



Experimental measurements of carbon dioxide solubility in aqueous tetra-*n*-butylammonium bromide solutions



Saneshiro Muromachi ^{a,*}, Atsushi Shijima ^b, Hiroyuki Miyamoto ^b, Ryo Ohmura ^c

^a Methane Hydrate Research Centre, National Institute of Advanced Industrial and Science Technology (AIST), 14-1 Onogawa, Tsukuba 305-8569, Japan

^b Department of Mechanical Systems Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama 939-0311, Japan

^c Department of Mechanical Engineering, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

ARTICLE INFO

Article history:

Received 17 September 2014

Received in revised form 15 January 2015

Accepted 17 January 2015

Available online 28 January 2015

Keywords:

Carbon dioxide

Solubility

Water

Tetra-*n*-butylammonium bromide

Semiclathrate hydrate

Gas hydrate

ABSTRACT

In this paper, we report the absolute measurements of CO₂ solubility in aqueous tetra-*n*-butylammonium bromide (TBAB) solution. The measurement range was 0.2 MPa < P < 4 MPa, 286.15 K < T < 298.15 K, with 0 (pure water) < w_{TBAB} < 0.4, where P , T , and w_{TBAB} denote the pressure, temperature, and mass fraction of TBAB in the aqueous feed solutions, respectively. These thermodynamic conditions are outside the hydrate formation region. We evaluated salting-in and -out effects based on the experimental data, and confirmed that the CO₂ salting-out effect of TBAB clearly appeared at $T = 292$ K with $w_{\text{TBAB}} < 0.32$ and the salting-in effect may exist for $P > 3$ MPa and $T > 292$ K with $w_{\text{TBAB}} \geq 0.4$ mass fraction of TBAB.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Among the numerous potential technologies for carbon capture and storage (CCS), applications using gas hydrates are the ones being presently developed. Gas hydrates are formally known as clathrate hydrates and are crystalline *guest-host* compounds that consist of water (*host*) and other molecules (*guest* or clathrate hydrate former). In the crystal structure, the water molecules form hydrogen-bonded cage-like voids, and guest gases can occupy the cages. Because gases that are important for environmental reasons, e.g., carbon dioxide, hydrocarbons, and hydrofluorocarbons, have suitable sizes for the cages, they can be easily captured in the hydrate cage. Ionic clathrate hydrates, which are composed of water and ionic guest substance [1], can encapsulate guest gases under moderate pressure–temperature conditions. Many potential applications relevant to CCS technology are presently being developed, e.g., gas storage and separation. Among the numerous ionic clathrate hydrate formers, tetra-*n*-butylammonium bromide (TBAB) has been tested for various applications because of its availability and low toxicity [2–5]. Ionic clathrate hydrates form from an aqueous solution of an ionic guest substance pressurized with a guest gas, and therefore the guest gas solubility is a factor for the formation reaction.

The phase equilibrium conditions of TBAB + CO₂ hydrate, which is characterized by the pressure (P) – temperature (T) – composition of TBAB in the aqueous phase (x_{TBAB}), are highly sensitive to the composition of TBAB in the aqueous phase [8–10] because of the stoichiometry of the crystal. Furthermore, the (TBAB + CO₂) hydrate has at least two crystal structures, which have compositions of TBAB · 38H₂O and TBAB · 26H₂O [11]. Thus, mass transfer of the hydrate formation is a complex of CO₂ and TBAB in the aqueous phase. Therefore, CO₂ solubility in the aqueous TBAB solution (x_{CO_2}) is necessary for crystal engineering of the ionic clathrate hydrate [12].

Some thermodynamic models have been suggested to interpret the equilibration mechanism [13,14]. In the calculation process of the aqueous phase, the solubility of the guest gas is in a framework, because the ionic clathrate former is usually an electrolyte and there are interactions between the ions and gas molecules. To understand such a complicated system and develop a more precise thermodynamic model, reliable equilibrium data, such as gas solubility, hydrate formation conditions, and cage occupancy, are required. The solubility data of CO₂ in aqueous TBAB solutions can be found in the literature [15–17]. It is of interest that these studies report salting-in and -out effects, which depend on the aqueous TBAB concentration. To clarify the effects, accurate solubility data are required. However, previous reports used the equations of state, which usually has 5 to 10% accuracy to obtain the CO₂ content in the aqueous sample.

* Corresponding author. Tel.: +81 29 861 4287; fax: +81 29 861 8706.

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

In this paper, we report experimental values of solubility of CO₂ in aqueous TBAB solutions obtained by absolute gravimetric measurements. The measurement range was $0.2 \text{ MPa} \leq P \leq 4 \text{ MPa}$, $286.15 \text{ K} \leq T \leq 298.15 \text{ K}$, and $0 \text{ (pure water)} \leq w_{\text{TBAB}} \leq 0.4$, where P , T , and w_{TBAB} denote the pressure, temperature, and mass fraction of TBAB in aqueous feed solutions, respectively, and these conditions are outside the hydrate formation region. The gravimetric measurements were conducted on the mass of the liquid samples before and after separation of CO₂ from water using the difference in the freezing point. The salting-in and -out effects were evaluated with the solubility data and the range is clarified in detail.

2. Experimental

2.1. Materials

Table 1 shows the specifications of the materials used in this study. The materials used in this study were water, tetra-*n*-butylammonium bromide salt, and carbon dioxide gas. Water was deionized and twice distilled before use. The TBAB salt of 0.995 mass fraction certified purity (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and CO₂ gas of 0.9998 volume fraction certified purity (Hokusan Co. Ltd., Japan) were directly used as received

from their respective manufacturers. Aqueous TBAB solutions were prepared with the aid of a dead weight balance that had $\pm 1 \text{ mg}$ uncertainty.

2.2. Apparatus

Figure 1 shows the dissolution apparatus used in this study. The aqueous TBAB solution was injected into a high pressure cell volume of which was 505 cm³. The electromagnetically induced stirrer was set on the top lid and the liquid phase was stirred at 400 rpm. The cell was equipped with glass windows, and it was possible to observe the inside of the cell. The cell was immersed in a temperature-controlled bath and maintained at a given temperature within $\pm 0.1 \text{ K}$. A platinum resistance thermometer (RD-185; Shimaden Co. Ltd.) was inserted into the cell. A strain-gage type pressure sensor (KH15; Nagano Keiki Co. Ltd.) was connected to the lid. The P - T data in the cell were acquired by a data logger (Daqstation DX220; Yokogawa Electric Corp., Tokyo, Japan). Carbon dioxide gas was supplied from a CO₂ gas cylinder. Two syringe-type pumps were connected to the cell. Their volumes were 300 cm³ and the temperature was controlled by a coolant circulator to be the same temperature as that of the cell. When liquid was sampled from the cell, the pumps worked and supplied CO₂ gas to compensate for the lost volume and maintain a constant

TABLE 1
Specifications of the materials used in this study.

Chemical name	Chemical formula	Supplier	Certified purity
Tetra- <i>n</i> -butylammonium bromide	(<i>n</i> -C ₄ H ₉) ₄ NBr	Wako pure Chemical Industries, Ltd.	0.995 mass fraction
Carbon dioxide	CO ₂	Hokusan Co. Ltd.	0.9998 volume fraction

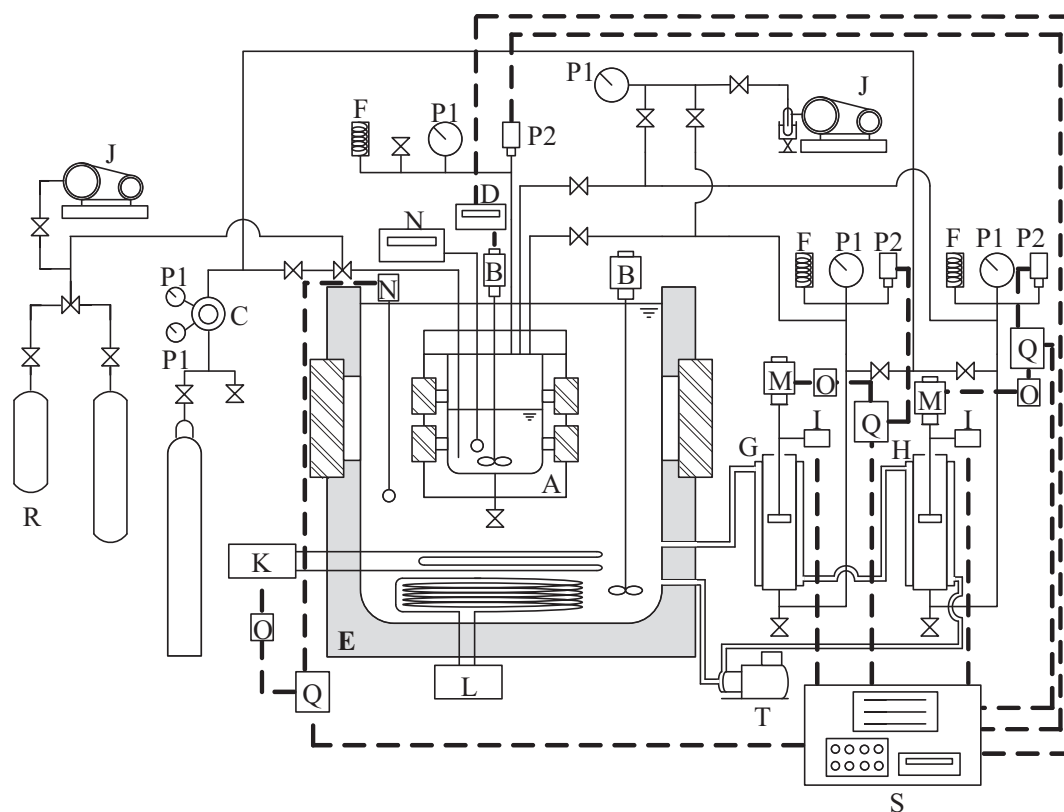


FIGURE 1. Schematic of the apparatus: A, high-pressure cell; B, stirrer; C, reducing valve; D, tachometer and torque sensor; E, thermostatted water bath; F, safety valve; G, recovery gas cylinder; H, sampling gas cylinder; I, linear gauge; J, vacuum pump; K, heater; L, chiller; M, motor; N, platinum resistance thermometer; O, thyristor regulator; P1, pressure gauge; P2, pressure sensor; Q, PID controller; R, sampling vessel; S, data logger; T, circulating pump.

Download English Version:

<https://daneshyari.com/en/article/6660537>

Download Persian Version:

<https://daneshyari.com/article/6660537>

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