12). The boroscope and video camera allowed observation of phase equilibria and provided a significant magnification of the viewable area. The entire cell was placed in a thermostated air bath (modified Varian 3400 gas chromatograph oven) (part 1) with temperature control to ±0.5 °C. The temperature was measured with a hand-held readout (HH-22 Omega) and thermocouple (Omega Type K) inserted into the phase equilibria vessel (part 8). The thermocouple response time was on the order of a few seconds. The combination of thermocouple and readout was accurate to ±0.2 °C. These devices were calibrated against platinum RTD (Omega PRP-4) with a DP 251 precision RTD benchtop thermometer (DP251 Omega).

The initial mixture (accurate to ±0.005 g) was loaded in the cell at atmospheric pressure using a volumetric pipet.

The solution in the cell was compressed by displacing the movable piston (part 4) using water pressurized by a high-pressure pump (ISCO 100D) (part 9) to ensure that no air was present in the vessel. The pressure was measured using a Druck DPI 260 gauge with PCDR 910 transducer accurate to ±0.001 MPa (part 7). Pressure measurement was performed at the backside of the piston; this pressure differed from that of the mixture by as much as 0.15 MPa and may vary slightly with the temperature. CO_2 was stored in an ISCO model 500D syringe pump (part 10) operated in the constant-pressure mode and was introduced to the cell through a six-port valve (Valco) (part 6). The moles of added CO_2 were calculated from the displaced volume of the syringe pump and molar density calculated from the Span−Wagner equation of state.[34] The uncertainty in mole fraction was estimated using standard error propagation techniques based on partial derivatives assuming that the sources of error were independent and included for each component in Tables 1−5. Specifically, the sources of error considered were weighing of the liquid sample and estimating the CO_2 loading and based on accuracy of the instruments involved in the measurement. All experiments were repeated at least 3 times in order to establish the reproducibility.

After the cell reached thermal equilibrium, the contents of the cell were compressed into a one-phase region by moving the piston forward. Subsequently, the piston was slowly retracted until the two-phase region appeared. The phase behavior was obtained in the pressure interval between these two states. A bubble point was obtained when small bubbles appeared in the cell; a dew point was obtained if a fine mist appeared in the vessel. The phase-transition pressure was reproduced at least 3 times within ±0.03 MPa for a specific cell loading. After the data points were obtained, a known mass of CO_2 was added to the cell and the procedure repeated at the new concentration.

Materials. The 25% tetramethylammonium hydroxide (TMAH) in methanol and all high-pressure-liquid-chromatography-grade methanol and water were obtained from Aldrich Inc. Water content in this solution was determined by Karl−Fisher titration using Aquamicron AX and Aquamicron CXU reagents (Mitsubishi). TMAB was obtained by bubbling CO_2 through the TMAH solution until a clear solution (no precipitate) was observed. The presence of

Table 1. Pressure-Composition Data for the Methanol(1)/Water(2)/CO_2 System

$100x_1$	$100x_2$	t/°C	P/MPa
This Work ($x_2/x_1 = 0.3324 \pm 0.0008$)			
54.05 ± 0.17	17.98 ± 0.068	69.7	11.92
41.19 ± 0.18	13.70 ± 0.066	70.3	16.83
36.81 ± 0.18	12.24 ± 0.065	69.6	17.70
33.18 ± 0.17	11.04 ± 0.062	69.8	18.45
27.98 ± 0.16	9.31 ± 0.058	69.7	20.03
Literature[27] $x_2/x_1 = 0.2490$			
72.29	18.17	69.7	3.85
66.9	16.7	69.6	6.13
60.1	15	69.9	9.60
54.71	13.62	69.6	10.54
48.85	12.16	69.5	12.83
41.44	10.32	70.2	15.38
34.85	8.68	70	16.27
24.38	6.07	69.9	16.85
21.48	5.35	70	17.55
$x_2/x_1 = 0.3318$			
40.34	14.86	69.9	14.26
45.53	13.57	70	15.69
54.51	11.33	70.3	17.98
$x_2/x_1 = 0.4298$			
10.8	26.8	69.6	5.68
20.3	24	69.4	10.02
27.63	21.75	69.5	12.25
37.94	18.66	69.6	15.52
43.34	17.03	69.5	18.98

Table 2. Pressure-Composition Data at 70 °C for Methanol(1)/Water(2)/CO_2/$TMAHCO_3$(5) with $x_5/x_1 = 0.127$[a]

$100x_1$	$100x_5$	$100x_2$	P/MPa
Experiment 1			
72.09 ± 0.25	9.12 ± 0.031	10.24 ± 0.035	4.87
68.02 ± 0.28	8.61 ± 0.035	9.66 ± 0.040	8.55
64.05 ± 0.26	8.11 ± 0.033	9.10 ± 0.037	9.83
56.34 ± 0.22	7.13 ± 0.028	8.00 ± 0.032	15.97
51.53 ± 0.20	6.52 ± 0.025	7.32 ± 0.028	24.08
Experiment 2			
75.91 ± 0.23	9.61 ± 0.029	10.78 ± 0.032	1.57
67.18 ± 0.29	8.50 ± 0.037	9.54 ± 0.041	6.61
57.07 ± 0.24	7.22 ± 0.031	8.11 ± 0.035	11.58
54.43 ± 0.23	6.89 ± 0.029	7.73 ± 0.033	13.63
47.92 ± 0.19	6.07 ± 0.025	6.81 ± 0.028	26.33
Experiment 1 (Water Addition)			
55.59 ± 0.22	7.04 ± 0.028	29.19 ± 0.19	7.36
52.31 ± 0.26	6.62 ± 0.033	27.47 ± 0.20	9.98
50.01 ± 0.28	6.33 ± 0.036	26.27 ± 0.20	11.46
47.77 ± 0.31	6.05 ± 0.039	25.09 ± 0.21	12.95
44.11 ± 0.34	5.58 ± 0.043	23.17 ± 0.21	25.03
Experiment 2 (Water Addition)			
55.46 ± 0.22	7.02 ± 0.028	29.13 ± 0.19	5.92
53.49 ± 0.24	6.77 ± 0.031	28.09 ± 0.19	7.52
50.82 ± 0.23	6.43 ± 0.029	26.69 ± 0.18	9.87
46.66 ± 0.20	5.91 ± 0.026	24.50 ± 0.16	14.62
40.19 ± 0.16	5.09 ± 0.020	21.11 ± 0.13	20.11

[a] $TMAHCO_3$ is a reaction product of original solution of TMAH(4) with CO_2(3) at elevated pressure; the mole fraction of CO_2 and $TMAHCO_3$ was calculated according to eq 4.

bicarbonate was confirmed by titration with HCl of known concentration. The equilibrium point was determined by a pH glass-membrane electrode using a Corning pH meter. Carbon dioxide (bone-dry grade, 99.99% purity) was supplied by Air Products.

Results and Discussion

Table 3. Pressure-Composition Data at 70 °C for Methanol(1)/Water(2)/CO_2/$TMAHCO_3$(5) with $x_5/x_1 = 0.127$[a]

$100x_1$	$100x_5$	$100x_2$	P/MPa
Experiment 1			
70.79 ± 0.16	8.96 ± 0.020	10.05 ± 0.023	6.48
64.80 ± 0.19	8.20 ± 0.024	9.20 ± 0.027	7.29
59.13 ± 0.22	7.49 ± 0.028	8.40 ± 0.031	12.39
53.11 ± 0.20	6.72 ± 0.025	7.54 ± 0.028	17.68
Experiment 2			
70.85 ± 0.16	8.97 ± 0.020	10.06 ± 0.022	5.70
68.65 ± 0.17	8.69 ± 0.021	9.75 ± 0.024	9.16
62.22 ± 0.20	7.88 ± 0.026	8.84 ± 0.029	13.78
56.72 ± 0.19	7.18 ± 0.024	8.06 ± 0.027	21.48
Experiment 3			
71.97 ± 0.15	9.11 ± 0.019	10.22 ± 0.021	4.95
65.81 ± 0.18	8.33 ± 0.023	9.35 ± 0.026	9.71
62.45 ± 0.20	7.91 ± 0.026	8.87 ± 0.029	11.93
59.28 ± 0.20	7.50 ± 0.025	8.42 ± 0.028	14.38
57.01 ± 0.19	7.22 ± 0.024	8.10 ± 0.027	16.33
Experiment 1 (Water Addition)			
55.23 ± 0.10	82.54 ± 0.013	29.31 ± 0.16	8.20
53.47 ± 0.11	59.43 ± 0.013	28.37 ± 0.16	9.27
50.81 ± 0.11	40.70 ± 0.014	26.96 ± 0.16	12.50
49.16 ± 0.12	33.57 ± 0.015	26.09 ± 0.15	18.24
Experiment 2 (Water Addition)			
51.67 ± 0.11	6.54 ± 0.013	27.79 ± 0.16	12.07
49.95 ± 0.11	6.32 ± 0.014	26.86 ± 0.15	15.09
46.83 ± 0.12	5.93 ± 0.015	25.18 ± 0.15	27.12

[a] $TMAHCO_3$ formed prior to experiment by bubbling of original solution of TMAH with CO_2 at atmospheric pressure.

To verify the accuracy and reproducibility of our experimental apparatus, the phase behavior of the CO_2/methanol/water system was measured and compared to literature data (Figure 2 and Table 1). As demonstrated in Figure 2, our experimental data are in good agreement with those reported in the literature.[27,28]

Since CO_2 is an acidic gas, it reacts with TMAH to form carbonate and bicarbonate salts of the tetramethylammonium ion. No more than two of these three components (eq 1) coexist in any solution because an acid−base reaction eliminates the third component. The initial product of the TMAH reaction with CO_2 is TMAB (eq 1). However, this intermediate product further reacts with excess hydroxide and shifts the equilibrium toward formation of tetramethylammonium carbonate (eq 2) according to LeChatelier's principle

$$(CH_3)_4NOH + CO_2 \rightleftharpoons (CH_3)_4NHCO_3 \tag{1}$$

$$(CH_3)_4NOH + (CH_3)_4NHCO_3 \rightleftharpoons [(CH_3)_4N]_2CO_3 + H_2O \tag{2}$$

When excess CO_2 is added, the equilibrium between carbonate and bicarbonate is shifted toward bicarbonate formation

$$[(CH_3)_4N]_2CO_3 + CO_2 + H_2O \rightarrow 2(CH_3)_4NHCO_3 \tag{3}$$

Thus, the overall reaction of TMAH in the presence of excess CO_2 can be written as

$$(CH_3)_4NOH + CO_2 \rightleftharpoons (CH_3)_4NHCO_3 \tag{4}$$

Our previous studies have shown that, with excess CO_2, all tetramethylammonium hydroxide is consumed and converted to TMAB.[22] To obtain additional confirmation of the suggested reaction mechanism, two sets of experiments were performed. In the first set, the original solution (as purchased) of TMAH was loaded into the cell and its phase behavior observed as a function of added CO_2; the mole fraction of components (CO_2, TMAB, methanol, water) was calculated on the basis of eq 4 (Table 2). The second set of

Table 4. Pressure-Composition Data for Methanol(1)/Water(2)/CO_2/$TMAHCO_3$(5) with $x_5/x_1 = 0.020$[a]

70 °C				25 °C			
$100x_1$	$100x_5$	$100x_2$	P/MPa	$100x_1$	$100x_5$	$100x_2$	P/MPa
Experiment 1							
81.35 ± 0.20	1.60 ± 0.0039	2.01 ± 0.0049	5.55	84.84 ± 0.22	1.67 ± 0.0043	2.10 ± 0.0054	2.89
75.18 ± 0.21	1.48 ± 0.0042	1.86 ± 0.0053	7.32	69.76 ± 0.34	1.37 ± 0.0066	1.73 ± 0.0083	4.70
70.49 ± 0.23	1.39 ± 0.0044	1.75 ± 0.0056	8.48	61.17 ± 0.38	1.20 ± 0.0075	1.51 ± 0.0094	5.45
66.62 ± 0.24	1.31 ± 0.0046	1.65 ± 0.0058	9.18	55.77 ± 0.40	1.10 ± 0.0079	1.38 ± 0.0099	5.56
58.14 ± 0.25	1.14 ± 0.0049	1.44 ± 0.0062	11.17	49.37 ± 0.41	0.97 ± 0.0080	1.22 ± 0.010	5.78
53.55 ± 0.25	1.05 ± 0.0050	1.33 ± 0.0063	12.01	45.65 ± 0.41	0.90 ± 0.0080	1.13 ± 0.010	5.84
49.58 ± 0.26	0.98 ± 0.0050	1.23 ± 0.0063	12.99				
Experiment 2							
90.08 ± 0.18	1.77 ± 0.0035	2.23 ± 0.0044	2.79	43.47 ± 0.34	0.86 ± 0.0068	1.08 ± 0.0085	6.21
83.97 ± 0.20	1.65 ± 0.0040	2.08 ± 0.0050	4.87	32.38 ± 0.30	0.64 ± 0.0060	0.80 ± 0.0075	6.33
73.64 ± 0.26	1.45 ± 0.0051	1.82 ± 0.0064	7.80	28.19 ± 0.28	0.56 ± 0.0055	0.70 ± 0.0069	7.17
67.08 ± 0.29	1.32 ± 0.0058	1.66 ± 0.0072	9.29	24.73 ± 0.26	0.49 ± 0.0051	0.61 ± 0.0064	8.67
61.18 ± 0.32	1.20 ± 0.0062	1.51 ± 0.0078	10.53	22.26 ± 0.24	0.44 ± 0.0047	0.55 ± 0.0059	10.25
56.72 ± 0.33	1.12 ± 0.0064	1.40 ± 0.0081	11.44				
53.33 ± 0.29	1.05 ± 0.0058	1.32 ± 0.0073	11.85				
Experiment 3							
53.76 ± 0.32	1.06 ± 0.0064	1.33 ± 0.0080	12.68	57.73 ± 0.42	1.14 ± 0.0083	1.43 ± 0.010	6.16
49.59 ± 0.32	0.98 ± 0.0063	1.23 ± 0.0079	13.97	46.72 ± 0.43	0.92 ± 0.0084	1.16 ± 0.011	6.23
44.12 ± 0.27	0.87 ± 0.0053	1.09 ± 0.0066	15.26	40.68 ± 0.41	0.80 ± 0.0081	1.00 ± 0.010	6.21
40.35 ± 0.23	0.79 ± 0.0046	1.00 ± 0.0058	16.00	34.07 ± 0.39	0.67 ± 0.0076	0.84 ± 0.0096	6.21
36.41 ± 0.20	0.72 ± 0.0039	0.90 ± 0.0049	17.15	29.14 ± 0.36	0.57 ± 0.0070	0.72 ± 0.0087	6.58
32.56 ± 0.17	0.64 ± 0.0033	0.81 ± 0.0042	18.64	27.80 ± 0.35	0.55 ± 0.0068	0.69 ± 0.0085	6.88
29.90 ± 0.15	0.59 ± 0.0029	0.74 ± 0.0037	20.32	25.66 ± 0.33	0.51 ± 0.0065	0.64 ± 0.0081	7.27
28.59 ± 0.14	0.56 ± 0.0027	0.71 ± 0.0034	20.95	24.43 ± 0.32	0.48 ± 0.0063	0.60 ± 0.0079	7.99
				23.58 ± 0.31	0.46 ± 0.0061	0.58 ± 0.0078	8.44
				21.28 ± 0.29	0.42 ± 0.0057	0.53 ± 0.0072	10.51
Experiment 1 (Water Addition)							
62.59 ± 0.17	1.23 ± 0.0033	19.68 ± 0.14	7.89	58.77 ± 0.17	1.16 ± 0.0036	20.83 ± 0.15	5.64
59.14 ± 0.17	1.16 ± 0.0033	18.60 ± 0.14	9.63	55.05 ± 0.19	1.08 ± 0.0039	19.51 ± 0.14	6.21
56.79 ± 0.17	1.12 ± 0.0034	17.86 ± 0.13	10.42	49.01 ± 0.21	0.97 ± 0.0043	17.37 ± 0.14	9.60
51.03 ± 0.18	1.00 ± 0.0035	16.05 ± 0.12	13.43	47.89 ± 0.21	0.94 ± 0.0044	16.97 ± 0.13	10.01
47.90 ± 0.18	0.94 ± 0.0035	15.06 ± 0.12	15.09	46.79 ± 0.22	0.92 ± 0.0044	16.58 ± 0.13	11.38
43.77 ± 0.18	0.86 ± 0.0036	13.77 ± 0.11	18.97	43.57 ± 0.22	0.86 ± 0.0045	15.44 ± 0.13	19.22
Experiment 2 (Water Addition)							
66.21 ± 0.18	1.30 ± 0.0036	18.59 ± 0.16	6.50	60.31 ± 0.18	1.19 ± 0.0036	23.94 ± 0.20	5.27
62.24 ± 0.18	1.23 ± 0.0036	17.47 ± 0.15	8.89	56.70 ± 0.21	1.12 ± 0.0042	22.50 ± 0.20	6.02
58.20 ± 0.18	1.14 ± 0.0036	16.34 ± 0.14	10.39	52.15 ± 0.25	1.03 ± 0.0049	20.70 ± 0.19	6.68
50.86 ± 0.19	1.00 ± 0.0037	14.28 ± 0.13	14.58	48.91 ± 0.27	0.96 ± 0.0053	19.41 ± 0.19	9.70

[a] $TMAHCO_3$ formed prior to experiment by bubbling of original solution of TMAH with CO_2 at atmospheric pressure.

experiments was designed to compare this phase behavior with the phase behavior of TMAB solution prepared a priori by bubbling CO_2 through the solution of TMAH at atmospheric pressure (the existence of TMAB was confirmed by acid−base titration with standardized solution of HCl) (Table 3). The initial equilibrium temperature was chosen to be 70 °C, to match our previous studies in photoresist and plasma etch residue cleaning.[22−24]

Initial addition of CO_2 to the original solution of TMAH at elevated pressure caused a sharp increase in the mixture temperature, indicating the exothermic nature of the reaction. The same effect was observed during the preparation of TMAB solutions at atmospheric pressure.[22]

Figure 3 compares the experimental results (Tables 2 and 3) obtained from the mixture with the original TMAH loading (circles in upper part of the figure) and from the mixture with the original TMAB loading (circles in bottom). Clearly both systems demonstrate similar trends and show similar phase-transition pressures. These results support our previous studies and initial assumption that TMAB is a final reaction product of tetramethylammonium hydroxide and CO_2. However, it is interesting to note that the system TMAB/CO_2 provides more reproducible results than does the system TMAH/CO_2. This means that the in situ neutralization reaction between TMAH and CO_2 has some impact on the mixture phase behavior. Temperature and pressure change can alter the rate of the neutralization reaction as well as the necessary time to achieve the overall thermal and chemical equilibrium of the system.

The effect of the addition of water to the CO_2 mixtures was also investigated, and results are presented in Tables 3 and 4 and in Figure 3 (squares). As expected, the addition of water sharply increases the phase-transition pressure. In addition, the same improvement (as in the mixture without intentional water addition) in reproducibility was noted as when the TMAB solution was used.

Figure 4 shows the phase behavior of TMAB as a function of methanol concentration. An increase in methanol concentration causes a decrease in phase-transition pressure as a result of the higher miscibility of methanol/salt mixtures in CO_2. These results demonstrate that it is possible to achieve a single phase mixture at moderate pressures with CO_2 concentrations up to 70 mol %. Addition of water results in an increase in transition phase pressures.

The phase behavior of the mixture was also measured at 25 °C and compared to that obtained at 70 °C (Figure 5, Tables 4 and 5). At higher salt concentrations, initial addition of CO_2 at elevated pressure at 25 °C resulted in the formation of a solid phase, which was not soluble upon further CO_2 addition. Further increase of pressure gave additional precipitation. It is interesting to note that the mixture with the higher methanol concentration at elevated pressures does not reveal the same phenomenon;

Table 5. Pressure-Composition Data for Methanol(1)/Water(2)/CO_2/$TMAHCO_3$(5) with $x_5/x_1 = 0.021$[a]

$100x_1$	$100x_5$	$100x_2$	P/MPa
	70 °C		
86.43 ± 0.18	1.85 ± 0.0039	2.07 ± 0.0044	3.79
81.73 ± 0.21	1.75 ± 0.0046	1.96 ± 0.0051	5.45
69.88 ± 0.28	1.49 ± 0.0061	1.68 ± 0.0068	8.88
65.27 ± 0.30	1.40 ± 0.0065	1.56 ± 0.0073	9.98
60.49 ± 0.32	1.29 ± 0.0069	1.45 ± 0.0077	11.07
54.98 ± 0.27	1.18 ± 0.0058	1.32 ± 0.0066	12.36
51.92 ± 0.25	1.11 ± 0.0053	1.25 ± 0.0060	13.14
49.90 ± 0.23	1.07 ± 0.0050	1.20 ± 0.0056	15.07
45.56 ± 0.20	0.97 ± 0.0043	1.09 ± 0.0048	16.55
41.98 ± 0.17	0.90 ± 0.0037	1.01 ± 0.0042	18.28
	Water Addition		
68.70 ± 0.17	1.47 ± 0.0037	21.02 ± 0.15	4.98
63.55 ± 0.18	1.36 ± 0.0038	19.45 ± 0.14	7.82
60.15 ± 0.18	1.29 ± 0.0039	18.40 ± 0.14	9.65
57.40 ± 0.19	1.23 ± 0.0040	17.56 ± 0.13	10.38
51.09 ± 0.20	1.09 ± 0.0042	15.63 ± 0.12	14.19
	25 °C		
84.11 ± 0.25	1.80 ± 0.0053	2.02 ± 0.0059	3.02
77.37 ± 0.30	1.65 ± 0.0065	1.86 ± 0.0073	4.03
74.01 ± 0.33	1.58 ± 0.0071	1.77 ± 0.0079	4.45
67.38 ± 0.37	1.44 ± 0.0080	1.62 ± 0.0090	5.14
62.03 ± 0.40	1.33 ± 0.0087	1.49 ± 0.0096	5.54
59.49 ± 0.41	1.27 ± 0.0088	1.43 ± 0.0098	5.58
55.24 ± 0.42	1.18 ± 0.0090	1.32 ± 0.010	5.67
52.39 ± 0.43	1.12 ± 0.0091	1.26 ± 0.010	5.81
50.08 ± 0.43	1.07 ± 0.0091	1.20 ± 0.010	5.87
47.27 ± 0.43	1.01 ± 0.0091	1.13 ± 0.010	5.92
44.91 ± 0.42	0.96 ± 0.0090	1.08 ± 0.010	5.94
	Water Addition		
59.32 ± 0.067	1.27 ± 0.0014	18.22 ± 0.13	6.00
54.91 ± 0.062	1.17 ± 0.0013	16.87 ± 0.12	6.49
52.04 ± 0.059	1.11 ± 0.0013	15.99 ± 0.11	7.54
49.50 ± 0.056	1.06 ± 0.0012	15.21 ± 0.11	12.98
48.55 ± 0.055	1.04 ± 0.0012	14.92 ± 0.10	13.52
45.24 ± 0.051	0.97 ± 0.0011	13.90 ± 0.10	22.06

[a] $TMAHCO_3$ is a reaction product of original-solution TMAH(4) with CO_2 at elevated pressure; the mole fraction of CO_2 and $TMAHCO_3$(5) was calculated according to eq 4.

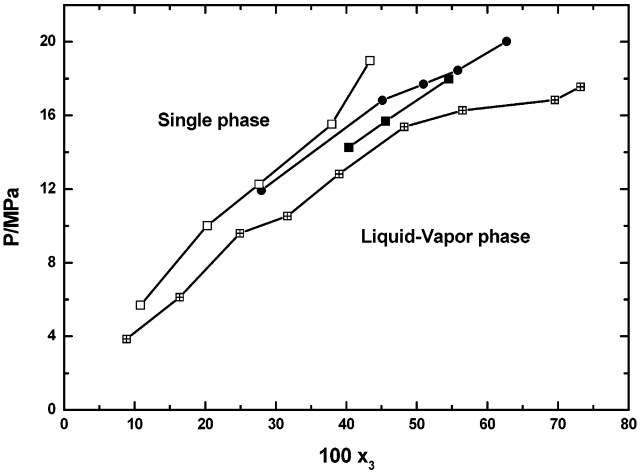

Figure 2. Comparison of pressure-composition data for methanol(1)/water(2)/CO_2(3) obtained in this work and previously reported in the literature:[25] ●, this work, 70 °C ($x_2/x_1 = 0.3324$); ⊞, Olesik et al.,[27] 70 °C ($x_2/x_1 = 0.2490$); ■, Olesik et al.,[27] 70 °C ($x_2/x_1 = 0.3311$); □, Olesik et al.,[27] 70 °C ($x_2/x_1 = 0.4298$).

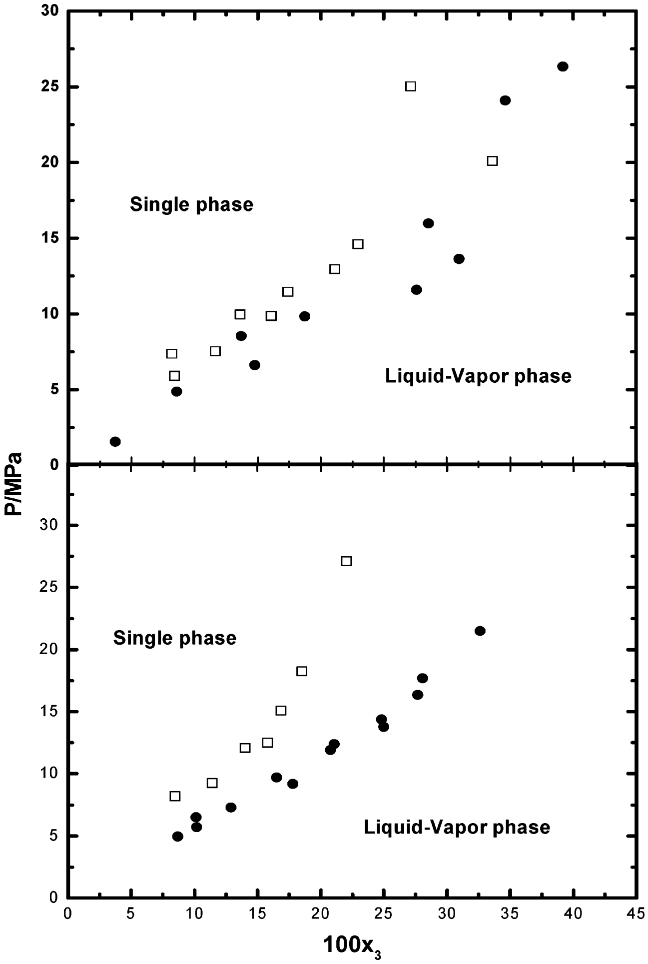

Figure 3. Experimental isotherm data at 70 °C for the 25 wt % original solution TMAH(4)(as purchased)/methanol(1) (with and without additional water(2)/CO_2 (3)) (top) ●, $x_4/x_1 = 0.127$; □, $x_4/x_1 = 0.127$, $x_2/x_1 = 0.525$ compared to experimental data isotherm obtained for TMAB solution(5)/methanol(1) (prepared a priori by bubbling CO_2 through the solution of TMAH at atmospheric pressure) (with and without additional water(2)/CO_2 (3)) (bottom) ●, $x_5/x_1 = 0.127$; □, $x_5/x_1 = 0.127$, $x_2/x_1 = 0.531$.

no precipitate was observed in this case. Moreover, the pressure necessary to achieve a single phase was almost two times lower than that required at 70 °C for the same salt−methanol composition. As seen in Figure 5, addition of CO_2 up to mole fraction of 60%, to the system at 25 °C, results in very little change in phase-transition pressure. A sharp increase in pressure occurs when more than 60 mol % of CO_2 was added. This implies that the effect of salt on the miscibility of the system is more dramatic at higher CO_2 concentrations. The system behaves differently upon addition of higher water concentrations (Figure 5, bottom). In comparison to the system at 70 °C where a linear increase in pressure was observed with addition of CO_2, at 25 °C the pressure increased sharply with addition of 30 mol % of CO_2 and showed almost exponential growth. These results, in fact, are close to literature values for methanol/CO_2, methanol/CO_2/water systems.[27−28] Lee et al. demonstrated previously that 6.3 MPa represents an inflection point in the above-mentioned systems.[27−28] In this study (Figure 5), the shape of the single phase transition isotherm changes at the same pressure of 6.3 MPa from concave down to concave up. In the absence of intentionally added water, and at relatively low salt concentrations (mole ratio of $TMAHCO_3/CH_3OH = 0.020$), at 25 °C, the phase-transition pressure sharply exceeds this inflection point at high mole fractions of CO_2. Methanol and CO_2 have been found to associate in supercritical and liquid phases.[35−36] However at high mole fractions of CO_2, its solubility in methanol decreases. Furthermore, the presence of ionic species in the mixture causes a further decrease of the CO_2 solubility in the mixture. This decrease in solubility results

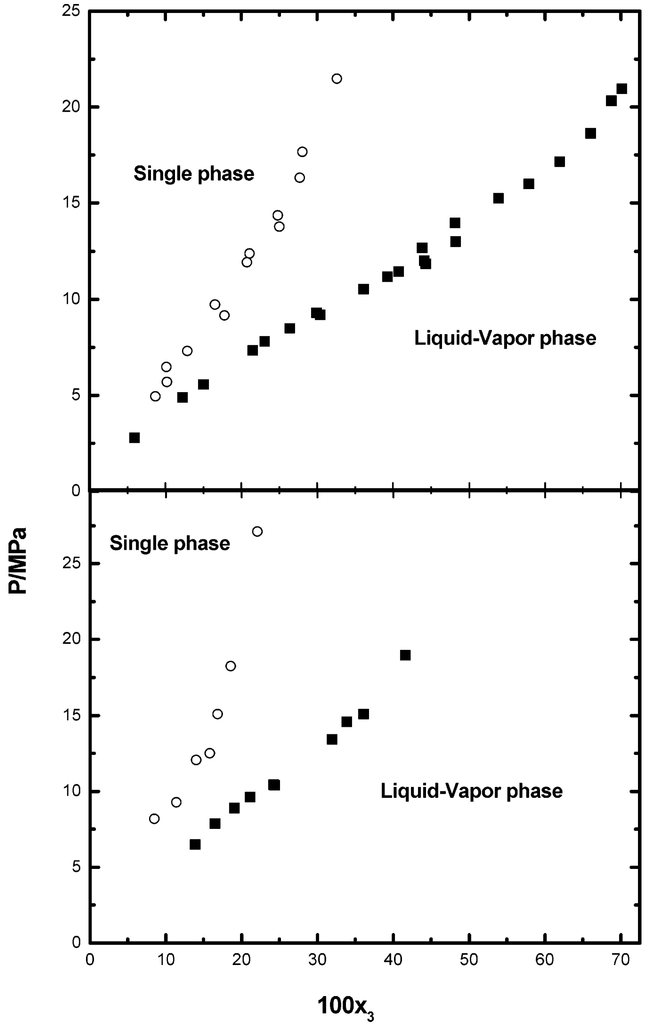

Figure 4. Effect of methanol concentration on phase behavior of TMAHCO$_3$(5)/methanol(1)/CO$_2$(3) (top) ○, $x_5/x_1 = 0.127$; ■, $x_5/x_1 = 0.021$ and TMAHCO$_3$(5)/methanol(1)/water(2)/CO$_2$(3) (bottom) ○, $x_5/x_1 = 0.127$, $x_2/x_1 = 0.531$; ■, $x_5/x_1 = 0.020$, $x_2/x_1 = 0.315$. Data was measured at 70 °C.

in higher phase-transition pressures. Upon addition of water, the transition pressure goes above 6.3 MPa with addition of 30 mol % of CO$_2$. Pure water and CO$_2$ are immiscible in each other except in relatively low proportions.[37−38] However, substantially higher mole fractions of H$_2$O and CO$_2$ can coexist in a single liquid phase (at 25 °C) in the presence of methanol. The later has been attributed to the high capacity of methanol to associate both with water and carbon dioxide. Salt addition to the mixture results in additional polar interactions in the systems.

As mentioned above, the isotherm shape is altered at higher temperature. This result is in good agreement with literature data for methanol/CO$_2$ and methanol/CO$_2$/water systems. A temperature increase in these systems results in a less distinct inflection point.

Modeling. Our goal was to use parameters fitted only to binary data to predict the ternary system CO$_2$/methanol/water and then to fit the quaternary systems that included TMAB with as few parameters as possible. We chose to model the systems with the PR[39] equation of state, the Stryjek−Vera attractive-term α function,[40] and the Wong−Sandler (WS) mixing rules.[42] Critical properties, acentric factors, and κ_1 values are listed in Table 6.

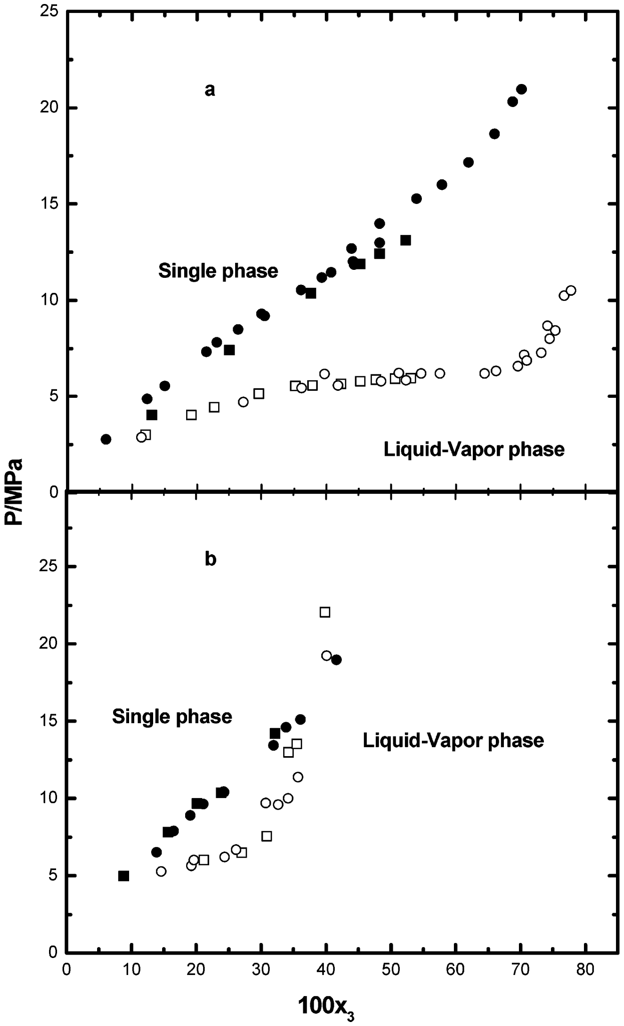

Figure 5. Phase behavior of original solution TMAH(4)(as purchased)/methanol(1)/CO$_2$(3) (top) and TMAHCO$_3$(5) (prepared a priori by bubbling CO$_2$ through the solution of TMAH at atmospheric pressure) (a) compared to that obtained for the same systems with intentional addition of water(2) (bottom) (b) at 25 and 70 °C. (a) At 25 °C: □, $x_4/x_1 = 0.021$; ○, $x_5/x_1 = 0.020$. At 70 °C: ■, $x_4/x_1 = 0.021$; ●, $x_5/x_1 = 0.020$. (b) At 25 °C: □, $x_4/x_1 = 0.021$, $x_2/x_1 = 0.307$; ○, $x_5/x_1 = 0.020$, $x_2/x_1 = 0.354$. At 70 °C: ■, $x_4/x_1 = 0.021$, $x_2/x_1 = 0.305$; ●, $x_5/x_1 = 0.020$, $x_2/x_1 = 0.315$.

Table 6. Pure Component Properties

	CO$_2$	methanol	water	TMAB
T_c/K	304.1	512.5	647.13	1021
P_c/bar	73.8	80.84	220.55	67.0
w	0.225	0.565831	0.3438	0.6822
κ_1	0	−0.15781	−0.06635	0

Two previous correlations have been reported for the system CO$_2$/methanol/water. Yoon et al.[26] measured ternary data at pressures up to 10 MPa. Adrian et al.[25] reported good predictions of these data with the PR equation of state with Huran−Vidal mixing rules and a modified NRTL g^E model[41] where the parameters were obtained only from correlations of binary data. By use of these parameters, we did not find good predictions for the data set measured by Lee et al.,[27] which covered much larger temperature and pressure ranges, (298−373) °K and (5−20) MPa. We used the WS mixing rule because parameters from low-pressure correlations were to be combined and some cross-second virial coefficient data were available. For the g^E portion of the mixing rule, the NRTL equation was used with α_{ij} set to 0.3 to reduce the number of adjustable parameters. In this formulation, the PR−WS equation has 3 adjustable parameters, k_{ij}, g_{ij}, and g_{ji}, per

Table 7. Binary Interaction Parameters for the PR−WS Equation[a]

	k_{ij}				g_{ij}			
	1	2	3	4	1	2	3	4
1	0	0.301897	0.318	0.65	0	912.6	1285	2000
2	0.301897	0	−0.5	0.4	101.35	0	419.7	600
3	0.318	−0.5	0	0.4	1380	14301	0	150
4	0.65	0.4	0.4	0	2000	600	150	0

[a] (1) CO_2, (2) methanol, (3) water, and (4) $TMAHCO_3$.

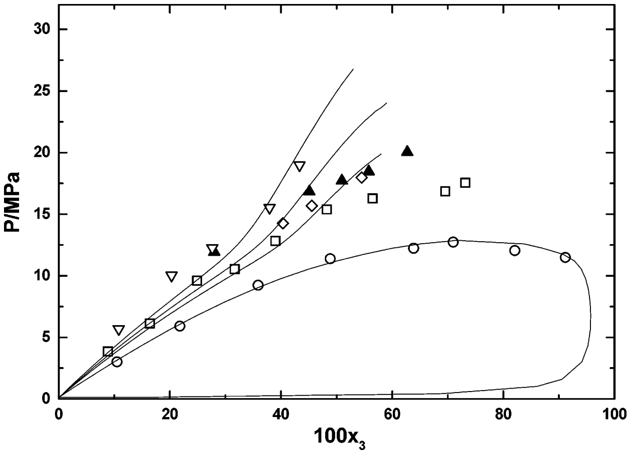

Figure 6. Data (symbols) and modeling results (lines) for the phase behavior of CO_2(3)/methanol(1) with constant ratios of water(2) to methanol(1). ▲, this work ($x_2/x_1 = 0.33$), at 70 °C; □, Olesik et al.[27] ($x_2/x_1 = 0.25$), at 70 °C; ◇, Olesik et al.[27] ($x_2/x_1 = 0.33$), at 70 °C; ○, Olesik et al.[27] ($x_2/x_1 = 0.43$), at 70 °C; ▽, Reighard et al.[28] ($x_2/x_1 = 0.0$), at 70 °C.

binary pair. The components are numbered 1 for CO_2, 2 for methanol, 3 for water, and 4 for TMAB. All adjustable parameters are listed in Table 7.

The three binary parameters for methanol/CO_2 were fit to the bubble pressure data of Reighard.[28] Shyu et al. had previously reported good correlations for the binary system water/CO_2 with the WS mixing rule using the van Laar g^E model.[43] Shyu's value for k_{13} was invoked and was fit to cross-second virial coefficient data; NRTL parameters were fit to the (g_{13} and g_{31}) water/CO_2 data of Bamberger et al.[44] For the methanol/water system, we initially fit the low-pressure data from Gmehling[45] to only the NRTL model and then adjusted only k_{23} when fitting the PR−WS. For these three binary systems, the correlation was within experimental error. Unfortunately, these parameters gave poor predictions of the ternary data of Lee et al.[27] Ternary predictions were quite sensitive to the methanol/water parameters, but by adjusting k_{23}, much improved results were obtained. Since the parameters in the methanol/water system are highly correlated, i.e., three parameters are more than needed, k_{23} could be varied to give a good ternary fit while changing g_{23} and g_{32} to allow a very good fit of the binary. The prediction of the ternary data is shown in Figure 6. The fit slightly underpredicts the bubble pressures at low concentrations of CO_2 and slightly overpredicts the pressures at higher concentrations, which is a limitation of the model.

The quaternary system containing TMAB adds complications to the model. First, the degree of disassociation in solutions with carbon dioxide is unknown, but we can assume that they would be much less than in pure water or methanol/water. The pK_a of TMAB in methanol was measured to be 5.2 by titration. Second, TMAB decomposes at modest temperatures and in aqueous solutions when not saturated with CO_2; therefore, little pure component data or binary solution equilibria is available. As a first approximation, we chose to model the salt only as a pure species. The critical properties were estimated by assuming that TMAB would be similar to glycine, which allowed the group contribution method of Lyderson[46] to be used.

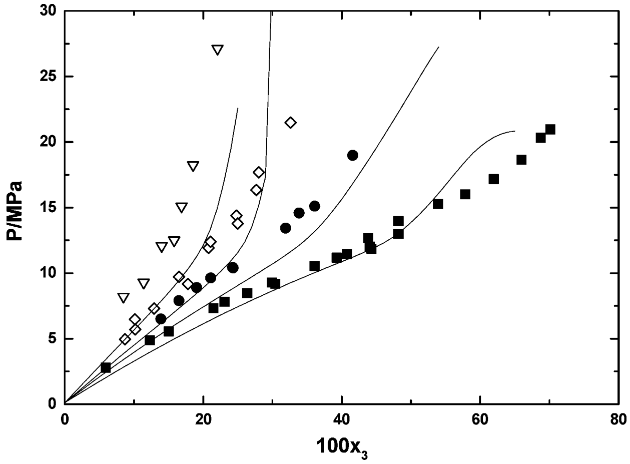

Figure 7. Bubble-point data (symbols) and modeling results (lines) for CO_2(3)/methanol(1)/water(2)/$TMAHCO_3$(5): ◇, $x_5/x_1 = 0.127$; ▽, $x_5/x_1 = 0.127$, $x_2/x_1 = 0.531$; ■, $x_5/x_1 = 0.021$; ●, $x_5/x_1 = 0.020$, $x_2/x_1 = 0.315$. Data was measured at 70 °C. The critical properties of $TMAHCO_3$ were estimated by similarity to glycine and use of group contribution method of Lyderson.[46]

To reduce the number of parameters, g_{i4} was assumed to be equal to g_{4i} and were chosen to give γ^{∞} of 1.5, 5, and 60 in water, methanol, and CO_2, respectively. The initial k_{i4} values were chosen to be 0.4. However, the predictions were most sensitive to k_{14}, which was changed to 0.65 for an improved fit. The correlation of the ternary data with 1 adjustable parameter is shown in Figure 7.

Conclusions

The phase behavior of the CO_2/methanol/TMAB and CO_2/methanol/TMAB/water systems has been studied using a high-pressure variable-volume view cell. For the system CO_2/methanol/water where literature data are available, our measurements were in good agreement. At higher methanol concentrations, the single-phase mixture could be achieved at moderate pressures with up to 70 mol % CO_2. These data can be used to design novel surface cleaning approaches in semiconductor device fabrication. The PR equation of state was capable of modeling this quaternary system, but the sensitivity to adjustable parameters necessitates that it must be used for correlation rather than prediction.

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