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Phase equilibrium and Raman spectroscopic studies of semi-clathrate hydrates for methane, nitrogen and tetra-butyl-ammonium fluoride

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ABSTRACT

The experimental study on phase equilibrium conditions for semi-clathrate hydrates formed in the systems of CH_4/N_2 gas mixture and tetra-butyl-ammonium fluoride (TBAF) with different ratios (0.210, 0.293 and 0.500 mol%) to water was conducted in this paper. The experiments were carried out under the conditions of 281.15–291.15 K and 0.30–3.70 MPa. The structures of the hydrates were characterized using *in-situ* Raman spectroscopy at 276.15 K and 2.50 MPa. At a certain given pressure, the equilibrium temperature of the semi-clathrate hydrates formed in the systems with 0.500 mol% TBAF is significantly higher than that of semi-clathrate hydrates formed the systems with 0.210 or 0.293 mol% TBAF, and even higher than that of structure II hydrates formed in the systems with THF-SDS. Moreover, TBAF has more positive influence on enhancing dissociation enthalpies of the hydrates than THF. Due to the quite weak signal of N—N triple bond vibration or/and seldom N_2 molecules encaged into the cavities, only CH_4 molecules could be determined clearly in the mixed hydrates. In addition, the crystal morphology of the semi-clathrate hydrates is affected by the ratio of TBAF to water.

1. Introduction

Gas Hydrate is a kind of inclusion crystalline compound, which consists of host water molecules and guest molecules such as light-carbon molecules, dioxide carbon (CO_2), hydrogen (H_2), nitrogen (N_2) cyclopentane (CP), tetrahydrofuran (THF), etc., under the high pressure and/or low temperature [1]. During the hydrate formation, the water molecules construct the various cavities via hydrogen bonds, while the guest molecules encage into the certain cavities via van der Waals forces. The hydrate technology which is environmental friendly and relatively simply has been widely studied in various applications, such as natural gas storage and transportation, gas separation and desalination. Especially, the hydrate-based gas separation has been vastly investigated into CO_2 capture from fuel gas (CO_2/H_2) [2] and flue gas (CO_2/N_2) [3], and CH_4 recovery from biogas (CH_4/CO_2) [4] and coal mine methane gas mixture (CH_4/N_2) [3,5–10].

However, the hydrate-based gas separation is still not suitable for commercial applications owing to the low gas uptake, slow hydrate formation rate and poor separation efficiency. For this purpose, hydrate formation additives are injected into the hydrate formation systems to accelerate the hydrate formation and enhance the gas separation efficiency. Generally, hydrate formation additives are categorized into thermodynamic additives such as tetra-n-butylammonium (TBAB) [7], tetrahydrofuran (THF) [3,8] and cyclopentane (CP) [11], and kinetic additives such as sodium sodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) [3,12]. The thermodynamic additives take part in constructing the hydrate structures, and furthermore, moderating the hydrate formation conditions. For instance, THF and CP molecules encage into the hydrate cavities and make the hydrates present for structure II (sII). Nevertheless, TBAB molecules participates in building the hydrates structure and making the hydrates be semi-clathrate (sc) structure. The kinetic promoters have positive influence on increasing the gas/liquid interface, further improving the gas dissolving in the water, and further enhance the gas hydrate formation rate. In our previous work, the combined additives including thermodynamic and kinetic promoter were applied in CH_4 recovery from the coal-bed methane (CBM) gas mixture [3,13].

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It was proven that the combined additive containing 1.0 mol% THF and 500 ppm SDS was an appreciate hydrate additive for recovering CH_4 from the CBM gas mixture. However, due to the volatile properties of THF, the out entrainment of THF from the releasing gas leaded to the serious loss of THF during the hydrate dissociation. Consequently, the concentration of THF in the recycled reaction solution might be lower than 1.0 mol%, which would bring about the negative effect on the hydrate formation rate and CH_4 separation efficiency for the next gas separation process. In order to maintain the additives and warrant the required separation efficiency in the recycled reaction solution, it is necessary to exploit and evaluate other additives for the CH_4 recovery from CBM gas mixture via clathrate hydrates.

Quaternary ammonium salts (QAS) has been proven to form the semi-clathrate hydrates and have a positive effect on moderating the hydrate equilibrium conditions [7,9,10,14–18]. The structures of the hydrate containing QAS are different from the three typical hydrates (sI, sII and sH) [1]. During the hydrates formation, the anions (e.g., F^-, Br^-, Cl^-, NO_3^-) take part in building up the cavities of the hydrates together with water molecules while TBA^+ are partially encaged into the cavities [19–21]. It is possible that the equilibrium conditions of the CH_4/N_2/QAS semi-clathrate hydrates are milder than those of the CH_4/N_2/THF sII hydrates in the process of recovering CH_4 from the CBM gas mixture.

For developing the application of hydrate-based CH_4 separation technology from the CBM gas mixture, this paper represents the basic phase equilibrium data of the semi-clathrate hydrates obtained in the systems consisted of CH_4/N_2 gas mixture and TBAF with different concentrations. Moreover, the hydrate structures of the TBAF/CH_4/N_2 hydrates are characterized by *in-situ* Raman spectrometer and the dissociation enthalpies of these hydrates are calculated by the Clausius–Clapeyron equation based on the data of the hydrate phase equilibrium.

2. Experimental section

2.1. Materials

The gas mixture with composition of 50 mol% CH_4 and 50 mol% N_2 was supplied by Foshan Huate Special Gas Co., Ltd. Such gas mixture was adopted to simulate the typical CBM gas mixture collected from the coal mine [3]. TBAF (75% in water) was supplied by Aladdin Industrial Co., Ltd. The deionized water was produced by an ultrapure water system with a resistivity of 18.25 $m\Omega \cdot cm^{-1}$, and used in all experimental runs.

2.2. Apparatus

The experimental apparatus to perform the hydrate equilibrium conditions are illustrated in Fig. 1. For Fig. 1, it shows the semi-batch experimental apparatus with stirring, SHD-I, employed to perform the equilibrium experiments to determine equilibrium conditions of the hydrates containing TBAF. The experimental apparatus is comprised of supply vessel (SV) with 1350 ml and hydrate crystallizer (CR) with 336 ml. SV and CR are both made by 316 stainless steel and immersed into the water bath with the controlled temperature. Especially, two visible windows are located on the front and back of the CR and used to observe the hydrate formation process. In the CR, the gas and liquid solution are mixed thoroughly by a magnetic stirring at the speed of 500 rpm. The maximum operation pressure of the SV and CR are 25 MPa, and the pressures of the SV and CR are measured using two Setra smart pressure transducers (model SS2, Boxborough, MA) with an uncertainty of 0.02 MPa. The temperatures in the CR are measured with Pt1000 thermocouples (JM6081) with an accuracy of 0.1 K. All above data of pressures and temperature are acquired by a data acquisition system, and automatically recorded by a personal computer (PC). In addition, the hydrate structures are measured by another apparatus combining with an *in-situ* Raman spectrometer, which was described in our previous work [22].

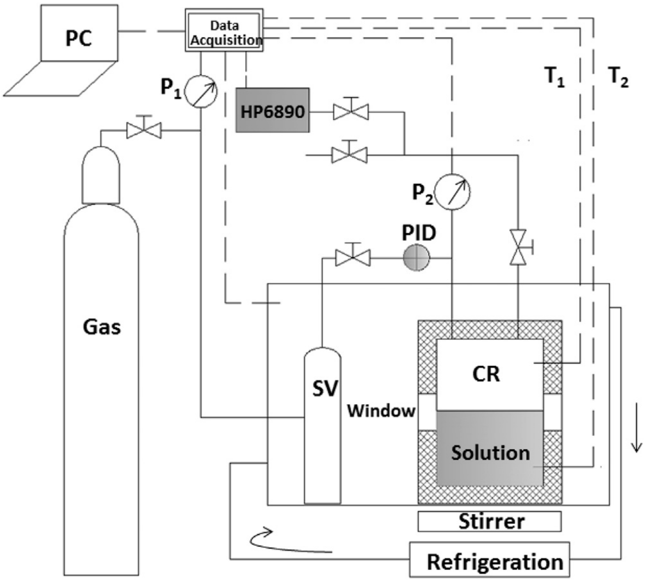

Fig. 1. Schematic of experimental apparatus.

2.3. Measurement procedure

The isochoric temperature method is employed to measure the hydrate formation equilibrium conditions, and the corresponding conditions are determined according to the temperature point of the last hydrate crystal dissociating. The solution of 180 ml is added into the hydrate formation CR. Subsequently, the CR is evacuated to air free. Then, under the setting temperature, the pressure is introduced to an operation pressure which is 2–3 MPa higher than the expected pressure to form the hydrates. During the hydrate formation, the content in the CR is mixed by a magnetic stirrer. Once the hydrates are formed, the temperature begins to be increased gradually to the point of the last hydrate crystal dissociation. The point when the last hydrate crystal disappearing completely is defined as the hydrate phase equilibrium point correspondingly. After that, the temperature is lowed to the formation point again as same as the above mentioned one, and the same process of hydrate dissociation are repeated three times.

The Raman spectrometer (Horiba, LabRAM HR) with a single Mono Chromator of 1800 grooves/mm grating and a multichannel air-cooled CCD (charge coupled device) detector is employed to determine the structures of the CH_4/N_2 mixed hydrates containing TBAF. A 532 nm incident laser beam was used. The Ar-ion laser was focused on the sample by a 1 × microscope objective. The spectroscopic data are detected by a CCD detector with an energy resolution of 100 mW and recorded with a 10 s integration time over 2–5 scans. The silicon (Si) crystal standard of 520.7 cm^{-1} is employed to calibrate the subtractive spectrograph.

3. Results and discussion

3.1. Phase equilibrium measurements

The reliability and accuracy of the experimental study were

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