ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 6341–6343

www.rsc.org/chemcomm

COMMUNICATION

Tuning ionic liquids for hydrate inhibition†

Ki-Sub Kim,[a] Jeong Won Kang[b] and Seong-Pil Kang*[c]

Received 20th December 2010, Accepted 18th April 2011
DOI: 10.1039/c0cc05676f

Pyrrolidinium cation-based ionic liquids were synthesized, and their inhibition effects on methane hydrate formation were investigated. It was found that the ionic liquids shifted the hydrate equilibrium line to a lower temperature at a specific pressure, while simultaneously delaying gas hydrate formation.

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]

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 allow gas hydrate formation but prevent 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(acryoyl 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 sub-cooling, 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 hydrate inhibition methods and introduce ionic liquids (ILs) as inhibitors.

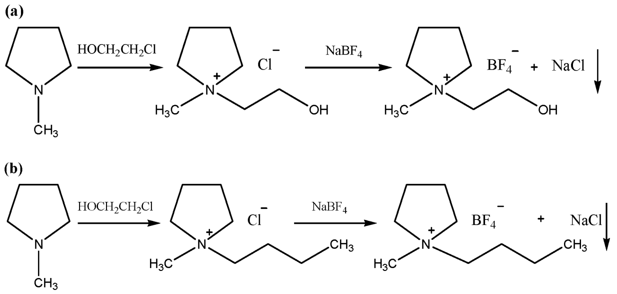
ILs are generally stable in the presence of air and water. Their physical properties strongly depend either on the length of the alkyl chain of the cation or on a specifically designed cation and anion. Therefore, ILs can be designed and synthesized for specific purposes. Adidharma and Xiao first identified 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 the 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".

Currently, we are attempting 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 two simple hypotheses. First, ILs must be hydrophilic or hygroscopic. If the materials are hydrophobic, then they will reside in a separate phase from water and will be unable to access water molecules. Second, special functional

---

[a] *Department of Chemical and Biological Engineering, Chungju National University, 50 Daehak-ro, Chungju, Chungbuk 380-702, Republic of Korea. E-mail: kks1114@cjnu.ac.kr; Fax: +82 43 841 5220; Tel: +82 43 841 5222*
[b] *Department of Computer Engineering, Chungju National University, 50 Daehak-ro, Chungju, Chungbuk 380-702, Republic of Korea. E-mail: jwkang@cjnu.ac.kr; Fax: +82 43 841 5340; Tel: +82 43 841 5466*
[c] *Clean Fossil Energy Research Center, Korea Institute of Energy, 101 Gaejong-ro, Yuseong-gu, Daejeon 305-343, Republic of Korea. E-mail: spkang@kier.re.kr; Fax: +82 42 860 3134; Tel: +82 42 860 3475*

† Electronic supplementary information (ESI) available: Synthetic method of ILs and the experimental measurement of hydrate equilibria and kinetic behavior. See DOI: 10.1039/c0cc05676f



Scheme 1 Synthesis of (a) [HEMP][BF$_4$] and (b) [BMP][BF$_4$].

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, *N*-(2-hydroxyethyl)-*N*-methylpyrrolidinium tetrafluoroborate ([HEMP][BF$_4$]) and *N*-butyl-*N*-methylpyrrolidinium tetrafluoroborate ([BMP][BF$_4$]) were synthesized as shown in Scheme 1. The procedure was carried out in two steps. The desired *N*-(2-hydroxyethyl)-*N*-methylpyrrolidinium and *N*-butyl-*N*-methylpyrrolidinium cations were formed, respectively, and they were then converted into the corresponding BF_4^- through an anion exchange. Details of the synthesis and purification procedures are provided in the ESI.†‡

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 new samples, the induction times for PVP, PVCap, and *N*-ethyl-*N*-methylimidazolium tetrafluoroborate ([EMIM][BF$_4$]) were measured at 0.1 and 1 wt%. [EMIM][BF$_4$] was the inhibitor that showed the best performance among imidazolium ILs as Adidharma and Xiao suggested.[5,6] 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 Fig. 1, the induction times for [EMIM][BF$_4$], [HEMP][BF$_4$] and [BMP][BF$_4$] at the same concentration were 88.4, 101.5, and 58.2 min, respectively.

Table 1 Induction time of methane hydrate formation

	Induction time/min			
Inhibitor	0.1 wt%	0.5 wt%	1 wt%	10 wt%
PVP	0.4 (0–1.1)	1.6 (0.4–2.3)	1.8 (0.8–2.4)	—
PVCap	11.7 (4–20)	19.9 (6–22)	43 (30–49)	—
[EMIM][BF$_4$]	35.3 (24–56)	—	88.4 (50–123)	97.3 (65–133)
[HEMP][BF$_4$]	61.5 (26–74)	—	101.5 (75–146)	342.8 (262–413)
[BMP][BF$_4$]	23.8 (15–46)	—	58.2 (53–70)	233.5 (180–303)

Numbers in parentheses: range of induction time. wt%: weight percentage of inhibitors. T = 274.15 K, ΔT(sub-cooling) = 15 K, P = 70 bar.

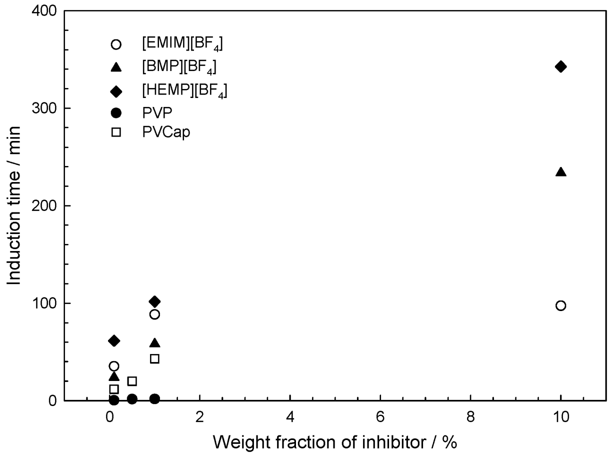


Fig. 1 Induction times of methane hydrate formation.

The induction time for [HEMP][BF$_4$] was 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][BF$_4$], [HEMP][BF$_4$], and [BMP][BF$_4$] were about 97.3, 342.8 and 233.5 min, respectively. In the case of [EMIM][BF$_4$], the induction time at 10 wt% was almost the same as the time at 1 wt%, though the values of [EMIM][BF$_4$] at 0.1 and 1 wt% were between those of [HEMP][BF$_4$] and [BMP][BF$_4$] at the same concentrations. It is found that the inhibition effects of PVP and PVCap at 0.1 wt% were very little. The times for PVP, PVCap, [EMIM][BF$_4$], [HEMP][BF$_4$] and [BMP][BF$_4$] were 0.4, 11.7, 35.3, 61.5, and 23.8 min, respectively. Even at the very low concentration, the inhibition effect of [HEMP][BF$_4$] was outstanding.

The common characteristics between [HEMP][BF$_4$] and the other ILs are summarized as follows: (1) they each have BF_4^-, which is a well known as a representative hydrophilic group that helps mix ILs and water together into one phase; (2) the short alkyl chain of cation allows ILs to access water molecules without any steric hindrance caused by a bulky group; (3) they have strong electrostatic charges leading to interaction between an ion and a dipole.

On the other hand, the presence of a hydroxyl group in [HEMP][BF$_4$] yields major differences in how long hydrate formation can be delayed although the ILs without a hydroxyl group also showed reasonable induction times. The functional group provides more chances for interrupting inter-molecular forces between IL and water molecules, thus the selected inhibitor can effectively delay hydrate formation. 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.[12] Pyrrolidinium-based ILs reduced the hydrate-aqueous liquid-vapor (HLV) equilibrium dissociation temperature by 1.3–1.6 K while

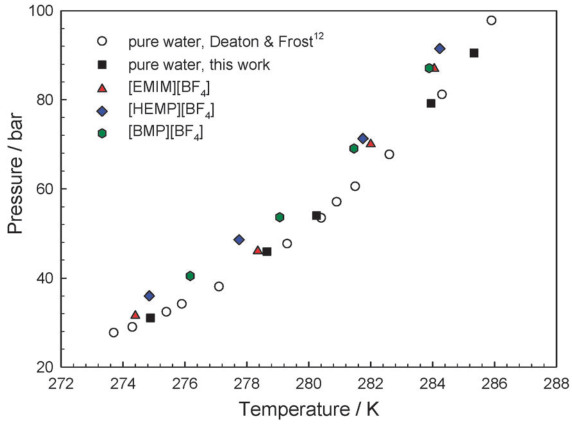


Fig. 2 Hydrate-aqueous liquid-vapor (HLV) equilibria of methane hydrate.

[EMIM][BF_4] presented a weaker inhibition effect. Therefore, the pyrrolidinium-based samples shifted the hydrate equilibrium curves to a lower temperature, as shown in Fig. 2. [HEMP][BF_4] and [BMP][BF_4] 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 equilibrium line. We synthesized [HEMP][BF_4] and [BMP][BF_4] for this purpose and found that the hydroxyl groups in [HEMP][BF_4] 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][BF_4] was used as an example to show that inhibition performance strongly relies on the IL structure. Therefore, [HEMP][BF_4] 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.

This work was supported by the Energy Efficiency & Resources Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 2010201030001A). K.-S. Kim acknowledges support by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0004788). We thank KBSI (Korea Basic Science Institute) for assistance with NMR.

Notes and references

‡ Representative synthesis: *1-butyl-1-methylpyrrolidinium bromide ([BMP][Br])*: 1-methylpyrrolidine (0.5 mol) in 200 mL of acetonitrile was added dropwise to 0.5 mol of 1-bromobutane 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 [BMP][Br] was dried under vacuum conditions at 323.15 K for more than 48 h: the ^{1}H-NMR(DMSO) spectrum consisted of the following peaks: 0.90–0.94(t, 3H), 1.26–1.35(m, 2H), 1.64–1.72(m, 2H), 2.08(s, 4H), 3.02(s, 3H), 3.36–3.40(m, 2H), and 3.47–3.54(m, 4H).

1-Butyl-1-methylpyrrolidine tetrafluoroborate ([BMP][BF$_4$]): [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: the ^{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). The ^{1}C-NMR(DMSO) spectrum consisted of the following peaks: 13.3 (CH_3 of butyl group), 21.0, 24.9, 62.9 (CH_2 of butyl group), 47.5 (CH_3 of methyl group), 19.3, 63.4 (CH_2 of pyrrolidinium). FAB MS (*m*/*z*) = $[BMP]^+$ ($C_9N_1H_{20}$) requires 142, exptl 142.

1 T. Kuznetsova, A. Sapronova, B. Kvamme, K. Johannsen and J. Haug, *Macromol. Symp.*, 2010, **287**, 168.
2 M. A. Kelland, *Energy Fuels*, 2006, **20**, 825.
3 K. Shin, Y. Park, M. Cha, D.-G. Huh, J. Lee, S.-J. Kim and H. Lee, *Energy Fuels*, 2008, **22**, 3160.
4 H. Lee, J.-W. Lee, D.-Y. Kim, J. Park, Y.-T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe and J. A. Ripmeester, *Nature*, 2005, **434**, 743.
5 C. Xiao and H. Adidharma, *Chem. Eng. Sci.*, 2009, **64**, 1522.
6 C. Xiao, N. Wibisono and H. Adidharma, *Chem. Eng. Sci.*, 2010, **65**, 3080.
7 K. N. Marsh, A. Deev, A. C. T. Wu, E. Tran and A. Klamt, *Korean J. Chem. Eng.*, 2002, **19**, 357.
8 K.-S. Kim, S. Choi, D. Demberelnyamba, H. Lee, J. Oh, B.-B. Lee and S.-J. Mun, *Chem. Commun.*, 2004, 828.
9 K.-S. Kim, D. Demberelnyamba and H. Lee, *Langmuir*, 2004, **20**, 556.
10 K.-S. Kim, S.-Y. Park, S.-H. Yeon and H. Lee, *Electrochim. Acta*, 2005, **50**, 5673.
11 K.-R. Seddon, A. Stark and M. Torres, *Pure Appl. Chem.*, 2000, **72**, 2275.
12 W. M. Deaton and E. M. Frost, *Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines*, U.S. Bureau of Mines Monograph, 1946, **8**, 101.