Kinetics of Mixed Amino Acid and Ionic Liquid on CO₂ Hydrate Formation

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Abstract. The formation of gas hydrate in oil and gas and carbon dioxide sequestration processing pipelines is unwanted and must be prevented for easy and safety processes. However, conventional kinetic hydrate inhibitors are less effective and thus, new inhibitors are required to effectively manage hydrate formation in the industry. Recently, ionic liquids and amino acids have been introduced as potential kinetic gas hydrate inhibitors (KHIs). But the quest for highly effective amino acids and ionic liquids hydrate inhibitors is still on going with no desired inhibition impact reported so far. Hence, a blend of these two classes of novel kinetic hydrate inhibitor may possibly perform better. Herein, the combined kinetic gas hydrate inhibition effect of some best performed amino acid (glycine) and ionic liquid (1-Ethyl-3-methylimidazolium chloride) is reported on CO₂ hydrate formation. The study was conducted in a sapphire hydrate cell using the constant cooling isochoric mode at 50/50 wt.% concentration of glycine and 1-Ethyl-3-methylimidazolium chloride at a total concentration of 1 wt.%. All experiments were performed at 3.5 MPa and 274.15 K. The results showed that, all studied systems (pure glycine and 1-Ethyl-3-methylimidazolium chloride and their mixture) inhibited CO₂ hydrate formation by increasing its induction time and reducing the total moles of CO₂ converted into hydrate. The inhibition impact of glycine was less than 1-Ethyl-3-methylimidazolium chloride, but surprisingly their combined effect was less than 1-Ethyl-3-methylimidazolium chloride but higher than glycine base on induction time and CO₂ uptake evaluation.

Keywords: Carbon dioxide; Gas hydrate; Kinetics; Glycine; 1-Ethyl-3-methylimidazolium chloride

1. Introduction

The formation of gas hydrate in oil and gas pipelines is undesired and must be prevented. During oil and gas production, the presence of reservoir water, hydrocarbons, low temperature and high-pressure condition assures serious gas hydrate threat which must be well predicted and avoided. Gas hydrates are ice-like compounds which are formed by the trapping of gas molecules in hydrogen bonded water cages at low temperatures and high pressures. [1–3]. There are three types of gas hydrate structures; structure
I, structure II and structure H. However, their structures are dependent on the type, size, and guest-to-cage size ratio of the gas molecule [4,5]. The formation of gas hydrates in oil and gas transmission pipelines may cause blockages due to its crystal solid nonflowing structures [6]. The formation of hydrate may also result in several safety problems, which in severe cases can lead to loss of lives. Hence, the formation of hydrates in hydrocarbon flow assurance are seriously unwanted. The oil and gas industries spend about 70% of their OPEX on the removal of hydrate plugs. Therefore, to ensure hydrate free operations, much attention is focused on the development of hydrate preventive methods form both academia and industry alike.

There are four methods of preventing hydrate formation and plugs; water removal, depressurization, thermal heating, and injection of chemical inhibitors. The best and practicable method is the injection of chemical inhibitors to disrupt the chemical potential of the water molecules either kinetically or thermodynamically. Thermodynamic inhibitors such as methanol, and glycols are used to reduce the risk of hydrate plugging in pipelines by shifting the hydrate phase equilibria to low temperature and high pressure regions [7]. However, conventional THIs have several problems. In particular, the toxic nature of these chemicals causes serious environmental pollution in ecological systems and critical damage to the polymer used to seal pipelines [8]. Therefore, low-dosage hydrate inhibitors (LDHIs) were introduced to replace the thermodynamic inhibitors. These class of inhibitors are used to reduce the nucleation time and at the same time reduced the hydrate formation rate and gas uptake. Generally, LDHIs are polymers such as PVP and PVCap. However, the capabilities of LDHIs to prevent hydrate formation are associated with uncertainties arising from the stochastic nature of hydrate nucleation and other kinetic factors [9]. In addition, the current LDHIs are not effective at lower subcooling conditions. Therefore, the development/discovery of new LDHIs is necessary for effective hydrate plug prevention, especially in deep sea operations.

Currently, there is a continuous search for novel LDHIs that can solve the problems that limits present techniques, especially kinetic gas hydrate inhibitors (KHIs). In searching for new KHIs inhibitors, ionic liquids (ILs) and amino acids are recently reported as novel KHIs for gas hydrate mitigations [3,10,11]. The kinetic hydrate inhibition impact of ionic liquids is attributed to their hydrogen bonding potentials and hydrophobic nature arising from the cations and anions of ionic liquids. [12–15]. On the other hand, amino acids are believed to perturbed water molecules via hydrogen bonding interaction with water molecules, thereby, delaying the hydrate nucleation time and growth kinetics [11,16–18]. These recent discoveries have led to much research [19–21] in discovering the best ILs or amino acids that can perform better than the conventional KHIs. Most especially imidazolium base ILs and natural amino acids have received much attention and studies in these regards. Literature shows that 1-Ethyl-3-methylimidazolium chloride and Glycine are one of the best gas hydrate inhibitors among the imidazolium ionic liquid family and naturally occurring amino acids. We previously reported that PVP slightly inhibits CO2 hydrate than 1-Ethyl-3-methylimidazolium chloride at 1 wt.% [19,22,23]. Sa et al[24] also presented that the kinetic inhibition strength of glycine and PVP are in the same range on the bases of subcooling and gas uptake [17,25].

Nonetheless, this inhibition performance is relatively weak as against the conventional KHIs, therefore a synergist study of the some of the best performed ILs and amino acids inhibitors is encouraging to develop effective KHIs. In addition, the scarcity of ILs + amino acids synergistic study in open literature is a motivating factor for conducting this study. In this study, the synergic kinetic effect of 1-Ethyl-3-methylimidazolium chloride (ILs) + glycine (amino acid) on carbon dioxide hydrate formation is studied in an isochoric mode at a total concentration of 1 wt.% synergy (0.5 wt.% 1-Ethyl-3-methylimidazolium chloride + 0.5 wt.% glycine).

2. Methodology

2.1. Materials

Fig. 1 shows the chemical structure of 1-Ethyl-3-methylimidazolium chloride and glycine. The 1-Ethyl-3-methylimidazolium chloride (EMIM-Cl) (purity 98%) and Glycine (purity 99.7%) were provided by Merck Malaysia and were used without further purification. Carbon dioxide (purity 99.995%) was supplied by Gas Walker Sdn Bhd, Malaysia. All samples were prepared with deionized water. The
chemicals were tested at 1 wt.% (50:50 % synergy of 1-Ethyl-3-methylimidazolium chloride and glycine).

Fig. 1. Chemical structure of 1-Ethyl-3-methylimidazolium chloride and glycine

2.2. Experimental apparatus and Kinetic measurement procedure

The experimental apparatus and methods used in this study are explained in details elsewhere [19,22,26–29]. To effectively evaluate the CO$_2$ hydrate formation kinetics in the presence of mixed EMIM-Cl and glycine, an Isochoric constant cooling method was adopted. A sapphire hydrate cell with volume of 29 ml was employed. The system can operate at a maximum pressure and temperature of 20 MPa and 338.15 K, respectively. Prior to all experiments, the cell is washed and dried thoroughly to remove all contaminants. The system temperature is then set to about 2–3 K above the desired hydrate equilibrium temperature of the testing experimental pressure (in this case 3.6 MPa). The desired testing solution (0.5 wt.% 1-Ethyl-3-methylimidazolium chloride + 0.5 wt.% glycine) is pumped into the reactor via a hand pump. Pure carbon dioxide is then pressurized into the cell and allowed to stabilize at 3.6 MPa with the stirrer on. After one hour, when the system is stabilized, the system temperature is reduced constantly to 274.15 K at 4 K/h for hydrate to form. The formation of hydrate in the reactor is noticed by observing a sharp system pressure drop and visually through the reactor and via the pressure time plot as shown in Fig 2. The experiment is considered done when the system pressure remains constant for about 3 – 5 hours after hydrate formation. A data acquisition system is attached to the system to continuously record the pressure and temperatures changes in the reactor with an accuracy of ± 0.1 K and ± 0.01 MPa, respectively.

Fig. 2. A typical Pressure vs time plot for CO$_2$ hydrate formation.

The induction time, $t_i$ describes the ability of a kinetic hydrate inhibitor to delay hydrate formation nucleation. It is defined in practice as the time taken for the formation of a detectable volume of hydrate phase or the time taken for an inhibitor to fail [3]. High induction time indicates greater inhibition. The induction time is a very important parameter for hydrate prevention during drilling of hydrate sediments. It characterizes the retention time the drilling can prevent hydrate agglomeration and growth in the wellbore. The induction time is calculated from the pressure – time plotted as illustrated in Fig. 2 as: 
\[ t_i = t_s - t_h \]  \hspace{1cm} (1)  

where \( t_i \) is time taken for the system temperature and pressure to stabilize at experimental pressure, and \( t_s \) is the time when detectable hydrate is noticed and grow rapidly, indicated by a sharp pressure drop due to gas consumption into hydrate. To calculate the amount of gas consumed into hydrate, the real gas equation is employed to determine the difference between the number of \( \Delta n_H \) of moles of gas at time zero and time \( t \) during hydrate formation process as given in equation 2.

\[ \Delta n_H = \left[ \frac{PV}{zRT} \right]_0 - \left[ \frac{PV}{zRT} \right]_t \]  \hspace{1cm} (2)  

where, \( P \), \( V \), \( T \) and \( R \) are system pressure, gas phase volume, temperature and universal gas constant respectively.

3. Results and Discussions

In this study, induction time and total gas uptake were used to evaluate the kinetic inhibition impact of mixed EMIM-Cl and glycine. Though adopting induction time to determine the KHI performance may sometimes lead to wrong judgment, since hydrate formation is a probabilistic process [30]. However, induction time is still the main important KHI indicators, because it describes the retention time of the gas stream to prevent hydrate formation, especially at high pressure and/or subcooling conditions [31]. In this work, the experiments were conducted at high pressure (3.6 MPa), thus using induction time will give a clear representation of hydrate prevention impact in the presence of the tested inhibitors. Table 1 presents the measured induction time of carbon dioxide hydrate in the presence of all studied systems in this work. Its observed that, the presence of both pure and mixed EMIM-Cl and glycine significantly delayed the \( \text{CO}_2 \) hydrate nucleation time. EMIM-Cl exhibited the highest induction time inhibition impact of about 114% delay in the hydrate formation nucleation. Glycine delayed the \( \text{CO}_2 \) hydrate induction time of about 42% against 64% for mixed 0.5wt%. EMIM-Cl + 0.5 wt%. glycine. This indicates that, instead of expecting a high inhibition strength when both inhibitors are combined, the presence of glycine reduces the inhibition strength of ionic liquids (EMIM-Cl). Contrary, the presence of EMIM-Cl increases the kinetic inhibition impact of amino acids (glycine).

| Systems | Induction time (min) |
|---------|---------------------|
| Pure water | 14.46 |
| Glycine | 20.67 |
| EMIM-Cl | 30.17 |
| 0.5 wt%. EMIM-Cl + 0.5 wt%. Glycine | 23.83 |
Interestingly, a similar trend of induction time inhibition is observed in Fig. 3 for the total CO$_2$ gas uptake. A CO$_2$ uptake inhibition of about 128% was exhibited by pure EMIM-Cl, followed by 34% for mixed 0.5wt%. EMIM-Cl + 0.5wt%. pure glycine, and 25.5% for glycine. It can be deduced that, in synergy of EMIM-Cl and glycine positively favors glycine but negatively affects EMIM-Cl.

In our previous studies on the synergic effect of EMIM-Cl and PVP a similar poor inhibition impact was observed compared with pure PVP [20,32]. These was found to be due to interactions between EMIM-Cl and PVP molecules which reduces the absorption ability of PVP and causes more CO$_2$ to dissolve into liquid phase, hence, enhancing hydrate formation. Herein, the presence of glycine and EMIM-Cl have similar interaction behavior which probably causes a steric orientation of the hydrogen bonded water structure to align in a way which promotes hydrate formation.

4. Conclusion
In this work, the induction time and total gas uptake for pure and mixed EMIM-Cl + glycine on CO$_2$ hydrate formation have been evaluated in an isochoric constant cooling mode at 1 wt.%. The results show that, the synergic effect of EMIM-Cl + glycine enhances the KHI performance of amino acids (glycine) but significantly reduces that of ionic liquids (EMIM-Cl). It is therefore recommended that, further studies on different hydrate formers at different operational conditions is needed for the development of effective KHI and to better understand the kinetic inhibition mechanism of gas hydrates in the presence of mix inhibitors.

5. Acknowledgments
The authors would like to acknowledge the Universiti Teknologi PETRONAS for their financial support.

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