

Supplementary Information

1. EXPERIMENTAL SECTION

1.1. Synthesis of ILs

We synthesized N-(2-hydroxyethyl)-N-methylpyrrolidinium tetrafluoroborate ([HEMP][BF₄]), N-butyl-N-methylpyrrolidinium tetrafluoroborate ([BMP][BF₄]) and purchased N-ethyl-N-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) from C-tri.

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

N-(2-hydroxyethyl)-*N*-methylpyrrolidinium chloride ([HEMP][Cl]): 1-methylpyrrolidine (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 at 323.15 K for more than 48 h.

¹H-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-(2-hydroxyethyl)-*N*-methylpyrrolidinium tetrafluoroborate ([HEMP][BF₄]): [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 at 323.15 K. The content of chloride anions was less than 200ppm. The water content was less than 150ppm.

$^1\text{H-NMR(DMSO)}$ 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).

N-butyl-N-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 at 323.15 K for more than 48 h.

$^1\text{H-NMR(DMSO)}$ 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).

N-butyl-N-methylpyrrolidine tetrafluoroborate ([BMP][BF₄]): [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 at 323.15 K. The content of bromide anions was less than 200ppm. The water content was less than 150ppm.

$^1\text{H-NMR(DMSO)}$ 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).

1.2. Apparatus and Procedure

To measure the induction time of the selected ionic liquids and their mixture with PVCap, we chose the detection of pressure difference as an indicator. During the formation of gas hydrate, methane is engaged into the hydrate structure, therefore the system pressure decreases. A sudden pressure drop and temperature rise indicates the formation of gas hydrates. Thus, from the beginning of the experiment, the temperature and pressure were continuously monitored while gas hydrate formation occurred.

To measure the induction time of methane hydrate formation, selected IL or the mixture of IL and PVCap samples were prepared as an aqueous solution with a specified concentration. PVCap was extracted from the Luviskol Plus (BASF, the solution of PVCap polymer and ethanol) by the vacuum

evaporation of ethanol. The molecular weight (M_n) and polydispersity of PVCap were 5,100 and 1.303, respectively. Solutions of about 90 ml were charged in a 220 mL autoclave cell that was prepared at 274 K and under vacuum to remove the possibility of remnant gases. Methane gas with a nominal purity of 99.999% was then injected into the cell at a pressure of 70 bar. The high-pressure autoclave cell was maintained at 274 K during the whole experiment, and its liquid content was stirred using a magnetic drive installed on the topside of the cell at 700 rpm after the pressure of the cell became stable. The induction time of each sample solution was measured during seven parallel experiments and their scattering values due to a natural phenomenon were averaged. In this study, we investigated the feasibility and basic characteristics of gas hydrate inhibition. The solution samples that exhibited 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 a 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. Once the formation of the hydrate began, 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".

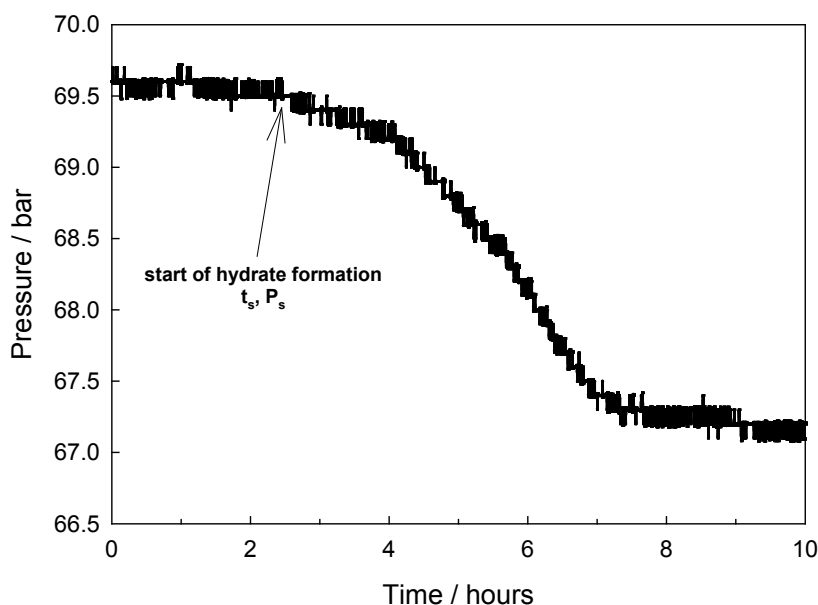


Fig. The P-T diagram for measuring induction time