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The phase equilibria of multicomponent gas hydrate in methanol/ethylene glycol solution based formation water

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ABSTRACT

In this paper, the three-phase coexistence points are generated for multicomponent gas hydrate in methanol (MeOH) solution for (0.05, 0.10, 0.15, and 0.35) mass fraction and ethylene glycol (EG) solution for (0.05, 0.10, 0.15, 0.35, 0.40 and 0.55) mass fraction. The phase equilibrium curves of different system were obtained by an isochoric pressure-search method on high pressure apparatus. The phase equilibrium regions of multicomponent gas hydrate were measured using the same composition of natural gas distributed in the South China Sea. And the different concentration solutions were prepared based formation water. The experimental data were measured in a wide range temperature from 267.74 to 298.53 K and a wide range pressure from 4.22 MPa to 34.72 MPa. The results showed that the hydrate phase equilibrium curves shifted to the inhibition region in accordance with the increased inhibitor concentration. In addition, the equilibrium temperature would decrease about 2.7 K when the concentration of MeOH increased 0.05 mass fraction. Besides, the suppression temperature was 1.25 K with the 0.05 mass fraction increase of EG concentration in the range of 0.05 mass fraction to 0.15 mass fraction. While in high EG concentration region, the suppression temperature was 3.3 K with the same increase of EG concentration (0.05 mass fraction).

1. Introduction

Gas hydrate are crystalline solid based water molecules, which was formed by host molecules (H_2O) and small guest gas (CH_4, C_2H_6, CO_2, C_3H_6 and so on) at low temperature and high pressure condition [1,2]. Due to small guest molecules trapped into the three-dimensional lattice structure of hydrogen-bonded water, gas hydrate can be applied to storage methane, separation mixture gas or sequestration greenhouse gases (CO_2) [3–7]. However, gas hydrate formation are also considered as a trouble in oil and gas industries, caused serious safety problem and economic loss [8–10].

In order to solve above problems, injection methanol or ethylene glycol to pipeline was a general option to inhibit formation of gas hydrate in industrial operation [15,16]. Many reports were available on the phase equilibrium region of single gas hydrate (especially for CH_4 hydrate) at different thermodynamic inhibitors, such as methanol (MeOH), ethylene glycol (EG), salts and their combination [9,17–22]. For example, Mohammadi et al. [20,21] published the dissociation data for methane hydrates in a wide range concentrations of thermodynamic hydrate inhibitors (THI) aqueous solutions (0.1, 0.2, 0.3 0.4 and 0.5 mass fraction) and also studied the methane hydrate equilibrium region in salt (NaCl, KCl, or $CaCl_2$) + MeOH aqueous solutions and salt (NaCl, KCl, or $CaCl_2$) + EG aqueous solutions. However, only a limited amount of work reported the effect of alcoholic material on the multicomponent gas hydrate equilibrium condition, especially the complex gas component from actual oil and gas field. Table 1 summarized the available literature information on the phase stability of multicomponent gas hydrate in system adding typical thermodynamic inhibitors. The phase equilibrium pressure was mainly focused on low pressure region (below 10.5 MPa). Besides, the oil and gas transportation was usually associated with saline water, electrolyte components such as NaCl and $CaCl_2$ should be taken into consideration as natural inhibitors as well. However, the investigation for the system containing mixed alcohol, glycol and salts were few.

In this work, the three-phase coexistence points are investigated for multicomponent gas hydrate in the presence of salts + methanol system, salts + ethylene glycol solution at wide pressure range (4.0 MPa–35.0 MPa). The mixture gas hydrate was measured using natural gas distributed in the South China Sea. And, the

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Table 1
Overview of phase equilibrium studies on multicomponent gas hydrate in alcoholic aqueous solution.

Sr. No.	Clathrate hydrate system	Additive mass fraction	p/MPa	References (year)
1	Quaternary gas + EG	(0.10–0.50)	(4.80–10.40)	Cha et al. (2013) [11]
2	Multicomponent gas + MeOH	(0.10–0.30)	(1.71–8.50)	Lee et al. (2011) [12]
3	Multicomponent gas + EG	(0.10–0. 50)	(0.99–9.21)	Lee et al. (2011) [12]
4	Multicomponent gas + Triethylene glycol	0.425	(2.31–8.59)	Ma et al. (2003) [13]
5	Quaternary gas + MeOH	(10.0–30.0)	(0.61–4.50)	Mei et al. (1998) [14]

different concentration solutions were prepared based formation water with high degree of mineralization.

2. Experimental section

2.1. Chemicals

Ethylene glycol with a purity of 99.0 mol% was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol with 99.8 mol% purity was obtained from Aladdin Co., Ltd. (Shanghai, China). The methane with 99.9 mol% purity was supplied by Guangzhou Zhuozheng Gas Industry Co. Ltd. The composition of multicomponent gas supplied by Guangzhou Zhuozheng Gas Industry Co. Ltd was shown in Table 2. Deionized water was made by our laboratory. Formation water used in all experiments was weighed on an electronic balance with an accuracy of ±0.1 mg. The composition of formation water and suppliers were shown in Table 3.

2.2. Experimental apparatus

In this paper, two apparatuses were used to perform the measurements.

2.2.1. Apparatus-1

The apparatus was used to measure the hydrate-phase equilibrium condition at the relative low pressure region (4.0–15.0 MPa). A detailed schematic and description of this setup have been demonstrated in our previous literature [10,23]. The main part of the apparatus was a stainless steel cylinder which could withstand pressures up to 20.0 MPa. The volume of the vessel was 300.0 cm^3. Two platinum resistance thermometers (PT100) and a pressure transducer with an accuracy of 0.1 K and 0.01 MPa were used to measure the internal temperature and pressure of the cell. The detailed diagram of apparatus-1 was shown in Fig. 1.

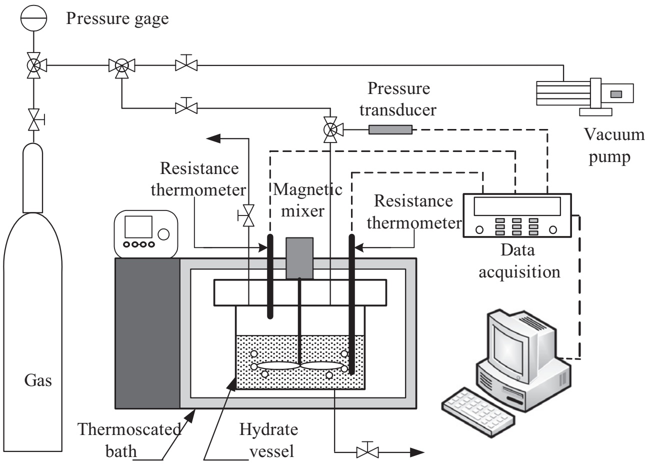

Figure 1. Schematic diagram of the experimental apparatus used for the measurement of the complex gas hydrate equilibrium conditions in the relative low pressure region.

Table 2
Composition of multicomponent gas used in this work.

Composition	Mole fraction (%)	Composition	Mole fraction (%)
CH_4	91.12	*iso*-Pentane	0.16
C_2H_6	5.03	*n*-Hexane	0.41
C_3H_8	1.49	*n*-Heptane	0.033
n-Butane	0.37	CO_2	0.48
iso-Butane	0.32	N_2	0.46
n-Pentane	0.12	Total	99.99

Table 3
The composition of formation water and the suppliers in this work.

Chemical	Supplier	Purity/mol%	Mass fraction (%)
KCl	Sinopharm Chemical Reagent Co., Ltd	99.5	0.207
NaCl	Tianjin Kermel Chemical Reagent Co., Ltd	99.5	1.769
$CaCl_2$	Sinopharm Chemical Reagent Co., Ltd	98.0	0.511

2.2.2. Apparatus-2

The apparatus was used to measure the hydrate-phase equilibrium condition at the relative high pressure region (15.0–40.0 MPa). A schematic diagram of the apparatus used to measure the dissociation points was shown in Fig. 2 and could also be found in our previous study [24]. The main part of the apparatus was a titanium cylindrical vessel with an effective volume of 450 cm^3. The allowable working pressure and temperature ranges are 0–70 MPa and 233.15–473.15 K, respectively. There was sapphire window which allows for visual observations on the information of hydrate formation occurred inside the vessel. Besides, a magnetic coupling stirrer (100–1300 rpm) was installed at the bottom of the vessel to mix the fluids. A platinum resistance thermometer (TC Direct-PT100) with an uncertainty of 0.01 K and a pressure transducer within 0.001 MPa in accuracy were used. The temperature of the vessel was controlled by a surrounding jacket filled with circulating silicone oil from a thermostatic bath, which temperature was controlled by a thermal resistance (HUBER) integrated in chiller/heater. All experimental data were recorded at 1 s interval and logged by the 4247 software.

2.3. Experimental method

The measuring hydrate phase equilibrium data for the multicomponent gas in the presence of different thermodynamic inhibitors was used the isochoric pressure-search method [24,25]. After the two vessels were well cleaned with experimental aqueous solution (3–4 times) and purged three times with multicomponent gas, they was loaded with approximately 250 cm^3 solution and then pressurized with multicomponent gas or by injecting THI solution with the hand pump. Then, the aqueous solution and gas were well mixed by the magnetic stirrer when the temperature