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Technical Note

Investigation of Hydrate Formation Conditions of Simulated Flue Gas in TBAB Solution with Potential Application in CO_2 Capture in Steel Industry

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ABSTRACT

The rising amount of CO_2 in the atmosphere is one of the most urgent environmental issues of our age. In order to reduce anthropogenic CO_2 emissions, carbon capture and storage (CCS) can be applied to large point sources like steel-making plants; In recent years, the new approach of hydrate-based CO_2 capture (HBCC) from flue gas has attracted considerable attention. Information on the hydrate equilibrium conditions of flue gas is the prerequisite for this method. In this study, semi-clathrate hydrate equilibrium conditions for the simulated flue gas (CO_2-N_2 mixture) in TBAB solution, as a good promoter for HBCC, were modeled in the temperature range of 281-288.1 K. The CO_2 concentration in the gas mixture was varied in the range of 15-40 mol%, and the TBAB concentration was varied in the range of 5-10 wt.%. The results clearly showed the promoting effect of TBAB on the hydrate equilibrium conditions. The modelling results showed good agreement with experimental data, with an average absolute percentage deviation of 9.5. Also, the model had better accuracy at lower CO_2 concentrations.

1. Introduction

Carbon dioxide is an important greenhouse gas that is thought to be a major contributor to the worsening of the climate situation due to global warming. The pressing need to cut CO_2 emissions across all sectors has become a crucial factor in reaching net zero emissions (NZE) by 2050, with the goal of limiting global warming to 1.5°C [1].

The iron and steel industry, being the most CO_2-emission-intensive sector among various industries, accounts for 29.7% of total industry-related CO_2 emissions and contributes around 6-7% of global CO_2 emissions. On a global scale, crude steel production has experienced significant growth over the past few decades and is projected to continue rising steadily, with an expected increase of more than one-third by 2050. In the iron and steel industry, flue gases are released at various stages of production, such as power generation (in power plants), sintering, coke production, and hot metal production. The CO_2 concentration in the flue gases from these different processes varies significantly, ranging from 4.8% to 27.3%. These variations are due to differences in the technologies used, the type of fuels consumed, and the operational conditions at each production stage. Overall, these gases represent a major source of carbon emissions in the steel industry, and reducing the CO_2 concentration in them is a critical challenge for achieving carbon reduction goals in this sector [1].

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In the past few decades, the iron and steel industry has achieved a 60% reduction in its energy consumption intensity. It is estimated that the potential for further improvement in energy efficiency within the iron and steel industry is limited to about 15–20%. This indicates that solely focusing on enhancing energy efficiency will not result in significant reductions in CO_2 emissions [2]. Therefore, it is essential to effectively implement CO_2 capture processes in the iron and steel industry to achieve significant emissions reductions. Among the available options, post-combustion capture, which does not require extensive retrofitting, emerges as the most suitable and practical solution for existing plants, allowing them to reduce their carbon emissions without the need for major infrastructure changes.

Over the past 50 years, large point sources, such as power plants and industrial facilities, have implemented a range of conventional CO_2 capture and storage (CCS) technologies. Despite their widespread use, recent analyses have revealed that these technologies significantly increase the energy consumption of power plants by 25-40%. This increase is largely attributed to the capture phase, which alone can account for up to two-thirds of the total cost of implementing CCS [3]. Therefore, use of new CCS technologies are needed to decrease both the overall cost as well as the environmental impact of traditional CCS absorbers and absorbers. Recently, hydrate-based CO_2 capture (HBCC) has attracted much attention as a low-cost strategy.

Clathrate hydrates are distinctive crystalline compounds that are created when small guest molecules become encapsulated within a three-dimensional network of hydrogen-bonded water molecules, resulting in a stable, ice-like structure. The formation of these compounds is determined by a delicate balance of temperature and pressure conditions, which are not fixed but instead vary widely based on the unique physical and chemical properties of the guest molecule, including its size, shape, and intermolecular interactions with the water lattice. Due to the significantly higher thermodynamic stability of CO_2 hydrates compared to the hydrates of other common industrial emission gases such as nitrogen (N_2), oxygen (O_2), and carbon monoxide (CO), carbon dioxide is more easily and preferentially trapped within solid hydrate structures. This characteristic makes CO_2 the dominant component in hydrate formation processes under favorable conditions. So, the gas phase will be contained a higher concentration of other compounds, and consequently CO_2 separation can occur effectively [4]. The requirement for high pressure and low temperature is the major challenge of this technology, which increases costs and decreases the rate of CO_2 separation.

To address this issue, the use of semi-clathrate hydrates (SCH) as an alternative to normal clathrate hydrates could offer a viable solution. Semi-clathrate hydrates are a group of organic compounds that can integrate into the hydrate lattice structure. Unlike traditional clathrate hydrates, SCH has the potential to form under atmospheric pressure and at relatively higher temperatures, making them more feasible under less stringent conditions. In this context, tetra-butyl ammonium halides have attracted a lot of attention due to their favorable thermodynamic properties [5]. Among these salts, tetra-butyl ammonium bromide (TBAB) has been identified as an environmentally friendly additive that not only reduces energy consumption but also enhances the formation of CO_2 hydrates. Its use in hydrate formation processes helps improve efficiency and promoting the capture and storage of carbon dioxide.

To assess the feasibility of the HBCC process, a comprehensive study must be conducted from both thermodynamic and kinetic perspectives. This analysis will provide insights into the process's efficiency, stability, and overall viability under various conditions. Currently, there is a noticeable lack of phase equilibrium data for the semi-clathrate of TBAB, which hinders a full understanding of its behavior and potential applications. Hence, in this research, the equilibrium conditions of TBAB semi-clathrate in various concentrations were obtained using a thermodynamic model.

2. Thermodynamic Modeling

As mentioned earlier, flue gas can contain small amounts of O_2 or CO in addition to N_2 and CO_2. Experiments studies have shown that the equilibrium conditions of single O_2 and CO hydrate formation are very close to N_2 [6, 7]. This suggests that, in the context of hydrate formation, flue gas can be effectively treated as a binary mixture consisting primarily of CO_2 and N_2, simplifying the analysis and modeling of the process.

In TBAB semi-clathrate hydrate structures, cages are created by the physical interaction of bromide ions and water molecules connected by hydrogen bonds. In a TBAB semi-clathrate hydrate unit cell, the structure consists of 4 large cavities and 3 small cavities, and it is assumed that TBA^+ cations are housed within large cages (two tetrakaidecahedral and two pentakaidecahedral cages), whereas the remaining dodecahedral small cages are filled with smaller gas molecules. The ionization of TBAB produces bromide and TBA^+ ions [8].

According to Chen and Guo [9], the fugacity of TBAB in aqueous phase (f_M^L) and in the hydrate phase (f_M^H) are equal at equilibrium conditions.

$$f_M^L = f_M^H \qquad \text{Eq. (1)}$$

where the subscript M refers to TBAB.

2.1. Calculation of Fugacity of TBAB in Hydrate Phase

According to the two-step formation mechanism proposed by Chen and Guo [9], the following equations proposed by Liao et al. [8] were used for calculation of TBAB fugacity in hydrate phase:

$$f_M^H = f_{M,0}^H(1-\theta)^{3/4} \quad \text{Eq. (2)}$$

Here, θ represents the fraction of linked small cavities that are occupied by gas molecules of CO_2 or N_2, which was determined using Langmuir correlations reported in the literature [8]. $f_{M,0}^H$ is also the fugacity of TBAB required to form hydrates without former gases occupying small cavities. Chen and Guo [9] proposed that $f_{M,0}^H$ is the product of three variables, each of them describes the contribution of T, P, and a_w, respectively.

$$f_{M,0}^H = f(P)f(T)f(a_w) \quad \text{Eq. (3)}$$

Where f(P) is considered as follow:

$$f(P) = \exp\left(\frac{\beta P}{T}\right) \quad \text{Eq. (4)}$$

Here, β can be considered as a constant, with a value of 3.5 K/bar for TBAB.

$$f(T) = exp\left(-\frac{\sum A_{Mj}\theta_j}{T}\right)A'\exp(\frac{B'}{T-C'}) \quad \text{Eq. (5)}$$

the Antoine constants, A' and B', C' and the corrected coefficients (A_{Mj}) between TBAB and small gas molecules were determined based on the hydrate formation data obtained from systems involving pure gases and TBAB aqueous solutions with different weight fractions [9].

$f(a_w)$ was also determined using the following equation:

$$f(a_w) = a_w^{-1/\lambda_2} \quad \text{Eq. (6)}$$

where λ_2 is equal to 4/38 for TBAB. The water activity (a_w) in the TBAB aqueous solution was determined based on the data provided by Lindenbaum and Boyd [10], along with values reported by Amado and Blanco [11].

$$a_w = \exp(-0.03321{w_M}^2 - 0.09463w_M - 2.5874\times10^{-4}) \quad \text{Eq. (7)}$$

Where, w_M denotes the weight fraction of TBAB in the solution.

2.2. Calculation of Fugacity of TBAB in the Aqueous Solution

The fugacity of TBAB in the aqueous phase was determined using Eq. (7):

$$f_M^L = x_M\gamma_M P_M^{sat,L}\emptyset_M^{sat,L}exp\left[\frac{v_M^L(P-P_M^{sat,L})}{RT}\right] \quad \text{Eq. (8)}$$

where x_M, γ_M, and $P_M^{sat,L}$ represent the mole fraction of TBAB in the aqueous phase, activity coefficient of TBAB, and TBAB vapor pressure, respectively [4]. The molar volume (v_M^L) of the TBAB aqueous solution was estimated through the empirical correlation developed by Sohnel and Novotny [12].

$$v_M^L = 1/(\rho_w + B_1(100w_M) + B_2(100w_M)^2 + B_3(100w_M)^3) \quad \text{Eq. (9)}$$

Where:

$$B_i = q_i + r_iT + s_iT^2 \quad \text{Eq. (10)}$$

The values of the parameters q_i, r_i, and s_i can be found elsewhere [12].

The activity coefficient of the TBAB salt was calculated using the proposed correlation by Eslamimanesh [4] as follows:

$$\gamma_M = -0.5050{w_M}^3 + 1.1603{w_M}^2 - 1.3689w_M + 0.7655 \quad \text{Eq. (11)}$$

Where w_M is weight fraction of the TBAB in aqueous solution.

3. Results

The experimental equilibrium data points of TBAB semi-clathrate hydrate of CO_2/N_2 gas mixture were collected from literature [5, 13-16].

Table 1. shows a summary of the temperature range, pressure, gas composition and TBAB salt concentrations used in these references. The accuracy of the model was examined using Eq. (12) which calculates the relative average deviation percentage of predicted equilibrium pressure (RADP%) for TBAB semi-clathrate compare to the experimental values.

$$AAD\% = \frac{1}{NP}\sum_{i=1}^{NP}|(\frac{P_{exp}-P_{cal}}{P_{exp}})|\times 100 \quad \text{Eq. (12)}$$

Fig. 1. illustrates the comparison between predicted and experimental equilibrium pressures. As can be seen from the figure, the modeling results are in good agreements with the experimental data. Also, the minimum, maximum and the mean of RADP% were equal to

0.05, 26, and 9.5, respectively. According to the results, the deviation of the model and experimental data increases with the increase of CO_2 concentration.

The results also show that by increasing the CO_2 concentration in the feed gas or increasing the TBAB salt concentration in the range of 5-10 wt.%, the semi-clathrate equilibrium pressure is reduced.

Fig. 2. shows the effect of TBAB salt on the equilibrium conditions of hydrate formation in a 0.15 mol% CO_2 - 0.85 mol% N_2 gas mixture in pure water and a 10 wt.% TBAB solution. As it is clear from the figure, the presence of TBAB shifts the equilibrium curve to the right, or in other words, it causes the gas hydrate to form at lower pressures and higher temperatures.

Table 1. The summary of experimental equilibrium conditions of TBAB + CO_2/N_2 gas mixture semi-clathrate reported in the literature.

Authors	CO_2 mol%	TBAB wt.%	T (K)	P (MPa)
Meysel et al. (2011) [13]	0.2	0.05,0.10	281.75-286.99	3-5.85
Mohammadi et al. (2012) [14]	0.15, 0.399	0.05	282.6-285.6	2.06-8.75
Belandria et al. (2012) [15]	0.15, 0.399	0.05	282.4-286.2	2.93-7.67
Sfaxi et al. (2014) [5]	0.15, 0.30	0.05,0.09	281-288.1	1.9-7.79
Tzirakis et al. (2016) [16]	0.15	0.05-0.1	281.45-287.97	2.31-7.21

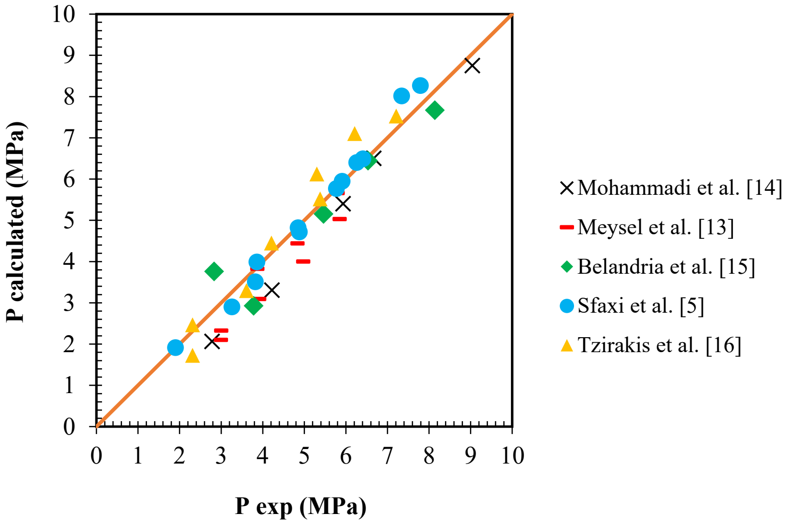

Fig. 1. Comparison of predicted hydrate equilibrium pressure and experimental equilibrium pressures of TBAB semi-clathrate hydrate of CO_2/N_2 mixtures in different TBAB concentrations.

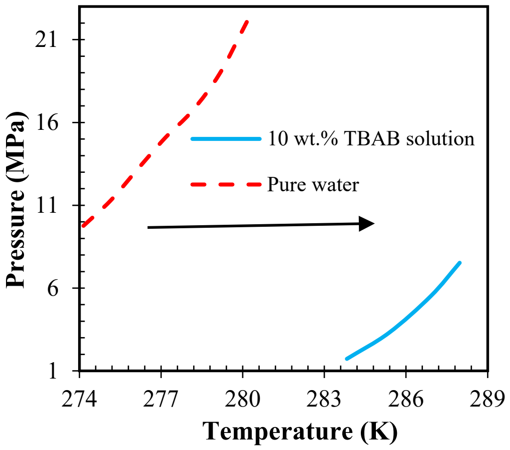

Fig. 2. Three-phase (H−L−V) equilibrium conditions for 0.15 mol% CO_2 - 0.85 mol% N_2 gas mixture in pure water and 10 wt.% TBAB salt solution, predicted using the model.

4. Conclusions

Phase equilibrium conditions of TBAB semi-clathrate in the presence of simulated flue gas (CO_2/N_2 gas mixture) were obtained using a thermodynamic model. Modelling was conducted at different concentration of CO_2 and TBAB salt. Modelling results showed good agreements with experimental data reported in the literature, achieving a mean RADP of 9.5%. The results also indicated that TBAB can be a good thermodynamic promoter for HBCC.

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