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Hydrate Equilibrium Conditions in Aqueous Electrolyte Solutions: Mixtures of Methane and Carbon Dioxide

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Three-phase equilibrium conditions (aqueous solution–vapor–hydrate) of methane + carbon dioxide mixtures in electrolyte solutions containing NaCl, KCl, $CaCl_2$, and their mixtures were measured in the temperature range of 262–285 K and in the pressure range of 1.5–10.6 MPa using a "pressure search" method. The ionic strengths of the solutions ranged from 0.7 to 6.76 *m*.

Introduction

Gas hydrates play an important role in the exploitation, transportation, and processing of natural gas. There is a risk of hydrate formation at all the stages of natural gas handling due to the operating conditions of pressure and temperature that favor hydrate formation. Large reserves of natural gas also exist as hydrates. In addition, natural gas may have to be drilled through a zone of hydrates. Carbon dioxide is normally present along with these hydrocarbons. CO_2 emission from the various combustion processes is identified to be the major reason for the greenhouse effect, and it is suggested that it be extracted and stored in deep sea waters as hydrates. Hydrate phase equilibrium data on CO_2 and its mixtures with hydrocarbons are, therefore, essential.

Hydrate equilibrium data on CO_2 and its mixtures in pure water are available in the literature (*1–7*). The gas industry uses methanol to inhibit hydrate formation. Ng and Robinson (*4, 8*) reported equilibrium data for CO_2 and a mixture of methane and CO_2 in the presence of methanol. Electrolytes, which are present in natural waters, also inhibit hydrate formation. As a part of a systematic research program, hydrate equilibrium data on CO_2 hydrates in aqueous solutions of electrolytes were obtained at the University of Calgary (*9*). In the present work, experimental data on the equilibrium conditions of two mixtures of methane and carbon dioxide in pure water and electrolyte solutions are reported.

Experimental Setup

The apparatus and the pressure search procedure employed were the same as those used by Dholabhai et al. (9) and Bishnoi and Dholabhai (11). The presence of hydrates in the solution was detected visually through the windows in the equilibrium cell. For easy reference a schematic of the apparatus is given in Figure 1. The experimental apparatus and procedure are briefly described below.

Experimental Apparatus. The main component of the apparatus consists of a stainless steel equilibrium cell equipped with two marine-type Plexiglass windows for visual observation, a magnetic stirrer, and suitable connections for charging/discharging of materials. The temperature of the cell contents is measured with two platinum resistance thermometers (RTDs). A 0–15-MPa Heise gauge is used to display the pressure. The pressure in the cell is measured with a differential pressure transmitter (DP). The signals from the RTDs and the DP are taken up by a data acquisition system. A computer receives the pressure and temperature values from the data acquisition system and saves them at preset sampling intervals. The cell is immersed in a cooling bath; a mixture of glycol and water is circulated from a refrigerated/heated bath. The set point of the temperature controller on this bath can be changed by multiples of 0.1 K. The temperature in the cell generally oscillates within 0.1 K during a period of 24 h.

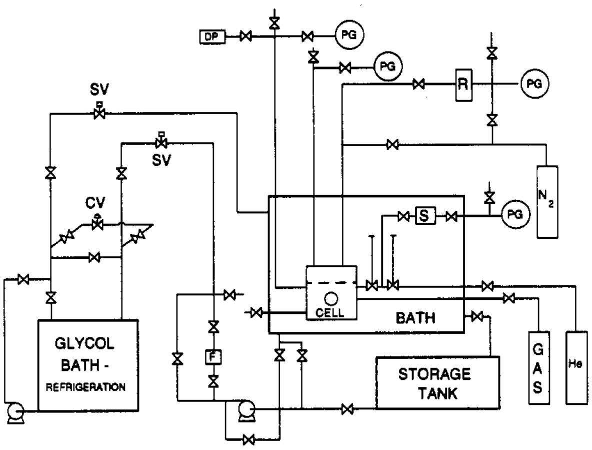

Figure 1. Schematic of the experimental apparatus: DP, pressure transmitter; R, nitrogen reservoir; S, sampling bomb; F, filter; PG, pressure gauge; SV, solenoid valve; CV, control valve.

The span of the DP was adjusted to 0–12 MPa. The low-pressure side of the DP was left open to the atmosphere. The stated accuracy of the DP was ±30 kPa (±0.25% of its span). The DP was calibrated against a dead weight tester. The standard deviation of the linear least-squares fit was 11.7 kPa. The accuracy of the RTDs was ±0.06 K.

Materials and Preparation of Electrolyte Solutions. The electrolytes used were certified ACS-grade supplied by Fisher Scientific Co. Deionized water was distilled in the laboratory before use. Gas mixtures having nominal compositions of 80 mol % methane + 20 mol % CO_2 and 50 mol % methane + 50 mol % CO_2 supplied by Union Carbide Canada Limited and Liquid Carbonic Inc. were used.

Appropriate quantities of the electrolyte were weighed on a top-loading Mettler balance with a readability of 0.01 g and added to a weighed quantity of the water. The mixture was stirred at room temperature to dissolve the electrolyte.

Analysis of the Vapor Phase. Samples from the vapor phase from the cell were analyzed on an HP 5840A gas chromatograph (GC) using a DC200 column. Pure-compo-

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Table 1. Compositions of the Aqueous Solutions

solution	composition/(mass % on wet basis) NaCl	KCl	$CaCl_2$	ionic strength/*m*
Na5	5.02			0.9044
Na10	9.99			1.8992
Na15	15.00			3.0197
Na20-1	20.00			4.2779
Na20-2	20.01			4.2806
K5		5.00		0.7060
K10		10.00		1.4904
K15		15.01		2.3690
Ca10			9.91	2.9733
Ca15			15.00	4.7699
Ca20			20.00	6.7574
Na5K10	5.00	10.00		2.5847
Na10K5	10.00	5.00		2.8022
K10Ca5		10.00	5.00	3.1681
Na5Ca10	5.01		10.00	4.1890
Na10Ca10	10.00		10.00	5.5176
Na10Ca5	10.17		5.08	3.6736
Na6K5Ca4-1	6.01	5.00	3.99	3.2677
Na6K5Ca4-2	6.00	5.00	4.00	3.2689

Table 2. Experimental Data on Hydrate Equilibrium Conditions of 80 mol % Methane + 20 mol % Carbon Dioxide

solution	*T*/K	*P*/MPa	% CO_2[a]	*T*/K	*P*/MPa	% CO_2[a]
pure water	277.56	3.41	15.3	274.10	2.36	16.4
	281.50	5.14	16.7	284.84	7.53	17.9
Na5	281.99	6.98	17.7	274.98	3.26	16.1
	279.23	5.08	17.2	271.59	2.30	15.2
Na10	278.98	6.56	17.4	276.14	4.66	19.4
	272.07	3.10	16.1	268.46	2.03	19.3
Na15	277.17	7.31	18.9	273.14	4.40	19.8
	269.12	2.88	19.4	264.78	1.86	17.3
	276.79	7.37	18.2			
Na20-1	270.37	5.42	19.3	267.48	3.85	19.8
	261.95	2.12	19.1			
Na20-2	274.31	9.15	19.9			
K5	271.38	2.04	19.7	274.97	2.96	19.8
	278.83	4.46	19.8	281.98	6.43	19.8
K10	275.90	3.94	19.6	272.16	2.59	19.8
	269.16	1.83	19.7	278.96	5.56	19.8
K15	266.96	1.89	18.4	272.69	3.45	19.5
	270.07	2.62	19.0	277.07	5.63	19.7

[a] Mole percent carbon dioxide in the vapor phase at equilibrium.

Table 3. Experimental Data on Hydrate Equilibrium Conditions of 80 mol % Methane + 20 mol % Carbon Dioxide

solution	*T*/K	*P*/MPa	% CO_2[a]	*T*/K	*P*/MPa	% CO_2[a]
Ca10	268.59	1.96	18.7	272.00	2.80	19.4
	276.04	4.32	19.7	279.13	6.08	19.7
Ca15	273.11	4.61	19.0	266.65	1.88	19.6
	269.13	3.00	19.7	276.88	7.09	19.7
Ca20	263.78	2.89	19.8	267.60	4.30	19.8
	271.34	7.24	19.9	273.69	9.46	19.9
Na5Ca10	273.67	5.04	19.4	265.54	2.06	19.7
	269.35	3.12	19.8	276.71	7.14	19.9
K10Ca5	265.07	1.65	19.8	269.35	2.46	19.8
	274.76	4.60	19.9	281.57	10.61	19.9
Na5K10	269.28	2.59	19.2	275.21	4.99	19.7
	281.27	10.41	19.8	265.09	1.66	20.3
Na10Ca5	275.13	6.07	19.5	269.18	3.10	20.0
	265.52	2.11	20.1	278.74	9.71	19.4
Na6K5Ca4-1	275.11	5.23	19.9	268.99	2.67	19.9
	278.25	7.65	19.7	265.48	1.85	20.3

[a] Mole percent carbon dioxide in the vapor phase at equilibrium.

Table 4. Experimental Data on Hydrate Equilibrium Conditions of 50 mol % Methane + 50 mol % Carbon Dioxide

solution	*T*/K	*P*/MPa	% CO_2[a]	*T*/K	*P*/MPa	% CO_2[a]
Na10Ca10	268.08	3.53	48.6	270.80	5.16	49.4
	264.14	2.15	49.7	268.21	3.52	49.7
Na10K5	275.48	4.59	46.5	268.04	1.82	49.8
	271.57	2.78	49.5	265.76	1.38	50.0
Na6K5Ca4-2	275.50	4.46	47.5	265.97	1.45	48.1
	271.86	2.80	50.0	268.08	1.81	49.6

[a] Mole percent carbon dioxide in the vapor phase at equilibrium.

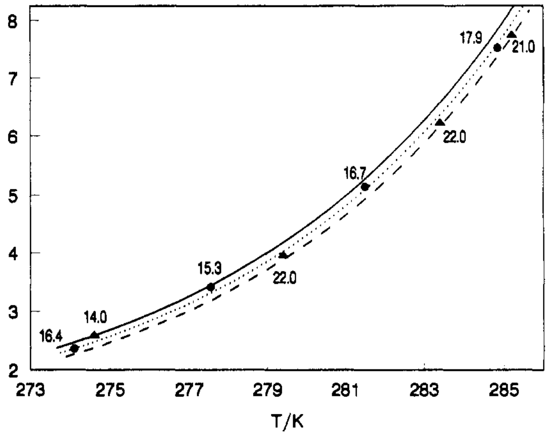

Figure 2. Hydrate equilibrium conditions for methane + CO_2 mixtures in pure water: (▲) ref 6; (●) this work. The constant CO_2 mole percent (in the vapor phase) curves were obtained using the correlation of ref 6: (—) 15 mol %; (···) 18 mol %; (- - -) 22 mol %. The numbers indicate the mole percent CO_2 in the vapor phase at equilibrium.

nent response factors for methane and CO_2 were obtained on the GC. Standard mixtures of methane and CO_2 were prepared gravimetrically and analyzed on the GC. The compositions of these mixtures were computed from the actual masses of the pure gases used as well from the GC analyses using the pure-component response factors. The two sets of compositions matched within 0.001 mole fraction.

Experimental Procedure. About 115 cm^3 of the solution was charged into the cell, and the vapor phase of the cell was purged with the gas mixture. A sample from the vapor phase of the cell was analyzed on the GC to ensure the absence of air. The solution was then allowed to cool to the required temperature. Once the desired temperature was reached, the pressure in the cell was increased beyond the expected equilibrium value by introducing the gas from the cylinder. When the hydrates formed, the pressure was reduced to a value slightly less than the expected equilibrium pressure by venting out the excess gas. The system was left to equilibrate. If the temperature and pressure of the system remained constant for 3–4 h with a negligibly small quantity of the hydrates present in the solution, the constant pressure and temperature were taken as the equilibrium conditions and the experiment was terminated. If the system pressure were higher than the equilibrium pressure, then the pressure would decrease continuously. In such a case the pressure was readjusted to a lower value. On the other hand, if all the hydrates had decomposed, then the hydrates were formed again as described above, the pressure was adjusted to a value slightly higher than that at which all the hydrates had decomposed, and the observations were continued. At the end of the experiment, the vapor phase was analyzed twice on the chromatograph. The results from the two samples did not differ from each other by more than 0.2 mol % and were averaged. The cell pressure was then lowered by approximately 30 kPa to verify that all the hydrates decomposed at the lower pressure.

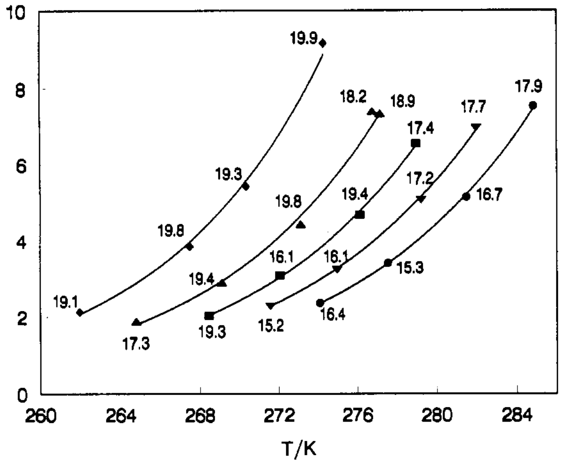

Figure 3. Experimental hydrate equilibrium conditions for the 80 mol % methane + 20 mol % CO_2 mixture in pure water and NaCl solutions: (●) pure water (this work); (▼) Na5; (■) Na10; (▲) Na15; (◆) Na20-1 and Na20-2. Each solid curve is a visual fit of the data for an electrolyte solution and is drawn to clarify the trend for the solution. The numbers indicate the mole percent CO_2 in the vapor phase at equilibrium.

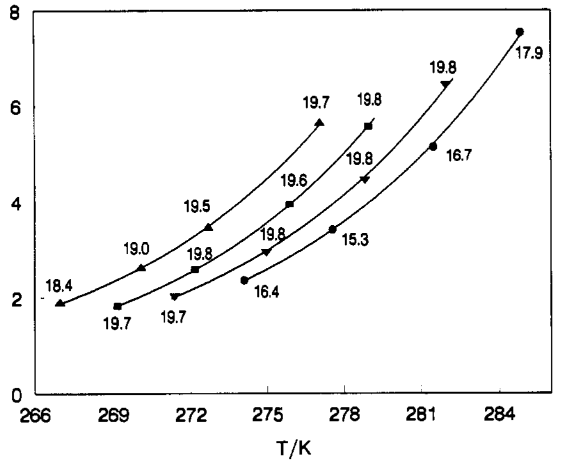

Figure 4. Experimental hydrate equilibrium conditions for the 80 mol % methane + 20 mol % CO_2 mixture in pure water and KCl solutions: (●) pure water (this work); (▼) K5; (■) K10; (▲) K15. Each solid curve is a visual fit of the data for an electrolyte solution and is drawn to clarify the trend for the solution. The numbers indicate the mole percent CO_2 in the vapor phase at equilibrium.

Experimental Results and Discussion

Experimental three-phase equilibrium data of aqueous electrolyte solutions, methane + CO_2 hydrate, and vapor are tabulated in Tables 2–4. The compositions of the electrolyte solutions are given in Table 1.

Pure water. In Figure 2 the experimental hydrate data of the 80 mol % methane + 20 mol % CO_2 mixture in pure water from this work are plotted. Adisasmito et al. (*6*) fit a polynomial to their data for methane + CO_2 binaries in pure water. Using this polynomial, constant concentration lines for CO_2 concentrations of 15, 18, and 22 mol % were computed. These lines, along with the applicable data from Adisasmito et al., are also plotted in Figure 2. The maximum absolute relative difference between the experimental and computed pressures was 1.74% for data from this work and 1.7% for data from Adisasmito et al.

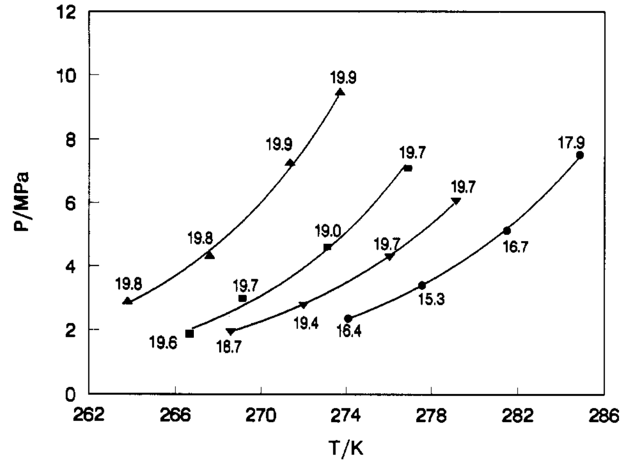

Figure 5. Experimental hydrate equilibrium conditions for the 80 mol % methane + 20 mol % CO_2 mixture in pure water and $CaCl_2$ solutions: (●) pure water (this work); (▼) Ca10; (■) Ca15; (▲) Ca20. Each solid curve is a visual fit of the data for an electrolyte solution and is drawn to clarify the trend for the solution. The numbers indicate the mole percent CO_2 in the vapor phase at equilibrium.

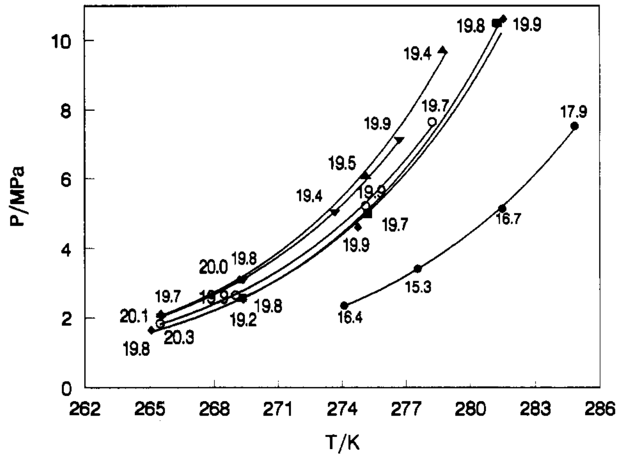

Figure 6. Experimental hydrate equilibrium conditions for the 80 mol % methane + 20 mol % CO_2 mixture in pure water and mixed electrolyte solutions: (●) pure water (this work); (▼) Na5Ca10; (◆) K10Ca5; (■) Na5K10; (▲) Na10Ca5; (○) Na6K5Ca4-1. Each solid curve is a visual fit of the data for an electrolyte solution and is drawn to clarify the trend for the solution. The numbers indicate the mole percent CO_2 in the vapor phase at equilibrium.

Electrolyte Solutions. The experimental data with the electrolyte solutions are plotted in Figures 3–7. The solid curves in these figures are "visually" drawn to clarify the trend for a given electrolyte solution. They are not obtained from any model or correlation. The inhibiting effect of the electrolytes can be seen clearly in these figures: at a given pressure, the equilibrium temperature is lower for higher ionic strengths. In Figure 6 the data for 5 mass % NaCl + 10 mass % $CaCl_2$ solution and those for 10 mass % NaCl and 5 mass % $CaCl_2$ solution are very close to each other. As has been observed with pure methane, propane, and CO_2 hydrates (*9–11*), this suggests that the inhibiting strengths of NaCl and $CaCl_2$ on a mass basis are close. Similar behavior can also be observed for 10 mass % KCl + 5 mass % NaCl and 10 mass % KCl + 5 mass % $CaCl_2$ solutions in Figure 6 and for 5 mass % KCl + 10 mass % NaCl and 5 mass % KCl + 6 mass % NaCl + 4 mass % $CaCl_2$ solutions in Figure 7.

Conclusions

Experimental three-phase equilibrium conditions of aqueous solution, methane + CO_2 hydrate, and vapor in pure water

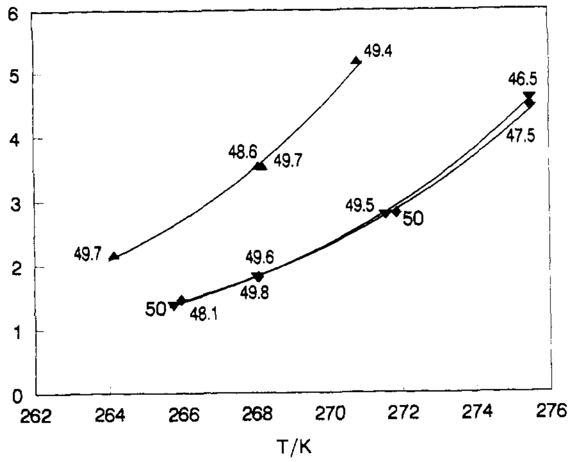

Figure 7. Experimental hydrate equilibrium conditions for the 50 mol % methane + 50 mol % CO_2 mixture in pure water and mixed electrolyte solutions: (▲) Na10Ca10; (▼) Na10K5; (◆) Na6K5Ca4-2. Each solid curve is a visual fit of the data for an electrolyte solution and is drawn to clarify the trend for the solution. The numbers indicate the mole percent CO_2 in the vapor phase at equilibrium.

and electrolyte solutions containing NaCl, KCl, and $CaCl_2$ and their mixtures were obtained in the temperature range of 262–285 K and the pressure range of 1.5–10.6 MPa. The data for pure water agreed with the literature values.

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