



Experimental and modelling studies on thermodynamic methane hydrate inhibition in the presence of ionic liquids

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ABSTRACT

This paper presents a series of experimental and modelling studies on the thermodynamic inhibition effects of four ionic liquids on the methane hydrate formation. The investigated ionic liquids are 1-methyl-3-octylimidazolium chloride [MOIM-Cl], 1-methylimidazolium hydrogen sulfate [H-MIM-HSO₄], tetraethylammonium iodide [TEA-I], and 1-hexyl-3-methylimidazolium iodide [HMIM-I]. The impact of 0.1 mass fraction concentration ionic liquids on the methane hydrate phase boundary was evaluated by measuring the dissociation temperature of methane hydrate in the pressure range of 5.1–11.1 MPa, using a high pressure differential scanning calorimeter. The molar dissociation enthalpy of methane hydrates was calculated using the Clausius–Clapeyron equation. The density was measured for 0.10 mass fraction of aqueous solutions of ionic liquids at 293.15 K, and then compared to the commercially available gas hydrate inhibitors. The results demonstrated that 1-methylimidazolium hydrogen sulfate [H-MIM-HSO₄] has the highest inhibitory performance among the four ionic liquids considered. Moreover, the Dickens and Quinby–Hunt (electrolyte) model was applied to predict the phase equilibrium data of the studied ILs. The predicted data is in agreement with the experimental data.

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1. Introduction

In the oil and gas industry, the term ‘flow assurance’ refers to the provision of the safe and economical delivery of hydrocarbon stream from the reservoir to the selling point through process facilities [1]. Flow assurance failures due to blockages in transmission pipelines can raise critical safety and economic problems [2]. The formation of natural gas hydrates is known as the main source of pipeline blockages in oil and gas flow assurance, which is a major concern to the oil and gas industry. At high pressures and low temperatures conditions, natural gas molecules are trapped in the cage molecules of frozen water, creating natural gas hydrates [3,4]. Severe safety issues such as loss of lives and massive production stoppage can occur if gas hydrates are accumulated in subsea pipelines. Water removal, depressurizing, heating, and chemical injection are techniques that can be used to mitigate or remove gas hydrate blockage. However, chemical inhibition is considered the most feasible and implemented technology by the oil and gas industry [4]. Chemical inhibition involves the injection of thermodynamic and low dosage gas hydrate inhibitors [4,5]. Thermodynamic gas hydrate inhibitor (THI) such as methanol (MeOH) and monoethylene glycol (MEG) are used at high concentrations 10–60 wt%, and are able to shift the hydrate equilibrium curve towards higher pressure and/or lower temperature regions [1,4,6]. Additionally, THIs form strong

hydrogen bonds with water, which prevent the formation of hydrate cages. On the other hand, LDHIs functions by postponing the nucleation and growth of gas hydrates to a time duration that is longer than the hydrocarbon fluid residence time in the pipelines, or prevents hydrate accumulation into larger masses [5]. However, the capabilities of LDHIs to prevent hydrate formation are associated with uncertainties that arise from the stochastic nature of hydrate nucleation and other kinetic factors. On the other hand, using THI is safer, since it can be used in high subcooling degree and extreme conditions [1]. There is currently active search for novel effective THIs that can solve problems that limit the present techniques such as the volatility of methanol.

Xiao and Adidharma (2009) reported imidazolium-based ionic liquids (ILs) as a new class of hydrate inhibitors [7]. They found that 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium dicyanamide, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, and 1-ethyl-3-methylimidazolium ethylsulfate perform as both thermodynamic and kinetic inhibitors for methane gas hydrates [7,8]. Generally, ILs are liquid organic salts at room temperature that have unique properties such as non-flammability, negligible vapor pressure, high thermal and chemical stability [9,10]. They are able to form hydrogen bonds and exhibit strong electrostatic charges when mixed with an appropriate solvent. These bonding interactions properties, specifically with water molecules, enable ILs to inhibit gas hydrate formation. On the other hand, the tunability of ILs cations and anions can result in the flexible design/development of environmentally-friendly, efficient,

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and low-cost ILs-based inhibitors for gas hydrate mitigation [11]. Researchers have investigated numerous types of ILs by varying the chain length, cations and anions in gas hydrate prevention studies [12–17]. To date, imidazolium-based ILs are the most commonly reported THIs and KHIs in the related body of literature. It is well established from the literature that ILs with shorter alkyl chains cations such as 1-ethyl-3-methylimidazolium are favorable as THI [12,18,19]. Furthermore, introducing functional groups to the cation structures can also potentially improve the performance of ILs [20]. Anions also play a crucial role in hydrate inhibition. For example, chloride [Cl][−] shows better inhibition than bromide [Br][−] and iodide [I][−]. It was reported that strong anions such as halides and hydrogen sulfate can disturb hydrogen bonds between water molecules, thus showing better hydrate inhibition impact. However, it was reported that the cations type have an impact on the inhibitory performance of ILs. For example, ILs cations such as morpholinium, piperidinium, ammonium, pyrrolidinium and pyrrolidine show different performance levels as gas hydrate inhibitors [12–15,17]. In order to investigate the potential applicability of ILs as gas hydrates inhibitors, a broad database is required by investigating numerous types of ILs.

In this work, four ILs were chosen and tested as THIs. Namely, tetraethylammonium [TEA-I], 1-methyl-3-octylimidazolium chloride [MOIM-Cl], 1-methylimidazolium hydrogen sulfate [H-MIM-HSO₄], and 1-hexyl-3-methylimidazolium iodide [HMIM-I]. The chosen ILs have not been investigated in the existing literature. Methane hydrate dissociation temperature was measured for (CH₄-0.1 mass fraction IL-water) systems using High-Pressure Differential Scanning Calorimeter (HPDSC). Quantitative analysis was carried out by calculating the average reduced temperature and molar hydrate dissociation enthalpies from the Clausius–Clapeyron equation. The density of 0.1 mass fraction of aqueous solutions ILs was measured and compared with commercial THI. Additionally, the Dickens and Quinby-Hunt (electrolyte) model was also applied in this study.

2. Experimental

2.1. Chemicals

The four selected ILs consisting of different cations and anions were supplied by Sigma-Aldrich (Table 1). The chosen cations are 1-methyl-3-octylimidazolium [MOIM]⁺, 1-methylimidazolium [H-MIM]⁺, 1-hexyl-3-methylimidazolium [HMIM]⁺, and tetraethylammonium [TEA]⁺; while the chosen anions (chloride [Cl][−], iodide [I][−], hydrogen sulfate [HSO₄][−]) have strong electrostatic charges. All ILs are water soluble and were used without further purification. Deionized water was dispensed from the Ultra-Pure Water System, Model: Lab Tower EDI 15 and used for the preparation of the sample solutions. All aqueous solutions were prepared with 0.1 mass fraction using an analytical balance with the accuracy of ± 0.001 g.

2.2. Apparatus and procedure

2.2.1. Hydrate dissociation temperature measurement

The main tool employed in this study is a High-pressure Micro Differential Scanning Calorimeter supplied by SETARAM. The experimental

setup is shown in Fig. 1. The HP μ DSC uses thermal analysis that measures the difference in heat flow between the sample cell and the reference cell as a function of temperature. The experimental setup was explained in-depth in previous work [12]. Approximately 0.05 g of a prepared aqueous ionic liquid solution or deionized water was placed in the high-pressure Hastelloy cell, while the reference cell remained empty. After that, these cells were placed inside the calorimetric block, followed by the frequent purging of the cells with a small amount of methane gas. This was done to filter out any remaining air. Next, the injection of methane gas into cells was performed at a specific pressure regulated by a pressure controller. The pressure points tested in this work are 5.1, 7.1, 9.6 and 11.1 MPa.

A non-isothermal mode was set to determine the offset dissociation temperature. It involves two procedures; cooling and heating. Initially, the cells were cooled from 293.15 K to about 253.15 K with a cooling rate of 0.5 K/min. During this stage, methane gas hydrates were formed. After this, the temperature was kept constant for 10–20 min to ensure hydrates formation. After hydrate formation, the cells were then reheated to 293.15 K at a rate of 0.01 K/min. In this experiment, the slow heating rate is important, as it allows the repeatability of measurements, since there is no agitation inside the HP Cells [8,12]. On the other hand, the high cooling rate was applied to ensure the fast formation of methane gas hydrates.

2.2.2. Density measurement

Density measurements for aqueous ionic liquid solutions were performed at a temperature of 293.15 K. The details and calibration of the apparatus used are available in prior work [21]. A digital vibrating tube density meter with an accuracy of ± 0.0006 g·cm^{−3} was employed to measure the IL solutions densities at 0.10 mass fraction. The temperature of the whole process was controlled and adjusted by an integrated thermostat.

3. Theory

Several thermodynamic models were proposed and applied to predict the phase equilibria of gas hydrate in the presence of additives. However, the prediction methods based on the influence of additives on the activity of water were shown to have accurate results. Therefore, to estimate the equilibrium points of methane hydrates in the presence of ILs, the electrolytes based model proposed by Dickens and Quinby-Hunt was adopted in this work [22]. This model can be applied, since ILs are molten salts composed of anions and cations [23]. The model is the adaptation of the Piroen model; and was adapted for the modelling of electrolytes and IL solutions on the methane hydrate phase boundary by many researchers [20,24–27]. The model was fundamentally established from the classical thermodynamic theory, which assumes that the amount of methane in the water phase is negligible. Moreover, the ILs decrease water activity (a_w), and at small temperature ranges, the hydrate enthalpy of dissociation (ΔH_d) remains constant. The derivation details were provided by Dickens and Quinby-Hunt [22] and Piroen [24].

Based on this model, the effect of ILs on the methane hydrate dissociation temperature can be denoted as follows;

$$\ln a_w = \frac{\Delta H_d}{nR} \left[\frac{1}{T_w} - \frac{1}{T_{IL}} \right] \quad (1)$$

where a_w denotes water activity, n is methane hydrate hydration number (6.0 [8]), H_d represents the dissociation enthalpy of methane hydrates (59.966 kJ/mol), R is the universal gas constant, and T_w and T_{IL} are the hydrate formation temperatures in pure water and aqueous ILs solution respectively. CSMGem software was used to calculate the water- methane hydrate dissociation temperature.

Table 1

Name and purity of studied ILs.

Name	Symbol	Purity
1-Methyl-3-octylimidazolium chloride	[MOIM-Cl]	97%
1-Methylimidazolium hydrogen sulfate	[H-MIM-HSO ₄]	95%
Tetraethylammonium iodide	[TEA-I]	98%
1-Hexyl-3-methylimidazolium iodide	[HMIM-I]	98%

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