Fluid Phase Equilibria 361 (2014) 208–214

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

# Phase equilibrium and morphology characteristics of hydrates formed by tetra-*n*-butyl ammonium chloride and tetra-*n*-butyl phosphonium chloride with and without $CO_2$

N. Ye, P. Zhang*

*Institute of Refrigeration and Cryogenics, MOE Key Laboratory for Power Machinery and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

ARTICLE INFO

*Article history:*
Received 6 September 2013
Received in revised form 23 October 2013
Accepted 30 October 2013
Available online 6 November 2013

*Keywords:*
Phase equilibrium
Hydrate
Tetra-*n*-butyl ammonium chloride
Tetra-*n*-butyl phosphonium chloride
Morphology

ABSTRACT

In this study, experimental investigations on hydrate equilibrium conditions of hydrates formed by tetra-*n*-butyl ammonium chloride (TBAC: $C_{16}H_{36}ClN$) and tetra-*n*-butyl phosphonium chloride (TBPC: $C_{16}H_{36}ClP$) with and without $CO_2$ are carried out using isochoric experimental method at mass fractions $w = 0.05$, 0.10, 0.20, 0.35 and 0.50. The equilibrium data of $CO_2$ + TBAC and $CO_2$ + TBPC hydrates are measured at pressures of 0.6 to 4.1 MPa and at temperatures from 279.0 to 292.0 K. Meanwhile, the equilibrium data of TBAC and TBPC hydrates without $CO_2$ are measured at atmospheric pressure and at temperatures from 279.0 to 286.0 K. Moreover, the visualization is conducted to characterize the morphologies of hydrate crystals forming at subcoolings of 4.0 to 6.0 K, and the results are discussed in comparison with those of tetra-*n*-butyl ammonium bromide (TBAB) and tetra-*n*-butyl phosphonium bromide (TBPB) hydrate crystals forming with and without $CO_2$ presented in our previous papers.

## 1. Introduction

Gas hydrates or clathrate hydrates are inclusion compounds with crystalline appearance similar to that of ice. Gas hydrates can form with water as host component and suitable gas as guest component at low temperature and high pressure. Within the structure of hydrate molecule, water molecules are strongly hydrogen-bonded to construct cage of hydrate molecule in which some cavities are occupied by guest molecules. More than 130 guest components are known being able to form gas hydrate with water, and gas hydrates are mainly categorized into three types of structure: $S_I$, $S_{II}$ and $S_H$ [1] depending on the size, shape and nature of guest molecules. Since 1934, gas hydrate was regarded as the reason for blockage by the oil and gas industries because the formation of gas hydrates can block pipelines [2]. However, with gradual discovery of huge reserve of natural gas hydrate, a new natural energy resource, in the earth, more attentions were focused on gas hydrate. In modern society, hydrate is also a promising medium to separate the greenhouse gas like $CO_2$ from flue gas emitted by industries. In addition, $CO_2$ hydrate can be used as two-phase secondary refrigerant for cold storage and transport in order to improve the efficiency of cold production system because the dissociation enthalpy of $CO_2$ hydrate is larger than that of ice [3].

Fowler et al. [4] first identified new hydrate forming from water as the host component and tetra-*n*-butyl ammonium salts as the guest component at atmospheric pressure and room temperature. Unlike gas hydrate, this kind of hydrate can form without the presence of gas, and it was named as semiclathrate hydrate due to its different molecular structure from the above-mentioned three usual structures of gas hydrates. The cage of gas hydrate molecule is solely comprised of water molecules; but for semiclathrate hydrate, one water molecule is replaced by one anion from tetra-*n*-butyl ammonium salt to construct a cage with many water molecules, and one cation from tetra-*n*-butyl ammonium salt is trapped in four cavities in the cage [5]. Among these semiclathrate hydrates, tetra-*n*-butyl ammonium bromide (TBAB) semiclathrate hydrate has been most investigated. As the phase equilibrium temperature is higher than that of ice, and the formation condition is milder than that of gas hydrate, TBAB semiclathrate hydrate is deemed as a promising medium for cold storage [6,7]. Furthermore, semiclathrate hydrate can also incorporate suitable gas in empty cavities under moderate condition, and it is named as double hydrate, for example, $CO_2$ + TBAB double hydrate, where there are two kinds of guest components, i.e., the gas and TBAB in the hydration formation. Such double hydrate can be used as the medium for gas storage and separation [8,9]. Recently, there are intensive researches on $CO_2$ + TBAB double hydrate because $CO_2$ is regarded as a main contributor to the greenhouse effect in modern society with high fossil fuel consumption. As a result, the technology based on double hydrate for $CO_2$ capture and separation [10–12] has a

---

* Corresponding author. Tel.: +86 21 34205505; fax: +86 21 34206814.
*E-mail address:* zhangp@sjtu.edu.cn (P. Zhang).

0378-3812/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fluid.2013.10.055

**Table 1**
List of experimental materials adopted in the current study.

| Component | Purity | Supplier |
|---|---|---|
| $CO_2$ | >0.999 mole fraction | Shanghai Cheng Gong Gas Industry Co., Ltd., China |
| TBAC | 0.99 mass fraction | Shanghai Richness Chemical Co., Ltd., China |
| TBPC | 0.99 mass fraction | Shanghai Weifang Fine Chemical Co., Ltd., China |
| Water | | Distilled |

good prospect for large-scale industrial application, in which phase equilibrium data is one of the key parameters. The hydrate with a higher equilibrium temperature at specified pressure is much more favorable for energy saving in industrial application. Therefore, to measure the phase equilibrium data of different hydrates is very necessary. Many studies have reported the phase equilibrium data of similar double hydrates with $CO_2$, such as $CO_2$ + TBPB and $CO_2$ + TBAC double hydrates [13–15]. However, it is found that the published equilibrium data of $CO_2$ + TBAC double hydrate are only in a narrow mass fraction range, and there are even no equilibrium data for $CO_2$ + TBPC double hydrate reported in open literature.

In this study, equilibrium data of TBAC and TBPC hydrates forming with and without $CO_2$ have been measured systematically in a wide mass fraction range. Moreover, in order to characterize TBAC and TBPC hydrate crystals, the visualization is also carried out, and the results are discussed in comparison with those of TBAB and TBPB hydrate crystals forming with and without $CO_2$ [16,17].

## 2. Experiments and methods

### 2.1. Materials

Table 1 shows the purities and suppliers of chemicals used in the current study. Distilled water as solvent and TBAC or TBPC as solute were used for solution preparation. TBAC and TBPC were supplied by Shanghai Richness Chemical Co., Ltd and Shanghai Weifang Fine Chemical Co., Ltd, respectively, and the purities of them were all 0.99 (mass fraction). In addition, carbon dioxide with a purity larger than 0.999 (mole fraction) was purchased from Shanghai Cheng Gong Gas Industry Co., Ltd. All the above-mentioned chemicals were used without further purification.

### 2.2. Apparatus and preparations

The experimental apparatus used for the phase equilibrium condition measurements and visualization is shown in Fig. 1, which has been described in detail in our previous works [16,17]. The main part of the apparatus was an in-house made cylindrical crystallizer (CR) made of stainless steel with inner volume of 1030.0 ml. The CR can provide a sealed high-pressure condition for hydration up to 15.0 MPa. In addition, the formation and dissociation of hydrate can be observed through two optic windows made of aluminosilicate glass embedded in CR. The images of hydrate crystals were taken by a charge-coupled device (CCD) camera (Grasshopper GRAS-50S5C, Point Gray Research, Inc., Canada). A magnetic stir bar in CR was used for agitating the aqueous solution. The stir bar was driven and controlled by an electric motor (H03-A, Shanghai Meiyinpu Instrument, Ltd., China) placed directly under CR. The CR was immersed in a thermostat bath covered by thermal insulation material. Ethylene glycol/water mixture (40:60 wt%) as coolant was circulated between a thermostat (DC2020, Shanghai Hengping Instrument Co., Ltd., China) and the thermostat bath to control the temperature of CR. The temperatures of the gas and liquid phases in CR were measured by two PT100 thermometers (WZP-270S, Shanghai Institute of Process Automation Instrumentation) with an uncertainty of 0.1 K, and the pressure in CR was measured by a pressure transducer (YSZK-311, Dinkey Instrument Co. Ltd., China, (0 to 15.0 MPa) F.S., uncertainty: 0.1%).

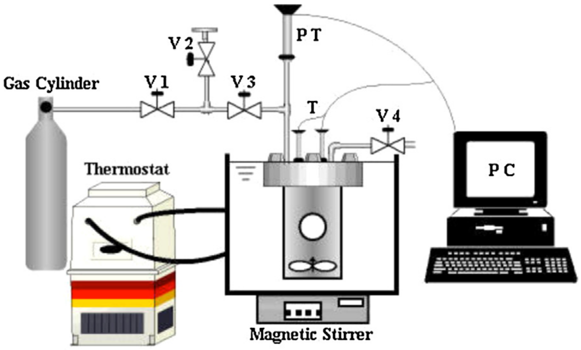

**Fig. 1.** Schematic diagram of the experimental apparatus. PT, pressure transducer; T, thermometer; V1 to V4, valves [16, 17].

An electronic balance with a high accuracy was used to weigh TBAC or TBPC and distilled water for aqueous solution preparation with the designated mass fraction. The uncertainty of this balance was 0.01 g (JM10002, Zhejiang Yuyao Jingming Weighing Sclae Co., Ltd., China). The mass fractions of TBAC and TBPC aqueous solutions adopted in this work were $w$ = 0.05, 0.10, 0.20, 0.35 and 0.50. Each time before charging the specified mass fraction aqueous solution, the CR was rinsed with aqueous solution at the same mass fraction. After solution charging, the CR was flushed with low-pressure $CO_2$ to remove any residual air. When $CO_2$ was introduced to CR at a designated pressure, the CR was sealed and the preparation procedure was completed.

### 2.3. Experimental procedure

#### 2.3.1. Measurements of hydrate phase equilibrium condition

The temperature of coolant was set low enough and the solution within CR was continuously agitated with a magnetic stir bar at a speed of 600 rpm to accelerate the formation of hydrate. The hydrate formation can be observed directly through the optic windows. There was a rapid drop in pressure and a rapid rise in temperature when hydrate formed. When there was no more change in the pressure and temperature versus time, the temperature of the system was increased at a step of 0.1 $K\,h^{-1}$ to dissolve hydrate. When infinitesimal amount of hydrate was detected in CR, the temperature increase rate was decreased to 0.0333 $K\,h^{-1}$. The heating up was stopped until there was no hydrate left in aqueous solution by observation, and the pressure and temperature were considered as the phase equilibrium data.

#### 2.3.2. Crystal morphologies of hydrate with and without $CO_2$

In the experiments, the hydrate crystals morphologies with and without $CO_2$ were observed and recorded by a CCD camera. The time when the first crystal was observed in the experiments was set as 0 s for determining the crystal growth. The subcooling $\Delta T_{sub} = T_{eq} - T_{ex}$ is in the range of 4.0 to 6.0 K, where $T_{eq}$ is the equilibrium temperature of TBAC and TBPC semiclathrate hydrates or $CO_2$ + TBAC and $CO_2$ + TBPC double hydrates corresponding to the equilibrium pressure $p$, and $T_{ex}$ is the bath temperature.

## 3. Results and discussion

The measurements of the phase equilibrium data of TBAC and TBPC semiclathrate hydrates forming at atmospheric pressure were conducted using the isochoric experimental method at different