Hydrate Equilibrium Conditions of (CH_4 + C_2H_6 + C_3H_8) Gas Mixtures in Sodium Dodecyl Sulfate Aqueous Solutions[†]

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Three-phase equilibrium conditions of (CH_4 + C_2H_6 + C_3H_8) mixtures (V) + hydrate (H) + aqueous solutions of sodium dodecyl sulfate (L_W) are determined using a sapphire cell apparatus according to an isochoric isothermal dissociation method at four temperatures, 275.2 K, 277.0 K, 278.8 K, and 280.6 K. The propane mole fraction in each equilibrium state is from 0.45 % to 16.98 %. Sodium dodecyl sulfate was used as a kinetic promoter as it has been shown that it has no influence on the phase equilibrium. The experimental data are in accord with those calculated by the hydrate thermodynamic models.

Introduction

Gas hydrates are solid crystalline compounds stabilized by the inclusion of guest molecules inside the cavities formed by water molecules through hydrogen bonding. Three kinds of hydrate structures (sI, sII, sH) have been confirmed. Hydrate forms at specific temperature−pressure conditions for a specific gas or gas mixture. Since CH_4, C_2H_6, and C_3H_8 are major components of natural gas, hydrates formed from them are of special concern. Many phase equilibrium measurements have been made, but most of them have been on pure or binary guest components.[1] There is limited quantitative experimental hydrate data for ternary guest components. (CH_4 + C_2H_6 + C_3H_8) mixtures (V) form sII hydrate (H) with water, but experimental equilibrium data are lacking.[1] Holder and Hand[2] measured three compositions of (CH_4 + C_2H_6 + C_3H_8) + hydrate V−H−L_W dissociation conditions by a pressure searching method. Sun et al.[3] measured a mole fraction mixture of CH_4 (0.9196) + C_2H_6 (0.0513) + C_3H_8 (0.0291) V−H−L_W equilibrium conditions in pure water and aqueous ethylene glycol solutions.

For a gas mixture hydrate system, gas phase compositions change as the hydrate forms and dissociates.[4] The relative concentration of each component in the hydrate phase and that in the residual vapor phase differ, which is a method to separate a gas mixture through the formation of hydrate.[5,6] In addition, the different solubility of each component in the gas mixture in water will change the gas phase compositions. If using the pressure searching method, the water quantity must be relatively small to avoid the variation of gas compositions due to the different solubility of gases in water, and the gas phase is generally replaced several times with the gas sample in the gas cylinder during the measurement to maintain the constant compositions in the gas phase.[7] The experimental procedure is thus time-consuming. In this work, the step-heating method or continuous-heating method which has been used for pure gas hydrate equilibrium[8] was modified and extended to determine the (V−H−L_W) three-phase equilibrium conditions for (CH_4 + C_2H_6 + C_3H_8) mixtures, which was called the isochoric−isothermal method. An anionic surfactant was added to reduce the formation time of hydrate. The hydrate dissociation equilibrium pressures at different gas compositions were determined for four temperatures, 275.2 K, 277.0 K, 278.8 K, and 280.6 K. The C_3H_8 mole fraction in the equilibrium gas phase was from 0.45 % to 16.98 %.

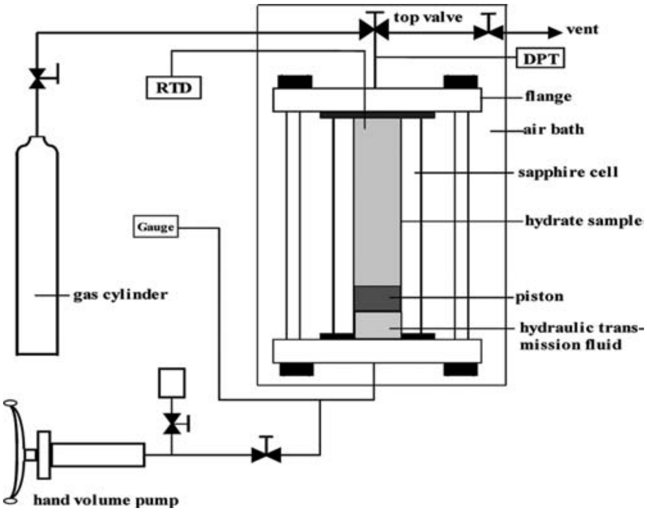

Figure 1. Schematic of the experimental apparatus.

Experimental Section

Apparatus. The experimental apparatus used in this work has been described in detail in previous papers.[9,10] A schematic of the apparatus is shown in Figure 1. The apparatus consists of a cylindrical transparent sapphire cell (2.54 cm in diameter, 10 cm in length) installed in an air bath with a view window and equipped with a magnetic stirrer for accelerating the equilibrium process. The formation and dissociation of the hydrate crystals in the solution can be observed directly. The pressure was measured by a MIDA-OEM pressure transducer manufactured by AdAstrA Company (Russia) with an uncertainty of ± 0.025 MPa. The temperature in the sapphire cell was measured by a PT-100 platinum resistance thermometer with an uncertainty of 0.1 K. The air bath temperature was stable within ± 0.1 K.

Materials and Preparation of Samples. Analytical grade CH_4 (99.99 %), C_2H_6 (99.95 %), and C_3H_8 (99.95 %) supplied by Beijing Beifen Gas Industry Corporation were used for preparing

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the gas mixtures. Compositions of gas mixtures were analyzed by an HP 6890 gas chromatograph with an uncertainty of ± 0.0002. The sodium dodecyl sulfate (SDS, analytical reagent) supplied by Beijing Reagents Corporation was used to reduce the formation time of hydrate. An electronic balance with a precision of ± 0.1 mg was used in measuring the mass of SDS. Deionized distilled water was used in preparing the aqueous solution with a mass fraction of SDS $= 6.5 \cdot 10^{-4}$.

Experimental Procedure. The isochoric isothermal dissociation method was used to determine hydrate phase equilibrium conditions. Compared with the pressure searching method, a large amount of hydrate is initially formed. After the sapphire cell had been washed three times by distilled water and dried, about 20 mL of SDS aqueous solution was added into the cell. The gas space of the cell was purged with the gas mixture four to five times to ensure the absence of air. The temperature of the air bath was then set to 273.7 K. Once the temperature of the solution was lower than 274 K, the gas mixture was fed in until the desired pressure was achieved. The feed pressure was much higher than the estimated equilibrium pressure value at the specified temperature to ensure hydrate formation. The magnetic stirrer was turned on to induce and accelerate the hydrate formation. During the formation of hydrate, the pressure in the cell decreased. When the pressure drop was less than 0.01 $\text{MPa} \cdot \text{h}^{-1}$, hydrate formation was considered to be complete, and part of the remaining gas was discharged slowly. The pressure in the sapphire cell was decreased to be about (0.3 to 0.5) MPa below the estimated equilibrium pressure which was calculated by CSMGem[1] from the feed gas compositions. At the same time, the air bath was set to the specified temperature which was in general higher than the hydrate formation temperature. Since the experimental pressure was lower than the equilibrium pressure at the specified temperature, the hydrate began to dissociate. The top valve of the cell was closed to make it be an enclosed system. The changes in the system pressure of the samples with elapsed time were recorded online by a computer. If the system pressure increased by less than 0.01 MPa in 3 h, the enclosed system was then considered as to be at equilibrium. The current temperature and pressure were then deemed to be the equilibrium conditions. About 35 cm^3 of the gas mixture (at atmospheric pressure) in the cell was sampled through the valve on the top flange of the cell. The gas sample was analyzed by HP 6890 GC immediately, and the corresponding compositions were then assumed as the equilibrium compositions at the equilibrium pressure and temperature.

Afterward, due to the drop of pressure as a result of sampling, the hydrate continued to dissociate at the constant temperature. Another group of equilibrium composition−pressure data was then obtained at the same temperature. The experimental procedure at this temperature was terminated until hydrate was almost completely dissociated.

The experimental equilibrium data at other temperatures were performed according to the above procedure.

Results and Discussion

Influence of SDS. SDS is a hydrate formation promoter used to shorten the induction time and enhance the formation rate of hydrate when a suitable (about $w = 6.5 \cdot 10^{-4}$) amount was added to the aqueous phase.[11−15] For the experimental method used in this work, an adequate amount of hydrate needed to be prepared. The influence of SDS on the equilibrium of hydrate was checked.

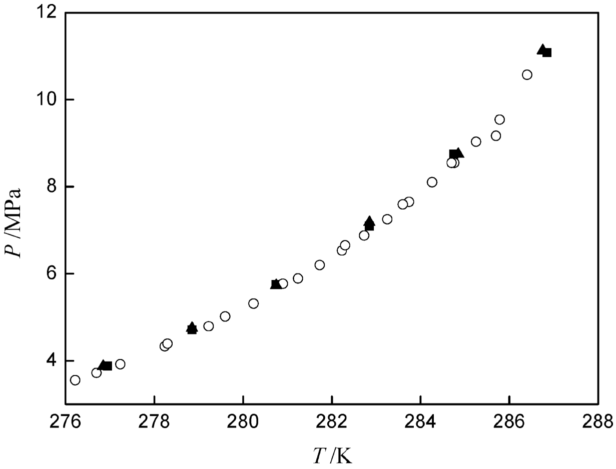

Figure 2. Comparison of measured CH_4 hydrate phase equilibrium conditions in deionized water and $6.5 \cdot 10^{-4}$ SDS aqueous solution with literature values. ■, deionized water; ▲, $w = 6.5 \cdot 10^{-4}$ SDS aqueous solution; ○, pure water, literature data[16,17] (pressure searching method).

The phase equilibrium data for CH_4 + deionized water and CH_4 + initial $w = 6.5 \cdot 10^{-4}$ SDS aqueous solution obtained by the isochoric isothermal dissociation method are shown in Figure 2. In comparison, the literature data[16,17] for CH_4 + pure water were also illustrated. The equilibrium conditions of the CH_4 hydrate formed with SDS agree with the literature data in the range of (276 ∼ 287) K and (3 ∼ 11) MPa. After adding SDS, the equilibrium data of temperature and pressure hardly changed. It should be noted that SDS concentration is not a constant in the formation/dissociation process. Since SDS could adsorb on hydrate particles,[18,19] the SDS concentration during hydrate formation/dissociation is difficult to determine. Lee et al.[20] found that the equilibrium dissociation pressures of CH_4 hydrates at SDS concentrations ranging from $w = 2.5 \cdot 10^{-4}$ to $100 \cdot 10^{-4}$ were not much different from pure water. Gayet et al.[21] also found SDS did not have any influence on the CH_4 hydrate equilibrium. However, with SDS, the nucleation and growth of the hydrate were more rapid.

Experimental Results for Gas Mixtures. The hydrate equilibrium pressure of ($CH_4 + C_2H_6 + C_3H_8$) mixtures at different gas compositions was determined for the four temperatures, 275.2 K, 277.0 K, 278.8 K, and 280.6 K, using the isochoric−isothermal method with initial $w = 6.5 \cdot 10^{-4}$ SDS added to enhance the hydrate formation rate. The mole fractions of the feed gas mixture were at CH_4 (86.82 %) + C_2H_6 (8.57 %) + C_3H_8 (4.61 %). The experimental results are listed in Table 1. For comparison, the equilibrium pressures for the CH_4 (85.97 %) + C_2H_6 (11.79 %) + C_3H_8 (2.24 %) gas mixture at 277.0 K in accord with that in Table 1 were also determined using the pressure searching method. During the experimental process using this method, the gas phase was replaced three times with the gas sample to maintain the constant compositions in the gas phase. The measurement equilibrium pressure value is 1.35 MPa, which is close to 1.33 MPa determined by the isochoric−isothermal method. Comparatively, the experimental procedure by the pressure searching method is time-consuming. It will need more than 24 h to determine one equilibrium temperature−pressure data point.

The calculated values by CSMGem[1] and the Chen-Guo model (a thermodynamic model for the prediction of the hydrate formation conditions based on a two-step hydrate formation mechanism)[22,23] are also listed in Table 1. The formation of sII hydrate was assumed during the calculation in this work. The average relative deviation between experimental pressure data

Table 1. Three-Phase Equilibrium (V−H−L_W) Condition Experimental Data for CH_4 (1) + C_2H_6 (2) + C_3H_8 (3), Feed Gas (V) Composition: x_1 = 0.8682, x_2 = 0.0857, x_3 = 0.0461

			T	P	calculated by CSMGem[1]		calculated by Chen-Guo model[22,23]	
100x_1	100x_2	100x_3	K	MPa	P_{cal}/MPa	100ARD[a]	P_{cal}/MPa	100ARD
95.44	4.11	0.45	275.2	1.83	1.67	8.74	1.65	9.84
92.32	6.79	0.89		1.28	1.37	7.03	1.33	3.91
91.01	7.77	1.22		1.31	1.26	3.82	1.22	6.87
87.78	10.58	1.64		1.16	1.14	1.72	1.09	6.03
80.42	15.55	4.03		0.79	0.87	10.13	0.83	5.06
72.37	17.16	10.47		0.61	0.64	4.92	0.60	1.64
93.93	5.58	0.49	277.0	2.10	1.92	8.57	1.89	10.00
90.77	8.22	1.01		1.68	1.60	4.76	1.56	7.14
85.97	11.79	2.24		1.33	1.29	3.01	1.24	6.77
81.49	14.16	4.35		1.08	1.06	1.85	1.02	5.56
75.98	16.31	7.71		0.83	0.89	7.23	0.85	2.41
92.41	6.60	0.99	278.8	2.02	2.03	0.50	1.99	1.49
88.45	8.95	2.60		1.65	1.56	5.45	1.52	7.88
87.79	9.29	2.92		1.46	1.50	2.74	1.46	0.00
82.43	11.84	5.73		1.24	1.21	2.42	1.18	4.84
74.83	16.64	8.53		1.03	1.08	4.85	1.04	0.97
72.38	16.60	11.02		0.93	0.99	6.45	0.95	2.15
69.52	13.50	16.98		0.80	0.85	6.25	0.81	1.25
94.06	5.43	0.51	280.6	2.98	2.89	3.02	2.86	4.03
94.25	5.03	0.72		2.86	2.75	3.85	2.73	4.55
91.22	7.58	1.20		2.34	2.36	0.85	2.32	0.85
89.37	8.72	1.91		2.24	2.09	6.70	2.05	8.48
87.09	10.69	2.22		1.98	1.98	0.00	1.94	2.02
82.29	13.74	3.97		1.71	1.68	1.75	1.64	4.09
77.33	13.56	9.11		1.21	1.30	7.44	1.27	4.96

[a] Average relative deviation (ARD) = ($|P_{exp} - P_{cal}|$)/(P_{exp}).

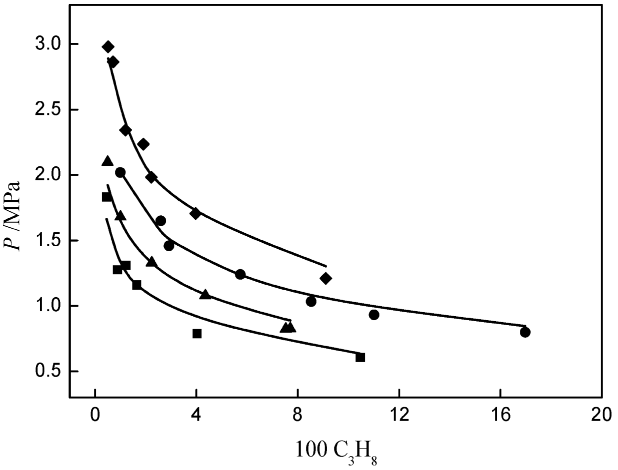

Figure 3. Comparison of measured and calculated equilibrium conditions at different compositions and temperatures for CH_4 + C_2H_6 + C_3H_8 (V)−hydrate (H)−aqueous solutions of $w = 6.5 \cdot 10^{-4}$ SDS (L_W). ■, 275.2 K; ▲, 277.0 K; ●, 278.8 K; ◆, 280.6 K; —, calculated line by CSMGem.[1]

with those calculated by CSMGem and the Chen-Guo model is 4.6 % and 4.5 %, respectively. The biggest difference between experimental and calculated pressures is 0.20 MPa. Figure 3 shows the comparison of measured and calculated equilibrium pressure at different C_3H_8 mole fractions and temperatures in Table 1. The measured data are in good agreement with the calculated values.

In addition, it was found that when C_3H_8 mole fraction in the equilibrium compositions is the lowest, the pressure difference between the experimental data and calculated values is the largest for temperatures of 275.2 K and 277.0 K. It is known that there exits a structure transition for the (CH_4 + C_2H_6) gas mixture hydrate[24] and the (C_2H_6 + C_3H_8) gas mixture hydrate.[25] sI and sII hydrate could coexist for the (CH_4 + C_2H_6 + C_3H_8) mixture.[25,26] Schicks et al.[25] indicated the presence of the (CH_4 + C_2H_6 + C_3H_8) hydrate structure transition from V + L + sII to V + sI + sII and confirmed the existence of sI for the CH_4 ($x = 0.98$) + C_3H_8 ($x = 0.02$) hydrate by Raman spectra. In this work, sI hydrate might also coexist with sII hydrate for the systems when C_3H_8 mole fraction is lower than 0.5 %, which results in the measured equilibrium pressures being higher than calculated value.

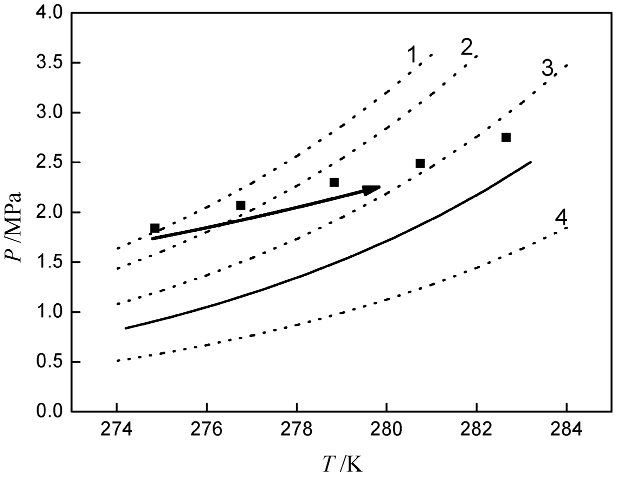

Figure 4. Comparison of experimental equilibrium conditions of CH_4 + C_2H_6 + C_3H_8 (V)−hydrate (H)−aqueous solutions of $w = 6.5 \cdot 10^{-4}$ SDS (L_W) with the calculated results using the Chen-Guo model[22,23] according to feed gas mixture mole fraction: CH_4 (89.3 %) + C_2H_6 (7.8 %) + C_3H_8 (2.9 %). ■, experimental data; solid line, calculated using the Chen-Guo model according to feed gas mixture compositions; dotted line, equilibrium line of different mole fractions calculated using the Chen-Guo model; 1, CH_4 (95.0 %) + C_2H_6 (4.9 %) + C_3H_8 (0.1 %); 2, CH_4 (94.0 %) + C_2H_6 (5.7 %) + C_3H_8 (0.3 %); 3, CH_4 (90.0 %) + C_2H_6 (9.0 %) + C_3H_8 (1.0 %); 4, CH_4 (85.0 %) + C_2H_6 (5.0 %) + C_3H_8 (10.0 %).

For the gas mixture system, gas phase compositions change as the hydrate forms and dissociates which may be called the distillation effect of the hydrate.[5,6] Figure 4 shows the hydrate equilibrium pressure data at different temperatures measured by the step-heating method. The feed gas mole fractions were set at CH_4 (89.3 %) + C_2H_6 (7.8 %) + C_3H_8 (2.9 %). In Figure 4, the solid line was calculated by the Chen-Guo hydrate model[22,23] according to the feed gas mixture compositions. The dotted lines are the calculated value by the Chen-Guo hydrate model at different gas mixture compositions. It is seen that there exists a considerable deviation between the measured data and calculated values. The deviation decreases with an increase of temperature. The calculated pressures are based on the single feed gas compositions. However, in fact, one should consider the equilibrium pressure at each temperature under the equilibrium mole fraction. Due to the distillation effect of the hydrate for $CH_4 + C_2H_6 + C_3H_8$ gas mixtures, the gas phase compositions at each equilibrium stage change with the formation or dissociation of hydrate. As shown in Figure 4, with an increase of temperature, the experimental equilibrium data are close to the dotted line with a higher C_3H_6 content in the mixture. At higher temperatures, most of the hydrate has dissociated, so the gas phase compositions are close to the feed gas content. Therefore, analyzing the equilibrium gas compositions at every stage is necessary for the measurement of equilibrium conditions of gas mixtures. The difference between feed gas compositions and the equilibrium gas phase compositions in Table 1 also clearly indicates a distillation effect of hydrate.

Conclusions

The isochoric isothermal dissociation method was used to measure the three phase ($V-H-L_W$) equilibrium conditions of a ($CH_4 + C_2H_6 + C_3H_8$) gas mixture. The equilibrium pressure data for 25 gas mixture compositions were determined at four temperatures (275.2 K, 277.0 K, 278.8 K, and 280.6 K). A low dose of SDS was added to the aqueous solution assuming no influence on the phase equilibrium. The average relative deviation between experimental pressure data with those calculated by CSMGem and the Chen-Guo model is 4.6 % and 4.5 %, respectively. The mole fraction of C_3H_8 in the equilibrium compositions was quite different from the feed gas. Compared with the pressure searching method, the experimental procedure using the isochoric−isothermal dissociation method was time-saving and simple.

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