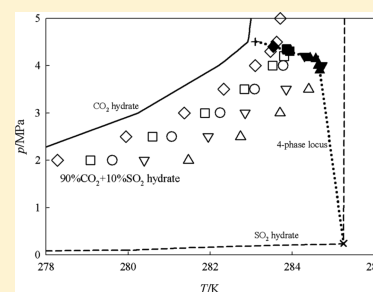# Phase Equilibria Containing Gas Hydrate of Carbon Dioxide, Sulfur Dioxide, and Water Mixtures

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ABSTRACT: Three- and four-phase hydrate equilibria for mixtures composed of carbon dioxide, sulfur dioxide and water were measured at pressures up to 5.00 MPa. Using Duhem's theorem on phase equilibrium, incipient hydrate-forming temperatures at given pressures with overall loading compositions of all components were measured, using an indirect visual phase equilibrium apparatus. In this study, effects of the relative amount of water to fixed composition of carbon dioxide and sulfur dioxide gas feed were studied. Phase equilibria were found to be sensitive to the water fraction at higher concentrations of sulfur dioxide in the gas feed but insensitive at lower concentrations. Four-phase equilibrium measurements showed the pseudoretrograde hydrate behavior.

■ INTRODUCTION

Hydrate-containing phase equilibria including carbon dioxide have been studied for flow assurance in applications such as carbon dioxide sequestration and enhanced oil recovery. In the carbon dioxide sequestration, carbon dioxide captured from flue gases may contain a small amount of water and sulfur dioxide as impurities despite efforts to remove them. Therefore, the influence of sulfur dioxide on incipient hydrate-forming conditions needs to be investigated.

Thermodynamic data for carbon dioxide, sulfur dioxide and water mixtures are available in only one literature source.[1] Such a system involves four different phases above the freezing point of water depending on temperature, pressure, and loading composition; water-rich liquid phase (L_W), hydrate phase (H), vapor phase (V), and guest-rich liquid phase (L_g). Beeskow-Strauch[1] reported $L_W-H_\infty-V$ three-phase equilibrium data with traces of hydrate phase (H_∞), which were given by temperatures, pressures, and 0.01 loading mole fraction of sulfur dioxide in the gas mixture without specifying the relative amount of water to guest contents. The literature data reported on the water-free basis are considered incomplete since equilibrium can be sensitive to the water contents at the same loading composition of the gas mixture. In the present study, experimental data are completely determined using Duhem's theorem, giving the incipient hydrate-forming temperature or pressure at a given pressure or temperature with known overall loading composition of all components.

$L_W-H_\infty-V-L_g$ four-phase behavior of binary guest and water system containing carbon dioxide has been investigated by several studies.[2−5] The four-phase behavior can be observed on the pressure−temperature plane when the $V-L_g$ two-phase loop of guests intersects with the incipient hydrate formation locus.[2] The degree of freedom is one for a four-phase system composed of three components. Therefore, a single four-phase curve is generated from the quadruple point of carbon dioxide

and water system to that of sulfur dioxide and water system, showing a pseudoretrograde hydrate behavior. The pseudoretrograde behavior denotes here that the incipient hydrate-forming temperature decreases as the pressure increases. Four-phase equilibrium data for these mixtures have not been reported by any other studies.

In the present study, three- and four-phase equilibrium data for carbon dioxide, sulfur dioxide, and water mixtures are determined by measuring temperatures, pressures, and overall loading compositions. Effects of the relative amount of water on the incipient hydrate-forming conditions are studied experimentally at a given loading ratio of the gas mixture. Phase behaviors for these mixtures are analyzed and discussed.

■ EXPERIMENTAL SECTION

Materials. Two different compositions of gas mixture composed of carbon dioxide and sulfur dioxide were investigated, and the sources and compositions were listed in Table 1. The mixed gas cylinder was prepared from PS Chemical Corp. (Busan, Korea), the composition of which was determined by measuring charged masses of each pure gas.

Table 1. Sources and Compositions of Gas Mixtures Used in Present Experiments

gas mixture name	source	composition[a]	
		carbon dioxide	sulfur dioxide
mixture 1	PS Chemical	0.990	0.010
mixture 2	PS Chemical	0.900	0.100

[a]Standard uncertainties of compositions are 0.001.

Triple distilled water was prepared by the water purification system from Human Corp. (Seoul, Korea) and degassed by ultrasonication for 30 min.

Apparatus and Procedures. Three- and four-phase equilibrium conditions were determined by measuring the isobaric dissolution temperatures of formed hydrates with an indirect visual phase equilibrium apparatus. The apparatus and procedure for this experiment were identical with those of Kim et al.[2] which were used for measurements of four-phase equilibria of mixtures composed of carbon dioxide, nitrogen, and water. While two pure gases of carbon dioxide and nitrogen were charged into the equilibrium cell separately in Kim et al., a single gas cylinder of the mixed gas with the predetermined composition was used in the present study for environmental and safety considerations. Schematic diagram of the apparatus and detailed procedures are available in Kim et al.

After the system was flushed and evacuated, triple-distilled water was introduced into the equilibrium cell through the vacuum suction. The mass difference of the water before and after its introduction to the system was measured using an Ohaus balance with an uncertainty of 0.03 g and taken as the amount of the water in the equilibrium cell. The mixed gas of carbon dioxide and sulfur dioxide in the gas buret was charged into the equilibrium cell. The amount of charged gases was determined by measuring the mass difference of the detached gas buret before and after its introduction to the system using the Ohaus balance. The whole system was immersed in the water bath of which the temperature was controlled within ± 0.03 K by an external circulator.

Hydrates were initially formed by lowering the temperature of the system. Then the mixtures were heated very slowly with an increase of temperature of 0.05 K every 10 h, while keeping the pressure constant manually using a pressure generator with an uncertainty of 0.01 MPa, until the hydrates visually disappeared. For the measurements at other pressures with the same loading compositions, the temperature was lowered again to form hydrate and the procedure was repeated. System pressures and temperatures were measured using a Sensys pressure transmitter with the resolution of 0.01 MPa and a Cole Parmer RTD thermometer with a resolution of 0.01 K, respectively. Expanded uncertainties of calibrated pressure and temperature gauges determined by the Korea Testing Laboratory were 0.01 MPa and 0.03 K with a coverage factor 2, respectively. Three- and four-phase equilibrium data were measured at (0.010 and 0.100) sulfur dioxide mole fraction in the gas mixture and listed in Tables 2 and 3 together with their uncertainties. The combined expanded uncertainties of equilibrium temperatures were estimated to be 0.16 K with coverage factor 2 ($k = 2$ with 99.7 % confidence level).

■ RESULTS AND DISCUSSIONS

Phase diagrams for 0.010 and 0.100 sulfur dioxide mole fraction of the gas mixture are shown in Figures 1 and 2 along with the incipient hydrate-forming loci for binary systems of carbon dioxide and water,[6] and sulfur dioxide and water.[7-10] Present data clearly indicate that the addition of sulfur dioxide to the system of carbon dioxide and water shifts the incipient hydrate-forming conditions to higher temperatures at the same pressures. At the same ratio of sulfur dioxide to carbon dioxide in the mixed gas, the loading mole fraction of water was varied from approximately 0.75 to 0.95 to examine the overall composition effect on the hydrate-forming conditions. L_W–H_∞–V and L_W–H_∞–L_g three-phase equilibrium for the ternary

Table 2. Experimental Values of Three- and Four-Phase Equilibrium Data at Loading Mole Fraction of Sulfur Dioxide in Gas Mixture y^a = 0.010, Overall Loading Mole Fraction z, pressure p, and temperature T for the System of Carbon Dioxide (1) + Sulfur Dioxide (2) + Water (3)^b

z_1	z_2	z_3	p/MPa	T/K
0.2483	0.0025	0.7492	2.00	277.52
$(0.0017)^c$	$(0.0002)^c$	$(0.0041)^c$	2.50	279.25
			3.00	280.57
			3.50	281.64
			4.00	282.62
			4.50^d	283.19^d
			5.00	283.22
0.1744	0.0018	0.8238	2.00	277.53
$(0.0020)^c$	$(0.0002)^c$	$(0.0048)^c$	2.50	279.25
			3.00	280.52
			3.50	281.70
			4.00	282.50
			4.30	282.95
			4.50^d	283.18^d
0.0878	0.0009	0.9113	2.00	277.41
$(0.0008)^c$	$(0.0001)^c$	$(0.0018)^c$	2.50	279.21
			3.00	280.57
			3.50	281.60
			4.00	282.52
			4.50^d	283.17^d
			4.64	283.15
			5.00	283.21
0.0497	0.0005	0.9498	2.00	277.37
$(0.0008)^c$	$(0.0001)^c$	$(0.0019)^c$	2.50	279.06
			3.00	280.44
			3.50	281.56
			4.00	282.30

$^a y = z_2/(z_1 + z_2)$. ^{b}Standard uncertainties u are $u(y) = 0.001$, $u(p) = 0.01$ MPa, and the combined expanded uncertainty U_c is $U_c(T) = 0.17$ K with coverage factor 2. ^{c}Standard uncertainties of loading compositions $u(z)$ are given in parentheses. ^{d}Four-phase equilibrium condition.

system has two degrees of freedom according to the Gibbs phase rule, allowing the equilibrium temperature to be dependent on the overall composition of the system at any given pressure. Kim and co-workers[11] also determined the overall composition effect for the system of carbon dioxide, water, and methanol, presenting different phase behavior when the amount of carbon dioxide was varied at the same methanol fraction in aqueous solution.

At the same sulfur dioxide fraction of 0.010 as shown in Figure 1, the three-phase equilibrium temperatures did not change significantly by the water loading fraction within their uncertainties since the amount of sulfur dioxide is so small that the overall composition effects become negligible. The literature data set of Beeskow-Strauch et al.[1] agreed with the present data sets within their uncertainties. As shown in Figure 2, incipient hydrate-forming conditions at the fraction of 0.100 sulfur dioxide were sensitive to the loading mole fraction of water or the overall mole fraction. The L_W–H_∞–V equilibrium temperatures decreased with the increase of the loading mole fraction of water at any given pressures. As the water fraction increases, the relative amount of sulfur dioxide to carbon dioxide in V or L_g decreases resulting from the difference of their solubilities to water, and thus the hydrate-containing
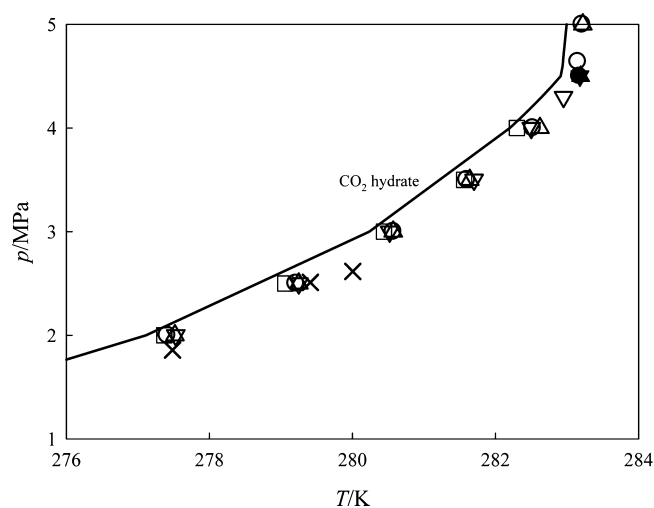
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Table 3. Experimental Values of Three- and Four-Phase Equilibrium Data at Loading Mole Fraction of Sulfur Dioxide in Gas Mixture y^a = 0.100, Overall Loading Mole Fraction z, Pressure p, and Temperature T for the System of Carbon Dioxide (1) + Sulfur Dioxide (2) + Water (3)^b

| z_1	z_2	z_3	p/MPa	T/K
0.2219	0.0247	0.7534	2.00	281.47
$(0.0034)^c$	$(0.0004)^c$	$(0.0083)^c$	2.50	282.74
			3.00	283.70
			3.50	284.40
			3.90^d	284.67^d
			4.00^d	284.63^d
			4.14^d	284.57^d
			4.16^d	284.43^d
0.1804	0.0200	0.7996	2.00	280.39
$(0.0019)^c$	$(0.0002)^c$	$(0.0046)^c$	2.50	281.95
			3.00	282.85
			3.50	283.85
			4.00^d	284.73^d
			4.20^d	284.30^d
0.1275	0.0142	0.8583	2.00	279.61
$(0.0008)^c$	$(0.0001)^c$	$(0.0020)^c$	2.50	281.06
			3.00	282.24
			3.50	283.08
			4.00	283.78
0.0833	0.0093	0.9074	2.00	279.08
$(0.0011)^c$	$(0.0001)^c$	$(0.0026)^c$	2.50	280.59
			3.00	281.87
			3.50	282.83
			4.00	283.52
			4.20	283.80
			4.30^d	283.94^d
			4.33^d	283.88^d
			4.35^d	283.86^d
0.0559	0.0062	0.9379	2.00	278.28
$(0.0009)^c$	$(0.0001)^c$	$(0.0021)^c$	2.50	279.95
			3.00	281.37
			3.50	282.33
			4.00	283.10
			4.30	283.47
			4.40^d	283.54^d
			4.50	283.62
			5.00	283.71

^{a} $y = z_2/(z_1 + z_2)$ ^{b}Standard uncertainties u are $u(y) = 0.001$, $u(p) = 0.01$ MPa, and the combined expanded uncertainty U_c is $U_c(T) = 0.17$ K with coverage factor 2. ^{c}Standard uncertainties of loading compositions $u(z)$ are given in parentheses. ^{d}Four-phase equilibrium condition.

Figure 1. Incipient hydrate-forming conditions at 0.010 loading mole fraction of sulfur dioxide in gas feed for systems of carbon dioxide (1) + sulfur dioxide (2) + water (3): △ (z_3 = 0.7492), ▽ (z_3 = 0.8238), ○ (z_3 = 0.9113), □ (z_3 = 0.9498), this work, 3-phase equilibria; ▲ (z_3 = 0.7492), ▼ (z_3 = 0.8238), ● (z_3 = 0.9113), this work, 4-phase equilibria; ×, ref 1; ——, ref 6, carbon dioxide hydrate.
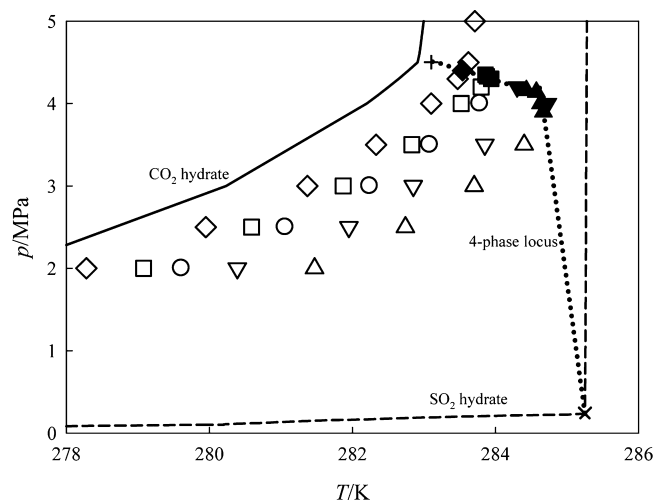
Figure 2. Incipient hydrate-forming conditions at 0.100 loading mole fraction of sulfur dioxide in gas feed for systems of carbon dioxide (1) + sulfur dioxide (2) + water (3): △ (z_3 = 0.7534), ▽ (z_3 = 0.7996), ○ (z_3 = 0.8583), □ (z_3 = 0.9074), ◇ (z_3 = 0.9379), this work, 3-phase equilibria; ▲ (z_3 = 0.7534), ▼ (z_3 = 0.7996), ● (z_3 = 0.8583), ■ (z_3 = 0.9074), ♦ (z_3 = 0.9379), this work, 4-phase equilibria; +, ref 12, quadruple point of carbon dioxide hydrate; ×, ref 10, quadruple point of sulfur dioxide hydrate; ——, ref 6, carbon dioxide hydrate; ref 7−10, sulfur dioxide hydrate; ·····, expected 4-phase locus.

phase equilibria of the ternary system shift toward those of the binary system of carbon dioxide and water, indicating a decreased effect of sulfur dioxide. In carbon dioxide sequestration including a very small amount of water, the effect of sulfur dioxide on the hydrate-forming conditions may increase showing higher equilibrium temperatures at given pressures.

Measured L_W−H_∞−V−L_g four-phase equilibrium data (filled points) are presented in Figure 2 together with quadruple points (Q2) of the binary systems of carbon dioxide and water,[12] and sulfur dioxide and water.[10] As the water mole fraction decreased, the pseudoretrograde hydrate behavior[13] was observed. For the water fraction of 0.7534, for example, at a

temperature of 284.2 K, formed hydrates dissociate with the pressurization from approximately 3.7 MPa to approximately 4.1 MPa. Similar behavior has been reported for other systems by a few researchers.[13−15] Ballard[13] noted that the pseudoretrograde behavior may be observed when sI and sII hydrate gases that have fairly low vapor pressures coexist in the mixture. Other systems[15] containing carbon dioxide, THF, and water exhibited the structural transformation from sII to sI hydrate, and it was believed to show the pseudoretrograde hydrate behavior. However, both carbon dioxide and sulfur dioxide form sI hydrate. The pseudoretrograde behavior in the present system may be produced by the relative Q2 position of two

binary systems. The univiariant four-phase locus is constructed from Q2 point of carbon dioxide and water system to that of sulfur dioxide and water system, showing the pseudoretrograde behavior as a dotted line in Figure 2. Predicted results by CSMGem[6] program showed the similar behavior for mixtures composed of carbon dioxide, hydrogen sulfide, and water without any structure changes.

CONCLUSIONS

In this work, hydrate-containing phase equilibria for mixed guests of carbon dioxide and sulfur dioxide were experimentally examined by measuring the incipient hydrate-forming temperatures at given pressures and accurately predetermined loading compositions in both three-phase ($L_W-H_\infty-V$ and $L_W-H_\infty-L_g$) and four-phase ($L_W-H_\infty-V-L_g$) regions. The incipient hydrate-forming conditions were found to shift to higher temperatures by the addition of sulfur dioxide. At a fixed sulfur dioxide mole fraction of 0.100 in the gas mixture, the increase of water fraction in feed significantly decreased the isobaric dissolution temperatures, whereas at a 0.010 sulfur dioxide fraction the measured equilibrium conditions were slightly affected by the water fraction. In the four-phase region, pseudoretrograde hydrate behavior was observed, and it arose from the relative position of two quadruple points of carbon dioxide and water, and sulfur dioxide and water systems.

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Notes

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