



## Full Length Article

# Tetramethyl ammonium chloride as dual functional inhibitor for methane and carbon dioxide hydrates



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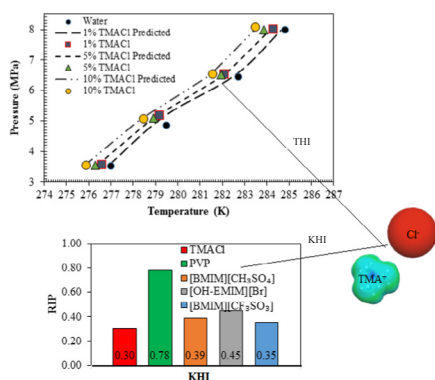
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## GRAPHICAL ABSTRACT



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## ABSTRACT

This experimental work evaluates the dual functional (thermodynamic and kinetic) behaviour of quaternary ammonium salt namely tetramethyl ammonium chloride (TMACl) for both methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) hydrates. The Hydrate Liquid Vapour Equilibrium (HL<sub>w</sub>VE) data for CH<sub>4</sub> and CO<sub>2</sub> are evaluated in the presence and absence of aqueous TMACl solutions (1, 5 and 10 wt%) through T-cycle method at different temperature and pressure conditions. The inhibition impact, i.e., average suppression temperature ( $\Delta T$ ) and Hydrate dissociation enthalpies ( $\Delta H_{diss}$ ) are also reported for the considered systems for both gases. The study is further extended to evaluate the formation kinetics of CH<sub>4</sub> and CO<sub>2</sub> hydrated in the presence and absence of aqueous TMACl systems. The impact of TMACl is reported via the induction time, the initial formation rate and a gas uptake at different subcooling temperatures for both gases. Furthermore, the kinetic inhibition performance of TMACl is also assessed via the relative inhibition performance (RIP) compared with literature systems for both CH<sub>4</sub> and CO<sub>2</sub> hydrates. Additionally, an electrolyte based thermodynamic model proposed by Dickens and Quinby-Hunt, (1997) is applied to predict the HL<sub>w</sub>VE temperatures of both gases (CH<sub>4</sub> and CO<sub>2</sub>) in the presence of TMACl. The obtained thermodynamic and kinetic results indicate that TMACl efficiently acts as a potential dual functional hydrate inhibitor for CH<sub>4</sub> and CO<sub>2</sub> gases. Therefore, the outcome of its efficacy, this study will envision the use of TMACl for both CH<sub>4</sub> and CO<sub>2</sub> hydrate systems and can potentially be applied in offshore flow assurance strategies.

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## Nomenclature

|                            |  |                           |  |
|----------------------------|--|---------------------------|--|
| $a_w$                      | Activity of water                              | $E_{Vdw}$                 | Van der wall energy                            |
| AIL                        | Ammonium based Ionic liquid                    | [EMMor][Br]               | N-ethyl-N-methyl morpholinium bromide          |
| AAs                        | Anti-agglomerates                              | [EMMor][BF <sub>4</sub> ] | N-ethyl-N-methylmorpholinium tetrafluoroborate |
| [BMIM]-[BF <sub>4</sub> ]  | 1-butyl-3-methyl imidazolium tetrafluoroborate | [EMPip][Br]               | N-ethyl-N-methyl piperidinium bromide          |
| [BMIM]-[Br]                | 1-butyl-3-methyl imidazolium chloride          | [EMPip][BF <sub>4</sub> ] | N-ethyl-N-methylpiperidinium tetrafluoroborate |
| [BMIM]-[Cl]                | 1-butyl-3-methyl imidazolium chloride          | $\Delta H_{diss}$         | dissociation enthalpies                        |
| [BMIM]-[HSO <sub>4</sub> ] | 1-butyl-3-methyl imidazolium hydrogen sulfate  | KHIs                      | kinetic hydrate inhibitors                     |
| Ch-But]                    | choline butyrate                               | LDHIs                     | Low dosage hydrate inhibitors                  |
| [Ch]-[iB]                  | choline iso-butyrate                           | PEO                       | Polyethylene oxide                             |
| [Ch]-Hex]                  | choline hexanoate                              | THI                       | Thermodynamic hydrate inhibitor                |
| [Ch]-[Oct]                 | choline octanoate                              | TMAAc                     | tetra-alkyl ammonium acetate                   |
| CH <sub>4</sub>            | Methane  | TMACl                     | Tetramethyl ammonium Chloride                  |
| CO <sub>2</sub>            | Carbon Dioxide                                 | TMAOH                     | Tetramethylammonium hydroxide                  |
| $E_{HB}$                   | Hydrogen bonding energy                        | TEAOH                     | Tetraethylammonium hydroxide                   |
| $E_{MF}$                   | Misfit energy                                  | TPrAOH                    | Tetrapropylammonium hydroxide                  |
| $E_T$                      | Total internal energy                          | $\Delta F$                | Average suppression temperature                |
|                            |  | $\Delta T$                | Suppression temperature                        |

## 1. Introduction

Gas or clathrate hydrates are well-defined as non-stoichiometric crystalline compounds that composed of hydrogen-bonded water molecules (host) and the trapped gas molecules (guest) and formed under thermodynamically feasible conditions (high-pressure 2.0–10.0 MPa and lower temperature 274.0–285.0 K [1]. Methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S), n-butane (n-C<sub>4</sub>H<sub>10</sub>) and iso-butane (i-C<sub>4</sub>H<sub>10</sub>) are amongst the common hydrate formers. Depending on the size and type of the guest molecule, three different hydrate structures are termed as cubical structure I (sI), cubical structure II (sII) and hexagonal structure H (sH) hydrates.

In flow assurance, gas hydrate formation appeared as leading impediment confronted in oil and gas pipelines that not only caused the obstruction of the hydrocarbon production but also hindered in transportation and processing phases as well [2,3]. Since the oil and gas production mainly operate in deep-sea regions (off-shore), therefore the hydrate formations are more favourable under low temperature and high-pressure conditions [4,5]. These conditions accompanied by undesired water transported in the pipelines impel to form gas hydrates that lead to disastrous economic losses and ecological risks. Oil and gas industry groans approximately 1 million US\$ per mile on insulation of off-shore pipelines annually and hundreds of million dollars further on various conventional approach to avoid hydrates in the pipeline [6].

Thermal heating; water removal; depressurization; and chemical insertion are the conventional methods that oil and gas industry apply to prevent the gas hydrate formation [7]. In most of the cases, chemical inhibition is the only feasible option remains for offshore gas pipelines [8,9]. There are three common types of chemical inhibitors used for gas hydrate mitigation namely Thermodynamic hydrate inhibitors (THIs); Anti agglomerates (AAs) and Kinetic Inhibitors (KHIs). THIs alter the hydrate phase equilibrium conditions of the system, hence able to shift equilibrium curves towards the lesser temperatures and higher-pressure regions. Instead of modifying the temperature and pressure conditions; KHIs delay the hydrate formation by interacting with the gas-water interface and provide steric hindrance among the water and gas. Since the petroleum industry applied THIs and KHIs separately, and it caused excessive load interims of cost and infrastructures mutually. For this reason, the focus is moving towards the compounds that can effectively behave as dual-functional inhibitors such as amino acids, quaternary ammonium salts (QAS) and ionic liquids (ILs) [10].

Room temperature ILs are ionic salts in the molten state; whereas QAS exist in the solid state at room temperature [11]. However, both types of compound possess the same ionic structure and behaviour [12,13]. The change in their physical states are attributed due to the presence of different anions, i.e., tetramethyl ammonium hydroxide (TMAOH) found in the liquid state whereas tetramethyl ammonium chloride (TMACl) occur in the solid state.

In 2009, Xiao & Adhirama [14] initiated the research on ILs as dual-functional gas hydrate inhibitors experimented with Imidazolium-based ILs and found better results for both KHI and THI inhibition. They discovered that studied ILs showed thermodynamic inhibition, and together they were able to delay the hydrate formation by slowing down the hydrate nucleation rate. The dual functionality of ILs is attributed due to their significant electrostatic charges and the ability to form hydrogen-bonding with water molecules [15–17]. Xiao et al. [18], further reported that some of the imidazolium-based ILs exhibited notable dual function inhibition performance as the kinetic and thermodynamic inhibitors of the CH<sub>4</sub> hydrates. Only a few numbers of researchers deal with THI of other ILs like ammonium, pyrrolidinium or phosphonium based ILs which can display better inhibition performances than the imidazolium-based ILs [10,19]. For this reason, the focus is moving from imidazolium-based ILs towards these kinds of ILs [20–25].

Even though the literature data for imidazolium ILs-CH<sub>4</sub> gas hydrates systems are available; however, fewer studies [3,10,19,26,27] have shed light on ammonium based ionic liquid (AIL-CH<sub>4</sub>). TMAOH was recently reported as a thermodynamic inhibitor of CH<sub>4</sub> gas hydrate by reducing the hydrate suppression temperature ( $\Delta T$ ) value up to 1.6 K (for 10 wt%) [19,27]. Tariq et al. [28], evaluated the different ammonium based ILs as methane hydrate inhibitors and found that all were able to reduce phase boundaries; some of them also worked as KHI inhibitors as well. Although few studies dealt with the dual functional behaviour of ILs and QAS for CH<sub>4</sub> hydrates; insufficient studies highlighted the dual functional behaviour of QAS for CO<sub>2</sub> hydrates [10].

Various modelling methodologies in the presence of electrolytes have been reported in the literature [15,29–34]. The activity coefficient approach is generally used since THI behaviour primarily induce the due activity of a chemical in the aqueous phase [35–38]. Most of the prior modelling studies only dealt with the pure CH<sub>4</sub> systems in the presence of electrolytes [3,15,39]. Similarly, the thermodynamic modelling is also limited in the case of CO<sub>2</sub> hydrates [3,40]. Therefore, it is essential to conduct the related investigations which could lead

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