Role of Ionic Liquids as Effective Thermodynamic Methane Hydrate Inhibitors

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ABSTRACT

In petroleum exploration, production and transportation operations, methane hydrates are considered problematic and nuisance as they pose acute flow assurance, economic and safety concerns. They have potency of blocking transmission lines, jeopardize foundations of deep-water platforms and may lead to casing and tubing collapse, bringing the entire production and/or transportation process to a cease. In this work, the performance of four ionic liquids (ILs) as thermodynamic methane hydrate inhibitors is investigated. The dissociation temperature of methane hydrates formed is determined by using high pressure micro-differential scanning calorimeter (HP-μ DSC) in the pressure range 35 bar to 140 bar. All aqueous ILs are studied at the 10 wt% concentration. It is found that the ILs shift the methane hydrate (liquid + vapor) equilibrium curve (HLVE) towards lower temperatures and higher pressures, with the exception of Tributyl methyl ammonium hydroxide solution (TBAOH) which acted otherwise, promoting the formation of methane hydrates. Our results manifested 1-ethyl-3-methyl imidazolium chloride [EMIM][Cl] to be the best amongst the ILs studied as thermodynamic methane hydrate inhibitors.

KEYWORDS: Methane Hydrates, Chemical Inhibitors, Thermodynamic Hydrate Inhibition, Ionic Liquids, Differential Scanning Calorimeter (HP-μDSC).

INTRODUCTION

Clathrate hydrates or gas hydrates are crystalline Euclidean meta-stable solid compounds that are formed at generally elevated pressures and low temperatures, which are comprised of water molecules connected through a network of hydrogen bonding that morph into a cage-like structure when hydrocarbon molecules such as methane is present in the vicinity [1-4]. These hydrogen bonded cage structures also called cavities can encapsulate or trap multifarious hydrocarbon molecules of different sizes and molecular combinations at relatively high pressures and low temperatures, resultantly forming stable hydrate units. Constant prevalence of appropriate high pressure and low temperature conditions tend to agglomerate together these individual stabilized hydrate units, gradually accumulating them into monolithic catastrophic blockages in pipelines and/or process equipment which consequently result into failure of flow assurance operations [5] as shown in Figure 1.

Figure 1: Developed gas hydrate plug in production line [6]

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The realm of 'Flow Assurance' has gained prominence and popularity as petroleum operations are moving off-shore into deeper waters involving high pressures and low temperatures, where methane hydrates are highly suspected to form in the system.

The financial loss incurred in terms of production cessation, asset damage, crew safety and ecological risks due to flow assurance failure can be profound and colossal. The oil and gas industry annually invests approximately US $1 million per mile on insulation of subsea pipelines [7] and myriad money sums on other conventional methods to mitigate hydrate formation and removal in petroleum exploration, production and transportation operations.

Various commercially practiced mitigation and removal methods exist for methane hydrate inhibition like water removal, thermal heating, pipeline depressurization and injection of chemical inhibitors. Even Standard Operating Procedures (SOPs) are established, documented and widely practiced for the removal of commonly encountered methane hydrate plugs in pipelines [8-9]. Among the mentioned methods, chemical inhibition is most widely adopted method, coupled with other method(s), depending upon the scenario. However, these methods seem inadequate and detrimental at times with limited inhibition effects.

Generally, chemical inhibitors are classified into two main groups namely thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs). LDHI can be further classified into kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAs). Ionic liquids (ILs) as inhibitors may find place under the umbrella of LDHI, as illustrated in Figure 2.
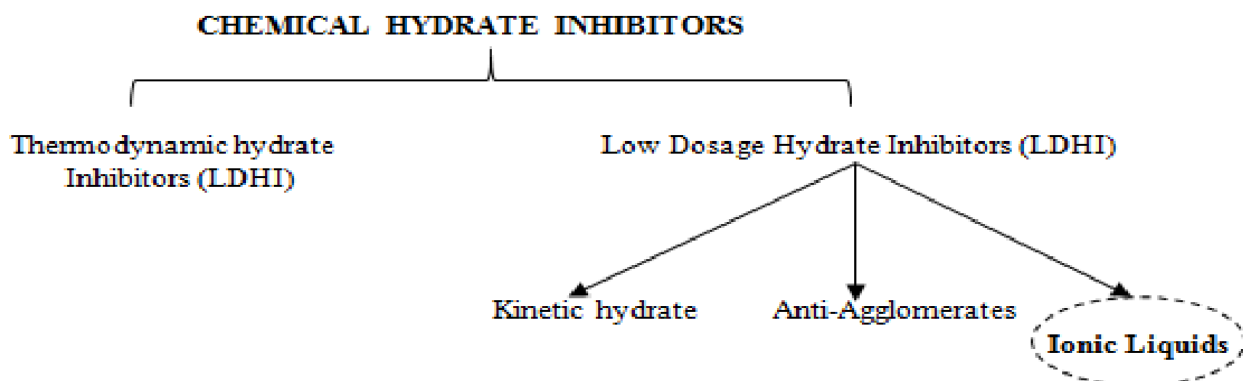

Figure 2: General classification of chemical hydrate inhibitors

Inhibition mechanism for thermodynamic hydrate inhibitors (THI) is based on distorting the geometry of hydrogen bonded water-cage, making it incapable to encapsulate hydrocarbon molecules, leading to the 'Salting out' phenomenon, which can be graphically analyzed by shifting of the Hydrate Liquid Vapor Equilibrium (HLVE) curve (HLVE) or Hydrate Stability curve towards lower temperatures and elevated pressures, as the chemical potential of the guest molecule in the aqueous phase is decreased [10]. In general, those chemicals having strong electrostatic charges and are able to form effective hydrogen bonding with water molecules are considered good contestants as hydrate inhibitors [11]. Ionic liquids possess these two fundamental attributes and are investigated as thermodynamic hydrate inhibitors (THI) for methane hydrates in this research work.

Ionic liquids (ILs) are organic salts that are generally in liquid state at room temperature. They are made of cationic and anionic parts. The cationic part is generally N-containing organic cations (e.g. Imidazole, Pyrrole, Pyridine etc.), while the anionic part comprise of anion ranging from simple inorganic ions (e.g. Halides), to more complex organic species [12]. They offer wide range of attractive characteristics such as negligible vapour pressure, non-flammability, high chemical and thermal stability, environmental compliance and chemical tunability [13] to dovetail various purposes earning them the title of 'magic solvents'. Above all this, from the perspective of ILs as hydrate inhibitors, they have manifested dual functionality i.e. they simultaneously act as thermodynamic inhibitors as well as kinetic inhibitors [14], which may exhibit their superiority as inhibitors over other conventional classes of hydrate inhibitors.

In this work, thermodynamic inhibition performance of four ILs is investigated. The dissociation temperatures of methane hydrates in the presence of these ILs at 10 wt% concentration at different pressures in the range of 35-140 bar are calculated. The ILs used in this work are 1-ethyl-3-methyl imidazolium chloride, 1-butyl-1-methyl pyrrolidinium chloride, 1-butyl-3-methyl imidazolium dicyanamide and Tributyl methyl ammonium hydroxide solution as illustrated in Table 1.

Table 1: Enumeration of ILs studied in this work

Chemical Name	Symbol	Percentage Purity
1-butyl-1-methyl pyrrolidinium chloride	ClN	98%
1-butyl-3-methyl imidazolium dicyanamide	[BMIM][N(CN)2]	97%
1-ethyl-3-methyl imidazolium chloride	[EMIM][Cl]	99%
Tributyl methyl ammonium hydroxide solution	[TBAOH]	99%

Note: These ILs were obtained from Centre for Research in Ionic Liquid (CORIL) Universiti Teknologi PETRONAS

METHODOLOGY

Materials

The ILs were obtained from Centre for Research in Ionic Liquid (CORIL) Universiti Teknologi PETRONAS. Their details are illustrated in Table 1. These ILs are water soluble with high purity and low viscosity. Before use, they were heated in an oven at 70°C for about 20 hours to drive off any moisture content present in them in order to further enhance their purity. 10 wt% concentration was prepared for each of the four ILs and were tested at four different pressures at 35bar, 70bar, 100bar and 140bar respectively. Deionized water obtained from Ultra-Pure Water system Model: Lab tower EPI 15, was used to prepare all sample solutions. All IL sample solutions were contained in air tight bottles. Analytical balance with accuracy of ±0.001 g was used to weigh all sample solutions. Methane gas with purity 99.9% was purchased from Linde Malaysia Sdn Bhd.

Apparatus and Procedure

SETARAM 7 evo high pressure micro-differential scanning calorimeter (HP-μ DSC) was used in this study to obtain the measurement values of methane hydrate dissociation temperatures. This equipment can operate between temperature range of -45°C to 120°C (228.15°K to 393.15°K) and pressures up to 400 bar (5800 psi). The equipment experimental cells are made of Hastelloy C276 steel metal alloy, which are highly resistant to corrosion and erosion. The equipment calorimetric block consist of two high pressure separate identical cells each having volume of 1ml. One is taken as reference cell and the other is taken as sample cell. These cells can be removed, cleaned and inserted back into the calorimetric block of the DSC equipment. The temperature scanning rate (heating and cooling) of this equipment is between 0.001 to 2.0K/min, which employ advanced Peltier elements for calorimetric measurement to create miniscule temperature difference by the application of controlled voltage. Data was generated and analyzed using Calisto software package provided by SERTARAM Inc. A SETARAM pressure controller was used to induce specific pressure into the experimental cells with an accuracy of ±0.1 MPa. Nitrogen gas was used to create dry environment around the experimental cells in order to avoid moisture condensation during low temperature operation. The experimental schematic is illustrated in Figure 3.
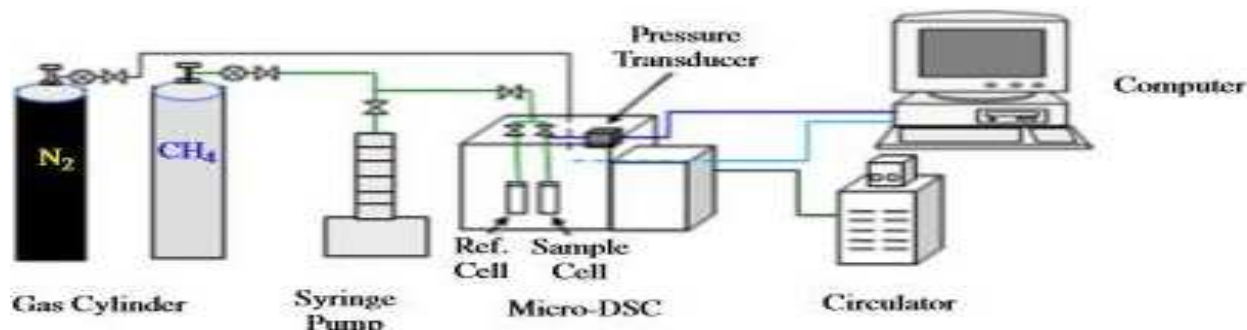

Figure 3: Schematic of experimental setup [15]

The phenomenon to determine hydrate dissociation temperature is based on the difference in the heat flow between sample and reference cells as a function of temperature during phase transition. Two drops of fresh sample solution were loaded into the sample cell, while the reference cell was left empty. The sample cell was carefully inserted back into the calorimetric block of the DSC equipment. The cells were purged thrice with small amounts of methane gas to remove any remaining air present inside the cells. Methane gas was then injected into the both cells simultaneously at desired pressure via pressure controller. In this study, non-isothermal mode setting was used to determine off-set dissociation temperature of methane hydrates [14-16]. This process cycle is comprised of two basic parts i.e. cooling followed by two-step heating. First the cells were cooled from 293.15° (20°C) to 253.15°K (-20°C) at a cooling rate of 0.5K/min succeeded by a short isothermal step of 10 minutes. The significance of this isothermal

step was to ensure formation of methane hydrate. Then, the cells were heated in two steps (i.e. at two different heating rates). The first rate was chosen to be 0.5K/min (fast heating) till the equilibrium temperature, followed by another heating rate of 0.05K/min (slow heating) till the complete dissociation of hydrate previously formed. Heating at slow rate is done in order to ensure accuracy of hydrate dissociation value. It took 7-8 hours to complete one full experimental run rendering only one methane hydrate dissociation value.

RESULTS AND DISCUSSION

The dissociation temperatures of methane hydrates with ILs acting as thermodynamic inhibitor of 10 wt% concentration at different pressure range (30 bar-140 bar) were measured using high pressure DSC. A standard thermogram of methane hydrate dissociation is depicted in Figure 4. An endothermic peak was formed during dissociation phase which manifests dissociation of methane hydrate and its area corresponds to the amount of hydrate formed and dissociated. The appearance of small exothermic peak prior to the endothermic peak depicts hydrate recrystallization from melted ice state before the dissociation process [17]. The hydrate dissociation temperature is determined by the point of intersection between the base line and tangent to the increasing (returning) section of the endothermic dissociation thermogram [15-17] as shown in Figure 4. This point is identified as the 'off-set temperature', which is considered to be the temperature at which the last hydrate crystal would dissociate. The pressure corresponding to this off-set temperature is termed as equilibrium pressure [16].
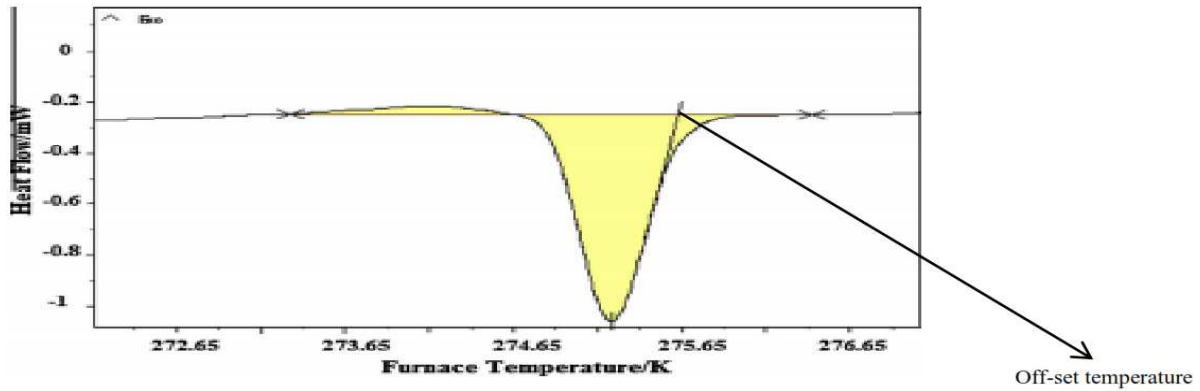

Figure 4: Specimen of DSC thermogram depicting methane hydrate dissociation at pressure of 3.6MPa

The hydrate dissociation temperatures for methane hydrate in the presence of afore-listed ILs at 10 wt% concentration in listed in Table 2 along with pure water data. The gauge pressure was converted to absolute pressure by taking into account the atmospheric pressure which was found to be 0.1MPa.

Table 2: Dissociation temperatures of pure water and methane hydrates at 10 wt% at different pressures

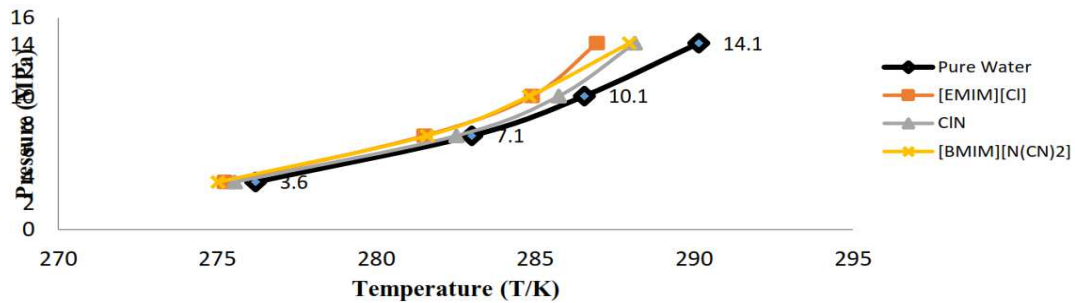| P/MPa	3.6T/K	7.1T/K	10.1T/K	14.1T/K
Water	276.21	283.01	286.55	290.15 (by extrapolation)
[BMIM][N(CN)2]	275.03	281.61	284.82	287.96
ClN	275.56	282.53	285.75	288.13
[EMIM][Cl]	275.25	281.52	284.91	286.95
[TBAOH]	276.33	283.82	287.71	290.87

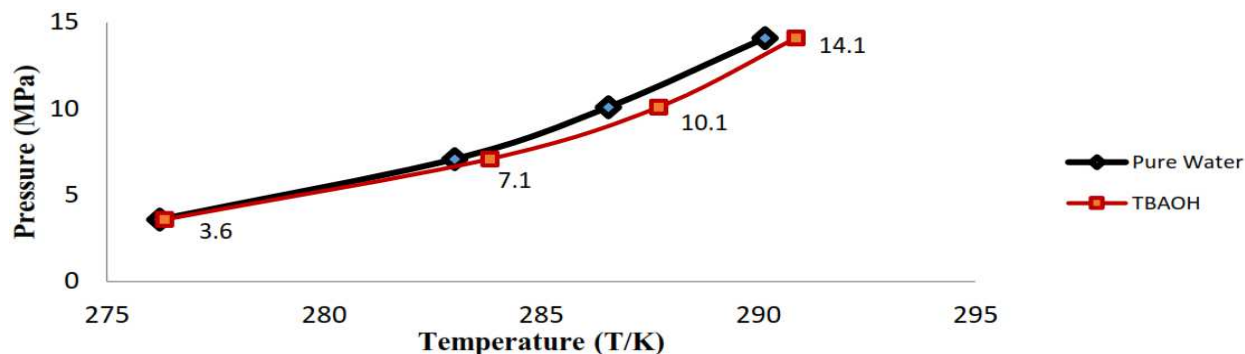**Figure 5: Methane hydrate dissociation comparison**

Figure 6: Dissociation comparison between pure water and TBAOH

In order to compare the inhibition strength of these ILs, the average reduced temperature (Ŧ) is calculated as follows:

$$\text{Ŧ} = 1/n \sum_{i=1}^{n} \Delta T$$

(1)

where n is the number of data points and ΔT is the difference between the measured hydrate dissociation temperature in the presence of IL and pure water at specified pressures.

Table 3: Average reduced temperature for studied ILs

Ionic Liquids	Ŧ/K
[BMIM][N(CN)2]	1.625
ClN	0.99
[EMIM][Cl]	1.83

Three of the four ILs ([BMIM][N(CN)2], ClN and [EMIM][Cl**]**) have exhibited thermodynamic inhibition which can be visually analyzed from Figure 5. The degree of shifting of hydrate dissociation curve towards lower temperatures and elevated pressures corresponds to the inhibition effectiveness, considering pure water (CH4 + water) as comparison reference base. As can be seen, the degree of inhibition becomes more profound at high pressures. [EMIM][Cl] showed highest degree of inhibition amongst other ILs, which may be hypothesized to its ability to form strong hydrogen bonding with methane hydrate water cage structure. Inhibition strength which is represented by average reduced temperature (Ŧ) (Equation (1)) is mathematically illustrated in Table 3 proving [EMIM][Cl] to have the highest value.

However, TBAOH showed anomaly as instead of methane hydrate inhibitor, it acted as methane hydrate promoter as shown in Figure 6. Instead of shifting the hydrate dissociation curve towards lower temperatures and higher pressures, TBAOH drifted the curve towards higher temperatures favouring the process of hydrate formation. No visible dissociation thermogram was generated during experimentation for TBAOH. The reason for its peculiar behaviour is not known at this time.

CONCLUSION

The methane hydrate dissociation conditions for four (04) ILs are scrutinized in this research work. Their inhibition ability on methane hydrate dissociation curve in the pressure range of 35 to 140 bar (3.6 to 14.1 MPa) at 10 wt% concentration is gauged using high pressure micro-differential scanning calorimeter. Three amongst four ionic liquids exhibited ability as thermodynamic hydrate inhibitor to shift the equilibrium curve with [EMIM][Cl] performing the best. The thermodynamic inhibition effectiveness is in the following order: [EMIM][Cl] > [BMIM][N(CN)2] > ClN. An anomaly was witnessed for TBAOH, which acted as moderate methane hydrate promoter instead of inhibitor. This research work is a step forward in the quest of better hydrate inhibitors that are more effective, inexpensive and environmentally friendly than the conventionally used ones.

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