

Influence of Ammonium based Compounds for Gas Hydrate Mitigation: A Short Review

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Abstract

Objectives: In natural gas transmission pipelines hydrate formation is major flow assurance challenge. This communication presents as brief review focuses on the potentially applicable area of Ammonium based compounds (ACs) as gas hydrate inhibition. **Methods/Statistical Analysis:** For avoiding gas hydrate formation, oil and gas industry spent millions of dollar annually without any permanent solution. In most of the cases insertion of chemicals (inhibitor) established as the utmost supreme route for gas hydrate mitigation. Quantary ammonium salts had widely been applied as commercial hydrate inhibitors. Ammonium based Ionic Liquids (AILs) also recently applies as work as potential gas hydrate inhibitor for hydrate mitigation. **Findings:** The systematic review on ACs proves that higher concentration of ACs provides more effective thermodynamic inhibition. The alkyl chain length of ACs plays an important part, as the chain length increases it decrease their effectiveness as inhibitors. Usually, imidazolium based ILs employed as gas hydrate inhibitors contains fluorinated anions which categorized as toxic compound. ACs holds the strong tendency to act as the dual function chemical inhibitor for possible replacement of widely used imidazolium based ILs due to their cheaper source, easy synthesis along with fairly better environmentally friendly nature. **Application/Improvements:** This study will highlight the recent advancements achieved in the field of ACs, highlighting the vigorous prospects of ACs as potential gas hydrate inhibitors and provide the avenue to accomplish flow assurance problems caused due to gas hydrates

Keywords: Ammonium based Compounds (ACs), AIL, Gas Hydrate, Inhibitors, KHI, THI

1. Introduction

Gas hydrates or clathrate hydrates are the ice-like crystalline structure formed when hydrogen bonded water molecules encapsulated by suitable gas particles grasping inside polyhedral cavities and are stabilized by engaged guest molecules via Van der Waals forces¹⁻³. The few key constituents, for example, gas molecule (visitors), water particles (hosts), and appropriate conditions including low temperatures (275K - 285K) and high pressure (3-10MPa) are a vital parameter for the formation of gas hydrate^{4,5}. Dependent on presence of the appropriate size and type of guest molecules, different structures of gas hydrate can be formed. The types of cavities that are shaped along with the distribution of those cavities within

a unit cell are used to differentiate a different clathrate hydrate structures. At present, there are three common types of hydrate structures known and studied are: structure I (sI), structure II (sII) and structure H (sH) hydrates³. The range of the guest molecules is from 0.40 nm to 0.90 nm in diameter. sI encases small molecules from 0.4-0.55 nm; sII and sH accommodate larger molecule typically propane or iso-butane for sII or combination of methane gas and nexoheptane of cycloheptanas shown in Figure 1⁶⁻⁹.

1.1 Applications of Gas Hydrate Inhibitors in Flow Assurance of Oil and Gas industry

For oil and gas industry, one of foremost impediment faced in flow assurance is the formation of gas hydrate in

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pipelines, which can cause the blockage of the production of hydrocarbon, hindrances in transportation and processing of the oil and gas. Formation of gas hydrate may perhaps lead to catastrophic economic losses and ecological risks. Hydrate problems also arise in production sites due to the drilling fluids used in deep offshore operations could lead to severe threats for operational safety. Hydrate formation issues are frequently faced in deeper oceans like; Caspian Sea, North Sea, Gulf of Mexico, etc., and permafrost region like Alaska. Annually, oil and gas sector bears approximately 1 million US\$ per mile on the insulation of offshore pipelines and further hundred of million dollars on other conventional approach to prevent hydrates in the pipelines¹⁰. These hydrate problems cost oil and gas sector additional billions of dollars annually to mitigate hydrates particularly without any permanent solution. To avoid hydrates; there are four conventional methods employed in oil and gas industry for preventing gas hydrate, which are 1. Thermal heating 2. Depressurization 3. Dehydration and 4. Chemical inhibitors. Extensive research activities are being performed to find better and effective mitigation solutions to avoid hydrate formation especially from chemical inhibitors¹¹. Chemical inhibition involves addition of certain chemicals which avoid or delay gas hydrate plug formation. Therefore, under many circumstances, the use of inhibitors for gas hydrate inhibition is the only feasible and viable option¹²⁻¹⁵.

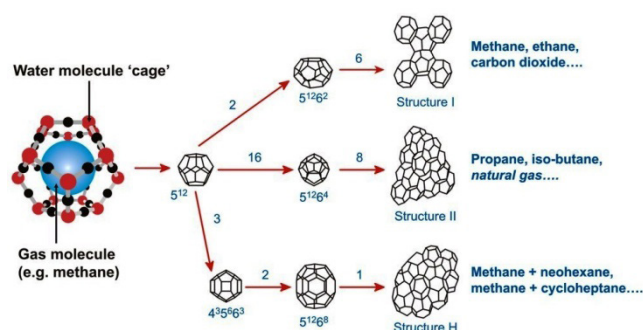


Figure 1. Common hydrate structures: sI, sII and sH⁽⁹⁾.

To mitigate hydrate complications, injection of inhibitors have been widely utilized as the highly efficient method¹². Based on their operating concentration, these inhibitors are classified into:

1. Thermodynamic Hydrate Inhibitors (THIs) 2. Low Dosage Hydrate Inhibitors (LDHI) which are classified to

1- Kinetic hydrate inhibitors (KHI), 2- Anti-Agglomerates (AA).

THIs shifting the Hydrate Liquid Vapour Equilibrium (HLVE) curve (hydrate stability/dissociation equilibrium towards the left side or low temperature and high pressure region. THIs applied in high concentrations such as 20-50wt% of water phase. Commercially, Sodium Chloride (NaCl), Methanol and Mono-Ethylene Glycol (MEG) are widely used THIs in oil and gas industry^{16,17}. LDHIs usually dosed at a very less concentration of 0.1-2.0wt % influenced by the water phase. The initial work on LDHIs was done by Russian Engineer named Kuliev in early 1970s by adding surfactants (alkylarylsulfonates) for avoiding gas hydrate problems in his wells¹⁵. Then in the mid of 1980s more researchers came and enhanced the LDHI research¹⁵. KHIs are water soluble light weight polymers which delayed the hydrate formation for acting as anti-nucleators. Industrially, Poly (vinylpyrrolidone) (PVP) and Polyvinylcaprolactam (PVCap) are commercially used as KHIs. AAs do not prevent hydrate formation instead these surface active molecules adhere to liquid and gas interface and keep disperse fine hydrate particles to become large agglomerate or plug. An AA allows hydrates to form as transportable non-stick or slippery slurry of fine particles easily dispersed in liquid phase. Mostly AAs are based on surfactant, common examples are Span 80, Span 60, Span 40, Span 20 and etc¹⁸.

Previous studies suggested that materials poses robust electrostatic charges or capability to form hydrogen bonds normally mitigate gas hydrates effectively^{19,20}. For instance, common THI like NaCl possess very strong electrostatic charges; Poly (Ethylene Oxide) (PEO), methanol, or KHI poly (N-vinylpyrrolidone) (PVP) are able to form effective hydrogen bonds with water. Grounded on this idea, more effective gas hydrate inhibitors need to be discovered in a form of Ionic Liquids (ILs) which possess both tendencies at a time^{21,22}.

1.2 Nature and Properties of Ammonium base Compounds

Industrially employed ACs commonly based on Quaternary Ammonium salts (quats) and Ionic Liquids (ILs) of Quaternary ammonium cation. Typical quats molecule encloses positively-charged nitrogen atom attached to four carbon atoms. ACs is considered as an economically beneficial class of industrial compounds.

They possess anti-microbial activity with efficient surface-active properties, and are recognized to be bioactive compounds used in fertilizer as well due to presence of quaternary ammonium group in their structure^{23,24}. Figure 2(a) shows the structure of quats molecule. AILs are composed of a poorly coordinating and large organic ammonium based cation combined with an organic or inorganic anion resulting as molten salt at room temperature. Figure 2(b) shown the structure of typical AIL molecule. Synthesis of AILs can easily be carried out from various tertiary amines and alkyl halides by ion exchange method or metathesis methods²⁵.

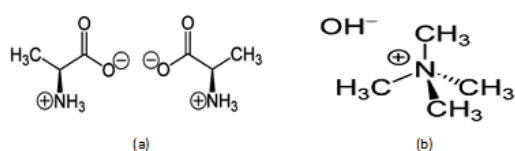


Figure 2. (a) Determine the structure of quats molecule Analine. (b) Determine the structure of Tetra methyl ammonium hydroxide (TMAOH).

2. Ammonium based Compounds (ACS) as Gas Hydrate Inhibitors

In 1980s Shell group initiated the research on quaternary ammonium surfactants as gas hydrate inhibitors which considered as ideal candidates as AAs due to their better particle dispersants in water. At comparatively low concentrations, the Quaternary ammonium salts (onium salts) inhibit the growth of hydrate crystals, therefore, suitable in LDHI formulations, and are able to prevent the growth of structure II (sII) hydrates and also used for prevention of plug formation^{18,26}. The detail functionality of ammonium based salts or Onium salts encompass hydrate-philic (hydrate liking for) headgroup and a hydrophobic tail. The headgroup (hydrate-philic), which based on the quaternary focus, stabto link with hydrate phase. The alkyl groups move in the larger cavities ($5^{12}6^4$) on the surface of hydrate phase and can even get to be fitted in the hydrate surface as it develops around the alkyl bunches^{15,27}. The extended hydrophobic tail evades the hydrate from on the surface, and also creates the surface further appealing towards the hydrocarbon phase. When AA atoms have appended to the surface, the molecule is able to scattered effectively in the hydrocarbon phase¹⁵.

ACs plays noteworthy part as synergists with other KHI inhibitors like PVP or PVCap polymers. Small amount of quaternary salts for example, Tetrabutylammonium Bromide (TBAB) have been utilized as a synergist for PVCap polymer for some years^{28,29}. TBAB is moreover efficiently works as synergist with Polyvinyl pyridine (PVP) as KHI inhibitor in industry²⁴. More biodegradable unique substitutes for TBAB with ester ties have also been asserted²⁴. TBAB is also a significant quaternary ammonium salt for the inhibition of THF hydrates crystal growth as well. Shorter alkyl chain, structures like quaternary ammonium zwitterionic particles, for instance, tributylammoniumpropylsulfonate have perfectly worked as synergists²⁴. The key component in all these quaternary particles is a quaternary nitrogen molecule with three or more pentyl or butyl groups. Their structures are related to the quaternary ammonium AA surfactants^{24,30}, finds that the compounds of tetra-n-alkyl ammonium are able to form hydrate crystals underneath surrounding temperature without applying high pressure. This recommends the particles possess longer ammonium alkyl chains have a solid tendency to facilitate the enclosed water atoms to form the clathrate-like structure in aqueous solutions^{21,30}. The researchers^{1,31}, determine the cationic tetra butyl ammonium or phosphonium ions and tetra pentyl ammonium ions are also performed as kinetic inhibitors by reducing the crystal growth of natural gas hydrate and have also been used as synergists for commercial KHIs¹. Thus, insertion of anion salts; such as TBAB or Tetra-Pentyl Ammonium Bromide (TPAB) with PVCAP significantly increased the KHI performance of the vinyl caprolactom polymer²⁶. It is noteworthy that, TBAB or TPAB alone showed no effect on inhibiting the nucleation of gas hydrates as described by elsewhere^{32,33}, studied the inhibition effect of dialkylimidazolium and tetra Alkyl Ammonium Ionic Liquids (AAILs) inhibition on the methane hydrate formation. An isochoric method was used to evaluate the data within the pressure range of 30 to 170 bars and temperature range of 276.15 to 289.15K. Comparative analysis provided by³³, also investigated different ILs families (IMILs/AILs) showed that $[N_{1,1,1,1}][Cl]$ displayed the most effective THI effect. Additionally, they extended their study to evaluate the influence of hydroxyl functional group $[OH^-]$ along with effect of alkyl chains substitution on methane (CH_4) hydrate formation. Results revealed that, ILs possess shorter alkyl chain length were performed better THI inhibitors for the CH_4 hydrate.

Furthermore, ILs showed different results with respect to IL family in presence of functional group [OH⁻]. For dialkylimidazolium based ILs, improved THI performance was observed while decreased inhibition value attained for tetra alkyl AILs in presence of [OH⁻] auxiliary group respectively³³. In³⁴, evaluate the tetraethyl-ammonium chloride (10wt %), 1-butyl-3-methylimidazolium dicyanamide (10wt %) and 1-butyl-3-methylimidazolium tetrafluoroborate (10, 15 and 20wt %) within the pressure and temperature ranges of 2.48-6.58MPa and 272.1–282K respectively, using an isochoric method. All the investigated ILs exhibited THI capabilities.

Recently³⁵, evaluated the five different structures of ammonium based ILs for determining dual functionality of the CH₄/AILs system (1 and 5 wt.%) at 40-120 bar pressures. All the ILs used; shown more thermodynamic inhibition at lower and moderate pressures (6<) for CH₄ hydrate. Tetramethyl Ammonium Acetate (TMAA) found to have maximum THI effect with ΔT 0.7-1.4 °C respectively. Additionally, some of the studied AILs (Ch-Oct, TMAA) were able to increase the induction time for hydrate formation. Moreover³⁶, used tetramethyl ammonium hydroxide (TMAOH) IL for THI inhibition of CH₄ and CO₂ gas hydrates. Results reveals that 10 wt. % TMAOH significantly reduce the hydrate equilibrium boundary for CO₂ is around 2.09 °C while inhibition influence have also evident on CH₄/TMAOH hydrate by reduction of ΔT around 1.53 °C³⁶.

Molecular dynamics simulations have been established to as influential technique to examine the solid/liquid interfaces at the molecular level. It offers valuable information about nucleation and growth mechanism of gas hydrates together with an understanding of the mechanism for LDHIs³⁷ in³⁸, analyzed the influence of quaternary ammonium zwitterions based inhibitor through molecular dynamics simulations approaches, results revealed that its activity was comparable with the PVP³⁹⁻⁴³.

ACs specially AILs also having a strong affinity to act as novel dual function chemical inhibitor for CH₄, CO₂ and mixture of CH₄/CO₂ clathrate hydrates to overcome earlier mentioned disadvantages and for preventing the gas hydrate formation in pipelines via strong hydrogen bonding network with water molecules^{20,36}. Since, these are comparatively more biodegradable, nontoxic to the sea organisms to their counter parts ILs^{44,45}. These advantages make them good candidates as inhibitors for assuring good flow in pipelines. Therefore, this study will

provide better alternative for the development of novel hydrate inhibitors, which can control the hydrate formation as thermodynamic along with kinetic gas inhibitors.

3. Conclusion

The higher concentration of ACs provides more effective thermodynamic inhibition by shifting the equilibrium curve towards lower temperatures and higher pressure regions. The length of the alkyl chain of ACs play the very vital part, increase the chain decrease their effectiveness as inhibitors. Imidazolium based compounds are applied mostly as gas hydrate inhibitors using fluorinated anions which are recognised as toxic, therefore, ACs are evaluated in this communication. ACs poses the strong tendency to act as novel dual function chemical inhibitor for possible replacement of widely used imidazolium based ILs due to their cheaper source, easy synthesis along with fairly better environmentally friendly nature. Recent studies also highlighted the effectiveness of AILs as dual functional gas hydrate inhibitors. From the literature survey of gas hydrate mitigation studies, it's obviously highlighted that ACs have the significant potential to influence the gas hydrate industry and more focus should be given towards AILs.

4. Acknowledgment

The authors would like to express their deep gratitude to Universiti Teknologi PETRONAS (UTP) for provided the laboratory facilities and financial support throughout the project.

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