Fluid Phase Equilibria 381 (2014) 102–107

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

# Phase equilibria of semiclathrate hydrates for methane + tetra n-butylammonium chloride (TBAC), carbon dioxide + TBAC, and nitrogen + TBAC aqueous solution systems

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ARTICLE INFO

*Article history:*
Received 18 May 2014
Received in revised form 7 August 2014
Accepted 8 August 2014
Available online 17 August 2014

*Keywords:*
TBAC
Phase equilibria
Gas hydrate
Clathrate hydrate
Semiclathrate hydrate

ABSTRACT

The equilibria of semiclathrate hydrates for the systems of tetra-n-butylammonium chloride (TBAC) + water + gas (methane, carbon dioxide, or nitrogen) and TBAC + water were measured. The experiments were performed in the temperature range of 277.1–293.2 K and the pressure range of 1.02–9.83 MPa at 0.05, 0.15, and 0.22 mass fraction of TBAC. An isochoric pressure-search method was employed to generate the phase equilibrium data. The experimental results show that the presence of TBAC moderates the hydrate formation (dissociation) conditions remarkably (in the concentration ranges studied in this work). Moreover, pressure reduction is dependent on TBAC concentration. By increasing the concentration of TBAC from 0.05 mass fraction to 0.22 mass fraction, its promotion effect increases and the pressure–temperature curves of the double gas + TBAC semiclathrate shift to the stabilized regions. The isobaric dissociation temperature of TBAC + methane semiclathrates is close to that of TBAC + carbon dioxide semiclathrates.



## 1. Introduction

The greenhouse gases such as methane and carbon dioxide have the potential for harmful environmental effects and the emission of these gases is one of the main concerns of the international communities in recent years. Thus, it is important to find a safe and economic method to capture and separate greenhouse gases.

Clathrate hydrates, or gas hydrates, are crystalline inclusion compounds in which molecules of suitable size and shape such as methane, carbon dioxide and nitrogen remain engaged as guest inside the host lattice of water molecules [1]. Clathrates consist of two dissimilar molecules physically intermingled but not truly chemically bonded. In the clathrate hydrates, the guest molecules occupy the cavities formed by hydrogen-bonded water molecules; and do not participate in the hydrate lattice structure.

Three typical hydrate structures have been reported in the literature, including structure I (sI), structure II (sII) and structure H (sH) [1]. Gas hydrates have the potential for many industrial applications. However, high pressure and low temperature conditions in the process of hydrate formation is a critical problem to benefit its application. Thus, moderating the hydrate formation conditions seems to be very important and economic. In 1940, some new hydrate structures (in the systems of water + tetra n-butyl and tetraisoamyl quaternary salts) were discovered by Fowler et al. [2]. In 1967, Jeffrey and McMullan [3] analyzed the structure of hydrates formed by a large number of these salts and found that the structural nature of these hydrates is different from clathrate hydrates. In this type of hydrates the guest molecules participate in the lattice structure; therefore these structures are called semiclathrates. The most common compounds that form semiclathrates are tetra n-butylammonium salts (TBAX), in which "X" can stand for a monoatomic halide anion such as bromide, chloride and fluoride. In crystal structure of semiclathrate hydrates a part of the cage structure is broken in order to encage the large guest ion species (e.g. $TBA^+$ in the case of TBAX aqueous solution) and water molecules with participate of guest anions ($X^-$) build up a polyhedral hydrogen-bonded framework [3–12].

Recently, some researchers have shown that the small cavities of TBAX semiclathrate hydrates can be occupied by gas molecules having appropriate size such as methane, carbon dioxide, nitrogen

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http://dx.doi.org/10.1016/j.fluid.2014.08.012
0378-3812/

(they are called auxiliary gas) [4,6,10,12–21]. When the dodecahedral ($5^{12}$) cavities in the structures of semiclathrate hydrates are filled with auxiliary gas molecules, double gas + TBAX hydrates are formed.

The hydrate promotion effects (shifting hydrate phase equilibria in curve to low pressures and high temperatures) of various water-soluble organic compounds such as acetone, 1,4-dioxane, and tetrahydrofuran (THF), have been studied by some researchers [22–26]. THF moderates the hydrate formation conditions sharply and its hydrate forms at atmospheric pressure [22,25]. Nevertheless, toxicity and volatility are some of the problems of using these compounds as a thermodynamic promoter.

Tetra n-butylammonium salts such as TBAB, TBAC and TBAF form semiclathrate hydrates with water molecules at ambient conditions and the presence of these compounds can dramatically moderate the gas hydrate formation conditions [6,10,21,27–30]. Tetra n-butylammonium salts are environmental friendly compounds. These materials are not toxic, volatile or flammable. These positive features of tetra n-butylammonium salts, result in significant attention to these compounds as a suitable additive for different applications of gas hydrate formation such as gas separation, sequestration of greenhouse gases [31–35], gas storage [36,37] and air-conditioning systems [38,39].

Because TBAB semiclathrate shows a favorable stability conditions, it has been studied more extensively than other tetra alkylammonium salts in the recent years [5,40,41]. However, some researchers have reported the remarkable effect of TBAC on the stabilization regions of gas hydrates [12,16,17,28]. However, there are not enough phase equilibrium data on TBAC + gas semiclathrate hydrate systems and more equilibrium data should be obtained in order to better understand gas enclathration behavior of TBAC semiclathrate, which are applicable in industrial application of gas hydrates.

The main objective of this work is to show that tetra n-butylammonium chloride greatly moderate the (methane, carbon dioxide or nitrogen) hydrates formation (dissociation) conditions.

**Table 1**
Purities and suppliers of materials used in this work.

| Purity | Supplier | Chemical name |
|---|---|---|
| 0.95 mass fraction | Merck | TBAC[a] |
| 0.99995 mol fraction | Varian gas | Methane |
| 0.9995 mol fraction | Varian gas | Nitrogen |
| 0.999 mol fraction | Varian gas | Carbon dioxide |

[a] TBAC: tetra n-butyl ammonium chloride.

In the present work, we mainly report the experimental data on the equilibrium conditions and stability regions for the water + TBAC (mass fraction = 0.05, 0.15, 0.22) + methane, +carbon dioxide, and +nitrogen systems.

## 2. Experimental

### 2.1. Materials

The purities and suppliers of the materials used in this work are reported in Table 1. Distilled water was used to prepare the TBAC aqueous solutions with $W_{TBAC}$ = 0.05, 0.15 and 0.22 mass fraction. Aqueous solutions were prepared with a gravimetric method using an accurate analytical balance (mass uncertainty: ±0.0001 g).

### 2.2. Apparatus

The schematic diagram of the apparatus is shown in Fig. 1. The reactor is a jacketed stainless steel cell (with an effective volume of 460 $cm^3$). It has a valve for charging and discharging aqueous solution and gas. For appropriate mixing of the gas and aqueous solution, an electromotor is used to rock the cell. The rocking motion of the cell always makes the existing phases in the reactor; (hydrate, liquid, and gas phases) being in contact together even after the hydrate formation, which is necessary for obtaining true equilibrium data. The jacket of the reactor has an inlet and an outlet

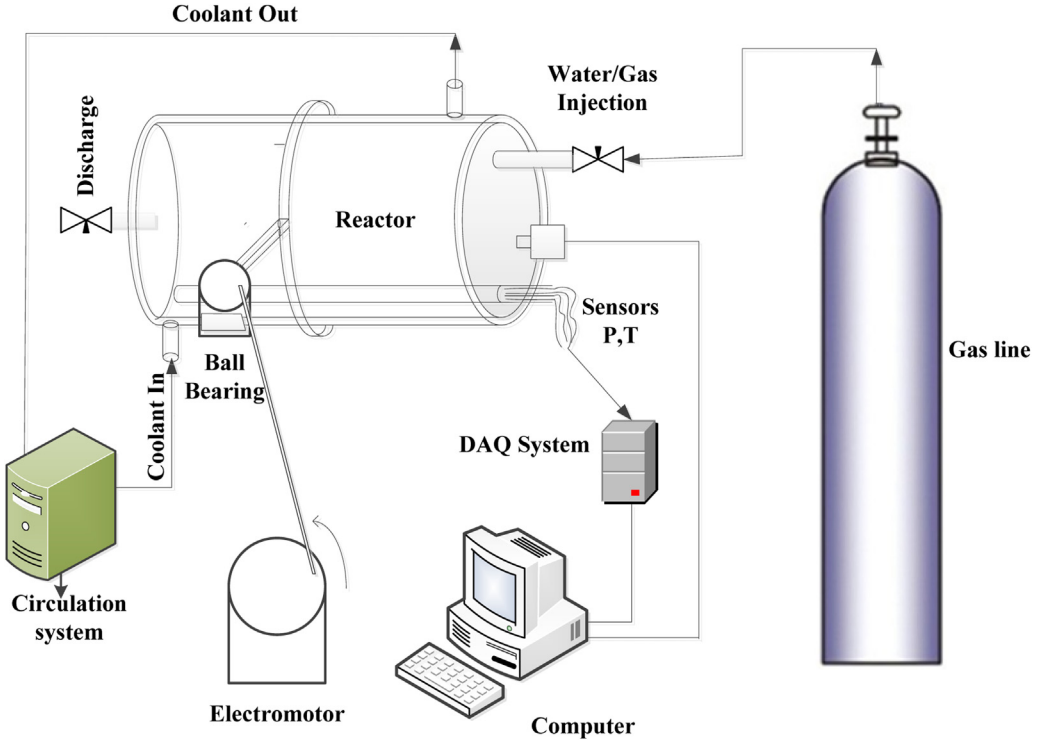


**Fig. 1.** Schematic illustration of the apparatus.