



Investigation on methane recovery from low-concentration coal mine gas by tetra-*n*-butyl ammonium chloride semiclathrate hydrate formation

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HIGHLIGHTS

- TBAC semiclathrate hydrate was used for CH₄ recovery from a coal mine gas.
- Phase equilibrium data at different TBAC concentrations were measured.
- Phase behaviors of TBAC-coal mine gas mixed semiclathrate hydrate were tested by HP μ -DSC.
- An optimum condition for semiclathrate-based CH₄ separation was determined.

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ABSTRACT

This work presents an investigation of using tetra-*n*-butyl ammonium chloride (TBAC) semiclathrate hydrate to separate CH₄ from a low-concentration coal mine gas containing 30 mol% CH₄, 60 mol% N₂, and 10 mol% O₂. Phase equilibrium data of TBAC semiclathrate hydrate formed in the presence of low-concentration coal mine gas with TBAC concentration ranging from 0.49 mol% to 3.3 mol% were measured and reported. A high pressure micro-differential scanning calorimeter (HP μ -DSC) was employed to characterize the phase behaviors of TBAC semiclathrate hydrate formed in the presence of coal mine gas with TBAC concentration fixed at 3.3 mol% (the stoichiometric concentration of TBAC semiclathrate). It was found that pure TBAC semiclathrate hydrate co-exists with the TBAC-coal mine gas mixed hydrate in the pressure range of (1.4–6.2 MPa). In addition, kinetic experiments were performed to elucidate the effects of TBAC concentration, subcooling, and sodium dodecyl sulfate (SDS) concentration on CH₄ separation efficiency and an optimum experimental condition for semiclathrate-based CH₄ recovery was screened. The highest CH₄ recovery and separation factor were obtained at the conditions of 0.49 mol% TBAC, $\Delta T = 8$ K, and 900 ppm SDS. It was found that CH₄ recovery obtained at 0.49 mol% TBAC is comparable with that obtained at 0.29 mol% TBAB, whereas CH₄ concentration of the gas mixture released from the TBAC hydrate (49.6 mol%) is increased substantially comparing to that obtained at 0.29 mol% TBAB (42.5 mol%).

1. Introduction

Coal mine gas is a type of unconventional natural gas stored in coal seams. It has been recognized as a clean energy resource to supplement the conventional fossil fuels (coal, oil, and natural gas) due to its huge reserve around the world [1–3]. During the coal mining process coal mine gas is mixed with air and thus becoming a low-concentration coal mine gas in which the CH₄ content is usually lower than 30 mol%. The low CH₄ concentration will hinder the utilization of coal mine gas [4]. Each year in China about 65% of the underground drained coal mine gas is not properly used as most of the recovered coal mine gas belongs to the low-concentration coal mine gas that is usually released into

atmosphere as a waste gas. Therefore, developing an efficient technology to utilize the low-concentration coal mine gas is of great importance to promote natural gas supply, reduce greenhouse gas (CH₄) emission, and ensure the operation safety of coal mines.

Gas hydrates are non-stoichiometric icelike inclusion compounds formed at low temperature and high pressure conditions with small-sized gas molecules (CH₄, C₂H₆, CO₂, etc.) trapped in hydrogen-bonded water cages. Structure I, structure II, and structure H are three well-known hydrate structures that have been identified so far [5,6]. Gas hydrates naturally occurring in ocean sediments and permafrost zones have been considered as a potential energy resource for the 21st century [7]. Besides, the hydrate-based technology has wide applications in gas

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separation (flue gas, fuel gas, shale gas, and coal mine gas) [8–16], solid natural gas transportation [17], and seawater desalination [18,19] owing to the unique properties of gas hydrates such as large gas storage capacity and superior gas selectivity.

The basis of hydrate-based gas separation (HBGS) process for CH₄ separation from the low-concentration coal mine gas is that CH₄ molecules can be preferentially entrapped in the hydrate cavities while N₂ and O₂ molecules are remaining free in the gas phase at certain conditions. As a consequence, the low-concentration coal mine gas is purified and CH₄ can be recovered via hydrate dissociation. Large gas storage capacity, moderate operating conditions, and high CH₄ selectivity are three pronouncing advantages of the HBGS technology in comparison with conventional CH₄ separation methods like adsorption, membrane separation, and liquefaction. Therefore, the HBGS technology has been viewed as a promising method for CH₄ separation from the low-concentration coal mine gas [20–22].

In order to reduce energy consumption in the gas separation process, the HBGS technology needs to be implemented at higher temperature and lower pressure conditions. This requirement can be achieved by adding some promoters such as cyclopentane (CP), cyclohexane (CH), and tetrahydrofuran (THF) into the aqueous solution. It has been reported in the literature that the phase equilibria of gas hydrates formed with coal mine gas shift to lower pressures and higher temperatures in the presence of THF, CP, or CH, and CH₄ recovery obtained in the presence of these promoters has been found to increase at the same time [23–25]. Recently, quaternary ammonium salts (QAS) have been employed to form semicathrate hydrates for gas mixture separation like capturing CO₂ from fuel gas [26–28]. This is because in QAS semicathrate hydrates the large cavities that are formed by water molecules and halide anions would trap the butyl groups while the small dodecahedral cavities (5¹²) formed by water molecules remains empty to entrap the small gas molecules (CH₄, CO₂, etc.). Besides, the phase equilibrium pressure for semicathrate hydrate formed at a fixed temperature is usually lower than that of structure I and structure II hydrates formed at the same temperature. For example, tetra-*n*-butyl ammonium bromide (TBAB) semicathrate hydrate was successfully employed to separate CH₄ from the low-concentration coal mine gas, and the impacts of TBAB concentration and driving force (overpressure, subcooling) on CH₄ selectivity were revealed [29,30]. However, other QAS such as tetra-*n*-butyl ammonium chloride (TBAC) and fluoride (TBAF) have not been used for CH₄ separation from low-concentration coal mine gas, and the thermodynamic and kinetic behaviors of semicathrate hydrate formed in the presence of low-concentration coal mine gas have not been well understood. The objective of this work is to report the phase equilibria of TBAC semicathrate hydrate formed in the presence of low-concentration coal mine gas and disclose the effects of TBAC concentration, subcoolings, and sodium dodecyl sulfate (SDS) concentration on the efficiency of CH₄ separation from the low-concentration coal mine gas. The results presented in this work will provide insights into the possibility of employing TBAC semicathrate hydrate to purify CH₄ from low-concentration coal mine gas.

2. Experimental methods

2.1. Materials

The low-concentration coal mine gas used in this work is a gas mixture containing 30 mol% CH₄, 60 mol% N₂, and 10 mol% O₂, and was supplied by Chongqing Jiarun Gas with a reported uncertainty of 0.05 mol%. Tetra-*n*-butyl ammonium chloride (TBAC) with a certified mass purity of 97% and sodium dodecyl sulfate (SDS) with a mass purity of 99% were purchased from Chongqing Oriental Chemical Co., Ltd. Deionized water was used in all experimental runs.

2.2. Apparatus

2.2.1. Stirred tank reactor

Detailed description of the apparatus used for the thermodynamic and kinetic experiments can be seen in the previous work [31]. Briefly, it consists of a high pressure stainless steel reactor with a volume of 600 cm³. It was immersed in a temperature-controlled water bath and can be operated at a maximum pressure of 10 MPa. An electromagnetic stirrer (0–1000 rpm) was inserted into the reactor to agitate the aqueous solution. Two platinum resistance probes with an uncertainty of 0.1 K were used to measure the gas and liquid temperature, respectively. A pressure transducer (Yokogawa Electric Corp., Japan) with an uncertainty of 0.06% of the span 0–10 MPa was employed to measure the gas pressure. A data acquisition unit (Agilent 34970A, USA) was used to collect the temperature and pressure data and was connected to a computer for data storage. A gas chromatograph (GC-2014, Shimadzu Corp., Japan) with an uncertainty of 0.1 mol% was used to measure the composition of the gas mixtures remaining in the reactor and released from hydrate dissociation at the end of the experiments.

2.2.2. High pressure micro-differential scanning calorimeter

A high pressure micro-differential scanning calorimeter (HP μ -DSC VII evo, Setaram Inc., France) was used to test the phase behaviors of TBAC semicathrate hydrate formed in the presence of low-concentration coal mine gas. The differential scanning calorimeter is composed of a reference cell and a sample cell which were made of Hastelloy C276 to avoid contamination and corrosion. The cells with an internal volume of 0.33 cm³ can be operated at the maximum pressure of 40 MPa. The temperature range for the calorimeter is between 228 K and 393 K while the temperature scanning rate can be set in the range of 0.001–1 K/min. The resolution of the HP μ -DSC is 0.02 μ W.

2.3. Procedures

The phase equilibrium data of TBAC semicathrate hydrate formed with the low-concentration coal mine gas were measured using the isothermal pressure search method [32]. Three TBAC concentrations of 0.49 mol%, 1.0 mol%, and 3.3 mol% were used in this work. Detailed description of the procedure can be seen in the previous work [21].

The procedure used for HP μ -DSC characterization was given as follows. The TBAC solution (3.3 mol%) with a mass of ~ 2 mg was charged in the sample cell by a micro syringe. Then, the sample cell was inserted into the DSC furnace and connected to the gas tubes. The sample cell was purged with the low-concentration coal mine gas at least five times to expel any air remaining in the system. During the experiments the pressure in the sample cell was kept constant using a supply vessel (inner volume of 150 cm³) and was measured by a pressure transducer (EJX430A, Yokogawa Electric Corp., Japan) with an uncertainty of 4 kPa. The dynamic method and isothermal temperature program [33–35] were used to characterize the phase behaviors of hydrate formation and dissociation at 3.3 mol% TBAC. The sample cell was cooled down from 293.2 K to 253.2 K at a constant rate of 0.3 K/min and the temperature was kept constant at 253.2 K for 3 h to ensure the complete formation of gas hydrates. Subsequently, the sample cell was heated from 253.2 K to 303.2 K at a constant rate of 0.3 K/min to obtain endothermic peaks, which reflect the process of hydrate melting. The experiment was repeated three times at each experimental condition to obtain a reproducible result.

The experiments employing TBAC semicathrate hydrate for CH₄ separation were performed in the stirred tank reactor (kinetic experiments). Three TBAC concentrations (0.49 mol%, 1.0 mol%, and 3.3 mol%) were used and the initial pressure was fixed at 3.0 MPa. The equations that were used to calculate normalized gas uptake ($\Delta n_{\text{normalized}}$), rate of hydrate formation, CH₄ recovery (R), and separation factor (S) for the separation experiments were described in detail in the literature [36]. The experiments were carried out in batch mode. Prior to the

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