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# Unusual behavior of propane as a co-guest during hydrate formation in silica sand: Potential application to seawater desalination and carbon dioxide capture



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## H I G H L I G H T S

- Unusual behavior of hydrate formation in presence of propane as co-guest is reported.
- Mechanism of enhanced kinetics of hydrate formation in sand with propane as co-guest is presented.
- Conceptual process flow sheet applying the clathrate process for desalination is proposed.
- An innovative approach is proposed for simultaneous CO<sub>2</sub> capture and desalination.

## A R T I C L E I N F O

### Article history:

Received 16 May 2014

Received in revised form

20 June 2014

Accepted 29 June 2014

Available online 11 July 2014

### Keywords:

Gas hydrates

Propane hydrate: pre-combustion capture

Carbon dioxide capture

Enhanced kinetics

Desalination

## A B S T R A C T

We report an unusual behavior of hydrate formation in silica sand with gas mixtures containing propane as a co-guest. Based on morphology study we observed that propane as a co-guest has the ability to draw water dispersed in silica sand to the hydrate formation region and showed a tendency to result in drastic hydrate growth due to the migration of water molecules to the gas phase region. Hydrate nucleation occurred in the interstitial pore space between the silica sand particles and hydrate growth occurred in the gas phase above the silica sand bed and to sustain the hydrate growth, dispersed water was drawn towards the hydrate growth front. In addition, we elucidated the effect of sand bed height to maximize the growth rates utilizing this behavior that results in enhanced kinetics. We propose conceptual designs for utilizing this behavior of propane as a co-guest in sand for seawater desalination and an innovative approach to simultaneously capture carbon dioxide and desalinate seawater.

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## 1. Introduction

Gas hydrates are crystalline compounds in which water molecules through hydrogen bonding form cavities that enclose small guest molecules like methane, carbon dioxide, hydrogen (Englezos, 1993; Sloan and Koh, 2008). Due to the high gas storage capacity, non-explosive nature and selective fractionation, gas hydrates have a wide range of applications including gas storage, gas separation, desalination, natural gas storage and transport and CO<sub>2</sub> capture and sequestration (Chatti et al., 2005; Eslamimanesh et al., 2012; Lee et al., 2005; Linga et al., 2007; Park et al., 2011; Rufford et al., 2012; Veluswamy et al., 2014b; Xu and Li, 2014). Among the applications, CO<sub>2</sub> capture has received significant attention as water is used a solvent to capture CO<sub>2</sub> from flue and fuel gas streams employing the

clathrate process (Babu et al., 2014; Duc et al., 2007; Gholinezhad et al., 2011; Kang and Lee, 2000; Kumar et al., 2013; Li et al., 2010, 2011a, 2011b; Linga et al., 2010; Park et al., 2013; Tajima et al., 2004; Xu et al., 2013; Yang et al., 2012).

Linga et al. (2012) employed several gas/gas mixtures and presented kinetic data in a silica sand bed dispersed with water and reported enhanced kinetics in a sand bed compared to a stirred tank reactor. Significantly higher formation rates for the gas mixtures containing propane as a co-guest was also observed. Recently, Babu et al. (2013a) employed a fixed bed column with silica sand bed for pre-combustion CO<sub>2</sub> capture and reported 38% water conversion to hydrate in presence of 2.5 mol% propane in fuel gas mixture. They concluded that propane not only reduces the operating pressure from 9.0 MPa to 6.0 MPa but also significantly enhances the kinetics of hydrate formation. Fig. S1 (Supporting Information) shows literature data for enhanced water conversion to hydrate in presence of propane as a co-guest in silica sand bed (Babu et al., 2013a, 2013b). The presence

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of 2.5 mol% propane allows the fuel gas mixture to form structure sII instead of sI, however, the significant increase in gas uptake and water conversion to hydrate cannot be attributed to the structure change alone as the gas uptake measurements were at comparable driving force of 3.4 and 3.7 MPa for the fuel gas mixture without (Babu et al., 2013b) and with propane (Babu et al., 2013a) as a co-guest. At the molecular level, it has been shown that in presence of propane, the resulting sII hydrate contains almost similar amount of CO<sub>2</sub> as in sI CO<sub>2</sub>/H<sub>2</sub> hydrate (Kumar et al., 2009a, 2009b). While kinetic data in the literature and our recent works present evidence of significantly enhanced rate if propane is present as a co-guest in water dispersed in silica sand, the reason for this peculiar behavior is not yet known.

The objective of this work is to elucidate the behavior of propane as a co-guest in hydrate formation in silica sand. Based on our morphology and kinetic observations we have proposed innovative conceptual ideas for the application of gas hydrate technology.

## 2. Experimental

The gas mixtures employed in this study were supplied by Soxal Private Limited. Silica sand was supplied by Sigma-Aldrich (Catalog number 274739). The average particle size of the silica sand was 329 μm (ranges from 150 to 630 μm). The pore volume and porosity of the sand used was 0.217 cm<sup>3</sup>/g and 0.35 respectively. Silica gel of particle size distribution of 75–200 μm and 100 nm pore diameter supplied by Silicycle was employed. Deionized and distilled water was used in all experiments.

### 2.1. Morphology experiments

Morphology experiments were conducted by employing a morphology apparatus described in detail in our previous work (Lim et al., 2013). Briefly, the morphology apparatus consists of a crystallizer immersed in a water bath. The crystallizer has two stainless steel lid and central transparent acrylic column. A thermocouple was inserted in the top port of the crystallizer to measure the gas phase temperature. A pressure transducer and an analog pressure gauge were used to measure the pressure of the crystallizer. An external refrigerator was used to maintain the temperature of the setup. A microscope coupled with digital camera was used to observe and capture the images of the crystallizer during the hydrate formation experiment. All experiments were conducted in batch manner.

18.43 g of silica sand was placed inside the crystallizer. 4.0 ml of water was then dispersed into the interstitial pore space of the silica sand particles to achieve 100% water saturation. The crystallizer was closed and the thermocouple was connected. The crystallizer was placed inside the water bath and then cooled to 274.2 K (experimental temperature). The crystallizer was flushed three times with the gas mixture and then pressurized to experimental pressure. Microscopic images are recorded for every 20 s and the hydrate crystal growth is observed using the microscope.

### 2.2. Kinetic experiments

The detailed description of the apparatus is available in the literature (Babu et al., 2013b). Briefly, the apparatus consists of a crystallizer of volume 1.2 L and an inner diameter of 10.16 cm. The crystallizer was immersed in a temperature controlled water bath. A pressure transmitter is used to measure the pressure of the crystallizer. A thermocouple was placed at the height of 1.2 cm from the bottom of the bed to measure the temperature of the silica sand bed in the crystallizer. An external refrigerator was used to maintain the temperature of the setup. A DAQ coupled with computer was used to record the data. All experiments were conducted in batch manner.

The detailed description of the preparation of silica sand bed and hydrate formation procedure is given in detail elsewhere (Babu et al., 2013b). Briefly, 645.16 g of silica sand was placed inside the crystallizer for bed height of 5 cm. 140 ml of water was then dispersed into the interstitial pore space of the silica sand particles. All the experiments were conducted with 100% water saturation in silica sand. The crystallizer was closed and the thermocouples were connected. The crystallizer was placed inside the water bath and then cooled to experimental temperature. The crystallizer was flushed three times with the gas mixture and then pressurized to experimental pressure. The data was recorded for every 20 s. Time zero corresponds to the time at which the pressure and temperature of the crystallizer reaches the experimental conditions. The crystallizer pressure drops as a result of gas dissolution and hydrate formation. When no significant pressure drop was observed, the experiment was terminated. The crystallizer was depressurized to atmospheric pressure and the system was heated to room temperature for decomposing of the hydrate crystals. After 2 h of standby time, the formation experiment for cycle 2 was repeated. Memory water refers to the water that has undergone hydrate formation.

The procedure for formation experiments were the same for silica sand bed heights of 1.5 and 3.5 cm except the amount of silica sand and water taken. For 1.5 cm bed height, 184.33 g of silica sand and 40 ml of water was taken. For 3.5 cm bed height, 96.8 ml of water was dispersed in 445.93 g of silica sand. The procedure to calculate gas uptake, water conversion and normalized rate (NR<sub>30</sub>) of hydrate formation are given below.

*Calculation of normalized gas uptake:*

Normalized gas uptake (NG<sub>t</sub>) at any given time *t* can be calculated using the following equation

$$NG_t = \frac{\Delta n_t}{n_w} = \frac{V(P/zRT)_0 - V(P/zRT)_t}{n_w} \quad (1)$$

where Δ*n<sub>t</sub>* is the moles of gas consumed at any time *t*. *P*, *V*, *T* are the crystallizer pressure, volume of gas phase and temperature of the liquid phase in the crystallizer. *R* is the ideal gas constant, *Z* is the compressibility calculated by Pitzer's correlation and *n<sub>w</sub>* is the number of moles of water employed in the experiment. The following equation is used to further represent the normalized gas uptake in a volume free basis

$$NG_t(v/v) = \frac{\Delta n_t \times 22,414}{V_w}$$

*V<sub>w</sub>* is the volume of water taken for the experiment in cm<sup>3</sup>.

*Calculation of Water conversion to hydrate:*

Conversion of water to hydrate is determined by using the following equation

$$\text{Conversion of water to hydrates (\%)} = \frac{(\Delta n_{H_2O})_t}{n_{H_2O}} \times \text{hydration number} \times 100 \quad (2)$$

where (Δ*n<sub>H<sub>2</sub>O</sub>*)<sub>*t*</sub> is the number of moles of gas consumed for hydrate formation at the end of the experiment.

*Calculation of the normalized rate of hydrate formation (NR<sub>30</sub>):*

Normalized rate of hydrate formation can be calculated by using the following equation

$$NR_{30} = \frac{(R_{30})}{V_w} \text{ (mole of gas min}^{-1} \text{ m}^{-3}\text{)} \quad (3)$$

where *R<sub>30</sub>* is the rate (mol of gas/min) of hydrate growth calculated by fitting the gas uptake data for the first 30 min of hydrate growth with time and *V<sub>w</sub>* is the volume of water taken for the experiment in m<sup>3</sup>.

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