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EFFECT OF 1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE AND POLYVINYLPYRROLIDONE ON KINETICS OF CARBON DIOXIDE HYDRATES

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***Abstract*— In this study, the kinetics effects of Polyvinylpyrrolidone (PVP) and 1-Ethyl-3-methylimidazolium chloride (EMIM-Cl) on the induction time, initial rate of formation and moles consumed of carbon dioxide simple gas hydrate formation has been evaluated and compared at a concentration of 1 wt% using an isochoric constant cooling with stirrer on method at pressure and temperature condition of 3.6 MPa and 274.15 K, respectively, in a sapphire cell gas hydrate reactor. Results suggests that both 1-Ethyl-3-methylimidazolium chloride and Polyvinylpyrrolidone delayed carbon dioxide hydrate nucleation time by about 50% compared with pure sample. In addition, the presence of PVP reduced carbon dioxide hydrate initial formation rate and moles consumed into hydrate by about 86% and 21%, respectively, compared with 1-Ethyl-3-methylimidazolium chloride. Furthermore, synergically using 0.5 wt% PVP and 0.5 wt% EMIM-Cl significantly decreased the induction of carbon dioxide hydrate and increased both the initial rate of carbon dioxide hydrate formation and moles consumed into hydrate compared with the inhibition effect of pure Polyvinylpyrrolidone and 1-Ethyl-3-methylimidazolium chloride on CO_2 gas hydrates formation.**

***Keywords*—** *Gas hydrates; Carbon dioxide; Kinetics; 1-Ethyl-3-methylimidazolium chloride; Polyvinylpyrrolidone*

I. INTRODUCTION

Gas hydrates are non-stoichiometric solid inclusion compounds formed by the physical trapping of hydrogen bonded water molecules and guest gases of appropriate size through van der Waals forces [1]–[4]. The presence of water and appropriate gases at high pressure and low temperature are the basic conditions necessary for gas hydrate formation. Common gas hydrate formers are methane, ethane, propane and carbon dioxide. Gas hydrates contain about 85 mol% water cage-like molecules and depending on the size, shape and properties of the gas (guest) molecule, three common gas hydrate structures ca be formed; cubic structure I, cubic structure II and hexagonal structure H as shown in Fig. 1. The size and shape of the cavities in the cages determines the difference in structure, also the size of gas molecule accommodated by the water shows the type of hydrate formed. Mostly subsea pipelines flow streams contain methane, propane and ethane, therefore structure I and structure II hydrates are commonly formed in oil and gas pipelines. For simple hydrates, pure carbon dioxide and methane form structure I hydrates [5].

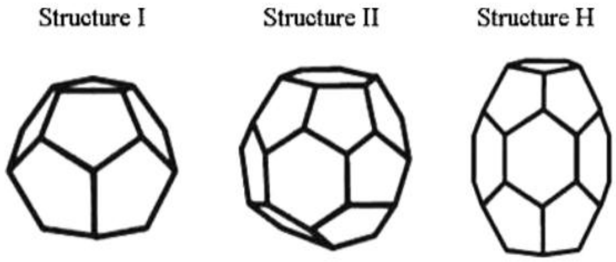

Fig. 1. Commonly formed gas hydrate structures

Natural methane gas hydrates are known as potential future sources of energy that will replace fossil fuel. Gas hydrates also has applications in gas transportations and storage of natural gas and as a technology for carbon dioxide sequestration and capture. However, gas hydrate is considered as threat to oil and gas flow assurance. Unfortunately, transportation of oil and gas activities and sequestration of carbon dioxide through pipelines into reservoirs operate in condition favorable for hydrate formation leading to hydrate formation in oil and gas pipelines which may further result in pipeline blockages, well shutdown, high financial loss and loss of human lives [6].

Heating, depressurizing, water removal and chemical inhibition are the available gas hydrate prevention methods [7]. However, chemical Inhibitors are practically applicable and widely used in the industry. Thermodynamic chemical inhibitors (such as methanol and ethylene glycol) are injected in flow streams to inhibit gas hydrate by disrupting the activity of water molecules in hydrate formation, shifting the hydrate formation phase boundary to high pressure and temperature conditions. However, the high injection of thermodynamic inhibitors resulting to increasing operating expenses and environmental challenges motivated the discovery of low dosage hydrate inhibitors (LDHIs) or kinetic hydrate inhibitors (KHIs). KHIs basically delays the hydrate nucleation formation time (induction time) and/or prevent further hydrate crystal growth once gas hydrates are formed. Polyvinylpyrrolidone (PVP) is one of the commonly used commercially KHI in the oil and gas industry. They inhibit hydrate by adsorbing to the hydrate crystal surface and prevent further increase in hydrate crystal growth through hydrogen bonding. Nevertheless these inhibitors perform poorly at high subcooling therefore, the need for new environmentally and effective KHI [5], [8]–[10].

Recently, some imidazolium base ionic liquids(ILs) was introduced as dual functional gas hydrate inhibitors [11] (i.e they have the ability to delay hydrate formation and growth and also shift the equilibrium hydrate curve to low temperatures and/or high pressure regions) due to their strong electrostatic force and hydrogen boding with water molecules. Since then, more research has been conducted regarding the use of ILs in gas hydrate mitigation [12]–[17]; findings from a recent review [18] showed that, ILs inhibit gas hydrate through the formation of hydrogen bond with water molecules minimizing the activity of water molecules in hydrate formation. In addition, the alkyl chain length of ILs cation and hydrophobicity of ILs affect its effectiveness as gas hydrate inhibitor as both thermodynamic and kinetic gas hydrate inhibitor.

Xiao et al. [19] studied the effect of EMIM-Cl as KHI using the measurement of induction time method, results showed that EMIM-Cl was a good kinetic gas hydrate inhibitor by delaying the gas hydrate induction time of methane hydrate. In other for ILs gas hydrate inhibitor to move from research point to industrial applications as KHI, one critical factor that needs to be considered is its effectiveness over the existing commercially used KHIs (e.g. PVP). For good and effective comparison of KHI, the induction time is not enough to make conclusions, other gas hydrate kinetic inhibition parameter that can be considered are initial hydrate growth rate and amount of mole consumed into hydrate. These parameters describes the ability of an inhibitor to delay further growth and crystallization of gas hydrates [3].

This work seeks to determine the effects of EMIM-Cl on the kinetics of CO_2 gas hydrate formation and compare its inhibition abilities to that of commercial used KHI (PVP). This work is relevant to the ongoing gas hydrate research committed to developing new KHIs which will be environmentally friendly and effective at high subcooling for safe flow assurance operations for oil and gas production and carbon dioxide sequestration process.

II. EXPERIMENTAL SECTION

A. *Experimental Materials.*

The experimental materials used in this work are shown in Table 1. All solutions were prepared using deionized water. The materials were used without further purification.

Table 1. Details of experimental materials used in this work

Chemical	**Molecular weight ($g \cdot mol^{-1}$)**	**Purity (mol%)**	**Supplier**
Carbon dioxide	44.01	0.9995	Gas Walkers SDN BHD
1-Ethyl-3-methy-limidazolium chloride	146.62	0.99	Sigma-Aldrich
Polyvinylpyrrolidone	160,000	0.99	Benua Sains Sdn. Bhd

B. *Experimental Apparatus.*

A costumed fabricated hydrate sapphire cell rector modeled for gas hydrate studies was used in this work as shown in Fig. 2. The apparatus consist of a 29 ml transparent sapphire cell, in which experiments can be monitored by physical observation through the cell. The setup is designed to function up to 20 MPa and a temperature range of 253.15 to 338.15 K. Temperature in the cell measured with two thermocouples (located at the top and bottom of the sapphire cell), it also consists of a pressure transducer for pressure measurement. The sapphire cell is place in a water bath using ethanol as refrigerant liquid. The temperature of the water bath is controlled by Lauda R24 thermostats. In order for adequate stirring, a magnetic torque stirrer is placed in the cell. Connected to the sapphire cell is a gas booster compressor to pressurize the cell with the gas to be studied, in addition is a manual pump used to load the cell with liquid sample. The whole apparatus is connected to a data acquisition source which continuously records pressure and temperature changes in the cell every 10 s with an accuracy of ± 0.01 MPa and ± 0.5 K respectively.

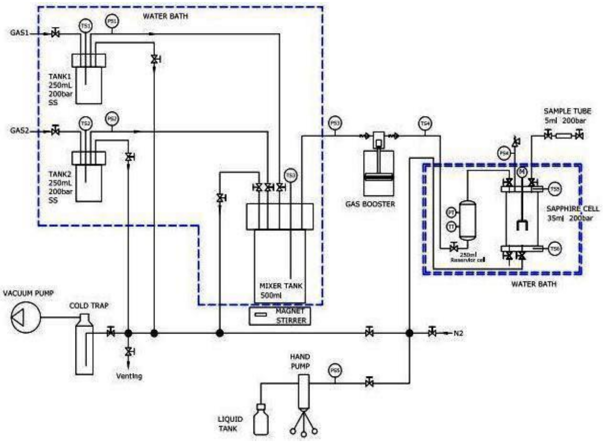

Fig. 2. Schematic diagram of the experimental apparatus in this work

C. Experimental Method.

In all experimental runs, an isochoric constant cooling method was used. EMIM-Cl and PVP solutions were prepared using deionized water at 1 wt%. In every run, before the liquid sample is loaded in the sapphire cell, the cell is vacuumed to remove excess air in the cell. The cell is then loaded with 18ml of liquid sample. The system temperature is set to about 1-2 K above the hydrate equilibrium temperature of the experimental pressure (3.5 MPa). This is to prevent the initial formation of hydrate when pressurizing the cell with the carbon dioxide.

The cell is pressurized to the experimental pressure, then the stirrer is turned on. The system is left until the pressure become stable at the experimental pressure. The experimental temperature for all experiment in this work is fixed at 274.15 K. The system temperature was reduce to the experimental temperature for hydrate to form simultaneously with the data acquisition system recoding the changes in pressure and temperature of the system for every 10 seconds. The experiment is considered completed by observing a constant pressure and temperature in the cell for 2-3 hours.

D. Determining of Induction Time, Gas Consumed and Apparent Rate Constant.

The induction time, ti, describes the ability of a kinetic hydrate inhibitor to delay the formation and/or growth of gas hydrate. It is defined in practice as the time taken for the formation of a detectable volume of hydrate phase [3] or the time taken for and inhibitor to fail. High induction time indicates greater inhibition. The induction time in this work is calculated from the pressure – time plotted as illustrated in Fig. 2 as;

$$t_i = t_s - t_h \qquad (1)$$

where ts is time taken for the system temperature and pressure to stabilize at experimental pressure, and t_h is the time when detectable hydrate is noticed and grow rapidly, indicated by a sharp pressure drop due to gas consumption into hydrate. However, the initial pressure drop between t_s and t_h in Fig. 3, is the amount of gas consumed in gas hydrate nucleation.

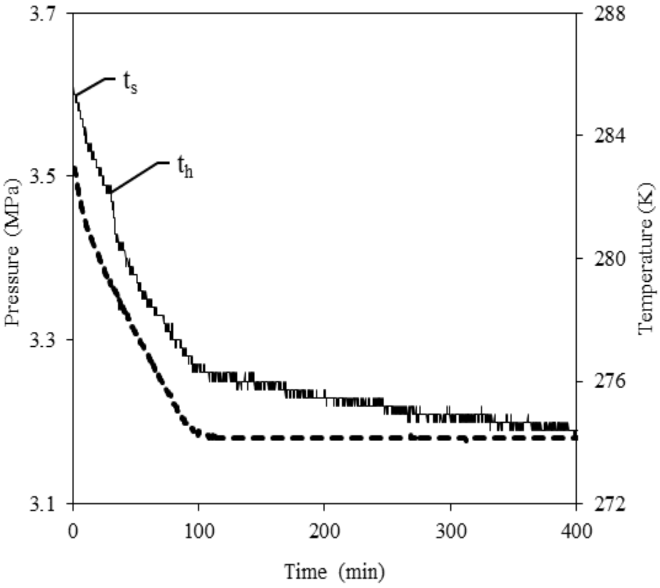

Fig. 3. A typical Temperature (- - -) and pressure (—) vs time plot for CO_2 hydrate formation in 1 wt.% EMIM-Cl solution.

The gas consumed is determined by using the real gas equation of state. The apparent rate constant is determined as described by Partoon et al [19] as finding the gradient of the plot of calculated gas consumed verses time. The Peng–Robinson equation of state is used to calculate the compressibility factor, *Z*.

III. RESULT AND DISCUSSION

Prior to the study, the accuracy of the experimental setup employed in this work was validated by determining the hydrate phase equilibrium data of CO_2 and compared to data presented in existing literature (see Fig. 4). In Fig. 4, the hydrate phase equilibrium data measured by the experimental setup in this work agrees with data in existing literature and validates the accuracy of the setup.

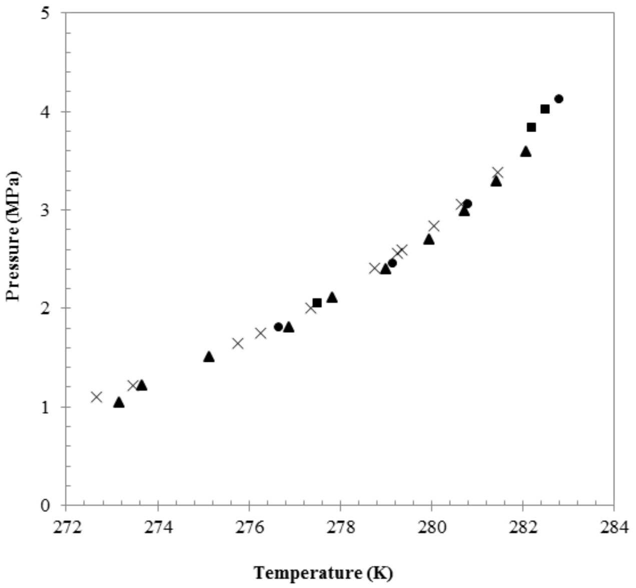

Fig. 4. Carbon dioxide (CO_2) H-L-V equilibrium data: ●, this work; ■, Mohammadi et al [20]; ▲,×, Sabil et al [21], [22].

A. *Induction Time*

The induction of carbon dioxide gas hydrate formation with and without PVP and EMIM-Cl is shown in Fig. 5. In Fig. 5, both PVP and EMIM-Cl delayed hydrate nucleation time about twice that of deionized water, with PVP slightly higher than EMIM-Cl comparatively. Since hydrate formation is a stochastic process [23], using induction alone to analyze the effectiveness and KHI maybe sometimes be misleading. However induction time can be very good gas hydrate inhibition indicator when experiments are performed at high pressure and or subcooling [24], as in the case of this work.

B. *Hydrate Crystal Growth*

Preceding hydrate nucleation is hydrate growth and crystallization. The hydrate growth rate and crystallization analyzes the effectiveness of a KHI, revealing the true ability of the inhibitor to reduce hydrate growth rate and the total amount of gas that will be consumed into hydrates when hydrates are completely formed.

The initial hydrate formation rate for PVP and EMIM-Cl is shown in Fig. 6. EMIM-Cl and PVP reduces the initial hydrate formation rate of CO_2 and deionized water about 21% and 86%, respectively. However, the percentage initial CO_2 hydrate formation rate reduction of PVP compared to EMIM-Cl was about 84% (see Fig. 6). In addition, Fig. 7 shows a plot of consumed gas (carbon dioxide) verse time. In Fig. 7, PVP adsorbs on hydrate nuclei and prevent further carbon dioxide consumption into hydrate than EMIM-Cl which prevents carbon dioxide consumption by forming hydrogen bonding with water molecules [19].

The synergic effect of 0.5 wt.% PVP and 0.5 wt.% EMIM-Cl on carbon dioxide hydrate was also studied. Results show that the synergy of PVP and EMIM-Cl significantly decreased the induction time of CO_2 hydrate and increased the initial rate of CO_2 hydrate formation and consumption in comparison with pure EMIM-Cl and PVP as shown in Fig. 5, 6, & 7.

The poor inhibition effect observed by the synergy of EMIM-CL and PVP may be due reduction in surface tension of the vapor – bulk liquid interface which leads to more CO_2 consumption to hydrate formation. The synergy results in this work contradicts with earlier work reported by Del Villano and Kelland [12] on the synergic effect study on two ILs (EMIM-BF_4 and BMIM-BF_4) and commercial KHIs based on vinyl lactam polymers on structure II hydrates. They reported that, the studied ILs performed very poor as KHIs for structure II hydrates at 5000–10000 ppm when used alone, but synergically good with vinyl lactam polymers based commercial KHIs.

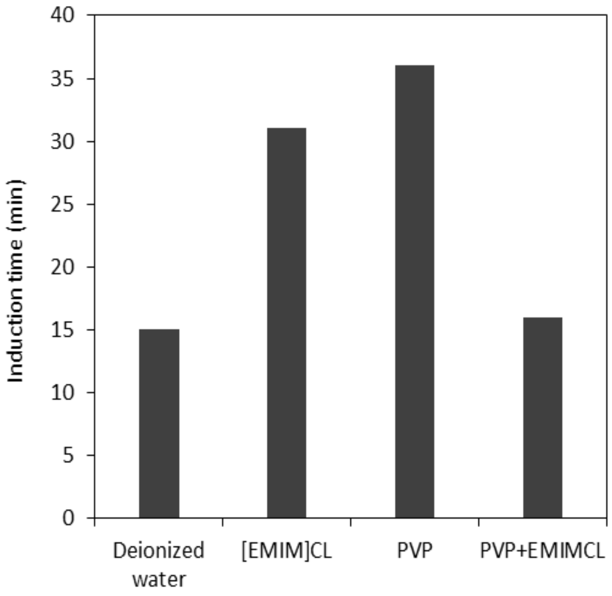

Fig. 5. CO_2 hydrate induction time in the presences for deionized water, EMIM-Cl, PVP and 0.5 wt% PVP+ 0.5 wt% EMIM-Cl.

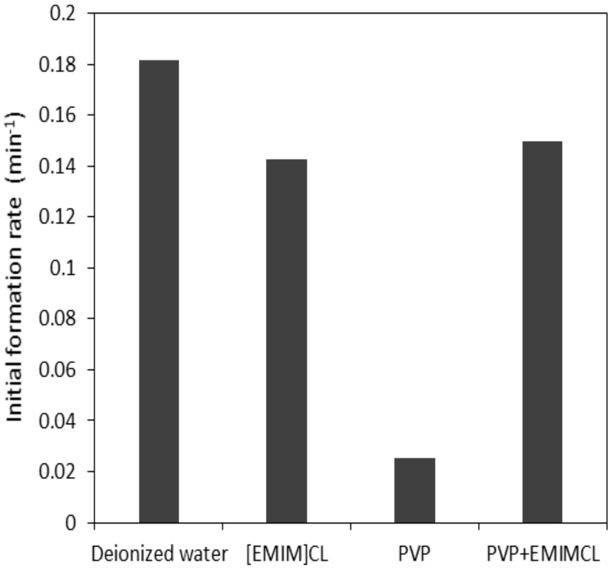

Fig. 6. CO_2 hydrate apparent rate constant in the presences for deionized water, EMIM-Cl, PVP and 0.5 wt% PVP + 0.5 wt% EMIM-Cl.

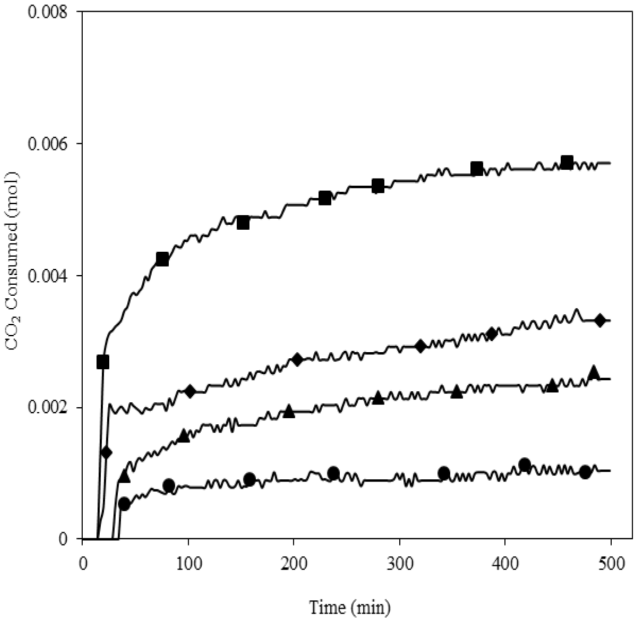

Fig. 7. Amount of CO_2 moles consumed during hydrate growth for CO_2 hydrate; ■: Deionized water; ◆: 0.5 wt% PVP + 0.5 wt% EMIM-Cl ; ▲: 1 wt. % EMIM-Cl ; ●: 1 wt.% PVP.

IV. CONCLUSION

The kinetic inhibition effect of PVP and EMIM-Cl has been studied at 1 wt.%, the study showed that, PVP and EMIM-Cl delays CO_2 hydrate nucleation time and at the same time decrease CO_2 hydrate initial formation rate and consumption. However, EMIM-Cl perfumed poorly as a KHI for CO_2 compared to PVP. Furthermore, synergic effect of PVP performed poorly in kinetic inhibition of CO_2 hydrate compared to the kinetic inhibition effect of pure PVP and EMIM-Cl on CO_2 hydrates.

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