Experimental Evaluation of a Novel Thermodynamic Inhibitor for CH₄ and CO₂ Hydrates

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Abstract

In natural gas transmission and processing, gas hydrate formation is a major flow assurance challenge which led scientists towards conducting new and more detailed studies on different aspects of gas hydrates inhibitors. Ionic liquids (IL) recently revealed as novel hydrate inhibitors due to their unique properties like electrostatic charges together with ability to form hydrogen bonding with water molecule lead them viable research area in the field of gas hydrate mitigation. This paper highlighted the experimental evaluation of thermodynamic measurements of tetra methyl ammonium hydroxide (TMAOH) for Methane (CH₄) and Carbon Dioxide (CO₂) gas hydrates. TMAOH belongs to ammonium based ionic liquids (AILs) which is comparatively economical ILs among the other ILs families. Traditional T-cycle technique with isochoric step heating method was adopted for determining thermodynamic inhibition in this work. Results reveal that TMAOH effectively shift the hydrate equilibrium curve to upper pressure and lesser temperature regions for CH₄ + TMAOH + water system and CO₂ + TMAOH + water system. The average reduced temperature obtained for CH₄ + TMAOH + water system is around 1.06 °C while for CO₂ + TMAOH + water system, the inhibition effect found to be around 2.09 °C. Therefore, this study provides roadmap for superior alternative for the development of novel thermodynamic hydrate inhibitor, which can efficiently control the gas hydrate formation.

Keywords: CH₄ Hydrate; CO₂ Hydrate; Hydrate Inhibitor; Ionic Liquids; TMAOH; THI
1. Introduction

Gas hydrates are ice-like crystalline structure formed by hydrogen bonded water molecules, in presence of suitable gas particles grasping inside polyhedral cavities. The few key constituents, for example, gas molecule (visitors), water particles (hosts), and appropriate conditions including high pressure/low temperature are vital conditions for formation of gas hydrate [1]–[3].

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
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<tbody>
<tr>
<td>AIL</td>
<td>Ammonium based Ionic liquid</td>
</tr>
<tr>
<td>BMIM-Cl</td>
<td>Butyl methyl imidazolium chloride</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>MEG</td>
<td>Monoethylene Glycol</td>
</tr>
<tr>
<td>THI</td>
<td>Thermodynamic hydrate inhibitor</td>
</tr>
<tr>
<td>TMACI</td>
<td>Tetra Methyl Ammonium Chloride</td>
</tr>
<tr>
<td>TMAOH</td>
<td>Tetra Methyl Ammonium Hydroxide</td>
</tr>
<tr>
<td>THI</td>
<td>Thermodynamic Hydrate Inhibitor</td>
</tr>
</tbody>
</table>

In oil and gas industry, one of foremost impediment faced in flow assurance is the formation of gas hydrate in pipelines, which can caused the blockage of during the production, transportation, and processing of hydrocarbons. Gas hydrate formation may perhaps lead to disastrous economic damages besides inordinate ecological risks. Hydrates also arise in the drilling fluids that are used in deep offshore drilling operations could lead to severe threats towards the operational safety. Hydrate formation issues are frequently encountered in deeper oceans like Gulf of Mexico, North Sea, Caspian Sea and permafrost regions like Alaska. Annually, oil and gas industry spends approximately US$1 million per mile on insulation of subsea pipelines and further hunderand of million dollars on other conventional approach to prevent hydrates in the pipeline. This problem costs the industry billions of dollars to mitigate annually with no permanent solution in focus. Inititally Hammer Schmidt (1934) has found the hydrate blockage problem in the gas pipeline and since then extensive research activities are being performed to find better and effective mitigation solutions especially chemical inhibitors [4]. There are four conventional methods employed in oil and gas industry for preventing gas hydrate, which are (i) heating (ii) depressurization (iii) dehydration and (iv) chemical inhibitors [5]–[8].

Ionic Liquids (ILs) have a strong potential to work as dual function gas hydrate inhibitors, since the compounds which exhibit hydrogen bonding can effectively act as gas hydrate inhibitors. ILs must be hydrophilic or hygroscopic in nature. Since hydrophobic material reside in a separate phase from water, therefore unable to access water molecules. Second, special functional groups such as oxygen or hydroxyl groups need to be introduced in the IL structure since they would create intermolecular hydrogen bonding with the hydroxyl groups of water molecules, leading to disrupting the great number of hydrogen bonds between water molecules, thus effectively preventing hydrate formation. ILs are used as thermodynamic and LDHIs inhibitors for methane and CO₂ hydrate formation [5], [6]. Xiao & Adhirama [6] initiated the research of ILs as gas hydrate inhibitors in 2009, experimentered for Imidazolium based ILs and found better results for both THI and KHI inhibition. They found that ionic liquids could show thermodynamic inhibition; and at the same time delay hydrate formation by slowing down the hydrate nucleation rate. This dual function was endorsed to their strong electrostatic charges and hydrogen bond with water. This means that ionic liquids work as both thermodynamic and kinetic inhibitor. Xiao et al. [7] further reported that imidazolium-based ILs having halides as anion showed significant dual function performance as the kinetic and thermodynamic inhibitors on the methane hydrate formation. Their effects on the shift in equilibrium curve and induction time of CH₄ hydrate formation were measured in a high-pressure DSC. Their study revealed that ILs must have strong electrolyte charges and capable of hydrogen bonding with the water molecule which causes the shift in H–L–V equilibrium conditions to a lower temperature at a given pressure and also slow down the hydrate nucleation...
growth rates. In another article, they extended the study to six dialkylimidazolium halide ILs and among all [EMIM]-Cl is the most effective thermodynamic inhibitor from their study [7].

Li et al., [8] studied the inhibition effect of dialkylimidazolium and tetra alkyl AILs Inhibition on the methane hydrate formation. An isochoric method was used to evaluate the data within the pressure range of 3.0 to 17.0 MPa and temperature range of 276.15 to 289.15K. Comparative analysis of the investigated ILs showed that [N1,1,1,1][Cl] displayed the most effective THI effect. Their study was further extended on the influence of hydroxyl functional group and alkyl chain substitution of the studied ILs for understanding the inhibition effect on methane hydrate formation, and showed that ILs having shorter alkyl chain length are better inhibitors for the methane hydrate formation. Further, ILs showed increased inhibition performance for hydroxyl functional group present in dialkylimidazolium based ILs and decreased inhibition performance for the case of tetra alkyl AILs, respectively [8]. Keshavarz et al., [9] evaluate the tetraethyl-ammonium chloride (10 wt%), 1-butyl-3-methylimidazolium dicyanamide (10 wt%) and 1-butyl-3-methylimidazolium tetrafluoroborate (10, 15 and 20 wt%) within the pressure and temperature ranges of 2.48–6.58 MPa and 272.1–282 K respectively, using an isochoric method. All of their investigated ILs exhibited THI capabilities.

Preceding studies emphasized that the materials, which possesses substantial electrostatic charges or having tendency to farm higher hydrogen with water commonly more prevent the gas hydrate formation. It can be concluded from the most of the previously researches; better inhibition can be attains from ILs which are hydrophilic in nature along-with anion group which possess the tendency to form hydrogen bonding with water molecules. This present work initiated the study on the new class of AILs based inhibitor (TMAOH) which are comparatively easy to synthesize, significantly cheaper in cost accompanied by enhanced environmental properties compare to their counterpart Imidazolium based ILs [10]. TMAOH poses these advantages, therefore, this study will provide better alternative for the development of novel hydrate inhibitor, which can efficiently control the hydrate formation as thermodynamic inhibitor.

2. Methodology

2.1. Materials

The details of materials used for gas hydrate mitigation study are presented in Table 1. RO membrane TKA-LabTowe plant was used for deionized water and purified with r from Thermo Scientific with resistivity of 18 MΩ for produced deionized water. Both gases, de-ionized water and TMAOH were employed without any further purification in all experiments. Gravimetric method was employed an accurate measurements of aqueous solutions through analytical balance (AND) (uncertainty in grams: ±0.0001 g). For evaluation of AIL effectiveness as THI inhibitor 10wt% of TMAOH is used throughout in this study for CH₄ and CO₂ gas hydrates.

<table>
<thead>
<tr>
<th>No</th>
<th>Symbol</th>
<th>Chemical Name</th>
<th>Purity</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>Methane</td>
<td>CH₄</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Tetramethylammonium hydroxide</td>
<td>TMAOH</td>
<td>99.95 %</td>
</tr>
</tbody>
</table>
2.2. Equipment

In this work, high pressure stainless steel cell, contrived by Dixson FA engineering Sdn. Bhd. is employed for the formation/dissociation measurement of the gas hydrate as used by Partoon et al., for their study [11]. Figure 1 represents the detailed schematic diagram of the experimental setup. The apparatus consists of high pressure equilibrium cell with volumetric capacity of 500 cm$^3$, with temperature ranges from (253 – 523) K with maximum operating pressure of 20 MPa. Conditions such as temperature, volume and pressure are recorded for every subsequent sec with an accuracy of ±0.1K, ±0.001 cm$^3$ and ±0.01 MPa respectively. Furthermore, the apparatus is fitted with magnetic motor to provide adequate mixing of sample under test conditions.

![Figure 1. Schematic diagram of Experimental setup.](image)

2.3. Procedure

A well renowned T-cycle technique with isochoric step heating method was employed in this work [12]. Prior to experiments cell was thoroughly washed with distilled water, then put 100 ml liquid phase sample has filled with or without TMAOH. Now, the cell was inserted and let the system to cool it down until desired operating condition. Small amount of gas inserted in the cell then vacuumed to ensure there is no traces of the air remains in the cell. Once the desired temperature condition achieved, then pressurized gas charged into the cell according to desired pressure. In this experiments, pressure range for CH$_4$ gas hydrate was selected from 3.5-8.0 Mpa pressure while pressure range for CO$_2$ Gas hydrate ranges from 2.0-4.0 MPa pressure. Once the temperature-pressure conditions stabilized, the mechanical stirrer was set at 300 rpm. Then the temperature of the system was slowly condensed step-wise for a rate of 0.01 K/min. The span of each step usually varies from 2 to 6 hours. Hydrate formation was observed both visually through sapphire window along with sudden pressure drops observed in the data. Once the hydrate is fully formed with no further pressure drop observed, then the cell was heated slowly for complete dissociation of gas hydrate.
3. Results and Discussion

3.1. Thermodynamic Analysis of CH₄ & CO₂ Gas Hydrate

In thermodynamic testing of methane hydrate equilibrium data was achieved and plot the pressure vs temperature relation. H-Lw-V data shown in Figure 2 reflect that cooling line initially meeting with the heating line which also considered as H-Lw-V equilibrium point at point E (282.5 K and 6.45 MPa). Figure 2 further highlighted the different states existing during the various parts of the H-Lw-V curve of CH₄ hydrate. Initially at A position only gas vapors and liquid water exists while cooling the system continually, system enters into B state where hydrate nucleation is started and considered as metastable zone where condition are favorable to hydrate formation. Sudden pressure drop observed (from 274 K at 6.26 MPa) reflect the stating of hydrate nucleation along with complete hydrate formation from point C to point D (272.5 K at 5.6 MPa). Point C and D possess three phases vapor, Hydrate, and liquid water which make sure complete formation of hydrate. After that again step hating is performed in order to dissociate hydrate slowly, increase in pressure shown the dissociation curve until point E where no further increase in pressure was observed. Point E is also have vapor, liquid and nucleation at the same time. Finally point F achieved after further heating for ensuring the complete dissociation of hydrate. The temperature differences among point E to D considered as degree of sub cooling, as sub cooling temperature higher there is more chance of hydrate formation. Furthermore, degree of sub cooling is also withdrawn from this graph is around 10.2 K due to complete hydrate formation around 272 K. Similar, method is correspondingly adopted for CO₂ gas hydrate alongside presence of TMAOH.

![Figure 2. H-Lw-V Equilibrium Curve for Pure CH₄ gas hydrate at 6.5 MPa Pressure](image)

3.2. H-L-V Equilibrium Curve Measurement

1. H-L-V Equilibrium Curve of CH₄ Hydrate

Ever since this study is for preliminary evaluation of newly design apparatus for gas hydrate thermodynamic and kinetic studies. Equilibrium data collected and compared with the existing literature data for CH₄ hydrate. Figure 3 shows the calibration data which revealed that the values lie within the range of hydrate. For instance it’s stated earlier that Figure 3 refers to the numerous chronological work done on CH₄ hydrates. Besides this data also
approaching in line with the preceding efforts therefore it can be said that the apparatus is ready for further experiments.

2. H-L-V Equilibrium Curve of CO₂ Hydrate

For reliability of the data, Equilibrium data for CO₂ also collected and compared with the existing literature data for CO₂ gas hydrate. Figure 4 revealed that the values of pure CO₂ hydrates satisfactory lies within the range of chronological work done on CO₄ hydrates in available literature. Besides this data also approaching in line with the preceding efforts therefore it can be said that the apparatus is ready for further experiments.

![Figure 3. Comparison of H-Lw-V equilibrium data for Pure CH₄ Hydrate from Literature Data [13]–[16].](image)

![Figure 4. Comparison of H-Lw-V equilibrium data for Pure CO₂ Hydrate from literature data [17]–[19].](image)

### 3.3. Influence of TMAOH on H-L-V Equilibrium Curve as THI inhibitor for CH₄ & CO₂

Previously, although there are a number of ILs tested for gas hydrate mitigation; mostly based on imidazolium-based ILs, very few ILs based on other cations like phosphonium, pyrrolidinium or Ammonium based ILs [20]. In order to record inhibition influence of TMAOH on CH₄ hydrate, H-LV Equilibrium temperature for pure gas
without TMAOH was measured at three different pressure points within the range (3.5-6.5) MPa. Subsequently, for pure CO\(_2\) hydrates same procedure was adopted at five different pressure points within the range (2-4) MPa. The effectiveness of TMAOH as THI evaluated by investigating the temperature shift towards the lower temperature and higher pressure regions at the above mentioned conditions.

The Hydrate- Liquid- Vapor (H-Lw-V) equilibrium data of CH\(_4\) + TMAOH + water system (Figure 5) revealed that the AIL, TMAOH has significantly reduce H-Lw-V equilibrium temperature by shifting the Equilibrium curves headed for lower temperature and higher pressure regions. Figure 5 similarly indicate that at higher pressure conditions the inhibition effect enhanced significantly. This behavior is also reported by the Qazi et al. in their study for mix gas hydrate [21]. For instance, at 6.5, 50 and 35 MPa pressures, the reduction in reduced temperatures between pure CH\(_4\) +water and CH\(_4\) + TMAOH + water system are 1.56, 0.92 and 0.70 °C, respectively. The overall average reduced temperature accomplished by the CH\(_4\) + TMAOH + water system in this study is 1.062 °C which is quite acceptable value for ILs perspective.

Figure 6 illustrate the Hydrate- Liquid- Vapor (H-Lw-V) equilibrium data of CO\(_2\) + TMAOH + water system. Data also revealed that TMAOH has expressively reduce H-Lw-V Equilibrium curve by significantly shift the equilibrium curves headed for lower temperature and higher pressure regions. Shin et al. [22], recently reported the BMIM-Cl as best IL inhibitor for CO\(_2\) gas hydrate, by reducing hydrate formation temperature around 1.65-1.75 °C at higher pressure range of 5-20 MPa. The average reduction temperature was observed as 2.09 °C in this study which is quite higher for 10 wt. % concentration of ILs [20]. Furthermore, at 2, 2.5, 3, 3.4 and 4 MPa pressures, the reduction between pure CO\(_2\) +water and CO\(_2\) + TMAOH + water system are 1.84, 2.15, 2.46, 2.32 and 1.69 °C respectively. The possible reason of strong TMAOH inhibition is the possible hydrogen bond formation tendency of TMAOH with water molecules in a form of -OH functional group, significantly increases the non-ideality of the system [9]. Tariq et al.[20], discussed the inhibition influence of OH-based anion which easily integrated with the hydrogen bonding of water molecule. TMAOH also contain shortest alkyl chain (methyl) which also provide adequate linkage at the surface of gas and water interface, consequently making the gas hydrate formation difficult [20]. Additional important reason for possible inhibition through TMAOH is their influence over activity coefficient of water in aqueous solution, which unswervingly disturbs the hydrate phase boundary.

![Figure 5. H-Lw-V equilibrium data of CH\(_4\) + TMAOH + water](image-url)
4. Conclusion

In this work, initially H-Lw-V equilibrium data of pure methane and carbon dioxide were measured along with the thermodynamic characterization. Obtained result were compared against literature data for pure CH$_4$ and CO$_2$ hydrate, and found acceptable agreement for existing literature H-L-W-V data. Additionally, Hydrate- Liquid-Vapor (H-Lw-V) Equilibrium data of CH$_4$ + TMAOH + water system along with H-Lw-V Equilibrium data of CO$_2$ + TMAOH + water system were measured thermodynamically. Results revealed that, presence of TMAOH decreased the hydrate phase boundary of CH$_4$ + TMAOH + water system to approximately 1 °C. While inhibition effect is also even more evident for CO$_2$ + TMAOH + water system around 2.09 °C. Therefore, it is highly recommended that to prolong this work for cage occupancy analysis together with kinetic study; which could lead to innovation of novel AILs, possible replacement for conventional THI inhibitor.

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References


