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Ionic Liquid as Low Dosage Hydrate Inhibitor for Flow Assurance in Pipeline

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ABSTRACT

1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF4) was explored in carbon dioxide (CO_2) gas mixture for its potential application as gas hydrate inhibitors for CO_2 hydrate (Type I). Induction time was the parameter obtained using High Pressure Kinetics Measurement (HPKM) for a bulk volume of 130 mL. The temperature for all the experiments was kept constant at 275.0 K (2°C) with the pressure varied at 25, 30 and 35 bar. The ionic liquid was tested as a kinetic inhibitor as well as thermodynamic inhibitor. In practice, kinetic inhibitors are typically used at concentrations of 1 wt.% or less, thus, the experiment was conducted for three different concentrations of the ionic liquid; 0.1, 0.5 and 1.0 wt.% at varying pressures. EMIM BF4 at a concentration of 10.0 wt.% was also tested but at 30 bar only to study the effectiveness of ionic liquid as thermodynamic inhibitors. It was found that the induction time for CO_2 hydrate formation increases in the presence of more highly concentrated ionic liquid. However, at high concentration of 10.0 wt.%, EMIM BF4 does not show significant changes in the induction time as CO_2 hydrate inhibitor.

Key words: Carbon dioxide hydrate, induction time, kinetic hydrate formation, ionic liquid, EMIM BF4, CO_2

INTRODUCTION

In the production of natural gas fields and oil fields, flow assurance is most critical especially for deep water production due to the high pressure and low temperature condition involved. This condition could induce the formation of gas hydrates and eventually, if not mitigated early, could cause catastrophic blockages and restrictions leading to the impairment of flow.

In a survey of 110 energy companies, flow assurance was listed as the major technical problem in offshore energy development (Perry and Green, 2008). Every few years, somewhere in the world a major injury occurs and a major equipment or asset damage is done and subsequent financial loss, due to hydrate formation and blockage.

Gas hydrates are crystalline solid compounds formed by water and natural gas (e.g., methane) or volatile liquids under suitable temperature and pressure conditions (~2000 psig). The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules (Perry and Green, 2008). Gas hydrates also form in vast amounts naturally, especially methane-hydrate which forms in the sea bed and below permafrost.

Various mitigation methods such as depressurization (hydraulic methods), heating (thermal methods), removal of water or natural gas, mechanical methods and chemical injection inhibitors can be deployed to prevent or delay the hydrate formation, either by controlling or eliminating the agents for the formation. Most of these methods, however, are often impractical and under many circumstances, chemical injection seems to be the only feasible solution with chemical inhibitor to be the most chemically viable option.

Two types of inhibitors are utilized nowadays: thermodynamics and kinetic. Thermodynamic inhibitors are known to be expensive and hazardous. The kinetic approach generally attempts to prevent the smaller hydrocarbon hydrate crystals from agglomerating into larger ones and to inhibit and/or retard initial hydrocarbon hydrate crystal nucleation and/or crystal growth (Moraveji, 2012).

This study is aimed to study the effectiveness of ionic liquid as LDHI to delay the formation of gas hydrates within the hydrate formation region at low temperature and high pressure conditions. In addition, this study investigated the effect of different concentrations of ionic liquid as LDHI on the hydrate formation.

LITERATURE REVIEW AND THEORY

Hydrate formation process: The hydrate formation can be divided into 2 processes - nucleation process and stable growth process (Sloan and Koh, 2007). Hydrate nucleation process is a process of formation and growth of hydrate nuclei to a critical size. The simultaneous growths of water and gas molecule act as precursors to the process which requires a supersaturated environment. The gas molecules will dissolve in liquid water to form a supersaturated condition through the liquid phase or locally near the interface between gas molecule and liquid water. At some point during the dissolution, the precursors of hydrate phase (nuclei) appear. The nuclei will tend to grow if sufficient gas is present in the system and will continue until the nuclei achieve a critical size. Induction time, an important indicator to characterize the kinetics of gas hydrate crystallization, is the time elapsed during the nucleation process which includes the formation of gas water cluster and their growth to stable nuclei with a critical size (Sloan and Koh, 2007). It can be obtained by observing the pressure-time relationship in Fig. 1 during hydrate formation. For heterogeneous nucleation, the nucleation rate depends on many factors such as the cell wall roughness and the presence of impurities and particles in the sample, including the driving force.

Hydrate growth is a process that refers to the growth of stable hydrate nuclei as solid hydrates where mass and heat transfers play important roles. In Fig. 1, a sudden pressure drop (beyond t2) indicates the hydrate growth. The decrease in pressure is due to the consumption of gas molecule to form the hydrate structure. When the pressure of the system remains unchanged (beyond t3 in Fig. 1), the hydrate formation is complete.

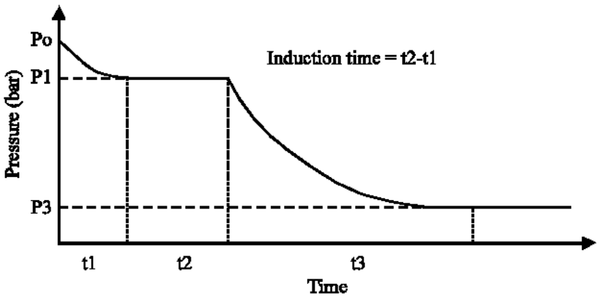

Fig. 1: Schematic diagram of pressure changes with time during hydrate formation (Sloan and Koh, 2007)

Gas hydrate: Gas hydrate is a crystalline solid compound formed in the mixture of water and non- or slightly polar low molecular weight natural gases or volatile liquids under suitable temperature (5-25°C) and pressure conditions (~2000 psig). No chemical reaction is involved during the hydrate formation but the hydrogen bonded network creates cavities that are filled with guest molecules. Low molecular weight gases such as nitrogen, carbon dioxide, methane, ethane, propane, hydrogen sulfide are suitable guest molecules for hydrate formation as they are generally stable at low temperature and high pressures and are present in natural gas.

Gas hydrates may form at low temperatures and so do ice. However, there are marked differences between gas hydrate and ice as listed below:

- Gas hydrate may form at temperatures above 0°C while ice cannot
- Water molecules diffuse at two orders of magnitude slower in hydrates than in ice
- With respect to the mechanical strength, hydrate is more than 20 times stronger (creep resistant) than ice
- CO_2 hydrate is significantly more compressible than ice
- Hydrate formation involves larger thermal expansion due to the guest molecule, with the different arrangements of oxygen atoms in hydrate and ice to play only a minor role

There are three common crystallographic structures for gas hydrates which differ in type and size of cavities and shape; Structure I (sI), Structure II (sII) and Structure H (sH).

SI is a centered face cubic system which appears with light components such as methane, CH_4 or carbon dioxide CO_2 and is the simplest type of gas hydrate. SII is diamond type with 24 cavities per mash while SH is hexagonal type constituted of 6 cavities and is the least common.

Ionic liquid: Ionic liquids (ILs) are organic salts with low melting point that are being considered as green replacements for industrial volatile organic compounds. The reputation of these solvents as ‘environmental friendly’ chemicals is based primarily on their negligible vapor pressure. Ionic liquids are attracting interest as a greener alternative to conventional hydrate inhibitors due to properties such as their stabilities, tuneable organic cations and anions, extremely low vapor pressures and ease of preparations from relatively inexpensive materials.

The uniqueness of the structural tenability of the cations and anions in the ionic liquids suggests that there is a great possibility for the potential application of the ionic liquids. Since, the cations and anions of the ionic liquids can be chosen or tailored to form hydrogen bonds with water, it can interfere with the hydrate formation condition.

MATERIALS AND METHODS

The details of the chemical used in this work are tabulated in Table 1. The dialkylimidazolium based ionic liquid with the short alkyl and hydroxyl groups is utilized. The ionic liquids were obtained from Merck with a mass purity of 99.8%. The Carbon dioxide gas was supplied by Mox-Linde. Different concentrations of ionic liquid were tested with deionized water used as a solvent.

Table 1: Details of ionic liquids utilized

Chemical name	Chemical symbol	Chemical structure
1-ethyl-3-methylimidazolium tetrafluoroborate	EMIM BF_4	

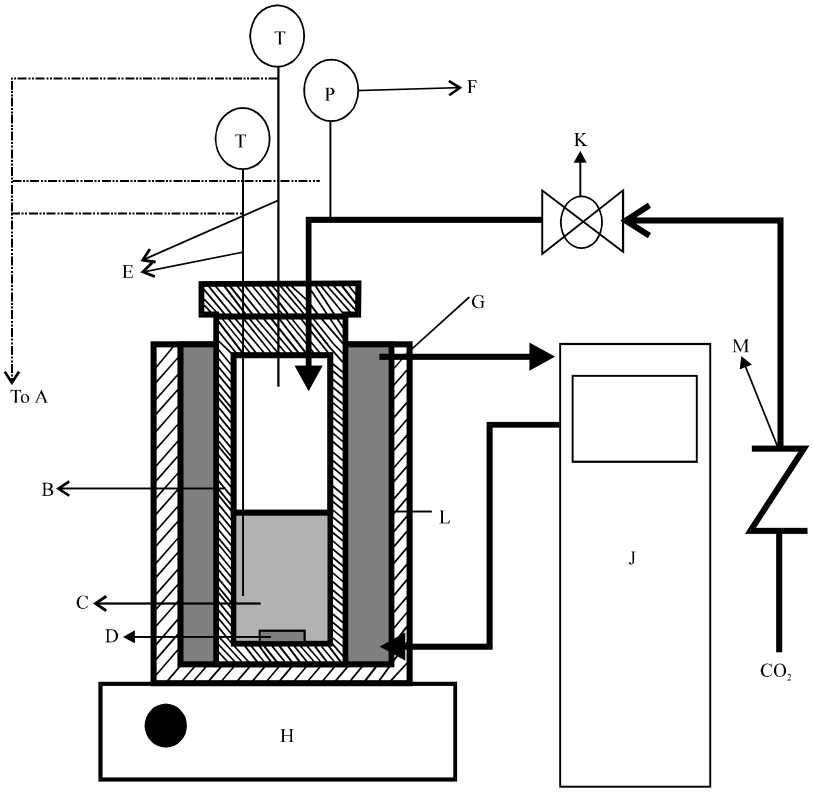

Fig. 2: Schematic representation of high pressure kinetic measurement, A: Data acquisition system, B: High pressure vessel, C: Liquid sample, D: Stirre, E: Thermocouple, F: Pressure gauge, G: Thermostatic bath, H: Magnetic stirrer and J: Cryostat (Sabil, 2009)

Experimental apparatus and procedure: The experimental apparatus utilized for this study is as shown in Fig. 2.

One hundred and thirty milliliter of deionized water and a magnetic stirrer were placed in the high pressure reactor. To ensure no leakage during the experiment, the bolts of the reactor were locked tightly. The reactor was purged with carbon dioxide several times to remove excess air.

It was then submerged into a cooling bath and allowed to cool down to the desired temperature. The temperature of the system was set to be 278.0 K at the specified pressure to avoid instant hydrate formation during loading of the carbon dioxide. Sufficient carbon dioxide gas was then introduced into the reactor until the desired experimental pressure was reached.

As presence of other gases can affect the temperature and pressure at which hydrate will form, the type of hydrate formed and the occupation of hydrate cavities, carbon dioxide loading was repeated several times to ensure least gas contamination.

Upon loading, a subsequent decrease in pressure was detected. This is due to the dissolution of carbon dioxide in the liquid mixture. When pressure regains stability, the temperature of the system was then reduced to 275.0 K.

The changes in pressure and temperature were then recorded by a data acquisition system. The hydrate formation was considered complete when pressure of the system remains unchanged for 2-3 h.

The above steps were conducted without ionic liquid, then, with the addition of several concentrations of ionic liquid at the pressure of 25, 30 and 35 bar with a constant temperature of 275.0 K.

Ionic liquid sample preparation: Four different ionic liquid concentrations were utilized in this study; 0.1, 0.5, 1.0 and 10.0 wt.%. The 0.1 wt.% ionic liquid solution was initially prepared by addition of 11.83 µL of ionic liquid into deionized water. Subsequent solution concentrations were obtained with the equations below to calculate the required amount of the pure ionic liquid solution to produce the desired ionic liquid concentration. A basis of 100 kg solution was used for the utilization of the following formulas:

$$\text{Mole fraction} = \frac{\text{n EMIM BF4}}{\text{n EMIM BF4} + \text{nH}_2\text{O}} \tag{1}$$

where, n is the number of moles. The molar mass of EMIM BF_4 used is 197.97 kg $kmol^{-1}$. Assuming that, Mole Fraction = Volume Fraction.

The following formula was used to calculate the volume of ionic liquid required:

$$\text{Volume fraction (x)} = \frac{\text{Volume of EMIM BF}_4}{\text{Volume of solution}} \tag{2}$$

$$\text{Volume of EMIM BF}_4 = \text{Volume of solution} \times \text{Volume fraction (x)} \tag{3}$$

RESULTS AND DISCUSSION

Figure 3 shows samples of CO_2 hydrate formed at 30 bar while Fig. 4 through Fig. 6 show the temperature variation with time throughout the experiment.

The induction time which is the time at which nucleation occurs, is determined by visual observation. At the point of nucleation, a sudden increase in the temperature is detected as seen in Fig. 4-6, where the initial sudden increase was taken as the induction time. This is due to the

Fig. 3(a-b): Example of CO_2 hydrate formed at 30 bar

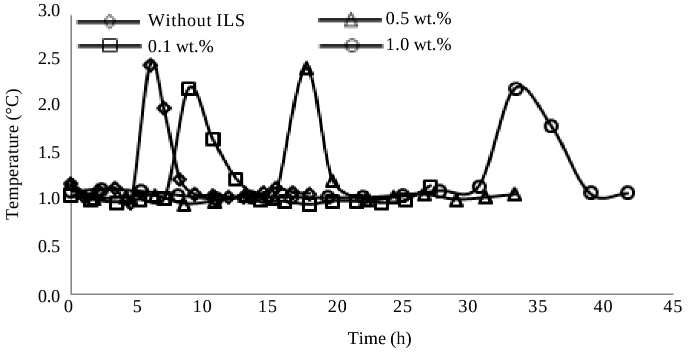

Fig. 4: CO_2 hydrate temperature vs. time at 25 bar for different ionic liquid's concentrations

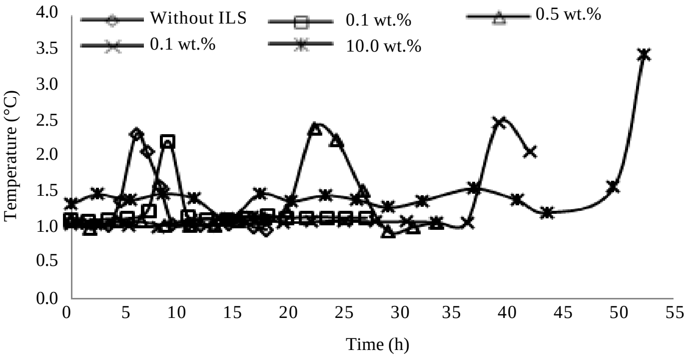

Fig. 5: CO_2 hydrate temperature vs. time at 30 bar for different ionic liquid's concentrations

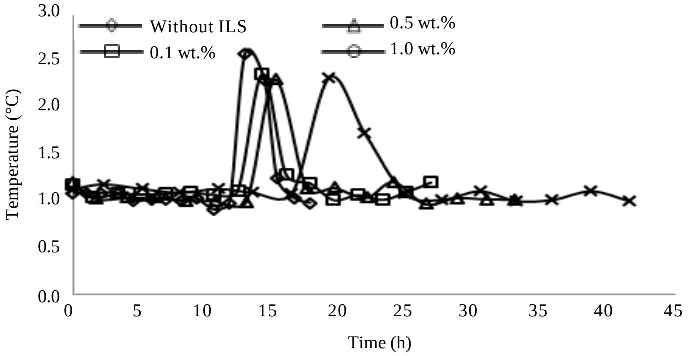

Fig. 6: CO_2 hydrate temperature vs. time at 35 bar for different ionic liquid's concentrations

exothermic process of the hydrate formation. During the hydrate formation process, the pressure was found to decrease tremendously (not shown in the figures) as gas was consumed and eventually, reaches a plateau. At this point, it is believed that no more hydrate is formed.

Figure 4 through 6 also show that additions of ionic liquids (IL) delay the CO_2 hydrate formation as indicated by the induction time tabulated in Table 2. The 0.1 wt.% of EMIM BF_4 has the least effect on the hydrate formation with the delay time increasing with the increase of ionic liquids concentrations to 0.5 and 1.0 wt.%.

Table 2: Hydrate induction time

	Range of induction time (h)		
Samples	25 bar	30 bar	35 bar
Pure deionized water	3.1	3.5	11.5
0.1 wt.% (EMIM BF_4)	6.3	6.0	13.2
0.5 wt.% (EMIM BF_4)	16.1	20.0	14.6
1.0 wt.% (EMIM BF_4)	30.2	36.3	17.1
10.0 wt.% (EMIM BF_4)	-	48.0	-

wt.%: weight percentage of inhibitors at Temperature: 275 K

In Fig. 4 and 5, the data trends show that the increasing of ionic liquid's concentrations do prolong the induction time accordingly. For example, the 0.5 wt.% concentration has roughly 3 times longer delay time compared to 0.1 wt.% concentration. However, in Fig. 5, 10 wt.% of ionic liquids does not show significant increase in the delay time of the hydrate formation which indicates that the delay time is not linearly increasing with the ionic liquids concentration.

While in Fig. 6, the gap between each sudden increase in the temperature data trend is small which indicates a shorter delay time. It is because the pressure parameter for this experiment was run at 35 bar which is near to CO_2 hydrate equilibrium line according to phase behavior diagram; therefore the delay time is shorter as the hydrate formation rate is higher at this condition (Sabil, 2009).

CONCLUSIONS

In general, the development of ionic liquids as LDHI can reduce the amount of chemical used and the cost for conventional hydrate inhibition method in pipeline. The use of ionic liquid as hydrate inhibitor will also have low environmental impact.

From the study, it can be concluded that using ionic liquid as kinetic inhibitor is effective in delaying the hydrate formation. The study also proves that induction time is longer with addition of ionic liquid as the time increases but not proportionally. On the other hand, the ionic liquid used as a thermodynamic inhibitor at high concentration did not achieve a significant difference in the induction time of the hydrate formation.

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