



# Thermodynamic stability conditions for semi-clathrate hydrates of CO<sub>2</sub>, CH<sub>4</sub>, or N<sub>2</sub> with tetrabutyl ammonium nitrate (TBANO<sub>3</sub>) aqueous solution



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## ABSTRACT

In this communication, the effect of tetrabutyl ammonium nitrate (TBANO<sub>3</sub>) on CO<sub>2</sub>, CH<sub>4</sub>, or N<sub>2</sub> hydrate was studied. Hydrate dissociation conditions for CO<sub>2</sub> + TBANO<sub>3</sub> + water, CH<sub>4</sub> + TBANO<sub>3</sub> + water and N<sub>2</sub> + TBANO<sub>3</sub> + water were investigated at different concentrations of TBANO<sub>3</sub>, viz. (0.05, 0.10, and 0.15) mass fraction, and over a temperature and pressure range of  $T = (275.1 \text{ to } 285.1) \text{ K}$  and (1.21 to 7.27) MPa, respectively. The results show that the presence of TBANO<sub>3</sub> causes the phase equilibrium curve to be shifted to moderate conditions (lower pressure and higher temperature), especially at higher concentrations of TBANO<sub>3</sub>.

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## 1. Introduction

Separation using gas hydrate (or clathrate hydrate) technology is an attractive and cost effective method/technique for carbon dioxide capture and storage [1–3]; cold storage for air conditioning systems [4]; separation of different gases [5], etc. Gas hydrate are non-stoichiometric solid compounds which are composed of small guest (gas or volatile liquid) and host (water) molecules. Water molecules form a hydrogen bonded framework to capture the gas molecules.

The formation of gas hydrates typically needs conditions of high pressure and low temperature, which makes the process costly. In order to have moderate conditions for hydrate phase formation, as well as speed up the hydrate formation process, gas hydrate promoters were developed in crystallization processes. Tetrabutyl ammonium nitrate (TBANO<sub>3</sub>) can be used as a promoter to enable hydrate formation at moderate pressure and temperature conditions [6].

TBANO<sub>3</sub> forms an unusual hydrate structure which is called a semi-clathrate hydrate. In the TBANO<sub>3</sub> semi-clathrate, water

molecules and anions (NO<sub>3</sub><sup>-</sup>) form a cage structure which encloses the tetra-*n*-butyl ammonium cations (TBA<sup>+</sup>). In addition, TBANO<sub>3</sub> semi-clathrates have empty cages capable of entrapping gas molecules such as CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. TBANO<sub>3</sub> semi-clathrates can form two different types of structures, viz. TBANO<sub>3</sub> · 26H<sub>2</sub>O and TBANO<sub>3</sub> · 32H<sub>2</sub>O [6].

The addition of TBANO<sub>3</sub> can remarkably affect the hydrate formation conditions. Mayoufi *et al.* [7] investigated the equilibrium conditions and dissociation enthalpies of semi-clathrate hydrates formed from CO<sub>2</sub> + TBANO<sub>3</sub> + water. They used differential scanning calorimetry (DSC) for the determination of hydrate–liquid–vapor (H–L–V) equilibrium conditions at a concentration of 0.3707 mass fraction of TBANO<sub>3</sub> and at pressures in the range of (0.5 to 0.15) MPa. Du *et al.* [8] measured phase equilibrium data for {CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>} + TBANO<sub>3</sub> + water systems at a TBANO<sub>3</sub> mass fraction of 0.3941 and at temperature and pressure ranges of  $T = (281.5 \text{ to } 290.9) \text{ K}$  and (1.19 to 32.89) MPa, respectively.

In another study, Du *et al.* [6] investigated the thermodynamic stability conditions for hydrogen semi-clathrate hydrates in the presence of TBANO<sub>3</sub> aqueous solutions at two mass fractions, viz. 0.394 and 0.344.

Shi *et al.* [9] investigated the hydrate phase equilibrium conditions for the system of methane and carbon dioxide (50 mol% methane and 50 mol% carbon dioxide) at different concentrations of TBANO<sub>3</sub>, viz. (0.050, 0.170, 0.340, and 0.394) mass fraction in

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the pressure range of (1.90 to 13.83) MPa and temperature range of  $T = (280.0 \text{ to } 288.3) \text{ K}$ . To the best of our knowledge, there are no additional data in the open literature for equilibrium conditions of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  in the presence of  $\text{TBANO}_3$  solutions.

The main aim of this study is to evaluate the possibility of using lower concentrations of  $\text{TBANO}_3$  to promote the formation of clathrate hydrates and find the optimum processing conditions (concentration, temperature, and pressure).

In the present study, experimental data on the equilibrium conditions of semi-clathrate hydrates formed from  $\text{CO}_2 + \text{TBANO}_3 + \text{water}$ ,  $\text{CH}_4 + \text{TBANO}_3 + \text{water}$ , and  $\text{N}_2 + \text{TBANO}_3 + \text{water}$  are reported. The experimental data were measured using the isochoric pressure search method at mass fractions of (0.05, 0.10 and 0.15)  $\text{TBANO}_3$ , in the temperature range of  $T = (275.1 \text{ to } 285.1) \text{ K}$  and in the pressure range of (1.21 to 7.27) MPa.

## 2. Experimental section

### 2.1. Materials

Table 1 presents the purities and suppliers of the chemicals used in this study. Ultrapure Millipore Q water with an electrical conductivity of  $18 \text{ M}\Omega \cdot \text{cm}$  was used to prepare the  $\text{TBANO}_3$  aqueous solutions in all experiments.

### 2.2. Experimental apparatus

The equipment used for the measurements was designed and commissioned in the Thermodynamics Research Unit (TRU) in the School of Engineering, University of KwaZulu-Natal [10]. The apparatus allows for the measurement of phase equilibrium data within the pressure range of (0.1 to 10) MPa with an expanded uncertainty (95% confidence level) of 0.05 MPa in the reported pressure. The operating temperature range of the apparatus is  $T = (243.15 \text{ to } 323.15) \text{ K}$ , and the expanded uncertainty in the reported temperature is 0.1 K.

A schematic diagram of the apparatus used in this study is shown in figure 1.

The apparatus consists of a stainless steel equilibrium cell which has an effective volume of approximately  $64 \text{ cm}^3$ . The cell is equipped with a magnetic stirrer to agitate the fluid and hydrate crystals formed during the measurements. The stirring device is located at the bottom of the cell which enables agitation of the liquid and hydrate contents. The stirring device is coupled to a Heidolph RZR 2041 overhead stirrer. The overhead stirrer drives a gear chain at the bottom of the cell which drives the magnetic stirrer. The temperature of the cell is controlled using a Grant temperature bath controller (Grant Optima™ TX150) which provides a stable and uniform temperature profile across the equilibrium cell. Two platinum (Pt) resistor temperature sensors, Pt100s, are inserted into the cell wall to monitor the temperature. Each Pt100 is fixed to the top or bottom of the equilibrium cell, corresponding to the vapor and liquid phases, respectively. A WIKA P-10 pressure transducer is used to measure the cell pressure.

TABLE 1

Purities and suppliers details of the chemicals used in this study.

| Chemical  | Formula  | Purity                 | Supplier      |
|---|--|------------------------|---------------|
| Carbon dioxide                                      | $\text{CO}_2$                                    | $\geq 0.9999$<br>(vol) | AFROX Ltd     |
| Methane   | $\text{CH}_4$                                    | $\geq 0.9999$<br>(vol) | AFROX Ltd     |
| Nitrogen  | $\text{N}_2$                                     | $\geq 0.9999$<br>(vol) | AFROX Ltd     |
| Tetrabutyl ammonium nitrate<br>( $\text{TBANO}_3$ ) | $\text{C}_{16}\text{H}_{36}\text{N}_2\text{O}_3$ | 0.97 (mass)            | Sigma-Aldrich |

The temperature and pressure readings of the cell are recorded and logged using a data acquisition unit (Agilent 34972A LXI).

### 2.3. Procedure

The isochoric pressure-search method [11,12] was used to measure the hydrate dissociation conditions. A typical temperature–pressure plot of the experimental method is shown in figure 2.

After flushing the equilibrium cell with distilled water to remove any contaminants, the cell is evacuated (pressure down to 0.01 kPa) for an hour. The cell is thereafter charged with the aqueous solution (approximately 30% of the cell volume is filled with aqueous solution). Once charged with the aqueous solution, the cell is pressurized to the desired pressure by supplying an appropriate amount of gas (carbon dioxide, methane, or nitrogen). The solution within the cell is then vigorously mixed using the stirrer. Once the pressure within the cell stabilizes, the flow of gas into the equilibrium cell is stopped. The temperature of the equilibrium cell is then slowly decreased at a rate of  $10 \text{ K} \cdot \text{h}^{-1}$  until hydrate is formed. The initial hydrate formation is detected by a rapid decrease in pressure due to encapsulation of the hydrate former. After the completion of hydrate formation, the system is slowly heated at a rate of  $1 \text{ K} \cdot \text{h}^{-1}$  to dissociate the hydrate. The temperature is thereafter slowly increased at a rate of  $0.2 \text{ K} \cdot \text{h}^{-1}$ . At each increment of temperature, the temperature is kept constant for sufficient time to obtain an equilibrium state within the cell. Thereafter, a pressure–temperature diagram is sketched for each experimental run to determine the hydrate dissociation point. The intersection between the cooling curve and the dissociation curve is taken as the dissociation point.

## 3. Results and discussion

Semi-clathrate hydrate formation conditions for  $\text{CO}_2$ ,  $\text{CH}_4$ , or  $\text{N}_2$  in the presence of  $\text{TBANO}_3$  are tabulated in tables 2–4 and plotted in figures 3–5.

For validation of the experimental procedure and the experimental setup, a few experimental dissociation data for  $\text{CO}_2$  in the presence of pure water were measured in the temperature range of  $T = (279.3 \text{ to } 283.3) \text{ K}$  and pressures ranging from (2.57 to 4.45) MPa. The measured data are presented in table 2 and compared with literature data [13]. figure 3 provides a graphical comparison of the data and shows that there is good agreement between the measured data and that reported in literature [13].

It can be seen from figure 3 and table 2 that the influence of the  $\text{TBANO}_3$  solution at 0.05 mass fraction, is unlike that for solutions at 0.15 and 0.394 mass fraction. The salt solution with a 0.05 mass fraction of  $\text{TBANO}_3$  shows a small/negligible promotion effect at pressures lower than 2.5 MPa because the phase equilibrium curve shifts to a higher temperature and lower pressure, while the phase equilibrium curve of  $\text{CO}_2 + \text{TBANO}_3 + \text{water}$  and the phase equilibrium curve of  $\text{CO}_2 + \text{water}$  [13] are identical at a higher pressure. This means that the  $\text{TBANO}_3$  solution at 0.05 mass fraction at a pressure higher than 2.5 MPa does not influence semi-clathrate hydrate formation condition.

For salt solutions with a mass fraction of 0.1  $\text{TBANO}_3$ , the pressure drops due to the semi-clathrate formation. At pressures higher than 3.7 MPa,  $\text{TBANO}_3$  does not have a significant promotion effect on  $\text{CO}_2$  semi-clathrate hydrates, and as can be seen in figure 3 the phase equilibrium curves for  $\text{CO}_2 + \text{TBANO}_3 + \text{water}$  and  $\text{CO}_2 + \text{water}$  are identical.

Increasing the mass fraction of  $\text{TBANO}_3$  in solution from 0.1 to 0.15, leads to a decrease in the equilibrium pressure with regard to the temperature. The equilibrium pressure for  $\text{CO}_2$  semi-clathrate hydrates in the presence of  $\text{TBANO}_3$  at a mass fraction

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