

# Effects of Tetrabutyl-(ammonium/phosphonium) Salts on Clathrate Hydrate Capture of CO<sub>2</sub> from Simulated Flue Gas

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**ABSTRACT:** Quaternary salts can form semi-clathrate hydrates, caging gas molecules in the empty small cages, which have the potential for the separation of mixtures, such as the simulated flue gas [CO<sub>2</sub> (17 mol %)/N<sub>2</sub> mixtures]. To enhance the CO<sub>2</sub> separation from CO<sub>2</sub>/N<sub>2</sub> binary mixtures, three quaternary salts, tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylphosphonium bromide (TBPB), and tetra-*n*-butylammonium nitrate (TBANO<sub>3</sub>), are investigated at different operating conditions by a one-stage hydrate separation process. The results indicate that the induction time for each quaternary salt system can be shortened to less than 5 min under the optimal operating condition. Meanwhile, each quaternary salt can significantly promote the CO<sub>2</sub> separation under its optimal condition. TBANO<sub>3</sub> displays the strongest capability in terms of gas consumption and CO<sub>2</sub> separation with the pressure drop of 0.72 MPa and the highest split fraction of 67% and separation factor of 15.54 compared to the other two salts. Besides, CO<sub>2</sub> can be further removed from 17 to 7 mol % in the presence of TBANO<sub>3</sub>. TBPB also has a potential effect on CO<sub>2</sub> separation with the pressure drop of 0.57 MPa and the separation factor of 14.06. The result demonstrates that TBANO<sub>3</sub> and TBPB are two better additives for efficient hydrate capture of CO<sub>2</sub>.

## 1. INTRODUCTION

With the increasing development of environmental problems, such as the greenhouse effect, energy savings and emission reduction have become the main topics in the world. The emission of carbon dioxide (CO<sub>2</sub>) from the combustion of fossil fuels has been considered as the dominant contributor to global warming and climate change.<sup>1</sup> Electric power generation remains the largest source of CO<sub>2</sub> emission, emitting as much CO<sub>2</sub> as that from the rest of the industries combined.<sup>2</sup> To cope with the challenge of these environmental concerns and to develop the low-carbon economy effectively, it is imperative to reduce the emission of CO<sub>2</sub> (especially CO<sub>2</sub> emitted from fossil fuel power plants). Many ways to reduce CO<sub>2</sub> emissions have been proposed, such as absorption, adsorption, and membrane separation.<sup>3,4</sup> However, these methods have their own critical issues related to high corrosion, large energy consumption, high cost, and low capacity. Hence, other new efficient and more cost-effective technologies that are different from the conventional methods need to be explored. CO<sub>2</sub> capture and storage through gas-hydrate-based technology is one of them.<sup>5</sup> Besides, in a recent review,<sup>6</sup> it is reported that gas hydrate formation technology will play a significant role in the future in separation processes and has the potential to be a more sustainable technique than current comparable commercial technologies for separation.

Gas hydrates are non-stoichiometric crystals formed by water molecules and a number of small gas molecules, such as CO<sub>2</sub>, nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), etc. There are three main crystallographic structures (I, II, and H), which differ in cavity size and shape. The structure is mainly determined by the size of the gas molecules trapped in the cavities.<sup>7</sup> When gas hydrates are formed, there is a selective

partition of the target component between the hydrate phase and the gas phase. Therefore, the component that formed the hydrate more easily might be enriched in the hydrate phase. It is the basis of CO<sub>2</sub> separation using hydrate formation and decomposition. In the present work, the flue gas contains N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, and NO<sub>x</sub>. Among them, the main components of flue gas become CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> after a suitable pretreatment method.<sup>8</sup> General characteristics of N<sub>2</sub> and O<sub>2</sub> for gas hydrates are nearly similar. Besides, H<sub>2</sub>O is not important for gas formation because the separation process occurs in the aqueous solution. Thus, the flue gas can be considered as CO<sub>2</sub>/N<sub>2</sub> mixtures, in which the CO<sub>2</sub> molar concentration is approximately 15–20 mol %. With regard to CO<sub>2</sub>/N<sub>2</sub> gas mixtures, the equilibrium pressure of CO<sub>2</sub> is much lower than that of N<sub>2</sub> at the same temperature; therefore, it is expected that CO<sub>2</sub> can be preferentially incorporated into the hydrate phase.<sup>9</sup>

Up to now, the investigations on hydrate-based CO<sub>2</sub> separation from the flue gas have been basically classified into three types: (1) thermodynamic research referring to hydrate phase equilibrium and hydrate crystallographic structure analysis,<sup>8,10</sup> (2) kinetic research on hydrate induction, formation, and decomposition,<sup>11</sup> and (3) separation research on CO<sub>2</sub> recovery and separation efficiency.<sup>12–14</sup> The flue gas with the CO<sub>2</sub> concentration of 15–20 mol % presents a high equilibrium pressure and low hydrate formation rate when forming hydrates in pure water, which is an obstacle for the separation process. Some promoters and additives have been

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investigated to resolve the problem. Tetra-*n*-butylammonium bromide (TBAB), tetrahydrofuran (THF), and cyclopentane (CP) have been found to be good hydrate promoters, which effectively reduce the equilibrium pressure and affect the formation rate. In comparison to the pure water system, these three promoters have shown improvements in both hydrate thermodynamics and kinetics.<sup>9–13,15–18</sup> However, their effects on CO<sub>2</sub> separation efficiency were limited by the one-stage hydrate process. Linga et al.<sup>14</sup> have studied the process of hydrate capture of CO<sub>2</sub> without any additive. They found that the flue gas with the 16.9 mol % CO<sub>2</sub> concentration could form hydrates, which approximately contained 55–57 mol % CO<sub>2</sub> under a high pressure (10–11 MPa) and low temperature (273.75 K). Meanwhile, the CO<sub>2</sub> concentration in the residual gas phase approximately decreased to 9.7–10.9 mol % after the hydrate formation process. THF was studied by Englezos et al.<sup>8</sup> for CO<sub>2</sub> capture from the simulated flue gas via a medium-pressure hydrate process. The result showed that THF had little improvement on CO<sub>2</sub> separation efficiency compared to the pure water system. On the contrary, CO<sub>2</sub> was only concentrated to 38 mol % in the hydrate slurry, and the gas uptake was relatively low by a one-stage hydrate process. CP was used by Li et al.<sup>17</sup> as an additive to capture CO<sub>2</sub> from the CO<sub>2</sub> (16.6 mol %)/N<sub>2</sub> mixture. It was found that the effect of CP/H<sub>2</sub>O emulsion was much better than CP on the hydrate formation rate and separation efficiency. However, they both had limited capacities for raising the storage of CO<sub>2</sub> in the hydrate. TBAB was proven to be another excellent hydrate promoter, which could favor the CO<sub>2</sub> separation process. Studies<sup>12,13,15,19</sup> showed that TBAB would significantly reduce the equilibrium pressure, shorten the induction time, and accelerate the formation rate. Besides, the separation efficiency was slightly improved in comparison to the other systems (CP and THF).

As a promising hydrate promoter, TBAB hydrate has empty dodecahedral cages that can selectively trap small gas molecules, such as CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>S.<sup>20</sup> Kamata et al.<sup>21</sup> proposed that gases with small molecular size and high solubility in water could be effectively separated using TBAB semi-clathrate hydrate. In their following work,<sup>22</sup> it was reported that >90% H<sub>2</sub>S was removed from the biogas mixture by a one-stage TBAB hydrate formation process because of its high solubility and small molecular size. As for the CO<sub>2</sub>/N<sub>2</sub> system, the molecular size of CO<sub>2</sub> (5.12 Å) and N<sub>2</sub> (4.1 Å) were both suitable for fitting into the dodecahedral cage.<sup>7</sup> Besides, Lin et al.<sup>23</sup> reported that the CO<sub>2</sub> solubility in TBAB solution was slightly lower than that in pure water. Therefore, separation efficiency was limited for CO<sub>2</sub> removal from the CO<sub>2</sub>/N<sub>2</sub> mixture using TBAB as a promoter. On the basis of the work by predecessors,<sup>24</sup> tetra-*n*-butylammonium nitrate (TBANO<sub>3</sub>) was another typical quaternary salt that could form a semi-clathrate hydrate with water molecules. The melting point and the hydrate number of the TBANO<sub>3</sub> hydrate were both close to that of the TBAB hydrate. It was inferred that TBANO<sub>3</sub> had a similar ability for CO<sub>2</sub> storage with TBAB. Furthermore, TBA<sup>+</sup> was a typical kind of cation of ionic liquids, in which CO<sub>2</sub> presented excellent high solubility.<sup>25,26</sup> It was proven that NO<sub>3</sub><sup>−</sup> could significantly increase the CO<sub>2</sub> solubility as a suitable anion of ionic liquid by Brennecke et al.<sup>27</sup> Thus, TBANO<sub>3</sub> could be considered to have the double characteristics of both quaternary salt and ionic liquid. Recently, tetra-*n*-butylphosphonium bromide (TBPB) was reported by Mayoufi et al.<sup>28</sup> as a CO<sub>2</sub> storage media. The

TBAB hydrate could store 2–4 times more CO<sub>2</sub> per water molecule than other similar compounds [e.g., tetra-*n*-butylammonium chloride (TBAC) or TBANO<sub>3</sub> hydrate]. Therefore, TBPB and TBANO<sub>3</sub> might have large capacities for CO<sub>2</sub> separation from the CO<sub>2</sub>/N<sub>2</sub> mixture, which would be beneficial for the hydrate-based CO<sub>2</sub> separation and sequestration process.

In this work, three quaternary salts were used for enhancing the CO<sub>2</sub> separation from CO<sub>2</sub>/N<sub>2</sub> binary mixtures. The CO<sub>2</sub> solubility in three salt solutions with 1.00 mol % concentration at different operating conditions was first measured. Then, the effects of three quaternary salts on hydrate formation and separation efficiency were studied. The effects of the salt concentration, pressure of feed gas, and system temperature were discussed and compared. Additionally, the CO<sub>2</sub> recovery and separation factor were calculated.

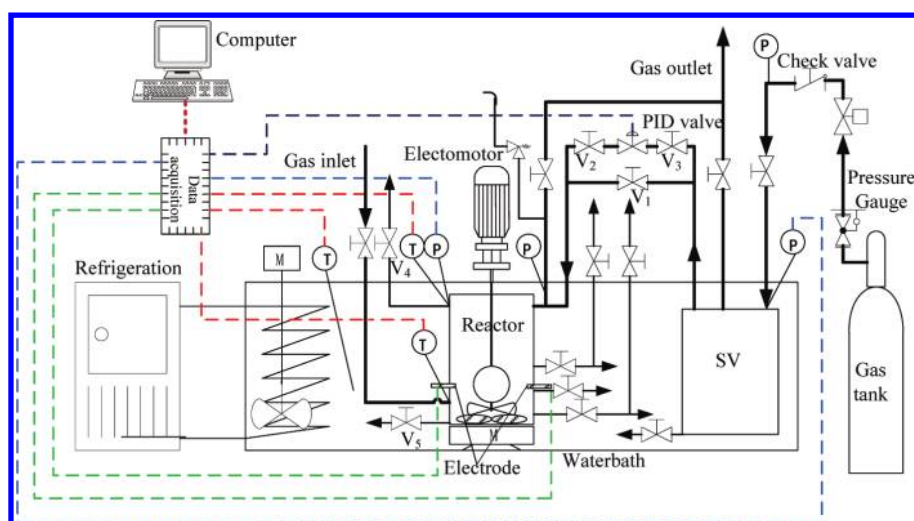
**Table 1. Tetrabutyl-(ammonium/phosphonium) Salts Studied in This Work**

| Symbol             | Chemical name                              | Structure | Purity                              | Supplier                 |
|--------------------|--|-----------|-------------------------------------|--------------------------|
| TBAB               | tetra- <i>n</i> -butyl ammonium bromide    |           | Br <sup>−</sup> ≥99.0%              | Chengdu Best Reagent Co. |
| TBANO <sub>3</sub> | tetra- <i>n</i> -butyl ammonium nitrate    |           | NO <sub>3</sub> <sup>−</sup> ≥98.0% | Chengdu Best Reagent Co. |
| TBPB               | tetra- <i>n</i> -butyl phosphonium bromide |           | Br <sup>−</sup> ≥98.0%              | Chengdu Best Reagent Co. |

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The tetrabutyl-(ammonium/phosphonium) salts studied were listed in Table 1. TBAB, TBANO<sub>3</sub>, and TBPB were weighed on an electronic balance (readability of ±0.1 mg). The deionized water with the resistivity of 18.25 mΩ cm<sup>−1</sup> was produced by a ultrapure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China. The simulated flue gas containing CO<sub>2</sub> (17 mol %)/N<sub>2</sub> was supplied by Huate Gas Co., Ltd., China.

**2.2. Apparatus and Procedure.** The schematic of the experimental apparatus is shown in Figure 1. It mainly consisted of a cylindrical hydrate crystallizer (CR) with an effective volume of 398 mL. The CR was made of 316 stainless steel and immersed in a temperature-controlled water bath. On the front and back of the CR, there were two circular viewing windows made of Plexiglas. The maximum working pressure of the CR was 30 MPa. A mechanical stirrer with the stirring speed range from 0 to 3500 revolutions/min ensured sufficient agitation to facilitate reaching equilibrium. The pressure in the vessel was measured by a MBS3000 absolute pressure transducer (range of 0–25 MPa) with an accuracy of ±0.02 MPa. The



**Figure 1.** Schematic of the experimental apparatus. T, thermoprobe; P, pressure transducer; V<sub>1</sub>, V<sub>2</sub>, V<sub>3</sub>, V<sub>4</sub>, and V<sub>5</sub>, valves; SV, supplied vessel; and M, mechanical stirrer.

temperature in the vessel was measured by a Pt 1000 thermocouple (JM6081) with an uncertainty of  $\pm 0.05$  K. The temperature and pressure data were collected every 5 s by an Agilent model 34970A recording system, which was controlled by the Agilent data acquisition software application BenchLink.

Each separation experiment was carried out at a constant temperature and volume condition. Prior to the experiments, the crystallizer was washed using the deionized water and allowed to dry. The tetra-butyl-salt aqueous solution (150 mL) at a desired concentration was introduced into the high-pressure hydrate crystallizer. Subsequently, the reactor was cooled to the desired temperature. When the temperature was stabilized, the reactor was evacuated with a vacuum pump and flushed with CO<sub>2</sub>/N<sub>2</sub> gas mixtures at least 4 times to ensure the absence of air. The mixture gas was then supplied into the CR through a pressure-regulating valve until the crystallizer reached the given pressure. Then, the stirrer was started to initiate the hydrate formation; meanwhile, the experimental time also began to be recorded. During the experiments, the temperature and pressure were recorded. After the completion of hydrate formation (the system pressure was stable for more than 0.5 h), the stirrer was stopped and the residual gas sample was transferred and analyzed with a gas chromatograph (GC, Agilent 6890 with an accuracy of gas composition analysis of  $\pm 0.01\%$ ). The vent valve was opened; the remaining gas was purged; and the CR was depressurized quickly to atmospheric pressure. Then, the vessel was warmed to room temperature to make the hydrate dissociate completely. The dissociated gas composition was also determined with a GC. The phase equilibrium for the TBAB/CO<sub>2</sub>/N<sub>2</sub> system had been completely investigated by the previous work.<sup>18,29</sup> Meanwhile, Mayoufi et al.<sup>28</sup> reported that the TBAB/CO<sub>2</sub> system had a similar equilibrium condition as the TBPB/CO<sub>2</sub> system, while the TBANO<sub>3</sub>/CO<sub>2</sub> system showed a relatively difficult equilibrium condition. Therefore, on the basis of the equilibrium data for the TBAB/CO<sub>2</sub>/N<sub>2</sub> system, we determined our initial operating conditions for all separation experiments, which are shown in Table 2.

### 2.3. Solubility of CO<sub>2</sub> in the Quaternary Aqueous Solution.

The solubility of CO<sub>2</sub> in the solution was a main factor for CO<sub>2</sub> separation using the tetra-butyl-salt semi-clathrate hydrate.<sup>21</sup> In this work, the solubility of CO<sub>2</sub> in different tetra-butyl-salt solutions was measured as follows: an amount of solution (150 mL) was introduced into the CR at a fixed temperature. The CR was evacuated to remove the air and then pressurized by CO<sub>2</sub> injection. The stirrer was started to accelerate the gas dissolution, resulting in a pressure decrease. When the CO<sub>2</sub> dissolution equilibrium was reached (pressure was stable), the pressure and temperature were recorded and then the temperature was

**Table 2.** Experiment Plans for CO<sub>2</sub> Separation Efficiencies

| run   | system             | conditions            |                        |                        |
|-------|--------------------|-----------------------|------------------------|------------------------|
|       |                    | concentration (mol %) | initial pressure (MPa) | temperature (K)        |
| 1–18  | TBAB               | 0.29, 0.65, 1.00      | 2.0, 2.5, 3.3          | 275.15, 276.15, 277.15 |
| 18–36 | TBPB               | 0.29, 0.65, 1.00      | 2.0, 2.5, 3.3          | 275.15, 276.15, 277.15 |
| 36–45 | TBANO <sub>3</sub> | 0.65, 1.00            | 2.5, 3.3, 4.0          | 274.15, 275.15         |

changed to measure another condition. The mole fraction of CO<sub>2</sub> in solution can be calculated as follows:<sup>23</sup>

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{L}}}{n_{\text{CO}_2}^{\text{L}} + n_{\text{salt}}^{\text{L}} + n_{\text{H}_2\text{O}}^{\text{L}}} \quad (1)$$

where  $n_{\text{salt}}^{\text{L}}$  and  $n_{\text{H}_2\text{O}}^{\text{L}}$  are the number of moles of tetra-butyl-salt and water in the liquid phase, respectively. The quantity of CO<sub>2</sub> in the liquid phase  $n_{\text{CO}_2}^{\text{L}}$  is given by

$$n_{\text{CO}_2}^{\text{L}} = n_{\text{CO}_2}^{\text{total}} - \frac{PV_{\text{CO}_2}}{ZRT} \quad (2)$$

where  $n_{\text{CO}_2}^{\text{total}}$  is the total number of moles of CO<sub>2</sub> in the system, which is determined by the pressure decrease of CO<sub>2</sub> in the supply vessel (SV).  $Z$  is the compressibility factor calculated by the Soave–Redlich–Kwong (SRK) equation of state.  $T$  is the average temperature of the system.

**2.4. Calculation of the Amount of Gas Consumed.** The amount of gas that has been consumed during hydrate formation can be calculated as follows:<sup>11</sup>

$$\Delta n_{\text{g}} = n_{\text{g},0} - n_{\text{g},t} = \frac{P_0 V}{z_0 R T} - \frac{P_t V}{z_t R T} \quad (3)$$

$$\Delta n_{\text{g}}^i = n_{\text{g},0}^i - n_{\text{g},t}^i = \frac{y_0^i P_0 V}{z_0^i R T} - \frac{y_t^i P_t V}{z_t^i R T} \quad (4)$$

where  $z$  is the compressibility factor calculated by the SRK equation of state, superscript  $i$  refers to component of the gas mixture, and  $y$  is the composition of the gas mixture. The volume of gas was assumed to be constant throughout the hydrate formation process.

**2.5. CO<sub>2</sub> Recovery and Separation Factor.** In this work, the CO<sub>2</sub> recovery or split fraction (S.Fr.) and the separation factor (S.F.)



were used to assess the hydrate-based separation process. They were defined and expressed by Linga et al.<sup>14</sup> as follows:

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2}^{\text{feed}}} \quad (5)$$

where  $n_{\text{CO}_2}^{\text{feed}}$  is the number of moles of  $\text{CO}_2$  in the feed gas and  $n_{\text{CO}_2}^{\text{H}}$  is the number of moles of  $\text{CO}_2$  in the hydrate phase at the end of the experiment.

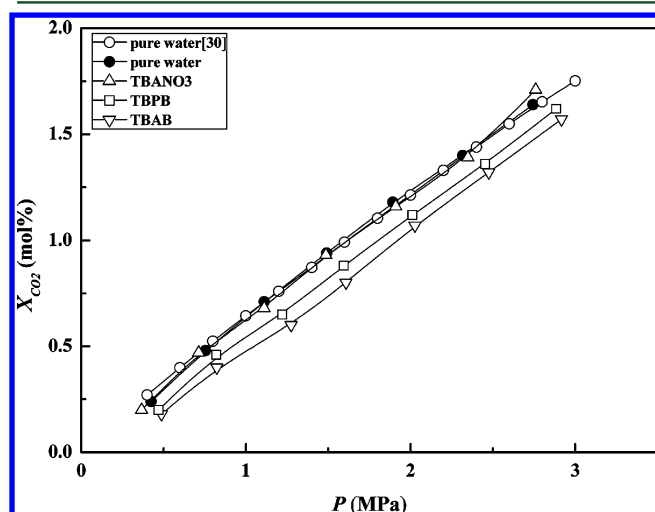
$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} n_{\text{N}_2}^{\text{gas}}}{n_{\text{N}_2}^{\text{H}} n_{\text{CO}_2}^{\text{gas}}} \quad (6)$$

where  $n_{\text{N}_2}^{\text{gas}}$  and  $n_{\text{CO}_2}^{\text{gas}}$  are the number of moles of  $\text{N}_2$  and  $\text{CO}_2$  in the gas phase at the end of the hydrate formation, respectively, and  $n_{\text{N}_2}^{\text{H}}$  is the number of moles of  $\text{N}_2$  in the hydrate phase at the end of the experiment.

### 3. RESULTS AND DISCUSSION

#### 3.1. $\text{CO}_2$ Solubility in the Quaternary Salt Solutions.

Figure 2 shows the relationship between  $\text{CO}_2$  solubility (in



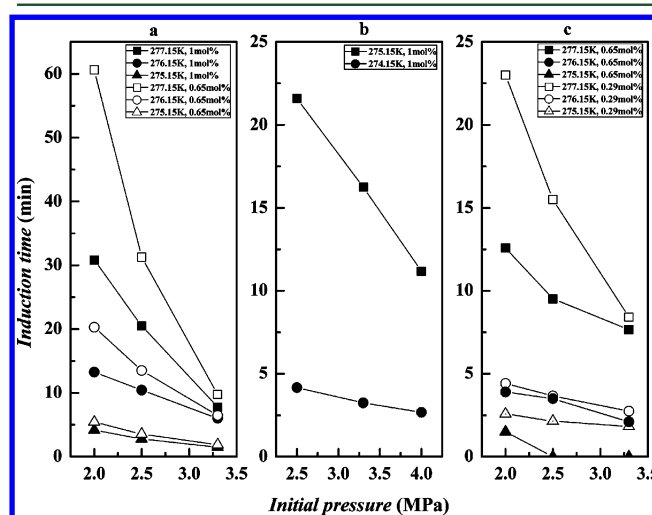
**Figure 2.** Solubility of  $\text{CO}_2$  in three quaternary salt solutions (1.00 mol % and 293.15 K).

mole fraction) and the pressure (from 3.0 to 0.5 MPa) in three salt solutions with the same concentration. As seen from Figure 2, on one hand, the experimental data for  $\text{CO}_2$  solubility in pure water in this work is in excellent agreement with the literature values.<sup>30</sup> On the other hand, at a fixed temperature (293.15 K), the  $\text{CO}_2$  solubility in TBAB solution is lower than that in pure water, which is similar to the result studied in the literature.<sup>23</sup> Besides,  $\text{CO}_2$  presents a higher solubility in  $\text{TBANO}_3$  solution than that in other solutions. The salt effects on  $\text{CO}_2$  solubility are summarized as below:  $\text{TBANO}_3 \approx \text{H}_2\text{O} > \text{TBPB} > \text{TBAB}$ . Meanwhile, it is also observed that the solubility increases with the increasing of the initial pressure in each solution, which means more  $\text{CO}_2$  entered into the solution in a higher pressure. It can be concluded that  $\text{CO}_2$  has the highest solubility in  $\text{TBANO}_3$  solution because of its characteristic of the ionic liquid. The result is favorable for the  $\text{CO}_2$  separation.

**3.2.1. Hydrate Formation Process. Induction Time.** The induction time in gas hydrate crystallization is an important characteristic of the kinetics of the process. Generally, it is defined as the period necessary for the

appearance of the very first hydrate cluster of supernucleus size.<sup>31</sup> For the  $\text{CO}_2/\text{N}_2$  system, some additives can shorten the induction time and accelerate the formation process. Linga et al.<sup>11</sup> studied whether the addition of THF could reduce the induction time and, more importantly, the operating pressure for a  $\text{CO}_2/\text{N}_2$  separation process. Li et al.<sup>15</sup> reported that the induction time of the  $\text{CO}_2/\text{N}_2$  hydrate process was within 5 min in the presence of TBAB. Here, the effects of three different quaternary salts on the induction time are compared.

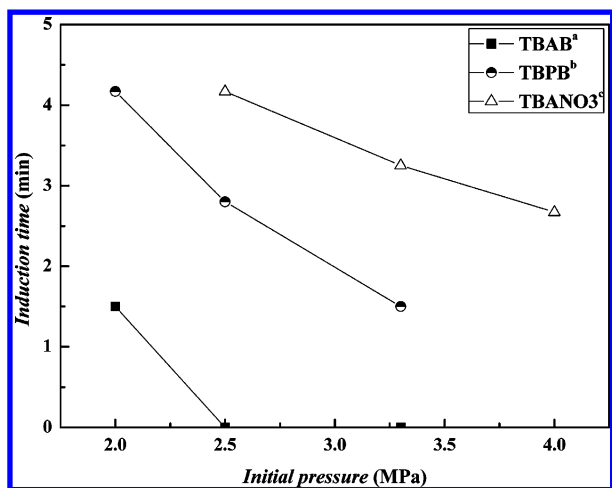
Figure 3 gives the effects of the operating conditions and the concentration of the additive on the induction time. As shown



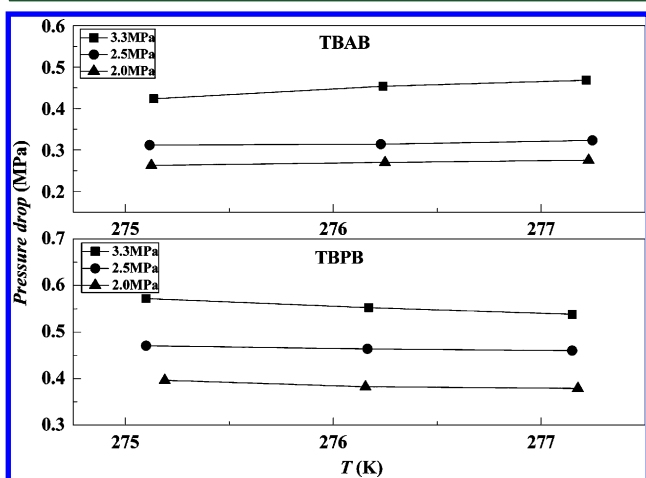
**Figure 3.** Induction time versus the initial pressure in quaternary salts with different operating conditions: (a) TBAB, (b)  $\text{TBANO}_3$ , and (c) TBAB.

in Figure 3, either the increase of the initial pressure, the drop of the temperature, or the rise of the concentration can significantly shorten the induction time. A similar phenomenon can be observed for the three quaternary salt systems. It can be attributed to a higher initial pressure, a lower temperature, or a higher concentration, which creates a higher driving force and further results in a higher degree of supersaturation. A similar result is also demonstrated by Nataraja et al.<sup>32</sup> The suitable operating conditions for each quaternary salt system (TBAB, 275.15 K and 0.65 mol %; TBPB, 275.15 K and 1.00 mol %; and  $\text{TBANO}_3$ , 275.14 K and 1.00 mol %) can be obtained from Figure 3. Corresponding to the suitable operating conditions, the shortest induction time during the hydrate formation is obtained. It is essential for the hydrate-based  $\text{CO}_2$  separation process for three systems. As seen from Figure 4, the induction time for each quaternary salt system can be shortened within 5 min under the optimal operating conditions. Consequently, it can be concluded that three quaternary salts (TBPB,  $\text{TBANO}_3$ , and TBAB) have the potential on the flue gas treatment by the hydrate method.

**3.2.2. Pressure Drop during Hydrate Formation.** In a system with the constant volume and temperature, the pressure drop during the hydrate formation can be used as a key parameter to measure the amount of gases that entered into the hydrate slurry. Figure 5 shows the pressure drops in the system versus the temperature in different salt solutions with the same concentration (1.00 mol %). It is obviously noted that the pressure drop has few changes with the change of the temperature; however, the pressure drop increases with the



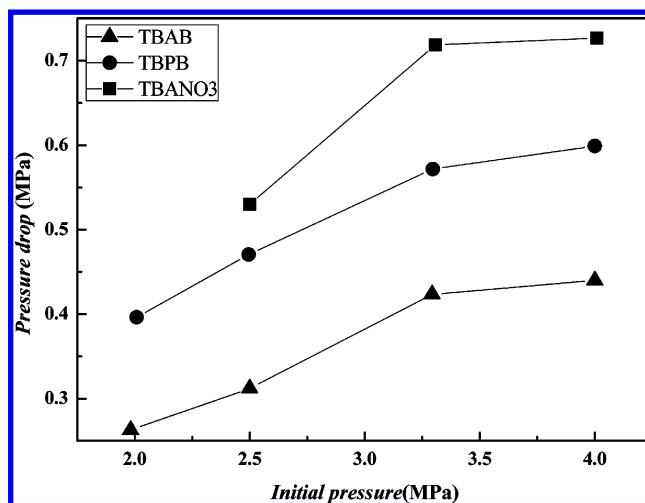
**Figure 4.** Induction time versus the initial pressure for each solution under its suitable operating conditions: (a) 275.15 K and 0.65 mol %, (b) 275.15 K and 1.00 mol %, and (c) 274.15 K and 1.00 mol %.



**Figure 5.** Pressure drops versus the temperature in salt (TBAB and TBPB) aqueous solutions (1.00 mol %).

increase of the initial pressure in both TBAB and TBPB solutions. It means that the effect of the temperature on the pressure drop can be negligible.

Figure 6 shows the change of the pressure drop at a fixed temperature and concentration in different solutions. It can be seen that the pressure drop increases with the increase of the initial pressure for all three salts. However, the shape of the TBANO<sub>3</sub> curve is slightly different from the others at the same operating conditions. The pressure drop first has a dramatic increase when the initial pressure varies from 2.5 to 3.3 MPa, while it increases slowly after the initial pressure exceeds 3.3 MPa. With the comparison of three salts under the same condition, it is found that TBANO<sub>3</sub> has the strongest effect on the pressure drop during the hydrate formation. For example, with the initial pressure of 3.3 MPa, the pressure drop is 0.42, 0.57, and 0.72 MPa for TBAB, TBPB, and TBANO<sub>3</sub> systems, respectively. The pressure drop for the TBANO<sub>3</sub> system is over 1.5 times higher than that for the TBAB system. The TBPB system also presents a better result for the pressure drop compared to the TBAB system. The experimental results prove that the hydrate cannot be formed in the TBANO<sub>3</sub> system at pressures under 2.5 MPa (2.0 MPa) at the same temperature (275.15 K). The equilibrium hydrate formation pressure for the



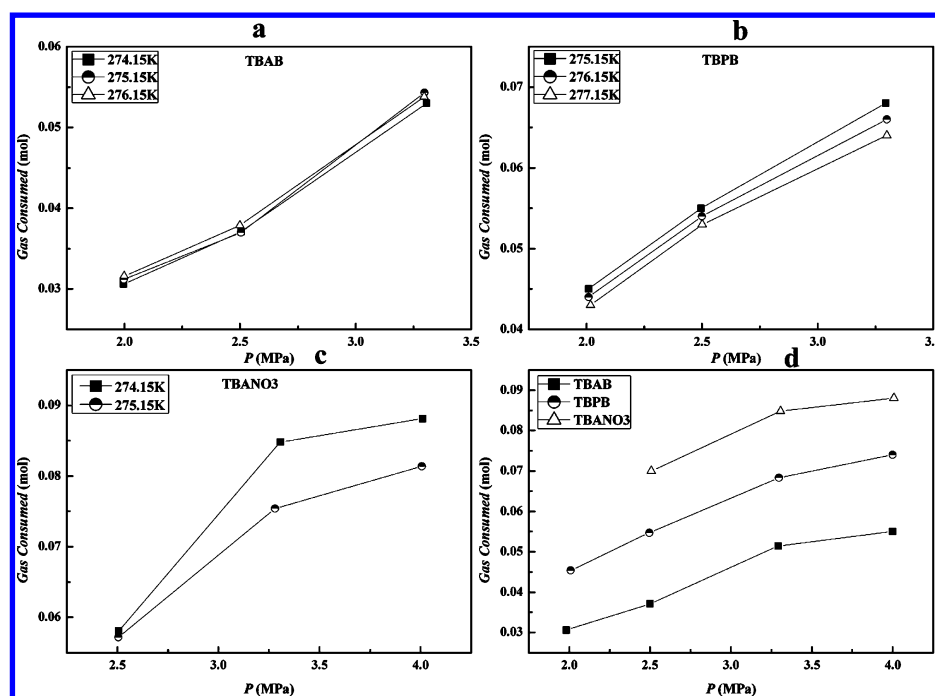
**Figure 6.** Pressure drops versus the initial pressure in different solutions (1.00 mol % and 275.15 K).

TBANO<sub>3</sub>/CO<sub>2</sub>/N<sub>2</sub> system is much higher than those for the other two systems. When the pressure is the same, the driving force for TBANO<sub>3</sub> system is quite smaller than those for the other systems. Hence, it is noted that TBANO<sub>3</sub> can guarantee a higher pressure drop at a lower driving force. It may be due to the fact that CO<sub>2</sub> has the highest solubility in the TBANO<sub>3</sub> solution, which causes more gas to dissolve and promotes the hydrate formation. Thus, it is comprehensively concluded that both TBANO<sub>3</sub> and TBPB have a better potential ability for hydrate-based CO<sub>2</sub> separation.

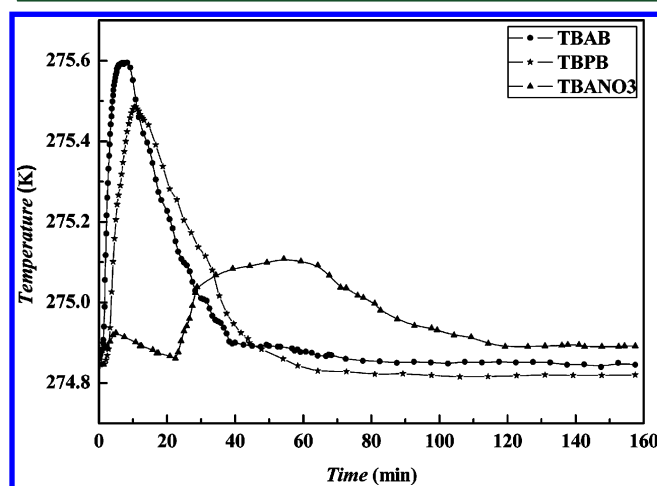
The gas consumption calculated using eq 3 versus the initial pressure is shown in Figure 7 for solutions with the same concentration of 1.00 mol %. As seen from panels a–c of Figure 7, the temperature has little effect on the gas consumption for both TBAB and TBPB systems at different pressures, while it plays a role in the gas consumption for the TBANO<sub>3</sub> system at a higher pressure. Meanwhile, gas consumption increases with the increase of the initial pressure for three solutions, which is in agreement with the change of the pressure drop noted in Figure 5 in the process of the hydrate formation. The gas consumptions of three quaternary salts with 1.00 mol % concentration at 275.15 K are compared in Figure 7d. It is obviously observed that the amount of gas consumption in TBANO<sub>3</sub> solution is the highest among three solutions. The trend of gas consumption can also correspond to the pressure drop curve shown in Figure 6.

### 3.2.3. Temperature Change during Hydrate Formation.

The temperature changes in hydrate formation experiments are shown in Figure 8 in different salt solutions with the same concentration of 1.00 mol % under the initial pressure of 3.3 MPa and the temperature of 275.15 K. It is found that the increases of the temperatures are approximately 0.80, 0.65, and 0.35 K in TBAB, TBPB, and TBANO<sub>3</sub> systems, respectively. In the process of the hydrate formation, TBANO<sub>3</sub> presents the lowest temperature increase compared to the other two salts. According to the result obtained by Nakajima et al.,<sup>33</sup> a large increase in the temperature corresponds to a higher rate of hydrate formation and vice versa. Therefore, the hydrate formation rate in the TBANO<sub>3</sub> solution is lower than that in other solutions under the operating conditions. Meanwhile, it can also be seen from the figure that the induction time with TBANO<sub>3</sub> is relatively longer. The hydrate formation rate in the TBPB solution is close to that in the TBAB solution. The



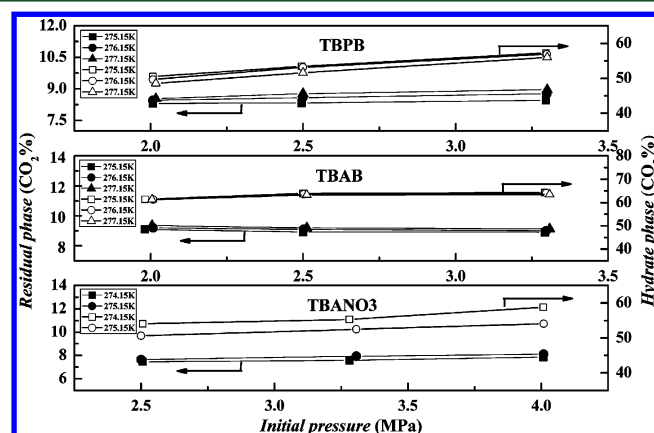
**Figure 7.** Mixed gas consumption curve for hydrate formation in different salt solutions: (a, b, and c) gas consumption versus the initial pressure in TBAB, TBPB, and TBANO<sub>3</sub> solutions (1.00 mol %), respectively, and (d) gas consumption versus the initial pressure in different solutions (1.00 mol % and 275.15 K).



**Figure 8.** Temperature in hydrate formation experiments with three salt solutions (1.00 mol %, 3.3 MPa, and 275.15 K).

reason is that the driving force of the TBANO<sub>3</sub> system is quite lower than those of the other two systems, resulting in a lower hydrate formation rate.

**3.3.1. Separation Characteristics.** *Effects of the Operating Conditions.* It is proven in Figure 5 that the system temperature is not a main factor to determine the pressure drop during the hydrate formation for three salt systems. It is also found in Figure 9 that the temperature change has little influence on separation efficiency. The CO<sub>2</sub> concentrations in both residual and hydrate phases present little variation with the increase of the system temperature. Besides, it is noted that the initial pressure also has little effect on the CO<sub>2</sub> concentration in the residual gas phase for salt solutions with the concentration of 1.00 mol %. Nevertheless, the CO<sub>2</sub> concentration in the hydrate slurry phase goes up with the increase of the initial pressure in a lower pressure range.

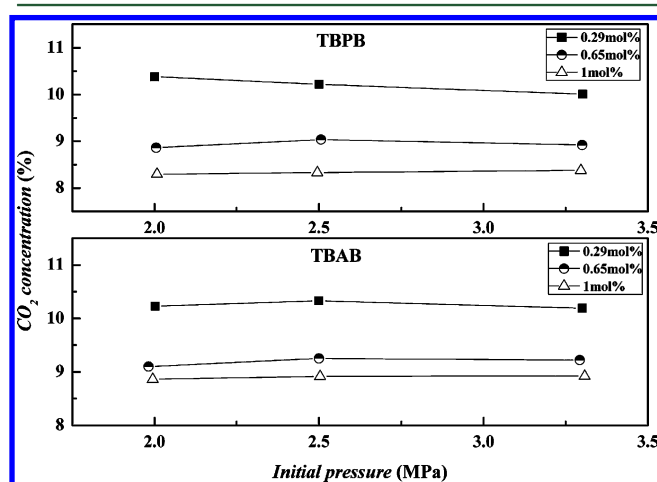


**Figure 9.** CO<sub>2</sub> concentrations in the hydrate slurry phase and residual gas phase for three salt solutions with 1.00 mol % under different operating conditions.

According to the phase equilibrium data given by Mohammadi et al.,<sup>34</sup> CO<sub>2</sub> can preferentially incorporate into hydrate at a lower initial pressure compared to N<sub>2</sub>. A suitable initial pressure can increase CO<sub>2</sub> storage in the hydrate slurry and enhance the separation process, and the result is presented in the three salt systems in this work, as shown above. Therefore, a fixed temperature of 275.15 K and the initial pressure in the range of 2.0–4.0 MPa are considered as suitable operating conditions for separation experiments.

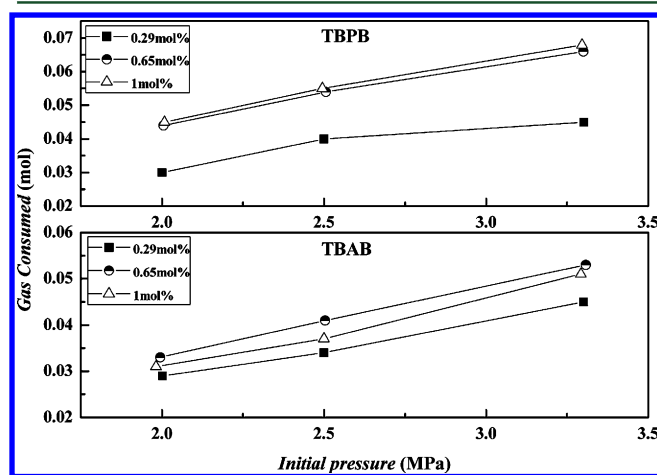
**3.3.2. Effects of Concentrations.** It should be explained in advance that there is no comparison of the TBNO<sub>3</sub> solution with different concentrations because it needs a high-pressure condition to form the hydrate in the TBANO<sub>3</sub> solution with 0.29 and 0.65 mol % concentration (e.g., no hydrate forms at 275.5 K and 3.3 MPa in the TBANO<sub>3</sub> solution with 0.65 mol %). The high-pressure condition is unfavorable for the practical

hydrate-based CO<sub>2</sub> separation technology. Thereby, the effects of the concentrations of the salts (TBAB and TBPB) on the CO<sub>2</sub> separation process at 275.15 K have been investigated. Paricaud<sup>35</sup> proposed a thermodynamic model that predicted well that the TBAB concentration can significantly affect the stability of the gas hydrate for the TBAB/CO<sub>2</sub> system. An increase of the TBAB concentration will lead to a destabilization of the hydrate at TBAB concentrations above the stoichiometric composition. It indicates that a suitable concentration of quaternary salt is essential for the CO<sub>2</sub> hydrate-based separation process. The CO<sub>2</sub> concentration in the residual gas phase versus the initial pressure for TBAB and TBPB solutions with different concentrations is shown in Figure 10. It can be seen that the CO<sub>2</sub> concentration in the



**Figure 10.** CO<sub>2</sub> concentration in the residual gas phase versus the initial pressure for TBPB and TBAB solutions with different concentrations at 275.15 K.

residual gas phase decreases with the increase of the concentration of the tetra-butyl-salt solution. Besides, when the concentration of the salt solution increases, the difference of the CO<sub>2</sub> concentration between two different concentrations of the solution becomes smaller (the CO<sub>2</sub> concentrations at 0.65 and 1.00 mol % are close). A similar phenomenon is also revealed in Figure 11, which depicts the effects of different



**Figure 11.** Mixed gas consumption versus the initial pressure for TBPB and TBAB solutions with different mole concentrations at 275.15 K.

concentrations of the solutions on gas consumption. As seen from Figure 11, gas consumption goes up with the increase of the concentration of the salt solution. However, when the concentration of the solution reaches 0.65 mol %, the gas consumption no longer increases for the TBPB system, while there is a drop for the TBAB system instead. It can be explained that, when the solution is at a low concentration, the semi-clathrate hydrate structure of the quaternary salt can provide enough dodecahedral cages. The dodecahedral cages are more favorable for CO<sub>2</sub> engagement, further resulting in the increase of gas consumption and the drop of the CO<sub>2</sub> concentration in the residual gas phase. It is helpful for CO<sub>2</sub> selection for the mixture gas separation. Nevertheless, it is found in the experiments that the hydrate sharply forms and substantially agglomerates at the gas/liquid interface when there is a higher concentration (0.65 or 1.00 mol %). A similar phenomenon can be found elsewhere.<sup>11</sup> Meanwhile, either pure TBAB hydrate or pure TBPB hydrate has probably formed at a higher concentration. These two barriers prevent gas molecules from incorporating into the hydrate. Especially for TBAB, the pure TBAB hydrate with the dissociation temperature of 284.8 K can more easily form than the pure TBPB hydrate with the dissociation temperature of 281.1 K.<sup>28,33</sup> It is concluded that more pure TBAB hydrate forms and gas incorporation is prevented at higher concentrations. Thus, gas consumption presents a slight drop from a high concentration (0.65 mol %) to a higher concentration (1.00 mol %) for the TBAB solution.

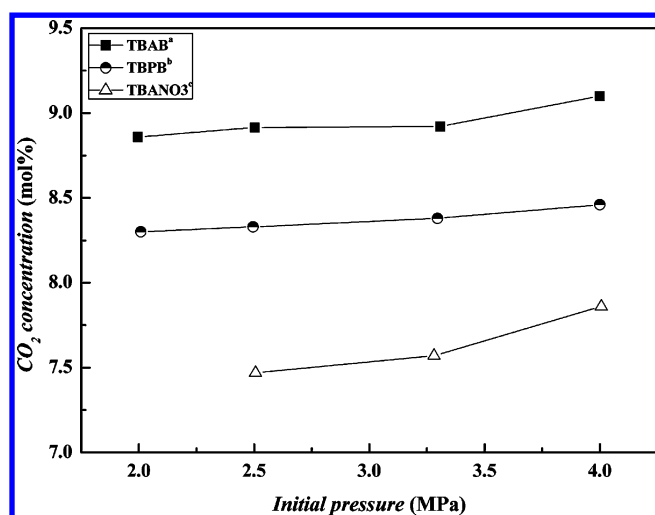
**3.3.3. Effects of Quaternary Salts.** On the basis of the above discussion and the phase equilibrium discrepancies among three quaternary salt systems, suitable operating conditions are chosen in Table 3 to make a comparison of the effects of

**Table 3.** Optimal Operating Conditions Chosen for Each Quaternary Salt System

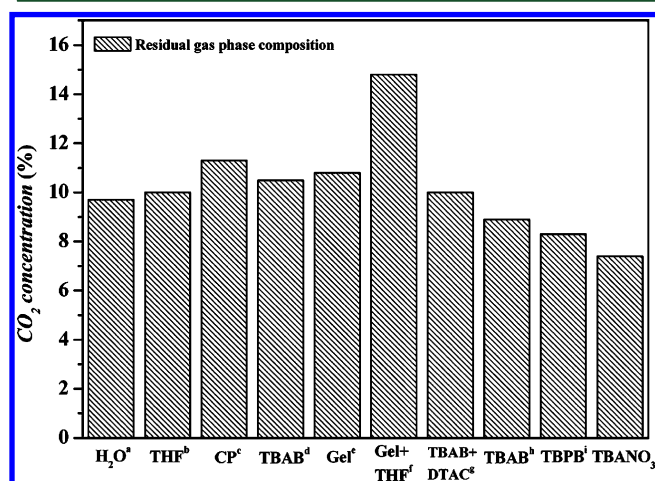
| quaternary salt    | temperature (K) | initial pressure (MPa) | concentration (mol %) |
|--------------------|-----------------|------------------------|-----------------------|
| TBAB               | 275.15          | 2.0–3.3                | 0.65                  |
| TBPB               | 275.15          | 2.0–3.3                | 1.00                  |
| TBANO <sub>3</sub> | 274.15          | 2.5–3.3                | 1.00                  |

quaternary salts on separation efficiency. Figure 12 shows the CO<sub>2</sub> concentration in the residual gas phase versus the initial pressures for each salt solution under suitable operating conditions. It is noted that the CO<sub>2</sub> concentration in the residual gas phase has a significant drop from 17.0 to 7.4 mol % with the TBANO<sub>3</sub> system, which indicates the strongest capability for CO<sub>2</sub> removal from the gas mixture compared to other systems. Meanwhile, it is found that TBPB has the potential ability in the CO<sub>2</sub> removal process by the concentration drop to about 8.3 mol %. The previous studies<sup>8,13,14,17,19,36</sup> referring to the effects of additives on hydrate-based CO<sub>2</sub> removal under suitable conditions are summarized in Figure 13. It is shown that additives (THF, CP, and TBAB) or the gel system cannot further decrease the CO<sub>2</sub> concentration in the residual gas phase. The CO<sub>2</sub> concentration in the residual gas phase maintains approximately 10.0 mol % in the systems with the additives above as well as that in pure water. Especially in the gel system with THF, the concentration has slightly dropped from 17.0 to 14.0 mol % by a one-stage hydrate separation. In comparison to the other systems, TBPB and TBANO<sub>3</sub> can not only have a more significant effect on CO<sub>2</sub> removal but also guarantee a suitable operating condition





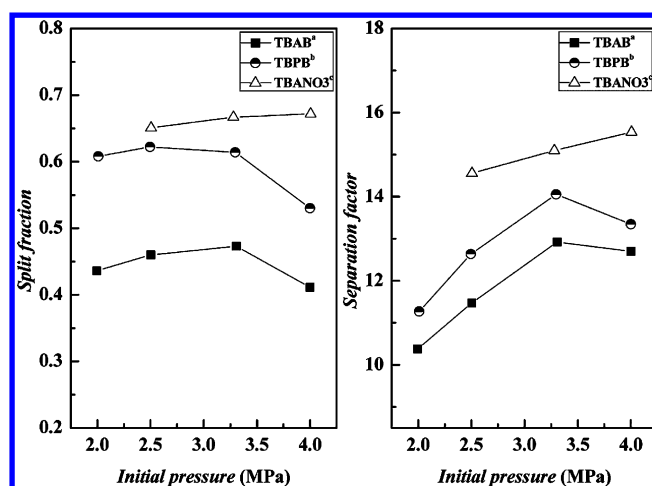
**Figure 12.**  $\text{CO}_2$  concentration in the residual gas phase versus the initial pressure for each salt solution under suitable operating conditions: (a) 275.15 K and 0.65 mol %; (b) 275.15 K and 1.00 mol %; and (c) 274.15 K and 1.00 mol %.



**Figure 13.**  $\text{CO}_2$  concentration in the residual gas phase for systems with different additives under suitable operating conditions: (a) water, 273.75 K and 10 MPa;<sup>14</sup> (b) THF (1.00 mol %), 273.75 K and 2.5 MPa;<sup>8</sup> (c) CP (1:5), 281.25 K and 2.9 MPa;<sup>17</sup> (d) TBAB (0.16 mol/L), 274.95 K and 3.35 MPa;<sup>13</sup> (e) gel (100 nm), 272.15 K and 8 MPa;<sup>36</sup> (f) gel (100 nm) + THF (1.00 mol %), 272.15 K and 5 MPa;<sup>36</sup> (g) TBAB (0.29 mol %) + dodecyltrimethylammonium chloride (DTAC) (0.028 mol %), 272.15 K and 5 MPa;<sup>19</sup> (h) TBAB (0.65 mol %), 275.15 K and 2.5 MPa; (i) TBPB (1.00 mol %), 275.15 K and 2.5 MPa; and (j) TBANO<sub>3</sub> (1.00 mol %), 274.15 K and 2.5 MPa.

(temperature, 274.15–275.15 K; pressure, 2.0–4.0 MPa) for a real hydrate-based  $\text{CO}_2$  separation technology. All of these demonstrate that TBANO<sub>3</sub> as well as TBPB are more likely to promote a one-stage hydrate-based  $\text{CO}_2$  separation process.

The S.Fr. and S.F. are two important factors to assess the separation efficiency by a one-stage hydrate formation process. According to eqs 5 and 6, the S.Fr. and S.F. are calculated. It can be seen from the equations that the S.Fr. and S.F. are obtained when the system is at thermodynamic equilibrium. Figure 14 shows the changes of S.Fr. and S.F. versus the initial pressure for each quaternary salt under its optimal operating conditions obtained above. It is clearly observed that effects of quaternary salt on S.Fr. and S.F. have the same results: TBANO<sub>3</sub> > TBPB > TBAB. The S.Fr. of TBANO<sub>3</sub> reaches



**Figure 14.** S.Fr. and S.F. versus the initial pressure for each salt solution under suitable operating conditions: (a) 275.15 K and 0.65 mol %; (b) 275.15 K and 1.00 mol %; and (c) 274.15 K and 1.00 mol %.

0.67, which is much more than that of TBAB (0.47) at each suitable operating condition. Meanwhile, TBPB presents a good effect on S.Fr. for  $\text{CO}_2/\text{N}_2$  mixtures. As shown in Figure 14a, the same trends that the S.Fr. increases and then drops with the increase of the initial pressure are found for both TBAB and TBPB systems. It reaches the maximum value at 3.3 MPa. It may be due to the fact that  $\text{N}_2$  competes with  $\text{CO}_2$  for cage occupancy with a higher driving force, resulting in a drop of the  $\text{CO}_2$  concentration in the hydrate slurry phase. As for the TBANO<sub>3</sub> system, the S.Fr. increases constantly within the initial pressure range of 2.5–4.0 MPa. This is because the TBANO<sub>3</sub>/ $\text{CO}_2/\text{N}_2$  system can guarantee a relatively lower driving force within the pressure range investigated.  $\text{CO}_2$  does more competitively incorporate into the hydrate compared to  $\text{N}_2$  in the TBANO<sub>3</sub> system. It is advantageous for the  $\text{CO}_2$  separation. Likewise, similar phenomena for S.F. of the three quaternary salts are revealed in Figure 14b. The maximum separation factors for TBANO<sub>3</sub>, TBPB, and TBAB systems under the operating conditions are 15.54, 14.06, and 12.92, respectively. The results of S.Fr. and S.F. obtained are superior to those with  $\text{H}_2\text{O}$ , THF, and CP systems discussed by others.<sup>8,14,17</sup> Hence, quaternary salts can significantly promote the  $\text{CO}_2$  separation by a one-stage hydrate process. In summary, TBANO<sub>3</sub> is proven to have the strongest effect on gas consumption, S.Fr., and S.F. under suitable operating conditions. It indicates that TBANO<sub>3</sub> shows the biggest potential to deal with the flue gas compared to other systems.

#### 4. CONCLUSION

The effects of three quaternary salts on hydrate formation and separation efficiency were investigated for the capture of  $\text{CO}_2$  from simulated flue gas [ $\text{CO}_2$  (17 mol %)/ $\text{N}_2$ ] at different operating conditions by a one-stage hydrate separation process. The main conclusions are obtained as follows: (1) The quaternary salt effects on  $\text{CO}_2$  solubility are summarized as follows: TBANO<sub>3</sub>  $\approx$   $\text{H}_2\text{O}$  > TBPB > TBAB. The higher solubility of  $\text{CO}_2$  in TBANO<sub>3</sub> solution is more beneficial for the  $\text{CO}_2$  separation compared to the other two solutions. (2) During the hydrate formation process, the induction time for each quaternary salt system can be shortened to less than 5 min at each optimal operating condition. Meanwhile, TBANO<sub>3</sub> has



the strongest effect on the pressure drop, which is approximately 1.5 times higher than that for the TBAB system. TBPB also presents a better effect for the pressure drop compared to TBAB. Similar results are seen in the gas consumption of three quaternary salts. (3) On the basis of this work, suitable operating conditions for CO<sub>2</sub> separation by the hydrate method with quaternary salts are proposed for the CO<sub>2</sub> (17 mol %)/N<sub>2</sub> mixture. Each quaternary salt can significantly promote the CO<sub>2</sub> separation under its optimal condition by a one-stage hydrate process. On the basis of the good kinetic behavior of CO<sub>2</sub> in TBANO<sub>3</sub> solution, TBANO<sub>3</sub> displays the strongest effect on CO<sub>2</sub> separation with the highest S.F. of 67% and S.F. of 15.54 compared to the other two salts. Besides, CO<sub>2</sub> can be further removed from 17 to 7 mol % in the presence of TBANO<sub>3</sub>.

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### Notes

The authors declare no competing financial interest.

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