

Thermodynamic inhibition effects of ionic liquids on the formation of condensed carbon dioxide hydrate



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ABSTRACT

Ionic liquids (ILs) have been proposed as potential inhibitors for preventing gas hydrate formation because their ion pairs effectively interrupt the hydrogen bonding between water molecules. ILs also have broad inhibitory capabilities depending on the specific cation and anion combinations. The final structural design of ILs for hydrate inhibition must be performed after an inhibition mechanism is suggested. In this study, the inhibitory thermodynamic effects of ILs were measured by the hydrate–aqueous liquid–liquid carbon dioxide (CO₂) equilibrium, and the experimental results were analyzed based on the hydration free energy of ILs calculated through molecular dynamics study. 1-Hydroxyethyl-1-methylpyrrolidinium chloride showed the best inhibitory performance of the suggested candidates. The anions mostly contributed to the thermodynamic inhibition, but the cations had a marginal impact on CO₂ hydrate inhibition. Through fundamental understanding of the inhibition mechanism by both experimental and computational approaches, it is highly possible to provide crucial information for effective ILs to be designed as the CO₂ hydrate inhibitor.

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1. Introduction

During the carbon dioxide (CO₂) capture and sequestration (CCS) process through pipeline, CO₂ hydrates, which are ice-like solids where CO₂ molecules are trapped, are formed. The phenomenon happens at hydrate formation conditions of high pressure and low temperature since water inevitably exists. As one of many impurities in pipeline, water would consequently causes harmful side effects such as pipe plug and pressure drops by forming CO₂ hydrates [1]. In order to keep pipeline under hydrate-free condition, thermodynamic hydrate inhibitors (THIs) have been used. For example, ethylene glycol or methanol is widely used in industrial applications [1,2]. While the alcohol-based inhibitors are effective for the hydrate inhibition, a huge cost is unavoidable due to usage of a significant amount of them. For the reason, studies on low dosage hydrate inhibitors (LDHIs) such as poly

(*N,N*-dialkylacrylamide) [3] and poly(*N*-vinylcaprolactam) (PVCap) [4] have been recently initiated and received growing attention for their kinetic inhibition merits. Kinetic hydrate inhibitors (KHIs) delay gas hydrate formation and elongate the induction time by the addition of just 0.5–2 wt% to the amount of produced water.

Recently, researchers have turned to a new class of inhibitors, ionic liquids (ILs). According to recent studies, ILs have been reported to act as both a THI and a KHI for methane hydrate [5,6]. These dual function inhibitors not only shift the dissociation temperatures of hydrates at constant pressure by changing the phase equilibrium but can retard the rate of hydrate formation through a kinetic inhibition effect. Xiao et al. [6] reported that dual function inhibitor ILs contain the three types of imidazolium-based cations, 1-ethyl-3-methylimidazolium ([Emim]⁺), 1-propyl-3-methylimidazolium ([Pmim]⁺) and 1-butyl-3-methylimidazolium ([Bmim]⁺), combined with seven anions, [BF₄][−], [N(CN)₂][−], [CF₃SO₃][−], [EtSO₄][−], Cl[−], Br[−] and I[−]. They identified the IL electrical conductivity to elucidate the inhibitory mechanisms, which depends on IL structures. When the electrostatic IL charges increased, IL had a greater chance to disrupt the hydrogen bonding between water molecules. Meanwhile, Hu and coworkers [7,8] presented the first account of the imidazolium-based ILs used as CO₂. They reported that Cl[−] was more effective than [BF₄][−] for thermodynamic inhibition and suggested that degree of inhibition

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Table 1
Abbreviation, sources, purities and impurity contents of the ILs used in the work.

Ionic liquid	Abbreviation	Source	Mass fraction purity (wt%)	Water in mass fraction (ppm)	Halides in mass fraction (ppm)
1-Hydroxyethyl-1-methylpyrrolidinium chloride	[Hemp]Cl	Synthesis	–	<150	–
1-Butyl-3-methylimidazolium chloride	[Bmim]Cl	Synthesis	–	<133	–
1-Hydroxyethyl-1-methylpyrrolidinium tetrafluoroborate	[Hemp]BF ₄	Synthesis	–	<145	<183
1-Ethyl-3-methylimidazolium tetrafluoroborate	[Emim]BF ₄	Sigma–Aldrich	≥99	≤200	≤10
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	[Bmmim]BF ₄	Sigma–Aldrich	≥97	≤1000	–
1-Butyl-3-methylimidazolium tetrafluoroborate	[Bmim]BF ₄	C-Tri	≥99	<100	<30
1-Butyl-3-methylimidazolium methylsulfate	[Bmim]MeSO ₄	C-Tri	≥99	<100	<30
1-Butyl-3-methylimidazolium hexafluorophosphate	[Bmim]PF ₆	C-Tri	≥99	<100	<30

was related to the disparity of hydrogen bonding between ILs and water molecules. In similar studies, Tumba et al. [9] showed phase equilibrium data for CO₂ and methane hydrates in the presence of a phosphonium-based IL with thermodynamic modeling that could predict experimental data. However, the reported CO₂ hydrate phase equilibria were *H–L_W–V_{CO₂}* regions. This low pressure equilibrium data are ineffective in applying CCS processes since the conditions of CO₂ transportation are liquid phase at high pressures (>5 MPa) and low temperatures. Furthermore, the previous work mentioned above focused on conventional ILs as inhibitors of hydrate formation. As reported in our previous study [10], special functional groups in cation, such as oxygen or hydroxyl groups, showed significant kinetic inhibition on methane hydrate even at the small concentrations, but these ILs have a limitation on their thermodynamic inhibitory effects.

In this paper, pyrrolidinium-based ILs were synthesized to improve the thermodynamic inhibitory effects on CO₂ hydrate. Unlike the mentioned studies [7–9], which reported inhibitory effects of ILs on vapor CO₂ hydrate, the hydrate–aqueous liquid–liquid CO₂ (*H–L_W–L_{CO₂}*) three-phase equilibrium was measured up to 20 MPa. The inhibitory effects of newly-designed ILs were compared with typical imidazolium-based ILs. The ILs suggested in

this study are as follows: [Hemp]Cl, [Bmim]Cl, [Hemp]BF₄, [Emim]BF₄, [Bmim]MeSO₄, [Bmim]BF₄, [Bmmim]BF₄, [Bmim]PF₆, [Bmim]Tf₂N. The inhibition effect of ILs was indirectly elucidated with the hydration free energy calculated by the density functional theory (DFT) calculation combined with the molecular dynamics simulation using the COMPASS II force field [11,12].

2. Experimental

2.1. Chemicals

Ultra-high purity CO₂ (99.999 wt%) from PS Chem. Corp. (Pusan, Korea) was used without further treatment. [Emim]BF₄ and [Bmmim]BF₄ ILs were purchased from Sigma–Aldrich (USA). Purities of these two ILs were estimated to be greater than 97 wt%. The halogen and water contents were less than or equal to 10 and 200 ppm for [Emim]BF₄, [Bmim]BF₄, [Bmim]MeSO₄, [Bmim]PF₆ and [Bmim]Tf₂N ILs were supplied by C-Tri Co. (Suwon, Korea). The halogen and water contents were less than 30 and 100 ppm, respectively (Ultra grade). Purities of the ILs were estimated to be greater than or equal to 99 wt%. The specifications of all ILs are shown in Table 1. The IL samples were degassed using a vacuum

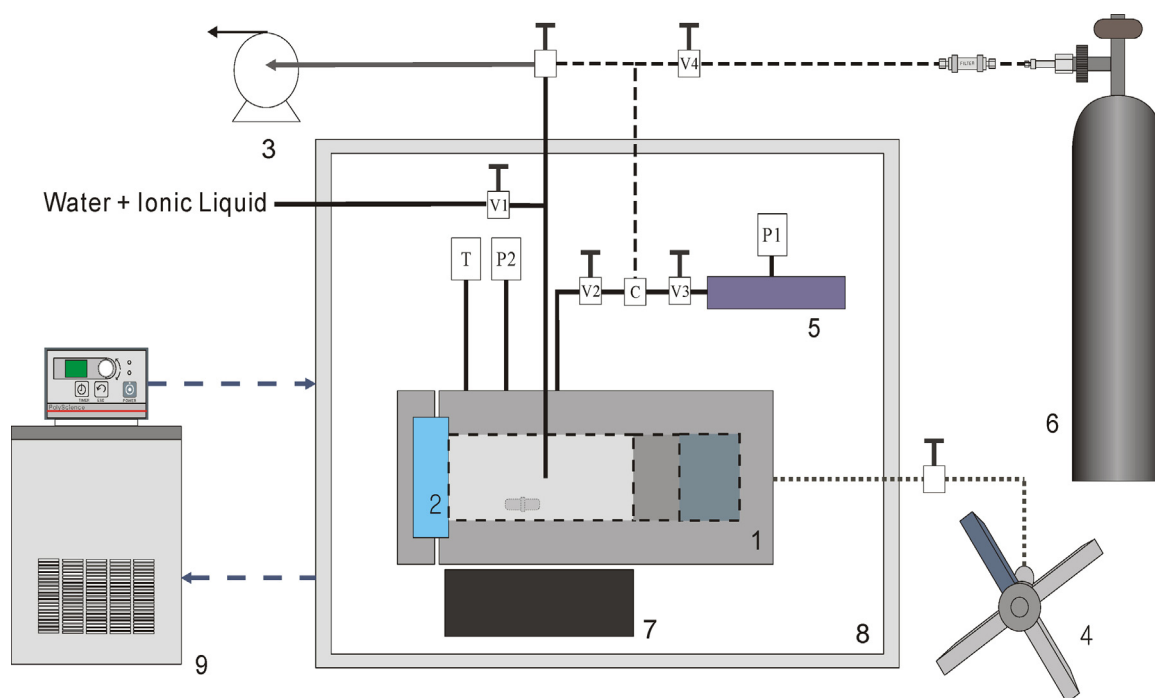


Fig. 1. Experimental apparatus; (1) variable-volume cell; (2) viewing glass; (3) vacuum pump; (4) pressure generator; (5) detachable CO₂ reservoir; (6) gas cylinder; (7) magnetic stirrer; (8) water bath; (9) circulator.

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