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Phase Equilibria of Mixed Gas Hydrates of Oxygen + Tetrahydrofuran, Nitrogen + Tetrahydrofuran, and Air + Tetrahydrofuran

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ABSTRACT: In this work, hydrate phase equilibrium data for oxygen + tetrahydrofuran (THF) + water, nitrogen + THF + water, and air + THF + water systems were measured in the temperature range of (281.84 to 303.63) K and the pressure range of (0.981 to 29.527) MPa at (5.13 or 5) mol % of THF. All hydrate phase equilibrium data were measured using an isochoric method. The hydrate dissociation conditions for methane + sodium dodecyl sulfate (SDS) + water system and oxygen + SDS +water system were measured and compared with the data reported in the literature, and the good agreement between them demonstrates the reliability of method and the experimental apparatus used in this work. The results show that THF can enlarge the hydrate stability zone compared with the corresponding single gas hydrates system. In the air + water system, the hydrate equilibrium pressure can be reduced to 0.981 MPa at the temperature of 281.84 K by addition of 5 mol % of THF, which provides valuable information for research on the air separation by hydrate crystallization.

INTRODUCTION

Clathrate hydrates are ice-like compounds in which guest molecules of suitable size are trapped in cages that are composed of hydrogen-bonded water molecules. Clathrate hydrates are classified into three distinct structures, sI, sII, and sH.[1] There is considerable interest in the application of hydrate crystallization technology, such as gas storage,[2−6] gas separation and transportation,[7−14] etc. However, high pressure and low temperature are required to form pure gas hydrates. Reducing hydrate formation pressure is a bottleneck issue for the wide application of hydrate technology.

It has been demonstrated that tetrahydrofuran (THF) can form stable sII hydrates with water at atmospheric pressure when the temperature is below 278 K.[15] There are 16 small cages and 8 large cages per unit cell of THF hydrate, and THF molecules reside only in the large cages, and the small ones are left to be free.[16] With the help of THF hydrate, gas molecules can stabilize the small cages at low pressure and high temperature compared with those for formation of single gas hydrates.[1]

The information of hydrate phase equilibrium data is critical for the aforementioned process based on hydrate formation. So, there are experimental results or thermodynamic data available about adding THF as a guest molecule to help stabilize the hydrate cages to reduce the synthesis pressures of single gas hydrates. There are reports on the phase equilibrium conditions for the mixed hydrate systems of THF + hydrogen + water,[15,17−19] THF + methane + ethane + water,[20] THF + nitrogen + water,[21,22] THF + carbon dioxide + water,[22] THF + methane + water,[21−23] THF + hydrogen sulfide + water,[23] THF + krypton + water,[24] THF + methyl fluoride + water,[25] THF + carbon dioxide + nitrogen + water,[26] THF + carbon dioxide + hydrogen + water,[27] THF + methane + hydrogen + water,[28] and THF + methane + ethylene + water.[29] However, to the best of our knowledge, the experimental hydrate equilibrium data for oxygen + THF + water and air + THF + water systems have not been reported.

It is well-known that air is mainly composed of 78 mol % of nitrogen and 21 mol % of oxygen. During the formation process of THF-air mixed hydrate, oxygen molecules can stabilize the small cages more easily than nitrogen molecules due to the greater size ratio(guest diameter to cage diameter) of the former.[1] It is possible that oxygen could be concentrated in the hydrate phase of THF + air + water system. If this assumption can be proved, there would be a novel method can be developed for air separation by hydrate crystallization, which is wide required in many industries.[30]

The objective of this work is to measure the hydrate equilibrium data for the systems of oxygen + THF + water, nitrogen + THF + water, and air + THF + water, which are essential for air separation by hydrate crystallization.

EXPERIMENTAL SECTION

Preparation of Materials. The materials used in this work are provided in Table 1, along with their purities and suppliers. In this work, the solution used is the mixture of water + THF or sodium dodecyl sulfate (SDS). All of the solutions were prepared at the room temperature and atmospheric pressure. The preparation of THF solution was done by the following steps: A certain amount of water and THF were weighted successively, then the water was poured into THF as quickly as one can to avoid volatilization of THF, and subsequently the solution was introduced into the vessel after being stirred with a glass rod to make them well-distributed. The process of preparation of SDS solution is as follows: A certain amount of water and SDS were weighted successively at first, then SDS was added into water, and finally the SDS aqueous solution was stirred with a glass rod to make them well-distributed. Water, SDS, and THF were weighed on an electronic balance with an accuracy of ± 0.1 mg. Distilled water was used in all experiments.

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Experimental Apparatus. A schematic diagram of the experimental apparatus used to determine the phase equilibrium data is shown in Figure 1. The main part of the apparatus is a titanium cylindrical vessel with an effective volume of 450 cm^3 (SEPAREX, France). The allowable working pressure and temperature ranges are (0 to 70) MPa and (233 to 473) K, respectively. There are three sapphire sight glasses (20 mm in diameter) which allows for visual observations on the phase transformation inside the vessel. In addition, a digital camera (Philips) and a TV adapter (HIPP) with an optical lens and an endoscope, located at the right side window, are used to record the hydrate formation and dissociation.

A magnetic coupling stirrer (M310, (100 to 1300) rpm, PREMEX) is installed at the bottom of the vessel to agitate the fluids and hydrate crystals. A platinum resistance thermometer (TC Direct-PT100) with an uncertainty of 0.01 K is inserted horizontally into the vessel from the center of the back side to measure the temperature. A pressure transducer (TP14LRBH31R, REP) within 0.001 MPa in accuracy is used to measure the pressure. The temperature of the vessel is controlled by a surrounding jacket filled with circulating silicone oil from a thermostatic bath (OPTIMUS) and the bath temperature is controlled by a thermal resistance (HUBER) integrated in chiller/heater.

The gas in the vessel can be pressurized by a hand pump (Hai'an Scientific Research Apparatus Co., China). All temperature and pressure data are recorded every second and controlled by the 4247 software (SEPAREX, France).

Table 1. Materials Used in the Experiments

component	purity (%)	supplier
methane	99.99	Guangzhou Yinglai Gas Co., Ltd.
oxygen	99.999	Foshan Analytical Instrument Co., Ltd.
nitrogen	99.9	Guangzhou Yinglai Gas Co., Ltd.
air		Guangzhou Yinglai Gas Co., Ltd.
sodium dodecyl sulfate(SDS)	≥9 9.0	Shanghai Bio Science & Technology Co., Ltd.
tetrahydrofuran (THF)	≥ 99.0	Sinopharm Chemical Reagent Co., Ltd.
water		distilled

Experimental Method. The experimental apparatus was adjusted with a standard thermal resistance and pressure gage. Before every experiment, the hand pump and the vessel were well cleaned with distilled water and SDS or THF aqueous solution, successively. The vessel was subsequently purged with oxygen or nitrogen for at least three times to remove any residual air and vacuumized to 10 Pa. After the solution was introduced into the vessel, the reactor is pressurized to the desired level by supplying gas from a cylinder and by injecting SDS or THF solution with the hand pump. When the temperature and pressure inside the vessel were stable, the magnetic stirrer was initiated and the thermostatic bath was started to decrease the temperature gradually inside the vessel to form hydrate. Hydrate formation in the vessel was detected by a decrease in pressure and an increase in temperature, and this also could be confirmed by visual observation.

The isochoric method was used to measure hydrate phase equilibrium data for systems of oxygen + SDS + water, methane + SDS +water, oxygen + THF + water, and nitrogen + THF + water. Once the hydrate formation process was finished, the temperature was increased at 1 $K \cdot h^{-1}$ and $P-T$ curve was plotted. The point at which the slope of the $P-T$ curve sharply changed was considered as the critical point. Above this point, the temperature was increased gradually to a desired value and 4 h was required to establish equilibrium adequately at this temperature. The final temperature and pressure were regarded as three phase equilibrium data.

As for measuring hydrate phase equilibrium data for the air + THF + water system, the isochoric pressure-search method was used.[31] For each round, both cooling and heating curves were required to be plotted. To obtain the cooling curve, three points should be measured in the large temperature steps of (3 to 5) K and 30 min was required at each temperature for achieving adequate equilibrium.[31] Once the hydrate had formed, the temperature was increased gradually at (1 to 3) $K \cdot h^{-1}$, and the temperature and pressure were measured continuously. The hydrate crystals inside the vessel were began to dissociate when there was an increase in pressure. Above this temperature, three points should be measured in order to obtain the heating $P-T$ curve, and 4 h was required to establish sufficient equilibrium at each temperature. The intersection point of the cooling and heating $P-T$ curves was confirmed to be a phase equilibrium data.

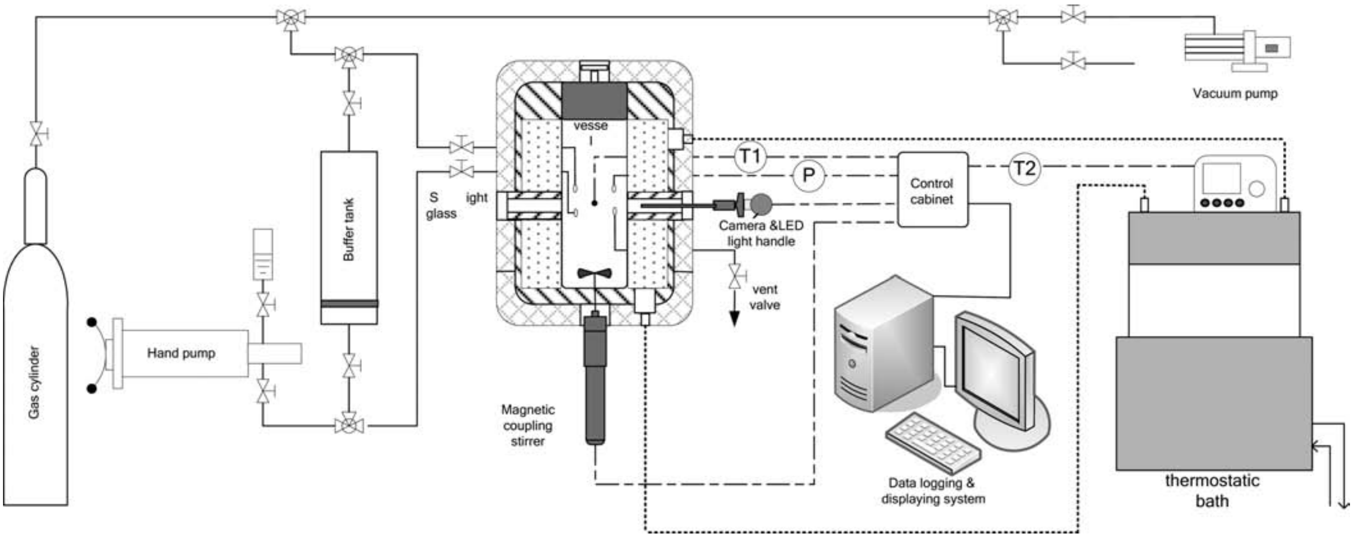

Figure 1. Experimental apparatus for measuring hydrate phase equilibrium.

Table 2. Hydrate Phase Equilibrium Data for Methane + SDS + Water System Measured at 500 ppm of SDS

T/K	P/MPa
273.31	2.941
275.23	3.474
277.14	4.145
279.17	5.044
281.18	6.112
283.21	7.457

Table 3. Hydrate Phase Equilibrium Data for Oxygen + SDS + Water System Measured at (200 and 500) ppm of SDS, Respectively

SDS concentration	T/K	P/MPa
200 ppm	276.42	17.394
	278.35	21.470
	280.27	26.627
	282.21	33.205
	284.19	41.994
500 ppm	283.20	38.420
	285.98	46.075
	287.14	58.525
	288.08	64.745

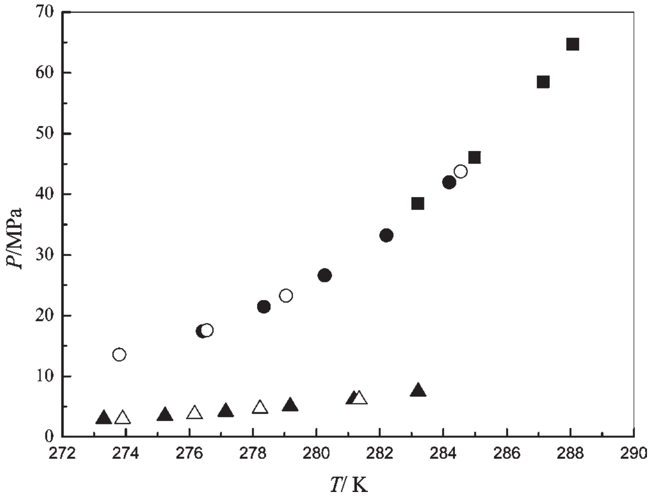

Figure 2. Hydrate dissociation conditions for oxygen + SDS + water and methane + SDS + water systems. Oxygen + SDS + water system: (○) without SDS, Mohammadi et al.;[32] (●) 200 ppm of SDS, this work; (■) 500 ppm of SDS, this work; methane + SDS +water system: (Δ) 500 ppm of SDS, Le et al.;[33] (▲) 500 ppm of SDS, this work.

■ RESULTS AND DISCUSSION

To check the reliability of the experimental apparatus and method used in this work, the hydrate equilibrium data for methane + SDS + water and oxygen + SDS + water systems were measured. The results are presented in Tables 2 and 3, respectively, and are plotted in Figure 2. The data measured in this work are consistent with those from the literature,[32,33] which confirms the accuracy of experimental apparatus and the feasibility of the phase equilibrium method used in this work.

Table 4. Hydrate Phase Equilibrium Data for Oxygen + THF + Water System Measured at 5.13 mol % of THF

T/K	P/MPa
286.10	2.130
289.95	3.879
293.91	7.192
297.79	11.956
303.63	25.812

Table 5. Hydrate Phase Equilibrium Data for Nitrogen + THF + Water System Measured at 5 mol % of THF

T/K	P/MPa
295.75	10.930
297.72	14.034
299.63	17.701
301.64	23.071
303.60	29.527

Table 6. Hydrate Phase Equilibrium Data for Air + THF + Water System Measured at 5 mol % of THF

T/K	P/MPa
281.84	0.981
286.85	2.909
289.00	4.287
291.54	6.230
294.18	9.296
296.74	11.646
299.41	16.685

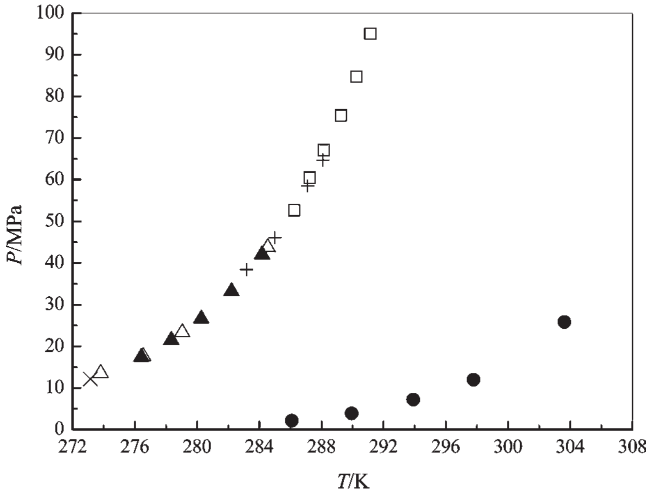

Figure 3. Hydrate dissociation conditions for oxygen + water, oxygen + SDS + water, and oxygen + THF + water systems. Oxygen + water system: (Δ) Mohammadi et al.;[32] (×) van Cleeff et al.;[35] (□) van Cleeff et al.;[36] oxygen + SDS + water system: (▲) 200 ppm of SDS, this work; (+) 500 ppm of SDS, this work; oxygen + THF + water system: (●) 5.13 mol % of THF, this work.

In our test experiment in the higher pressure range, SDS was used to reduce the induce time of hydrate formation.[34] The

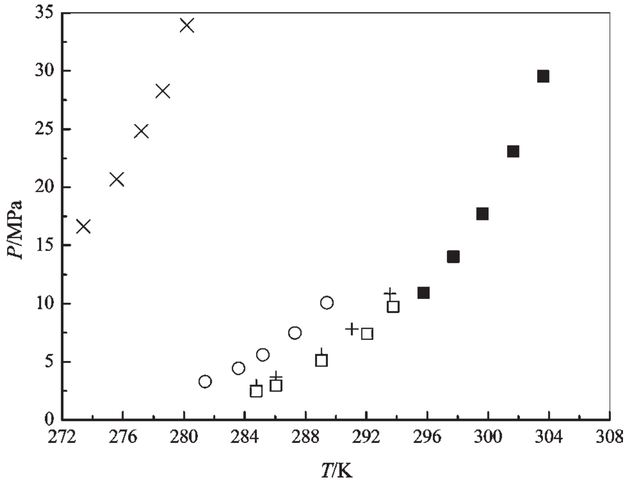

Figure 4. Hydrate dissociation conditions for nitrogen + THF + water system: (×) without THF, Sloan et al.;[1] (○) 1.1 mol % of THF, Mohammadi et al.;[22] (+) 3 mol % of THF, Seo et al.;[21] (□) 5 mol % of THF, Seo et al.;[21] (■) 5 mol % of THF, this work.

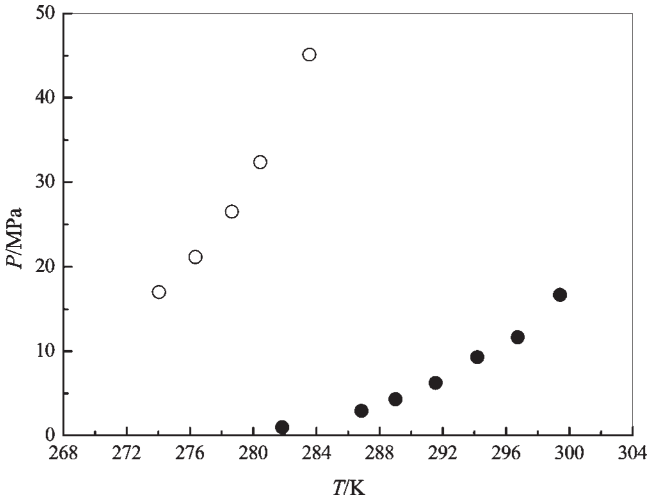

Figure 5. Hydrate dissociation conditions for air + THF + water system: (○) without THF, Mohammadi et al.;[32] (●) 5 mol % of THF, this work.

measured hydrate dissociation conditions for oxygen + SDS + water system at (200 and 500) ppm of SDS are listed in Table 3 and plotted in Figure 2, along with those for the oxygen + water system. The results show that SDS has little effect on the phase equilibrium, which agrees with the previous work.[33]

Measured hydrate phase equilibrium data for systems of oxygen + THF + water, nitrogen + THF + water, and air + THF + water at (5.13 or 5) mol % of THF are listed in Tables 4, 5, and 6, respectively, and are also plotted in Figures 3, 4, and 5, respectively.

Figure 3 shows the hydrate dissociation conditions for oxygen + THF + water system measured at 5.13 mol % of THF, and those for oxygen + water system[32,35,36] and oxygen + SDS + water system are also presented for comparison. As shown in Figure 3, the hydrate equilibrium pressures are reduced dramatically by addition of THF. The higher the temperature, the more reduction the pressure. In our measured temperature scope, the hydrate phase equilibrium pressures are reduced by at least 50 MPa in the oxygen + water system by addition of THF.

The same promoter effect of THF on hydrate formation was found in nitrogen + water system. The phase equilibrium data for nitrogen + THF + water system measured at 5 mol % of THF are listed in Table 5 and presented in Figure 4, along with those selected from the literature for comparison.[1,21,22] The hydrate equilibrium temperatures in the nitrogen + THF + water system are higher by at least 26 K than those in nitrogen + water system. As shown in Figure 4, the hydrate stability zone is enlarged with the increase of THF mole concentration, However, it seems that the influence of THF on hydrate stability zone becomes tiny, when the THF concentration is greater than 3 mol %, especially in the low temperature range.

Figure 5 displays the hydrate phase equilibrium data for the air + THF + water system measured at 5 mol % of THF along with the comparison data for air + water system,[32] and the results are also listed in Table 6. The results show that the phase equilibrium pressures in air + water system are reduced by at least 38 MPa with addition of THF.

■ CONCLUSIONS

This work reports the hydrate phase equilibrium data for the systems of oxygen + THF + water, nitrogen + THF + water, and air + THF + water, which were measured in the temperature range of (281.84 to 303.63) K and the pressure range of (0.981 to 29.527) MPa at (5.13 or 5) mol % of THF. The isochoric method was used in the all measurements, there is a good agreement between the hydrate phase equilibrium data for methan + SDS + water system or oxygen + SDS + water system measured in this work and those reported in the literature, which demonstrates the reliability of data we measured in this work. The comparison results between the hydrate phase equilibrium data for the systems for oxygen + THF + water, nitrogen + THF + water, and air + THF + water and those for the systems in the absence of THF show that THF can enlarge the hydrate stability zone. The hydrate phase equilibrium data we have measured are essential to the research on air separation by hydrate crystallization.

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