

# Tetra-*n*-butyl ammonium bromide semi-clathrate hydrate process for post-combustion capture of carbon dioxide in the presence of dodecyl trimethyl ammonium chloride

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## ABSTRACT

To determine the appropriate operating conditions for separating carbon dioxide from flue gas via the hydrate formation, the effects of the concentrations of dodecyl trimethyl ammonium chloride (DTAC) in 0.29 mol% Tetra-*n*-butyl ammonium bromide (TBAB) aqueous solution and the initial pressures on the induction time of the hydrate formation and CO<sub>2</sub> separation efficiency are investigated. The experiments are conducted at the DTAC concentration range of 0–0.056 mol%, initial pressures range of 0.66 MPa–2.66 MPa and temperature range of 274.95 K–277.15 K. The results indicate that the initial pressure of 1.66 MPa in conjunction with the concentration of 0.028 mol% DTAC is most favorable for CO<sub>2</sub> separation. At the condition, the induction time of forming the hydrate can be shortened considerably and CO<sub>2</sub> can be purified from 17.0 mol% to 99.4% with the two-stage hydrate separation process. CO<sub>2</sub> split fractions for Stage 1 and Stage 2 are 0.54 and 0.39, respectively, and the separation factors are 9.60 and 62.25, respectively.

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) as one main greenhouse gas contributes itself to greenhouse effect accounted for about 60% [1]. In order to deal with the challenge of global warming and carry out the Kyoto protocol, it is imperative to reduce the emission of CO<sub>2</sub>, especially for the CO<sub>2</sub> emitted from fossil fuel power plants. Various methods such as cryogenic fractionation, selective adsorption, gas absorption and membrane process, have been proposed. However, the above methods have their individual issues of either high corrosion, large energy consumption, high cost, or low capacity [2]. Accordingly, a new efficient and more cost-effective technology which is different from the conventional methods needs to be explored.

The hydrate separation method for gas mixtures is a novel gas separation technique. Since Glew [3] applied the first patent and successfully separated propane and propylene from gas mixture by forming the hydrate with structure II (sII), the method for gas

separation has been proposed [3,4]. Recently, separating CO<sub>2</sub> from Integrated Gasification Combined Cycle (IGCC) syngas or flue gas via the hydrate formation has attracted many attentions. Preliminary economic assessment shows that the cost of the hydrate technique for CO<sub>2</sub> separation from IGCC power plant is approximately 10 U.S. dollars/ton of CO<sub>2</sub>, which is less than half of that of others [5].

The basis for the separation is the selective partition of the target component between the hydrate phase and the gaseous phase. Because the equilibrium hydrate formation pressure of CO<sub>2</sub> is much lower than that of N<sub>2</sub> at the same temperature, it is expected that CO<sub>2</sub> preferentially encaged into the hydrate crystal phase. The hydrate crystals are separated and subsequently decomposed to create the CO<sub>2</sub>-rich stream, while the rest constitute the CO<sub>2</sub>-lean one. For CO<sub>2</sub> hydrate separation from flue gas, the first task is to decrease the operating pressure to save the separation cost. The equilibrium hydrate formation pressure of flue gas is between those of pure CO<sub>2</sub> and pure N<sub>2</sub>, and it increases with the decrease of the CO<sub>2</sub> concentration. Due to the fact that flue gas from the power plant usually consists of CO<sub>2</sub> from 15 to 20 mol% [6], the equilibrium pressure for this kind of gas is relatively high. For example, the equilibrium pressures for gas containing CO<sub>2</sub> of 17.61% are 7.60 MPa and 11.00 MPa at 274.00 K and 277.00 K, respectively [7]. The main challenge of hydrate technique for CO<sub>2</sub> separation is

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that it needs the high equilibrium hydrate formation pressure. Hence, a suitable promoter is essential to help in reducing the hydrate formation pressure and the energy consumption without impacting the separation efficiency or CO<sub>2</sub> recovery.

Tetrahydrofuran (THF) was chosen as a hydrate promoter by Kang and Lee [8] studying on the thermodynamic verification of recovery of CO<sub>2</sub> from flue gas using gas hydrate through phase equilibrium measurements. The result showed that, in principle, CO<sub>2</sub> can be purified to 99% from flue gas containing 17% CO<sub>2</sub> in the presence of THF through a three-stage separation process. Meanwhile, it showed that THF, as an effective additive, can greatly reduce hydrate formation pressure at the temperature range of 273–283 K. However, the induction time was not shortened remarkably. THF was also used by Linga et al., [6] for CO<sub>2</sub> capture from flue gas containing 16.9% CO<sub>2</sub> via a medium-pressure clathrate hydrate process. It showed that THF (1.0 mol %) could substantially decrease the pressure from 7.8 MPa to 2.5 MPa at 273.75 K. In addition, THF was found by Kumar et al. [9] to have the function on shortening the induction time and accelerating the hydrate growth compared to the pure water system. Ding [10] used sodium dodecyl sulfate (SDS) associated with an anionic fluorosurfactant (FS-62) (FS-62/SDS: 100/1000 ppm) as a joint additive to capture and sequester CO<sub>2</sub> from CO<sub>2</sub>/N<sub>2</sub> mixture. However, its effect on raising the storage of CO<sub>2</sub> in hydrate was limited.

As an environmental friendly compound, Tetra-*n*-butyl ammonium bromide (TBAB) is also an excellent hydrate promoter and it can form semi-hydrate with water molecules and small gas molecules and moderate the hydrate formation condition significantly [11]. The properties of this semi-hydrate such as temperature and enthalpy of dissociation have already been studied [12–14]. TBAB semi-clathrate hydrates technology is also applied for CO<sub>2</sub> separation from flue gas. Ahmadloo et al. [15] have done a research on gas separation and storage by forming CO<sub>2</sub>-TBAB semi-clathrate hydrates at a moderate pressure. His work verified that the concentration of TBAB in the aqueous solution positively impacted the separation of CO<sub>2</sub>. However, when the concentration of TBAB is higher than 35 mass%, the recovery of gas has no considerable change. Phase behavior of TBAB semi-clathrate hydrate crystal with several gas components was investigated by Oyama et al. [16]. They found that TBAB was not a gas hydrate formation promoter; but it can promote the hydrate stability. However, Nguyen Hong Duc et al. [2] used TBAB as a hydrate formation promoter to separate CO<sub>2</sub> from CO<sub>2</sub>/N<sub>2</sub> mixture gas by forming gas hydrate. In their work, the hydrate formation conditions and gas storage capacity of the hydrate for a wide range of additive concentrations were determined. Meanwhile, based on the thermodynamic results, they made a commercial flow-sheeting simulator to estimate the operative cost of a continuous CO<sub>2</sub> capture by hydrate system. However, the further studies required to carry out efficiently shorten the induction time of the hydrate formation and the gas storage capacity of the hydrate based on the function of TBAB to enhance CO<sub>2</sub> recovery efficiency from the flue gas.

In this work, a novel hydrate promoter is used for enhancing the CO<sub>2</sub> separation from the CO<sub>2</sub>/N<sub>2</sub> mixture gas, based on our previous study [17]. The experiments are conducted to separate CO<sub>2</sub> from the CO<sub>2</sub>/N<sub>2</sub> gas mixture by forming semi-clathrate hydrates using 0.29 mol% TBAB in conjunction with dodecyl trimethyl ammonium chloride (DTAC) with the different concentrations as an additive. DTAC is compatible with cationic or nonionic surfactants and is widely used as an environmental friendly surfactant for textile materials, pictures, paintings, construction materials, carpentry, etc. [18]. The effects of the concentration of DTAC and the initial pressure on the induction time of forming hydrate and CO<sub>2</sub> recovery efficiency are investigated. In addition, a two-stage hydrate separation process is proposed to obtain CO<sub>2</sub> with high purity.

## 2. Experimental

### 2.1. Experimental apparatus and materials

The experimental apparatus is shown in Fig. 1A crystallizer (CR) is immersed in a temperature-controlled bath. The crystallizer with an inner volume of 56.4 cm<sup>3</sup> is made of 316 stainless steel. The crystallizer has two circular viewing windows made of Plexiglass on the front and back. Mixing of the contents in the CR is accomplished using a magnetic stir bar which is magnetically coupled to a set of rotating magnets (Shanghai Hongpu instrument, Ltd., China) placed directly underneath the crystallizer. The temperature of the liquid phase in the CR is measured using a Pt1000 thermoprobe (JM6081) with an uncertainty of ±0.1 K. All pressure measurements are determined with Setra smart pressure transducers (model 552, Boxborough, MA, USA) with the pressure range of 0–25 MPa with ±0.02 MPa accuracy. The signals of the pressure and temperature are acquired by a data acquisition system. A gas chromatography (HP6890) is connected with the CR to measure the composition of the gas phase in the CR.

CO<sub>2</sub>/N<sub>2</sub> gas mixture containing 17.0 mol% CO<sub>2</sub> and 65.0 mol% CO<sub>2</sub> are used in the work to simulate flue gas mixture, which is supplied by Foshan Huate Gas Co. TBAB and DTAC are supplied by Xiamen Pioneer Chemical Reagent Co. with a purity of 99.9%. The de-ionized water used with the resistivity of 18.25 mΩ cm<sup>-1</sup> was produced by an ultra-pure water system supplied by Nanjing Ultrapure Water Technology Co.

### 2.2. Experimental procedure

In our previous work [17], it was found that the TBAB concentration has no significant effect on reducing the pressure in the system (the pressure change reflects the gas storage capacity of the hydrate) in the process of hydrate formation when its concentration is more than 0.29 mol% [3,17]. Hence, in this work, TBAB of 0.29 mol% is used as the main promoter for CO<sub>2</sub> hydrate formation in the experiment. DTAC (0, 0.014%, 0.028%, and 0.056%) as a secondary promoter is dissolved into the TBAB solution. The water bath temperature (T) is set at 274.95 K and 277.15 K respectively.

Prior to the experiment, the CR was cleaned using the de-ionized water and allowed to dry. Then 0.29 mol% TBAB aqueous solution in conjunction with DTAC prepared at a desired concentration was introduced into the CR to a desired volume. Subsequently, the CR with the solution was flushed with CO<sub>2</sub>/N<sub>2</sub> mixture gas at least four

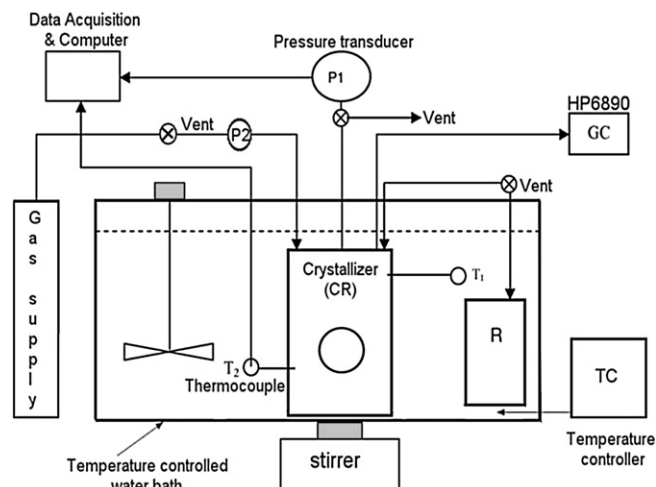


Fig. 1. Schematic of experimental apparatus.

times to ensure that it was air-free, and then CO<sub>2</sub>/N<sub>2</sub> mixture gas was charged into the cell until the desired pressure. Once the temperature was stabilized (typically within 2 min) the stirrer in the CR was started at the speed of 600 rpm and the experimental time also began to be recorded. During the experiment, the temperature and pressure in the system were recorded. After the system pressure is maintained constant for more than half an hour, the hydrate formation is considered to complete. The stirrer was stopped and the residual gas was sampled and analyzed with the gas chromatography. Then, the vent valve was opened, and the residual gas was quickly purged. Subsequently, the vent was closed, and the vessel was warmed to room temperature to allow the hydrate dissociate completely. The decomposed gas and dissolved gas at the relative high pressure released from the hydrate slurry phase were collected and analyzed by the gas chromatography (GC). The method was adopted elsewhere [15].

### 2.3. CO<sub>2</sub> recovery and efficiency

CO<sub>2</sub> separation efficiency can be given from the two following equations [9]. The CO<sub>2</sub> recovery or split fraction (S. Fr.) of carbon dioxide is expressed as:

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2}^{\text{Feed}}} \quad (1)$$

The separation factor (S.F.) is expressed as:

$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} \times n_{\text{N}_2}^{\text{gas}}}{n_{\text{N}_2}^{\text{H}} \times n_{\text{CO}_2}^{\text{gas}}} \quad (2)$$

where  $n_{\text{CO}_2}^{\text{gas}}$ ,  $n_{\text{CO}_2}^{\text{H}}$  and  $n_{\text{CO}_2}^{\text{Feed}}$  are the moles of CO<sub>2</sub> in the gas phase, in the hydrate slurry phase at the end of the hydrate formation, and in the initial gas mixture, respectively.  $n_{\text{N}_2}^{\text{gas}}$ ,  $n_{\text{N}_2}^{\text{H}}$  are the moles of N<sub>2</sub> at the end of the hydrate formation and the moles of N<sub>2</sub> in the hydrate slurry phase, respectively.

## 3. Results and discussion

### 3.1. Induction time of hydrate formation

In the experiment, we firstly determined whether CO<sub>2</sub>/N<sub>2</sub> gas mixture could form gas hydrate in pure DTAC solution at the bath temperature range from 274.95 K to 277.15 K and the initial pressure range from 0.66 MPa to 2.66 MPa. The result showed that CO<sub>2</sub>/N<sub>2</sub> mixture gas could not form any gas hydrate in DTAC solution in absence of TBAB under the above condition.

Fig. 2 gives the change of the induction time of the hydrate formation for the CO<sub>2</sub>/N<sub>2</sub> gas mixture with 17.0 mol% CO<sub>2</sub> in the 0.29 mol% TBAB aqueous system in the presence of DTAC with the different concentrations vs. the initial pressure at 274.95 K. It can be seen from Fig. 2 that the addition of DTAC results in a remarkable reduction of the induction time, and the induction time decreases with the increase of concentration of DTAC at the fixed initial pressure. For example, when the initial pressure is 1.66 MPa, the induction time for pure TBAB aqueous solution is 31.0 min. However, when DTAC with the concentration from 0.014 mol% to 0.056 mol% is added into the 0.29 mol% TBAB aqueous solution, the induction time is shortened from 7.1 min to 3.0 min. It may be due to the fact that DTAC as a surfactant can change the surface activity of the solution and lower its surface tension. As a result, the addition of DTAC promotes the dissolving ability of mixture gases in the TBAB solution, and furthermore enhances the degree of super-saturation of CO<sub>2</sub>. According to the expression for the rate of hydrate nucleation ( $J$ ) given by Nataraja [19],

$$J = k \times (S - 1)^n \quad (3)$$

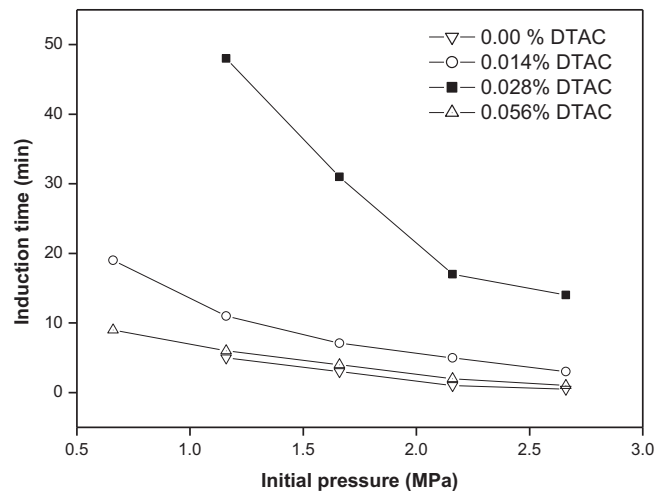


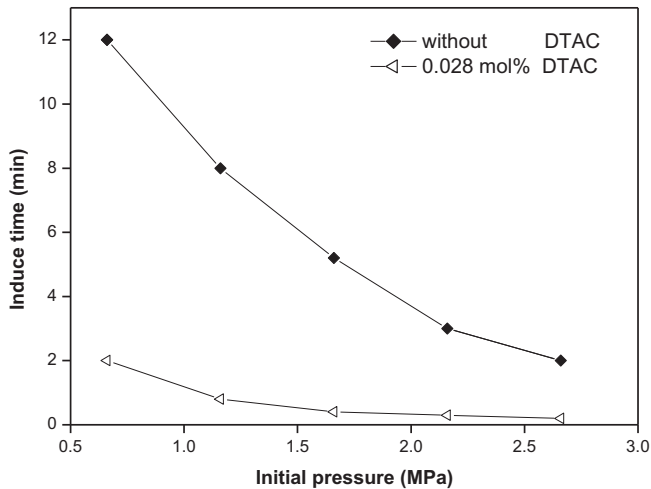
Fig. 2. Induction time of the hydrate formation for 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> gas mixture in TBAB aqueous system in the presence of DTAC with different concentrations vs. initial pressure at 274.95 K.

where  $k$  and  $n$  are the constants, and  $S$  is the super-saturation ratio; it can be seen that the nucleation rate increases with the degree of super-saturation resulting in the decrease of the induction time. However, as shown in Fig. 2, the reduction of the induction time is quite small, when the concentration of DTAC changes from 0.028 mol% to 0.056 mol% at the fixed initial pressure. According to the characteristics of the surfactant [20,21], the surface tension of solution is the smallest when the concentration of DTAC is critical micellar concentration (CMC) of  $1.6 \times 10^{-2}$  mol/L which is estimated by use of the way of Zhong [22]. Its mole percentage is approximately 0.028 mol%. However, when the concentration exceeds its CMC, the increase of concentration cannot change surface activity any more, and the surface tension cannot be also further decreased. Thus, the super-saturation of CO<sub>2</sub> in the solution can also not rise any more. Hence, the induction time of the hydrate formation cannot be shortened in spite of the increase of the DTAC concentration. This is the reason why the induction time has little change with the increase of the DTAC concentration from 0.028 mol% to 0.056 mol%. The similar phenomenon was found by Watanabe et al. [23]. In addition, it can be also seen from Fig. 2 that the induction time reduces with the increase of the initial pressure. This is because the higher initial pressure creates the higher super-saturation which results in the higher nucleation rate.

Likewise, Fig. 3 gives a typical comparison for the induction time of hydrate formation for 65.0 mol% CO<sub>2</sub>/N<sub>2</sub> gas mixture as the feed gas for the second-stage separation with and without the addition of DTAC. It can be seen from Fig. 3 that a small amount of DTAC reduces the induction time significantly at 277.15 K. For example, the induction time with 0.028 mol% DTAC is about 0.4 min and is one thirteenth of that without DTAC at initial pressure of 1.66 MPa. In addition, it can be found from Figs. 2 and 3 that for 65.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas as the feed gas for the second-stage separation, the addition of DTAC can remarkably reduce the induction time of the hydrate formation, compared with that for 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas. It is because 65.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas has the higher component of CO<sub>2</sub>. Furthermore, it is easier to be induced to form the hydrate under the function of DTAC.

### 3.2. Pressure drop during hydrate formation

Fig. 4 gives the pressure drops in the system vs. the DTAC concentration in 0.29 mol% TBAB aqueous solution with the different initial pressures at 274.95 K using 17.0 mol% CO<sub>2</sub>/N<sub>2</sub>



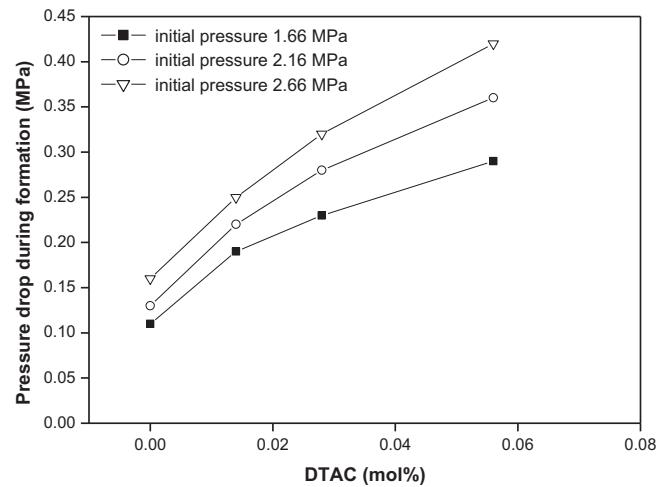
**Fig. 3.** Induction time of the hydrate formation for 65.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas in 0.29 mol% TBAB aqueous system in the presence of 0.028 mol% DTAC vs. initial pressure at 277.15 K.

mixture gas as the feed gas. As shown in Fig. 4, with the increase of the concentration of DTAC, the pressure drop ( $\Delta P_1$ ) increases obviously. In the process of formation of gas hydrate, when the concentration of DTAC is less than CMC, the gas super-saturation in the solution increases, that is the amount of gas dissolving in water increases, with the increase of DTAC. When the concentration of DTAC is more than CMC, the DTAC molecules associate as the micelles containing solubilized gas, and the concentration of the micelles also increases with increasing concentration of DTAC resulting in the increase of the solubilized gas corresponding to the decrease of the pressure in the system and that is the increase of  $\Delta P_1$ . Likewise, as shown in Fig. 4, the higher initial pressure causes the bigger pressure drop in the process of the hydrate formation. It attributes to the fact that more gas dissolves in the solution and forms the hydrate with the increase of the initial pressure, resulting in bigger pressure drop.

### 3.3. CO<sub>2</sub> concentration in hydrate slurry phase

The effect of DTAC on promoting the gas to go into the hydrate slurry phase can be seen from Fig. 5, which shows the pressure increase ( $\Delta P_2$ ) in the system after the hydrate dissociation vs. the initial pressure in the presence of DTAC with the different concentrations in 0.29 mol% TBAB aqueous solution at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> feed gas. As seen, the pressure increase ( $\Delta P_2$ ) rises with the increases of the concentration of DTAC and initial pressure. It is noted that there is a remarkable increase of  $\Delta P_2$  due to the presence of DTAC with the concentration of 0.014 mol%–0.056 mol %, compared with that for the pure TBAB solution. It demonstrates that either DTAC or the increase of initial pressure can lead to the increase of the gas storage in the hydrate slurry phase.

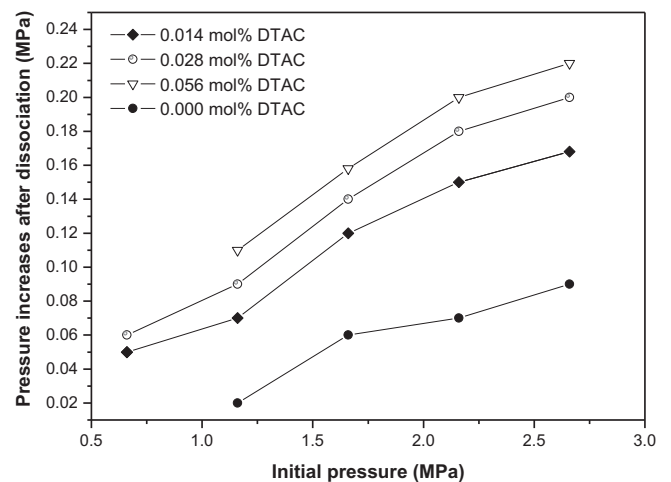
The changes of CO<sub>2</sub> concentration in the hydrate slurry vs. the initial pressures in the presence of DTAC with the different concentrations in 0.29 mol% TBAB aqueous solution at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> feed gas are shown in Fig. 6. As seen, the concentration of CO<sub>2</sub> in hydrate slurry phase decreases with the increase of DTAC at the fixed initial pressure, and a substantial reduction occurs at the DTAC concentration of more than 0.028 mol %. As mentioned above, the addition of DTAC lowers the surface tension of TBAB solution and promotes the dissolving ability of the mixture gas. Thus, it enhances not only the amount of CO<sub>2</sub> but also the amount of N<sub>2</sub> dissolved into the TBAB solution. However,



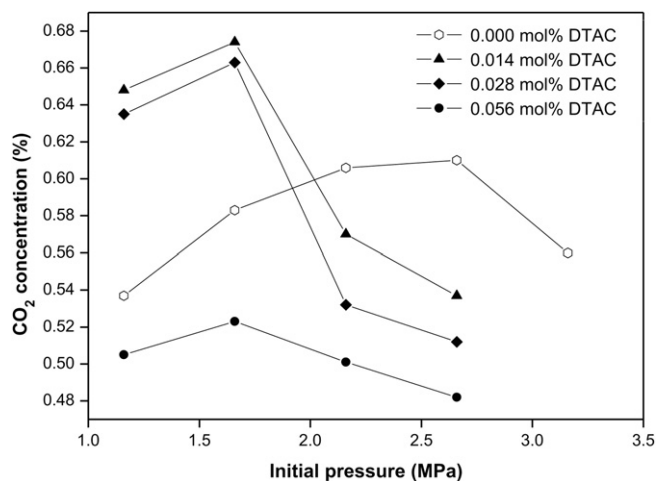
**Fig. 4.** Pressure drops ( $\Delta P_1$ ) in the system vs. DTAC concentration in 0.29 mol% TBAB aqueous solution with different initial pressures at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas.

relative to CO<sub>2</sub>, more N<sub>2</sub> goes into the solution. This is due to the hydrophobic groups of DTAC molecules which preferentially adsorb N<sub>2</sub> molecules and thus results in the reduction of CO<sub>2</sub> concentration in the hydrate slurry phase with the increase of the DTAC concentration. In addition, when the concentration of DTAC is more than its CMC, the DTAC molecules in the solution form the Water/Oil micelles, and, with the function of the hydrophobic group of the surfactant molecules micellized, substantial N<sub>2</sub> can be preferentially enclosed into the micelles compared to CO<sub>2</sub>. This causes the remarkable reduction of concentration of CO<sub>2</sub> at the DTAC concentration of 0.056 mol%, as shown in Fig. 6.

It is noted, as shown in Fig. 6, that the CO<sub>2</sub> concentration goes up with the increase of initial pressure, and then it goes down after an inflexion point occurs. The inflexion point is also the largest point of CO<sub>2</sub> concentration. According to the phase equilibrium data given by Deschamps et al. [24] and Arjmandi et al. [25], CO<sub>2</sub> is prior to form CO<sub>2</sub> hydrate at low initial pressure, compared to N<sub>2</sub>. The driving force increases with the increase of initial pressure. Furthermore, N<sub>2</sub> can compete with CO<sub>2</sub> for hydrate cage (5<sup>12</sup>) occupancy with higher driving force [26] resulting in the dramatic



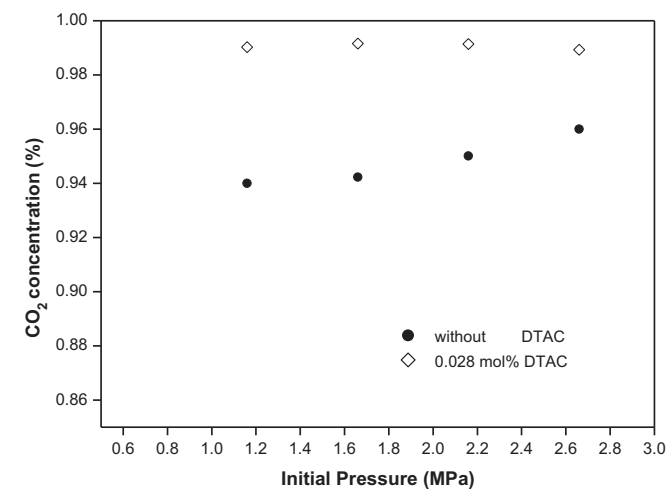
**Fig. 5.** Pressure increase ( $\Delta P_2$ ) in the system after hydrate dissociation vs. initial pressure in the presence of DTAC with the different concentrations in 0.29 mol% TBAB aqueous solution at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas.



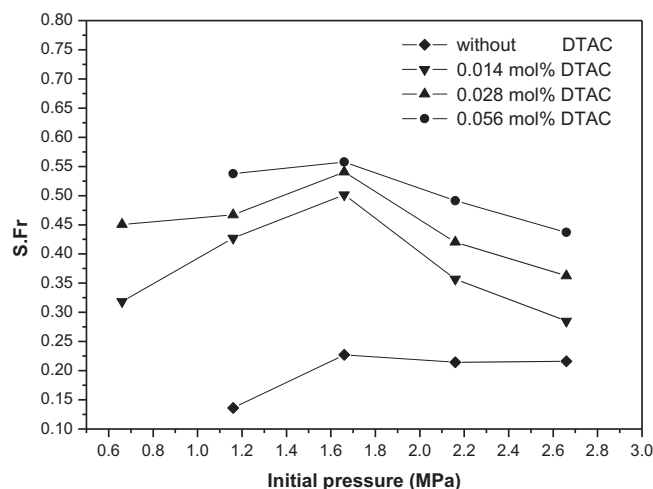
**Fig. 6.** CO<sub>2</sub> concentration in hydrate slurry vs. initial pressures in the presence of DTAC with different concentration in 0.29 mol% TBAB aqueous solution at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas.

decrease of the concentration of CO<sub>2</sub> in the slurry phase after the inflexion point. The similar experimental phenomenon is also found by Fan et al. [27]. However, it can be found from Fig. 6 that the inflexion point for pure TBAB solution lags behind that for TBAB + DTAC solution. Compared with those inflexion points occurring at the initial pressure of 1.66 MPa in the presence of DTAC, the inflexion point in the absence of DTAC is shifted to 2.66 MPa. It may be attributed to the fact that the addition of DTAC actually lowers the equilibrium hydrate formation pressure of mixture gas. Meanwhile, the equilibrium pressures of CO<sub>2</sub> and N<sub>2</sub> are also lowered, resulting from the reduction of the surface tension with the function of the surfactant [28–32]. Thus, N<sub>2</sub> can begin to compete with CO<sub>2</sub> for hydrate cage (5<sup>12</sup>) occupancy at the relative lower driving force.

As discussed above, in order to shorten the induction time of hydrate and increase CO<sub>2</sub> storage in the hydrate slurry phase to meet the requirement of CO<sub>2</sub> separation from the flue gas (17.0 mol % CO<sub>2</sub>/N<sub>2</sub> mixture gas), it is found that the 0.29 mol% TBAB + 0.028 mol% DTAC aqueous solution is chosen as optimizing joint promoter for the CO<sub>2</sub> separation at the initial pressure of



**Fig. 7.** CO<sub>2</sub> concentration in hydrate slurry vs. initial pressures in the presence of 0.028 mol% DTAC in 0.29 mol% TBAB aqueous solution at 277.15 K with 65.0% CO<sub>2</sub>/N<sub>2</sub> mixture gas.

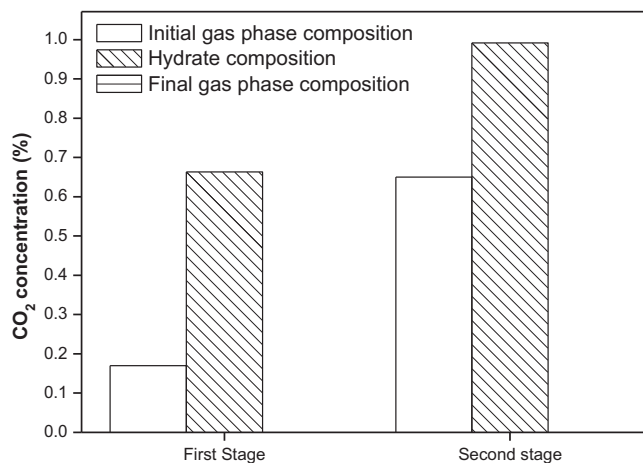


**Fig. 8.** Split fraction (S. Fr.) vs. initial pressure in the presence of DTAC with different concentration in 0.29 mol% TBAB aqueous solution at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> mixture gas.

1.66 MPa. The similar result can also be obtained from the experiment in which the 65.0 mol% CO<sub>2</sub>/N<sub>2</sub> gas mixture is used as the feed gas at 277.15 K. As shown in Fig. 7, under the function of DTAC, the concentration of CO<sub>2</sub> can be purified from 65.0 mol% to 99.2 mol% by forming the semi-clathrate hydrates at initial pressure 1.66 MPa and temperature 277.15 K. Compared to the operating pressure of 2.5 MPa given by Linga et al. [6], the operating pressure to obtain CO<sub>2</sub> of 99.2 mol% in the stage 2 in this experiment is much lower. However, the highest concentration of CO<sub>2</sub> in the hydrate slurry phase in the absence of DTAC is only 94.0 mol% at 273.75 K. Thereby, it is possible to realize the target of capturing CO<sub>2</sub> through a two-stage hydrate separation in industry.

#### 3.4. Two-stage separation for CO<sub>2</sub> recovery

The separation efficiency with the two-stage hydrate separation was determined from the split fraction (S. Fr.) and the separation factor (S.F.) [9]. Fig. 8 shows the change of S. Fr. vs. the initial pressure in the presence of DTAC with the different concentrations in the aqueous solution of 0.29 mol% TBAB at 274.95 K with 17.0 mol% CO<sub>2</sub>/N<sub>2</sub> feed gas. As seen from Fig. 8, there is a significant enhancing of S. Fr.



**Fig. 9.** CO<sub>2</sub> concentration in feed gas, hydrate slurry phase and residual gas phase for two-stage separation with 0.028 mol% DTAC in 0.29 mol% TBAB aqueous solution at 1.66 MPa.

**Table 1**  
Split fraction and Separation factor for the two-stage CO<sub>2</sub> separation.

Feed gases	Experimental Conditions	Split Fraction	Separation Factor
17.0 mol% CO <sub>2</sub> /N <sub>2</sub>	Stage 1 274.95 K 1.66 MPa DTAC 0.028 mol%	0.54	9.60
65.0 mol% CO <sub>2</sub> /N <sub>2</sub>	Stage 2 277.15 K 1.66 MPa DTAC 0.028 mol%	0.39	62.25

in the presence of DTAC, compared with that without DTAC. The value of S. Fr. increases with the increase of the concentration of DTAC. However, the values of S. Fr. reach an extreme point with the four different DTAC concentrations of 0 mol%, 0.014 mol%, 0.028 mol% and 0.056 mol% when the initial pressure is 1.66 MPa, as shown in Fig. 8, and the S. Fr. values with 0.028 mol% and 0.056 mol% DTAC are almost the same at the initial pressure of 1.66 MPa. Hence, the operational condition at the DTAC concentration of 0.028 mol% and the initial pressure of 1.66 MPa is an optimal one for the CO<sub>2</sub> separation via the hydration crystallization.

Fig. 9 gives CO<sub>2</sub> concentration in the feed gas, the hydrate slurry phase and the residual gas phase for two-stage separation with 0.028 mol% DTAC at 1.66 MPa. The results indicate that after the separation for the CO<sub>2</sub>/N<sub>2</sub> mixture gas (simulated flue gas) at 274.95 K and 1.66 MPa, a CO<sub>2</sub>-rich gas containing more than 65.0 mol% CO<sub>2</sub> can be obtained, as shown in Figs. 6 and 9. As the industrial objective is to obtain purified CO<sub>2</sub> with the high concentration, 65.0 mol% CO<sub>2</sub> gas needs to be treated further with a second-stage hydrate separation. As seen in Figs. 7 and 9, the CO<sub>2</sub> content is increased from initial 65.0 mol% to 99.2% after the second separation stage at 277.15 K and 1.66 MPa.

Table 1 shows the values of the split fraction and the separation factor for the two-stage CO<sub>2</sub> separation with the DTAC concentration of 0.028 mol% at the initial pressure of 1.66 MPa. It can be seen from Table 1 that CO<sub>2</sub> split fractions for Stage 1 and Stage 2 are 0.54 and 0.39, respectively, and the separation factors are 9.60 and 62.25, respectively, which are superior to those given by Linga et al. [6].

#### 4. Conclusion

The induction time of the hydrate formation and CO<sub>2</sub> recovery from the flue gas (N<sub>2</sub>/CO<sub>2</sub>) mixture are investigated in 0.29 mol% TBAB aqueous solution with the functions of DTAC and the different initial pressures. The result shows that DTAC as a surfactant considerably shortens the induction time of hydrate formation. The induction time decreases dramatically with the increase of the concentration of DTAC. However, when the concentration exceeds its CMC value, the DTAC micelles forms and the induction time cannot be shortened any more. Meanwhile, substantial N<sub>2</sub> is preferentially solubilized into the micelles compared to CO<sub>2</sub>, resulting in the remarkable reduction of CO<sub>2</sub> recovery. Therefore, the optimizing concentration of DTAC for the CO<sub>2</sub> separation is its CMC, approximately 0.028 mol%. On the other hand, the induction time reduces and the CO<sub>2</sub> concentration in the hydrate slurry phase increases with the increase of initial pressure. However, when the pressure is more than 1.66 MPa, the CO<sub>2</sub> concentration in the hydrate slurry phase and CO<sub>2</sub> separation efficiency reduce due to the increase of the concentration of N<sub>2</sub> which can compete with CO<sub>2</sub> for hydrate cage (5<sup>12</sup>) occupancy. Hence, the initial pressure of 1.66 MPa in conjunction with 0.028 mol% DTAC is most favorable for CO<sub>2</sub> separation. At this condition, the induction time can be shortened to 4.0 min for the first stage separation and 0.4 min for second-stage

separation. These are only one eighth and one thirteenth of those without DTAC. Meanwhile, CO<sub>2</sub> can be purified from 17.0 mol% to 99.2 mol% with the two-stage hydrate separation process, CO<sub>2</sub> split fractions for Stage 1 and Stage 2 are 0.54 and 0.39, respectively, and the separation factors are 9.60 and 62.25, respectively.

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