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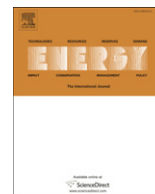


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Hydrate-based pre-combustion carbon dioxide capture process in the system with tetra-n-butyl ammonium bromide solution in the presence of cyclopentane

Xiao-Sen Li ^{a,b,*}, Chun-Gang Xu ^{a,b,c}, Zhao-Yang Chen ^{a,b}, Hui-Jie Wu ^{a,b}

^a Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China

^b Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, PR China

^c Graduate University of Chinese Academy of Sciences, Beijing 100083, PR China

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ABSTRACT

Effects of 0.29 mol% tetra-n-butyl ammonium bromide (TBAB) solution in conjunction with cyclopentane (CP) on the hydrate-based pre-combustion CO₂ capture are investigated by the measurements of the gas uptakes, CO₂ separation efficiencies and induction time of the hydrate formation at the different temperature–pressure conditions. The results show that the volume of the TBAB has an effect on the CO₂ separation and the induction time, and the addition of the CP into the TBAB solution remarkably enhances the CO₂ separation and shortens the induction time. The system with the CP/TBAB solution volume ratio of 5 vol% and TBAB solution/reactor effective volume ratio of 0.54 is optimum to obtain the largest gas uptake and the highest CO₂ separation efficiency at 274.65 K and 4.0 MPa. Compared to the results with tetrahydrofuran (THF) as an additive [1], the gas uptake is enhanced by at least 2 times and the induction time is shortened at least 10 times at the similar temperature–pressure condition. In addition, the CO₂ concentration in the decomposed gas from the hydrate slurry phase reaches approximately 93 mol% after the first-stage separation at 274.65 K and 2.5 MPa. The gas uptakes of more than 80 mol% are obtained after 400 s at the temperature range of 274.65–277.65 K and the pressure range of 2.5–4.5 MPa.

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1. Introduction

Carbon dioxide discharged from the burning of fossil fuels has been identified as the main contributor to the greenhouse gases and the global warming [2]. Among all the CO₂ emissions worldwide, about one third of CO₂ emissions come from fossil fuel electric power plants [3]. In order to deal with the challenge of the global warming, the technique of CO₂ sequestration (capture and storage) has been developing. The current main techniques for the CO₂ capture include physical adsorption, chemical adsorption, cryogenic fractionation and membrane process. However, these techniques have their individual issues of either high cost, large energy consumption, low capacity or high corrosion [4]. Therefore, for the purpose of utilizing fossil fuels in the power plants continuously, it is necessary to develop the new technologies to capture CO₂ efficiently and cost-effectively.

* Corresponding author. Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, No. 2, Nengyuan Road, Wushan, Guangzhou 510640, PR China. Tel.: +86 20 87057037; fax: +86 20 87034664.

E-mail address: lixs@ms.giec.ac.cn (X.-S. Li).

A novel method for separating CO₂ is via the gas hydrate crystallization [4–7]. The basis for the separation is the selective partition of the CO₂ component between the hydrate phase and the gaseous phase. Spencer et al. [8] gave an economic assessment that the cost of the hydrate technique for CO₂ separation from IGCC (Integrated gasification combined cycle) power plant was approximately 10 U.S. dollars per ton of CO₂, which is much lower than that of other methods. Hence, the hydrate separation technique is promising for separating CO₂ from IGCC syngas.

Linga et al. [1] studied on the hydrate kinetics of CO₂/H₂ mixture in pure water system. They found that the induction time is 9.7 min and the hydrate formation rate is 0.0048 mol/min for the first 5 min for CO₂/H₂/H₂O system at 273.7 K and 7.5 MPa. Especially, the operating pressure of 7.5 MPa was higher than the outlet pressure of the fuel gas. Hence, there is a continuous interest in using the additives to shorten the induction time, accelerate the formation rate, and reduce the operating pressure. Tetrahydrofuran (THF) is identified to have a significant effect on reducing the equilibrium hydrate formation condition for the CO₂/H₂/H₂O mixture [1], and the 1.0 mol% THF was found to be the optimum concentration for the CO₂ capture based on the thermodynamic experiments. Zhang and Lee found that the H₂/cyclopentane (CP) hydrate system has

a lower equilibrium pressure at the same temperature, compared with the H_2/THF hydrate system [6]. Furthermore, they studied on the phase equilibria of the $\text{CO}_2/\text{H}_2/\text{CP}$ ternary hydrate systems and proposed a hydrate-based pre-combustion CO_2 capture process [7]. The results showed that the equilibrium hydrate dissociation pressure of the $\text{CO}_2/\text{H}_2/\text{CP}/\text{H}_2\text{O}$ system is lower than that of the $\text{CO}_2/\text{H}_2/\text{THF}/\text{H}_2\text{O}$ system with the same initial gas compositions at the same temperature. Thus, the operating pressure of the hydrate-based pre-combustion CO_2 capture can be reduced. However, in the $\text{CO}_2/\text{H}_2/\text{CP}/\text{H}_2\text{O}$ system, the selectivity of CO_2 over H_2 in the hydrate phase reduces significantly due to H_2 competed with CO_2 for the small cages of the hydrates with structure II [7]. Kumar et al. studied on the incipient hydrate phase equilibria for the gas mixtures containing hydrogen, carbon dioxide and propane, and found that the propane (C_3H_8) as a promoter can reduce the equilibrium hydrate formation pressure [9]. Afterwards, C_3H_8 was employed in a two-stage clathrate hydrate process for pre-combustion capture of carbon dioxide and hydrogen, and the results showed that the 3.2 mol% C_3H_8 can reduce the operating pressure from 7.5 MPa (in a system without propane) to 3.8 MPa in the first stage [10].

Recently, tetra-*n*-butyl ammonium bromide (TBAB) as an environmental friendly compound is investigated in the process of hydrate-based gas capture, which can significantly reduce the equilibrium hydrate formation pressures of the CO_2/H_2 mixtures [11,12]. Li et al. found that approximately 0.29 mol% TBAB is the optimum concentration to obtain a high gas storage capacity based on the experiments of the gas hydrate formation process for the CO_2 separation from the fuel gas mixture [13]. Although some work [1,7,10,11] has carried out the investigations into the gas uptakes, the CO_2 separation efficiencies, the induction time of hydrate formation etc. in the processes of the hydrate-based pre-combustion gas separations, the CO_2 capture still needs to be further improved to meet the requirement of the industrial application. As mentioned above, the TBAB and CP are excellent promoters for the hydrate-based gas separation. However, few studies on the kinetic behaviors

of the hydrate formation for the CO_2/H_2 gas mixtures in the TBAB solution in the presence of CP are reported.

In this work, the gas uptakes, the CO_2 separation efficiencies and the induction time of the hydrate formation for the hydrate-based pre-combustion CO_2 capture process in the systems with the different amount of the 0.29 mol% TBAB solution in the presence of CP with various corresponding volume ratios with the TBAB solution are investigated at the pressure range from 2.5 MPa to 4.5 MPa and the temperature range from 273.65 K to 277.65 K. In the following, the ratio of the volume of CP to the volume of the TBAB solution is abbreviated as the CP/TBAB ratio.

2. Experimental

2.1. Materials

A treated synthesis gas coming out of an IGCC power station consists of approximately 40 mol% CO_2/H_2 gas mixture at the pressure of 2.5–5.0 MPa [5]. Thus, a CO_2/H_2 gas mixture containing the 38.6 mol% CO_2 is used in the work to simulate a pretreated fuel gas mixture. The gas mixture is supplied by Foshan Huate Gas Co., Ltd. TBAB with 99.9% purity is supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd., China. CP with the purity of more than 99.0% is supplied by Xiamen Pioneer Chemical Reagent Co., Ltd. The de-ionized water used with the resistivity of $18.25 \text{ m}\Omega \text{ cm}^{-1}$ is produced by an ultra-pure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China.

2.2. Apparatus

The experimental apparatus in this work is shown in Fig. 1. The crystallizer (CR) with inner volume of 336 ml and the supply vessel (SV) with the inner volume of 1350 ml are made of 316 stainless steels, respectively. They are immersed in a temperature-controlled water bath. On the front and back of the CR, there are two circular

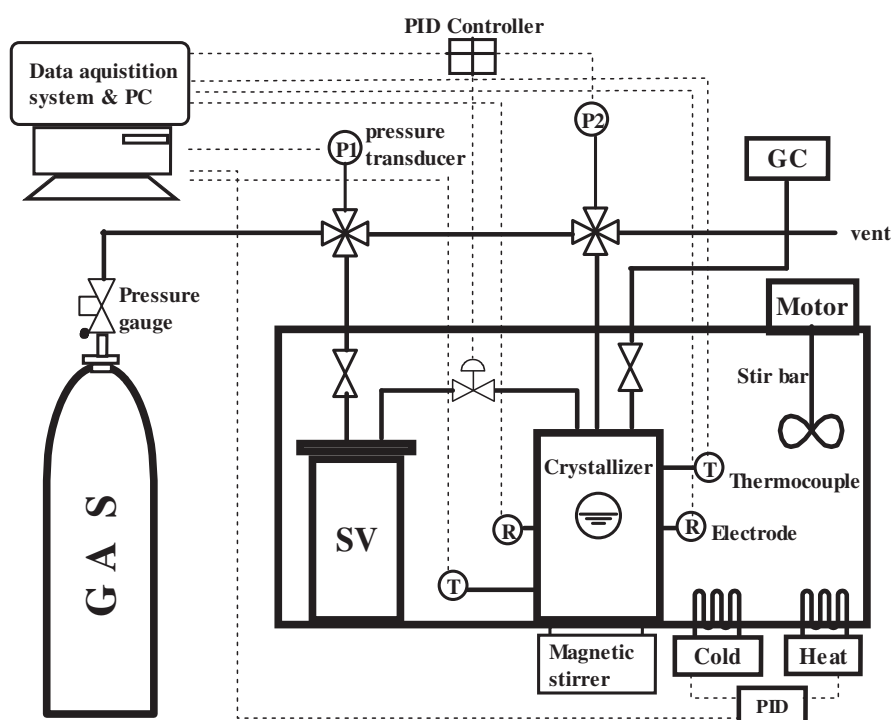


Fig. 1. Experimental apparatus.

viewing windows made of Plexiglas. The maximum working pressure of the CR is 25 MPa. A magnetic stirrer (500 r/min) is employed to mix the contents in the CR. The temperatures of the gas phase and the liquid phase in the CR are measured using two Pt1000 thermocouples (JM6081) with uncertainties of ± 0.1 K. The pressures in the SV and the CR are measured with two Setra smart pressure transducers (model 552, Boxborough, MA, USA) with the uncertainty of 20 kPa. In addition, the composition of the gas phase in the CR is determined with a HP6890 gas chromatography (GC) connected on-line with CR and automated with a personal computer (PC).

2.3. Procedure

In our previous work [11,13], the TBAB concentration of 0.29 mol % is identified to be the optimum concentration for the CO₂ capture from the CO₂/H₂ mixture. Therefore, in this work, the 0.29 mol% TBAB solution in conjunction with the CP, as an additional additive, with the different volume ratios with the TBAB solution is used for the separation experiments.

Prior to the experiment, the CR is cleaned using de-ionized water and allowed to dry. Then the TBAB aqueous solution and CP liquid with individual desired volumes are introduced into the high-pressure hydrate CR. Subsequently, the hydrate CR is flushed with the CO₂/H₂ gas mixture at least four times to remove any residual air or mixed gas, and then the CO₂/H₂ gas mixture is charged into the CR until the desired pressure. Once the temperature is stabilized (typically within 1 min) the stirrer with the rate of 500 r/min is started, and the experimental time also began to be recorded once every 2 s. The time when the stirrer is started is defined as t_0 . The temperature, the pressure and the resistance in the system are recorded during the experiment. As the gas in the CR is consumed on account of the hydrate formation, the additional gas mixture in the SV is supplied and the pressure in the CR is maintained constant with a proportional integral derivative (PID) controller.

The composition of the gas phase is measured with GC in the process of the hydrate formation. It is assumed that the small amount of gas sampled to GC does not affect the whole gas uptake in the process [5]. Once the pressure and the temperature are stable and have no change for 60 min, the process of the hydrate formation is considered to be completed and the time is defined as t . The moles of the gas (Δn_H), the moles of gas uptake, that has either gone into the water or been consumed from the hydrate formation can be calculated as follows [1]:

$$\Delta n_H = n_{H,t} - n_{H,0} = \left(\frac{PV}{zRT} \right)_{G,0} - \left(\frac{PV}{zRT} \right)_{G,t} + \left(\frac{PV}{zRT} \right)_{SV,0} - \left(\frac{PV}{zRT} \right)_{SV,t} \quad (1)$$

where z is the compressibility factor calculated by Pitzer's correlation [14]. Subscript t refers to time t . Subscript 0 refers to the initial time. Subscript G refers to the gas phase in the CR. Subscript SV refers to the gas phase in the supply vessel. The solution used in the experiments comes from the fresh solution and the memory solution. The memory solution is obtained 2 h after the fresh CO₂/H₂/TBAB hydrate has decomposed.

After the end of the hydrate formation, the CR is quickly depressurized to atmospheric pressure and then it is closed. Thus, the hydrate is allowed to dissociate completely by being heated to 293.15 K. Subsequently, the gas evolved from the decomposed hydrate and released from the solution is collected and analyzed by GC. The method is also used elsewhere [10]. When the hydrate nucleation completes and the hydrate growth starts, the system temperature and gas uptake instantaneously have an obvious rise. This can be attributed to the fact of the substantial

hydrate formation and the extensive release of the heat in the process [1,15]. The induction time can be experimentally determined by the abrupt points of the gas uptake and temperature curves in the process of the hydrate formation.

3. Results and discussion

The orthogonal-test design is used for selecting the optimum condition of experimental factors [16]. In order to investigate into the effects of the different volumes of the 0.29 mol% TBAB solution in the presence of the CP with various corresponding CP/TBAB ratios on the gas uptakes, the CO₂ recovery efficiencies and the induction time in the processes of the hydrate-based CO₂ separations from the CO₂/H₂ gas mixture at the different temperatures and pressures, twenty-five runs of the experiment plans with four factors (i.e. the temperature, pressure, volume of TBAB solution and CP/TBAB ratio) and five levels (each factor has 5 levels), $L_{25}(5^4)$, are adopted in the experiments. The experimental plans are shown in Table 1. The following discussions in detail are carried out based on the experimental plans.

3.1. Gas uptake

Before doing the formal experiments, we carry out a group of the contest experiments for the CO₂/H₂/CP/H₂O system, in which the composition of the feed gas mixture is CO₂ of 38.6 mol% and H₂ of 61.4 mol%, at 4.5 MPa and 273.15 K for the purpose of confirming whether the CP added in the water can enhance the amount of final gas uptake after the gas hydrate forms. As shown in Fig. 2, the gas uptake changes only from 0.0264 to 0.0305 with the increase of the amount of the CP. Fig. 3(a) and (b) shows the gas uptake profiles for the different systems with the same feed gas with the above components at 274.65 K and 4.0 MPa. As seen, the gas uptake for the CO₂/H₂/CP/H₂O system is quite low, compared to those for the CO₂/H₂/TBAB/H₂O and CO₂/H₂/TBAB/CP/H₂O systems. Furthermore, it can be found that the gas uptake for the CO₂/H₂/TBAB/CP/H₂O system is more than the sum of those for the CO₂/H₂/TBAB/H₂O and CO₂/H₂/CP/H₂O systems at any time. Therefore, the addition of the

Table 1
Experimental plans along with CO₂ separation efficiencies.

Run	CP/TBAB ratio (vol%)	Volume of TBAB solution (ml)	Temperature (K)	Pressure (MPa)	S.Fr.	S.F.
1	3	150	273.65	3.0	0.49	17.3
2	3	160	274.65	3.5	0.50	19.1
3	3	170	275.65	4.0	0.51	22.4
4	3	180	276.65	4.5	0.52	24.2
5	3	200	277.65	2.5	0.49	19.3
6	5	150	277.65	2.5	0.54	16.9
7	5	160	276.65	3.0	0.56	18.2
8	5	170	275.65	3.5	0.57	26.5
9	5	180	274.65	4.0	0.58	30.6
10	5	200	273.65	4.5	0.55	30.2
11	8	150	276.65	4.5	0.47	16.1
12	8	160	275.65	2.5	0.46	17.9
13	8	170	274.65	3.0	0.53	25.4
14	8	180	273.65	3.5	0.52	25.7
15	8	200	277.65	4.0	0.49	21.0
16	15	150	275.65	4.0	0.47	14.5
17	15	160	274.65	4.5	0.45	16.7
18	15	170	273.65	2.5	0.44	17.2
19	15	180	277.65	3.0	0.49	16.3
20	15	200	276.65	3.5	0.48	16.6
21	20	150	274.65	3.5	0.44	13.3
22	20	160	273.65	4.0	0.41	15.4
23	20	170	277.65	4.5	0.42	12.1
24	20	180	276.65	2.5	0.43	12.9
25	20	200	275.65	3.0	0.44	14.9

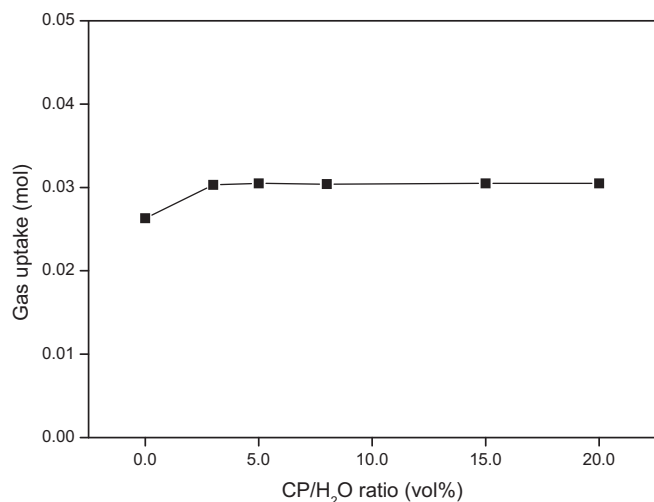


Fig. 2. Gas uptake at the end of the hydrate formation vs. volume ratio of CP/H₂O in 180 ml pure water at 273.15 K and 4.5 MPa.

CP in the pure water/gas system has little effect on the gas uptake. This illustrates that the hydrate phase existing in the CO₂/H₂/CP/H₂O system is mainly the CP hydrate rather than the CP–gas hydrate, and the addition of the CP into the TBAB solution remarkably enhances the gas uptake. This may be attributed to the fact that the synergistic effect of the CP and TBAB results in the more amount of gas going into the hydrate phase. The mechanism of the promotion of the TBAB in conjunction with the CP still requires to be further investigated in our next work.

Fig. 4 shows the final gas uptake change vs. the CP/TBAB ratio with the 0.29 mol% TBAB solution of 180 ml at 4.0 MPa and the different temperatures. As shown in Fig. 4, the value of the gas uptake firstly rises and then drops with the increase of the CP/TBAB ratio from 0 vol% to 20 vol% at the fixed temperature. The peak value of the gas uptake occurs when the CP/TBAB ratio is 5 vol%, and the moles of gas consumed are less than ones in the pure TBAB solution when the ratio is higher than 15 vol%. In addition, it is found that the moles of gas consumed decrease with the increase of the temperature at the fixed CP/TBAB ratio. Because the equilibrium hydrate formation pressure increases with the temperature, the driving force for the gas hydrate formation decreases with the increase of the temperature at the fixed pressure, resulting in the decrease of the moles of the gas consumed. The phenomenon can be found elsewhere [5].

Compared to the results in others' work at the similar conditions [1,10], the gas uptake in this work is enhanced remarkably by approximately 2 times on account of the synergistic effect of the TBAB and CP. For example, the gas uptake obtained by Lee et al. [5] from the system with the 135 ml THF aqueous solution is 0.06 mol at 4.12 MPa and 279.6 K. However, that obtained in this work is 0.12 mol at 4.0 MPa and 277.65 K when the volume of the TBAB solution with the CP/TBAB ratio of 5 vol% is 150 ml, as seen from Fig. 4.

Fig. 5 shows the change of the gas uptake vs. the amount of the 0.29 mol% TBAB solution with the corresponding CP/TBAB ratio at 274.65 K and 4.0 MPa. As seen from Fig. 5, the gas uptake increases with the increase of the amount of the TBAB solution at the given CP/TBAB ratio. However, the increase is little when the amount of the TBAB solution exceeds 180 ml. It is due to the fact that the more amount of liquid phase means the more moles of TBAB existing in the solution for the hydrate formation. Thus, at the given condition, the larger number of the TBAB results in the formation of the more

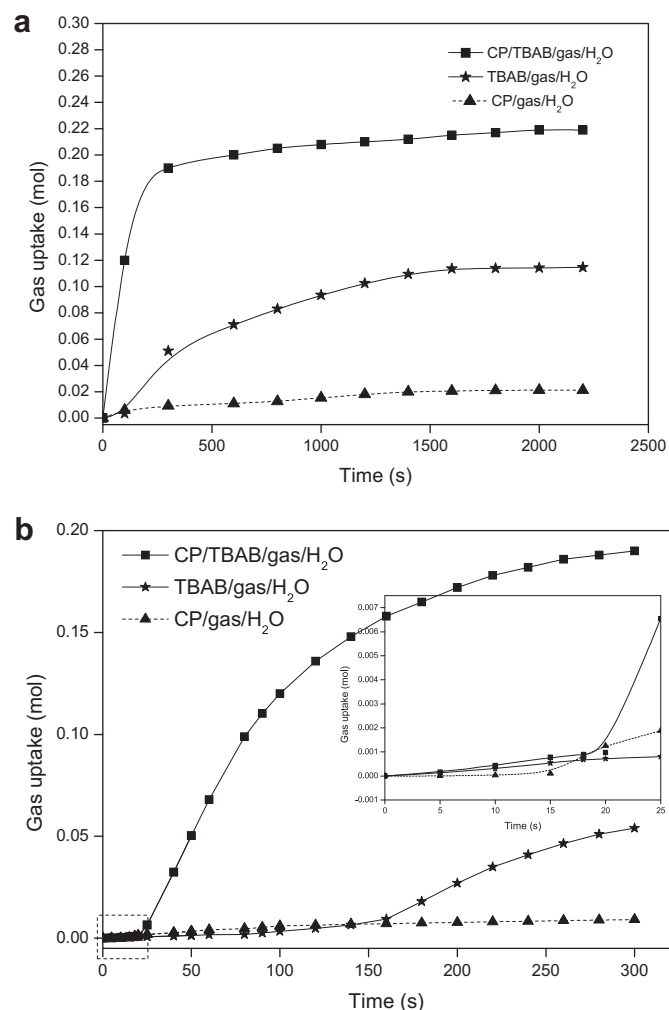


Fig. 3. Gas uptake change for hydrate formation vs. time from different systems at 276.15 K and 4.0 MPa. ■: 0.29 mol% TBAB solution of 180 ml with CP/TBAB ratios of 5 vol%; ★: 0.29 mol% TBAB solution; ▲: pure water of 180 ml with CP/H₂O ratios of 5 vol%.

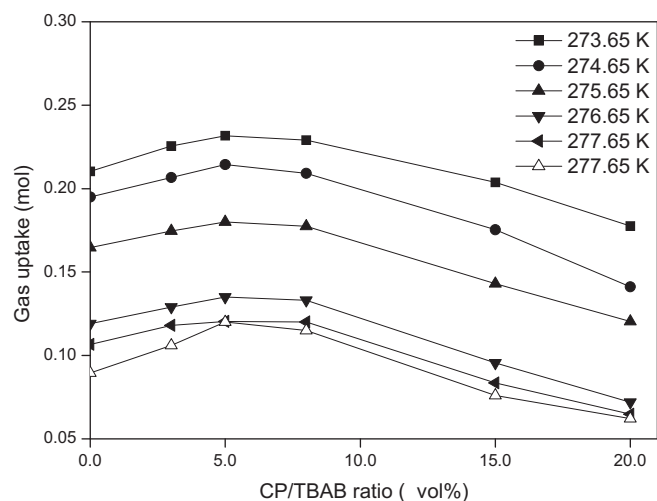


Fig. 4. Gas uptake change vs. CP/TBAB ratio in 180 ml TBAB solution at 4.0 MPa and the different temperatures (△: TBAB solution of 150 ml at 4.0 MPa).

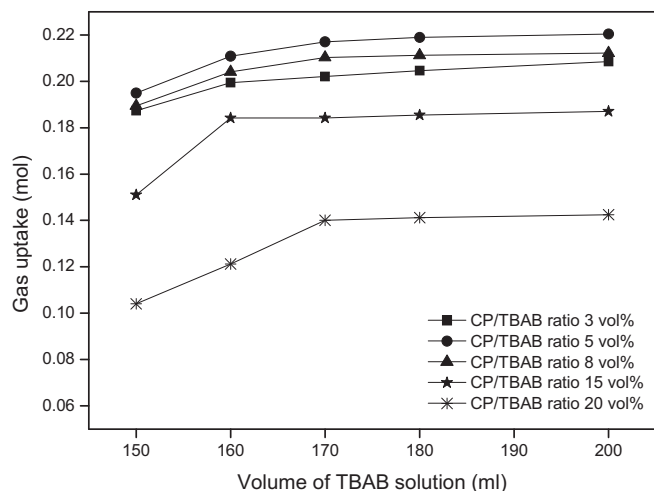


Fig. 5. Gas uptake change vs. volume of 0.29 mol% TBAB solution with different CP/TBAB ratios at 274.65 K and 4.0 MPa.

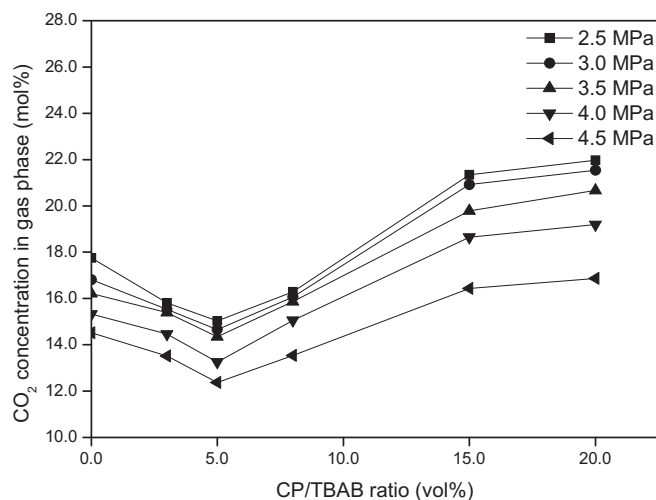


Fig. 6. Change of CO₂ concentration in gas phase vs. CP/TBAB ratio in 180 ml TBAB solution at 274.65 K and different pressures.

hydrate containing the TBAB with more enclosed gas. This is why the moles of the gas consumed increase with the amount of the TBAB solution. On the other hand, for the given CP/TBAB ratio, the increase of the amount of the TBAB solution accompanies the corresponding increase of the amount of CP liquid on the top of the TBAB solution. Thus, as the experiment proceeds, the more CP hydrate can form, and further the thicker layer of the CP hydrate occurs at the CP–TBAB solution interface. The layer dramatically prevents the gas from contacting with the TBAB solution and dissolving into the TBAB solution to form the gas hydrate containing the TBAB, and the degree of the hindrance is bigger with the increase in the layer of the CP hydrate. However, when the amount of the TBAB solution exceeds 180 ml, the effect of the hindrance resulting from the continuous increase of the thickness of the corresponding CP hydrate layer reaches to a maximum value, and, at the time, little gas permeates the CP hydrate. Therefore, the amount of the gas uptake has little increase when the solution exceeds 180 ml. It can be also seen from Fig. 5 that when the amount of the solution is fixed, the gas uptake firstly rises with the increase of the CP/TBAB ratio from 3 vol% to 5 vol%, then drops with the increase of the CP/TBAB ratio from 5 vol% to 20 vol%. The same phenomenon has been explained for Fig. 4.

3.2. CO₂ selectivity

Fig. 6 shows the change of the CO₂ mole concentration in the gas phase at the end of the hydrate formation vs. the CP/TBAB ratio at 274.65 K and the different pressures. As seen from Fig. 6, the CO₂ mole concentration reduces with the increase of the driving force. In addition, each of the CO₂ mole concentration curves is saddle-shaped with the increase of the CP/TBAB ratio from 0 vol% to 20 vol%. Compared to the pure TBAB solution, the addition of a small amount of CP can efficiently reduce the mole concentration of CO₂ in the gas phase as the CP/TBAB ratio increases from 0 vol% to 5 vol%. However, the tendency of the change turns in opposite direction when the CP/TBAB ratio exceeds 5 vol% and even the mole concentration of CO₂ is higher than that of the pure TBAB solution when the CP/TBAB ratio is more than 15 vol%. As described in Zhang et al.'s work, the CP hydrate formation at the CP–water interface can catalyze CO₂ going into the hydrate phase [17]. Similarly, in this work, with the addition of a small amount of the CP, the occurrence of the CP enclathration may catalyze the gas, which is mainly CO₂ because CO₂ easily forms the hydrate, compared to H₂, transferring into the gas hydrate containing the TBAB other than the CP/gas hydrate, because, as

shown in Figs. 2 and 3, the addition of the CP has little effect on the gas uptake in the H₂/CO₂/CP/H₂O system. This also means that there is little gas enclathrated in gas/CP hydrate. However, with the further increase of the amount of the CP, the amount of gas consumed and the selectivity of CO₂ over H₂ entrapping into the hydrate containing the TBAB significantly reduces. It is because the CP hydrate sharply forms and substantively agglomerates at the gas/liquid interface when the CP/TBAB ratio is relatively high. The layer of the agglomeration prevents the gas from contacting with water and transferring into the solution, and further results in the relatively small amount of gas dissolving into the solution. However, H₂ molecule is smaller than CO₂ molecule in the CO₂/H₂ gas mixture, and thus H₂ goes through the layer of the agglomeration diffusing into the aqueous solution more easily. Consequently, this causes the increase of the CO₂ composition of the residual gas phase [17]. Linga et al. did also find the similar phenomenon in their work [1].

Fig. 7 shows the change of the CO₂ concentration in the gas phase vs. the amount of the TBAB solution with the different CP/TBAB ratios at 274.65 K and 4.0 MPa. As shown in Fig. 7, the CO₂ concentration decreases with the increase of the amount of TBAB solution

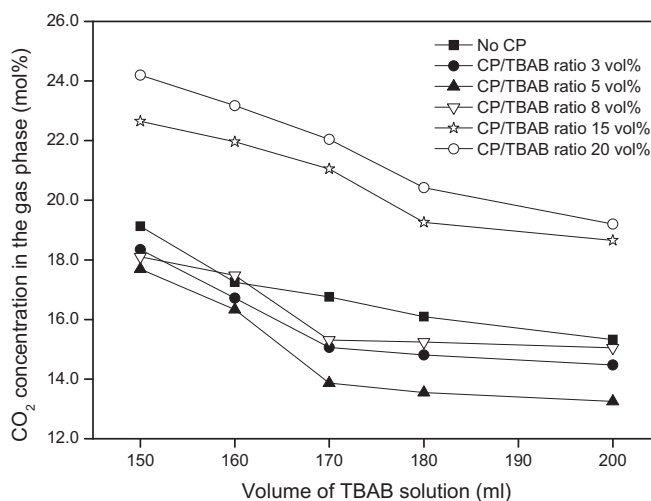


Fig. 7. Change of CO₂ concentration vs. volume of 0.29 mol% TBAB solution with different CP/TBAB ratios at 274.65 K and 4.0 MPa.

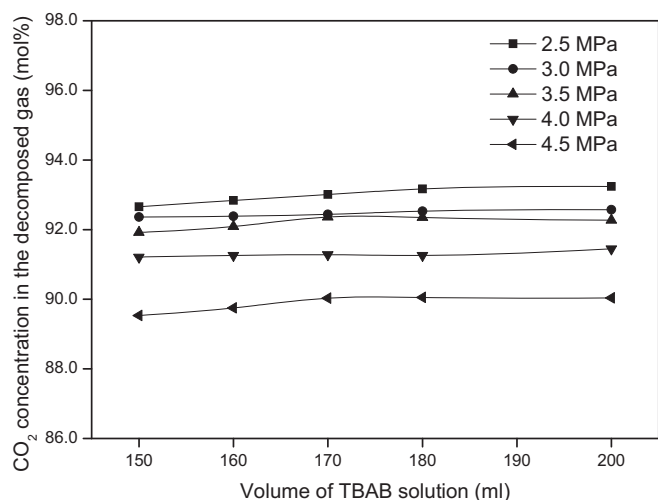


Fig. 8. CO₂ concentration change in the decomposed gas from hydrate phase vs. the volume of TBAB solution with CP/TBAB ratio of 5 vol% at 274.65 K and different pressures.

at the fixed CP/TBAB ratio. On one hand, because CO₂ has much more solubility than H₂ in the TBAB solution at the same condition and the equilibrium hydrate formation pressure of CO₂ is remarkably lower than that of H₂, the CO₂ with the higher solubility and lower equilibrium hydrate formation pressure is more easily incorporated in the hydrate [18]. Therefore, once the CO₂ dissolved in the solution is incorporated in the hydrate containing the TBAB, CO₂ in gas phase is supplied into the TBAB solution to keep the thermodynamic equilibrium of the mass transfer. On the other hand, the volume of the gas phase reduces with the increase of the TBAB solution at the fixed effective volume of the cell in the CR. In addition, the gas with the constant component from the SV is continuously supplied into the gas phase to maintain the pressure constant as the gas hydrate forms. The more amount of the solution result in the more gas supplied from SV going into the system enclosed in the hydrate. Furthermore, according to the law of mass balance, the increased amount of the TBAB solution leads to the lower CO₂ concentration in the gas phase, based on the above given conditions. It can also be seen from Fig. 7 that when the volume of the solution is fixed, the change trend of the CO₂ concentration with the CP/TBAB ratio is the same with that showed in Figs. 4 and 5. The similar reason can be found for Fig. 4.

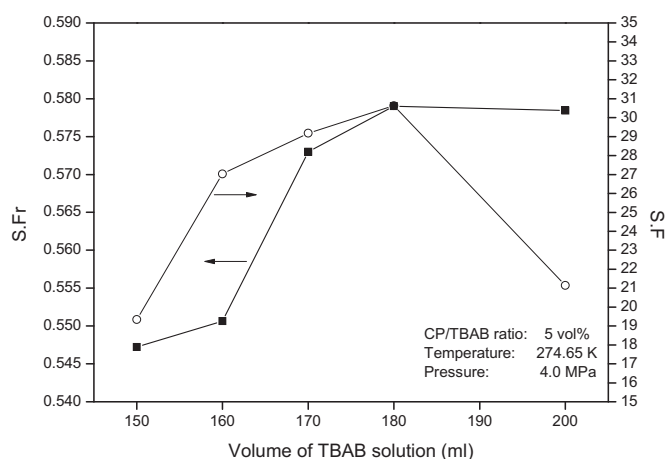


Fig. 9. Changes of CO₂ recovery (S.Fr.) and separation factor (S.F.) vs. volume of TBAB solution with CP/TBAB ratio of 5 vol% at 274.65 K and 4.0 MPa.

Fig. 8 shows the CO₂ content change in the hydrate phase vs. the amount of the 0.29 mol% TBAB solution with the CP/TBAB ratio of 5 vol% at 274.65 K and the different pressures. As shown in Fig. 8, the CO₂ content in the hydrate phase decreases with the increase of the pressure at the fixed amount of the TBAB solution. It is due to the fact that H₂ can compete with CO₂ for the hydrate cage occupancy with the higher driving force [12], and thus this leads to the decrease of the CO₂ content in the hydrate phase. The similar phenomenon and explanation can also be found elsewhere [1]. It can be also seen from Fig. 8 that the CO₂ content in the hydrate slurry increases with the increase of the amount of TBAB solution, but the degree of the increase is quite small compared to the effect of the pressure. By the law of conservation of mass, the CO₂ content in the hydrate phase has to be high if it is low in the gas phase [19]. Thus, the reason for the change trend of the CO₂ content in the hydrate slurry phase with the amount of TBAB solution is the same as that explained for Fig. 7. It is noted from Fig. 8 that the CO₂ mole concentration in the decomposed gas from the hydrate phase reaches approximately 93 mol% after the first-stage separation at 274.65 K and 2.5 MPa. It illustrates that the process provided in this work can be a promising one for separating CO₂ from IGCC syngas in the future.

3.3. CO₂ separation efficiency

The separation efficiency can be determined by the CO₂ recovery or split fraction (S.Fr.) and CO₂ separation factor (S.F.), which can be obtained according to the following equations [20].

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2}^{\text{Feed}}} \quad (2)$$

$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} n_{\text{H}_2}^{\text{gas}}}{n_{\text{H}_2}^{\text{H}} n_{\text{CO}_2}^{\text{gas}}} \quad (3)$$

where $n_{\text{CO}_2}^{\text{Feed}}$, $n_{\text{CO}_2}^{\text{H}}$, $n_{\text{CO}_2}^{\text{gas}}$, are the moles of CO₂ in the feed gas, hydrate phase and gas phase, respectively, and $n_{\text{H}_2}^{\text{H}}$, $n_{\text{H}_2}^{\text{gas}}$ are the moles of H₂ in the hydrate phase and gas phase, respectively.

The values of the CO₂ recovery fractions (S.Fr.) and separation factors (S.F.) for all 25 experimental runs can be calculated from Eqs. (1)–(3), based on the experimental data. The results are shown in Table 1. It is found from Table 1 that the values of the CO₂ recovery (S.Fr.) and separation factor (S.F.) for run 9 are optimum at the conditions of the volume ratio of CP/TBAB of 5 vol%, volume of TBAB

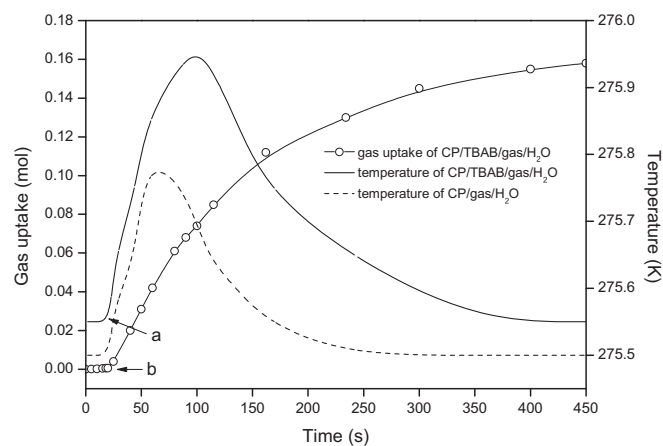


Fig. 10. Changes of the temperature and gas uptake for the hydrate formation over time from 180 ml TBAB solution with CP/TBAB ratio of 5 vol% and 180 ml water with CP at 274.65 K and 4.0 MPa.

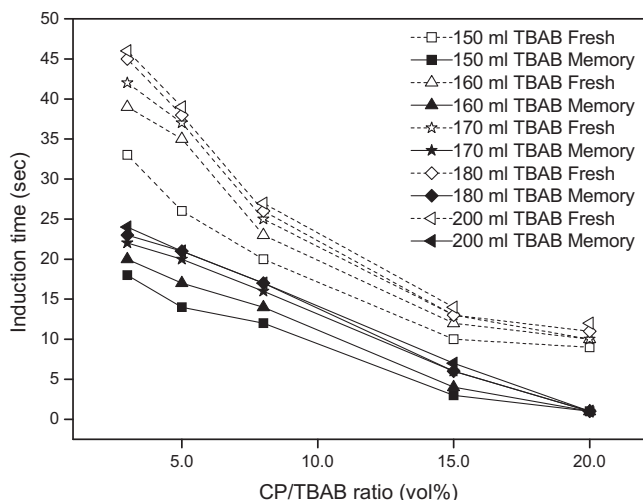


Fig. 11. Induction time change for hydrate formation from the systems with the fresh and the memory TBAB solution vs. CP/TBAB ratio with different volumes of TBAB solution at 274.65 K and 4.0 MPa.

solution of 180 ml, 274.65 K and 4.0 MPa. As a typical example, Fig. 9 shows the curves of the S.F.r. and S.F. for CO₂ vs. the amount of 0.29 mol% TBAB solution with the CP/TBAB ratio of 5 vol% at 274.65 K and 4.0 MPa after the first-stage separation. Both the S.F.r. and S.F. increase with the increase of the amount of the 0.29 mol% TBAB solution and they reach the maximum values, 0.58 and 30.61, respectively, when the amount of TBAB solution is 180 ml. However, when the amount of the TBAB solution exceeds 180 ml, the S.F.r. has a remarkable reduction and the S.F. has little change.

In addition, the optimum results for the S.F.r. and S.F. in the work are compared with those determined by Kumar et al. [10] at the similar condition. In the work of Kumar et al. [10], they are 0.47 and 27.84, respectively, after the first-stage separation with C₃H₈ as a promoter at 273.7 K and 3.8 MPa. Therefore, it is found that the separation efficiency in this work is relatively better than that given by Kumar et al. [10]. Meanwhile, the above results indicate that for the purpose of obtaining an optimum process of the hydrate-based pre-combustion CO₂ capture in an IGCC plant, it is necessary to find out the one appropriate ratio of the volume of the TBAB solution to the volume of the CR. In this work, the 0.29 mol% TBAB solution of 180 ml with the CP/TBAB ratio of 5 vol% loaded in the CR of 336 ml is the optimum. According to the theory of scaling up [21], it means the volume ratio of TBAB solution/CR of approximately 0.54 may be the suitable ratio for the potential industrial application.

3.4. Induction time

As mentioned in the section “Procedure”, the induction time can be determined by the abrupt points of the gas uptake and temperature curves in the process of the hydrate formation.

Fig. 3(b) shows the gas uptake profiles for the three systems, CP/gas/H₂O, TBAB/gas/H₂O, CP/TBAB/gas/H₂O, at 274.65 K and 4.0 MPa. The induction time for the above three systems is 15, 160 and 19 s, respectively. Therefore, it can be found from the above results that the addition of CP can efficiently shorten the induction time of the hydrate formation for the CP/TBAB/gas/H₂O system, and remarkably enhance the gas uptake.

Fig. 10 gives the typical curves of the temperature and gas uptake changes for the hydrate formation over time from the 180 ml TBAB solution with the CP/TBAB ratio of 5 vol% and the 180 ml water with the CP at 274.65 K and 4.0 MPa. For the CP/TBAB/gas/H₂O mixture, there may be at least 2 different hydrate (the CP hydrate and the gas hydrate involving in the CP and TBAB, at least including the gas hydrate containing the TBAB) forming at the certain experimental condition, and thus resulting in the temperature rise on account of the heat released by their individual hydrate formation. As seen from Fig. 10, the temperature abrupt point (point a) for the CP/TBAB/gas/H₂O system is at the 15th second. The time is in agreement with that for the CP/gas/H₂O system. On the other hand, it can be also seen from Fig. 10 that the abrupt point (point b) of the gas uptake curve is at the 19th second. Therefore, it can be identified from the above analysis that the CP hydrate firstly forms, and then the gas hydrate involving in the CP and TBAB forms in the process of the hydrate formation. As seen from Figs. 2 and 3, the gas uptake for the hydrate formation from the CP/gas/H₂O system is quite low. Thus, it can be determined that the induction time for the formation of the gas hydrate involving in the CP and TBAB is 19 s, as shown from the abrupt points of the gas uptake curves in Figs. 3(b) and 10. In addition, it is found that the temperature rises immediately after nucleation due to the hydrate formation is an exothermic process. The temperature reaches a high level and then gradually drops to the surrounding temperature because the temperature controller brings the temperature back to the set point value. The similar phenomenon is also observed in other experimental runs.

Fig. 11 and Table 2 show the induction time of the hydrate formation from the systems with the fresh and memory 0.29 mol% TBAB solution with the various CP/TBAB ratios at 4.0 MPa and 274.65 K. The induction time with the memory TBAB solution is much smaller than that with the fresh TBAB solution and the phenomenon has been explained elsewhere [22,23]. Additionally, the induction time decreases with the increase of the amount of the CP at the fixed amount of the TBAB solution. This illustrates that the

Table 2

Experimental conditions along with measured induction time at 274.65 K and 4.0 MPa.

CP/TBAB ratio (vol%)	Sample	P_{exp} (MPa)	Induction time (s)				
			150 ml TBAB	160 ml TBAB	170 ml TBAB	180 ml TBAB	200 ml TBAB
3	Fresh	4.0	33	39	42	45	46
	Memory	4.0	18	20	22	23	24
5	Fresh	4.0	26	35	37	38	39
	Memory	4.0	12	17	18	19	21
8	Fresh	4.0	20	23	25	26	27
	Memory	4.0	12	14	16	16	17
15	Fresh	4.0	10	12	13	13	14
	Memory	4.0	3	4	6	6	7
20	Fresh	4.0	9	10	10	11	12
	Memory	4.0	<1	<1	<1	<1	<1

Table 3

Comparison of measured induction time in this work with that in other work.

System	Temperature (K)	Sample	Driving force (MPa)	P_{exp} (MPa)	Induction time (min)	Source
CO ₂ /H ₂ /H ₂ O	273.7 K	Fresh	3.4	8.5	5.0	[1]
		Memory	3.4	8.5	3.7	
		Fresh	2.4	7.5	7.7	
		Memory	2.4	7.5	5.3	
CO ₂ /H ₂ /C ₃ H ₈ /H ₂ O Gas phase: 3.2 mol% C ₃ H ₈	273.7 K	Fresh	2.7	4.8	11.0	[10]
		Memory	2.7	4.8	5.0	
		Fresh	1.7	3.8	31.0	
		Memory	1.7	3.8	28.3	
CO ₂ /H ₂ /THF/H ₂ O Solution phase: 1.0 mol% THF	279.6 K	Fresh	0.89	3.14	25	[5]
		Memory	0.89	3.14	6.6	
		Fresh	1.87	4.12	10	
		Memory	1.87	4.12	3.3	
CO ₂ /H ₂ /TBAB/H ₂ O Solution phase: 0.29 mol% TBAB	278.15 K	Fresh		2.5	13.4	[13]
		Memory		2.5	5.8	
CO ₂ /H ₂ /TBAB/CP/H ₂ O Solution phase: 0.29 mol% TBAB CP/TBAB ratio: 5 vol%	276.65 K	Fresh		4.0	0.87	This work
		Memory		4.0	0.27	
		Fresh		3.5	0.92	
		Memory		3.5	0.35	

addition of the CP promotes the nucleation of gas hydrate containing the TBAB and the nucleation rate increases with the amount of CP. The explanation of the reason is not too clear, and it may due to the fact that the CP hydrate crystals, which firstly form, catalyze the gas going to the TBAB solution, and furthermore enhance the degree of the gas super-saturation, resulting in the increase of the nucleation rate. It can be also seen from Fig. 11 that decreasing the amount of TBAB solution leads to the decrease of the induction time at the fixed CP/TBAB ratio.

In addition, it is interestingly noted that the induction time with memory water is even lower than 1 s when the CP/TBAB ratio is 20 vol%. It means that the gas hydrate containing the TBAB can be formed instantaneously with the CP/TBAB ratio of 20 vol%. However, it is at the cost of the increase of the CO₂ concentration in the gas phase, as shown in Figs. 5 and 7.

The comparisons of the induction time at the moderate conditions obtained from the different studies are showed in Table 3 [1,5,10,13]. As given in Table 3, the induction time in this work is much smaller than those in other work [1,5,10,13]. For example, compared to the previous results [1,10,24], the induction time from the system of either the fresh or memory 0.29 mol% TBAB solution

with the CP/TBAB ratio of 5 vol% is reduced by at least 10 times at the temperature ranges from 273.7 K to 279.6 K and pressure ranges from 3.14 MPa to 8.5 MPa. Accordingly, it is expected that the system with the TBAB solution of 0.29 mol% as well as the CP/TBAB ratio of 5 vol% can be the one potential choice for the hydrate-based CO₂ separation from IGCC plants.

3.5. Hydrate formation rate

Figs. 12 and 13 show the changes of the gas uptakes in the processes of the hydrate formation at the different temperatures and different pressures, respectively. As shown in Fig. 12, the amount of gas consumed and the gas uptake rate increase with the drop of the temperature. It is because the lower temperature leads to the higher driving force for the hydrate formation. The same behavior can be also found by Zhong et al. [25]. As seen in Fig. 13, the amount of gas consumed and the gas uptake rate also increase with the pressure. This is also attributed to the fact that the higher pressure results in the higher driving force for the hydrate formation. However, it is found from Figs. 12 and 13 that the degree of the effect of the pressure on the amount of gas consumed and the gas uptake rate is not significant, compared with the temperature. In

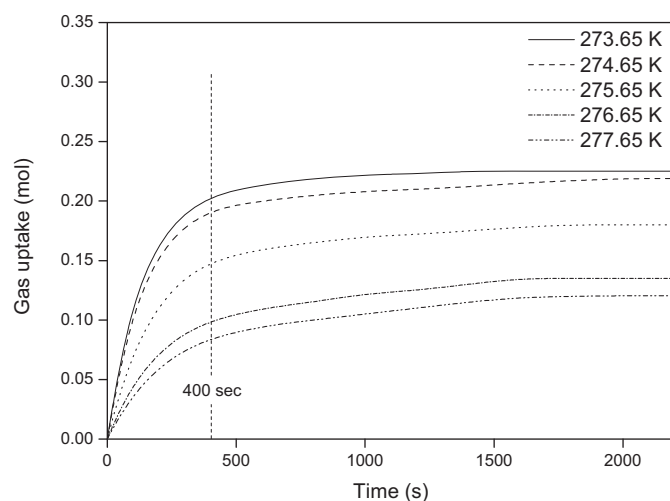


Fig. 12. Gas uptake changes with time in 180 ml TBAB solution with CP/TBAB ratio of 5 vol% at 4.0 MPa and different temperatures.

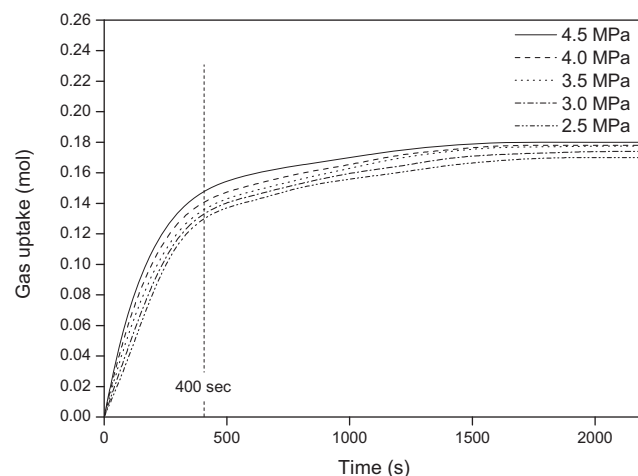


Fig. 13. Gas uptake changes with time in 180 ml TBAB solution with CP/TBAB ratio of 5 vol% at 275.65 K and different pressures.

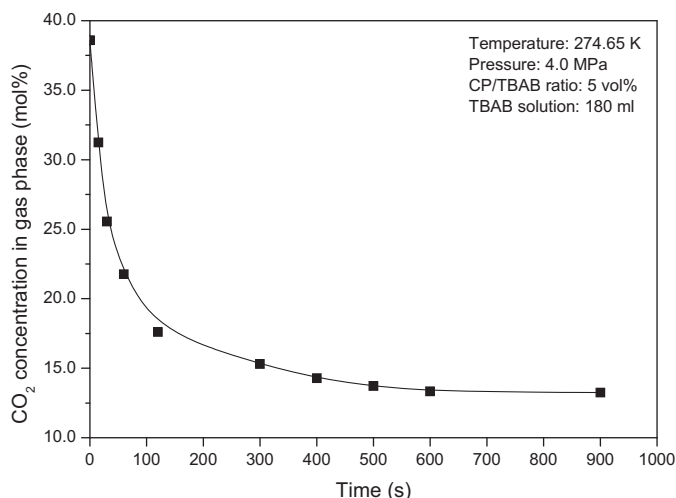


Fig. 14. Change of CO₂ concentration in the gas phase with time at 274.65 K and 4.0 MPa.

addition, it can be also seen from Figs. 12 and 13 that more than 80% of the total amount of gas consumed are obtained within 400 s. For example, the 84% of the total amount of gas consumed are obtained within 400 s at 274.65 K and 4.0 MPa. It means that most of the gas uptakes can be achieved within a relative short time. Fig. 14 gives also a typical curve showing the change of the CO₂ concentration in the gas phase in the process of the hydrate formation at 274.65 K and 4.0 MPa. As shown in Fig. 14, the CO₂ concentration decreases rapidly in the period from 0 s to 115 s, then it decreases slowly. After 400 s, the decrease is quite small. It illustrates that the main process of hydrate formation occurs before 400 s, and this also means that the CO₂ separation process can be completed within a shorter time. Furthermore, this work lays a foundation for the CO₂ capture from the IGCC syngas in industry in the future.

4. Conclusion

The effects of the 0.29 mol% TBAB solution in conjunction with CP on the hydrate-based pre-combustion CO₂ separation are investigated by the measurements of the gas uptakes, CO₂ selectivity, CO₂ separation efficiencies, the induction time of the hydrate formation and the hydrate formation rates at the different conditions. The results illustrate that the addition of the CP into the pure water/gas system has little effect on the gas uptake, whereas the addition of the CP into the TBAB solution remarkably enhances the CO₂ separation and speeds up the hydrate nucleation rate. The volume of the TBAB has also an effect on the CO₂ separation and the induction time. The biggest gas uptake and the highest CO₂ separation efficiency are obtained at 274.65 K and 4.0 MPa when the CP/TBAB ratio is 5 vol% and the volume ratio of the TBAB solution/CR is 0.54. The gas uptake is at least 2 times compared to the other work at the similar conditions [1,5,10]. The maximum CO₂ mole concentration in the decomposed gas from the hydrate phase can reach approximately 93 mol% after the first-stage separation. The induction time reduces with the increase of the CP/TBAB ratio and the decrease of the amount of the TBAB solution. When the CP/TBAB ratio is 20 vol%, the induction time is less than 1 s. This means the hydrate can be formed instantaneously. Compared to the results obtained from the other studies, the induction time is shortened by at least 10 times at the similar conditions [1,5,10]. More than 80 mol% of the total gas uptake can be obtained after 400 s in the process of the separation. These results support the development of the continuous process for the recovery of CO₂ and H₂ from the fuel gas mixtures.

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Notation

The following symbols are used in this study:

- Δn = the gas uptake in the process of hydrate-based pre-combustion CO₂ capture;
- $n_{\text{CO}_2}^{\text{Feed}}$ = number of moles of CO₂ in feed gas mixture;
- $n_{\text{CO}_2}^{\text{H}}$ = number of moles of CO₂ in hydrate phase;
- $n_{\text{CO}_2}^{\text{gas}}$ = number of moles of CO₂ in gas phase;
- $n_{\text{H}_2}^{\text{H}}$ = number of moles of H₂ in hydrate phase;
- $n_{\text{H}_2}^{\text{gas}}$ = number of moles of H₂ in gas phase;
- P = pressures desired;
- V_{gas} = number of volume of gas phase;
- V_{SV} = number of volume of supplier vessel;
- z = compressibility factor;
- R = gas constant;
- T = temperatures desired.

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