Supplementary Information

1. EXPERIMENTAL SECTION

1.1. Synthesis of ILs

1.1.1. Materials

The materials used in this work were as follows: 1-methylpyrrolidine (Fluka, 99%), 2-chloroethanol (Aldrich, 99%), 1-bromobutane (Aldrich, 99.5%), sodium tetrafluoroborate (Aldrich, 98%), dichloromethane (SAMCHUN, 99.5%), acetone (DAEJUNG, 99.8%), and acetonitrile (JUNSEI, 99.5%).

1.1.2. Synthesis

1-hydroxyethyl-1-methylpyrrolidinium chloride ([HEMP][Cl]): 1-methylpyrrolidine (0.5 mol) in 200 mL of acetonitrile was added dropwise to 0.5mol 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).

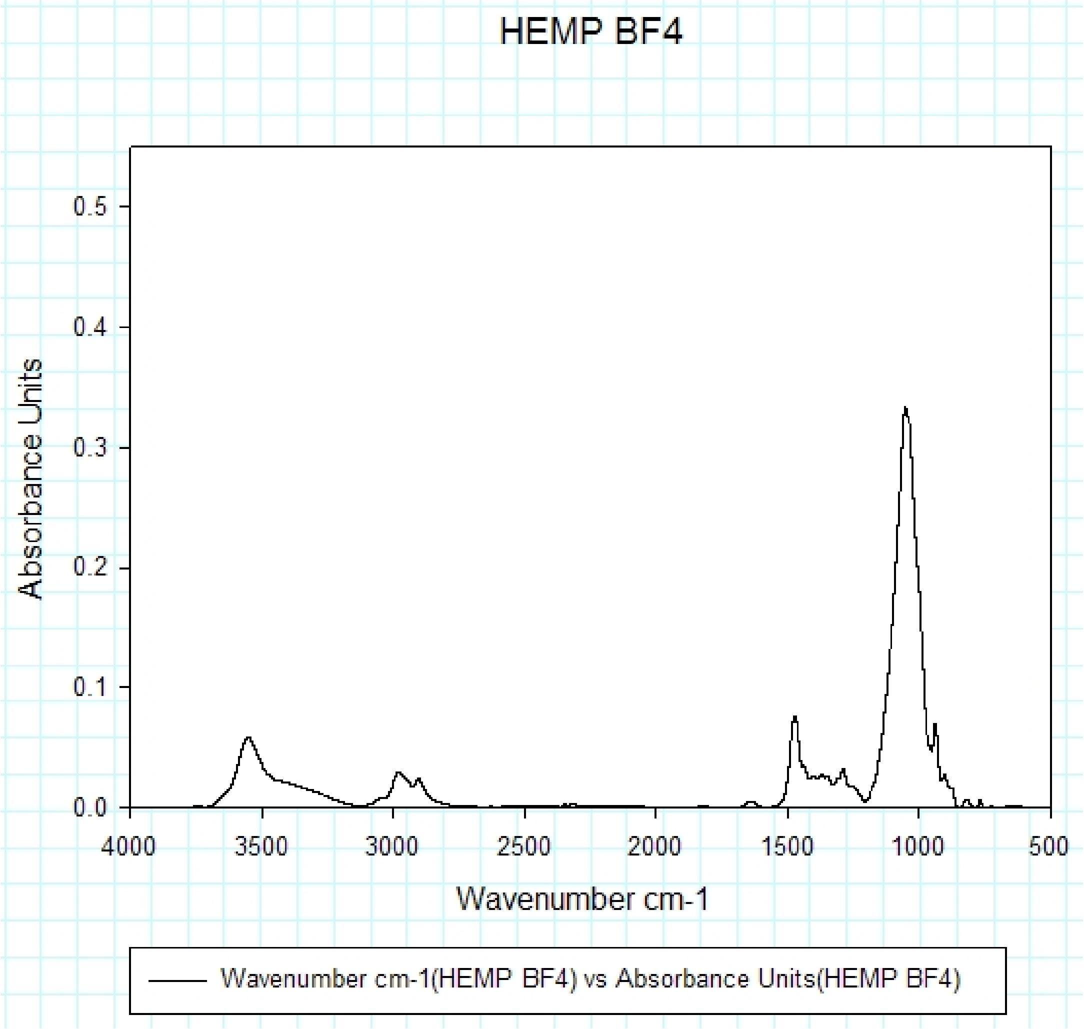
1-hydroxyethyl-1-methylpyrrolidinium tetrafluoroborate ([HEMP][BF$_4$]): [HEMP][Cl] (0.2 mol) in acetone was reacted with 0.2 mol of sodium tetrafluoroborate in a round-bottom flask. After 24 h of stirring, the resulting NaCl precipitate was filtered through a plug of filter paper, and the volatiles 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 chloride 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: 2.08(s, 4H), 3.03(s, 3H), 3.41~3.43(m, 2H), 3.49~3.52(m, 4H), 3.82~3.85(m, 2H), 5.27~5.30(t, 1H).

^{1}C-NMR(DMSO) spectrum consisted of the following peaks: 20.8, 65.2 (CH$_2$ of pyrrolidinium), 48.2 (CH$_3$ of methyl group), 56.0, 65.2 (CH$_2$ of hydroxyethyl group).

FAB MS (m/z) = [HEMP]$^+$ ($C_7N_1O_1H_{16}$) requires 130, exptl 130.

IR image:



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.

^{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).

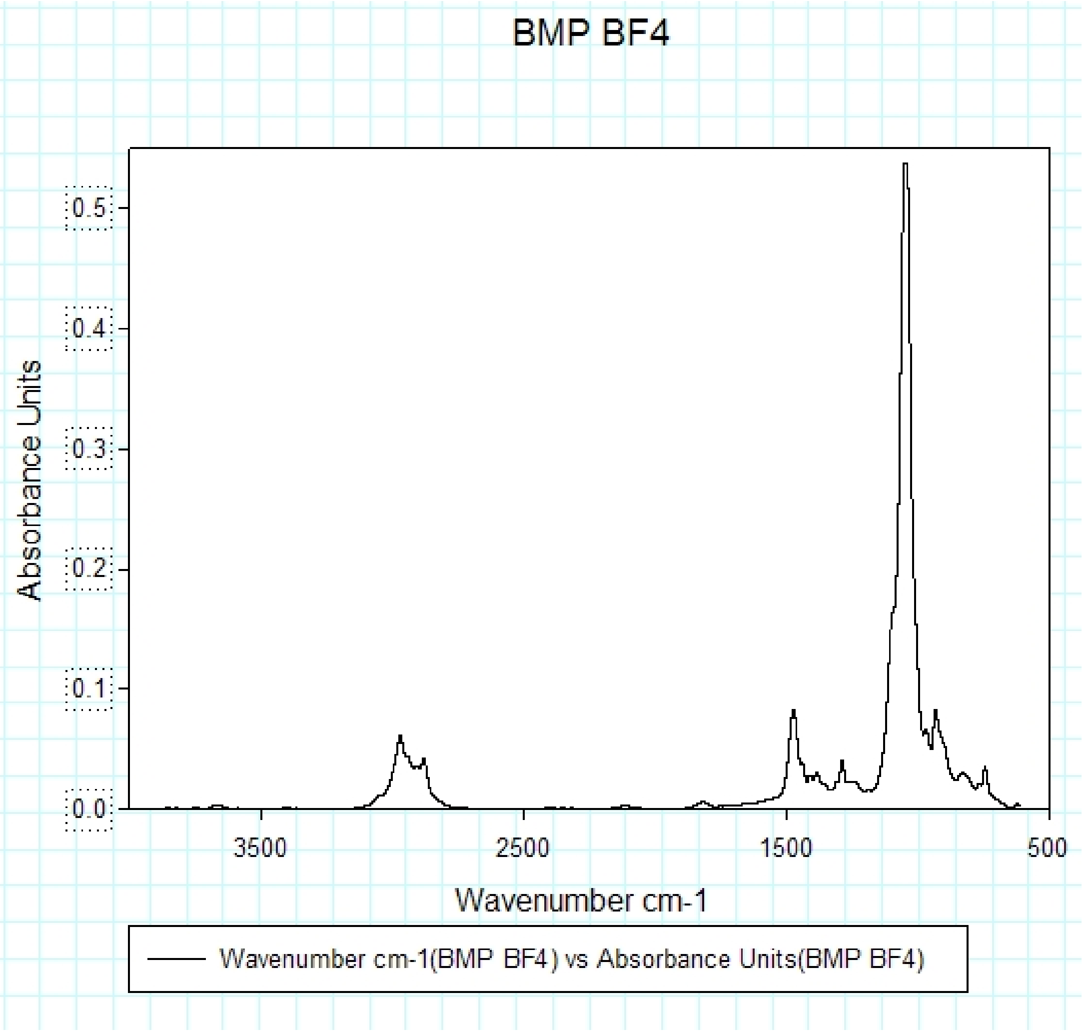
1-butyl-1-methylpyrrolidine tetrafluoroborate ([BMP][BF$_4$]): [BMP][Br] (0.2 mol) in acetone was reacted with 0.2 mol of sodium tetrafluoroborate in a round-bottom flask. After 24 h of stirring, the resulting NaBr precipitate was filtered through a plug of filter paper, and the volatiles were removed 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.

^{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).

^{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.

IR image:



	Cl^- / ppm	Br^- / ppm	water / ppm
[HEMP][BF_4]	< 200	-	< 150
[BMP][BF_4]	-	< 200	< 150

1.2. Apparatus and procedure

All ILs synthesized in this work are listed in Table 1. The 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 figure 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_s and P_s, were detected and chosen as the onset of the hydrate formation. Time from the beginning to t_s is named for "the induction time".

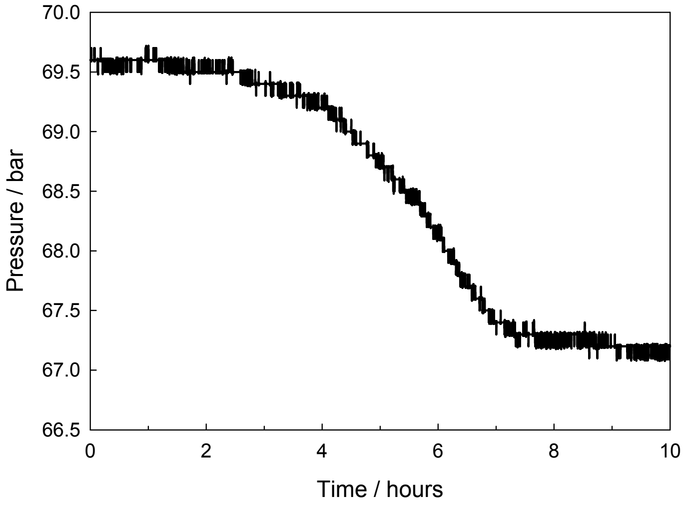
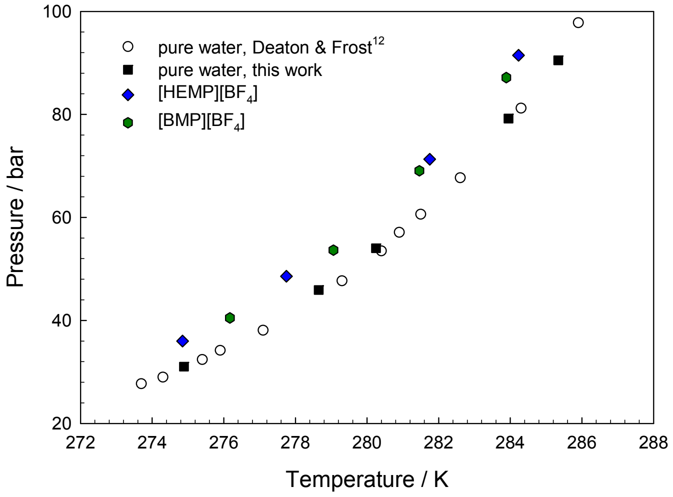


Fig. The P-T diagram for measuring induction time.

1.3. Uncertainties

1.3.1. Equilibrium measurement

The error between our experiment and the reference is within about 0.25 %.



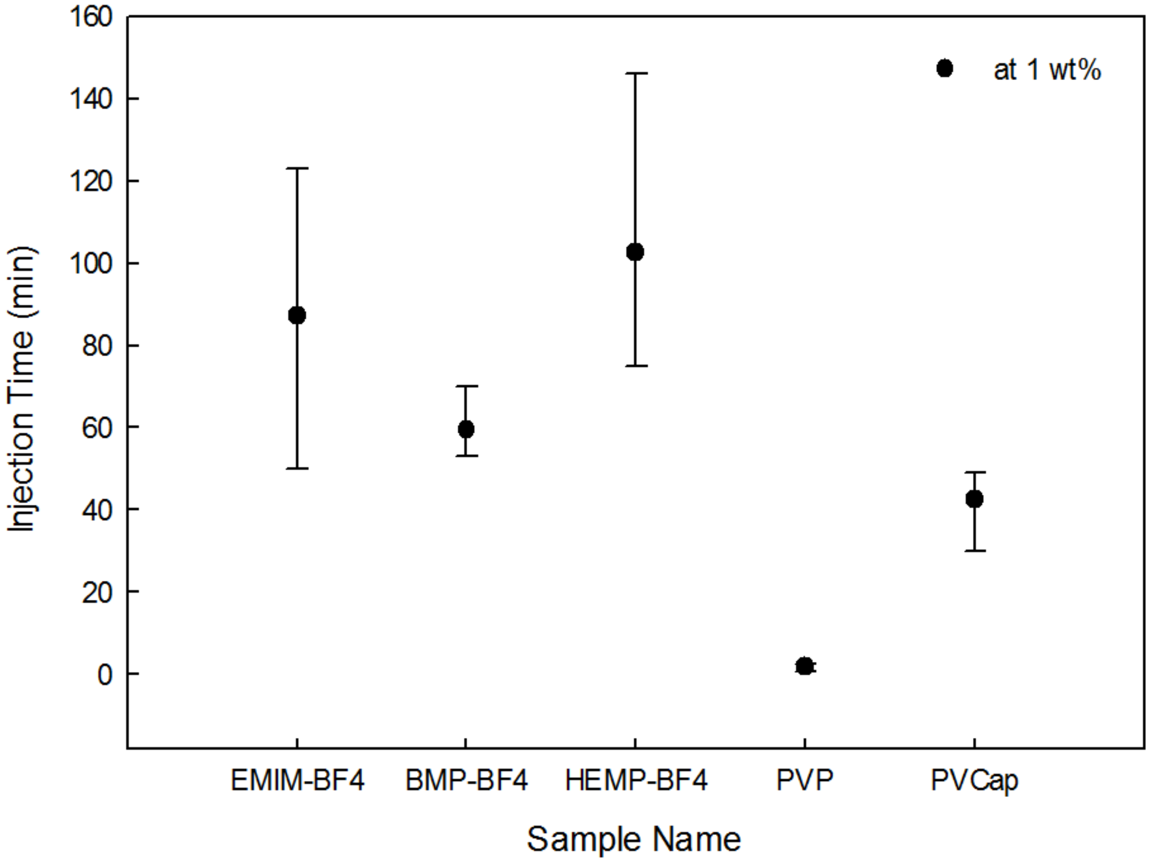
1.3.2. Ranges of induction times

Table 1. Induction time of methane hydrate formation

Inhibitor	Induction time / min			
	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

The numbers in parentheses indicated ranges of induction times.



These inhibitors can be generally applied to industries at 0.5~3 wt%, and particularly 1 wt%. We prepared a comparison figure with minimum and maximum range at 1 wt%.