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Semi-clathratic impact of tetrabutylammonium hydroxide on the carbon dioxide hydrates

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Abstract. In the present experimental study, the phase behaviour of Tetrabutylammonium hydroxide (TBAOH) on Carbon dioxide (CO\textsubscript{2}) hydrates is evaluated via the T-cycle method. All the experiments performed in high-pressure hydrate reactor for various concentrations of TBAOH (1, 5 and 10 wt\%) at moderate pressure and temperature ranges of 2.0-4.50 MPa and 276.0-285.0 K, respectively. The hydrate dissociation enthalpy (\(\Delta H_{\text{diss}}\)) is also calculated for all the studied systems via Clausius Clapeyron equation. Results revealed that the TBAOH able to shift the hydrate liquid vapour equilibrium (HL\textsubscript{w}VE) curve towards higher temperature and lower pressure regions hence provide the promotional impact on all the studied concentrations. 10 wt\% TBAOH able to heighten hydrate promotional impact (\(\Delta T\)) up to 1.15 K. Additionally, enthalpy (\(\Delta H_{\text{diss}}\)) data revealed that the promotional impact of TBAOH attributed due to the semi-clathratic nature of TBAOH. Thus, it can be concluded that the studied TBAOH in the present work has the immense potential for the industrial applications like natural gas separation and gas storage.

1. Introduction

Gas hydrates are non-stoichiometric crystal-like inclusion compounds formed under thermodynamically favourable conditions and stabilized via hydrogen bonding network of water. In gas hydrates, the water molecules are acted as host molecule while smaller molecules gases like methane (CH\textsubscript{4}), ethane (C\textsubscript{2}H\textsubscript{6}), Carbon dioxide (CO\textsubscript{2}) and others are entrapped (as a guest molecule) within the hydrate structures. Usually, there are three types of hydrate structures are often found which known as structure I (sI), structure II (sII) and structure H (sH) hydrates [1]. The type of hydrate structure mainly depends upon the presence of guest molecules together with thermodynamic condition accounted for hydrate formation.

Earlier, gas hydrate often saw as a perennial problem in flow assurance. The mitigation of gas hydrates accounted for almost 70 percent of all the flow assurance problems which leads towards the spending of 100s of Million dollars ($) without any permanent solutions [2]. Therefore, much research on gas hydrates focused on mitigation of gas hydrate via conventional [3] and unconventional inhibitors [2,4–6]. The conventional thermodynamic hydrate inhibitors include alcohols like methanol, ethylene...
glycol together with conventional salts for instance sodium chloride (NaCl) and potassium chloride (KCl) [7]. The unconventional inhibitors include various novel chemicals that possess relatively superior environmentally friendly properties especially lower vapour pressure. The prime examples are amino acids [4] and ionic liquids [4,8–10].

Recently, researchers receiving more attraction on developing novel hydrate based technologies, applicable to the energy and environmental fields. Since hydrate formation is the tedious process, which involves high pressure, low temperature alongside lower rate of hydrate formations that causes hindrances for their potential applications. Therefore, for the numerous applications of gas hydrates, thermodynamic gas hydrate promoters (THP) are inserted to decrease the equilibrium hydrate formation pressure and to increase the hydrate formation temperatures [11]. Shahnazar and Hasan [12] intensely reviewed the formation studies of gas hydrate promoters to evaluate the emergence of the novel applications of gas hydrate. Energy recovery, gas separation gas storage and transportation alongside seawater desalination are the potentials applications which triggered gas hydrate to be in the continual research during recent years.

Ammonium based hydrate promoters take up an essential part of the formation of clathrate and semi-clathrate hydrate, for instance, tetra-n-alkyl ammonium salts formed some unusual hydrate structures even at atmospheric pressure. Contrasting from clathrate hydrates where water atoms form hydrate cages, and small guest molecules like CH₄ or CO₂ entrapped inside the hydrate lattice structure. In semi-clathrate hydrates, the anion of halide uproots the water particle in the system, shaping Hydrogen bond with water molecules, then the tetra-n-alkylammonium cation also participated in hydrate crystalline structure [13].

Initially, Karimi et al. [14] thermodynamically evaluated the tetrabutylammonium hydroxide (TBAOH) as hydrogen (H₂) hydrate promoter for the storage of hydrogen gas. Results revealed that TBAOH could shift HLₜVE boundary towards higher temperature and pressure regions around 0-40 MPa pressures. They further reported that the promotional impact of TBAOH found to be pressure dependent as the pressure increased the promotional impact also found higher due to more hydrate enthalpation. Similar hydrate promotional behaviour was also observed by the Su et al. [15] with CH₄ gas. TBAOH was able to promote CH₄ hydrate at higher-pressure conditions (4.46–16.05 MPa).

Previously, Nashed et al. [16] reported the physical-chemical properties of TBAOH; they further reported that in the presence of the TBAOH, the gas uptake of CO₂ gas significantly enhanced compared to deionized water. Recently, Khan et al. [17,18], evaluated the impact of alkyl chain on the AILs and reported that TBAOH able to promote hydrate formation in CO₂ and CH₄ enrich hydrate systems.

Therefore, the focus of this study is to report the impact of TBAOH on the HLₜVE boundaries of CO₂ hydrates at different concentrations (1, 5 and 10 wt%) for the first time. The experiments are performed at the moderate pressure and temperature range of 277 K-286 K and 2.0 MPa - 4.5 K respectively. The average hydrate promotional temperature (∆T) values of all the studied systems are also reported. The Clausius Clapeyron equation is employed to determine the enthalpy of hydrate dissociation (∆Hₜ₅₀) for all the studied systems. Also, an attempt is also made to define the hydrate promotional mechanism of TBAOH in the presence of CO₂ hydrates.

2. Methodology

2.1. Materials
The table 1 provide the details of the materials used in this work. The all chemicals are employed without any further purification. The gravimetrically analytical balance is used for all the sample preparations.

2.2. Details of the Experimental Apparatus and Method
The high-pressure hydrate reactor is used in this study. The details of the experimental setup and methods can be found elsewhere [19,20]. The HLₜVE data of pure CO₂ + H₂O and CO₂ + TBAOH + H₂O hydrate systems are measured via the isochoric T-cycle with step heating method. The complete details of the experimental method can also be found in others places [1,4,21,22].
Table 1. Materials used for this gas hydrates study.

| No | Chemical Name            | Symbol | Purity          | Chemical Structure |
|----|--------------------------|--------|-----------------|--------------------|
| 1  | Carbon dioxide           | CO₂    | 99.95 mole %    | O=C=O              |
| 2  | Water                    | H₂O    | Deionized       |                    |
| 3  | Tetrabutylammonium hydroxide | TBAOH | 40 wt% aqueous solution | ![Chemical Structure](image) |

2.3. HLwVE data and Enthalpy (ΔH_{diss}) Analysis

In this study, the average promotional temperature (ΔT) is calculated via Equation 1 determined by Xia and co-workers [23].

\[
\Delta T = \frac{1}{n} \sum_{i=1}^{n} \left( T_{0,p_i} - T_{1,p_i} \right)
\]

where, \( T_{0,p_i} \) and \( T_{1,p_i} \) represents the hydrate equilibrium temperatures of CO₂ gas for deionized water and an aqueous solution of TBAOH respectively. The values of both dissociation temperatures attained at the uniform pressure \( p_i \), and \( n \) denotes the number of considered pressure points. The dissociation enthalpies (ΔH_{diss}), of gas hydrates, are obtained through the Clausius Clapeyron equation (see Equation 2) which also used in preceding studies [4,24–26].

\[
\frac{\partial \ln P}{\partial \frac{1}{T}} = -\frac{\Delta H_{diss}}{R}
\]

where \( T \) and \( P \) are the equilibrium temperature and pressure, \( R \) denotes the universal gas constant, \( z \) represents the compressibility factor of CO₂ gas (calculated via Peng Robinson Equation of state), and \( \Delta H_{diss} \) represents the enthalpy of CO₂ hydrates for all the studied systems.

3. Results and Discussions

The experimental characterization and analysis of CO₂ hydrate in the presence of TBAOH is presented in this section.

3.1. HLwVE Analysis of CO₂+TBAOH+H₂O hydrates

As mentioned afores very inadequate data offered on the thermodynamic promotional impact of ILs on CO₂ hydrate systems[5]; most of the system dealt with hydrate inhibition impacts [5,27]. The phase behaviour of the various concentrations (1, 5 and 10 wt%) of CO₂ + TBAOH + H₂O system is presented in figure 1.

The acquired results expose that all the studied concentrations of TBAOH can enhance the CO₂ hydrate equilibrium curves to a higher temperature and lower pressure regions, which reveals the thermodynamic promotional impact. It can be evident from the results that the hydrate promotional influence is composition-dependent. As the quantity of TBAOH increasing from 1 – 10 wt%, the promotional impact is also increased (see figure 1). The prior ILs studies revealed that shorter alkyl chain ILs (like TMAOH, TMACl, TEAOH, TEAI and TPrAOH) were performed as hydrate inhibitors [20,21,24]. The hydrate promotional behaviour of TBAOH is observed perhaps attributed due to the longer chain of AIL. It should be noted that this promotional impact might cause due to the
semiclathratic nature of TBAOH, which is evaluated in next section (see section 3.2). For further quantifying the hydrate promotional impact, the $\Delta T$ values of different concentrations of TBAOH are depicted in figure 2. For different concentrations of CO$_2$ + TBAOH + H$_2$O systems; 1 wt% showed the very less $\Delta T$ value of 0.04 K, while higher concentrations of 5 and 10 wt% are found to be enhanced the $\Delta T$ values up to 0.37 K and 1.15 K, respectively.

Figure 1. HL$_w$VE data for 1 wt%, 5 wt% and 10 wt% concentrations of TBAOH.

![Figure 1](image1.jpg)

Figure 2. Average promotional temperature ($\Delta T$) for different concentrations (1, 5 and 10 wt%) of CO$_2$ + TBAOH + H$_2$O systems.

![Figure 2](image2.jpg)

3.2. Enthalpy of dissociation ($\Delta H_{diss}$) of CO$_2$+TBAOH+H$_2$O hydrates

To investigate the semi-clathratric influence of TBAOH on the cage occupancy, the Clausius Clapeyron equation is used to calculate the $\Delta H_{diss}$ of CO$_2$ hydrates in the presence and absence of TBAOH. The calculated $\Delta H_{diss}$ of CO$_2$+TBAOH + H$_2$O systems are presented in table 2.

The average $\Delta H_{diss}$ of H$_2$O + CO$_2$ is 64.73 kJ/mol lies within the range of CO$_2$ hydrate enthalpy data which means structure I hydrate formed [3]. Referring to the table 2, it can be observed that the enthalpies of all the studied TBAOH + CO$_2$ + H$_2$O systems appear very different to the pure CO$_2$ hydrate. This behaviour proposes that the presence of TBAOH have a substantial impact on the $\Delta H_{diss}$ of the system and therefore participate in the CO$_2$ hydrate structure and cages occupancy. Hence, semiclathrate impact of TBAOH found on CO$_2$ hydrate structure which is in line with the preliminary data.
The enthalpy results further rationalize the promotional influence of TBAOH, which predominantly comes owing to higher alkyl chain together with its semi-clathrate effect. The probable mechanism of semi-clathrate nature of TBAOH further underpinning via the structural representation of TBAOH as observed in figure 3.

Table 2. Calculated molar enthalpies of hydrate dissociation, $\Delta H_{diss}$ (kJ/mol) of CO$_2$ hydrate in the presence of CO$_2$ + TBAOH + H$_2$O solutions

| Pressure (MPa) | TBAOH concentration in the solution |
|---------------|-------------------------------------|
|               | 0 wt%  | 1 wt%  | 5 wt%  | 10 wt% |
| 4.0           | 57.481 | 59.664 | 62.538 | 63.648 |
| 3.5           | 61.071 | 63.647 | 66.521 | 68.078 |
| 3.0           | 65.052 | 66.807 | 70.390 | 71.842 |
| 2.5           | 67.655 | 70.527 | 74.226 | 75.516 |
| 2.0           | 72.435 | 74.575 | 77.902 | 79.131 |
| Overall       | 64.739 | 67.044 | 70.315 | 71.643 |

Figure 3. The graphical representation of TBAOH molecule in the semi-clathrate structure.

4. Conclusions
In this work, the HL$_w$VE measurement for CO$_2$ + TBAOH + H$_2$O is reported for different concentrations (1, 5 and 10 wt%). The attained results revealed that the occurrence of TBAOH increases the HL$_w$VE phase boundary towards higher temperature and lower pressure regions. The promotional impact of TBAOH seems to be concentration dependent since 10 wt% can shift the $\Delta F$ value up to 1.15K. The hydrate promotional impact of TBAOH found perhaps attributed due to the presence of large cation (TBA$^+$) which induce semi-cathartic behaviour. Furthermore, the molar enthalpies of dissociation for the CO$_2$ + TBAOH + H$_2$O hydrate systems suggested that TBAOH actively participated in the hydrate crystalline structure and its impacts on the hydrate promotion caused due to its semi-clathrate nature. Therefore, the outcome of this study would highlight the importance of TBAOH for designing the hydrate based technological applications such as hydrate-based desalination of saline water, storage of natural gas and designing of separation processes for gas phase separations.

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