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Equilibrium Conditions for Carbon Dioxide Hydrates in the Presence of Aqueous Solutions of Alcohols, Glycols, and Glycerol

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Equilibrium conditions for carbon dioxide hydrates in the presence of aqueous solutions of methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol were experimentally measured at temperatures ranging from (264.1 to 283.1) K and pressures up to 4.54 MPa using an isochoric method. On a mass fraction basis, the inhibiting effect on the carbon dioxide hydrate equilibria decreased in the following order: methanol > ethanol > ethylene glycol > glycerol > diethylene glycol > triethylene glycol. The order is the same as predicted by the Hammerschmidt equation.

Introduction

Gas hydrates are crystalline compounds formed by hydrogen-bonded water molecules enclathrating small gas molecules such as methane, ethane, and propane. They are generally stable at low temperatures and high pressures and are of interest to the oil and gas industry because their formation can result in the blockage of pipelines and processing facilities. Addition of chemicals such as alcohols and glycols, which shifts the hydrate equilibria to lower temperatures and higher pressures, is a widely used method in the industry for inhibiting hydrate formation.

Carbon dioxide can also form a hydrate with water under suitable temperature and pressure conditions. It is present in natural gases produced from some reservoirs and also often used in the enhanced oil recovery process. In this process, carbon dioxide is injected into a reservoir and then flows from the production wells along with the natural gases. Understanding the equilibrium data for carbon dioxide hydrates in the presence of alcohols and glycols could aid in the design of such processing facilities.

The equilibrium conditions of natural gas hydrates have been studied extensively over many years.[1] Although many experimental data have been reported for equilibrium conditions of gas hydrates in the presence of methanol, information for gas hydrate equilibria in the presence of other alcohols and glycols is limited, especially for high concentration solutions. This work is part of a continuing study of gas hydrate equilibria in solutions containing chemical inhibitors. Previously, the inhibiting effects of various chemicals on propane hydrate equilibria were experimentally investigated.[2] The object of this work was to obtain new data for carbon dioxide hydrate equilibria in the presence of alcohols, glycols, and glycerol using an isochoric method. Moreover, as with propane hydrate, the inhibiting effects of the chemicals on carbon dioxide hydrate equilibria were investigated.

The chemicals used for the present study included methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol. The measurements of carbon dioxide hydrate equilibria were made at temperatures ranging from (264.1 to 283.1) K and pressures up to 4.54 MPa using an isochoric method.

Table 1. Components Used for the Experiments with the Corresponding Supplier and Purity

chemical	supplier	purity (mass fraction basis)
methanol	Kanto Chemical Co., Inc.	99.8 %
ethanol	Wako Pure Chemical Industries, Ltd.	99.5 %
ethylene glycol	Kanto Chemical Co., Inc.	99.5 %
diethylene glycol	Wako Pure Chemical Industries, Ltd.	99.0 %
triethylene glycol	Alfa Aesar	99.0 %
glycerol	Kanto Chemical Co., Inc.	99.0 %

Experimental Section

Materials. Deionized water was distilled in the laboratory before use. Carbon dioxide of research grade purity was supplied by Showa Tansan Co. Ltd. The alcohols, glycols, and glycerol used in the present study were supplied as listed in Table 1. Appropriate amounts of the chemicals and distilled water were weighed on an electronic balance with a resolution of 0.01 g and mixed thoroughly at room temperature. The uncertainties in the composition of the solutions were less than ± 0.0002 on a mass fraction basis.

Experimental Apparatus. The experimental apparatus used in the present study is similar to that used by Maekawa.[3] Briefly, the main part of the apparatus is a cylindrical stainless steel cell with a volume of approximately 1000 cm^3. The cell is equipped with a mixer to agitate the solution and hydrate. The temperature and pressure inside the cell are measured with a platinum resistance thermometer and a semiconductor pressure transducer calibrated by a precise Bourdon tube gauge, respectively. The estimated uncertainties of the temperature and pressure are ± 0.2 K and ± 0.04 MPa, respectively. The hydrate equilibrium cell is immersed in a glycol−water bath of which the temperature is controlled by an external heater and refrigeration unit.

Experimental Procedures. Hydrate equilibrium conditions were measured using an isochoric procedure similar to those described by Maekawa[3] and Ohmura et al.[4] In each experimental run, approximately 700 cm^3 of solution was charged into the

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cell. After sealing the lid, the cell was immersed in the temperature-controlled bath. The cell was repeatedly flushed with carbon dioxide, and carbon dioxide was then introduced into the cell until the desired pressure was reached. The vent valve of the cell was closed, and the temperature was then lowered for hydrate formation.

When hydrate formed in the cell, a rapid pressure drop was observed because of the encapsulation of carbon dioxide in the hydrate. After hydrate formation, the temperature was raised to a temperature slightly lower than the predicted equilibrium temperature. Subsequently, the temperature was raised in steps of 0.1 K to dissociate the hydrate. At every step, the temperature was kept constant for 4 h to achieve a steady equilibrium state. While the temperature was raised in the presence of hydrate, a marked increase in pressure was observed at each step because of partial dissociation of the hydrate. In contrast, once all of the hydrate was dissociated, only a small pressure increase was observed because of thermal expansion and fluid phase equilibria.

The point at which the slope of measured pressure to temperature abruptly changed is considered to be the hydrate dissociation point. Therefore, the hydrate equilibrium conditions were determined by measuring the pressure and temperature of the hydrate dissociation point. To obtain another equilibrium condition, the initial pressure was changed, and the procedure was repeated.

Results and Discussion

The equilibrium conditions obtained for carbon dioxide hydrates in aqueous solutions of different chemicals are summarized in Tables 2 and 3. A graphical representation of the conditions along with corresponding data from previous studies is shown in Figures 1 to 6.[5−8,10−14] To validate the experimental technique performed in the present study, the results for carbon dioxide hydrate in pure water were compared to previously reported data (Figure 1). The comparison indicates that the present results obtained using the isochoric procedure are consistent with the previous data.

The equilibrium conditions for pure water obtained in the present study were correlated from a least-squares regression to obtain the equation:

$$\ln(p/\mathrm{MPa}) = -3063.51 + 120336/(T/\mathrm{K}) + 467.5923\,\ln(T/\mathrm{K}) \qquad (1)$$

where p and T are the equilibrium pressure and temperature, respectively. The equation indicates the phase equilibria for a carbon dioxide-rich vapor + water-rich liquid + carbon dioxide hydrate system. The absolute mean deviation of the calculated pressure (AAD %) is 0.79 % from the following equation:

$$\mathrm{AAD}\ \% = \frac{1}{N}\sum |(P_{\mathrm{exp}} - P_{\mathrm{cal}})/P_{\mathrm{exp}}| \cdot 100 \qquad (2)$$

where N is the number of data. The regression curves are also shown in Figures 1 to 6. As is seen in these figures, the data sets for carbon dioxide hydrate equilibria in each solution essentially parallel the regression curve for pure water. The best-fit curves for each solution that are parallel to the regression curve for pure water are also shown in the figures.

The experimental data generated for methanol solutions are shown in Figure 1 along with results reported for previous investigations. As can be seen in the figure, there is some disagreement between the data from Ng and Robinson[5] and others for the 0.10 mass fraction methanol solution. The data obtained in the present study for methanol solutions are consistent with those from Dholabhai et al.[6,7] and Fan et al.[8] Dholabhai et al.[6] evaluated two different procedures to determine the equilibria and concluded that their data are reliable. The results of the present study and those of Fan et al.[8] support their conclusion. The reason why the discrepancy occurred remains obscure but may be due to the use by Ng and Robinson[5] of an isothermal procedure with visual observation. Using visual techniques could lead to inaccurate results for determining the hydrate point.[9] The results of Ng and Robinson[5] for a 0.20 mass fraction solution are also overestimated when compared to the data obtained in the present study.

Table 2. Equilibrium Conditions of Carbon Dioxide Hydrates in the Presence of Pure Water and Aqueous Solutions of Alcohols (w = Mass Fraction of Alcohol)[a]

T/K	p/MPa
Pure Water	
273.6	1.33
274.9	1.54
276.2	1.78
277.7	2.13
278.9	2.47
279.1	2.57
280.0	2.86
280.1	2.90
281.1	3.28
281.1	3.29
282.1	3.80
282.8	4.24
283.1	4.54
Methanol (w = 0.100)	
269.3	1.35
270.5	1.55
272.4	1.92
273.9	2.33
275.0	2.67
276.5	3.30
277.3	3.72
Methanol (w = 0.200)	
265.6	1.67
267.0	1.98
269.0	2.53
270.4	3.10
Ethanol (w = 0.100)	
273.0	1.75
273.8	1.94
274.9	2.23
276.0	2.55
277.1	2.98
278.2	3.42
Ethanol (w = 0.200)	
268.1	1.55
269.8	1.91
271.5	2.33
273.1	2.85
274.4	3.45

[a] Uncertainties on temperatures and pressures are ± 0.2 K and ± 0.04 MPa, respectively.

The results for ethanol solutions are presented in Figure 2. The data reported herein are in good agreement with the data previously published by Mohammadi et al.[10] for a 0.10 mass fraction ethanol solution. New data for a 0.20 mass fraction ethanol solution are provided in the present study. The results for ethylene glycol solutions with (0.10, 0.20, and 0.30) mass fractions are shown in Figure 3. These data agree with the data previously reported for ethylene glycol solutions of (0.10 and 0.30) mass fraction.[8,11] Data generated in the present study for (0.10, 0.20, and 0.30) mass fraction solutions of diethylene glycol are presented in Figure 4. Previously published data for (0.074 and 0.163) mass fraction solutions of diethylene glycol are not shown.[12] For triethylene glycol solutions, the data for

Table 3. Equilibrium Conditions of Carbon Dioxide Hydrates in the Presence of Aqueous Solutions of Glycols and Glycerol (w = Mass Fraction of Glycol or Glycerol)[a]

T/K	p/MPa	T/K	p/MPa
Ethylene Glycol (w = 0.100)			
272.0	1.48	276.8	2.62
272.4	1.55	277.8	3.01
273.6	1.78	279.3	3.68
275.1	2.13	279.8	3.95
Ethylene Glycol (w = 0.200)			
270.1	1.71	275.3	3.32
272.1	2.15	276.1	3.74
273.7	2.65		
Ethylene Glycol (w = 0.300)			
264.1	1.39	269.5	2.69
266.2	1.77	270.8	3.19
267.7	2.14		
Diethylene Glycol (w = 0.100)			
274.9	1.82	278.9	3.03
277.0	2.33	280.9	4.06
Diethylene Glycol (w = 0.200)			
272.3	1.73	277.0	3.10
273.9	2.10	278.1	3.65
274.9	2.37		
Diethylene Glycol (w = 0.300)			
269.3	1.72	273.2	2.77
271.4	2.19	275.0	3.56
Triethylene Glycol (w = 0.100)			
273.9	1.56	279.0	2.89
275.7	1.92	280.3	3.47
277.5	2.38	281.3	4.04
Triethylene Glycol (w = 0.200)			
273.0	1.70	277.6	3.00
274.3	1.98	279.4	3.85
276.1	2.46		
Triethylene Glycol (w = 0.300)			
270.7	1.70	274.7	2.80
273.1	2.27	276.1	3.42
Triethylene Glycol (w = 0.400)			
267.0	1.68	271.6	2.95
269.0	2.12	272.6	3.41
270.2	2.46		
Glycerol (w = 0.100)			
274.5	1.77	279.2	3.21
276.8	2.35	280.9	4.13
Glycerol (w = 0.200)			
272.0	1.70	275.8	2.73
272.9	1.90	277.1	3.23
274.5	2.30	278.4	3.94
Glycerol (w = 0.300)			
269.3	1.73	272.9	2.74
271.0	2.14	274.6	3.49

[a] Uncertainties on temperatures and pressures are ± 0.2 K and ± 0.04 MPa, respectively.

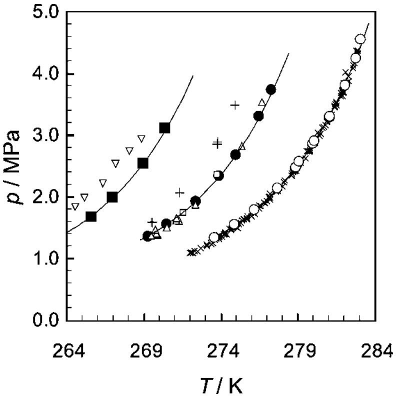

Figure 1. Carbon dioxide hydrate equilibrium conditions in pure water and aqueous methanol solutions. The solid curves indicate the regression curve for pure water and the best-fit curves for different solutions parallel to the regression curve. ○, present study (pure water); ●, present study (w = 0.100); ■, present study (w = 0.200); ×, ref 1 (pure water); +, ref 5 (w = 0.1000); △, refs 6 and 7 (w = 0.10); □, ref 8 (w = 0.10); ▽, ref 5 (w = 0.2002).

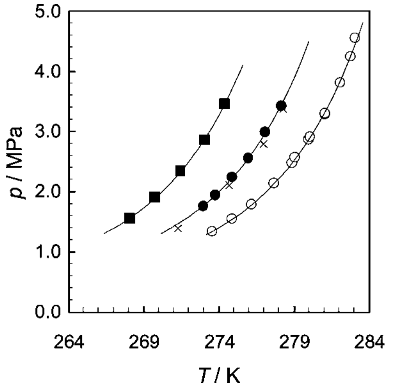

Figure 2. Carbon dioxide hydrate equilibrium conditions in aqueous ethanol solutions. ○, present study (pure water); ●, present study (w = 0.100); ■, present study (w = 0.200); ×, ref 10 (w = 0.10).

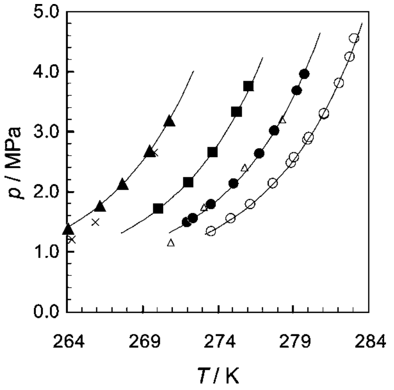

Figure 3. Carbon dioxide hydrate equilibrium conditions in aqueous ethylene glycol solutions. ○, present study (pure water); ●, present study (w = 0.100); ■, present study (w = 0.200); ▲, present study (w = 0.300); △, ref 8 (w = 0.10); ×, ref 11 (w = 0.30).

solutions of up to 0.20 mass fraction have been previously presented.[13] The additional data for higher concentration solutions (0.30 and 0.40 mass fraction solutions) were generated in the present study (Figure 5). The equilibrium data for glycerol solutions of (0.10, 0.20, and 0.30) mass fraction, including previously reported data, are shown in Figure 6.[14] The data obtained in the present study are in good agreement with the previous results.

To investigate the effect of the chemicals on carbon dioxide hydrate equilibria, the temperature difference, ΔT, between carbon dioxide hydrate equilibria in pure water and that in an aqueous solution of the chemical was obtained, assuming that each set of carbon dioxide hydrate equilibria ran parallel to the regression curve obtained for pure water. The temperature difference was calculated using the following equation:

$$\Delta T = T_0 - T_s \tag{3}$$

where T_0 and T_s are the hydrate equilibrium temperature for pure water and a solution at a given pressure, respectively. The ΔT values are shown in Table 4.

Alternatively, to approximate the temperature difference due to the presence of added chemicals, Hammerschmidt[15] presented a semiempirical equation:

$$\Delta T = \frac{1297W}{100M - MW} \tag{4}$$

where ΔT is the temperature difference in K, M is the molecular weight of the chemical, and W is the concentration of the chemical measured as mass percent in the solution. The calculated values from the Hammerschmidt equation and previously reported data are also shown in Table 4.

The inhibiting effects of the different chemicals on carbon dioxide hydrate equilibria can be seen by comparing the temperature differences for solutions containing the same mass fraction of each chemical. As shown in Table 4, on a mass fraction basis, the effect of chemicals on carbon dioxide hydrate equilibria decreases in the following order: methanol > ethanol > ethylene glycol > glycerol > diethylene glycol > triethylene glycol. The order of inhibiting effect is the same as that obtained for propane hydrate equilibria,[2] although the temperature difference for carbon dioxide hydrate is slightly smaller than that for propane hydrate for each of the same solutions. In addition, the measured temperature differences for solutions of chemicals are on the same order as those estimated using the Hammerschmidt equation; however, there is some disagreement in numerical values.

Table 4. Temperature Differences in Carbon Dioxide Hydrate Equilibria between an Aqueous Solution of the Chemical (Mass Fraction w) and Pure Water

chemical	w	ΔT^a/K	ΔT^b/K	ΔT^c/K	ΔT^d/K	refs
methanol	0.100	4.5	4.9	4.5	6.1, 4.3, 4.6	5, 6, 8
	0.200	10.1		10.1	11.7	5
ethanol	0.100	3.2	3.5	3.1	2.8	9
	0.200	6.9		7.0		
ethylene glycol	0.100	2.6	2.8	2.3	2.4	8
	0.200	5.8	6.4	5.2		
	0.300	10.0		9.0	8.8	10
diethylene glycol	0.100	1.5	1.7	1.4		
	0.200	3.7	4.1	3.1		
	0.300	6.6		5.2		
triethylene glycol	0.100	1.1	1.2	1.0	1.1	11
	0.200	2.8	3.1	2.2	2.5[e]	11
	0.300	5.2		3.7		
	0.400	8.7		5.8		
glycerol	0.100	1.7	1.9	1.6	1.8	
	0.200	3.9	4.3	3.5	4.2	
	0.300	6.8		6.0	7.1	

[a] Present study. [b] Maekawa[2] for propane hydrate. [c] Hammerschmidt equation. [d] Previous study. [e] The value was obtained from data ($n = 2$) above 1 MPa.

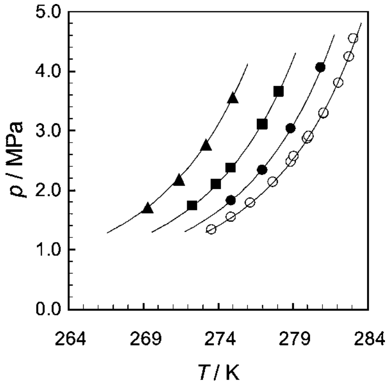

Figure 4. Carbon dioxide hydrate equilibrium conditions in aqueous diethylene glycol solutions. ○, present study (pure water); ●, present study ($w = 0.100$); ■, present study ($w = 0.200$); ▲, present study ($w = 0.300$).

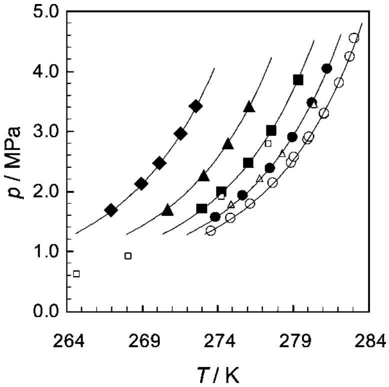

Figure 5. Carbon dioxide hydrate equilibrium conditions in aqueous triethylene glycol solutions. ○, present study (pure water); ●, present study ($w = 0.100$); ■, present study ($w = 0.200$); ▲, present study ($w = 0.300$); ◆, present study ($w = 0.400$); △, ref 13 ($w = 0.10$); □, ref 13 ($w = 0.20$).

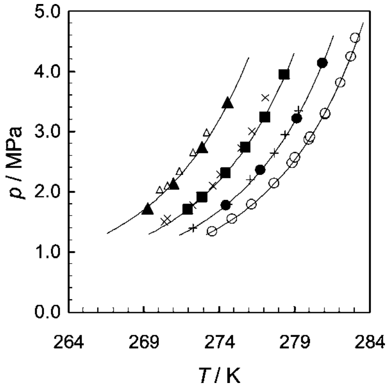

Figure 6. Carbon dioxide hydrate equilibrium conditions in aqueous glycerol solutions. ○, present study (pure water); ●, present study ($w = 0.100$); ■, present study ($w = 0.200$); ▲, present study ($w = 0.300$); +, ref 14 ($w = 0.10$); ×, ref 14 ($w = 0.20$); △, ref 14 ($w = 0.30$).

Conclusions

The equilibrium conditions for carbon dioxide hydrates formed in the presence of aqueous solutions of methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol were experimentally measured at temperatures ranging from (264.1 to 283.1) K and pressures up to 4.54 MPa using the isochoric method. The set of carbon dioxide hydrate equilibria for each chemical solution essentially parallel the results obtained for pure water. The inhibiting effect of chemicals on carbon dioxide hydrate equilibria on a mass fraction basis decreased in the following order: methanol > ethanol > ethylene glycol > glycerol > diethylene glycol > triethylene glycol. The order is the same as that obtained for propane hydrate equilibria and that estimated from the Hammerschmidt equation.

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