INVESTIGATION OF PYRROLIDINIUM- AND MORPHOLINIUM-BASED IONIC LIQUIDS INTO KINETIC HYDRATE INHIBITORS ON STRUCTURE I METHANE HYDRATE

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ABSTRACT
Kinetic hydrate inhibitors (KHI) are a kind of low dosage hydrate inhibitor (LDHI) that have been propagated in the oil and gas industries to prevent the blockages in pipelines with gas hydrates. In general, KHIs are water-soluble polymers, especially co-polymers, and sometimes mixed with additional organic materials to enhance their retarding strength on gas hydrate formation. However, more effective KHIs than existing inhibitors are still required for some severe cases of high degrees of sub-cooling and high pressures. For this reason, ionic liquids become attractive new inhibitors. Several imidazolium-based ionic liquids have been announced that they showed the KHI performance and sometimes dual functional performances of KHIs and thermodynamic inhibitors (THIs). This is very interesting results because there have been no other non-polymeric KHIs. In this paper we present some new KHIs based on pyrrolidinium and morpholinium ionic liquids. We synthesized these ionic liquid KHIs in our laboratory, and measured their effect on shifting the equilibrium curves (hydrate–water-rich liquid–vapor, HLV) and retarding the gas hydrate nucleation/growth by investigating their induction times during methane hydrate formation. The induction times of aqueous solutions were measured, and the effect of inhibition strength was investigated regarding the composed anion of tetrafluoroborate. Results show that the superior inhibition effect of the ionic liquids containing hydroxyl group was observed among the tested ionic liquids. It was found that ionic liquids shifted the hydrate equilibrium line to a lower temperature at a specific pressure, while simultaneously delaying gas hydrate formation.

Keywords: gas hydrates, kinetic inhibitors, ionic liquids, methane hydrates

INTRODUCTION
Gas hydrates have received increased attention recently as research on future green energy and carbon sequestration has become more urgent. Natural gas obtained from methane hydrates can be an alternative energy source, and carbon dioxide can be captured in void space in hydrates in the form of ice-like solids [1-2]. Recently, Lee et al. found a swapping phenomenon between gaseous carbon dioxide and methane hydrate deposits [3]. In a suggested process, carbon dioxide is directly sequestered into the methane hydrate layer while methane is simultaneously produced with a high recovery rate of higher than 90 %. In addition, they opened up a new research field of hydrogen storage based on hydrate materials. The new storage medium captured hydrogen up to 4 wt% [4].

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While gas hydrates have become a strategic material in solving the crises relating to future energy needs and global warming, the formation of hydrates in oil and gas industries has long been a severe problem [1-2]. Gas hydrate formation under the conditions typical of oil and gas production and transport can cause pipeline blockage or explosion, resulting in economic loss as well as ecological disasters. To deal with these problems, research on the development of new and effective inhibitors has been increased. Chemicals that possess inhibition activities at comparatively small amounts have been studied and named low-dosage hydrate inhibitors (LDHIs). Until now, there have been two kinds of LDHIs. The first type is a group of compounds called kinetic hydrate inhibitors (KHIs), which retard gas hydrate formation. Although KHIs do not shift the equilibrium temperature at a specific pressure and eventually allow hydrate formation, they do slow down the rates of hydrate nucleation and growth. The other type is anti-agglomerants (AAs), which prevent gas hydrate formation by preventing the agglomeration of particulates. KHIs retard gas hydrate formation and elongate induction time at low dosages of 1-2 wt%. Thus, KHIs are expected to possess significant economic and environmental advantages. All discovered KHIs to date are water-soluble polymers. Poly(N-vinylpyrrolidone) (PVP), poly(N-vinylcaprolactam) (PVCap), poly(N-methyl-N-vinylacetamide) (VIMA), poly(N-vinylvalerolactam) (PVVam), poly(acryloyl pyrrolidine) (PAPYD), and their copolymers are all representative examples of KHIs [2]. However, the economic application of KHIs is still under development, especially at a large degree of subcooling, meaning the temperature difference between the equilibrium and operational temperatures. Therefore, there is demand for new inhibitors or a combination of inhibitors that are cost effective and efficient. Herein, we present new methods to introduce ionic liquids (ILs) as inhibitors.

ILs are generally stable in the presence of air and water. Their physical properties strongly depend either on the length of the alkyl chain of cation or on a specifically designed cation and anion. Therefore, ILs can be designed and synthesized for specific purposes. Adidharma et al. first identified ILs as a novel methane hydrate inhibitor based on both thermodynamic and kinetic mechanisms [5-6]. Their discovery of a new inhibitor system, so called “Ionic Liquids”, is expected to bring about progress in the area of hydrate inhibition and help open up another phase in relevant industries. However, they tested only imidazolium cation-based ILs without optimizing the combination between the cation and anion. Whether or not there are other ILs that can be used as inhibitors is an interesting research question, the answer to which depends on how to design and synthesize suitable ILs. In this context, we adopted a systematic approach starting from IL design to synthesis, with the goal of tailoring ILs to a single purpose: “Tuning Ionic Liquids for Hydrate Inhibition”.

This paper presents the use of ILs as hydrate inhibitors and their duel function effects as the thermodynamic and kinetic inhibitors. ILs are carefully tailored for this goal. This dual function makes this type of inhibitors perform more effectively. In this study, we synthesized N-(2-hydroxyethyl)-N-methylpyrrolidinium tetrafluoroborate ([HEMP][BF4]), N-butyl-N-methylpyrrolidinium tetrafluoroborate ([BMP][BF4]), and N(2-hydroxyethyl)-N-methylmorphorinium Tetrafluoroborate [HEMM][BF4], and purchased N-ethyl-N-methylimidazolium tetrafluoroborate ([EMIM][BF4]). Their performances in shifting the HLVE curve and slowing down hydrate formation rate were experimentally investigated.

**EXPERIMENTAL SECTION**

**Synthesis of ILs**

**Materials**

The materials used in this work were as follows: 4-methylmorpholine (Aldrich, 99%), 1-methylpyrrolidinum (Fluka, 99%), 2-chloroethanol (Aldrich, 99%), 1-bromobutane (Aldrich, 99.5%), 2-bromoethanol (Aldrich, 95%), sodium tetrafluoroborate (Aldrich, 98%), dichloromethane (SAMCHUN, 99.5%), acetone (DAEJUNG, 99.8%), and acetonitrile (JUNSEI, 99.5%). N-ethyl-N-methylimidazolium tetrafluoroborate (Ctri)

**Synthesis**

N-hydroxyethyl-N-methylpyrrolidinium chloride ([HEMP][Cl]). 1-methylpyrrolidinum (0.5 mol) in 200 mL of acetonitrile was added dropwise to 0.5 mol of 2-chloroethanol in a three-necked round-bottom flask. The mixture was refluxed under nitrogen gas for 72 h at 343.15 K. The molten salt was then decanted from the hot solution in a separatory funnel, washed three times with acetone, and dried on a rotary evaporator for 5 h at 323.15
K under low pressure. The solid product of [HEMP][Cl] was dried under vacuum conditions at 323.15 K for more than 48 h.

$^1$H-NMR(DMSO) spectrum consisted of the following peaks: 2.06 (s, 4H), 3.10 (s, 3H), 3.48–3.51 (m, 2H), 3.56–3.59 (t, 4H), 3.80–3.81 (m, 2H), 5.76–5.79 (t, 1H).

N-butyl-N-methylpyrroldinium tetrafluoroborate ([BMP][BF₄]), scheme 1(B): [BMP][Br] (0.2 mol) in acetone was reacted with 0.2 mol of sodium tetrafluoroborate in a round-bottom flask. After 24 h of stirring, the resulting NaBr precipitate was filtered through a plug of filter paper, and the volatiles were removed using a rotary evaporator at 323.15 K. The product was dissolved in dichloromethane, and the organic phase was washed twice with water to ensure complete removal of the bromide salt. Then, the product was dried for more than 24 h under vacuum conditions at 323.15 K.

$^1$H-NMR(DMSO) spectrum consisted of the following peaks: 0.67–0.71 (t, 3H), 1.03–1.12 (m, 2H), 1.40–1.48 (m, 2H), 1.84 (s, 4H), 2.73 (s, 3H), 3.02–3.07 (m, 2H), and 3.18–3.23 (m, 4H).

N-(2-hydroxyethyl)-N-methylmorpholinium tetrafluoroborate ([HEMM][BF₄]), scheme 1(C): [HEMM][Br] (0.2 mol) in acetone was reacted with 0.2 mol of sodium tetrafluoroborate in a round-bottom flask. After 24 h of stirring, the resulting NaBr precipitate was filtered through a plug of filter paper, and the volatiles were removed using a rotary evaporator at 323.15 K. The product was dissolved in dichloromethane, and the organic phase was washed twice with water to ensure complete removal of the bromide salt. Then, the product was dried for more than 24 h under vacuum conditions at 323.15 K.
salt. Then, the product was dried for more than 24 h under vacuum conditions at 323.15K. 

$^1$H-NMR(DMSO) spectrum consisted of the following peaks: 3.21 (s, 3H), 3.47 (t, 2H), 3.53 (t, 2H), 3.6 (t, 2H), 3.89 (s, 2H), 3.95 (s, 4H) 5.32 (t, 1H).

**Apparatus and procedure**

The synthesized and purchased ILs were highly hygroscopic and water-soluble. Short alkyls were chosen as cations, and BF$_4^-$ were chosen as anions for the induction of hydrogen bonding with water. To examine hydrate formation, the concentrations of the ILs in water were 10, 1, and 0.1 wt%.

To measure the dual function inhibition effects of ILs on methane hydrate formation, both the equilibrium dissociation pressures and induction times were measured. Equilibrium dissociation pressures were measured in order to determine the sub-cooling shift with methane hydrate at specific pressures with and without inhibitors.

To measure the induction time of methane hydrate formation, IL samples were prepared as aqueous solutions. Solutions of 90 ml were charged in a high-pressure cell with a volume of 220 mL at 274 K and degassed under vacuum conditions. Methane gas of 99.999% purity was then introduced into the cell at a pressure of 70 bar. The temperature of the cell was maintained at 274 K, and the contents of the cell were stirred using a magnetic spin bar at 700 rpm after the pressure of the high-pressure cell had become stable. The pressure and temperature of the high-pressure cell were measured throughout the whole experiment, and a sudden pressure drop was detected when gas hydrate formation occurred. The induction times of each sample solution were measured five times. Scattering of the measured induction times did occur due to a natural phenomenon, which was dependent on the number of repeated experiments. In this study, we investigated the feasibility and basic characteristics of gas hydrate inhibition. The solution samples that experienced gas hydrate formation were heated up to 313 K and maintained for at least 3 h in order to minimize any memory effect. Although gas hydrate formation progressed through the well-known steps of gas dissolution, crystal nucleation, and growth, we determined the induction times of the corresponding sample under specific conditions at the end of dissolution.

We presented the following Figure 1 to explain for readers' understanding. The pressure of the gas and temperature of the solution were recorded while stirring the solution with a magnetic spin bar. Since onset of the hydrate formation becomes, a sudden drop in pressure was noted as seen in the following figure. Time and pressure, $t_i$ and $P_s$, were detected and chosen as the onset of the hydrate formation. Time from the beginning to $t_i$ is named for “the induction time”.

![Figure 1. The P-T diagram for measuring induction time](image)

**RESULTS AND DISCUSSION**

We attempted to develop new and powerful ILs as inhibitors of methane hydrates and evaluate their inhibition activities. The design of ILs for hydrate inhibition was based on simple two hypotheses. First, ILs must be hydrophilic or hygroscopic. If the materials are hydrophobic, then they will reside in a separate phase from water and be unable to access water molecules. Second, special functional groups such as oxygen or hydroxyl groups need to be introduced in the IL structure since they would create intermolecular hydrogen bonding with the hydroxyl groups of water molecules, leading to disrupting the great number of hydrogen bonds between water molecules, thus effectively preventing hydrate formation [7-11].

According to the selected criteria, as shown in Scheme 1, [HEMP][BF$_4^-$], [BMP][BF$_4^-$], and [HEMM][BF$_4^-$] were synthesized and [EMIM][BF$_4^-$] was purchased from C-tri (Korea). The pressure and temperature were recorded with time and consequently the induction time was decided according to the result. The induction time is an important indicator to characterize the kinetics of gas hydrate crystallization. Each sample was prepared at concentrations of 0.1, 1, and 10 wt% in water. For comparison with IL samples, the induction times for PVP and PVCap...
at 0.1 and 1 wt% were measured. The induction times on average for 1 wt% PVP and PVCap were 1.8 and 43 min, respectively, whereas, as shown in Table 1 and Figure 2, the induction times for [EMIM][BF₄], [BMP][BF₄], [HEMP][BF₄] and [HEMM][BF₄] at the same concentration were 88.4, 58.2, 101.5, and 107.5 min, respectively. The induction times for [HEMP][BF₄] and [HEMM][BF₄] were found to be much higher compared to those of the others. The differences in induction time with 10 wt% of ILs were more distinguishable, although typical polymer LDHIs are not available at high concentrations. The induction times at 10 wt% for [EMIM][BF₄], [BMP][BF₄], [HEMP][BF₄], and [HEMM][BF₄] were about 97.3, 233.5, 342.8, and 364.8 min, respectively. It is found that the inhibition effects of PVP and PVCap at 0.1 wt% were very little.

### Table 1. Induction time of methane hydrate formation

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Induction time / min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 wt%</td>
</tr>
<tr>
<td>PVP</td>
<td>0.4</td>
</tr>
<tr>
<td>PVCap</td>
<td>11.7</td>
</tr>
<tr>
<td>[EMIM][BF₄]</td>
<td>35.3</td>
</tr>
<tr>
<td>[BMP][BF₄]</td>
<td>23.8</td>
</tr>
<tr>
<td>[HEMP][BF₄]</td>
<td>61.5</td>
</tr>
<tr>
<td>[HEMM][BF₄]</td>
<td>26.7</td>
</tr>
</tbody>
</table>

( ), numbers in parentheses; range of induction time wt% : weight percentage of inhibitors

\[ T = 274.15 \text{ K}, \quad \Delta T (\text{sub-cooling}) = 15 \text{ K}, \quad P = 70 \text{ bar} \]

The introduction of the functional group into the IL structure is the key point in this research.

It is also of interest to test whether or not ILs can function as thermodynamic inhibitors (THIs). The concentration of ILs used was 10 wt%. Thermodynamic inhibitors are usually used at a concentration of 10 wt% or more while kinetic inhibitors are usually used at a concentration of less than 2 wt%. All of the IL samples tested in this work definitely showed inhibition effects on methane hydrate formation. Pyrrolidinium-based ILs reduced the hydrate-aqueous liquid-vapor (HLV) equilibrium dissociation temperature by 1.3-1.6 K while [EMIM][BF₄] and [HEMM][BF₄] presented weaker inhibition effect. Therefore, the pyrrolidinium-based samples shifted the hydrate equilibrium curves to a lower temperature, as shown in Figure 3. [HEMP][BF₄] and [BMP][BF₄] showed nearly the same degree of HLV shift over the entire range of experiments. This is a favorable outcome since pyrrolidinium-based IL inhibitors play a homogeneous role over a wide range of pressures, even though experiments over an expanded pressure range are still necessary. In the case of conventional THIs such as MEG and methanol, 10 wt% aqueous solution decreased the HLV equilibrium curve by about 2.5-5 K, which was superior to IL-based solutions at identical concentrations. Although ILs showed no remarkable inhibition effects on the gas hydrate equilibrium state, ILs, in theory, can also be classified as THIs.

This research has shown that specifically designed ILs for hydrate inhibition can tremendously improve induction time while shifting the original

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**Figure 2. Induction times of methane hydrate formation**
equilibrium line. We synthesized [HEMP][BF4] and [BMP][BF4] for this purpose and found that the hydroxyl groups in [HEMP][BF4] effectively interrupted the hydrogen bonding between water molecules. This study also showed the potential application of ILs as dual function inhibitors that not only shift the equilibrium dissociation conditions but also slow down the rates of nucleation and growth. [HEMP][BF4] was used as an example to show that inhibition performance strongly relies on IL structure. Therefore, [HEMP][BF4] can be a benchmark material for future research. It is also expected that more effective thermodynamic or kinetic inhibitors will be developed based on molecular design.

REFERENCES