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► To cite this version:

Ihtisham Ul Haq, Ali Qasim, Bhajan Lal, Dzulkarnain Zaini, Khor Siak Foo, et al.. Ionic liquids for the inhibition of gas hydrates. A review. *Environmental Chemistry Letters*, In press, 10.1007/s10311-021-01359-9 . hal-03616013

HAL Id: hal-03616013

<https://hal.science/hal-03616013>

Submitted on 25 Apr 2022

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Ionic liquids for the inhibition of gas hydrates. A review

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Abstract

In the recent years, application of ionic liquids in flow assurance has been enhanced due their potential as viable candidates for chemical mitigation of gas hydrates. Such clathrate compounds, in which gas molecules are trapped in hydrogen bonded cages formed by water molecules, comprise a major part of flow issues in pipeline conditions of low temperatures and higher pressures. Their formation can cause plugging, thereby disrupting the normal oil and gas flow. One flow assurance strategy consists in injecting different chemicals acting as gas hydrate inhibitors (GHIs). Ionic liquids have a strong potential for this application. Therefore, challenges, issues and current trends on their use as GHIs have been discussed in detail. Contrary to usual GHIs, Ionic liquids can act both as on thermodynamic (THI) and kinetic (KHI) hydrate inhibitors (as well as anti-agglomerates). This dual functionality of ionic liquids is advantageous for gas hydrate mitigation. In preceding open literature, the studies on the applications of dual functional behavior of ionic liquids for mixed gases are found to be limited. The discussion on mixed gas hydrates behavior is novel and the factors influencing are highlighted. It is found that imidazolium based ionic liquids have been studied frequently in THI and KHI applications for pure CO₂ and CH₄ hydrates as their performance is better. While in the case of mixed gas hydrates, only quaternary ammonium salts have been studied yet. They showed better performance in terms of THI and KHI. Furthermore, the prospects of the use of ionic liquids in gas hydrate inhibition applications in flow assurance are also considered.

Keywords; Flow assurance; gas hydrates; ionic liquids; kinetic hydrate inhibitors; thermodynamic hydrate inhibitors.

1. Introduction

In 2010, the Deepwater Horizon disaster which is considered the largest marine oil spill ever, started with fatal explosion which took the life of eleven men. A recent research work on the cause

of this explosion [REF] suggest that gas hydrates played a central role in these tragic events. Also known as gas clathrate, gas hydrates are a long known cause of fluid flow assurance issues in the petroleum industry. These ice like solid compounds can form in pipelines and cause plugging. They result from the contact between the natural gas components and water molecules present in the pipeline under certain conditions of pressure and temperature. Water molecules form hydrogen bonded crystalline lattices in which gas molecules are encaged [REF]

Carbon dioxide and methane are commonly hydrates forming gases under the thermodynamically suitable conditions. Other than these gases, ethane, propane and butane can also form hydrates during routine pipeline operations [1][2]. The favorable conditions of hydrate formation are at low temperature and high pressure. Gas hydrates pose problems in the deep sea as well as the permafrost zones. Most natural gas hydrates reserves exist in deep sea. It is estimated that about 97% of hydrate content resides in the undersea hydrate residues [3][4]. Gas hydrates acquired huge consideration both academically and industrially for several reasons. Firstly, amount of enormous energy potential hotspot recommended that the quantity of energy secured in hydrate form is double to that all other forms of fossil fuels energy all across the planet [5]. In addition, gas hydrates are not suitable for climate and environmental system sustainability, when huge amount of methane gas is discharged unexpectedly from hydrate reserves [6][7]. Moreover, many suitable engineering applications are under research using gas hydrate as a convenient technology for example, sea water desalination [8][9][10], hydrate-based carbon storage and capture [11] [12], natural gas storage and delivery [4], hydrogen storage and advanced air conditioning system [13]. When it comes to the occurrence of gas hydrate within the treatment and transportation of hydrocarbons, they are not preferred. Since, the formation of hydrate is deemed an industrial nuisance and may cause several difficulties for instance, the gas pipeline congestion/ blockage, unexpected production shutdown/losses and unendurable economical loss, in addition threatening to personal integrity [14][15]. Gas hydrates are formed more quickly as the drilling activities move

deeper into sea water because of the harsh subsea conditions of colder water (higher pressure and low temperature) [16,17]. Therefore, different strategies for the mitigation of hydrates and their treatment in the hydrocarbon transmission line is more problematic and vital for safe operation [18][19]. There are various kinds of methodologies implemented for avoidance and treatment of hydrate in oil and gas industry is shown in **Figure 1**.

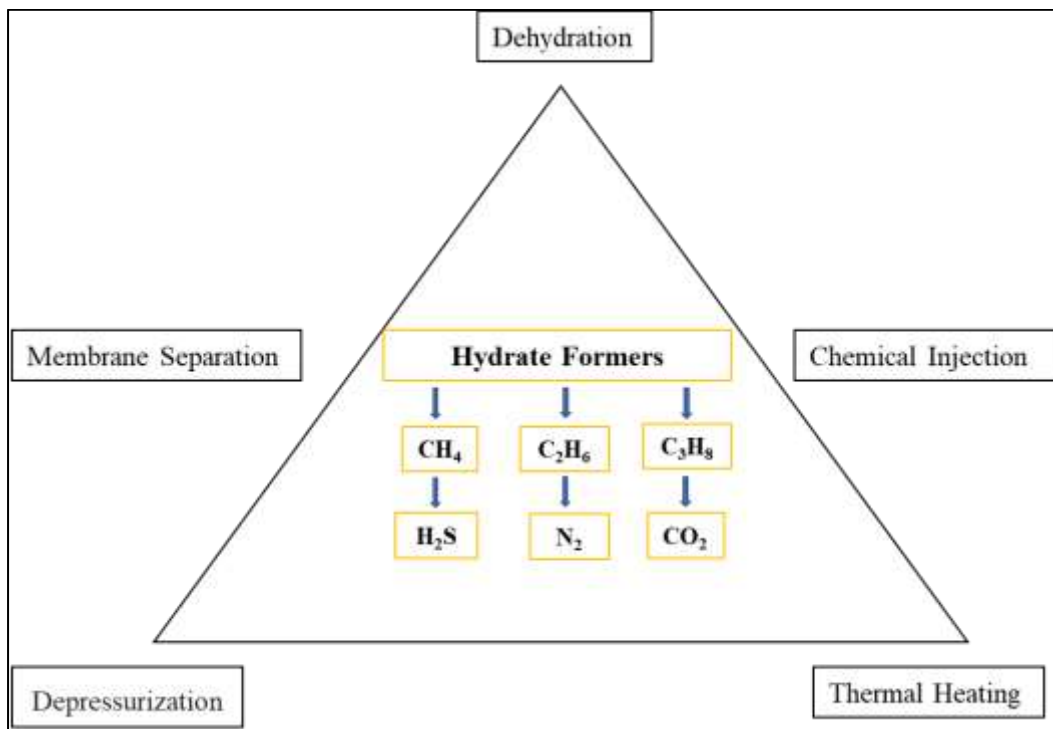


Figure 1. The gas hydrate mitigation strategies described in literature. The present review focuses on the injection of chemicals, including ionic liquids.

By reducing the pressure or heating up the fluid line, the system is kept out of the hydrate zone. In most of the cases, such strategies may not ideal or practical particularly in deep ocean environment [20]. The reduction of pressure and increment of heating to cope with formed hydrate can even pose a threat to personnel safety as well as system facilities significantly, if improper temperature control is taken or an inaccurate depressurization area [21,22] [23]. As an alternative, dehydration is suggested which is the most effective way to for hydrate development as the amount

of water in hydrate is about 85 percent, there is no probability of hydrate formation when H₂O is fully eliminated from the hydrocarbon flow regime. Practically, there is no such technique that can be implemented to eliminate water from the hydrocarbons stream flow entirely [24]. Apart from all these methodologies, the injection of chemicals known as Gas Hydrate Inhibitors (GHIs) can be a cost-effective and practical approach for hydrate preventive treatment. All other strategies require a huge amount of chemical solvent, in addition, it increases the operating cost and places a detrimental effect on the atmosphere of the oil and gas facilities [25] [26]. Therefore, under many circumstances, such chemical remediation approach is a feasible option industrially [27,28]. Traditionally, three types of GHIs have been researched to prevent issues related to gas hydrate formation [29] [30]. They have different mechanisms of action : thermodynamic hydrates inhibitors (THIs) prevent the formation of hydrates, while kinetic hydrate inhibitors (KHI) only delay their formation , and anti-agglomerants (AA), just keep the hydrate particles small. KHI and AA chemicals are also referred as low dose hydrates inhibitors (LDHIs) since much smaller quantities are required than for KHI chemicals

This review addresses the challenges and recent trends on ionic liquids-based GHIs. It considerer subsequently fundamental aspects of hydrate structure, favourable formation conditions and inhibition performance of ionic liquids critically. In addition, novel routes towards for hydrate formation and their hindrance, are reviewed, and research gap is reported. A detailed discussion concerns the dual potential of ionic liquids as both THI and KHI chemicals..

2. Current trends in gas hydrate formation

2.1 Process optimization

In oil and gas transmission flowlines, water is also accompanied and therefore the flow is multiphase. Due to the presence of water, the formation of gas hydrates at pipeline operational conditions becomes inevitable. Different types of systems in subsea conditions may prevail which

are further classified into four categories [19]. The oil dominating system is the first type amongst these four models. As the name suggests, it is dominated by oil and gas and water are lesser constituents. Another type is gas dominated system in which the quantity of liquid hydrocarbons is small. This particular type is not noticed frequently in practical field applications and this system seldom cause hydrate impediment. It is totally variant from oil dominated system in which they may not dissolve water in the in liquids hydrocarbon phase. The other system is condensate due to high shear action. In this type of system water is suspended in droplets or present as a condensate itself. Finally, high water cut system is another type of flow in flowline. In it, the water percentage can reach up to 70 % and it is immiscible with oil. Gas hydrate formation typically occurs in a mixture of water and slightly dissoluble hydrocarbons [31], when it is subjected to thermodynamic conditions of high pressure and low temperature [32]. These conditions usually vary from 30 to 100 bar in pressure range and 275-285 K for temperature range in subsea pipelines. Referring to **Figure 2** [33], water availability and presence of gases such as CO₂, CH₄, C₂H₆ and C₃H₈ lead to the formation of gas hydrate [34]. Hydrogen bonded water molecules form cages in which the gas molecules are hosted. Meanwhile, the structure of hydrate gets stable with the increment of duration of the guest molecules trapped inside the cages by the action of van der Waals forces [33].

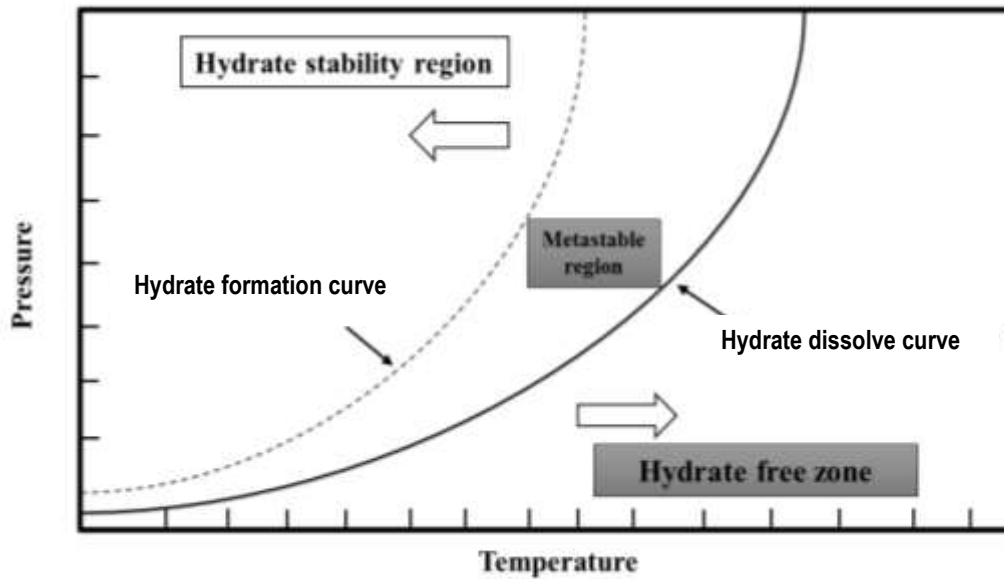


Figure 2: Process optimization of gas hydrate formation curve [33].

2.2 Structures of Gas hydrate

Figure 3 shows three distinct crystallographic structures of natural gas hydrates, also known as clathrate hydrates (from the Latin *clathratus* meaning “lattice”). Gas hydrate structures are categorized into structure I, II, and H abbreviated as sI, sII and sH respectively. Structure I and II consist of cubic structure while sH has hexagonal shape [35]. Hydrate cage structure and cavity size determine the kind of hydrate structure. Apart from this, the type as well as the gas particle structure can be fitted via water demonstrates the hydrate category. Gases such as CH_4 , CO_2 , C_2H_6 , C_3H_8 are commonly encountered in subsea flowlines. The hydrate structures formed inside the pipeline are shown in Figure 3. As the structure I comprises of two distinct cage types: (a pentagonal dodecahedral cage with 12 pentagonal faces), denoted 5^{12} , and tetrakaidecahedral is large cage designated as $5^{12}6^2$ (comprised 12 pentagonal also 2 hexagonal faces. likewise, sII includes the small 5^{12} cages as well as a large hexakaidecahedral cage, designated $5^{12}6^4$ containing 12 pentagonal, 4 hexagonal faces. structure sH is the last one that is made up of small

cages 5^{12} , a medium-sized cage with three triangles, six pentagonal along with three hexagonal faces, in addition, icosahedral is a large cage, connoted as $5^{12}6^8$ including, 12 pentagonal, 8 hexagonal faces. The size of guest molecule impacts significantly on the type of formed structure, as methane can be accommodated more into the small or even large cages of structure I, while propane can produce sII which is too wide to fit into the large cage of sI. However, sII can be adjusted into the large cage of structure II hydrate formation. For structure H, two guest molecules are needed for hydrate formation and stabilization. The ‘sI’ is mostly found in naturally produced gas hydrate reservoirs, since they comprise CH_4 frequently as a guest molecule which make structure ‘I’ hydrate. Nonetheless, in oil and gas transmission line, the found gas hydrate is primarily ‘sII’ hydrates due to the existence of CH_4 and other small quantities of hydrocarbons as for instance, propane, isobutane etc, contacting in natural gas [36][37].

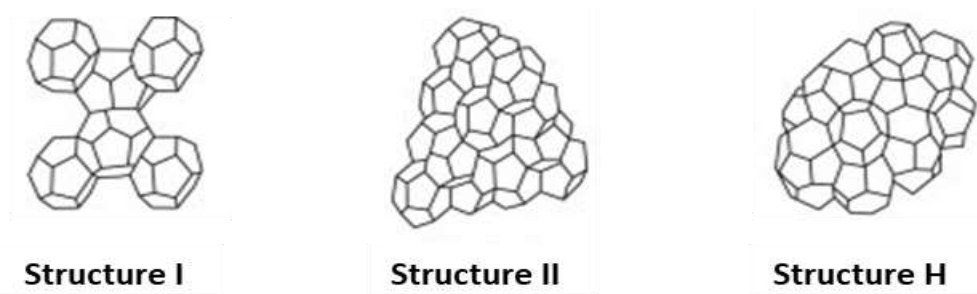


Figure 3. Different crystallographic structures of gas hydrates [37].

The gas hydrate formation comprehension is significant in terms of process economics as well as in safety perspective. In the previous few decades, numerous investigations have revealed that the knowledge of mechanism of gas hydrates can create new avenues for safe hydrocarbon transmission. Based on the above discussion, it is concluded that gas hydrate mitigation study can be examined in further detail and efficient methods need to be developed for the hydrate control in flow assurance applications.

3. Evaluation of THI and KHI chemicals' performances

The thermodynamic hydrate inhibitors [THI] and kinetic hydrate inhibitors [KHI] assessment is generally carried out through experimental methodologies. These involve rocking cell equipment [38], high pressure autoclaves, and other apparatus that can withstand high pressures such as sapphire cell reactors [39] [40] [41]. The formation of gas hydrates inside the flow loop is also currently being studied. The most important parameters for gas hydrate experiments are volume of the solution and gas, temperature and pressure [42]. Along with these parameters, time required for hydrate formation and dissociation is another very important factor to be considered for hydrate inhibition studied. On the other hand, for characterization study, magnetic resonance imaging, RAMAN spectroscopy, magnetic resonance [NMR] spectroscopy and X-ray diffraction have been used [42], [43],[44].

3.1 Thermodynamic hydrate inhibitors (THI)

In order to determine the hydrate aqueous liquid vapor equilibrium temperature T_{HLVE} , an isochoric temperature/T-cycle technique is mostly used by researchers [41][45][46][47]. Initially, in this process, the thermodynamic hydrate inhibitor in a solution is charged firstly into a reactor. After that, the pressure value for which the experiment needs to be performed is set and the gas is infused at that particular condition. It requires some time for stabilization. When the temperature and pressures values become constant, then the reactor temperature is dropped gradually. Hydrate formation is materialized through gradual decrease in temperature value. Sudden pressure drop in the system is the key indicator of complete hydrate formation. In contrast, for hydrate dissociation usually two heating techniques (continuous heating and step heating) are used to find out the measurement of equilibrium points. A slow heating rate ranging from 0.2 to 0.5 K/h is maintained for continuous heating. Whereas the system temperature in step heating technique is incremented

stepwise to about 0.5 K for individual step. The holding time is set to be 4-8 hours to obtain the equilibrium state, consequently, it takes 24-48 hours measuring equilibrium points of hydrate dissociation [46].

Figure 4 schematically shows the typical pressure temperature phase diagram obtained for slow cooling / step heating procedure. The hydrate dissociation point is defined on the pressure temperature phase diagram as the equilibrium point where heating and cooling lines converge [41]. The corresponding T_{HLVE} equilibrium temperature can thus be determined.

When thermodynamic GHI (or THI) chemicals are added to the water / gas mixture, the inhibition effect of the inserted chemicals shifts the equilibrium to the left side of the pressure-temperature (P-T) curve. (T_{HLVE} decreases). The efficiency of the THI is thus quantified by the average hydrate depression temperature [ADT] which is the difference between T_{HLVE} equilibrium temperatures obtained for gas-water hydrates system and gas-water-inhibitor hydrates system.

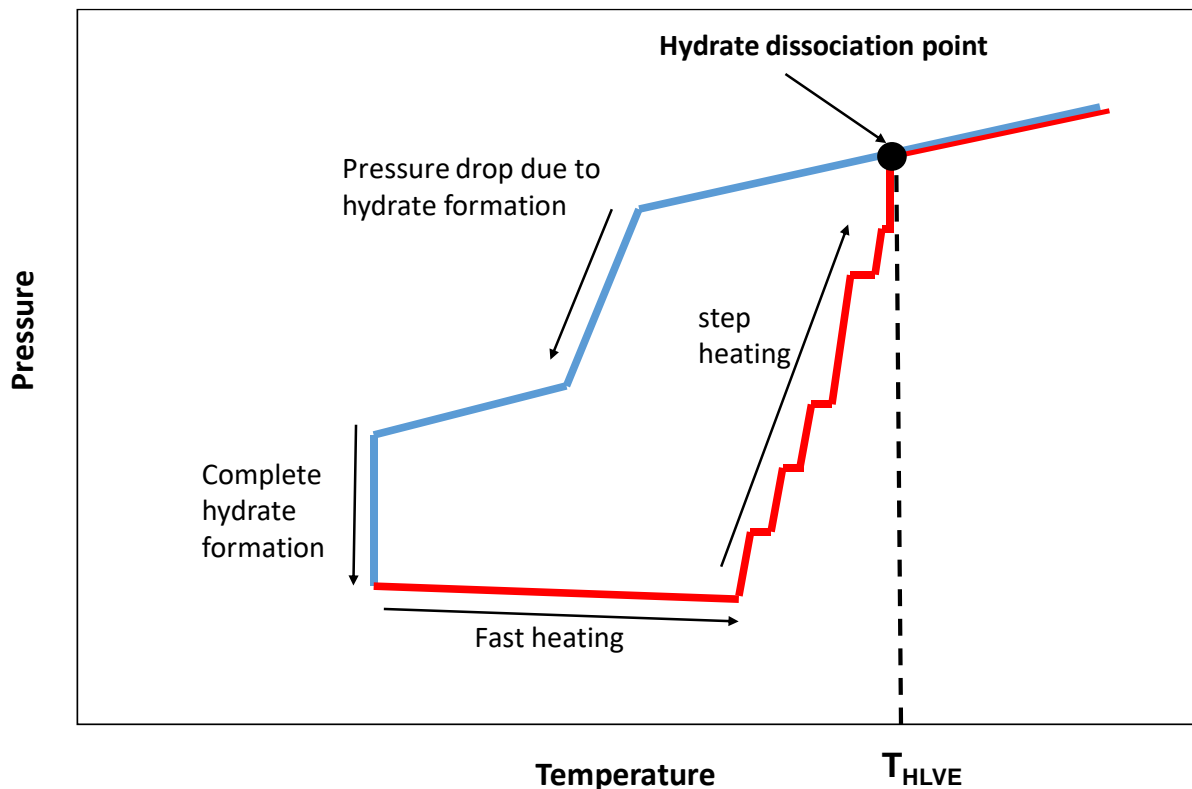


Figure 4. Determination of hydrate dissociation point and hydrate aqueous liquid vapor equilibrium temperature T_{HLVE} , on a standard P-T diagram obtained through T-cycle technique (slow cooling curve in blue and step heating curve in red).

3.2 Kinetic hydrate inhibitors (KHI)

When temperature becomes lower than T_{HLVE} , the typical hydrate crystallization process typically involves first an induction time during which the gas molecules are solubilized in liquid water followed by nucleation and growth of the hydrate particles [REF]

The induction time is used to experimentally quantify KHIs. It is defined as the point where water molecules encage hydrocarbon gas and the process of nucleation is initiated. The thermodynamic conditions favour the generation of nuclei during induction in the system under consideration [48]. The suitability of pressure and temperature is a crucial factor in KHI. The nucleation and crystallisation of hydrates are probabilistic and stochastic processes. As a result, there are some degree of uncertainties in experimental results and screening but as repeating the experiments in comparable conditions can reduce the uncertainties because it confirms the potential performance of KHI. The majority researchers have used the constant cooling method to determine the induction time. However, hydrate formation in pipelines can be avoided by having a precise understanding of the induction time. Stirring rate and degree of sub-cooling are crucial parameters in induction time control [49].

Dues to these experimental issues, in order to quantify the KHI efficiency , the Relative Inhibition Power (abbreviated RIP) is preferred to the raw induction time [50][51]. It is defined as follows : [51].

$$RIP = \frac{T_i - T_o}{T_o} \quad (1)$$

Where T_i stands for the induction time in presence of KHI and T_o denotes the induction time without inhibitor.

The memory impact is another significant parameter in KHI studies that is linked to hydrate history. The maintenance of hydrate structure in a solution is attributed to memory effect. The solution with memory effect is more likely to form hydrate swiftly than a fresh solution, it is therefore, an important factor in reducing the induction time. For the gas sector, it has significant implications for instance, the hydrate begins to form, if the transmission is without using KHI. Once the hydrate is dissociated, the water needs to be removed. In the event where water removal is not possible, the hydrate plug has more chances of quick reformation. The memory effect can be avoided by using a fresh sample for every run of experiment. Furthermore, induction time at a given pressure is also affected by sub-cooling temperature. In KHI investigation, the temperature for sub-cooling plays a very important role. It is the difference between theoretical HLVE temperature value and experimentally determined equilibrium temperature. A kinetic inhibitor's induction time should be at least so long as the gas stream's residence time in the pipeline [52].

4. Challenges with gas hydrate inhibitors

4.1 THI inhibitors

Mostly organic solvents such as methanol, polyethylene glycol, polyethylene oxide, and certain conventional salts as an instance, NaCl and KCl are used as thermodynamic gas hydrate inhibitors. The thermodynamic hydrate suppressors cause the phase boundary of hydrates to move toward a lower temperature and higher-pressure phase. As a consequence, they can preclude the development of hydrates. [53],[54],[55].

Basically, organic based chemical substances impart interference of water activities via hydrogen bonding ability among H_2O molecules. The presence of hydroxyl (OH^-) groups in organic

solvents like as ethylene glycol and alcohols offer hydrogen bonding capacity, as illustrated in **Figure 5**. Conventional salts such as KCl and NaCl effectiveness is due to coulombic effect. The presence of anionic and cationic moieties in these chemicals are responsible for the coulombic effect. It is caused by charge particles that contribute a crucial role in disintegrating the hydrogen bonds of the crystal structure of water molecules. To maximize the amount of charged ions, more hydrogen bonds between gas and water molecules are disrupted., resulting in increased hydrate inhibition [56] [57].

Koh and co-workers [58], presented an excellent illustration of an oilfield in Gulf of Mexico which is 80 kilometre in length from the wellhead to the downstream. They used traditional thermodynamic inhibitor, methanol, and filled it at varying percentages by mass into the natural gas pipeline to ensure that the operation state is to delay the hydrate formation zone. The methanol inhibitory effect shifts the equilibrium from hydrate forming domain to a region which is free of gas hydrates [58], [28]. In this way, it affects the hydrate stability zone. On the contrary, in oil and gas production activities, a large volume of produced water is generated, which comprises of several distinct salt species in varied mass percentages. The presence of salt species can act as preventative agent as it diminishes the potential of the gas formation.

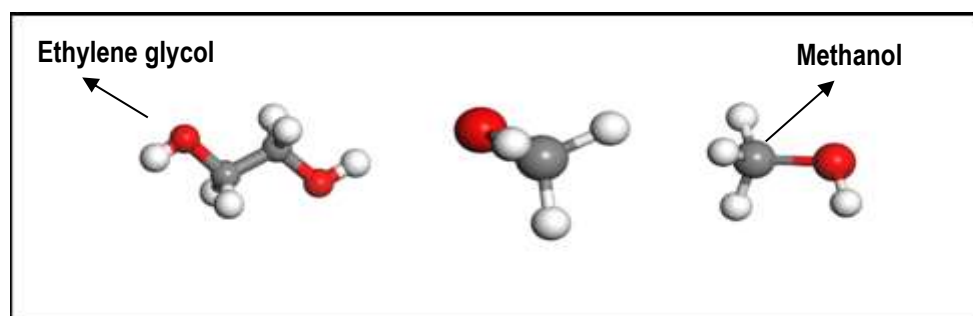


Figure 5. Mono ethylene glycol and methanol structures.

Contrastingly, salty water constraint is deficient, thus, water solutions containing organic-based inhibitors such as as mono ethylene glycol (MEG) and methanol are fed into long flat

conduits. The presence of shorter alkyl chain and hydroxyl moiety, MEG is considered to be an effective THI in offshore applications of flow assurance. In comparison to methanol, mono ethylene glycol is most commonly utilised in the petroleum industry as it has a higher density and lower volatility. THIs are used in high concentrations often up to 40 wt% [59]. Currently the use of conventional THIs is proving costly to flow assurance industry in terms of chemical consumption. Methanol coupled with LPG, propane, and mixed butane constituents, according to John, produces azeotropes, which are difficult to extract using a simple approach. Methanol applications may also cause corrosion issues, making these compounds more expensive and environmentally unfavourable [25]. As a result, in the 1990s, low-dose hydrate inhibitors were developed [LDHIs] that comprise kinetic inhibitors (KHIs) and anti-agglomerates (AAs).

4.3 Low dosage hydrate inhibitors

LDHIs were first employed for gas hydrate mitigation applications in Russia in 1970s in a natural gas field. They were used in the aftermath of commercialized surfactants in relatively small amounts on petroleum reservoirs, and thus the gas hydrates problems were promptly rectified [60]. Meanwhile, as the hydrate prevention mechanism was not complicated, in this approach the discovery of LDHIs were developed in the early 1990s.

The advanced hydrates obstruction strategies are transitioning from hydrates mitigation to handling by using LDHIs. LDHIs are employed in small quantities, especially (0.5-0.2) mass fraction of water cuts; consequently, the benefits of low dosage inhibitors over high dosage inhibitors are as follows: they are moderately lower in cost and optimize production, take up less space on production platforms, and are more environment friendly contrasting with THIs. Therefore, they can also be used with certain other treatment chemicals [14]. The processing of methanol in refineries usually cost up to an extra of \$2/bbl [61]. The use of LDHIs will decrease the methanol consumption as a THI or act as its replacement. In terms financial and operational expenditure, the use of LDHIs is beneficial as they are used in lower concentrations, which gives

them preference over THIs. Also, LDHIs are relatively benign as well. Economical LDHIs include KHIs and AAs. They are mostly water-soluble polymers and surfactants [62]. The detailed discussion is presented in following sections.

4.3.1 Kinetic hydrate inhibitors (KHI)

The use of KHIs in industry has been going on since 1995, and their gas hydrate inhibition efficiency is attributed to form H-bonding with water molecules. Hydrogen bonding suppresses hydrate formation by slowing the hydrate induction/nucleation duration [63],[50]. KHIs are polymers with water dissolution abilities, such as PVCap and PVP, that are typically utilised at concentrations i.e. less than 2 wt.%. Biomolecules, anti-freezing proteins, and ionic liquids (ILs) are also employed as KHI [64].

Sloan et al. 1998 [65] reported binary KHIs methods, and it was found that these chemicals restrict hydrate particles growth to materialize fully by disrupting the local water structure through hydrophobic interlinkages [66]. Additionally, the kinetic hydrate inhibitors may impede any hydrate growth by interacting with the freshly grown crystal of hydrate. KHIs' alkyl chains replace the incoming gas molecule as acts as their counterpart in action. They mix and attach onto the hydrate surface with accessible free cavities. PVP molecules demonstrate adsorbing on crystals of methane gas hydrate with hydrogen bonds at hydrate development sites upon contact [67]. As it is clearly apparent that PVP follows the suggested process [68], it accumulates on water's open pores, providing steric deterrents to water and gas inter-linkages by hydrophobic interactions.

The operational pressure and subcooling temperature are the most important factors in terms of KHI effectiveness. KHIs frequently act poorly at greater subcooling pressures. At higher subcooling temperatures, usually the performance of KHIs is depreciated. In deep-water scenarios, the sub-cooling temperature reaches up to 7 to 10 K [36]. Moreover, KHIs improve as hyper-stretched polymers, which are quite non-hazardous, cheaper, and biodegradable KHIs [PVCap or

PVP]. Anti-agglomerates [AAs] also consist of long chain polymeric compounds. In one scenario, they can be produced by combining dialkanolamine and anhydride. It allows of a polymer having a $[\text{OH}^-]$ group at the front ends. The hyper-branching in the polymer being generated by the three reactive groups of dialkanolamine. Furthermore, with addition of third molecule, e.g., an auxiliary amine to the blend reaction, the polymer ends show electronegative behaviour and inhibit hydrate materialization. It is, however, proven that KHI, such as PVCap, decreases the commercial cost of hydrate inhibition over methanol by 16 percent to 50 percent. But on the other hand, when extremely subcooled, these KHIs are environmentally misanthropic and inefficient.

4.3.2 Anti-agglomerates (AAs)

Surfactants have been used as AAs in industrial offshore applications. Quaternary Ammonium Salts (QAS) are typically used AA compounds. QAS are employed as AAs due to the presence of long chains in the cationic structure and these compounds possess both hydrophobic and hydrophilic ends. Cation is hydrophobic and anion is hydrophilic. The anion forms bond with water ends; however, in the oil and natural gas regimes, the cation is dissolved and disintegrated. The action of anti-agglomerants as hydrate disintegrating agents makes them valuable in the field application particularly in the environment where hydrate formation inside the pipeline is not bothered as long as they are small in size to threaten safe operation. Among QAS, n-butyl, n-pentyl, and isopentyl groups were used by Shell Oil Company in 1993. These salts showed enhanced anti-agglomeration capabilities [69]. In QAS category, Tetrapentylammonium bromide (TPAB) has shown anti-agglomerant properties also [69]. Moreover, twin-tailed quaternary AAs are being utilized which comprise of tetraalkylammonium salts. Amongst the salts, the Dutch shell group evaluated dicocoyldibutylammonium bromide, that was significantly more applicable for the industry. However, it did not perform up with the desired expectations in terms of biocompatibility.

Huo et al. 2001 [70], investigated the use of commonly available surfactants which were Sorbitan based compounds comprising of Span 20-80. The findings showed that the investigated salts could retain the hydrate particles suspended at 277 K and 8.20 MPa.

Despite the substances that were synthesised, well disbandment was observed at a relatively high cut phase, as an example, 0.75 wt. percent. Kelland et al. 2001 [71], worked on developing efficient LDHIs for the oil exploration and production industry, expanding the AAs study with the use of polypropoxylyates. In well-agitated scenarios, polyamine polypropoxylyates as well as its branches affected gas hydrates to scatter inside flowlines.

AAs have been investigated to expand the LDHI sub-cooling range to that of KHIs. AAs permit their formation at certain rates, on the contrary, KHIs postpone the hydrate formation. AAs act as to disperse the hydrate crystals in oil phase by breaking them into very small size. The development of AAs is considered in terms of extension of the subcooling temperature higher than that of KHIs. Although, KHIs fundamentally postpone hydrate formation, but on the other side, AAs allow the formation of gas hydrates. The gas hydrates form at the normal rate in the presence of AAs. The formation of hydrate crystals is miniscule as they are disintegrated inside the oil system thus avoiding large crystal accumulation. Due to some limitations regarding water salinity, water cut, emulsification and de emulsification. the water cuts are supposed to be less than 50% otherwise, at larger cuts of water can render AAs inefficient due emulsion formation. According to the latest literature review, ionic liquids and their various types are applicable in hydrate reduction practices owing to dual functionality.

5. Current trends in ionic liquids (ILs) based gas hydrate inhibitors

The ionic character of these liquids, on the other hand, gives a variety of innovative and exciting physicochemical features that enable a variety of applications. With relation to inorganic,

organic, and organometallic compounds, some of the fundamental qualities of practically all ionic liquids include being very thermally stable, having a low vapour pressure, being non-combustible and having a high dissolvent potential [72]. The various cation structures are relayed on. As a result, ionic liquids can be divided into many families, including imidazolium, phosphonium, pyridinium, ammonium, thiazolium, and triazolium.

One of the most appealing features of ILs is their ability to structure or create them for specific functions, especially intermingling with additional eminent traits, like low vapour pressure, in comparison to molecule counterparts. Due to non-volatile nature of ILs, these compounds exhibit better performance in comparison to some typical natural solvents. The other advantages of the use of ILs include low toxicity due to being eco-friendly and non-flammability. These properties render their use in a variety of applications [73]. The tuneable characteristics of ILs render them advantageous as they can make hydrogen bonds in aqueous solutions [74]. Pertaining to above-mentioned clarification, the unique feature of ILs have got interest in a wide range of industrial applications, including fuels energy and fuels, solvent catalysts and processes, electrochemical applications, and biomass conversions [74],[75]. Furthermore, ILs are being considered as a feasible alternative to traditional gas hydrate inhibitors [GHIs]. ILs have demonstrated an excellent potential to act as dual gas hydrate inhibitors due to the hydrogen bond forming capabilities [76],[77]. Because of the thermodynamic hydrate barrier, ILs must be hydrophilic in their nature. If ILs show hydrophobicity, then they will exist as a separate distinct phase in the solution and not participate in hydrogen bonding with water. Moreover, particular function groups in the ionic liquids structure, like the hydroxyl [OH⁻] and oxygen [O⁻] groups, affect the intermolecular disruptions with water molecules, thereby inhibiting hydrate nucleation [8]. Nevertheless, ILs can be employed as THIs as well as LDHIs in the presence of CH₄, CO₂, and mixed gas hydrates impediment. [76] [78] [79]. A detailed study on ILs is done in the following sections.

5.1 Ionic liquids based THIs for CH₄ gas hydrate.

Imidazolium based ILs are kinetic inhibitors for the methane + water hydrate forming system as well as thermodynamic inhibitors. The studied Ionic liquids were continued with the anions included tetrafluoroborate, dicyanamide, trifluoromethanesulfonate, ethylsulfate, chlorine, bromide, and iodide, while the cations included 1-ethyl-3-methylimidazolium, 1-propyl-3-methylimidazolium, and 1-butyl-3-methylimidazolium. Besides, Li et al. 2011 [80] detailed the equilibrium data for the CH₄ hydrate in the presence of five different chloride anion-containing ILs: 1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-hydroxyethyl-3-methylimidazolium, tetramethylammonium, and hydroxyethyl trimethylammonium. Partoon et al. [81], tested the influence of [Emim]Cl and 1-hydroxyethyl-3-methylimidazolium chloride [OH-c₂mim]Cl as THIs for CH₄ hydrates Employing Hydreval . So, the [OH-c₂mim]Cl inhibited CH₄ hydrates greater than [Emim]Cl at 1wt%. Furthermore, they determined that at pressures greater than 7MPa, the impacts were stronger. While evaluating the CH₄ hydrates stability line data with 5% salts in aqueous solutions to particular ILs, this was revealed that the salts seemed to have a substantially larger thermodynamic inhibitory impact than the ILs, which was due to the lower concentration of the ionic liquids. **Table 1** shows the performance of various ILs for gas hydrate formation.

Table 1. THI for CH₄ hydrates system using ionic liquids.

Name of ILs	Chemical formula	Concentration (wt.%)	ILs Test	(ΔT) K
1-ethyl-3-methylimidazolium bromide	[Bmim]Br	0.10 mf	THI	0.75
1-ethyl-3-methylimidazolium chloride	[Bmim]Cl	0.10 mf	THI	0.88
1-ethyl-3-methylimidazolium perchlorate	[Bmim][ClO ₄]	0.10 mf	THI	0.37
1,3-dimethyl-imidazolium iodide	[Mmim]I	0.1 mf	THI	1.00
1-ethyl-3-methyl-imidazolium iodide	[Emim]I	0.1 mf	THI	0.96
1-ethyl-3-methyl-imidazolium chloride	[OH-C ₂ mim]Cl	0.1 mf	THI	0.99
Tetra-methyl ammonium chloride	[N _{1,1,1,1}]Cl	0.1 mf	THI	0.95
1-ethyl-trimethyl-ammonium chloride	[N _{1,1,1} , eOH]Cl	0.1 mf	THI	0.95
1-(2-hydroxyethyl) 3-methylimidazolium chloride	[OH-Emim]Cl	5-25	THI	1.32
1-(2-hydroxyethyl) 3-methylimidazolium bromide	[OH-Emim]Br	5-25	THI	0.92
1-ethyl-3-methyl-imidazolium chloride	[Emim]Cl	5-40	THI	4.80 (at 40 wt.%)
1-ethyl-3-methyl-imidazolium bromide	[Emim]Br	20	THI	2.70
1-ethyl-3-methyl-imidazolium bromide + 1-ethyl-3-methyl-imidazolium chloride	[Emim]Br + [Emim]Cl [1:1]	20	THI	3.70
1-ethyl-3-methyl-imidazolium chloride + Monoethylene glycol	[Emim]Cl + [MEG] [1:1]	10-30	THI	8.00 (at 30 wt.%)
1-ethyl-3-methyl-imidazolium chloride + Sodium chloride	[Emim]Cl + [NaCl] [1:1]	10	THI	3.80
Tetramethyl-ammonium hydroxide	[TMAOH]	10	THI	1.52
1-ethyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	0.20 mf	THI	1.00
Tetraethyl-ammonium chloride	[N _{2,2,2,2}]Cl	0.10 mf	THI	0.30
Tetra-methyl ammonium chloride	[TMAB]	10	THI	1.34
Tetra-ethyl ammonium bromide	[TEAB]	10	THI	1.07
Tetra-ethyl ammonium iodide	[TEAI]	10	THI	0.82
Tetra-methyl ammonium bromide + Mono-ethylene glycol	[TMAB] + [MEG]	10	THI	2.36

Sabil et al. 2015 [56] reported nine distinctive aqueous imidazolium based ILs solutions at pressures ranging from 3.6 to 11.2 MPa. The electrical conductivity and pH of these aqueous solutions of ILs were measured as to correlate their performance as hydrate inhibitors with other physical properties. It was demonstrated from the findings that all the nine ILs have ability to act as thermodynamic hydrate inhibitor by moving the hydrate equilibrium curve till $T = (0.37 \text{ and } 1.32) \text{ K}$, respectively. Among the studied ILs the [OH-Emim]Cl was the most effective. Chu et al. 2016 further explored the alkyl chain impact of various imidazolium based ILs. It was indicated from the findings that the greater inhibition impact is achieved when the alkyl chain is shorter [82]. Furthermore, Long et al. [83] studied the phase equilibrium conditions of CH_4 in the sight of imidazolium based ILs and their blend namely, 1-ethyl-3-methylimidazolium nitrate, 1-ethyl-3-methylimidazolium chloride pressure ranging from 35 bar to 150 bar by using T-cycle method. It is revealed that the inhibitory impact of all the systems including [Emim][NO_3], [Emim]Cl increments with high concentration and pressure.

At low concentration, the inhibition effect is found to be less significant. In another analysis, Menezes et al. 2020 [84], explored the effectiveness of [Bmim]Br and [Bmim]Cl for CH_4 hydrates at high pressure. The findings revealed that both additives act as THI, the results were further compared with methanol which shows that at lower concentration these solvents acted as promoters, but as increasing the concentration of ILs all of them inhibit the hydrate growth, particularly [Bmim]Cl. Xiao et al. 2010 also found the dual functional effectiveness of other halide anions apart from chloride anion in combination with imidazolium-based compounds for CH_4 hydrates inhibition [2]. Their efficacy was observed in both THI and KHI investigations. The influences of these compounds on hydrate stability curve changes and induction time of methane hydrates development were studied using calorimetric method. In this regard, differential scanning calorimetry (DSC) was employed. Also, their study indicated that ILs had strong positive and negative charges. Hydrogen bonding of these compounds with water is easier to occur in the

presence of strong charges. This propensity allows them to alter their H–L–V phase of stability to a low temperature at a certain pressure, slowing hydrate nucleation rate. On the contrary, contrarily, due to strong surfactant phenomenon, surfactants reduced the pace of hydrate nucleation formation. They decided to expand the study to six Dialkylimidazolium halide ILs in another article and found that [Emim]Cl had the best THIs of all.

Sulaimon et al. 2020 [85], very recently studied the three innovative ILs, 1-ethyle-3-methylimidazolium dihydrogen phosphate, [1-(3-cyanopropyl)-3-methyl imidazolium hydrogen phosphate] and [1-butyle-3-methyl imidazolium dihydrogen phosphate] as both THIs and KHIs for CH₄ hydrate, the result revealed that all the studied ILs were able to avert the HLVE Curve to lower temperature below the hydrate formation temperature, at the same time, they were decreasing the hydrate nucleation growth rate [85].

Initially, Li et al. 2011 [80] reported the effectiveness of tetramethylammonium chloride and dialkyl imidazolium chloride on methane hydrate prevention, which disclosed better impediment amongst the ILs studied for CH₄ hydrates. Likewise, Keshavarz et al. 2013 [86], performed both computational and research investigation on [TEA]Cl based ILs, achieving a hydrate HLVE point of 0.72 K. Results showed that all evaluated AILs displayed CH₄ hydrate thermodynamic suppression at high pressures. However, the inhibitory impact dropped by all accounts at 7.0 MPa, and a small proportion of ILs functioned as gas hydrates promoters. In addition to analysed AILs as for instance, tetramethylammonium acetate was shown to be an excellent THI, whilst choline octanoate was found to be an effective KHI [87].

Choline based IL were also investigated for hydrate inhibition with methane by Mohamed et al [REF] who insisted on the fact that this cation is biocompatible. The highest efficiency (ADT= 0.8K) was obtained for Choline Actetate which is well known as an environmental friendly IL.

Khan et al. 2019 recently determined the effects of AILs like tetraethylammonium chloride [TMACl] on the stability of CH₄ hydrates, finding that [TMACl] at 10 wt.% reduced the temperature by 0.9 K, the effect of ILs depends on length of the alkyl chain, the smaller the alkyl chain, the larger the inhibition influence [88]. **Figure 6** illustrates the alkyl chain length of ILs at a concentration of 10 wt. percent on CH₄ hydrate liquid vapour [HLVE]. In our previous work [89], research on quaternary ammonium salts (QASs) as THI for CH₄ hydrates was conducted and it was discovered that the inhibitory impact of QAS increases with increasing the concentration, in addition, better inhibition performance is observed in the shorter alkyl chain length (cations + anions) of tested QASs. Furthermore, the ammonium salts are compared with methanol and glycols as they are commercial THIs.

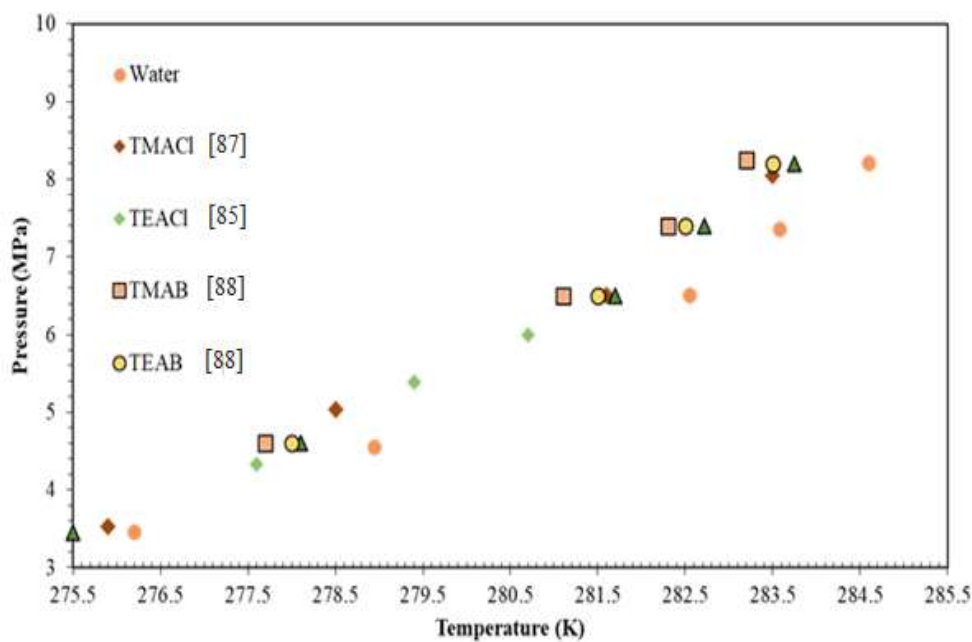


Figure 6. The influence of alkyl chain length of ILs at 10 wt.% concentration on phase behaviour of CH₄ hydrates.

5.2 Ionic liquid based THIs for CO₂ gas Hydrate.

Ionic liquids for CO₂ gas hydrate inhibition have significant impact as the ionic moieties present in their structure disrupt hydrogen bonding in aqueous solution. In this regard, Hu and co-workers studied the mitigation performance of ionic liquids from imidazolium family for CO₂ hydrates control. Different types of anions were examined with imidazolium cation including chloride and tetrafluoroborate anions. The performance of chloride ion was found to be better than tetrafluoroborate ion. It is due to the reason that chloride ion is more electronegative than tetrafluoroborate thus imparting higher inhibition effect. The degree of inhibition was found to be a dependent variable of the hydrogen bonding disparity between inhibitors and water molecules. Chen et al. 2008 [90] discovered 1-butyl-3-methylimidazolium tetrafluoroborate to be a good THI for CO₂ hydrate control. This shows the potential benefit of using ILs as THIs in practical applications due to their benign and environment friendly nature. The hydrate inhibition impact of ionic liquids originating from phosphonium family was predicted through thermodynamic modelling by Tumba et al. 2011 [91]. They modelled the THI effect for methane and carbon dioxide hydrates.

On the other hand, the investigated hydrate phase equilibria for CO₂ hydrate were H-LW-V_{CO₂} region. The transportation of CO₂ inside the pipeline is in liquid state and it operates under severe conditions of elevated pressures and lower temperatures, so the hydrate equilibrium data at relatively less pressure is not significant for practical purposes. For this purpose, in order to implement CCS operations in field, the HLVE data at higher pressure ranges is suitable. Besides, the previous research described above centred on traditional ILs as hydrate formation inhibitors. Even at low concentrations, the presence of hydroxyl or oxygen groups delayed methane hydrate formation, but their thermodynamic inhibitory effects were restricted. Furthermore, Shen et al. 2015 [92], synthesized pyrrolidinium-based ILs to enhance the THI influence on CO₂ hydrate, the result indicates that at the set pressures ranging from 50 to 200 bar with loading compositions of

CO₂, water and IL, the temperatures of the three-phase equilibrium [H–LW–LCO₂] involving CO₂ hydrate was determined. The CO₂ hydrate dissociation temperature was reduced by 0–1.75 K in aqueous solution containing 9 wt.% ILs, depending on anion type and molar mass. It was found that the IL cation had a minor impact on thermodynamic inhibition of CO₂ hydrate, while the anions were the most important factor in enhancing the IL inhibitory capacity.

Among the ILs analysed in this study, Chlorine Cl had the most powerful thermodynamic inhibitory impact.

Cha et al. 2016 [93] studied the phase equilibrium boundary of CO₂ in the presence of four types of ILs (morpholinium and piperidinium) namely, N-ethyl-N-methylmorpholinium bromide [Bmim]Br, N-ethyl-N-methylmorpholinium tetrafluoroborate [Emim][BF₄], N-ethyl-N-methylpiperidinium bromide [EMPip][Br], N-ethyl-N-methylpiperidinium tetrafluoroborate [Emm][EmPip][BF₄). The outcomes revealed that the phase boundary had moved into higher pressure, lower temperature zone, which is also known the hydrate free region. These two ILs had almost identical inhibition effects at higher temperatures. The piperidinium ILs, on the other hand, had a slightly stronger inhibitory impact as the temperature dropped, morpholinium ILs performed better than morpholinium ILs. Khan et al. 2017 [45], determined the influence of ammonium based ILs for CO₂ hydrates system, among the tested AILs at various concentration, Tetramethyl ammonium hydroxide-based IL [TMAOH] was observed with better inhibition influence, this better performance is achieved due to shorter alkyl chain length of [TMAOH] as well as the hydroxyl radical. In our previous work [94], it has been found that the tendency with QASs study for CO₂ hydrates as smaller alkyl length (cationic moiety) of ILs play better THI and the thermodynamic inhibition is also depending on anionic moiety of ILs specially the hydroxyl group (OH) which create strong hydrogen bonding with water molecules as shown in **Figure 7**.

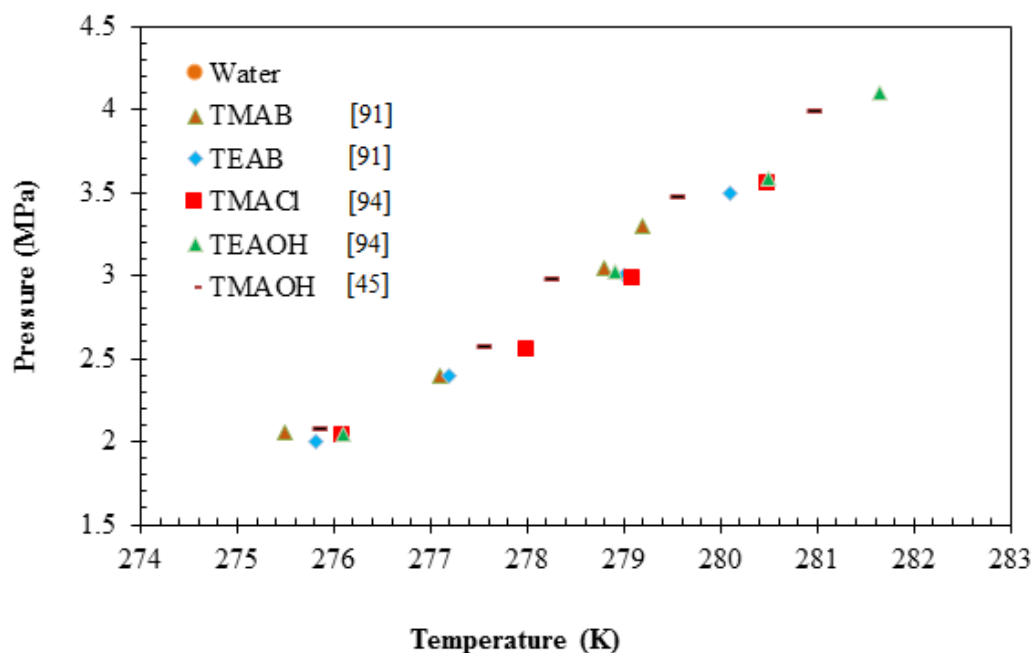


Figure 7. Alkyl chain length of ILs at 10 wt.% concentration on hydrate liquid vapour [HLVE] curve of CO₂ hydrates [44, 94, 97].

Hydrate inhibition is affected with the alkyl chain length of ILs. ILs with having short alkyl length possess superior hydrate hindrance capacity as compared to longer chain length of ILs. However, the effect of anionic moiety of ionic liquids also better work in gas hydrate impediment, since the anion moiety is certainly creating hydrogen bonding with H₂O molecules. Meanwhile, investigations on ionic liquids in CO₂ system are relatively limited. In addition, the study on distinct types of ionic liquids is confined. Further research is needed on other types of ionic liquids for carbon dioxide hydrates. Since, the CO₂ hydrate formation occurs rapidly in oil and gas pipeline as the compared to CH₄ hydrates, it is due to difference in molar mass of both gases although CO₂ and CH₄ reciprocally make structure I. **Table 2** summarizes the performances of ILs for CO₂ system, as well as the efficiency of studied ILs with respect to (ΔT) for THI.

Table 2. Ionic liquid hydrate as THI for CO₂ and CO₂+CH₄ hydrates system.

Name of ILs	Chemical Formula	Gases	Concentration (wt.%)
Tetramethylammonium hydroxide	[TMAOH]	CO ₂ + CH ₄ (70/30%)	10
Tetraethylammonium hydroxide	[TEAOH]	CO ₂ + CH ₄ (70/30%)	10
Tetrapropylammonium hydroxide	[TPrAOH]	CO ₂ + CH ₄ (70/30%)	10
Tetramethylammonium hydroxide	[TMAOH]	CO ₂ + CH ₄ (50/50%)	10
Tetraethylammonium hydroxide	[TEAOH]	CO ₂ + CH ₄ (50/50%)	10
Tetrapropyl-ammonium hydroxide	[TPrAOH]	CO ₂ + CH ₄ (50/50%)	10
N-ethyl-N-methylmorpholinium bromide	[Emm]Br	CO ₂	10
N-ethyl-N-methylmorpholinium tetrafluoroborate	[Emm][BF ₄]	CO ₂	10
N-ethyl-N-methylpiperidinium bromide	[EMPip-Br]	CO ₂	10
N-ethyl-N-methylpiperidinium tetrafluoroborate	[(EMPip)][BF ₄]	CO ₂	10
Tetraethyl-ammonium iodide	[TEAI]	CO ₂	10
Tetramethyl-ammonium bromide	[TMAB]	CO ₂	10
Tetraethyl-ammonium bromide	[TEAB]	CO ₂	10
Tetramethyl-ammonium bromide + methanol	[TMAB + MEG]	CO ₂	10
Tetraethyl-ammonium bromide + methanol	[TEAB + MEG]	CO ₂	10
Tetramethyl-ammonium chloride	[TMA]Cl	CO ₂	10
Tetramethyl-ammonium hydroxide	[TEAOH]	CO ₂	10
Tetrapropyl-ammonium hydroxide	[TPrAOH]	CO ₂	10

5.2.1 Summary of ILs applications as THIs

The THI impact of ILs is dependent on the selection of combination of anions and cations. It is also dependent on inhibitor concentration. All these factors have an influence on average depression temperature (ADT). It can be observed that among ionic liquids mostly imidazolium based ILs have been used in THI performance probe in previous literature for CH₄ and CO₂ hydrates [28], and few investigators have examined the impact of various gases and groups of ILs. Mainly, Imidazolium compounds are used because they are relatively cheaper and already in commercial use among other families of ILs. Generally, researchers have studied the effect of pure methane hydrates as methane hydrates are encountered frequently in the pipeline conditions in comparison to CO₂ hydrates [72].

Khan et al. 2018 [79], recently utilized ammonium based ionic liquids with hydroxide anion on binary mixed gas hydrates. The cationic hydrophobic moiety consisted of TMA⁺, TEA⁺, TPrA⁺ and TBA⁺. The anion employed for investigation was fixed as OH⁻. The experiments were performed for gas mixture with 50 mol % -50 mol % CO₂-CH₄ composition. The hydrate equilibrium was obtained at 10 wt% inhibitor concentration using T-Cycle method at pressure values of 20–65 bar for THI behaviour. The HLVE for all the examined compounds was obtained in the temperature range of 275.0–284.0 K.

The calculation shows the better performance of [TMAOH] among the studied AILs for the mixed gas system (decreased hydrate phase boundary by 1.38 K) through average suppression temperature (F). The findings are then compared to those obtained with industrial THI inhibitors. The results also included the values for hydrate dissociation enthalpy. In addition, Khan et al. 2017 [95], investigated the THI influence of four ammonium-based ionic liquids (AILs) on a CO₂-rich mix gas hydrate system (70–30 mol% CO₂ + CH₄), and the observed behaviour is modelled. [TMAOH], [TEAOH], [TPrAOH] and [TBAOH] were examined.

In binary gas mixture of high CO₂ content, the hydrate liquid vapor equilibrium is measured in between the pressure range of 1.90 to 5.10 MPa. The concentration of the AILs used during the equilibrium measurement is set to be 10 wt%. The effect of AILs on thermodynamic inhibition is quantified by measuring the hydrate suppression temperatures of the studied AILs. The evaluated results indicated that the shorter alkyl chain AILs namely [TMAOH], [TEAOH] and [TPrAOH] are able to change hydrate phase boundary of CO₂ rich gas mixture toward lower pressure and high temperature in the presence of 10 wt% inhibitor (as shown in **Figure 8**). In the case of TMAOH, the ADT increases with IL concentration (up to 1.7K at 10%). On the other hand, [TBAOH] acted as hydrate promotor. The length of alkyl chain in cationic part of IL showed a strong influence on the compound's inhibition behaviour. It is therefore observed that shorter alkyl chains offer superior thermodynamic inhibition [31][34].

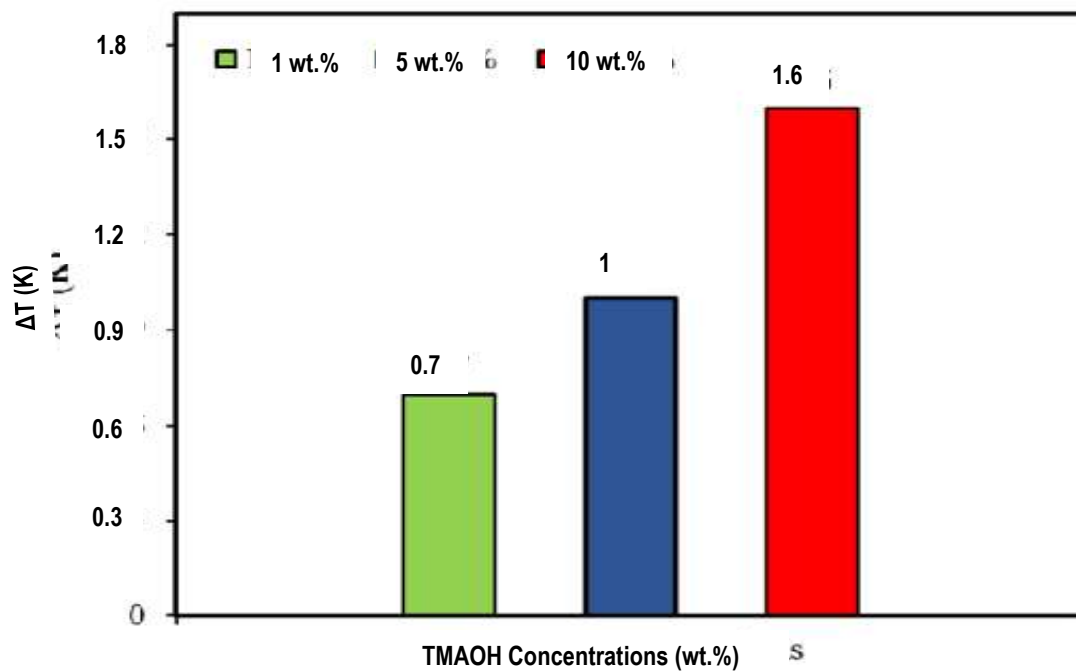


Figure 8. THI performance of [TMAOH] for mixed gas [70/30 CO₂/CH₄ mol%] [34].

Khan et al. 2018 [34], concluded that in case of binary gas mixture the role of guest cage occupancy for each gas plays an important role in gas hydrate structure as they are competitive. The composition of the gas in final stage in the mixed gas hydrate system was found to be different

as compared to that of the original composition. It is owed due to the variation in guest cage occupancy [34].

In recent years, the use of ionic liquids containing nitrogen atom in cationic structure i.e. AILs is widespread in GHI studies due to being more effective [96]. It is so because of the existence of a nitrogen atom in the centre of the cationic structure; ammonium based ILs display efficient hydration suppression. Furthermore, AILs offer considerably better or environmentally sustainable options than the most tested Imidazolium-based ionic liquids.[97]. Additionally, AILs have a wide range of applications in a variety of industries, including gas storage, nanomaterials, organic synthesis, heavy metal removal electrochemistry, and gas separation [97].

5.3 Ionic liquids based KHI for CH₄ gas hydrates.

Various researchers [79][98][64] have assessed the kinetic efficiency of hydrate inhibitors and their approach was based on analysing different physical properties, for instance, hydrate nucleation rate, amount of gas consumed during the process of hydrate crystallization and induction time which is a key property in evaluating inhibition performance. KHI performance relied on the following key factors, containing driving force (sub-cooling), equipment specifications, contaminants present in the chemical species and lastly technique and stirring, so it is therefore, the hydrate nucleation and induction time can be only compared to pure water induction time of the same system due to their probabilistic behaviour. Since Xiao & Adhirama [76] initiated the research of ILs as gas hydrate inhibitors in 2009, experimented for Imidazolium based ILs and found better results for both THI and KHI inhibition. The KHI efficiency is attributed to the ability of ILs for hydrogen bonding with water and the presence of both positive and negative ions. The research was further performed for CH₄ hydrates by varying dialkylimidazolium halides.

Xiao et al. 2010 [2]. conducted experiments on [Bmim]I and [Emim][BF₄] to probe their KHI influence. The chemicals were employed in 0.005 and 0.01 mf concentration. These compounds showed better KHI impact in comparison with PVCap and Luvicap at 0.01mf. Based on that concept ionic liquids have got more attention in gas hydrate research field. Kim et al. 2011 [99], investigated the performance effects of pyrrolidinium based ILs. The results revealed better inhibitory effects of these ILs as at 70 bar and 15 K subcooling and the induction time was longer than that of [PVP] and [PVCap]. They argued that the presence of hydroxyl group [OH] improves the hydrate hindrance by increasing the hydrophilicity of ILs and hydrogen bond ability with water molecules.

On the other hand, Villano and his co-workers (2010) [100] analysed the kinetic effect of standard natural gas [SNG] in the presence of [Emim][BF₄] and [Bmim][BF₄] ionic liquids. The study revealed that the investigated ILs were ineffective as GHI, in addition, it was found that the selected ILs were extremely weak kinetic hydrate inhibitors at 0.5 to 1.0 mass fraction.

Based on literature report it was found that ILs, including [Emim][BF₄] and [Emim][Br], promoted hydrate growth rather than showing the controlling effect [101]. Nashed et al. 2018 [50] analysed THI performance of ILs with imidazolium cation. The compounds included anionic halides in combination with 1 butyl 3 methylimidazolium and 1-[2-hydroxyethyl] 3 methylimidazolium cations as KHI. The findings showed that better induction time is attained by longer alkyl chain group and further argued that among the studied ILs [OH-emim] Br showed better KHI characteristics. It almost increased the induction time doubly at high pressure and low temperature. Zare et al. 2015 [101] has been described the behaviour of [C₂C₁im] [C₂SO₄] and [C₄C₁im] [C₁SO₄] as effective KHIs. The results expressed that the hydrate nucleation of [C₄C₁im] [C₁SO₄] at 13.7 MPa and 313.15 K was prolonged by 3 folds compared to [C₂C₁im] [C₂SO₄] with an induction time of 3.8 hours 2 folds than pure water) it is due to longer chain of alkyl possess in [C₄C₁im] [C₁SO₄]. As the sub cooling temperature was further lowered to 12.1 MPa, the hydrate

nucleation was postponed to a larger extent, at 12.1 MPa, the [C₂C₁im] [C₂SO₄] induction time was 6.8 hours, whereas it was 9.11 hours for that of [C₄C₁im] [C₁SO₄]. The analysis indicated that the intermolecular force amid anion moiety and water is directly proportion to inhibition. similarly, the methyl group of (C₁SO₄) attached with oxygen atom has more negative compared to [C₂SO₄] the ethyl group. Moreover, the hydrophobicity of an ionic liquid increases as the alkyl chain length increases, it is so, the butyl group in [C₄C₁im] [C₁SO₄] had a greater effect on the hydrate surface than the ethyl group in [C₂C₁im] [C₂SO₄]. As a result, [C₄C₁im] [C₁SO₄] had a greater kinetic hindrance capability than [C₂C₁im] [C₂SO₄]. It indicated that anions can also impart the hydrate mitigation and promotion effect and influence in their formation [101].

Lee et al. 2016 [102][103] studied the morpholinium based ionic liquid for CH₄ hydrates formation for example, 1-hydroxyethyl-1-methyl-morpholinium-tetra-fluoroborate and 1-hydroxyethyl-1-methyl-morpholinium chloride. It was noted that the CH₄ hydrate formation was promoted, and more methane was used as a result of the hydrate formation facilitated by 1-hydroxyethyl-1-methyl-morpholine chloride which could be because of the halide anion, i.e., Cl. Additionally, both cationic and anionic moieties of [OHeC₂C₁Mor]Cl have hydrogen bonding ability. Due to this ability it can break the hydrate structure surface. The kinetic inhibitory impact of [OHeC₂C₁Mor][BF₄] on the other hand postponed the nucleation of hydrates till 0.96 h. Consequently, concentration impact of [OHeC₂C₁Mor][BF₄] on induction time demonstrated that the induction time improved repetitively with the inhibitor quantity in the solution [102][103]. The induction time of ILs reported for KHI on CH₄ hydrate system is shown in the **Table 3**.

Table 3. Ionic liquid tested as KHI for CH₄ and CO₂+CH₄ hydrate system.

Name of ILs	chemical formula	Gases	Concentration (wt.%)	ILs Test	Induction time (h)
1-3-methylimidazolium chloride	[Emim]Cl	CH ₄	1	KHI	1.47
1-3-methylimidazolium chloride	[Bmim]Cl	CH ₄	1	KHI	1.85
1-3-methylimidazolium iodide	[Pmim]I	CH ₄	1	KHI	5.21
1-3-methylimidazolium iodide	[Bmim]I	CH ₄	1	KHI	1.29
1-3-methylimidazolium bromide	[Emim]Br	CH ₄	1	KHI	2.04
1-3-methylimidazolium bromid	[Bmim]Br	CH ₄	1	KHI	2.45
1-3-methylimidazolium dicyanamide	[Emim][N(CN) ₂]	CH ₄	10	KHI	1.03
1-3-methyl-3-methylimidazolium trifluoromethanesulfonate	[Emim][CF ₃ SO ₃]	CH ₄	10	KHI	0.40
1-3-methylimidazolium ethylsulfate	[Emim][EtSO ₄]	CH ₄	10	KHI	0.56
1-3-methyl-3-methylimidazolium tetrafluoroborate	[Emim][BF ₄]	CH ₄	10	KHI	6.48
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	CH ₄	10	KHI	3.94
1-methyl-ammonium hydroxide	[TMAOH]	CO ₂ +CH ₄ 50/50%	10	KHI	0.35 (277 K)
1-ethyl-ammonium hydroxide	[TEAOH]	CO ₂ +CH ₄ 50/50%	10	KHI	0.30 (277 K)
1-butyl-ammonium hydroxide	[TBAOH]	CO ₂ +CH ₄ 50/50%	1	KHI	0.74 (277 K)
1-propyl-ammonium hydroxide	[TPrAOH]	CO ₂ +CH ₄ 50/50%	1	KHI	0.50 (277 K)
1-methyl-ammonium hydroxide	[TMAOH]	CO ₂ +CH ₄ 50/50%	1	KHI	0.35 (274 K)
1-ethyl-ammonium hydroxide	[TEAOH]	CO ₂ +CH ₄ 50/50%	1	KHI	0.33 (274 K)
1-butyl-ammonium hydroxide	[TBAOH]	CO ₂ +CH ₄ 50/50%	1	KHI	0.61 (274 K)
1-propyl-ammonium hydroxide	[TPAOH]	CO ₂ +CH ₄ 50/50%	1	KHI	0.35 (274 K)
1-Butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	CH ₄	0.6	KHI	7.63
1-Ethyl-3-Methylimidazolium methylsulphonate	[Emim][MS]	CH ₄	(DW)+5	KHI	1.25
1-3-Methylimidazolium dicynamide	[Emim][CN]	CH ₄	(DW)+5	KHI	0.75
1-Ethyl-3-Methylimidazolium methylsulphonate	[Emim][MS]	CH ₄	(SW)+5	KHI	0.75
1-3-Methylimidazolium dicynamide	[Emim][CN]	CH ₄	(SW)+5	KHI	0.75

5.4 Ionic liquids based KHI for CO₂ gas hydrates

CO₂ is known as an appropriate guest molecule that combines physically with water at suitable temperature and pressure to form structure, I gas hydrates. In natural gas streams, CO₂ and water are frequently found together which can cause complications in extracting phase of natural gas. The kinetic inhibition efficiency of imidazolium based ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF₄] and 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄] indicated that imidazolium based ILs have weak kinetic inhibition. Khan et al. 2019 [88] recently studied ammonium based ILs specifically [TMACl] which acts as potential KHI on CO₂ hydrate hindrance. [TMACl] was discovered to be a much better KHIs than imidazolium based ILs. It delayed CO₂ hydrate formation about 45 min. The induction time of ILs, impacts of chemical species on induction as well as hydrate formation rate are reported for KHI on CO₂ hydrate system as shown in the **Table 4**.

Table 4. Ionic liquids tested as KHI for CO₂ and CO₂+CH₄ hydrate system.

Name of IIs	Ionic liquids	Gases	Concentration (wt.%)	ILs Test	Induction time (h)	Pressure (bar)	Temperature (K)
1-methyl imidazolium bromide	[Emim]Br	CO ₂	1	KHI	14.00	25	-
1-methyl-ammonium hydroxide	[TMAOH]	50% CO ₂ +50% CH ₄	10	KHI	0.35	-	277
1-methyl-ammonium hydroxide	[TEAOH]	50% CO ₂ +50% CH ₄	10	KHI	0.30	-	277
1-butyl-ammonium hydroxide	[TBAOH]	50% CO ₂ +50% CH ₄	1	KHI	0.74	-	277
1-propyl-ammonium hydroxide	[TPrAOH]	50% CO ₂ +50% CH ₄	1	KHI	0.50	-	277
1-methyl-ammonium hydroxide	[TMAOH]	50% CO ₂ +50% CH ₄	1	KHI	0.35	-	274
1-methyl-ammonium hydroxide	[TEAOH]	50% CO ₂ +50% CH ₄	1	KHI	0.33	-	277
1-butyl-ammonium hydroxide	[TBAOH]	50% CO ₂ +50% CH ₄	1	KHI	0.61	-	274
1-propyl-ammonium hydroxide	[TPAOH]	50% CO ₂ +50% CH ₄	1	KHI	0.35	-	274
1-propyl-ammonium chloride	[TMACl]	CO ₂	1	KHI	0.71	-	274
1-propyl-ammonium chloride	[TMACl]	CO ₂	2	KHI	0.91	-	274
1-propyl-ammonium chloride	[TMACl]	CO ₂	1	KHI	1.00	-	277
1-propyl-ammonium chloride	[TMACl]	CO ₂	2	KHI	1.32	-	277
1-methyl imidazolium chloride + Polyvinylpyrrolidone	[Emim]Cl +[PVP]	CO ₂	1	KHI	0.60	25	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	0.1	KHI	6.00	30	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	0.1	KHI	6.30	25	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	0.1	KHI	13.20	35	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	0.5	KHI	16.00	25	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	0.5	KHI	20.00	30	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	1	KHI	30.20	25	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	1	KHI	36.30	30	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	10	KHI	48.00	30	-
1-methyl imidazolium bromide	[Emim]Br	CO ₂	0.5	KHI	17.00	30	-

In another work, Khan et al. 2018 [77] reported, the performance of tetramethylammonium hydroxide [TMAOH] and tetra propylammonium ammonium hydroxide [TPrAOH] as KHI for the CO₂ and CH₄ mix gases in 50%, 50% composition. It was demonstrated that the ammonium based ionic liquid can work as better KHI on mixed gas system [77]. Meanwhile, **Figure 9** shows the results obtained by Khan et al. 2019 for CO₂ hydrates mitigation using TMACl ionic liquid in which KHI impact was observed at two different temperatures and concentration. The increment in TMACl concentration increased the induction time and it has proved to be a promising KHI [88].

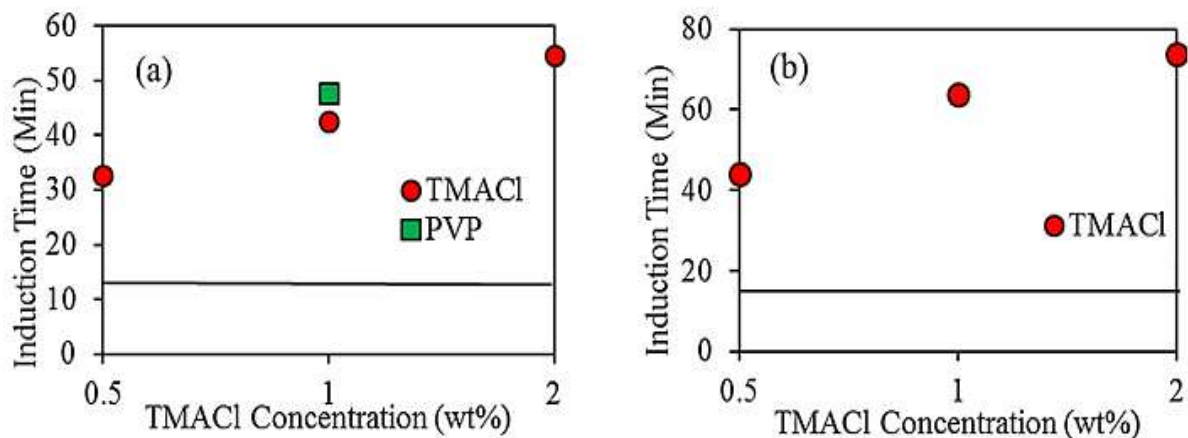


Figure 9. Effect of induction time on CO₂ hydrates at different temperature (a) 274 K (b) 277 K [88].

5.4.1. Summary of ILs utilized in KHI application.

The performance impact of kinetic hydrate inhibitors is measured through induction time. Induction time essentially reflects hydrate prolonging capability of inhibitor in the particular system. KHIs act to postpone or delay the hydrate formation and affect the induction time. Practically, it is defined as the time required to form a detectable volume of hydrate phase. In literature, induction time has

been reported as a probabilistic phenomenon. As a result, each experiment is replicated minimum twice and the average value is taken into account [107],[108],[109].

The inhibition mechanism of ionic liquids as KHIs is different from the thermodynamic hydrate inhibitors. Since, many researchers have claimed that the longer the alkyl chain of an ionic liquid, the better the kinetic suppression [110]. This is because the hydrophobicity of the ionic liquid increases as the alkyl chain lengthens. Consequently, the butyl group has a greater influence upon on hydrate surface than the ethyl group as already discussed above. The anions of ILs, on the other hand, have the effect of preventing or facilitating hydrate formation because the intermolecular attraction of anions and H₂O is responsible for significant inhibition. The performance of various types of tested ionic liquids as KHIs for both CH₄ as well as CO₂ hydrates, which indicate that among the studied ionic liquids for CH₄ hydrates, [Bmim][BF₄] represents maximum induction time at 0.6 concentration and [Bmim][MS] also showed decent induction time at 0.6 concentration perhaps due to the presence of longer alkyl chain. In case of ILs analysed for CO₂ hydrates, [Emim][Br] exhibited maximum induction time at different concentration and pressure. Most of the ILs systems contain methane, comparatively less studies have investigated the inhibition activity in the presence of pure CO₂ hydrates. Some researches in open literature have studied the gas hydrate mitigation performance of inhibiting chemicals in presence of multicomponent gas mixture. The literature data for ILs - mixed gas hydrates inhibitors systems is not reported with different types of ionic liquids. Subsequently, it is suggested that the study on other types of ionic liquids should be extended for mixed gas hydrates.

5.5 Dual Functional ILs based Gas Hydrate Inhibitors

In a case where many inhibiting chemicals are inserted simultaneously, they cause a stimulating impact thus creating inhibition power or influences that is greater than the inhibitors' individual impact. However, even so the utilizing of existing KHIs alone is not effective mainly as the exploration activities dig deeper offshore territories. As a result, most of the researches probed the development of new kinetic hydrate inhibitors but also synergistic effects for KHI [8],[62]. On that account, for excellent efficiency, a combination of low-cost, environmentally friendly THIs and KHIs are essential for gas hydrate remediation.

The recent idea of utilizing ILs for different applications containing gas hydrate impediment is acquiring interest due to lower heat capacity, ease in separation, high thermal stability and lastly the dual functional ability of ILs. Due to these reasons, ILs have received more interest in gas hydrate field that can replace the conventional inhibitors. Since Xiao and Adharma studied ILs as gas hydrate inhibitors in 2009, utilization of ionic liquids as GHI in the oil and gas sector is a novel field of research. [76]. They first explored the imidazolium based ILs for CH₄ hydrates, which displayed outstanding performance both THI and KHI as compared to polyethylene glycol. It was highlighted that ILs depicted THI hydrates interference, which delayed hydrate formation by lowering the hydrate crystallization process. It is due to the presence of strong electrostatic charge and the tendency to develop hydrogen bonds with water molecules which indicates dual functional behaviour. Altamash et al. 2019 [111], performed experimental study on the effect of imidazolium based ionic liquids as THI and KHI. The compounds included anions of sulphonate and dicyanamide in combination with cationic moiety of 1-ethyl-3-methylimidazolium. The obtained results were compared with the conventional KHIs and THIs performance.

Qureshi and his co-workers 2016 [29], conducted experimental analysis on a mixture of pyrrolidinium-based ILs and synergists compounds (polyvinyl caprolactam) on CH₄ hydrate. The findings indicated that adding synergists to ionic liquids enhanced their thermodynamic and kinetic hydrate inhibition performance instantaneously. Furthermore, Khan et al. 2019 [88], evaluated the

dual functional behaviour of ammonium based ILs (TMACl) on CO₂ and CH₄ hydrates. It is disclosed that the evaluated performance of THI at 10 wt.% (TMACl) reduced the phase boundary of CO₂ and CH₄ hydrates from 1.42 K to 1.60 K. likewise, performance effect of [TMACl] as KHI signified that the induction time of all the evaluated systems effectively enhanced in the presence of [TMACl] for both CO₂ and CH₄ hydrates.

In another work, Khan et al 2018 [79], investigated the performance investigation of THI and KHI in the presence of Quaternary ammonium salt such as [TMAOH], [TEAOH], [TBAOH], [TPrAOH] on binary mixed of 50% CH₄ and 50% CO₂ hydrates. Among the studied the ILs, the [TMAOH] worked better, and shifted the phase boundary to 1.38 K for both gasses' hydrates, it is because of having the shorter alkyl chain of [TMAOH]. on the other hand, kinetics influence of measured systems demonstrated the Quaternary ammonium salt may effectively improve the kinetic performance by enhancing induction time of all considered system. Compared to the previous work, the effect of the alkyl chain also observed in this study, as nucleation time of hydrates is dependent on the length of the alkyl chain and its elongation increase the nucleation time also. THI and KHI performance of ILs is stated in terms of average depression temperature [ΔT] for and induction time respectively on the CO₂ hydrate system is shown in Table 5.

Table 5. Ionic liquid tested as dual functional inhibitors for gas hydrate system.

Name of ILs	Ionic liquids	Gases	Concentration (wt.%)	ILs Test	ΔT (K)	Induction Time RIP (h)
1-methyl-3-methylimidazolium chloride	[Emim]Cl	CH ₄	10,1	KHI+THI	1.01	0.75
1-methyl-3-methylimidazolium bromide	[Emim]Br	CH ₄	10,1	KHI+THI	0.84	0.82
1-methyl-3-methylimidazolium iodide	[Bmim]I	CH ₄	10,1	KHI+THI	0.34	0.93
1-propyl-3-methylimidazolium iodide	[Pmim]I	CH ₄	10.1	KHI+THI	0.67	0.72
1-ethyl-3-methylimidazolium dicyanamide	[Emim][N(CN) ₂]	CH ₄	0.1-10 wt.%	KHI+THI	0.58	0.65
1-butyl-3-methylimidazolium methyl sulfate	[Bmim][CH ₃ SO ₄]	CH ₄	10.1 wt.%	KHI+THI	0.58	0.38
1-ethyl-3-methylimidazolium tetrafluoroborate	[Emim][BF ₄]	CH ₄	0.1-10 wt.%	THI-KHI	0.52	17
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	CH ₄	0.1-10 wt.%	THI-KHI	0.72	9.94
1-trimethyl-ammonium hydroxide	[TMAOH]	CO ₂ /CH ₄ (50/50)	10	THI-KHI	1.38	0.38
1-tetraethyl-ammonium hydroxide	[TEAOH]	CO ₂ /CH ₄ (50/50)	10	THI-KHI	1.05	0.30
1-tetrabutyl-ammonium hydroxide	[TBAOH]	CO ₂ /CH ₄ (50/50)	10	THI-KHI	0.58	1.75
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	CH ₄	0.6-7 wt.%	THI-KHI	0.70	-
1-ethyl-3-methylimidazolium tetrafluoroborate	[Emim][BF ₄]	CO ₂	0.10-1	KHI+THI	1.11	-2.09
1-ethyl-3-methylimidazolium methyl sulfate	[Bmim][MS]	CH ₄	0.6-7	KHI+THI	1.21	0.5
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	CH ₄	0.6-7	KHI+THI	0.74	0.79

A look into the literature reveals that imidazolium based ILs have been studied extensively for both KHI and THI in preceding years. Researchers have approached to the same conclusion that the dual functional performance of ILs depends on the suitable size of inhibitor as well as the dispersed charge on the inhibitor's edge [14]. Although ILs that can perform dual functions activity are linked to unique compounds, not all ILs own dually functionality. So, this dual behaviour of ILs is characterised by their tuneability in terms of cationic along with anionic components. For instance, the hydrophilic part $[\text{OH}]^-$ of tetramethyl ammonium hydroxide [TMAOH] based ILs make hydrogen bonds along with water molecules and eventually enhance thermodynamic hindrance [113][114]. Additionally, the hydrophobic part $[\text{TMA}]^+$ is having its own role. As increasing the chain length of alkyl in [TMAOH] decreases the capacity of hydrogen bonding of ILs [45]. Consequently, the thermodynamic hindrance become least because the cationic moiety of IL substantially induced the hydrophobicity due to expanded chain length and in this case, it imparted the thermodynamic promotion effect rather than inhibition. In conclusion, the hydrogen bonding is a significant factor that influences the dual function activity of ILs. The act of ILs could be explained by three factors: functional group, cations/anions, and alkyl chain length.

On the other hand, it is demonstrated that the majority researchers have conducted research in the existence of Imidazolium based ILs like KHI and THI for CH_4 hydrate system. though, it has not demonstrated substantial inhibition strength contrasted with conventional inhibitors. The dual functional effect in the presence of ILs for CO_2 hydrate system is very limited. Furthermore, it is disclosed that more research on other families of ionic liquids is required which is exceptionally negligible. Besides, in the presence of ILs, the performance analysis on mix gas hydrates is reported very least. It should be noticed vitally that dual functional influence for both mix gas and CO_2 is essential to be studied in the presence of ILs.

6. Conclusion

This review paper evaluates the routes towards the applications of ionic liquids as chemical inhibitors of gas hydrate formation for offshore pipeline applications. Ionic liquids have been investigated either as thermodynamic hydrate inhibitors (THI), or as kinetic hydrate inhibitors (KHI), and even as dual functional inhibitors (THI and KHI).

The factors influencing the hydrate inhibitors in terms of their performances have been reviewed and discussed. The present review of the available literature suggests that ionic liquids have been widely employed in CO₂ and CH₄ gas hydrates inhibition. Imidazolium based ionic liquids have extensively been used in gas hydrate inhibition applications as they show better results in terms of hydrate inhibition. Apart from imidazolium, some piperidinium based ILs have also been used. The utilization of quaternary ammonium salts in gas hydrate mitigation applications is novel and some researches have performed experiments involving ammonium based ionic liquids. The literature also demonstrated that THI application for CO₂ hydrates inhibition [Emim]Br show efficient inhibition potential at a higher percentage of 40 wt%. [Emim]Cl displayed better inhibition performance compared to the other ILs in case of CH₄ hydrate inhibition. In terms of KHI also, imidazolium based ILs show better performance. [Emim] Br has shown an induction time of 48 hours at 10 wt% of concentration for CO₂ hydrates. Meanwhile, [Bmim][BF₄] reveals an induction time of 7.63 hours for CH₄ hydrates. Mixed gas separation performance of [TBAOH] ionic liquid-based gas hydrate is new and yet to be investigated in detail which could enhance its potential application at industrial scale.

7. Future Recommendations

The use of ionic liquids in gas hydrate inhibition application shows a promising future. Currently most studies have been performed involving pure CO₂ and CH₄ gas hydrates. In future these studies can be extended to multicomponent gas mixtures involving up to pentane or even higher components as natural gas consists of mixture of hydrocarbons. Furthermore, different

families of ionic liquids such as pyridinium, phosphonium and thiazolium based can be employed to test their performance in this field of study. The use of quaternary ammonium salts is also new and can be explored further with different combination of anions and cations in this regard, in particular environmental friendly choline based ILs. In addition, the use of quantum mechanical techniques and softwares such as COSMO-RS can be employed as predicting tool for thermodynamic properties of ILs. The qualitative analysis assists researchers in developing better compounds with high polarity anions in the field of gas hydrate control.

Acknowledgement

We would like to thank Universiti Teknologi Petronas, Bandar Seri Iskandar, Malaysia for supporting the research work.

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