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Chain length effect of ionic liquid 1-alkyl-3-methylimidazolium chloride on the phase equilibrium of methane hydrate

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ABSTRACT

A high pressure differential scanning calorimeter was used to determine the dissociation temperature of methane hydrate in the presence of ionic liquid 1-alkyl-3-methylimidazolium chloride under a constant pressure ranging from 5 to 35 MPa. A homologous series of 1-alkyl-3-methylimidazolium chloride with different alkyl chain lengths: 1-ethyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride and 1-decyl-3-methylimidazolium chloride, were chosen to examine the chain length effect on the dissociation temperature for methane hydrates. All these ionic liquids have inhibition effect on methane hydrate formation. Moreover, the shorter the alkyl chain length is, the stronger the inhibition effect is. That is, the inhibition effect of these ionic liquids on the methane hydrate formation is in the order of 1-ethyl-3-methylimidazolium chloride > 1-hexyl-3-methylimidazolium chloride > 1-decyl-3-methylimidazolium chloride. The three-phase vapor–liquid–hydrate equilibrium condition of methane hydrate in the presence of 1-alkyl-3-methylimidazolium chloride was successfully described by a predictive thermodynamic model. The Peng–Robinson–Stryjek–Vera equation of state incorporated with COSMO-SAC activity coefficient model and the first order modified Huron–Vidal mixing rule were applied to evaluate the fugacity of vapor and liquid phase. An explicit pressure dependence of the Langmuir adsorption constant in the modified van der Waals and Platteeuw model was applied to determine the fugacity of hydrate phase. The average absolute relative deviation in predicted dissociation temperature from the predictive thermodynamic model was 0.54%. In addition, these experimental data of dissociation temperatures were further correlated to a general correlation of Østergaard et al. (J. Petroleum Sci. Eng. 48 (2005) 70–80) and the average absolute relative deviation in the correlated dissociation temperature was 0.05%.

1. Introduction

Gas hydrates are crystalline ice-like solids formed by encapsulating small gas molecules (such as, methane, ethane, carbon dioxide, etc.) in the cages of hydrogen bonded water molecules to stabilize the lattice structure at temperatures higher than ice point. The gas hydrate has three major structures: structure I (sI) with 2 small cages (5^{12}) and 6 large cages ($5^{12}6^{2}$), structure II (sII) with 16 small cages (5^{12}) and 8 large cages ($5^{12}6^{4}$) and structure H (sH) with 3 small cages (5^{12}), 2 medium cages ($4^{3}5^{6}6^{3}$) and one large cage ($5^{12}6^{8}$). Usually water and methane gas would form sI hydrate under the conditions of low temperatures and high pressures [1–3]. Gas hydrates have been widely investigated since 1930s due to formation of gas hydrates to plug natural gas pipelines [4]. Thermodynamic and kinetic inhibitors for gas hydrate are commonly used in oil and gas industry to prevent gas hydrate formation from plugging oil and gas pipelines and production wells. The kinetic inhibitors would hinder the hydrate formation by slowing down the hydrate nucleation and growth rates. The thermodynamic hydrate inhibitor would shift the hydrate stability zone to lower temperatures and higher pressures region to retard the hydrate formation. For example, electrolytes, alcohols, and polyols have been well studied and verified as thermodynamic inhibitors. Methanol and glycols are two most commonly used hydrate inhibitors in oil and gas industry [5,6].

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Recently Adidharma and coworkers [7,8] pointed out that imidazolium-based ionic liquids can act as both thermodynamic and kinetic inhibitors for methane hydrates, coined as dual function inhibitors, a new class of hydrate inhibitors. On the other hand, Del Villano and Kelland [9] found out that these imidazolium-based ionic liquids are rather weak kinetic inhibitors when used alone at low concentrations of 5000–10,000 ppm at typical subsea temperature and subcooling, but exhibit fairly good synergetic effect when applied along with commercial kinetic polymer inhibitors. Ionic liquids have been extensively studied as green solvents for chemical processes. They can be designed for specific application due to tunable cations and anions. For example, Kim et al. [10] synthesized and designed pyrrolidinium cation-based ionic liquids to demonstrate the potential application of ionic liquids as dual function inhibitors. Note that ionic liquids can act as not only thermodynamic inhibitors but also thermodynamic promoters. Richon and coworkers [11] pointed out that ionic liquid tetra-n-butylammonium bromide (TBAB) would act as a thermodynamic promoter for gas hydrates especially at low concentrations of TBAB.

Further investigation of effect of ionic liquids on the phase boundary of gas hydrate is still needed to provide basic information for engineering design. The equilibrium conditions of gas hydrates in the presence of some other ionic liquids have been experimentally determined and reported in literature [12–17]. Richard and Adidharma [18] reported dissociation temperatures of methane hydrates in the presence of 1-ethyl-3-methylimidazolium chloride, abbreviated by EMIM-Cl hereafter, at pressure ranging from 10.1 to 19.9 MPa. Recently, we investigated the inhibition effect of additive EMIM-Cl (10, 20, 30, and 40 wt%) on the phase equilibrium for the methane hydrates at pressure ranging from 5.00 to 35.00 MPa [19]. In this study, a homologous series of 1-alkyl-3-methylimidazolium chloride with different chain lengths: 1-ethyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride and 1-decyl-3-methylimidazolium chloride were chosen to further explore the effect of the alkyl chain length of 1-alkyl-3-methylimidazolium chloride on the phase equilibrium of methane hydrate. It was found that the increase of alkyl chain length of 1-alkyl-3-methylimidazolium chloride would weaken the inhibition effect on the methane hydrate formation. The experimental data of dissociation temperatures of methane hydrates in the presence of 1-alkyl-3-methylimidazolium chloride were successfully described by a predictive thermodynamic model composed of COSMO-SAC model and the modified van der Waals and Platteeuw model.

2. Experimental

2.1. Materials

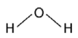
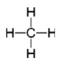
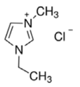
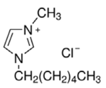
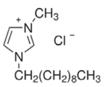
The ionic liquids 1-ethyl-3-methylimidazolium chloride (EMIM-Cl, purity ≥ 98%), 1-hexyl-3-methylim-idazolium chloride (HMIM-Cl, purity ≥ 97%) and 1-decyl-3-methylim-idazolium chloride (DMIM-Cl, purity ≥ 96%) were purchased from Sigma–Aldrich and used as received. Pure methane was purchased from Praxair Gas Inc. with a purity of ≥99.97%. Water was purified by active carbon, reverse osmosis and deionization process (pure water system RDI-30, Lotun Technic Co., Taiwan) in sequence and then followed by ultra-pure water system, Barnstead Nanopure (D11901, Thermo Fisher Scientific Inc., USA). The resistivity of the purified water was always ≥18.2 MΩ cm. All samples on mass fraction scale were gravimetrically prepared using an analytical balance (300-9205H 125A, Precisa Inc., Switzerland) with a precision of 1×10^{-4} g, and the uncertainty for mass fraction was less than $\pm 5.0 \times 10^{-4}$. The prepared sample was stirred at least 30 min to ensure the thorough mixing before used. Descriptions for all materials used in this work are listed in Table 1.

2.2. Apparatus and experimental procedure

A high pressure micro-differential scanning calorimeter (abbreviated by HP μDSC hereafter) was applied to measure the hydrate phase transition in this study. This HP μDSC was composed of a micro-differential scanning calorimeter (μDSC 7 evo, Setaram, France) and a high pressure gas panel (Setaram). The μDSC 7 evo (Setaram) had a resolution of 0.02 μW in large measurement range mode and temperature control ranging from 233.15 to 393.15 K with the temperature uncertainty of 0.02 K stated by the manufacture (Setaram). The high pressure gas panel applied a motorized pump connected to the μDSC to control the system pressure at a desired pressure with a resolution of 0.01 MPa and the precision of pressure regulation of ±0.005 MPa.

Two high pressure Hastelloy C276 cells with a volume of 0.3 mL and maximum operating pressure of 40.0 MPa (Setaram) were used as the reference cell and the sample cell. The reference cell was left empty. A drop of sample solution about 0.1 mL was loaded into the sample cell which was then connected to the motorized pump controlled at a prescribed pressure by the high pressure gas panel. The non-isothermal mode was used and the thermal cycle was consisted of two steps: The system was cooled from 298.15 to

Table 1
Descriptions for all materials used in this work.

Chemical name	Abbreviation	Chemical structure	Chemical formula	M.W.	Purity
Water	–		H_2O	18.015	Purified water with resistivity always ≥18.2 MΩ cm
Methane	–		CH_4	16.041	≥99.97%
1-Ethyl-3-methylimidazolium chloride	EMIM-Cl		$C_6H_{11}ClN_2$	146.603	≥98%
1-Hexyl-3-methylimidazolium chloride	HMIM-Cl		$C_{10}H_{19}ClN_2$	202.704	≥97%
1-Decyl-3-methylimidazolium chloride	DMIM-Cl		$C_{14}H_{27}ClN_2$	258.805	≥96%

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