Rapid and high capacity methane storage in clathrate hydrates using surfactant dry solution

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HIGHLIGHTS

- SDS dry solution (SDS-DS) combines dispersion of dry water and activity of surfactant solution.
- SDS-DS can enhance storage rate and capacity of methane hydrate.
- SDS-DS has similar storage rate as SDS solution and similar storage capacity as dry water.
- SDS-DS stores methane faster than dry water and has higher storage capacity than SDS solution.

ARTICLE INFO

ABSTRACT

Surfactant dry solution (DS) was prepared by mixing sodium dodecyl sulfate (SDS) solution, hydrophobic silica nanoparticles and air in a high speed blender. Flour-like SDS-DS combines the advantages of dispersed dry water and active SDS solution. Methane storage in clathrate hydrates using SDS-DS was investigated in a stainless steel vessel without stirring under the condition of 5.0 MPa and 273.2 K. The results demonstrated that highly dispersed SDS-DS could significantly enhance formation kinetics and storage capacity of methane hydrate. SDS-DS exhibited about the same methane storage capacity ($172.96 \, m^3 \, m^{-3}$) as dry water, but faster storage rates than dry water. Compared to SDS solution, SDS-DS had similar storage rates ($7.44 \, m^3 \, m^{-3} \, min^{-1}$) and higher methane storage capacity under the relative low pressure. However, the aggregation of partial SDS-DS powders destroyed its original dispersive property after hydrate dissociation.

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1. Introduction

Gas hydrates are crystalline compounds encaging noble gases or short chain hydrocarbons as guest molecules in a hydrogen-bonded water framework (Sloan and Koh, 2008). In recent years, natural gas hydrates have drawn significant attention not only as a new natural energy resource but also as a new economical medium for natural gas storage and transportation (Sloan, 2003; Englezos and Lee, 2005; Koh and Sloan, 2007). One standard volume of such hydrates can stably store about 180 standard volumes of natural gas (Sloan and Koh, 2008), which corresponds to approximately one-quarter energy density of liquefied natural gas. High storage capacity of hydrate has also contributed to carbon dioxide capture (Linga et al., 2007), flue gas separation (Kang and Lee, 2000; Fan et al., 2009),

hydrogen storage (Mao et al., 2002; Struzhkin et al., 2007), seawater desalination (Park et al., 2011) and solute purification (Yoon and Lee, 1997) in the form of hydrate.

However, the application on an industrial scale has been critically challenged by slow formation rate and low conversion ratio of gas to hydrate resulting in insufficient storage capacity. The causes of these problems lie in inadequate gas–water contacts and unreacted interstitial water trapped in the hydrate mass, neither of which favors hydrate nucleation and growth. Therefore, enhancing gas–water contacts is crucial for efficient hydration of gas to solid.

Mechanical methods, such as liquid stirring (Englezos et al., 1987; Hao et al., 2007), gas bubbling (Maini and Bishnoi, 1981; Luo et al., 2007), liquid spraying (Fukumoto et al., 2001; Ohmura et al., 2002), are often employed in experimental operations to increase the formation rate of gas hydrates. However, the substantial cost of mechanical mixing devices and energy requirements may be unfeasible in real gas storage application. The addition of

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surfactants to water can enhance gas hydrates formation without mechanical perturbation (Zhong and Rogers, 2000; Link et al., 2003; Zhang et al., 2007). Evidently, the presence of surfactants increases gas–water contacts by changing the hydrate morphology (Yoslim et al., 2010), but the gas storage medium remains a pool of stationary liquid. Silica sand saturated with water (fixed bed column) has recently been employed for enhancing the rate of gas hydrate formation and the percent of water conversion to hydrate (Linga et al., 2007). However, the volume "penalty" is high because the sand occupies quite a large space in the bed column. Grinding ice powder exposed in the gas provides considerable gas–ice contacts and increases hydrate formation rates (Staykova et al., 2003), but the material must be prepared laboriously without melting. Dispersed liquid such as dry water (DW) with higher specific surface than ice powder is used to dramatically enhance the methane uptake rate in hydrates under static conditions (Wang et al., 2008; Carter et al., 2010). Dry water can capture more methane than surfactant solution, but the enhanced rate of gas uptake is slightly inferior to the rate increased by the surfactant (Carter et al., 2010).

Considering storage advantages of DW and surfactant solution, in this work, we attempt to prepare a surfactant dry solution (DS) using sodium dodecyl sulfate (SDS) solution and hydrophobic silica nanoparticles. Formation kinetic behaviors of methane hydrate in the SDS-DS were investigated under given pressure and temperature. In order to distinctly observe the effect of SDS-DS on hydration kinetics, DW and SDS solution were also used for methane hydrate formation under the same operating conditions, respectively. The results are expected to provide useful information on kinetic properties of hydrate formation in static dispersed solution.

2. Experimental

2.1. Preparation of surfactant dry solution

Full details of the procedure for the preparation of dry liquid can be referred to elsewhere (Binks and Murakami, 2006). A sample of hydrophobic silica nanoparticles (HB630) with particle size range of 5–15 nm was supplied by Guangzhou GBS High-Tech & Industry Co., Ltd.. A sample of sodium dodecyl sulfate (SDS) with certified purity of > 99% was purchased from Shanghai Bio Science & Technology Co., Ltd. To prepare SDS-DS, SDS (0.03 g) was dissolved in deionized water (99.97 g) to form SDS solution beforehand. And then the solution was poured into a blender (Philips HR1727/06, 1.5 l) and silica HB630 was added to the solution. Mixing was carried out at a speed of 18,000 rpm for two 15 s under ambient conditions. SDS-DS sample looks like dry flour but can freely flow like liquid. Four mixing ratios of solution to silica were designed, as shown in Table 1. DW was also prepared by mixing 46.25 g of deionized water and 3.75 g of HB630 with the same operation as above.

2.2. Formation of methane hydrate

Gas consumption based on pressure-volume-temperature (PVT) measurements can be considered as an efficient method to conduct laboratory experiments, which has been reported in our previous

Table 1
Mixing ratios of 0.03 wt% SDS solution to silica HB630 for preparing SDS-DS.

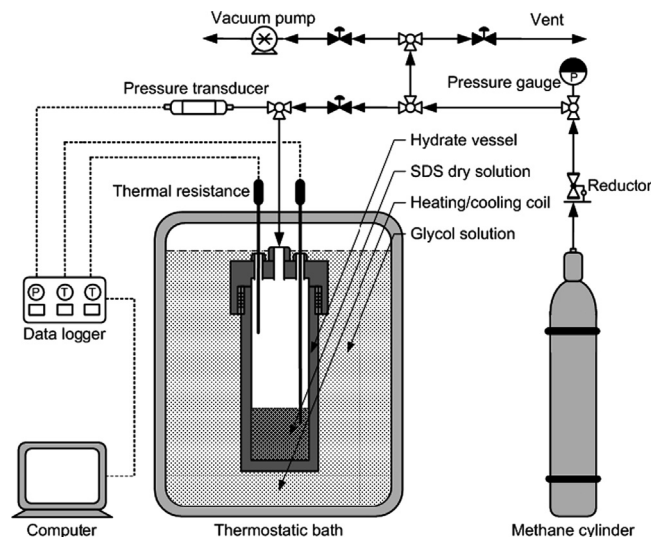| SDS solution weight (g)	Silica weight (g)	Silica contents (wt%)
48.75	1.25	2.5
47.50	2.50	5.0
46.25	3.75	7.5
45.00	5.00	10.0

Fig. 1. Schematic diagram of experimental apparatus.

paper (Yang et al., 2011). The apparatus employed in this work is shown schematically in Fig. 1. Before each experiment, a stainless steel high-pressure vessel (50 mm in diameter, 153 mm in height and effective volume of 300 cm³, Jiangsu Hai'an Scientific Research Instrument Factory) was washed with deionized water and loaded with 15.00 g of SDS-DS (or DW or SDS solution or bulk water). Subsequently, a vacuum pump (2XZ-4, Zhejiang Taizhou Qiujing Vacuum pump Co., Ltd.) was started to evacuate air from the apparatus, and then the vessel was flushed with methane (99.99% purity, Guangzhou Yinglai Gases Co., Ltd.) three times to ensure the absence of air. Afterward, a circulating coolant bath (THD-3010, Zhejiang Ningbo Tianheng Instrument Factory) with a heating/cooling coil was turned on to control the vessel temperature to 273.2 K. The coolant with a freezing point lower than 243 K is prepared by blending equivalent volume of water and glycol. Two thermal resistance detectors (Pt100, ± 0.01 K, − 30 to 200 °C Jiangsu Plaza Premium Electric Instrument Co., Ltd.) were used for measuring the temperatures of gas phase and liquid phase, respectively. Once the desired temperature was maintained constant for several minutes, methane was injected into the vessel until the given pressure (5.0 MPa) was reached, and then gas injection was cut off. The pressure of gas supply was monitored using a pressure gauge with a precision of ± 0.1 MPa. A pressure transducer (DG1300, ± 0.01 MPa, 0–40 MPa, Guangzhou Senex Instrument Co., Ltd.) was used for measuring the pressure in the vessel. The time, temperature and pressure information was collected (10 s between individual t–T–P points) by Agilent 34970A Data Logger (Agilent Technologies Co., Ltd.) and displayed on the computer screen. In the initial period of hydrate formation, liquid temperature increased while the gas pressure decreased obviously. When the pressure drop rate was less than 0.01 MPa over 30 min, hydration process was assumed to reach its destination. Experimental conditions of all tests conducted are listed in Table 2.

2.3. Calculation of methane storage rate and capacity

Methane storage rate and capacity during the hydration process could be determined from the t–T–P data. The formation rate, F, was defined as

$$F = \frac{d(V_{t,\text{gas}}^{\text{h}})_{\text{STP}}}{V_t^{\text{h}} dt} \approx \frac{(\Delta V_{t,\text{gas}}^{\text{h}})_{\text{STP}}}{V_t^{\text{h}} \Delta t}, \tag{1}$$

where V^{h}, $V_{\text{gas}}^{\text{h}}$ and $\Delta V_{\text{gas}}^{\text{h}}$ are the accumulative volume of hydrate