

Component of Clathrate Hydrates Formed in CH₄-TBAB-H₂O System

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Keywords: component; clathrate hydrates; Tetra-n-butyl Ammonium Bromide; magnetic suspension weight adsorption instrument

Abstract. Methane storage data of clathrate hydrates formed in ternary system, methane-tetra-n-butyl ammonium bromide-water (CH₄-TBAB-H₂O), was measured by a magnetic suspension weight adsorption instrument at the temperature of 273.64 ~ 278.23 K and the pressure of 2.01 ~ 7.07 MPa, for two concentration (20.8 wt % and 43.3 wt %) of TBAB solutions. The hydrates component was qualitatively analyzed. The results showed that the structure of CH₄-TBAB semi-clathrate hydrates was deformed at high pressure possibly due to methane molecules replacing TBAB molecules and forming structure I true methane hydrates for the 20.8 wt % TBAB solutions at 273.64 K. For 43.3 wt % TBAB solutions, at the same experimental temperature and pressure, the maximum mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates was only 1.64 wt % which was less than the ideal maximum value (3.08 wt %). It showed that for the 20.8 wt % TBAB solutions, TBAB molecules were not replaced by methane molecules but both CH₄-TBAB semi-clathrate hydrates and structure I true methane hydrates were formed simultaneously. For 43.3 wt % TBAB solutions, the reason of low methane storage capacity may be that the pressure was not high enough.

Introduction

Clathrate hydrates are a group of crystalline inclusion compounds formed by the combination of water molecules and suitable-sized molecules at atmospheric pressure and not very low temperature. Water molecules are linked through hydrogen bonding and form cage structure lattice (hosts) that can encage a large variety of molecules (guests) through van der Waals forces [1, 2]. The guest molecules generally include single or mixed low molecular diameter gases (e.g., methane, nitrogen), and organic compounds (e.g., tetrahydrofuran), ionic compounds (e.g., tetra-n-butyl ammonium bromide).

Unlike many guest molecules, ionic compounds molecules form semi-clathrate hydrates with water molecules under atmosphere pressure at near room temperature. The guests of semi-clathrate hydrates are salt ions, where the anions actually participate in the cage structure lattice and the cations are incorporated inside the clathrate cavities [3]. One typical semi-clathrate hydrates formed by TBAB and water consists of massive cavities composed of two 5¹²6² cavities, two 5¹²6³ cavities and several 5¹² cavities. In the semi-clathrate hydrates, the Br⁻ are part of cage structure lattice and the tetra-n-butyl ammonium (TBA) cations are engaged in the center of four larger cavities. Furthermore, the residual empty 5¹² cavities selectively encage small molecules such as methane, hydrogen. Shimada and coworkers [4] reported that the unit cell of TBAB·38H₂O consists of two 5¹² cavities for encaging small molecules, as presented in Figure 1. Therefore, the ideal maximum mass fraction of methane in it is 3.08 wt % for 2CH₄·TBAB·38H₂O semi-clathrate hydrates [5]. On the other hand, single methane molecules form structure I true clathrate hydrates, the unit cell of which includes six 5¹²6² cavities and two 5¹² cavities formed by forty-six H₂O molecules through hydrogen bonding. Therefore, if all the cavities are fully occupied by methane molecules and one cavity only encages one methane molecule, the ideal maximum mass fraction of methane in 8CH₄·46H₂O clathrate hydrates is 13.39 wt %.

In this communication, a novel hydration experimental platform which core equipment is one weight adsorption instrument [6, 7] is established. In the adsorption instrument, the mass of methane storage in CH₄-TBAB-H₂O clathrate hydrates can be directly measured by magnetic suspension balance with the accuracy of 0.01 mg. After analysis on mass fraction of methane in clathrate hydrates, comparing with the ideal maximum mass fraction of methane in CH₄-TBAB semi-clathrate hydrates and true methane hydrates, the component of clathrate hydrates formed in CH₄-TBAB-H₂O system can be predicted. The new method for measuring mass of gas in hydrates and predicting the component of multi-clathrate hydrates is helpful for further studying on gas hydrates.

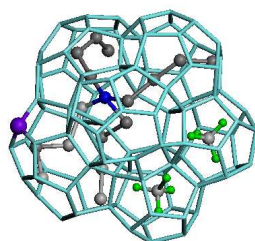


Fig.1 Structure of the CH₄-TBAB semi-clathrate hydrates unit cell.

Br atom and water molecules form the cage structure. TBA cation is located at the centre of four cages and methane molecules are encaged in the two empty cages. H atoms of methane molecules haven't been omitted while others' have been omitted for clarity.

Table 1 Materials Used in This Experiment

materials	purity / %	supplier
TBAB	> 99.5	Jiangsu Yonghua Fine Chemical Co. Ltd
methane	> 99.9	Guangzhou Shengying Gas Co. Ltd
helium	> 99.9	Guangzhou Shengying Gas Co. Ltd
nitrogen	> 99.9	Guangzhou Shengying Gas Co. Ltd
water	deionized	Laboratory

Experimental Section

Materials. Materials used in this experiment is presented in TABLE I. Deionized water was used to dissolve TBAB power, 20.8 wt % and 43.3 wt % TBAB solutions was prepared.

Apparatus. The experimental platform that consists of temperature control system, pressure control system, mass measurement system and data acquisition system, is clearly shown in Figure 2. The core part of weight adsorption instrument is a magnetic suspension balance (NL-2006-00384, ± 0.01 mg, Germany Rubotherm Co. Ltd) shown in Figure 3. The temperature control system contains two thermostat baths and each of thermostat baths has an inlet and outlet, allowing fluids to be pumped and cycled between thermostat bath and balance. The balance consists of coupling system and measurement system, which working temperatures in this experiment is controlled by two thermostat baths respectively. The temperature of coupling system of balance was controlled at room temperature by thermostat bath 1 (Julabo F25, -30 °C to 200 °C, ± 0.01 °C, Germany Julabo Co. Ltd) which cycling fluids is silicone oil, while the temperature of measurement system of balance is controlled in the range from 0 °C to 5 °C (hydration temperature) by thermostat bath 2 (THD-3015, -30 °C to 100 °C, ± 0.1 °C, Ningbo Tianheng Instrument Plant) whose cycling fluids is 50 volume % glycol solutions. The pressure control system (0 MPa to 15 MPa) consists of a vacuum pump (DUO 5 M, Germany PVA TePla Co. Ltd), two pressure sensors (± 0.001 MPa) and two gas flowmeters (± 0.01 mL / min). The data acquisition system, a digital PC, is used to obtain and deal with the data of temperature, pressure and mass.

Proceduce. Weight adsorption instrument is an unconventional experimental setup for forming clathrate hydrates because of its solid adsorbent and hydration experiment in the novel hydration setup hasn't been reported up to now. In this paper, CH₄-TBAB-H₂O clathrate hydrates was formed in magnetic suspension balance, meanwhile methane mass in clathrate hydrates was measured by

the balance. Before adsorption experiments of methane, TBAB semi-clathrate hydrates must be formed in balance firstly, and then methane was injected in adsorption instrument and encaged in the empty cavities (5^{12}) of semi-clathrate hydrates. a complete experiment needs four steps. First, nitrogen blank experiment: Nitrogen was injected into magnetic suspension balance without any sample and the gas flow rate was 60 mL / min. Mass of blank tank was measured under several pressure points (over five points, 30 min per point). True mass and volume of the tank was obtained through linear regression. Second, formation of TBAB semi-clathrate hydrates: Some dosage TBAB solutions (about 2 mL) were put into measurement tank, sealed in magnetic suspension balance at 0 °C to 5 °C. After three or four hours, TBAB semi-clathrate hydrates were formed in tank. Third, helium buoyancy experiment: Helium was injected into balance for buoyancy correction because of non-adsorption property and the gas flow rate was 60 mL / min. The true mass and volume of TBAB semi-clathrate hydrates was obtained in the same with the first step. Finally, methane adsorption experiment: methane was injected into the balance constantly at 3 °C with the gas flow rate of 60 mL / min and TBAB hydrate adopted at several pressure points (over five points, 7 h per point). The true mass and volume of CH_4 -TBAB- H_2O clathrate hydrates and measurement tank formed in the balance was measured. The mass of methane could be obtained combined with results of the first and third steps.

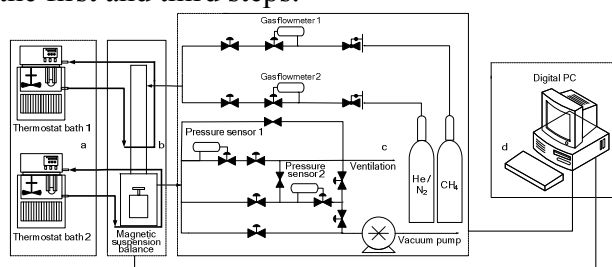


Fig.2 Schematic illustration of experimental platform.
a. temperature control system; b. mass measurement system;
c. pressure control system; d. data acquisition system

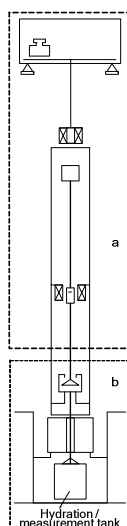


Fig.3 Schematic illustration of magnetic suspension balance.
a. coupling system; b. measurement system

Results and Discussion

The ideal maximum mass fraction of methane in CH_4 -TBAB semi-clathrate hydrates and true methane hydrates are 3.08 wt % and 13.39 wt % respectively. The mass fraction of TBAB in TBAB·38 H_2O semi-clathrate hydrates which reported by Shimada W.[4] is 32.0 wt %, meanwhile the mass fractions of TBAB solutions used in this experiment are 20.8 wt % and 43.3 wt %. In the CH_4 -TBAB- H_2O system of this experiment, for 20.8 wt % TBAB solutions, if TBAB·38 H_2O semi-clathrate hydrates is formed, the water will be superfluous and methane may form true

methane hydrates with the excess water besides encaged in TBAB·38H₂O semi-clathrate hydrates; for 43.3 wt % TBAB solutions, if TBAB·38H₂O semi-clathrate hydrates is formed, TBAB will be superfluous and usually methane will be only encaged in TBAB·38H₂O semi-clathrate hydrates. For the former, if methane forms true methane hydrates with the excess water, the mass fraction of methane in two kinds of hydrates will be between 3.08 wt % and 13.39 wt %, otherwise the mass fraction of methane in semi-clathrate hydrates will be less than 3.08 wt %. For the latter, the mass fraction of methane is usually less than 3.08 wt % because of the only CH₄-TBAB semi-clathrate hydrates present and insufficient water; if the mass fraction of methane is between 3.08 wt % and 13.39 wt %, it is possibly that the structure of CH₄-TBAB semi-clathrate hydrates is deformed under high pressure and methane molecules replace TBAB molecules, forming structure I true methane hydrates. With this method, the component of CH₄-TBAB-H₂O clathrate hydrates will be determined qualitatively and the predicted possible results are presented in TABLE II.

Table 2 Component of clathrate hydrates formed in ch4-tbab-h2o system.

Methane mass fraction (%)	<3.08	3.08	3.08 ~ 13.39	13.39
Component	H _{semi} ^a	H _{semi}	H _{true} ^b / H _{true} + H _{semi}	H _{true}

a. true methane hydrates; b. methane-TBAB semi-clathrate hydrates

The mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates (20.8 wt % TBAB solutions) at different temperature and pressure was shown in Figure 4. As presented in the Figure, when the temperature is 277.20 K or 278.23 K, the mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates is obviously less than the ideal maximum mass fraction of methane in CH₄-TBAB semi-clathrate hydrates 3.08 wt %, possibly because of a little higher temperature or no stirring. When the temperature is 273.64 K, over 4.04 MPa, the mass fraction of methane CH₄-TBAB-H₂O system clathrate hydrates is close to 3.08 wt % and with the increasing pressure, it exceeds 3.08 wt %. It was deduced that both CH₄-TBAB semi-clathrate hydrates and structure I true methane hydrates are formed simultaneously. There may be two reasons for two types hydrates formed, one is that the empty 5¹² cavities of TBAB semi-clathrate hydrates cannot encage more methane molecules and the amount of water in TBAB solutions is superfluous; the other is that the structure of CH₄-TBAB semi-clathrate hydrates is deformed under high pressure and methane molecules replace TBAB molecules, forming structure I true methane hydrates completely. To identify which explanation is reasonable, the experiment was done repeatedly using 43.3 wt % TBAB solutions at the same experimental temperature and pressure.

The mass fraction of methane from this experiment is shown in Figure 5. In this part, 43.3 wt % TBAB solutions displacing 20.8 wt % TBAB solutions was used to form clathrate hydrates with methane at 273.98 K. The high concentration TBAB solutions excluded the reason that methane formed structure I true methane hydrates with excess water. If the mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates is more than 3.08 wt %, the above reason may be that the structure of CH₄-TBAB binary hydrates is deformed under high pressure and methane molecules replace TBAB molecules, forming structure I true methane hydrates. If the mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates is less than 3.08 wt %, the above reason may be that both CH₄-TBAB semi-clathrate hydrates and structure I true methane hydrates are formed simultaneously. The mass fraction of methane from this experiment is shown in Figure 5. Seen from the Figure, the maximum mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates is only 1.64 wt %, which is less than 3.08 wt %. Due to high concentration TBAB solutions excluded the reason that methane formed structure I true methane hydrates with excess water, and according to former analysis, its structure was not deformed, thus, for 20.8 wt % TBAB solutions above 5.05 MPa and at 273.64 K, TBAB molecules are not replaced by methane molecules, but both CH₄-TBAB semi-clathrate hydrates and structure I true methane hydrates formed simultaneously. However, for 43.3 wt % TBAB solutions, the reason of low methane storage capacity may be that the pressure was not high enough. The experiment under more high pressure needs to do in the further work.

Summary

In this communication, the CH₄-TBAB-H₂O clathrate hydrates have been formed in magnetic suspension weight adsorption instrument and the component of the clathrate hydrates was studied. When the content of TBAB solutions is 20.8 wt %, above 5.05 MPa and at 273.64 K, both CH₄-TBAB binary hydrates and structure I true methane hydrates are possibly formed simultaneously. For 43.3 wt % TBAB solutions, at 273.98 K, the maximum mass fraction of methane in CH₄-TBAB-H₂O clathrate hydrates is only 1.64 wt%, which is less than 3.08 wt%. Whether the concentration of TBAB solutions is 20.8 wt % or 43.3 wt %, above 5.05 MPa and at about 273 K, TBAB molecules cannot be replaced by methane molecules. The reason of low methane storage capacity at 273.98 K (43.3 wt % TBAB) may be that the pressure is not high enough.

Acknowledgment

This study was supported by the National High Technology Research and Development Program ("863" Program) of China (2007AA03Z229).

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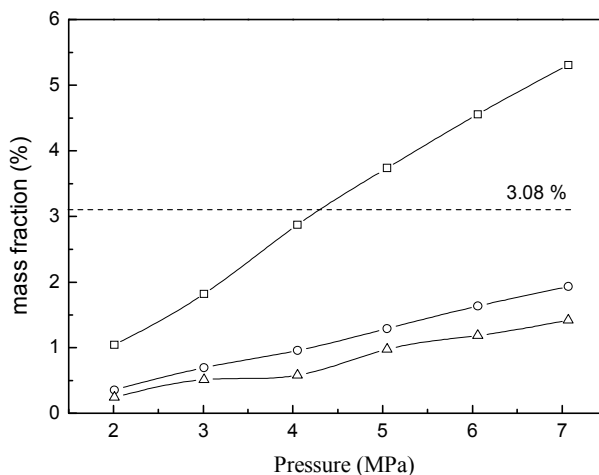


Fig.1 Methane storage capacity of CH₄-TBAB-H₂O clathrate hydrates for 20.8 wt % TBAB solutions. □, 273.64 K; ○, 277.20 K; △, 278.23 K

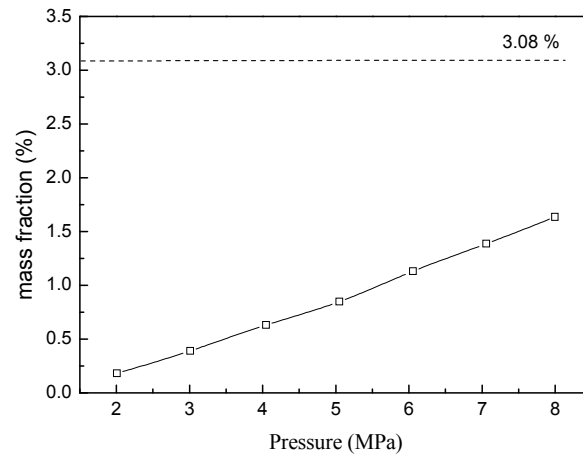


Fig. 2 Methane storage capacity of CH₄-TBAB-H₂O clathrate hydrates for 43.3 wt % TBAB solutions, □, 273.98 K