Equilibrium Conditions of Clathrate Hydrates Formed from Propane and Aqueous Solutions of Propanone and Sodium Chloride

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Equilibrium conditions of clathrate hydrates formed from propane and aqueous solutions of propanone and sodium chloride were experimentally measured at a temperature range of (264.7 to 276.9) K and pressures up to 0.514 MPa using an isochoric method. The equilibrium temperatures of the clathrate hydrates decrease as the propanone concentrations increase, indicating that propanone has an inhibiting effect on propane hydrate formation.

Introduction

Clathrate hydrates are crystalline solid compounds formed by hydrogen-bonded water molecules encapsulating relatively small guest molecules. The structures are generally classified into structure I, structure II, and structure H by the difference in the cavity size and shape formed by the water molecules.[1] Low molecular-weight gas molecules and organic components are captured into the suitable cavities in a clathrate structure. In general, small gas molecules such as methane can form a structure I hydrate, whereas larger gas molecules such as propane can form a structure II hydrate. Organic compounds such as tetrahydrofuran can also form a structure II hydrate.

Propanone is also known to form a solid clathrate hydrate as a single guest.[2] The phase diagram of the propanone + water system was considered in Dyadin et al.[3] It was shown that the structure II hydrate of propanone is stable from atmospheric pressure to 165 MPa.

For double hydrates containing propanone, Ng and Robinson[4] investigated clathrate hydrates formed from methane and aqueous propanone solutions. They concluded that propanone promotes or suppresses the methane hydrate formation depending on the propanone concentration. At lower propanone concentrations it acts as a hydrate promoter, whereas at higher propanone concentrations it suppresses methane hydrate formation. The investigation was followed by Mainusch et al.,[5] and Seo et al.[6] also investigated the hydrate equilibria of methane or nitrogen with an aqueous propanone solution (0.03 mole fraction).

Javanmardi et al.[7] investigated the effect of propanone on the R22 ($CHClF_2$) hydrate equilibria. They used aqueous propanone solutions having propanone mole fractions of 0.02, 0.04, and 0.06 and concluded that propanone has an inhibiting effect on the R22 hydrate formation in contrast to methane hydrate formation.

The clathrate hydrate equilibria for difluoromethane or krypton with an aqueous propanone solution (molar ratio of water to propanone of 17) were investigated by Imai et al.[8] They found that equilibrium temperatures of clathrate hydrates for the difluoromethane + propanone + water system are lower than those in the binary difluoromethane + water system under the same pressure above 0.2 MPa. In contrast to the presence of difluoromethane, equilibrium temperatures of clathrate hydrates for the krypton + propanone + water system were found to be higher than those in the binary krypton + water system.

However, few hydrate equilibria for other gases in propanone-containing systems have been investigated. In this study, equilibrium conditions of clathrate hydrates formed from propane and aqueous propanone solutions are experimentally measured using an isochoric method. In addition, aqueous solutions containing sodium chloride with propanone were also investigated. The investigated concentrations of propanone (1) and sodium chloride (2) were on a mass basis ($w_1 = 0.05$ to 0.30 and $w_2 = 0.03$ to 0.10, respectively).

Experimental Section

Materials. Deionized water was distilled in the laboratory before use. Propane of research grade purity was supplied by Takachiho Chemical Industrial Co., Ltd. Propanone and sodium chloride was supplied by Wako Pure Chemical Industries, Ltd. Their minimum purities are 0.998 and 0.995 on a mass basis, respectively. Appropriate amounts of propanone, sodium chloride, and distilled water were weighed on an electronic balance with a readability of 0.01 g and mixed thoroughly at room temperature. The uncertainties in composition of solutions are estimated to be less than ± 0.0004.

Experimental Apparatus. The apparatus used in this study is essentially the same as reported by Maekawa.[9,10] The main part of the apparatus consists of a cylindrical stainless steel cell with about 700 cm^3 volume. A magnetic mixer agitates the solution and hydrate inside the cell. The temperature and pressure inside the cell are measured by a platinum resistance thermometer (Pt100) and a semiconductor pressure transducer (model KH15, Nagano Keiki Co., Ltd.), respectively. The estimated uncertainties of temperature and pressure measurements are ± 0.2 K and ± 0.004 MPa, respectively. The cell is immersed in a glycol + water bath in which the temperature is controlled by a heater and refrigeration unit.

Experimental Procedures. In this study, the equilibrium conditions of clathrate hydrates were determined using an isochoric method. The isochoric method is similar to that described by Maekawa.[10] In each experimental run, about 400

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Table 1. Equilibrium Conditions of Clathrate Hydrates Formed from Propane and Aqueous Propanone Solutions (w_1 = Mass Fraction of Propanone)

T/K	p/MPa	T/K	p/MPa
	Pure Water		
276.0	0.317	276.9	0.386
276.6	0.356	277.6	0.462
	Propanone (w_1 = 0.05)		
273.4	0.224	275.4	0.358
274.0	0.259	276.1	0.417
274.7	0.303	276.9	0.501
	Propanone (w_1 = 0.10)		
272.3	0.222	274.6	0.387
273.2	0.272	275.1	0.437
273.9	0.325	275.5	0.482
	Propanone (w_1 = 0.15)		
270.8	0.209	273.1	0.368
271.1	0.224	273.5	0.402
272.0	0.283	274.0	0.452
272.7	0.328		
	Propanone (w_1 = 0.16)		
270.6	0.204	272.7	0.358
271.3	0.244	273.3	0.407
271.8	0.284	273.8	0.467
	Propanone (w_1 = 0.20)		
270.0	0.239	271.8	0.392
270.6	0.288	272.3	0.442
271.5	0.353		
	Propanone (w_1 = 0.25)		
267.7	0.194	270.1	0.358
268.4	0.239	270.7	0.426
269.1	0.283		
	Propanone (w_1 = 0.30)		
266.4	0.209	268.2	0.338
266.9	0.239	268.6	0.370
267.7	0.298	268.9	0.397

Table 2. Equilibrium Conditions of Clathrate Hydrates Formed from Propane and Aqueous NaCl Solutions (w_2 = Mass Fraction of NaCl)

T/K	p/MPa	T/K	p/MPa
	NaCl (w_2 = 0.03)		
273.0	0.224	275.9	0.422
273.7	0.258	276.4	0.482
274.2	0.288	276.6	0.506
274.9	0.338		
	NaCl (w_2 = 0.05)		
271.3	0.194	274.6	0.399
272.1	0.235	275.0	0.447
273.0	0.287	275.6	0.514
273.8	0.338		
	NaCl (w_2 = 0.10)		
268.6	0.194	271.0	0.343
269.3	0.239	271.7	0.402
270.3	0.293	272.1	0.442

cm^3 of a solution was charged into the cell. After sealing the lid, the cell was immersed in a glycol + water bath. The cell was repeatedly flushed with propane from the cylinder, and then propane was introduced into the cell until a desired pressure was reached. The compositional change in liquid during flushing was ignored because amounts of propanone and water in liquid were quite larger than those in vapor. The pressure is almost the same as the vapor pressure of propane because the vapor pressures of propanone and water are much smaller than that of propane at experimental temperatures. The vent valve was then closed, and the temperature was lowered to form hydrates. At the time of hydrate formation, a rapid pressure drop was observed because of encapsulation of gas within the hydrate.

Table 3. Equilibrium Conditions of Clathrate Hydrates Formed from Propane and Aqueous Solutions of Propanone (1) and NaCl (2) (w_1, w_2 = Mass Fraction of Propanone and NaCl)

T/K	p/MPa	T/K	p/MPa
	Propanone (w_1 = 0.05) + NaCl (w_2 = 0.05)		
270.2	0.204	272.8	0.373
270.8	0.239	273.5	0.447
271.6	0.283	273.9	0.482
272.5	0.342		
	Propanone (w_1 = 0.10) + NaCl (w_2 = 0.05)		
269.2	0.234	271.2	0.380
270.1	0.297	271.4	0.402
270.8	0.347	271.9	0.452
	Propanone (w_1 = 0.15) + NaCl (w_2 = 0.05)		
267.0	0.208	269.2	0.377
267.3	0.234	269.6	0.412
268.3	0.298		
	Propanone (w_1 = 0.05) + NaCl (w_2 = 0.10)		
267.0	0.204	269.4	0.368
267.6	0.239	269.9	0.417
268.8	0.314		
	Propanone (w_1 = 0.10) + NaCl (w_2 = 0.10)		
264.7	0.199	266.9	0.353
265.5	0.244	267.3	0.382
266.5	0.318	267.4	0.391

After hydrate formation, the temperature was raised to a value slightly below the predicted equilibrium temperature. Subsequently, the temperature was raised in steps of 0.1 K to dissociate the hydrate. The temperature was kept constant at every step for 3 h. 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 due to the change in the phase equilibria of the fluids. The point at which the slope of the pressure versus temperature plot changed abruptly was considered to be the hydrate dissociation point. Therefore, the equilibrium condition was determined on the basis of 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

Tables 1, 2, and 3 show experimentally measured equilibrium conditions of clathrate hydrates formed from propane and aqueous solutions of propanone, sodium chloride, and their mixtures, respectively. In the tables, w_1 and w_2 are represented to be concentrations of propanone and sodium chloride in solutions on a mass basis, respectively. To verify the experimental procedure, the equilibrium conditions for propane hydrates with pure water are compared with the previously reported values,[11−13] as shown in Figure 1. The comparison shows that the present results are consistent with the previous data.

The equilibrium conditions of clathrate hydrates with aqueous propanone solutions are shown in Figure 1. The investigated concentrations of propanone (1) were from w_1 = 0.05 to 0.30. The figure shows that the equilibrium temperatures of the clathrate hydrate decrease as the propanone concentrations increase. Therefore, propanone has an inhibiting effect on propane hydrate formation in contrast to methane hydrate formation.[4,5] The inhibition effect is suggested to be due to reduction of water activity by adding propanone to water. However, propanone can stabilize clathrate hydrates formed with methane, and adding propanone to propane hydrate can cause the destabilization of the propane hydrate.

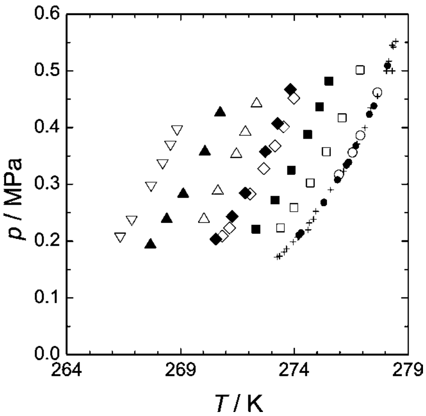

Figure 1. Equilibrium conditions of clathrate hydrates formed from propane and aqueous propanone solutions (1). ○, present study (pure water); □, present study ($w_1 = 0.05$); ■, present study ($w_1 = 0.10$); ◇, present study ($w_1 = 0.15$); ◆, present study ($w_1 = 0.16$); △, present study ($w_1 = 0.20$); ▲, present study ($w_1 = 0.25$); ▽, present study ($w_1 = 0.30$); ●, ref 10 (pure water); +, refs 11 to 13 (pure water).

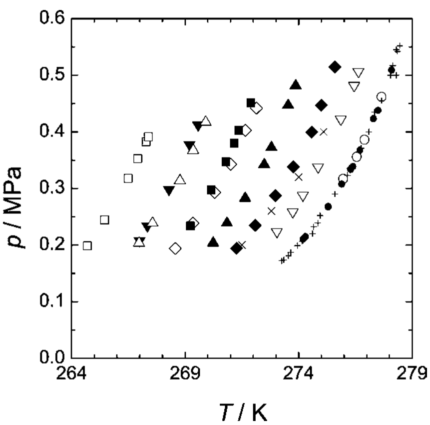

Figure 2. Equilibrium conditions of clathrate hydrates formed from propane and aqueous solutions of propanone (1) and sodium chloride (2). ○, present study (pure water); ▽, present study ($w_2 = 0.03$); ◆, present study ($w_2 = 0.05$); ▲, present study ($w_1 = 0.05$, $w_2 = 0.05$); ■, present study ($w_1 = 0.10$, $w_2 = 0.05$); ▼, present study ($w_1 = 0.15$, $w_2 = 0.05$); ◇, present study ($w_2 = 0.10$); △, present study ($w_1 = 0.05$, $w_2 = 0.10$); □, present study ($w_1 = 0.10$, $w_2 = 0.10$); ●, ref 10 (pure water); +, refs 11 to 13 (pure water); ×, ref 14 ($w_2 = 0.05$).

Table 4. Temperature Difference of Propane Hydrate Equilibria between Pure Water and an Aqueous Solution of Propanone and/or Sodium Chloride (x_1, x_2 = Mole Fraction of Propanone and NaCl)

w_1	w_2	x_1	x_2	ΔT/K
		Propanone		
0.05		0.0161		1.1
0.10		0.0333		2.2
0.15		0.0519		3.5
0.16		0.0558		3.7
0.20		0.0720		4.9
0.25		0.0937		6.4
0.30		0.1174		8.0
		NaCl		
	0.03		0.0094	1.4
	0.05		0.0160	2.6
	0.10		0.0331	5.4
		Propanone + NaCl		
0.05	0.05	0.0167	0.0166	3.9
0.10	0.05	0.0346	0.0172	5.6
0.15	0.05	0.0540	0.0179	7.5
0.05	0.10	0.0173	0.0344	7.2
0.10	0.10	0.0360	0.0358	9.5

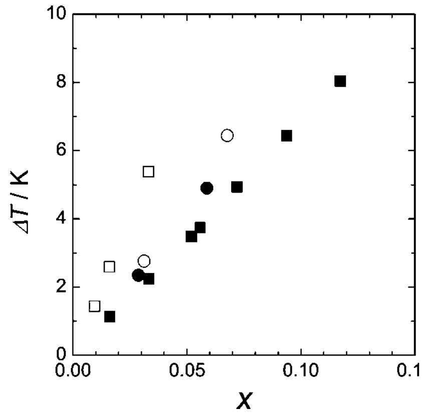

Figure 3. Comparison of inhibiting effect on propane hydrate formation (x = mole fraction of a chemical). ■, present study (propanone); □, present study (sodium chloride); ●, ref 10 (methanol: $w = 0.05$, 0.10 ($x = 0.0288$, 0.0588)); ○, ref 10 (ethylene glycol: $w = 0.10$, 0.20 ($x = 0.0312$, 0.0677)).

Equilibrium conditions of clathrate hydrates in the presence of propanone (1) and sodium chloride (2) are shown in Figure 2. As seen from the figure, the inhibiting effects on propane hydrate for the solutions of ($w_2 = 0.10$) and ($w_1 = 0.05$, $w_2 = 0.10$) are comparable to those for the solutions of ($w_1 = 0.10$, $w_2 = 0.05$) and ($w_1 = 0.15$, $w_2 = 0.05$), respectively.

These figures show that equilibrium temperatures of clathrate hydrates formed from propane and aqueous solutions of propanone and sodium chloride are lower than those formed from propane and pure water at the same pressures. The temperature differences of clathrate hydrates between each solution and pure water at a pressure of 0.3 MPa are calculated as shown in Table 4. In the table, x_1 and x_2 are the concentrations of propanone (1) and sodium chloride (2) on a mole basis, respectively. The temperature differences are also graphically shown as a function of the concentrations in solution in Figure 3. The inhibiting effects of propanone and sodium chloride on propane hydrate are compared with those of methanol and ethylene glycol reported in previous study.[10] As seen from the figure, sodium chloride is the most effective to inhibit propane hydrate formation than other compounds on a mole basis, and methanol and ethylene glycol are slightly more effective than propanone.

Conclusions

Equilibrium conditions of clathrate hydrates formed from propane and aqueous solutions of propanone and sodium chloride were experimentally measured in a temperature range of (264.7 to 276.9) K and pressures up to 0.514 MPa using an isochoric method. The investigated concentrations of propanone (1) and sodium chloride (2) were on a mass basis ($w_1 = 0.05$ to 0.30 and $w_2 = 0.03$ to 0.10, respectively). The equilibrium temperatures of the clathrate hydrates decrease as the propanone concentration in solution increases, indicating that propanone has an inhibiting effect on propane hydrate formation in contrast to methane hydrate formation. Propanone is less effective to inhibit propane hydrate formation than sodium chloride on a mole basis.

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