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The impact of pressure and temperature on tetra-n-butyl ammonium bromide semi-clathrate process for carbon dioxide capture

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Abstract

The pre-combustion capture of CO₂ in an IGCC power plant employing the hydrate based gas separation (HBGS) process is a novel method currently receiving attention around the world. Tetra-n-butyl ammonium bromide (TBAB) is a promoter that has been shown to improve the efficiency of hydrate formation. In this study, the effect of temperature and pressure on 0.3 mol% TBAB solution is investigated. The induction time for the experiments conducted at 6.0 MPa and 274.8 K was found to be lower, while nucleation became increasingly random as temperature is increased and pressure is reduced. Total gas uptake and normalized rate of hydrate formation (NR_s) is also the highest for the experiments conducted at 6.0 MPa and 274.8 K. However, it was found that the hydrate phase CO₂ composition remains relatively constant at both reduced temperatures and pressures.

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1. Introduction

Gas hydrates are non-stoichiometric crystalline materials that form at a certain temperature and pressure in which water molecules encage gas molecules [1, 2]. High storage capacity and selective fractionation of gas molecules have led to several applications for gas hydrates in recent years [3-6]. Application of hydrate based gas separation (HBGS) process for the pre-combustion capture of CO₂ from an IGCC power plant is a novel and environmentally benign method [7-9]. In order to operate in the

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pressure range of fuel gas mixture (2-7 MPa) coming out of IGCC power plant, there is a need for a promoter to reduce the operating pressure [10-13].

Tetra-n-butyl ammonium bromide (TBAB) has been reported to be promising promoter for CO₂ capture [14-17]. TBAB form semi-clathrate hydrates at mild conditions of 1 atm and 284.2 K, and can trap small gas molecules at favorable temperatures and pressures [18-20]. Thermodynamically, the presence of TBAB significantly shifts the equilibrium to lower pressure for all systems at a given temperature. Several studies in the literature have reported that 0.3 mol% is the optimum TBAB concentration for enhanced kinetics [12, 14]. Recently, in our lab we systematically evaluated the effect of TBAB concentration on the efficiency of the clathrate process at a pressure simulating the pre-combustion stream. We found out that the TBAB concentrations above 1.0 mol% are inefficient for the clathrate process to capture carbon dioxide [15]. Concentrations above 1.0 mol% resulted in lower gas uptake, lower hydrate growth rates, and significantly reduced separation efficiency [15].

The objective of this study is thus to evaluate the effect of temperature and pressure on the semi-clathrate hydrate formation using a 0.3 mol% TBAB solution. This concentration was chosen also based on our recent study that found that it had the best performance for CO₂ capture with a fuel gas mixture based on total gas consumed and separation factor [15].

2. Experimental Section

The gas used was supplied by Soxal Private Limited and consisted of 40% Carbon Dioxide (CO₂) and 60% Hydrogen (H₂). TBAB from Alfa Aesar with a >98% certified purity was used. Distilled water prepared was used in the experiments. A detailed description of the experimental apparatus and the procedures is available in our previous work [15]. The mole balance calculation for the formation experiment is given in our previous work [15]. Accordingly, the normalized gas consumption (NG_i) in mol of gas/mol of water, Normalized rate (NR₅) in mole of gas/min/m³ of water and the separation factor defined by Linga et al. [7] were calculated.

3. Results and Discussion

All experiments were carried out with 0.3 mol% TBAB solution which was reported to be the optimum in our previous study [15]. In our previous study, we evaluated the performance of 0.3 mol% TBAB at 6 MPa and 279.2 K. In order to investigate the effect of pressure and temperature, we carried out experiments at 4.5 MPa and 279.2 K and 6.0 MPa and 274.8 K respectively. The driving force for these conditions were 3.6 and 5.9 MPa respectively. Figure 1 presents a comparison of the effect of different experimental temperatures and pressures on the induction time (a), total gas uptake (b), the normalized rate of hydrate formation (c) and hydrate phase CO₂ composition (d) of a 0.3 mol% TBAB solution. The experiments conducted with the greatest driving force (at 6.0 MPa and 274.8 K) have the shortest induction time (10.8±14.7 min) compared to the lower driving force experiments. Induction time increases as the driving force decreases, and the occurrence of nucleation becomes increasing random: two out of the nine experiments reported in Babu et al. [15] at 6.0 MPa and 279.2 K; and two out of four experiments conducted at 4.5 MPa and 279.2 K did not nucleate. As the driving force decreases this stochastic nature becomes more prominent, resulting in some experiments not nucleating even after 100 min. This is also evident in the extent of the error bars presented in Figure 1, as the variability increases with the decrease in the driving force. This will be an important parameter in the deployment of the hydrate process for a large scale application like carbon dioxide capture. The induction time needs to be kept as short as possible for practical implementation.

The total gas uptake is highest for the conditions with a highest driving force (6.0 MPa and 274.8 K) and decreases as driving force decreases. This suggests that for 0.3 mol% TBAB solutions, a greater driving force would result in a higher gas uptake. This was again not the case at higher concentrations of TBAB that were investigated in our prior study [15], possibly due to the catastrophic formation of TBAB semi-clathrate hydrates at higher concentrations that lead to the decreased gas uptake due to mass transfer limitations.

The normalized rate of hydrate growth for semi-clathrate hydrate formation over the first 5 minutes of nucleation is an important parameter that has to be considered during process design is presented in Figure 1(c). The normalized rate is highest for the experimental conditions with the greatest driving force (6.0 MPa and 274.8 K) and slowest for experimental conditions with the lowest driving force (4.5 MPa and 279.2 K). It is however noted that the standard deviation for the experiments conducted at 6.0 MPa and 274.8 K is very large, and hence the difference between the normalized rate of the 6.0 MPa and 279.2 K may not be statistically significant. Hydrate phase composition of CO₂ seems to be relatively unaffected by the experimental conditions ($\leq 6.0\%$), although its composition seems to be slightly lower for both conditions with higher and lower driving forces.

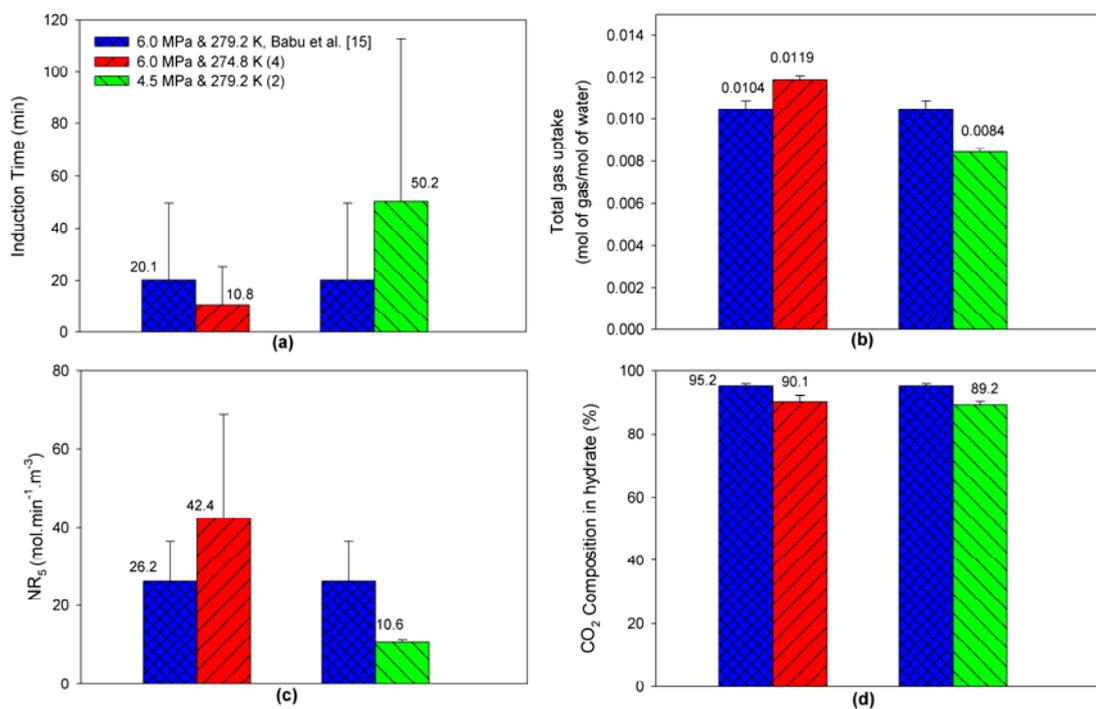


Figure 1. Effect of temperature and pressure on the (a) induction time, (b) total gas uptake, (c) normalized rate of hydrate formation over the first 5 min and on the (d) CO₂ composition in hydrate

4. Conclusions

In this study, the effect of temperature and pressure on semi-clathrate hydrate formation in a 0.3 mol% TBAB solution was investigated. Decreasing experimental temperature from 279.2 to 274.8 K at 6.0 MPa was found to reduce the induction time and increase both the total gas consumption and normalized rate of hydrate formation due to the increase in driving force. On the other hand, decreasing

the experimental pressure from 6.0 to 4.5 MPa at 279.2 K resulted in an increase in induction time and a decrease in both total gas consumption and normalized rate that is attributed to the decrease in driving force. The hydrate phase CO₂ composition was found to decrease very slightly at both lower temperatures and pressures, which could possibly be due to the reduced solubility of CO₂ at these conditions.

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Biography:

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