



# Gas separation of flue gas by tetra-*n*-butylammonium bromide hydrates under moderate pressure conditions



Hidenori Hashimoto <sup>a, b</sup>, Tsutomu Yamaguchi <sup>a, b</sup>, Takahiro Kinoshita <sup>c</sup>,  
Sanehiro Muromachi <sup>b, \*</sup>

<sup>a</sup> Graduate School of Environmental Science, Toho University, 2-2-1 Miyama, Funabashi-shi, Chiba, 274-8510, Japan

<sup>b</sup> National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569, Japan

<sup>c</sup> Mitsui Engineering and Shipbuilding Co., Ltd., 16-1, Tamahara 3-chome, Tamano, Okayama, 706-0014, Japan

## ARTICLE INFO

### Article history:

Received 18 January 2017

Received in revised form

11 April 2017

Accepted 14 April 2017

Available online 19 April 2017

### Keywords:

Gas separation

Ionic clathrate hydrate

Carbon dioxide

Nitrogen

Tetra-*n*-butylammonium bromide

CCS

## ABSTRACT

Ionic clathrate hydrates are composed of water and ionic guest substance, which can selectively capture gas under moderate conditions. We performed gas separation experiments with tetra-*n*-butylammonium bromide (TBAB) widely-used for an ionic guest substance. The experiments in a closed system showed good CO<sub>2</sub> gas selectivity of the TBAB hydrates even under the mild conditions: 1 MPa and 282 K. We also performed the gas separation with tetrahydrofuran (THF) which is a guest substance forming the structure II clathrate hydrate. Comparison with THF clearly revealed the better CO<sub>2</sub> selectivity of TBAB than that of the structure II clathrate hydrate. We further compared our data with the literature, and found that the condition of low pressure and dense TBAB concentration provided superior CO<sub>2</sub> selectivity. Gas separation with continuous gas flow was demonstrated. The hydrate formation behavior was similar to the cases without gas flow. The results showed that controlling the crystal growth temperature is important to capture gases by the TBAB hydrates.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

CO<sub>2</sub> in flue gases from industry, such as thermal power plants and iron mills, is an issue for development. In spite of much less emission compared to that in industry, agricultural green house gases including CH<sub>4</sub> and N<sub>2</sub>O are also an issue [1]. Although the CO<sub>2</sub> emission could almost balance with agricultural land, CO<sub>2</sub> capture and utilization in this area plays an important role with regard to atmospheric CO<sub>2</sub> mitigation. In horticulture, since CO<sub>2</sub> promotes photosynthesis of plants, CO<sub>2</sub> enrichment in a green house enhances crop increases. Recently, CO<sub>2</sub> capture and enrichment process in agriculture by clathrate hydrates are proposed [2,3]. The clathrate hydrates of CO<sub>2</sub> can preserve a lot of CO<sub>2</sub> under more moderate pressure conditions than liquefied CO<sub>2</sub> [4]. In a green house in winter, though a combustion heater is usually used for keeping the house warm during the night, the house temperature becomes high for plants in the daytime. The CO<sub>2</sub> hydrates can also provide cool energy for plants which are usually required in the

daytime in hot green houses. Therefore, to be suitable for an on-site CO<sub>2</sub> recovery system from a flue gas of a combustion heater, formation conditions of CO<sub>2</sub> hydrates need to be moderated, e.g., 1 MPa at ~285 K [5–9]. With this concept, an operation period of the system is also limited to be a few hours during the night.

Ionic clathrate hydrates are host–guest compounds which form from aqueous solutions of ionic guest substances, such as quaternary ammonium salts and quaternary phosphonium salts [10]. Tetra-*n*-butylammonium bromide (TBAB) is a widely used ionic guest substance, and the TBAB hydrates can form over 283 K under both atmospheric and moderately pressurized conditions [11–13]. In the crystal structure, the tetra-*n*-butylammonium (TBA) cation is incorporated in the cage-like network which consists of hydrogen-bonded water molecules, and the bromide anion makes bonds with water molecules [10,14,15]. Ionic clathrate hydrates usually have a couple of possible crystal structures, i.e., polymorphism, and the TBAB hydrates mainly have two crystal structures: tetragonal and orthorhombic, of which hydration numbers are 26 and 38, respectively [12]. Recently, we reported the irregular arrangement of water framework which may provide better selectivity even for similarly-sized gases [16–18], such as CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>, compared to canonical clathrate hydrates, i.e., structure I, II, and H hydrates.

\* Corresponding author.

E-mail address: [s-muromachi@aist.go.jp](mailto:s-muromachi@aist.go.jp) (S. Muromachi).

Since the mild conditions of ionic clathrate hydrates are advantageous for gas separation, many studies were performed [19–25]. Most of them evaluated gas separation performance of the TBAB hydrates based on separation factor which indicates performance on condensation of the target component in the separation medium. Based on the S.F. data, it was found that TBAB hydrates selectively captured CO<sub>2</sub> in high concentration from CO<sub>2</sub> + N<sub>2</sub> mixed gas [19–22] and CO<sub>2</sub> + CH<sub>4</sub> gas [23–25]. As well as S.F., gas storage capacity is crucial for gas separation and storage, which determines processing gas amount. So far, gas capacity of the TBAB hydrate was not enough discussed based on its stoichiometry. In the previous papers, aqueous TBAB solutions with low concentrations were used, probably to avoid the viscosity increase. Considering moderation of the formation pressure and temperature, denser aqueous solutions close to the stoichiometric compositions are suitable. Such mild thermodynamic conditions increase potential of these materials for the application in various situations.

In this study, we investigate gas separation properties of TBAB hydrates on CO<sub>2</sub> + N<sub>2</sub> mixed gas for developing CO<sub>2</sub> recovery system under moderate conditions: Mass fraction of TBAB in aqueous solution ( $w$ ) = 0.20 and 0.32, pressure ( $P$ ) = 1, 2, and 3 MPa, and temperature ( $T$ ) = 279–285 K. Gas capacity, selectivity, separation factor and their pressure dependency were discussed. We used two experimental setups: One had a small (223 cm<sup>3</sup>) volume hydrate formation reactor without gas flow, and the other had a large (1000 cm<sup>3</sup>) reactor with continuous gas flow. In the small system without gas flow, to compare the gas separation performance of the TBAB hydrates with canonical gas hydrates in a short operation period, we also used tetrahydrofuran (THF) which promotes hydrate formation. In the large system with gas flow system, the gas mixture in the reactor was refreshed and kept the feed gas composition, which means that the enrichment of N<sub>2</sub> in the gas phase caused by CO<sub>2</sub> capture by hydrates was controlled. Therefore, the driving force of the hydrate formation, subcooling temperature in this case, was maintained during the experiment with gas flow to maximize the captured CO<sub>2</sub> amount. Using these two different setups allow us to investigate potential of this material, scaling feasibility of the system and effects of driving force on gas separation.

## 2. Experimental

### 2.1. Materials

We used different materials for our two experimental systems: the gas separation experiments without gas flow and with continuous gas flow. For the experiments without gas flow, we used refined water which sterilized with ultraviolet lamp, purified by activated carbon, and deionized before use. For the gas separation experiments with continuous gas flow, we used deionized water

provided by KOGA Chemical Manufacturing Co.,Ltd (Saitama, Japan). The other materials were listed in Table 1.

### 2.2. Gas separation experiments without gas flow

The apparatus used in this study is shown in Fig. 1. The apparatus mainly consists of a high-pressure cell, a thermostated water bath, a pressure sensor, and a thermometer. We used a high-pressure cell with 223 cm<sup>3</sup> volume. The hydrate formation reactor has strain-gauge pressure sensor (VPRTF-A2-10MPaW-5, Valcom, Co. LTD., Osaka, Japan) and platinum resistance thermometer (Class A 2 mA, NRHS1-0, Chino, Co., Tokyo) in a sealed tube at upper part of the cell for measurement of system temperature and an electromagnetically induced stirrer on the lid. The cell was charged with ~30 g of an aqueous TBAB or THF solutions, of which volumes can be calculated with density reported in Table S1 in ESI<sup>†</sup>. Aqueous solutions were gravimetrically prepared using an electronic balance with 0.02 g of uncertainty (GX-6100, A&D Co., Tokyo) and supplied to the cell (~30 g). The bath temperature was controlled by a cooler, a PID (proportional-integral-derivative)-controlled heater, and stirring pump. We used 10 cm<sup>3</sup> cylinder for gas sampling. Gas composition analysis was performed by gas chromatograph (GC-2014, Shimadzu, Co., Kyoto, Japan).

Aqueous solutions were prepared with  $w = 0.200$  and  $0.320$  for

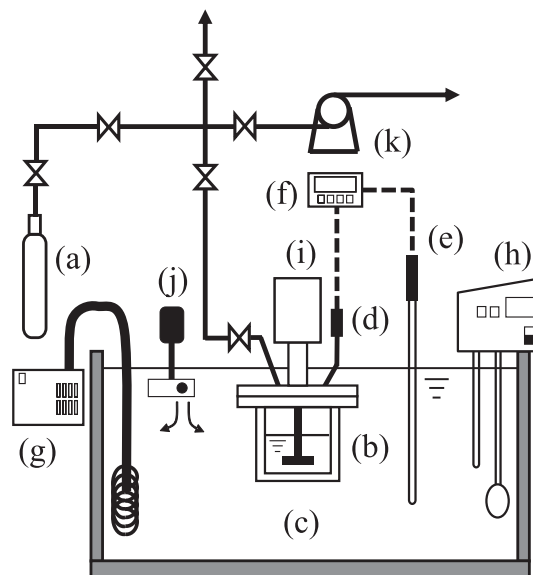


Fig. 1. Schematic of apparatus used in this study. (a) Gas cylinder (b) Hydrate formation reactor (c) Water bath (d) Pressure sensor (e) Thermometer (f) Data logger (g) Cooler (h) PID controlled heater (i) Stirrer (j) Jet pump (k) Vacuum pump.

Table 1

List of materials used in this study.

Name	Chemical formula	Supplier	Purity
Experiments without gas flow			
Tetra- <i>n</i> -butylammonium bromide	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NBr	Sigma-Aldrich, Co., Missouri	≥0.99 in mass fraction
Tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	Sigma-Aldrich, Co., Missouri	≥0.999 in mass fraction
Carbon dioxide (0.1524) + nitrogen (0.8476) mixed gas	CO <sub>2</sub> + N <sub>2</sub>	Takachiho Chemical Industrial Co., LTD., Tokyo	≥0.0001 in mole fraction (GC)
Argon	Ar	Taiyo Nippon Sanso, Co., Tokyo	≥0.99999 in mole fraction
Experiments with continuous gas flow			
Tetra- <i>n</i> -butylammonium bromide	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NBr	Wako Pure Chemical Industries, Ltd. Osaka, Japan	≥0.980 in mass fraction
Carbon dioxide (0.1342) + nitrogen (0.8658) mixed gas	CO <sub>2</sub> + N <sub>2</sub>	TOATSU YAMAZAKI Co.,Ltd, Tokyo	≥0.0001 in mole fraction (GC)
Carbon dioxide	CO <sub>2</sub>	Taiyo Nippon Sanso, Co., Tokyo	≥0.995 in mole fraction
Helium	He	Taiyo Nippon Sanso, Co., Tokyo	>0.9999995 in mole fraction
Nitrogen	N <sub>2</sub>	Taiyo Nippon Sanso, Co., Tokyo	>0.9999995 in mole fraction

Download English Version:

<https://daneshyari.com/en/article/5475930>

Download Persian Version:

<https://daneshyari.com/article/5475930>

[Daneshyari.com](https://daneshyari.com)