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Kinetic Assessment of Tetramethyl Ammonium Hydroxide (Ionic Liquid) for Carbon Dioxide, Methane and Binary Mix Gas Hydrates

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Bhajan Lal and Mohamad Azmi Bustam

Additional information is available at the end of the chapter

Abstract

This present work highlights the impact of ammonium-based ionic liquid tetramethylammonium hydroxide (TMAOH) on the formation kinetics of carbon dioxide (CO_2), methane (CH_4), and their binary mixed gas (50–50 mole%) hydrates. The TMAOH (IL) is applied in varying concentrations (0.5, 1, and 2 wt%) at different experimental temperatures, i.e., 1 and 4°C. The kinetic experiments are conducted in a high-pressure reactor equipped with two-bladed impeller, to provide sufficient agitation. The experimental pressures of CO_2, CH_4, and mixed 50% CO_2 + 50% CH_4 were 3.50, 8.0, and 6.50 MPa, respectively. Induction time, the initial apparent rate of formation and the total gas consumed are the kinetic parameters used to evaluate the performance of TMAOH as KHI. The results are further compared with commercial KHI (PVP), at higher subcooling condition of 1°C and 1 wt% of all the studied gaseous systems. Furthermore, the KHI performance of TMAOH is also evaluated via the relative inhibition performance (RIP) compared with other ILs for CO_2 and CH_4 hydrates. Results revealed that TMAOH delays the induction time for all the considered systems. The presence of TMAOH also reduced the total gas consumed and the initial rate of hydrate formation in most of the studied systems.

Keywords: CH_4 hydrate, CO_2 hydrate, ionic liquids, mix gas hydrate, KHI, RIP

1. Introduction

Gas hydrates are solid crystals formed when gas (C_1, C_2, C_3, C_4 and CO_2) molecules are trapped inside the hydrogen-bonded water cages under thermodynamically favourable conditions

(low-temperature and high-pressure conditions) [1, 2]. Typically, three types of gas hydrate structures are known, sI, sII and sH hydrates, depending on the type and size of the encaged gas molecules. For example, pure CH_4 and CO_2 mostly form sI hydrate, while C_2H_6 forms sII hydrate.

Gas hydrate formation in the pipelines is considered as one of the most perennial flow assurance problems, which consumes about 70% of flow assurance resources. The accumulation of gas hydrates plugs oil and gas pipelines, disturbing hydrocarbon flow, and causes several safety issues [3–5]. The removal of hydrate plugs from transmission pipeline amount to about 1 million/day shutdown [1]. The hydrate plugging risk increases when producing and transporting high carbon dioxide (CO_2) content natural gas, as CO_2 readily forms hydrates than methane (CH_4) at the same pressure [6, 7]. High CO_2 content natural gas reservoirs are frequently encountered in various areas around the world, such as Central European Pannonian Basin, Colombian Putumayo Basin, Gulf of Thailand, South China Sea, Ibleo platform, Taranaki Basin, Sicily, North Sea South Viking Graben and New Zealand [8]. Malaysia is among the leading natural gas exporters in the world [8]. The J5 and K5 gas fields located in offshore Eastern Malaysia produces about 70–87 mol% CO_2 content natural gas [9]. This significant amount of CO_2 together with the harsh offshore conditions poses various complications for the exploration and transportation of these enormous reserves. One of the core concerns from CO_2-enriched gas systems are their susceptibility to forming gas hydrates in the natural gas production lines [6, 7, 10]. Therefore, in-depth understanding of the mix gas hydrate systems will primarily provide an avenue for safe flow assurance operations when transporting such natural gas systems. Also, this will also provide some fundamental knowledge to design CO_2 separation system for the natural gas system together with the storage opportunity for CO_2 captured from richer CO_2 content natural gas [4, 11, 12].

Four methods can be used to combat gas hydrate formation in flow assurance; this includes removal of water, pressure reduction, thermal heating and chemical injection [4]. In most of the cases, chemical injection is the utmost economical preventive method among the others [8, 13]. These gas hydrate preventive chemicals are known as hydrate inhibitors and are extensively used in oil and gas transmission pipelines. There are three types of gas hydrate inhibitors; thermodynamic hydrate inhibitors (THIs), which mainly shift the hydrate equilibrium curves towards lower-temperature and higher-pressure regions. THIs are mostly required in large concentrations (10–50 wt% of water cuts). Commonly used THIs are methanol and glycols. Although these chemicals are still used in practical field applications till date, they face many drawbacks such as their high operational cost (transportation, storage, injection and pumping quantities and regeneration units) [14, 15].

The drawbacks of above THIs motivated researchers to develop a new kind of hydrate of inhibitors known as low-dosage hydrate inhibitors (LDHIs). This class of inhibitors are typically applied in very less concentration (<2 wt%). LDHIs consist of kinetic hydrate inhibitors (KHIs) and anti-agglomerates (AA). Kinetic hydrate inhibitors (KHIs) are primarily engrossed in delaying the hydrate nucleation time and formation growth rate. It remains quite problematic to evaluate the kinetics of hydrate formation [16–18], exclusively in the presence of KHIs, as it is a very dynamic

and complex process [19]. Commercially employed KHIs are water-soluble polymers such as polyvinylpyrrolidone (PVP) and polyvinyl caprolactam (PVCAP). Karaaslan and Parlaktuna [20] reported that PVP and PEO work as kinetic hydrate inhibitors but have carcinogenic materials which are capable of causing severe health and safety impact on human health. However, the impact of PEO is relatively less compared to PVP [20]. To address these environmental defies of current inhibitors, the quest for greener inhibitors is actively ongoing. Several chemicals such as ILs (mostly imidazolium-based ILs) have been tested for gas hydrate mitigation. ILs could efficiently work as dual-functional hydrate inhibitors (THIs alongside KHIs).

Xiao and Adidharma [21] initiated the research on ILs as gas hydrate inhibitors and found a dual functional effect through imidazolium-based ILs. Since ILs are salts in a molten state, their ability to exhibit electrostatic interaction and form hydrogen bonds with water molecules enhances their hydrate crystalline surface adsorption ability by retarding hydrate nucleation process [21]. Kim and Kang [22] used a high-pressure cell to evaluate pyrrolidinium- and morpholinium-based ionic liquids such as N-hydroxyethyl-N-methyl pyrrolidinium chloride ([HEMP][Cl]), N-hydroxyethyl-N-methyl pyrrolidinium tetrafluoroborate ([HEMP][BF$_4$]), N-butyl-N-methyl pyrrolidinium bromide ([BMP][Br]), N-(2-hydroxyethyl)-N-methyl morpholinium bromide ([HEMM][Br]) and N-(2-hydroxyethyl)-N-methyl morpholinium tetrafluoroborate ([HEMM][BF$_4$]) that can delay methane hydrate nucleation time than PVP and PVCAP at 0.1, 1 and 10 wt%. Furthermore, Nazari and Ahmadi [23] studied the effects of [BMIM][BF$_4$] and [BMIM][MS] on the CH$_4$ hydrate formation and suggested that [BMIM][BF$_4$] acts as better KHI than [BMIM][MS]. However, poor THI behaviour was observed from [BMIM][BF$_4$] in comparison with [BMIM][MS]. Norland and Kelland [24] and Lee et al. [25] elucidate that the type of anion/cation has a significant impact on IL effectiveness. They further suggested that ILs synergistically enhance the kinetic inhibition impact of PVCAP [25]. However, quaternary ammonium salts have also reported as potential KHIs, which open the door for the second-generation IL-based KHIs.

An earlier study suggested that quaternary ammonium salts (QAs) can reduce the nucleation time and hydrate growth rate of tetrahydrofuran (THF) hydrates [26]. The inhibition influence of trimethylpentane, trimethyl hexane and trimethyl octane (QAs) is attributed to the presence of alkyl (CH$_3$) groups in a polar moiety form, which shows high tendency to be adsorbed on the hydrate crystalline surface [27]. Most QAs were found to exhibit kinetic inhibition and anti-agglomeration tendency. However, prior study from Storr et al. [27] recommended that these chemicals should be tested in mixed gas or natural gas hydrate system to evaluate their suitability for field applications. The best kinetic inhibition performance for the studied QAs on THF hydrates were achieved by tetrapentylammonium bromide (TPAB) followed by tetrabutylammonium bromide (TBAB) [28–30].

On the other hand, a limited number of studies are found on the effect of ammonium-based ionic liquids (AILs) as gas hydrate inhibitors [4, 12, 31–33]. Few studies have reported that AILs could efficiently induce thermodynamic hydrate inhibition [3, 4, 14, 34]; however, kinetic evaluations of AILs are rarely available in open literature [15]. Tariq et al. [15] previously reported that the presence of OH$^-$ anion in ILs has a higher inhibition effect as it facilitates more water hydrogen bond cleavage, thus delaying hydrate formation nucleation time. As the

search for useful IL hydrate inhibitors is still ongoing, in our recent works [3, 4], tetramethylammonium hydroxide (TMAOH) was reported as an effective THI for both CH_4 and CO_2 gases with average suppression temperature ($\Delta \overline{T}$) of 1.53 and 2.23°C, respectively. However, its ability to delay hydrate formation kinetics has not been investigated in the open literature.

Therefore, herein, the kinetic influence of TMAOH on CO_2, CH_4 and binary mixed gas hydrate (50–50 CO_2 + CH_4) formation at different concentrations (0.5, 1 and 2 wt%) is comprehensively evaluated and reported for the first time. Induction time, moles consumption and initial apparent rate of hydrate formation are the kinetic parameters that are used to assess the performance of TMAOH at different subcooling experimental temperatures of 1 and 4°C. The obtained results for all gaseous systems are further compared with PVP (commercial KHI) at 1 wt% and 1°C (since the best and commercially applicable concentration of PVP is 1 wt%, and 1°C gives the highest subcooling conditions in the study.) conditions. Also, the performance evaluation of TMAOH via RIP with other ILs is reported. Also, an attempt is made to describe the TMAOH kinetic inhibition mechanism in the presence of the studied hydrate systems.

2. Methodology

2.1. Materials

Table 1 shows the materials used in this study. Only deionized water is used for all the sample preparations during the experiments. The sample concentration measurements are performed using a gravimetrical analytical balance.

2.2. Details of experimental equipment

A high-pressure stainless steel cell [3, 12, 32] with an internal volume of 650 mL, alongside a maximum working pressure of 30 MPa, is used in this study. The cell is immersed in a water bath to regulate the temperature in the cell at desired conditions during experimentations. Two thermocouples are used to measure the temperature inside the cell at an accuracy of ±0.01°C. To achieve appropriate agitation in the liquid phase, two-bladed pitch impeller stirrer is positioned in the equipment with a constant speed of 400 rpm (optimum speed) in all experimentations. The pressure inside the cell is noticed via a pressure transducer with an accuracy of ±0.001 MPa.

2.3. Kinetic measurement procedure

Before each experimental run, the cell is meticulously cleaned with distilled water, and then a 100 mL liquid phase sample (with or without TMAOH) is loaded into the cell. The cell is then introduced into the water bath, and the system is put under vacuum for about an hour to ensure there are no traces of the air in the cell. The desired gas is then pressurized into the cell to the desired experimental operating pressures; after that, the system is allowed to stabilize to the desired initial experimental pressure and temperature conditions by leaving it for about an hour. The mechanical stirrer is turned on at 400 rpm, and data logging system is started simultaneously with the commencement of the experiment (i.e. by reducing the
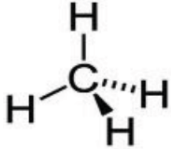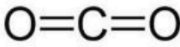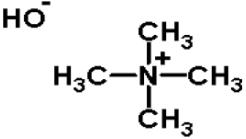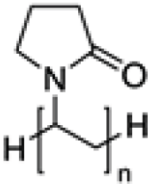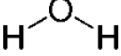
No	Chemical name	Symbol	Purity	Chemical structure
1	Methane	CH_4	99.99 mole %	
2	Carbon dioxide	CO_2	99.95 mole %	
3	Mixed gas	$CO_2 + CH_4$	50.009–49.991 mole %	—
4	Tetramethylammonium hydroxide	TMAOH	25 wt% aqueous solution	
5	Polyvinylpyrrolidone	PVP	99 wt%	
6	Water	H_2O	Deionized	

Table 1. Materials used for kinetic study of gas hydrates.

system temperature to the experimentally desired subcooling temperature of 1 or 4°C). The experimental pressures are set at 3.50, 8.00 and 6.50 MPa for CO_2, CH_4 and binary mixed gas 50–50 $CH_4 + CO_2$ hydrate systems, respectively. The experimental temperatures are kept constant at 1 and 4°C for all studied systems and concentrations. All the experiments are repeated for three times, and averages are reported. The kinetic inhibition influence of TMAOH is assessed within the range of 0.5–2 wt%, similar to the typical industrial application of KHIs.

2.4. Kinetic measurement parameter

In all experiments, the hydrate formation is observed through a sudden pressure drop in the pressure-time plot recorded by the data recording system. The experiments are considered complete after observing a constant pressure in the cell at each experimental temperature for about 3–5 hours. A typical pressure and temperature verse time profile during hydrate formation is illustrated in **Figure 1**. In **Figure 1**, the general hydrate formation process has three major stages: nucleation, crystal/hydrate growth and complete hydrate formation due to mass transfer limitation. The objective of effective KHIs is to increase the hydrate nucleation time (induction time) and at the same time reduce the hydrate crystal growth rate and the total amount of gas consumed into hydrates [35]. Hence, the kinetic inhibition influence of TMAOH is evaluated based on these three parameters.
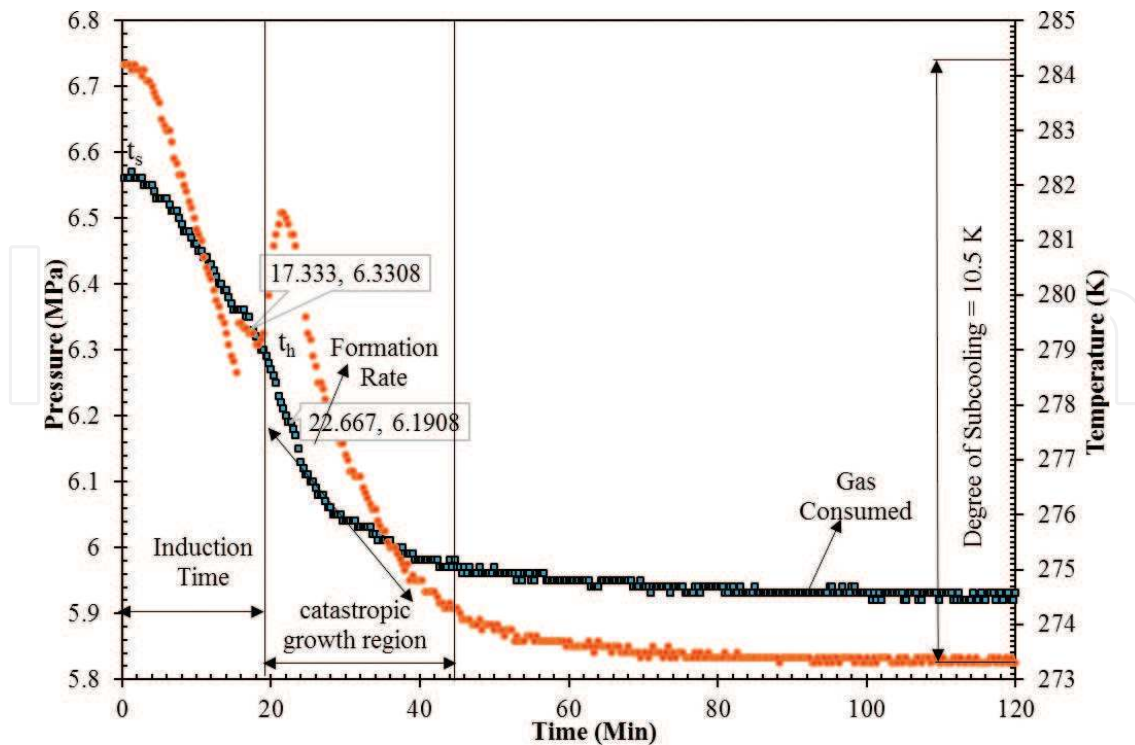
Figure 1. Pressure and temperature vs. time relationship (50–50 mixed gas hydrate).

2.4.1. Induction time measurement

The induction time is the most significant indicator to assess initiation of gas hydrate crystal-lization and growth. It is the time elapse for the occurrence of visible hydrate crystals of the critically stable-sized hydrate nucleus. Longer induction time than the fluid retention time would result in hydrate-free transportation for hydrocarbons in pipelines [36]. However, induction time is a probabilistic phenomenon which depends upon the heterogeneous nucle-ation parameters [2]. The nucleation rate could influence by the numerous factors, such as the existence of particles and impurities in the sample, the roughness of the cell wall and the pres-ence of driving force. Thus, diverse experimental approaches would apparently provide dif-ferent outcomes. For comparison of measurements of the induction time of hydrate inhibitors, the same apparatus is highly recommended/appropriate, and experimental method should is employed [15]. The induction time is measured in this study from the pressure–time data plotted in **Figure 1** as described in the literature [37, 38] as

$$t_i = t_s - t_h \tag{1}$$

where t_s is the time taken for the system pressure to decrease the experimental pressure and t_h and t_i is the actual induction time for hydrate formation (**Figure 1**). Usually, the induction time is recognized by the point at which there is a drastic drop in the reactor pressure accom-panied by a corresponding sudden spike in the reactor temperature, thus indicating the onset of hydrate formation (see **Figure 1** at point t_h).

2.4.2. Initial apparent rate of hydrate formation

The initial apparent rate of hydrate formation determines the rate of hydrate crystallization after the hydrate nucleation [39]. The initial apparent rate is measured with regard to the rate at which the initial moles of gas is consumed into hydrate formation, thereby defining fast hydrate crystal growth that takes place [40]. In these experiments, the initial rate of hydrate formations is accounted for initial 10 min of hydrate formations. The initial apparent rate of hydrate formation can be given by

$$dn/dt = k(n_0 - n_s) \tag{2}$$

where k is the initial apparent rate of any studied gas, n_0 is the mole of gas at initial stage 0 and n_s is the initial moles of consumed gas. The Peng-Robinson equation is employed for calculation of compressibility factor z, and the real gas equation is also used to calculate the mole of consumed gas.

2.4.3. Moles of gas consumed

Moles of gas consumed during hydrate formation determine the dissolved gas in hydrate phase which could form hydrate plug in the subsea condition. The total amount of consumed gas for complete hydrate formation is calculated by applying the real gas law [38, 41]:

$$\Delta n_{gas} = \frac{V}{R}\left[\left(\frac{P}{zT}\right)_0 - \left(\frac{P}{zT}\right)_f\right] \tag{3}$$

where V, R, P and T denote the system gas phase volume, universal gas constant, pressure and temperature, respectively. Δn_{gas} denotes the moles of gas consumed, z is the compressibility factor of the gas determined from the Peng-Robinson equation of state and the subscripts '$_0$' and '$_f$' denote the number of n of moles of gas at the time, zero and time of complete hydrate formation.

In the mixed gas hydrate system, the final gas composition in the gas phase is different from the original mix gas composition due to the guest cage occupancy ratio of the mix gas composition. A gas chromatograph (PerkinElmer) is used to accurately calculate the final composition of the mixed gas in the gas phase after complete hydrate formation. The gas chromatograph results are employed to calculate the moles of mixed gas in the gas phase after hydrate completion (denoted as 'f' in Eq. (3)). Also, the gas chromatograph values indicated that gas composition is more in the hydrate phase in the presence and absence of TMAOH.

3. Results and discussion

The kinetic inhibition effect of TMAOH on the hydrate induction time, formation growth rate and total gas consumption on the hydrate systems is assessed in this work. This is to efficiently evaluate the kinetic inhibition of TMAOH on the complete hydrate formation and growth stages.

3.1. Effect of TMAOH on the kinetics of CO_2 hydrates

The experimental pressure for CO_2 hydrates has been fixed at 3.50 MPa with operating temperatures of 1 and 4°C (subcooling of 8.32 and 5.32°C). These conditions are selected to provide sufficient driving force for hydrate formation as typically encountered in offshore operations of oil and gas production. The effect of various concentrations (0.5, 1 and 2 wt %) of TMAOH on the induction time of CO_2 hydrate at different experimental temperatures (1 and 4°C) is presented in **Figure 2(a)** and **(b)**, respectively. Results reveal that TMAOH could delay the growth of CO_2 hydrates at almost all studied systems by hindering its nucleation process. In the absence of TMAOH, the induction time of water is observed as 14.33 min at 1°C (see **Figure 2(a)**), while 4°C condition showed even lesser induction time of 12.35 min for pure water as evident in **Figure 2(b)**. The presence of 0.5 wt% TMAOH shows a slight improvement in hydrate nucleation time (induction time) with the base sample (pure water) for both 1 and 4°C, which are 23.2 and 21.45%, respectively. Upon increasing the concentration to 1 wt%, the induction time of pure water is improved up to 32.5 and 78.1% at 1 and 4°C, respectively, indicating an inhibition ability of TMAOH at the studied subcooling conditions. However, the inhibition impact at 4°C is relatively higher compared to 1°C, primarily due to the significant driving force existed at 1°C (8.32°C). Further increase in TMAOH concentration to 2 wt% resulted in a negligible delay of CO_2 hydrate induction time compared to the 1 wt% sample. Thus, the optimum TMAOH concentration to delay CO_2 hydrate nucleation is at 1 wt% as shown in **Figure 2**. For comparison purposes, the induction time data is also equated with PVP at 1°C condition in **Figure 2(a)**. The comparison results suggest that PVP still possess better hydrate holding efficacy than studied aqueous TMAOH solution perhaps due to the enhanced polymer linkage on the liquid-gas surface compared to TMAOH.

Since hydrate formation kinetic is a complex phenomenon, it is hard to compare with the previous studies due to the different experimental conditions and apparatus designs. However, [42] found the efficient method to compare different types of the system via relative inhibition power (RIP):

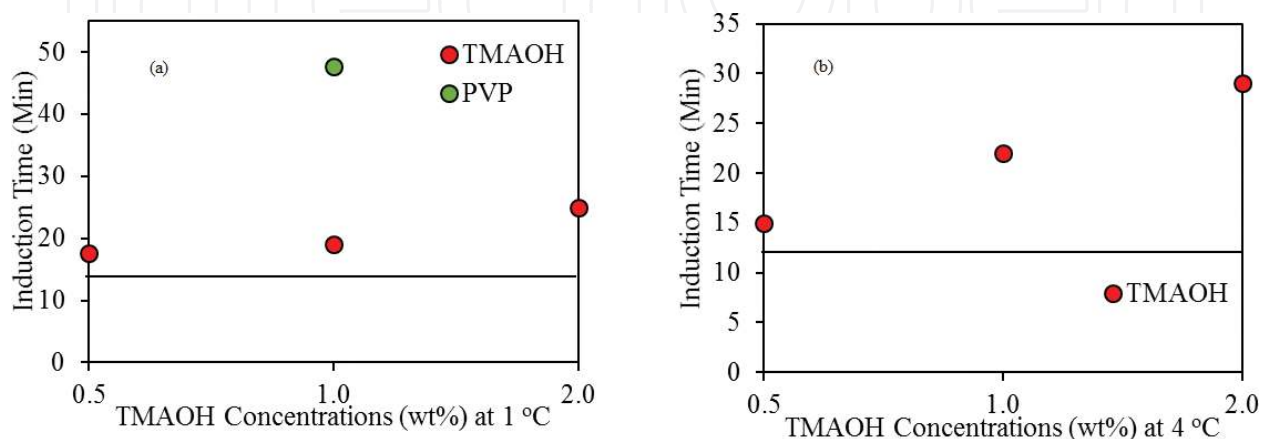$$RIP = \frac{\text{Induction time of KHI-Induction time of water}}{\text{Induction time of water}} \qquad (4)$$

Figure 2. Induction time of CO_2 hydrates in the presence of water (straight line) and TMAOH at different experimental temperatures (a) 1 and (b) 4°C.

The RIP values determine the kinetic inhibitory efficacy of the KHIs, as the RIP>0 corresponds to the better inhibitory performance of KHI. The RIP value of 1 wt% TMAOH concentration at a higher subcooling experimental temperature (1°C) is presented in **Figure 3** for CO_2 hydrate system. The RIP results are further compared with PVP and some reported ILs, namely, [EMIM][Cl] and [EMIM][BF$_4$] from Bavoh et al. [38] and Chun et al. [43], respectively. The RIP results further enlighten the kinetic inhibition performance of TMAOH. In fact, TMAOH possess enhanced RIP value (0.32) compared to [EMIM][BF$_4$] (0.27) earlier studied imidazolium-based IL. However, [EMIM][Cl] provides much better inhibition performance due to the presence of Cl$^-$ anion in its structure which leads towards better induction time [15]. However, PVP performs better than all studied ILs in **Figure 3**.

Figure 4 presents the initial rate constant of CO_2 hydrate formation in the presence of various TMAOH concentrations at 1 and 4°C, respectively. It is found that the rate of hydrate formation is inhibited in the presence of TMAOH compared with the pure water sample at all studied concentrations (see **Figure 4**). The CO_2 hydrate formation rate is reduced more at 4°C experimental temperature than 1°C, especially at 0.5 wt% system. This is attributed to the higher driving force existed at 1°C [15, 21]. At both 1 and 4°C, the samples with 0.5 wt% TMAOH concentration shows the maximum inhibition impact on CO_2 hydrate formation rates up to 0.0013 and 0.00065 min^{-1}, respectively. Unlike the induction time, whose inhibition impact is enhanced with increasing TMAOH concentration, the inhibition impact on CO_2 formation rate is condensed with increasing TMAOH concentrations from 0.5 to 1 and 2 wt% as shown in **Figure 4**. It is suggested that the hydrate kinetic inhibition impact of TMAOH is concentration and subcooling temperature dependent. The obtained formation rate data of PVP (see **Figure 4(a)**) suggests that 1 wt% TMAOH performed considerably superior to PVP at 1°C conditions perhaps due to superior steric hindrances ensued in very least formation rates for all the studied CO_2 systems.

The total moles of CO_2 consumption during hydrate formation in TMAOH solution is depicted in **Figure 5**. All concentrations of TMAOH solution reduce the CO_2 uptakes (moles) into hydrate phase. The maximum inhibition effect on mole consumption of TMAOH for CO_2
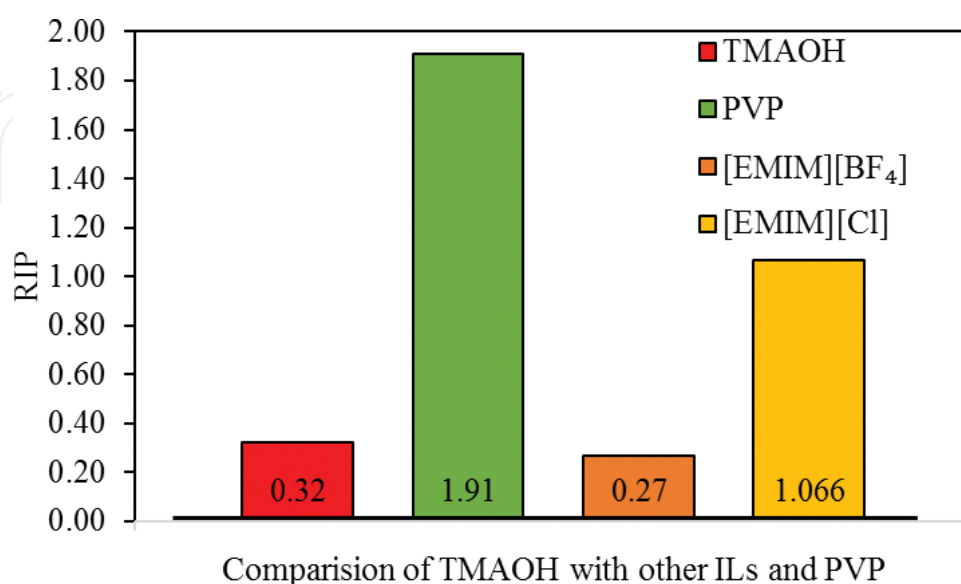

Figure 3. Influence of 1 wt% TMAOH on relative inhibition power (RIP) of CO_2 hydrates at 1°C, the solid line (0.00 RIP) represents pure water, and results are compared with commercial inhibitor (PVP) and ILs.
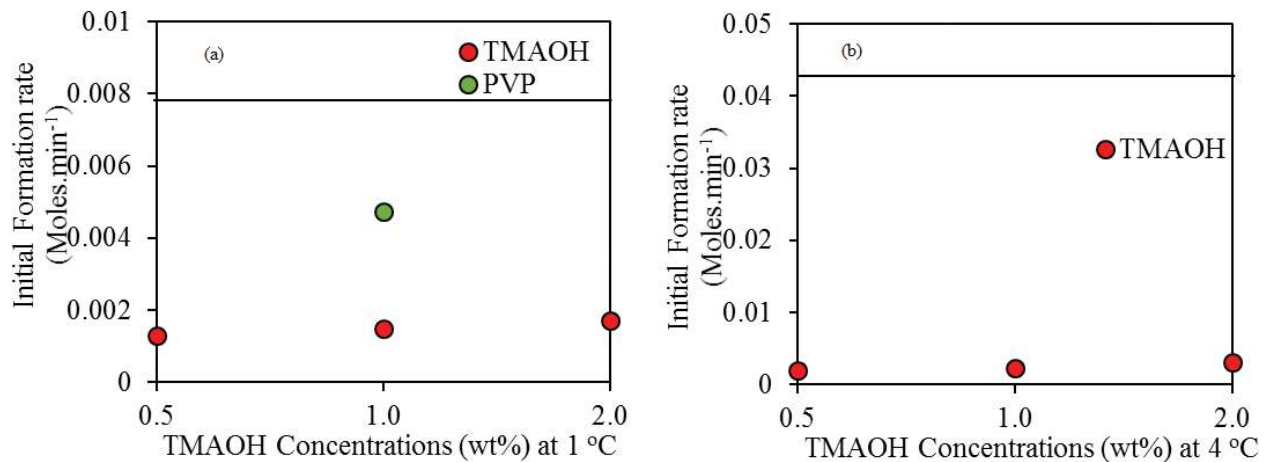
Figure 4. The initial apparent rate of CO_2 hydrate formation in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.

hydrate is observed at 1 wt% for both experimental conditions. The CO_2 uptake values are found to be 0.132 and 0.124 moles for 1 and 4°C, respectively. The complete moles consumed at 4°C at all concentration are significantly higher than 1°C, again affirming the effect of the active driving force at 1°C. This considerable driving force attributed further hydrate formation environs cause the formation of more CO_2 hydrates. Additionally, the CO_2 uptake result of 1 wt% TMAOH is further compared with PVP in **Figure 5(a)**. Referring to the comparison results of CO_2 consumed, it is detected that TMAOH can reduce the mole consumption of CO_2 more than PVP which signifies its usefulness as a potential KHI for CO_2 hydrate formation.

3.2. Effect of TMAOH on the kinetics of CH_4 hydrates

CH_4 hydrate formation is a bit different from CO_2 hydrate formation and required higher pressure (8.0 MPa) compared to CO_2 hydrate (3.5 MPa). **Figure 6** presents the influence of TMAOH on the induction time of CH_4 hydrate formation at various concentrations (0.5, 1 and 2 wt%) and different experimental temperatures (1 and 4°C).

In contrary to CO_2, higher concentrations of TMAOH do not reflect the linear induction time with mass concentration perhaps due to probabilistic nature of hydrate formation. Similarly,
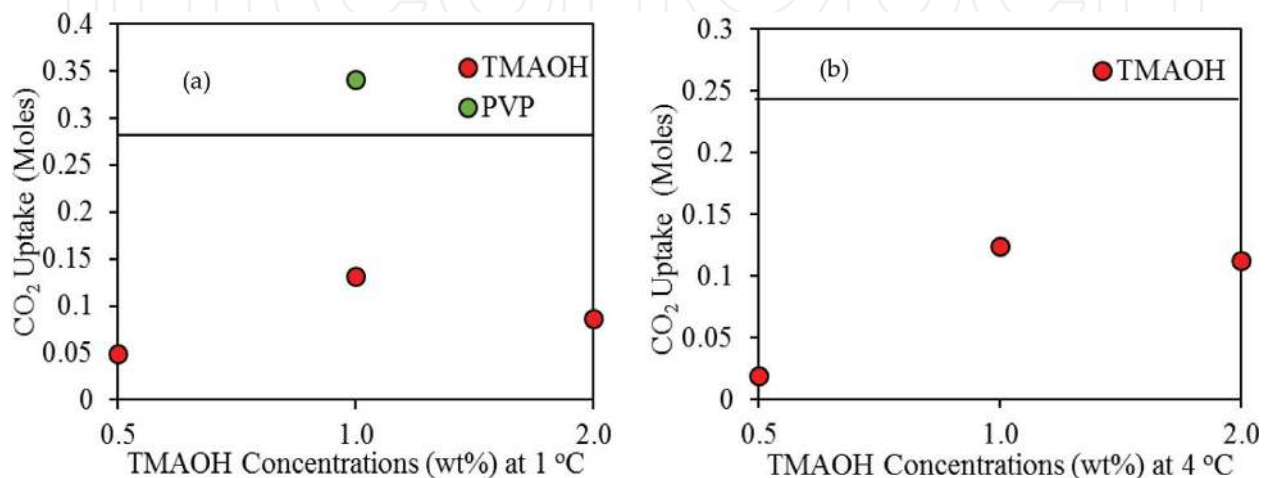

Figure 5. Moles of CO_2 consumption in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.

as overseen in CO_2 hydrate systems, the maximum TMAOH inhibition impact is observed at 1 wt% at 1 and 4℃. In the presence of 1 wt% TMAOH, the CH_4 hydrate induction time is enhanced nearly 41.4 and 81.1% for 1 and 4℃, respectively, compared to the pure water sample. However, the presence of 0.5 wt% TMAOH ensued little induction time value at 4℃ and however slightly enhanced CH_4 hydrate nucleation observed at 1℃. Increasing the TMAOH concentration above 1 wt% reduced the induction time inhibition impact on CH_4 hydrates (see **Figure 6**). Furthermore, the induction data of 1 wt% TMAOH at 1℃ condition is further compared with PVP data in **Figure 6(a)**. Similar to CO_2 hydrate, PVP is able to enhance the induction time of CH_4 more than TMAOH.

Additionally, obtained induction time results of 1 wt% TMAOH concentration of CH_4 hydrates at 1℃ are also compared with recently published imidazolium-based IL data of Nashed et al. [44] in the form of RIP and perceived in **Figure 7**. Moreover, RIP data of studied AILs could easily be compatible with the previous study [44] as shown in **Figure 7**. TMAOH possess better RIP values compared to most earlier studied imidazolium-based ILs reported by Nashed et al. [44] (see **Figure 7**).

The initial rates of CH_4 hydrate formation with and without TMAOH mass concentrations (0.5, 1 and 2 wt%) at 1 and 4℃ are illustrated in **Figures 8(a)** and **(b)**, respectively. At 4℃ condition, the formation rates of TMAOH found for concentration are driven; as the quantity of TMAOH increases, the rate of CH_4 hydrate formation decreases. The similar behaviour was observed in CO_2 hydrate systems as well (**Figure 4(a)**). However, unlike CO_2 hydrates (see **Figure 4**), at 1℃ the formation rates of CH_4 hydrates are found in non-linear trend (see **Figure 8(a)**) which demonstrates that the inhibition impact of TMAOH is not only concentration dependent but also significantly dependent on the type of hydrate formerly present. The presence of low driving force (subcooling = 7℃) at 4℃ enhanced the inhibition of the rate of hydrate formation than at 1℃, which holds the higher driving force (subcooling = 10℃) resulting in catastrophic crystal growth as discussed in the preceding study [45].

Furthermore, the formation rate of 1 wt% TMAOH is also compared with PVP data in **Figure 8(a)**. The formation rate data revealed that TMAOH is able to reduce the formation rate moderately than PVP as also evident in the above results of CO_2 hydrates in an earlier section (see **Figure 4(a)**).
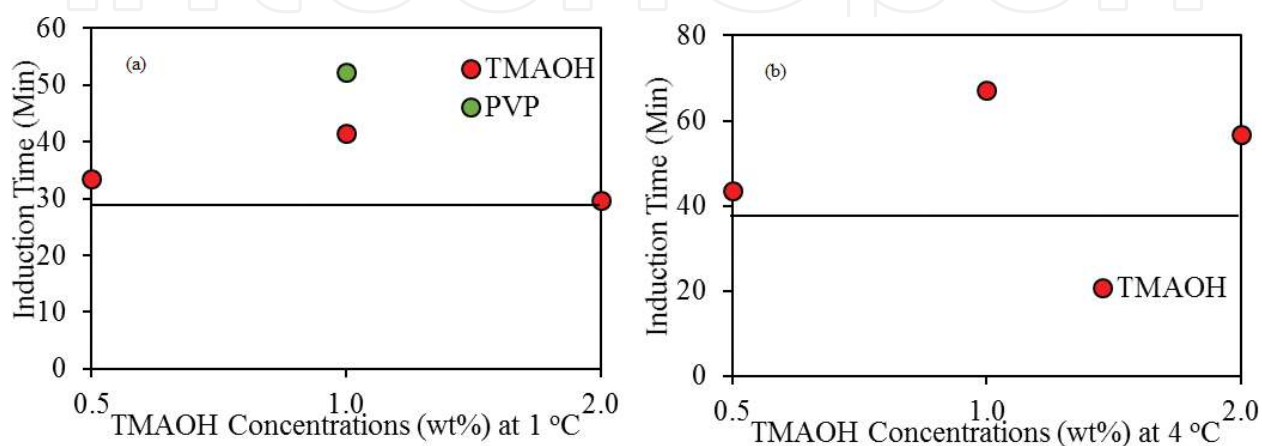

Figure 6. Induction time of CH_4 hydrate in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4℃.
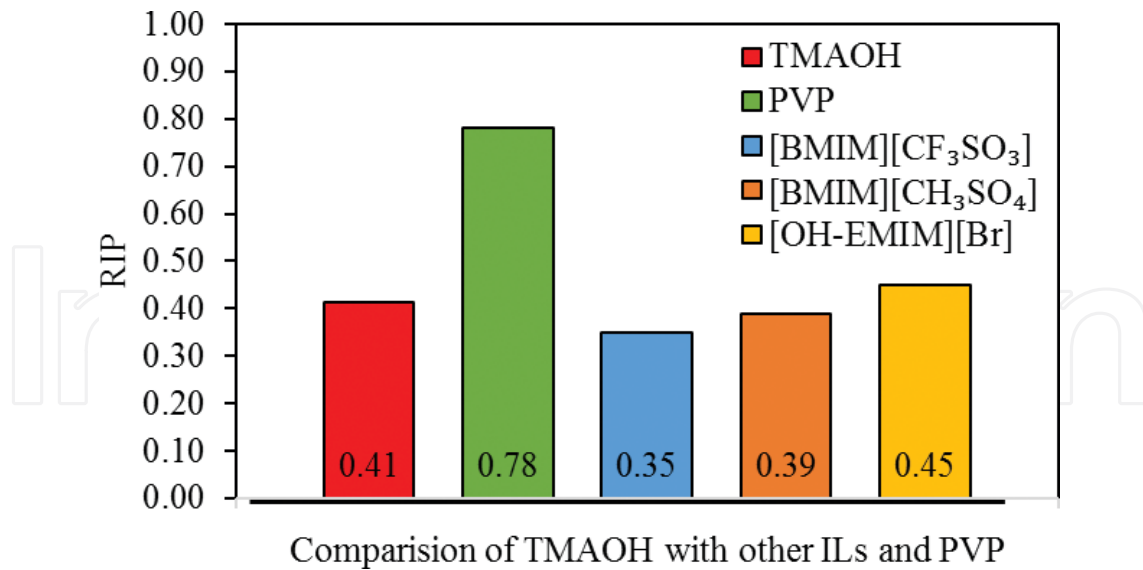
Figure 7. Influence of 1 wt% TMAOH on relative inhibition power (RIP) of CH_4 hydrates at 1°C, the solid line (0.00 RIP) represents pure water, and results are compared with commercial inhibitor (PVP) and ILs.

Figure 9 presents the CH_4 mole consumed into hydrate with and without TMAOH. The presence of TMAOH poorly inhibited the CH_4 consumption into hydrate formation at both studied experimental temperatures. Especially at 1°C, all tested TMAOH concentrations significantly enhanced CH_4 hydrate formation, thus showing hydrate promotional impact. However, the moles of CH_4 consumed into the hydrate at 4°C are similar to the water sample; this may be due to the low driving force existing at that temperature (4°C). Therefore, the presence of TMAOH in CH_4 hydrate can inhibit the hydrate induction time and formation rate but will cause hydrate plug upon formation with time due to its CH_4 mole consumption promotion effect. Previous studies have shown that some conventional KHIs such as PVP have similar behaviour [46]. They form large hydrate plugs upon hydrate formation (i.e. after hydrate nucleation).
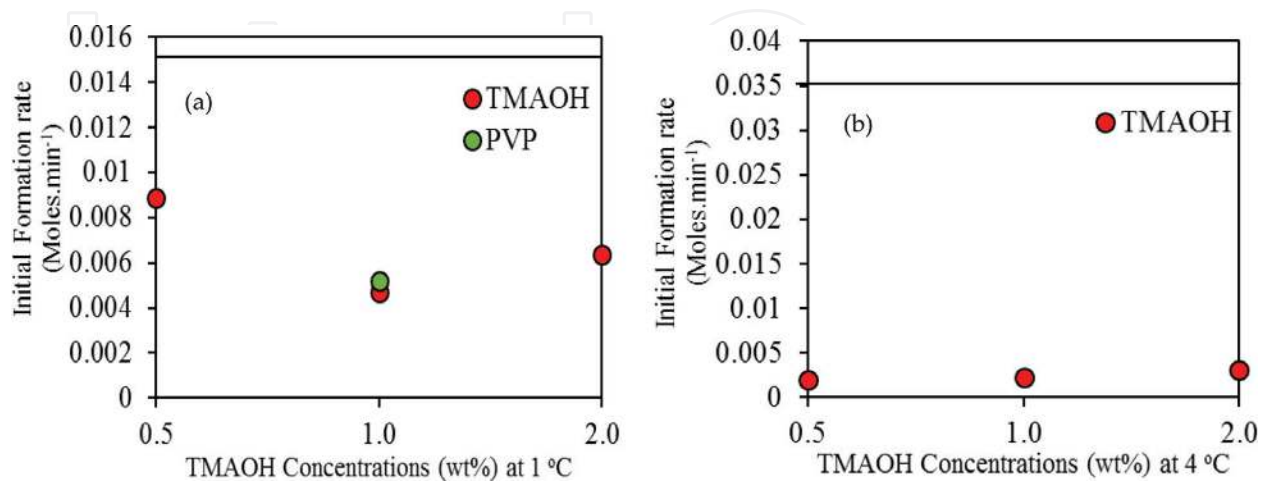

Figure 8. Rate of CH_4 hydrate formation in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.
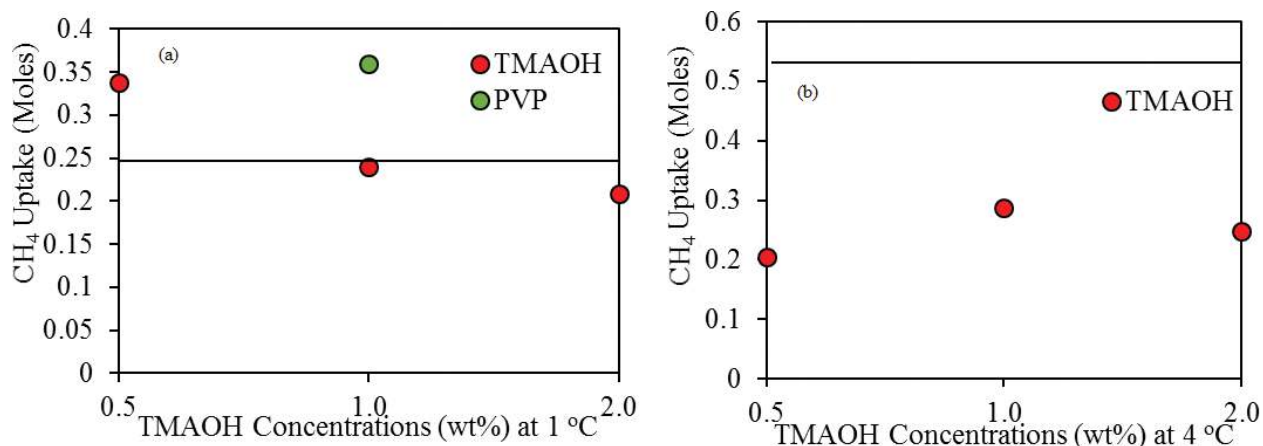
Figure 9. Moles of CH_4 consumption in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.

3.3. Effect of TMAOH on the kinetics of binary mixed gas hydrates (50–50 mole% CO_2 + CH_4)

The kinetic formation of mixed gas 50–50 CO_2 + CH_4 hydrates in the presence of various quantities of aqueous TMAOH solutions is discussed in this section. The hydrate induction time values for the mix gas hydrate systems are perceived in **Figure 10**. Results revealed that as TMAOH concentration increases the mixed gas hydrate induction time is further delayed, thus showing a significant inhibition impact for the mixed gas hydrates.

At the lowest concentration (0.5 wt%), TMAOH delayed the base sample induction time by about 1.2 times at both 1 and 4°C, while at 2 wt% about 1.5 and 2.3 times at 1 and 4°C, respectively. Additionally, the KHI impact (induction time) of 1 wt% TMAOH aqueous solution of the mixed gas is also compared with PVP data in **Figure 10(a)**. The comparisons of data are interestingly piercing that TMAOH can delay hydrate nucleation time further than commercial KHI inhibitor PVP. The potential of the improved delay time observed is perhaps due to the larger subcooling (11°C) conditions of studied mixed gas system compared to pure water
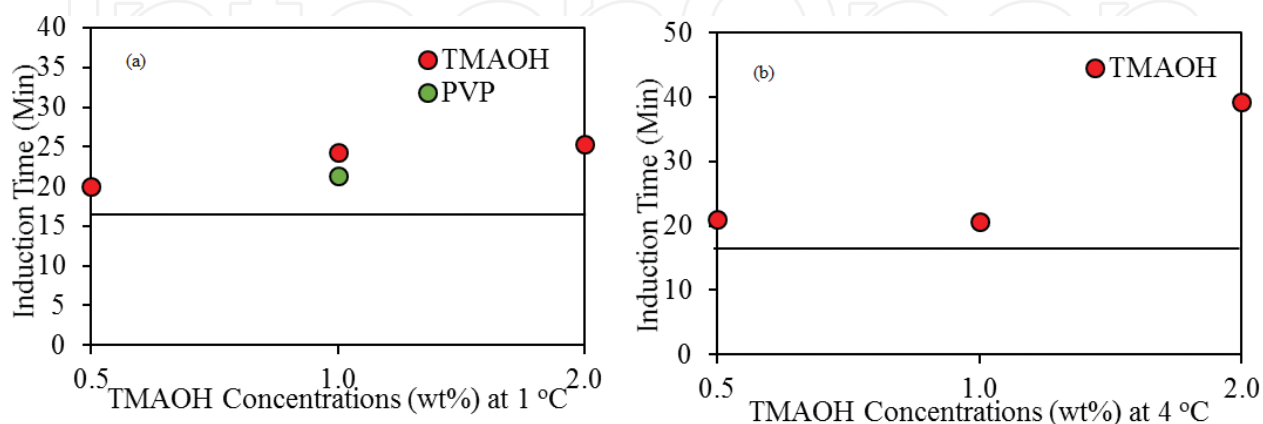

Figure 10. Induction time of binary mixed gas hydrate in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.

systems (CO_2 = 7.32°C; CH_4 = 10°C). This observation also highlighted the limitation of PVP (commercial inhibitor) efficacy over harsh deep-water condition which loses its strength at higher subcooling conditions [38, 47].

Figure 11 refers the initial formation rate of 50–50 CO_2 + CH_4 mixed gas hydrates. Results revealed that initial rate of hydrate formation for mixed gas hydrates reduced with increasing TMAOH mass concentrations for both 1 and 4°C. The presence of 1 wt% TMAOH shows the optimal hydrate rate diminution. The hydrate formation rate is found to be reduced about five times at 1 wt% TMAOH for all subcooling compared with the mixed gas hydrate (pure water sample). Furthermore, the result of 1 wt% TMAOH is further compared with PVP in **Figure 11(a)** at a similar concentration. Like the pure gases hydrates, TMAOH can further reduce the initial formation rate compared to the PVP-based system.

In **Figure 12**, it is observed that the presence of TMAOH significantly reduces the amount of mixed gas consumption in both experimental (subcooling) conditions, unlike the case of pure CH_4 hydrates. The inhibition of mixed gas consumed into hydrate is practically observed at all concentrations. However, the much significant inhibition impact is obtained at 2 wt% aqueous TMAOH solution. At 2 wt%, the amount of mixed gas consumed into hydrate is reduced about 1.7 times compared to the pure water system. This notable inhibition together with the THI impact [3] shows the potentials of applying TMAOH as a novel dual functional inhibitor for practical field operation, especially in high CO_2 content reservoir productions of fluid transportation and procession.

A gas chromatography (GC) is used to explore the mixed gas composition after hydrates are entirely formed in all the binary mixed gas experiments. The data are used to calculate the amount of gas remaining in the gas phase after hydrate formation. However, the GC readings are also useful to understand the percentage of each gas entrapped in the hydrate phase in the presence and absence of TMAOH. The inhibition selectivity of TMAOH for the binary mixed gas composition may be suggested. The measured GC readings are tabularized in **Table 2**. The data revealed that CO_2 compositions in the binary mixed gas are diminished after complete hydrate formation compared to original compositions (50–50% CO_2 + CH_4) for all experiments.
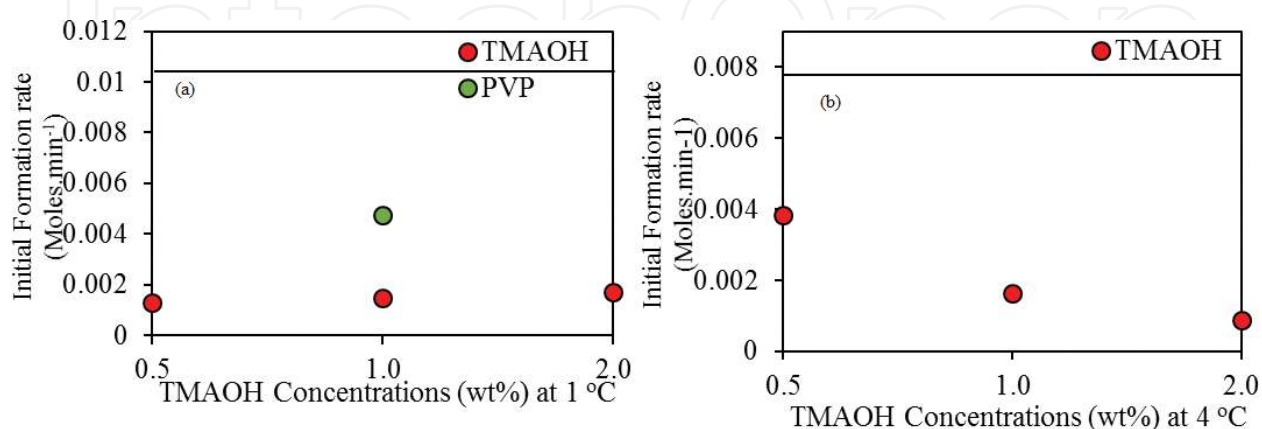

Figure 11. Initial apparent rate of binary mixed gas hydrate formation in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.
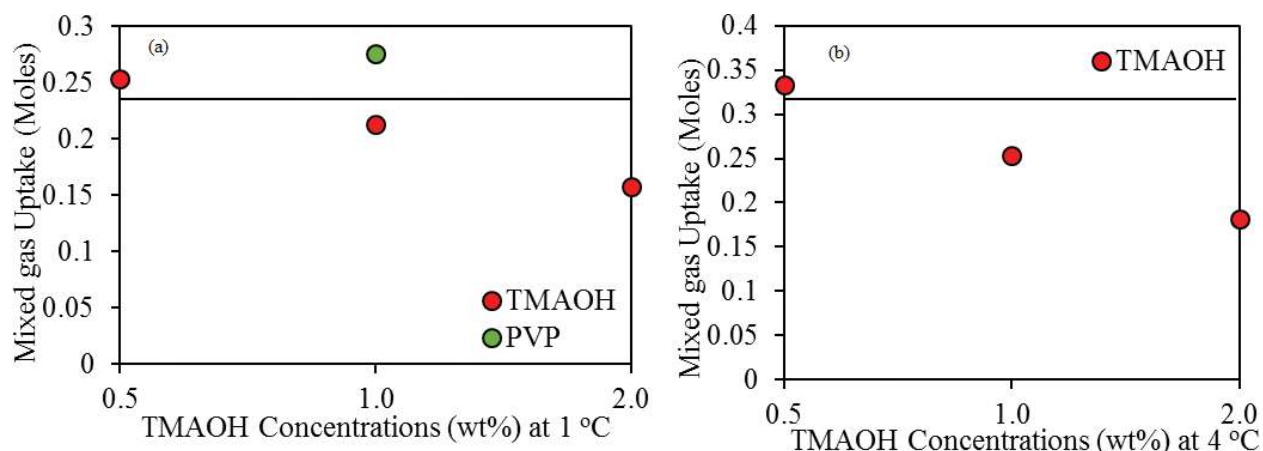
Figure 12. Moles of binary mixed gas consumption in the presence of water (straight line) and TMAOH at different temperatures (a) 1 and (b) 4°C.

Confirming that CO_2 hydrates are more formed in mixed gas hydrates compared to CH_4 hydrate, which is due to experimental pressure, provides more driving force to CO_2 than CH_4 hydrates as CO_2 is more prone to hydrate formation compared to CH_4 gas.

3.4. Kinetic mechanism of TMAOH

The kinetic inhibition influence of TMAOH observed for all studied gas systems in this work presents TMAOH as a potential KHI. TMAOH is speculated to demonstrate a kinetic inhibitory mechanisms effect via (1) coulombic forces of interactions and (2) hydrogen bonding affinity, which probably results in its kinetic hydrate inhibition influence. Firstly, TMAOH is an ionic liquid which can form hydrogen bonding with water molecules and thus disturb the hydrogen-bonded structure of water molecules owing to the presence of its anion and cation ions [4, 12, 15, 48]. TMAOH ionizes in aqueous solution as TMA^+ cation and OH^- anions which

Sample	Concentration (wt%)	Experimental temperature (°C)	CH_4	CO_2
Pure water	0.00	4	53.26	46.74
Pure water	0.00	1	54.1	45.9
TMAOH	0.50	4	53.1	46.9
	1.00	4	55.38	44.62
	2.00	4	54.1	45.9
TMAOH	0.50	1	53	47
	1.00	1	55.8	44.17
	2.00	1	54	46
PVP	1.00	1	55.3	44.7

Table 2. Gas chromatography (GC) data for the average composition of binary mixed gas hydrates after complete hydrate formation.

interacts with the dipoles of the aqueous molecules with strong coulombic forces in additions to its hydrogen bonding ability [49]. This combined effect easily overcomes the hydrogen bond structure or the van der Waals forces which causes clustering of water molecules in hydrate formation nucleation and growth [3, 4, 12]. As the water structures are distorted, it promotes the hindrance/delay in hydrate nuclei clustering and gas consumption into hydrate. Additionally, TMAOH possesses four methyl cations $[CH^{3+}]$ which is the least hydrophobic alkyl radical among other alkyl groups, which makes tetramethylammonium $[TMA^+]$ cation relatively more hydrophilic [3, 50–52]. Similarly, hydroxyl $[OH^-]$ anion is well known for its strong hydrogen bonding affinity for water molecules [3, 4, 32]. Therefore, TMAOH could adsorb on the gas-water interface, and retarded hydrate nucleation and crystal growth (through hydrogen bonding by the amide group and anion) and sterically block the hydrate formation [15, 53–56].

It is already proven from previous studies [1, 13, 35, 57, 58] that hydrate formation depends on the presence of a guest molecule. Therefore, the inhibition impact of TMAOH also differs according to the type of gas systems. For instance, CO_2 hydrates showed lesser induction time in comparison with CH_4 hydrates and 50–50 CO_2-CH_4 mix gas hydrates in this study. The overall better KHI performance of TMAOH is found with 50–50 CO_2-CH_4 mix gas hydrates for both experimental temperature conditions (1 and 4°C) for induction time, hydrate formation rate alongside moles of gas consumed. Additionally, although the kinetic inhibition is concentration dependent, as aqueous TMAOH concentration increases, the KHI performance enhances for most of the studied systems. However, for optimum performance evaluation, one% (1 wt%) TMAOH seems to be more efficient as not much differently observed (above results) between 1 and 2 wt% concentrations. It is also evident for all studied system that at higher experimental temperature condition 4°C TMAOH performs better in comparison to lower-temperature condition (1°C). It can be concluded that TMAOH successfully worked as a KHI inhibitor for all the studied system; earlier [3], TMAOH has already been proven as an efficient THI as well for CH_4 and CO_2 gas hydrates. Therefore, TMAOH possibly will work as dual-functional hydrate inhibitor and therefore could efficiently be contemplated for flow assurance strategies.

4. Conclusions

In the present work, ammonium-based ionic liquid, TMAOH, is tested as a potential kinetic inhibitor for pure CO_2, CH_4 and binary mixed (50–50) $CO_2 + CH_4$ hydrate systems at different mass concentrations (0.5, 1.0 and 2.0 wt%). The effect of subcooling was also investigated at two different experimental temperatures of 1 and 4°C at moderate pressures for all the studied TMAOH systems. Experimental results revealed that TMAOH kinetically inhibits hydrate formation by delaying hydrate nucleation through the enhancement of hydrate induction time and TMAOH also lessens the initial apparent rate of hydrate formation and accordingly decreased the mole consumptions for almost all studied systems. Influence of subcooling was also observed as the subcooling increased the hydrate formation due to the presence of excessive driving force. The effect of TMAOH concentration and the type of guest molecules under study are found to affect the TMAOH hydrate inhibition impact significantly. Furthermore, the experimental results of TMAOH were further compared with PVP at 1 wt% concentration at 1°C conditions. The induction time of PVP seems to be higher than TMAOH for both pure

gases; however, for binary mixed gas, the induction time of TMAOH is found to be higher than PVP due to enhanced subcooling conditions. The initial formation rate and mole consumption are found to be enhanced with TMAOH compared to the commercial counterpart. The TMAOH inhibitory mechanisms are driven by their coulombic forces of interactions and hydrogen bonding affinity for water molecules in hydrate formation environment. Therefore, the findings of this study highlighted the kinetic impact of TMAOH, which should be beneficial for gas hydrate-based technological applications such as storage and gas transportation, flow assurance and energy productions.

Acknowledgements

Nomenclature

ILs	ionic liquids
LDHI	low-dosage hydrate inhibitor
KHI	kinetic hydrate inhibitors
PVP	polyvinyl pyrrolidinium
RIP	relative inhibition performance
TMAOH	tetramethylammonium hydroxide

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References

[1] Koh CA. Towards a fundamental understanding of natural gas hydrates. Chemical Society Reviews. 2002;**31**(3):157-167

[2] Sloan ED, Koh CA. Clathrate Hydrates of Natural Gases. Fuel. New York: CRC Press Taylor & Francis; 2007. 3158p

[3] Khan MS, Partoon B, Bavoh CB, Lal B, Mellon NB. Influence of tetramethylammonium hydroxide on methane and carbon dioxide gas hydrate phase equilibrium conditions. Fluid Phase Equilibria. 2017;**440**(May 2017):1-8

[4] Khan MS, Lal B, Bavoh CB, Keong LK, Bustam A. Influence of ammonium based compounds for gas hydrate mitigation : A short review. Indian Journal of Science and Technology. 2017;**10**(5):1-6

[5] Nashed O, Sabil KM, Lal B, Ismail L, Jaafar AJ. Study of 1-(2-hydroxyethyle) 3-methylimidazolium halide as thermodynamic inhibitors. Applied Mechanics and Materials. 2014;**625**:337-340

[6] Roosta H, Dashti A, Mazloumi SH, Varaminian F. Inhibition properties of new amino acids for prevention of hydrate formation in carbon dioxide-water system: Experimental and modeling investigations. Journal of Molecular Liquids. Elsevier B.V. 2016;**215**:656-663

[7] Shen X, Shi L, Long Z, Zhou X, Liang D. Experimental study on the kinetic effect of N-butyl-N-methylpyrrolidinium bromide on CO_2 hydrate. Journal of Molecular Liquids [Internet]. Elsevier B.V. 2016;**223**:672-677

[8] Sloan ED, Koh CA. Clathrate Hydrates of Natural Gases. 3rd ed. New York: CRC Press Taylor & Francis; 2008. 758p

[9] Nasir Q, Lau KK, Lal B, Sabil KM. Hydrate dissociation condition measurement of CO_2 -rich mixed gas in the presence of methanol/ethylene glycol and mixed methanol/ethylene glycol + electrolyte aqueous solution. Journal of Chemical & Engineering Data. 2014;**59**(11):3920-3926

[10] Khodaverdiloo KR, Rad SA, Naeiji P, Peyvandi K, Varaminian F. Synergistic effects of nonylphenol ethoxylates and polyethylene glycols on performance of gas hydrate kinetic inhibitor. Journal of Molecular Liquids. Elsevier B.V. 2016;**216**:268-274

[11] Daraboina N, Linga P. Experimental investigation of the effect of poly-N-vinyl pyrrolidone (PVP) on methane/propane clathrates using a new contact mode. Chemical Engineering Science. 2013;**93**:387-394

[12] Khan MS, Bavoh CB, Partoon B, Lal B, Bustam MA, Shariff AM. Thermodynamic effect of ammonium based ionic liquids on CO_2 hydrates phase boundary. Journal of Molecular Liquids. Elsevier B.V. 2017;**238**(July):533-539

[13] Sloan ED Jr. Fundamental principles and applications of natural gas hydrates. Nature 2003;**426**(6964):353-363

[14] Qureshi MF, Atilhan M, Altamash T, Tariq M, Khraisheh M, Aparicio S, et al. Gas hydrate prevention and flow assurance by using mixtures of ionic liquids and Synergent compounds: Combined kinetics and thermodynamic approach. Energy & Fuels. 2016;**30**(4):3541-3548

[15] Tariq M, Rooney D, Othman E, Aparicio S, Atilhan M, Khraisheh M. Gas hydrate inhibition: A review of the role of ionic liquids. Industrial and Engineering Chemistry Research. 2014;**53**(46):17855-17868

[16] Rasoolzadeh A, Javanmardi J, Eslamimanesh A, Mohammadi AH. Experimental study and modeling of methane hydrate formation induction time in the presence of ionic liquids. Journal of Molecular Liquids. Elsevier B.V. 2016;**221**:149-155

[17] Zare M, Haghtalab A, Ahmadi AN, Nazari K, Mehdizadeh A. Effect of imidazolium based ionic liquids and ethylene glycol monoethyl ether solutions on the kinetic of methane hydrate formation. Journal of Molecular Liquids. 2015;**204**(4):236-242

[18] Shi L, Yi L, Shen X, Wu W, Liang D. The effect of tetrabutylphosphonium bromide on the formation process of CO_2 hydrates. Journal of Molecular Liquids—Elsevier B.V. 2017;**229**:98-105

[19] Mohammadi A, Manteghian M, Mohammadi AH, Jahangiri A. Induction time, storage capacity, and rate of methane hydrate formation in the presence of SDS and silver nanoparticles. Chemical Engineering Communications. 2017;**204**(12):1420-1427

[20] Karaaslan U, Parlaktuna M. Kinetic inhibition of methane hydrate by polymers. American Chemical Society Division of Fuel Chemistry. 2002;**47**(1):355-358

[21] Xiao C, Adidharma H. Dual function inhibitors for methane hydrate. Chemical Engineering Science. 2009;**64**(7):1522-1527

[22] Kim K, Kang S-P. Investigation of pyrrolidinium- and morpholinium-based ionic liquids into kinetic hydrate inhibitors on structure i methane hydrate. 7th International Conference on Gas Hydrates (ICGH) 2011. Edinburgh, Scotland; 2011. pp. 17-21

[23] Nazari K, Ahmadi AN, Moradi MR, Sahraei V, Taghikhani V, Ghobti CA. A thermodynamic study of methane hydrate formation in the presence of [BMIM][BF_4] and [BMIM][MS] ionic liquids. In: Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011); 2011 Jul 17. pp. 17-21

[24] Norland AK, Kelland MA. Crystal growth inhibition of tetrahydrofuran hydrate with bis- and polyquaternary ammonium salts. Chemical Engineering Science—Journal—Elsevier. 2012;**69**(1):483-491

[25] Lee W, Shin J, Cha J, Kim K, Kang S. Inhibition effect of ionic liquids and their mixtures with poly(N-vinylcaprolactam) on methane hydrate formation. Journal of Industrial and Engineering Chemistry. The Korean Society of Industrial and Engineering Chemistry. 2016;**30**:3541-3548

[26] Roosta H, Khosharay S, Varaminian F. Experimental study of methane hydrate formation kinetics with or without additives and modeling based on chemical affinity. Energy Conversion and Management. Elsevier Ltd. 2013;**76**:499-505

[27] Zanota ML, Dicharry C, Graciaa A. Hydrate plug prevention by quaternary ammonium salts. Energy and Fuels. 2005;**19**(11):584-590

[28] Storr MT, Taylor PC, Monfort JP, Rodger PM. Kinetic inhibitor of hydrate crystallization. Journal of the American Chemical Society. 2004;**126**(5):1569-1576

[29] Perrin A, Musa OM, Steed JW. The chemistry of low dosage clathrate hydrate inhibitors. Chemical Society Reviews. 2013;**42**(5):1996-2015

[30] Kelland MA. History of the development of low dosage hydrate inhibitors. Energy & Fuels. 2006;**20**(3):825-847

[31] Yasuda T, Kinoshita H, Miran MS, Tsuzuki S, Watanabe M. Comparative study on physicochemical properties of protic ionic liquids based on allylammonium and propylammonium cations. Journal of Chemical & Engineering Data. 2013;**58**(10):2724-2732

[32] Khan MS, Lal B, Partoon B, Keong LK, Bustam MA, Mellon NB. Experimental evaluation of a novel thermodynamic inhibitor for CH_4 and CO_2 hydrates. Procedia Engineering. 2016;**148**(2016):932-940

[33] Khan MS, Bavoh CB, Partoon B, Nashed O, Lal B, Mellon NB. Impacts of ammonium based ionic liquids alkyl chain on thermodynamic hydrate inhibition for carbon dioxide rich binary gas. Journal of Molecular Liquids. 2018 Apr 10

[34] Nashed O, Dadebayev D, Khan MS, Bavoh CB, Lal B, Shariff AM. Experimental and modelling studies on thermodynamic methane hydrate inhibition in the presence of ionic liquids. Journal of Molecular Liquids Elsevier B.V. 2018;**249**:886-891

[35] Kashchiev D, Firoozabadi A. Induction time in crystallization of gas hydrates. Journal of Crystal Growth. 2003;**250**(3-4):499-515

[36] Fazlali A, Keshavarz-Moraveji M, Farjami M, Mohammadi AH. Experimental study of the effect of kinetic inhibitor on methane hydrate formation. In: Taylor JC, editor. Advances in Chemistry Research. NY, USA: Nova Science Publishers, Inc; 2016. pp. 133-148

[37] Partoon B, Nurmala S, Malik A, Azemi MH, Sabil KM. Experimental investigations on the potential of SDS as low-dosage promoter for carbon dioxide hydrate formation. Asia-Pacific Journal of Chemical Engineering. 2013;**8**:916-921

[38] Bavoh CB, Lal B, Keong LK, binti JM, binti IM. Synergic kinetic inhibition effect of EMIM-Cl + PVP on CO_2 hydrate formation. Procedia Engineering. 2016;**148**:1232

[39] Kumar A, Bhattacharjee G, Kulkarni BD, Kumar R. Role of surfactants in promoting gas hydrate formation. Industrial and Engineering Chemistry Research. 2015;**54**(49):12217-12232

[40] Akhfash M, Boxall JA, Aman ZM, Johns ML, May EF. Hydrate formation and particle distributions in gas-water systems. Chemical Engineering Science. Elsevier. 2013;**104**:177-188

[41] Babaee S, Hashemi H, Mohammadi AH, Naidoo P, Ramjugernath D. Kinetic and thermodynamic behaviour of CF_4 clathrate hydrates. The Journal of Chemical Thermodynamics. Elsevier Ltd. 2015;**81**:52-59

[42] Koh CA, Westacott RE, Zhang W, Hirachand K, Creek JL, Soper AK. Mechanisms of gas hydrate formation and inhibition. Fluid Phase Equilibria. 2002;**194-197**:143-151

[43] Chun LK, Jaafar A. Ionic liquid as low dosage hydrate inhibitor for flow assurance in pipeline. Asian Journal of Scientific Research. 2013;**6**(2):374-380

[44] Nashed O, Sabil KM, Ismail L, Japper-Jaafar A, Lal B. Mean induction time and isothermal kinetic analysis of methane hydrate formation in water and imidazolium based ionic liquid solutions. The Journal of Chemical Thermodynamics. 2018 Feb 1;**117**:147-154

[45] Parent JS, Bishnoi P. Investigations into the nucleation behaviour of methane gas hydrates. Chemical Engineering Communications. 1996;**144**(1):51-64

[46] Sa J-H, Kwak G-H, Han K, Ahn D, Lee K-H. Gas hydrate inhibition by perturbation of liquid water structure. Scientific Reports. Nature Publishing Group. 2015;**5**:11526

[47] Bavoh CB, Nashed O, Saad Khan M, Partoon B, Lal B, Sharif AM. The impact of amino acids on methane hydrate phase boundary and formation kinetics. The Journal of Chemical Thermodynamics. 2018;**117**:48-53

[48] Tariq M, Connor E, Thompson J, Khraisheh M, Atilhan M, Rooney D. Doubly dual nature of ammonium-based ionic liquids for methane hydrates probed by rocking-rig assembly. RSC Advances. 2016;**6**(28):23827-23836

[49] Saw VK, Das BB, Ahmad I, Mandal a, Laik S. Influence of electrolytes on methane hydrate formation and dissociation. Energy Sources, Part A Recover Utilization, and Environmental Effects. 2014;**36**(15):1659-1669

[50] Filley TR, Minard RD, Hatcher PG. Tetramethylammonium hydroxide (TMAH) thermo-chemolysis: Proposed mechanisms based upon the application of 13C-labeled TMAH to a synthetic model lignin dimer. Organic Geochemistry. 1999;**30**(7):607-621

[51] Kavitha T, Attri P, Venkatesu P, Devi RSR, Hofman T. Influence of alkyl chain length and temperature on thermophysical properties of ammonium-based ionic liquids with molecular solvent. The Journal of Physical Chemistry. B. 2012;**116**(15):4561-4574

[52] Govinda V, Attri P, Venkatesu P, Venkateswarlu P. Evaluation of thermophysical properties of ionic liquids with polar solvent: A comparable study of two families of ionic liquids with various ions. The Journal of Physical Chemistry. B. 2013;**117**(41):12535-12548

[53] Abay HK, Svartaas TM. On the kinetics of methane hydrate formation: A time-dependent kinetic rate model. In: Proceedings of the 7th International Conference on Gas Hydrates. Edinburgh, Scotland, United Kingdom: 2011

[54] Makogon YF. Hydrates of Natural Gas. Tulsa, Oklahoma: Penn Well Books; 1981. 125p

[55] Servio P, Mahajan D. Kinetic reproducibility of methane production from methane hydrates. Preprints of Papers—American Chemical Society, Division of Fuel Chemistry. 2003;**48**(1987):881-882

[56] Hong SY, Il LJ, Kim JH, Lee JD. Kinetic studies on methane hydrate formation in the presence of kinetic inhibitor via in situ Raman spectroscopy. Energy & Fuels. 2012;**26**: 7045-7050

[57] Koh CA, Sloan ED, Sum AK, Wu DT. Fundamentals and applications of gas hydrates. Annual Review of Chemical and Biomolecular Engineering. 2011;**2**:237-257

[58] Daraboina N, Ripmeester J, Walker VK, Englezos P. Natural gas hydrate formation and decomposition in the presence of kinetic inhibitors. 3. Structural and compositional changes. Energy & Fuels. 2011;**25**:4398-4404