

Hydrate Phase Equilibrium of CH₄-Rich Binary and Ternary Gas Mixtures in the Presence of Tetra-*n*-butyl Ammonium Bromide

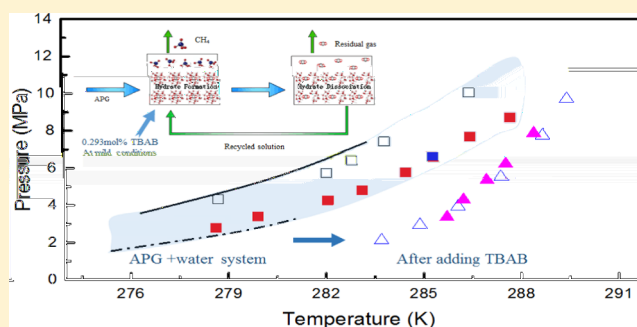
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ABSTRACT: In this work, binary gas mixtures of 92 mol % CH₄/CO₂ and ternary gas mixtures of 87 mol % CH₄/5 mol % C₂H₆/CO₂ were studied as simulate associated petroleum gas. It mainly consists of two parts: one is the hydrate phase equilibrium of the binary and ternary gas mixtures both in water and 0.293 mol % tetra-*n*-butyl ammonium bromide (TBAB) solution by isochoric pressure-search method, and the other is the enthalpy of hydrate dissociation calculated by the Clausius–Clapeyron equation. The hydrate phase equilibrium measured temperature ranged from 278.61 to 289.46 K and pressure from 2.12 to 10.06 MPa with 24 points in total. The results show that the hydrate phase equilibrium line of 87 mol % CH₄/5 mol % C₂H₆/CO₂ + water was shifted about 2.4 K toward the higher temperature compared to that of 92 mol % CH₄/CO₂ + water. After adding 0.293 mol % TBAB, it could be found that the hydrate phase equilibrium line of binary gas mixtures and ternary gas mixtures in 0.293 mol % TBAB(aq) were shifted about 5.3 and 2.7 K toward the higher temperature compared to that of water. Besides, the enthalpy of the hydrate dissociation in 0.293 mol % TBAB(aq) is much higher than that in water. Average enthalpy of the hydrate dissociation of binary gas mixture hydrate increased from 62.46 kJ/mol in water to 160.21 kJ/mol in 0.0293 mol % TBAB(aq). Meanwhile the average enthalpy of hydrate dissociation of ternary gas mixture hydrate increased from 72.89 kJ/mol in water to 181.61 kJ/mol in 0.0293 mol % TBAB(aq).



1. INTRODUCTION

Gas hydrates are crystalline clathrate compounds, that are formed by host molecules (H₂O) and guest molecules (CH₄, CO₂, H₂, etc.) at high pressure and low temperature.¹ Because guest molecules could be thermodynamically steady in clathrates, hydrate-based technology has been utilized in gas storage,^{2,3} sea water desalination,⁴ and gas separation.^{5–8} All these research studies required phase equilibrium data as the fundamental thermodynamic data. Associated petroleum gas (APG) is a high-caloric gas of variable composition and an important natural gas resource.⁹ Typical APG composition contains 80–90% methane, 5–10% ethane, 5–10% carbon dioxide, and others; APG needs to be purified before being used as an urban natural gas. Nowadays, conventional methods for separating CO₂ from associated petroleum gas include pressure swing adsorption,^{10,11} cryogenic separation,¹² absorption,¹³ membrane separation,¹⁴ and hydrate-based separation. Although the hydrate-based technology is still some distance away from industrial applications, it has shown good development prospects with the trend of low energy consumption and environmental friendly technology.

In 1940s, the semiclathrate hydrates were first discovered. It was often used in gas separation, gas storage, and desalination.

In recent years, the use of quaternary ammonium salts (QASs) as an additive to separate gas mixtures has been one of the important research directions. Luo et al.¹⁵ reported hydrate phase equilibrium data of CH₄ + H₂ in the presence of TBAB, and the results showed that the addition of TBAB can dramatically reduce the pressure required for hydrate formation at a fixed temperature, and the thermodynamic promoting effect of TBAB was better than that of THF below 284 K. Sánchez-Mora et al.¹⁶ reported the hydrate phase equilibrium data of CO₂ + N₂ + tetra-butyl-ammonium fluoride (TBAF) + water system, the mass fractions of TBAF were 0.05 and 0.10, results show that TBAF could thermodynamically promote hydrate formation.

Our earlier work tested the phase equilibrium data of 67 mol % CH₄/CO₂ binary gas as simulated biogas and flue gas with various additives, such as tetrabutylammonium halide (bromide, chloride, or fluoride),^{17–19} *n*-butyl peroxy-2-ethyl-hexanoate,⁸ 2-methyl-2-propanol, and 1,1-dichloro-1-fluoroethane.²⁰ However, phase equilibrium data of associated

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petroleum gas remained unavailable, which limited the application of hydrate–base separation. In this work, the ternary gas 87 mol % CH₄/5 mol % C₂H₆/CO₂ and binary gas 92 mol % CH₄/CO₂ were studied as simulated associated petroleum gas. Hydrate phase equilibrium data of binary and ternary gases in water and 0.293 mol % tetra-*n*-butyl ammonium bromide (TBAB) solution were tested. The results could provide the fundamental thermodynamic data for hydrate-based associated petroleum gas separation.

2. EXPERIMENTAL SECTION

2.1. Materials. Table 1 presents the chemicals and materials used in this work. Concentration of tetra-*n*-butyl

Table 1. Chemicals and Materials Used in This Work

component	purity/mol %	supplier
92 mol % CH ₄ /CO ₂	99.99	Foshan KODI Gas Chemical Industry Co.
87 mol % CH ₄ /5 mol % C ₂ H ₆ /CO ₂	99.99	Foshan KODI Gas Chemical Industry Co.
tetrabutylammonium bromide (TBAB)	99.0	Shanghai Aladdin Bio-Chem Technology Co.
water		deionized

ammonium bromide (TBAB) solution was 0.293 mol %. The gas mixtures in this work were 92 mol % CH₄/CO₂ and 87 mol % CH₄/5 mol % C₂H₆/CO₂, which was used as simulated associated petroleum gas.

2.2. Experimental Apparatus. Schematic of the experimental apparatus is shown in Figure 1, which described in detail in our previous works.^{20,21} Briefly, the apparatus was made of a 300 cm² stirred high-pressure stainless steel vessel, a Huber CC2-K20B cooling bath circulator, and an Agilent 34970A data logger. Two thermocouples (PT100) and a pressure sensor (Senex DG-1300) were installed to monitor the temperature and pressure during the experiments with a resolution of ±0.1 K and ±0.01 MPa, respectively.

Experimental method of this work is a isochoric pressure search method, which was similar to our previous work^{18,19,21,22} and literatures.^{23,24} First, high-pressure vessel was washed with deionized (DI) water. Then, about 200 mL of water or 0.293 mol % TBAB(aq) was added into the vessel. After that started data logger to record pressure and

temperature of experiment system, vacuumed the vessel and injected gas to the required pressure. Magnetic stirring (roughly 600 rpm) and cooling bath circulation were started; then, the experiment system was kept at room temperature and ensured no gas was leaking. The system started to cool down at a rate of 3 K/h. An abrupt pressure drop meant hydrate formation; the system pressure was maintained for 3 h and then heated up at the rate of 0.1 K/h. The pressure change of hydrate dissociation line during experiments was monitored. There was a change in the heating rate to 0.025 K/h when the pressure drop of the hydrate formation line and hydrate dissociation line in P – T curve was less than 0.5 MPa. The intersection points of the hydrate formation line and hydrate dissociation line in the P – T curve were considered as the hydrate phase equilibrium points.

2.3. Calculation of Enthalpy. The enthalpy of hydrate dissociation is one of the important parameters of hydrate stability. Currently, methods for measuring the enthalpy of hydrate dissociation are mainly differential scanning calorimetry (DSC)²⁵ and Clausius–Clapeyron equation.^{26,27} In this paper, the enthalpy of the hydrate dissociation for 92 mol % CH₄/CO₂ and 87 mol % CH₄/5 mol % C₂H₆/CO₂ in water and in 0.293 mol % TBAB(aq) is calculated with the Clausius–Clapeyron equation

$$\frac{d(\ln P)}{d(1/T)} = \frac{\Delta H_d}{zR} \quad (1)$$

where P is the equilibrium pressure of gas hydrate; T is the equilibrium temperature of gas hydrate; ΔH_d is the dissociation enthalpies of hydrate; and z and R are the gas compressibility factor and the molar gas constant, respectively; and $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Hydrate Phase Equilibrium Data. The results of hydrate phase equilibrium data of 92 mol % CH₄/CO₂ in water and 0.293 mol % TBAB(aq) are shown in Table 2 in the temperature range of 278.68–289.46 K and pressure range of 2.12–10.06 MPa with total of 11 points. Hydrate phase equilibrium data for different concentrations of CH₄/CO₂ in water are summarized in Figure 2.^{16,28–31} It can be seen in Figure 2 that the hydrate phase equilibrium line of 92 mol %

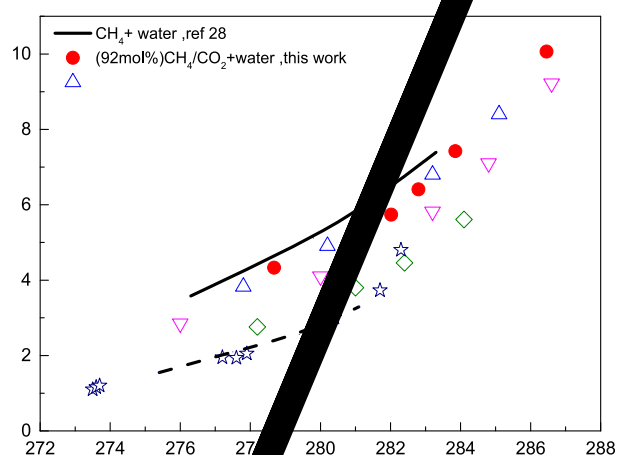


Figure 1. Schematic of experimental apparatus.

Table 2. Hydrate Phase Equilibrium Data and Enthalpy of Hydrate Dissociation of 92 mol % CH₄/CO₂ in Water and 0.293 mol % TBAB(aq)^a

system composition	temperature (K)	pressure (MPa)	enthalpy of hydrate dissociation (kJ/mol)
92 mol % CH ₄ /CO ₂ + water	286.46	10.06	59.35
	283.85	7.42	61.56
	282.85	6.41	62.69
	282.75	5.74	63.50
	279.75	4.33	65.22
92 mol % CH ₄ /CO ₂ + 0.293 mol % TBAB	286.46	9.71	147.65
	285.72	7.75	156.81
	285.38	5.53	157.99
	286.05	3.94	163.04
	284.88	2.95	166.40
	283.70	2.12	169.38

^aCombined standard uncertainties for TBAB(aq) mole fraction, temperature, and pressure are ± 0.002 mol %, ± 0.1 K, and ± 0.025 MPa, respectively, with the confidence level of 0.95.



CH₄/CO₂ binary gas was slightly shifted toward higher temperature (about 0.4 K) compared to that of CH₄. The reason was that the addition of CO₂ thermodynamically promotes hydrate formation.

The results of hydrate phase equilibrium data of 92 mol % CH₄/CO₂ in 0.293 mol % TBAB solution are shown in Table 2 and Figure 3. Hydrate phase equilibrium data of CH₄ + 0.293 mol % TBAB(aq) and CO₂ + 0.293 mol % TBAB(aq) in Figure 3 were obtained from Mohammadi et al.³² and our previous work.¹⁹ In Figure 3, the hydrate phase equilibrium line of 92 mol % CH₄/CO₂ + 0.293 mol % TBAB(aq) significantly shifted about 5.3 K toward a higher temperature compared to that of 92 mol % CH₄/CO₂ + water. Meanwhile, it could be clearly seen that the hydrate phase equilibrium lines of 92 mol % CH₄/CO₂ + 0.293 mol % TBAB(aq), CH₄ + 0.293 mol % TBAB(aq), and CO₂ + 0.293 mol % TBAB(aq) almost coincide, which indicated that TBAB dominated the hydrate phase equilibrium rather than gas components. TBAB could form a semihydrate in water, which is much more thermodynamically easier than either CH₄ or CO₂. During gas hydrate formation in the TBAB solution, TBAB semihydrate may be formed earlier and easier than CH₄, CO₂, or 92 mol % CH₄/CO₂ binary gas. CH₄ or CO₂ molecules migrated into empty cages of the TBAB semihydrates, which leads to same thermodynamic conditions as those of the gas-forming hydrate in TBAB solutions.

The results of hydrate phase equilibrium data of 87 mol % CH₄/5 mol % C₂H₆/CO₂ in water and 0.293 mol % TBAB(aq) are shown in Table 3 and Figure 4 in the temperature range from 278.61 to 288.45 K and the pressure range from 2.79 to 8.73 MPa, with a total of 13 points. In Figure 4, hydrate phase equilibrium line of 87 mol % CH₄/5 mol % C₂H₆/CO₂ + water shifted about 2.4 K toward a higher temperature compared to 92 mol % CH₄/CO₂ + water. Formation of C₂H₆ hydrate is easier thermodynamically. During hydrate formation, C₂H₆ molecules could occupy the 5¹²6² cages of the semihydrate and help CO₂ and CH₄ molecules occupy 5¹² cages and 5¹²6² cages, respectively. As a consequence, C₂H₆ acts as a thermodynamic promoter that shifts the hydrate phase equilibrium line toward a higher temperature in this work.

Figure 4 also shows that the hydrate phase equilibrium line of 87 mol % CH₄/5 mol % C₂H₆/CO₂ + 0.293 mol % TBAB(aq) was significantly shifted about 2.7 K toward a higher temperature compared to that of 87 mol % CH₄/5 mol % C₂H₆/CO₂ + water. Meanwhile, it could be clearly seen that the hydrate phase equilibrium line of 92 mol % CH₄/CO₂ + 0.293 mol % TBAB(aq) and 87 mol % CH₄/5 mol % C₂H₆/CO₂ + 0.293 mol % TBAB(aq) almost coincide, which proved that TBAB dominated the hydrate phase equilibrium rather than the gas components. Similar to the system of 87 mol %

CH₄/5 mol % C₂H₆/CO₂ + 0.0293 mol % TBAB(aq), TBAB as a guest molecule formed a semihydrate more easily than CH₄, CO₂, or C₂H₆ molecules. CH₄, CO₂, or C₂H₆ molecules migrated into the empty cages of the TBAB semihydrates, which leads to the same thermodynamic conditions as those of the gas-forming hydrate in TBAB solutions.

3.2. Enthalpy of Hydrate Dissociation. The enthalpies of hydrate dissociation of 92 mol % CH₄/CO₂ and 87 mol % CH₄/5 mol % C₂H₆/CO₂ in water and 0.0293 mol % TBAB(aq) are shown in [Tables 2](#) and [3](#), respectively. The calculation results are shown in [Figure 5](#). It could be seen that the dissociation enthalpy of the hydrate significantly increased by adding 0.0293 mol % TBAB. The average enthalpy of the hydrate dissociation of 92 mol % CH₄/CO₂ increased from 62.46 kJ/mol in water to 160.21 kJ/mol in 0.0293 mol % TBAB(aq). Meanwhile, the average enthalpy of the hydrate dissociation of 87 mol % CH₄/5 mol % C₂H₆/CO₂ increased from 54.91 kJ/mol in water to 165.8 kJ/mol in 0.0293 mol % TBAB(aq).

ternary gas hydrate formation in 0.293 mol % TBAB, TBAB as guest molecule forming semihydrate occurs easier than CH_4 , CO_2 or C_2H_6 molecules. CH_4 , CO_2 or C_2H_6 molecules migrated into empty cages of TBAB semihydrates, which leads to same thermodynamically conditions that gas forming hydrate in TBAB solutions.

Lastly, the calculation results show that the dissociation enthalpy of the hydrate significantly increased by adding 0.0293 mol % TBAB. The average enthalpy of hydrate dissociation of the binary gas mixture hydrate increased from 62.46 kJ/mol in water to 160.21 kJ/mol in 0.0293 mol % TBAB(aq). Meanwhile, the average enthalpy of the hydrate dissociation of ternary gas mixture hydrate increased from 72.89 kJ/mol in water to 181.61 kJ/mol in 0.0293 mol % TBAB(aq). The results could provide important fundamental thermodynamic data for hydrate-based associated petroleum gas separation.

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