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# Phase equilibrium measurements for semi-clathrate hydrates of the ($CO_2$ + $N_2$ + tetra-n-butylammonium bromide) aqueous solution system

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ABSTRACT

The application of semi-clathrate hydrate formation technology for gas separation purposes has gained much attention in recent years. Consequently, there is a demand for experimental data for relevant semi-clathrate hydrate phase equilibria. In this work, semi-clathrate hydrate dissociation conditions for the system comprising mixtures of {$CO_2$ (0.151/0.399 mole fraction) + $N_2$ (0.849/0.601 mole fraction) + 0.05, 0.15, and 0.30 mass fraction tetra-n-butylammonium bromide (TBAB)} aqueous solutions have been measured and are reported. An experimental apparatus which was designed and built in-house was used for the measurements using the isochoric pressure-search method. The range of conditions for the measurements was from 277.1 K to 293.2 K for temperature and pressures up to 16.21 MPa. The phase equilibrium data measured demonstrate the high hydrate promotion effects of TBAB aqueous solutions.

## 1. Introduction

Gas hydrates, or clathrate hydrates, are crystalline solid compounds composed of water and small molecules such as $CO_2$, $N_2$, methane ($CH_4$), hydrogen ($H_2$), *etc.*, which are formed under suitable conditions of low temperatures and specified pressures [1–5]. They are a subset of compounds known as clathrates (from the Greek word "khlatron") or inclusion compounds [1,2,5]. A clathrate compound is formed when a guest molecule or molecules are trapped in a structure or structures formed from a host molecule or molecules [1,2].

In the early 1930s, evidence was found indicating that the formation of gas hydrates was one of the main reasons for pipeline blockages in the petroleum industry [1,2]. However, there are many positive applications of clathrate hydrates, many of which have been reported in literature but have gained renewed interest in the past decade, *e.g.*, in $CO_2$ capture and sequestration, gas storage, air-conditioning systems in the form of hydrate slurry, water desalination/treatment technology, concentration of dilute aqueous solutions, separation of different gases, *etc.* [1,2,4,6–11].

The ever-increasing energy needs of human beings have contributed to greater utilization of fossil fuels such as coal, oil, and natural gas [10–18]. Several comprehensive studies show that large amounts of carbon dioxide, carbon monoxide, and hydrogen sulphide (called "greenhouse gases") are emitted every year into the atmosphere [10–18] as a result of combustion of fossil fuels. Accumulation of these gases in the earth's atmosphere is widely accepted to be the cause of global warming which has been related to harmful environmental effects including sudden and unexpected climate change. Therefore, separation of the aforementioned gases from their corresponding gas mixtures which are generally found in flue gas streams of, *e.g.*, power-plants is of great interest for the industry.

The $CO_2$ is considered, perhaps, the most important greenhouse gas due to the fact that about 64% of the greenhouse gas effects are related to carbon dioxide emissions [4,10–19]. Therefore, the objective of many research studies recently has been on the development of energy efficient and environmental friendly methods to capture $CO_2$ produced in large scale power-plants, where flue gases typically contain mostly $N_2$ and $CO_2$ [10–19].

The gas hydrate crystallization (formation) technique has recently been proposed to have great potential to separate carbon dioxide from combustion flue gas [10,18–48]. Based on the difference in chemical affinity between $CO_2$ and other gases in the hydrate structure when hydrate crystals are formed from a binary mixture of the aforementioned gases, the hydrate phase is enriched in $CO_2$ while the concentration of other gases is increased in the

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**TABLE 1**
Experimental hydrate dissociation conditions available in open literature for the (carbon dioxide + nitrogen + TBAB) aqueous solution system at different concentrations of TBAB.

| Authors | System | TBAB mass fraction | $T$ range/K | $p$ range/MPa | Number of experimental points |
|---|---|---|---|---|---|
| Deschamps and Dalmazzone [50] | $CO_2$ (0.249 mole fraction) + $N_2$ (0.751 mole fraction) | 0.4 | 284.8 to 293.3 | Up to 9.180 | 5 |
| Meysel *et al.* [69] | $CO_2$ (0.75 mole fraction) + $N_2$ (0.15 mole fraction) | 0.05, 0.1, 0.2 | 284.1 to 290.0 | 1.964 to 3.822 | 14 |
| Meysel *et al.* [69] | $CO_2$ (0.50 mole fraction) + $N_2$ (0.50 mole fraction) | 0.05, 0.1, 0.2 | 282.3 to 290.4 | 1.956 to 5.754 | 16 |
| Meysel *et al.* [69] | $CO_2$ (0.20 mole fraction) + $N_2$ (0.80 mole fraction) | 0.05, 0.1, 0.2 | 281.8 to 288.3 | 2.976 to 5.901 | 12 |
| Lu *et al.* [35] | $CO_2$ (0.159 mole fraction) + $N_2$ (0.841 mole fraction) | 0.05, 0.153, 0.348, 0.407, 0.457 | 278.05 to 287.85 | 1.17 to 5.84 | 12 |

**TABLE 2**
Purities and suppliers of chemicals.*

| Chemical | Supplier | Purity |
|---|---|---|
| Carbon dioxide (0.151 mole fraction) + nitrogen (0.849 mole fraction) | Air liquide | Purity of each gas > 0.99 (mole fraction) |
| Carbon dioxide (0.399 mole fraction) + nitrogen (0.601 mole fraction) | Air liquide | Purity of each gas > 0.99 (mole fraction) |
| TBAB | Sigma–Aldrich | 0.99 (mass fraction) |

Aqueous solutions were prepared following the gravimetric method, using an accurate analytical balance (mass uncertainty ±0.0001 g). Consequently, uncertainties on the basis of mole fraction are estimated to be <0.01.

* Deionised water was used in all experiments.

gas phase at equilibrium. The hydrate phase is then dissociated by depressurization and/or heating, and subsequently $CO_2$ can be recovered as a separated gas [18–22].

Generally the hydrate formation for these flue-gas systems occurs at high pressure and low temperature. Gas hydrate promoters are generally added to the gas hydrate formation processes to reduce the required hydrate formation pressure and increase the formation rate and/or temperature along with modification of the selectivity of hydrate cages for absorption of various gas molecules in the water cages [18]. The common hydrate promoters can be grouped into the following categories [18]:

1. Chemical additives that have no effect on the structures of the water cages *e.g.* tetrahydrofuran (THF), cyclopentane, acetone, *etc.* [23–38].
2. Those hydrate promoters which change the structures of the ordinary water cages in the traditional clathrate structures such as tetra-n-butylammonium salts and [$(n\text{-}C_4H_9)_4NBH_4$] [39–43].

The THF, from the first, and TBAB (tetra-n-butylammonium bromide), from the second category are the common thermodynamic promoters that have been proposed for separation processes recently.

The second category of hydrate promoters consists mainly of environmental friendly tetra-n-butylammonium ionic liquids. They form semi-clathrate hydrates in which a part of the cage structure is broken in order to trap the large tetra-n-butyl ammonium molecule [18]. This feature results in more gas storage capacity than the organic hydrate promoters such as THF. Although the promoters like THF can significantly decrease the hydrate formation pressure, they are volatile and may be consequently lost in considerable amounts during separation processes. More description about semi-clathrate hydrates, including the results of crystallography, NMR studies, *etc.* can be found in literature [6,39–68].

In order to design separation processes using semi-clathrate hydrate crystallization, reliable phase equilibrium data are required. Table 1 provides a summary of all experimental studies on semi-clathrate hydrates for mixtures of ($CO_2 + N_2$) in the presence of TBAB aqueous solution [35,50,69] that are available in the open literature. It is clear that there are not sufficient data available to undertake an efficient process design. Therefore, it is an imperative to generate more experimental phase equilibrium data to clarify complex phase behaviour of semi-clathrates, tune the future thermodynamic models, and for the investigation of the relevant separation capabilities through application of these structures. Consequently, in this study, the semi-clathrate hydrate dissociation conditions for the {$CO_2$ (0.151/0.399 mole fraction) + $N_2$ (0.849/0.601 mole fraction)} system in the presence of different concentrations of TBAB aqueous solutions (0.05, 0.15, and 0.30 mass fraction) are measured and reported.

## 2. Experimental

### 2.1. Materials

Table 2 lists the chemicals used in this work, their suppliers, and the purities. The chemicals were used without any further purification.

### 2.2. Equipment

In summary, the main part of the experimental apparatus is a cylindrical vessel made of Hastelloy, which can withstand pressures up to 20 MPa. The volume of the vessel is approximately 30 $cm^3$. A magnetic stirrer is installed in the vessel to agitate the fluids and hydrate crystals. A thermostatic bath (Lauda E100, Type RE112) is used to control the temperature of the equilibrium cell. Two platinum resistance thermometers (Pt100) are inserted into the vessel to measure temperatures and check for their equality within the measurement uncertainty, which is estimated to be less than 0.1 K. The estimated temperature uncertainty is determined by calibration against a 25 Ω reference platinum resistance thermometer. The pressure in the vessel is measured with a DRUCK pressure transducer (Druck, type PTX611 for pressures up to 16 MPa). The estimated pressure uncertainty is less than 5 kPa and is determined by calibration against a dead weight balance (Desgranges and Huot, model 520). A schematic diagram of the experimental apparatus is shown in figure 1.