

# Effect of imidazolium based ionic liquids and ethylene glycol monoethyl ether solutions on the kinetic of methane hydrate formation



Marziyeh Zare<sup>a</sup>, Ali Haghtalab<sup>a,\*</sup>, Amir Naser Ahmadi<sup>b</sup>, Khodadad Nazari<sup>b</sup>, Ali Mehdizadeh<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran

<sup>b</sup> Center of Chemistry and Petrochemical, Research Institute of Petroleum Industry, Tehran, Iran

## ARTICLE INFO

### Article history:

Received 2 January 2015

Received in revised form 18 January 2015

Accepted 19 January 2015

Available online 20 January 2015

### Keywords:

Methane hydrate

Imidazolium based ionic liquid

Ethylene glycol monoethyl ether

Kinetics

Promoter

## ABSTRACT

In a high pressure reactor, the methane hydrate formation experiments are carried out in the presence of the various imidazolium based ionic liquid solutions with 0.5 wt.% so that the induction time, gas consumption and temperature are measured. Moreover, methane hydrate formation experiments are performed in the presence of ethylene glycol monoethyl ether (EGME) as an inhibitor. The simultaneous effect of EGME and ionic liquid solutions on the methane hydrate formation is investigated so that influence of these materials depends on the type of ionic liquid and the concentration of EGME. The results indicate that using 0.75 wt.% EGME in the presence of [BMIM][MeSO<sub>4</sub>] and [OH-EMIM][BF<sub>4</sub>] solutions leads to the promotion of methane hydrate formation. In contrast, these systems with 10 wt.% EGME play as a kinetic inhibitor in methane hydrate formation.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Gas hydrates are ice-like crystalline compounds that are formed by water molecules through hydrogen bonding and gas molecules with suitable size trapping inside cages [40]. The several essential factors such as gas molecules (guests), water molecules (hosts), and proper conditions including low temperature/high pressures are necessary for gas hydrate formation [13,41]. The works on the gas hydrate formation have been performed in the two opposite directions [43]. One group of the research activities have been focused since the last decade not only on the inhibition of gas hydrates formation, which are related to petroleum and gas industries, but also some other works have been carried out to investigate the influence of promoters on gas hydrate formation [21].

The thermodynamic and low dosage kinetic inhibitors have been applied to prevent hydrate blockage in pipelines. Although, the thermodynamic inhibitors including alcohols, glycols and electrolytes effectively cause to inhibit the formation of gas hydrates, their large concentrations are needed (10–50 wt.%) with high cost [8,28,29,40]. The low dosage kinetic inhibitors (LDHIs) including anti-agglomerates (AAs) and kinetic hydrate inhibitors (KHIs) as a new group of inhibitors have been proposed to prevent hydrate formation so that these inhibitors not only don't change the thermodynamic conditions of gas hydrate formation but they are also able to delay hydrate nucleation and slow down the

rate of hydrate growth [20,40]. Many works have been carried out to applying LDHIs [2,8,9,20,22,26–29,48]. On the other hand, recently the gas hydrates have been considered as a new tool for storage and transport of natural gas [43]. Using this technique, several steps are required for storage and transport of natural gas hydrates that include hydrate formation, the processing of the formed hydrate, storage and transportation of the processed hydrate and hydrate dissociation so that the necessary technologies for these processes are still at early stages. The hydrate storage processes haven't been industrialized because of some shortcoming such as slow formation rates, volume of unintegrated water with gas (only a thin film is formed at the interface of water and gas), economy of process scale up and the reliability of hydrate storage capacity [19,35,42]. Therefore, the hydrate formation rate has the most important role in the natural gas hydrate storage and transport. Using enough amounts of kinetic or thermodynamic promoters, the mass transfer between gas and water is intensified so that the hydrate formation rate is enhanced [19]. Several researchers have presented that the hydrate formation rate is enhanced effectively through using promoters [14,15,21,23,24,33,35,36,42,43,50,51].

In recent research works, the ionic liquids as green solvents have been used in various applications. Ionic liquids are like electrolytes with low melting points that present specific characteristics such as low volatility (low vapor pressure) and good thermal stability so that they can be used for a particular application through tuning of their cation, anion and functional groups [3,17,39]. The limited works have been accomplished using ionic liquids as inhibitors/promoters for gas hydrate formation. Chen et al. [6] investigated the effect of 1-butyl-3-imidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) on the formation rates

\* Corresponding author.

E-mail address: [haghtala@modares.ac.ir](mailto:haghtala@modares.ac.ir) (A. Haghtalab).

**Table 1**  
List of materials used in this work.

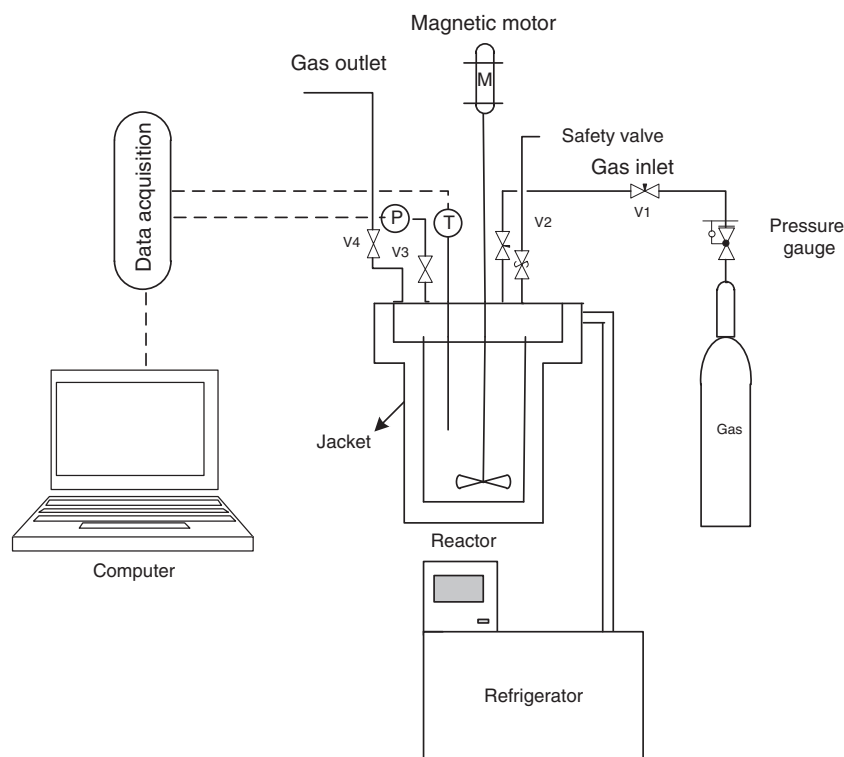
Name	Symbol	M <sub>w</sub> (g/mol)	Purity
Ethylene glycol monoethyl ether (EGEE)	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	90.12	≥ 99%
1-Ethyl-3-methylimidazolium ethyl sulfate	[EMIM][EtSO <sub>4</sub> ]	236.29	≥ 95%
1-Ethyl-3-methylimidazolium hydrogen sulfate	[EMIM][HSO <sub>4</sub> ]	208.24	≥ 94%
1-Butyl-3-methylimidazolium methyl sulfate	[BMIM][MeSO <sub>4</sub> ]	250.32	≥ 95%
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF <sub>4</sub> ]	226.02	≥ 97%
1-(2-Hydroxyethyl)-3-methylimidazolium tetrafluoroborate <sup>a</sup>	[OH-EMIM][BF <sub>4</sub> ]	213.97	>99.5

<sup>a</sup> The [OH-EMIM][BF<sub>4</sub>] was prepared in the lab of Research Institute of Petroleum Industry (RIPI), and the characteristic of the ionic liquid was presented by Shokouhi et al. [38].

of carbon dioxide hydrate so that the rate of gas consumption was enhanced by lowering the experimental temperature when the mass percent of [BMIM][BF<sub>4</sub>] was kept constant. The performance of some imidazolium-based ionic liquids with various cations and anions was investigated [46,47] so that they found that ionic liquids are able to act as dual function (kinetic-thermodynamic) inhibitors for methane hydrate formation. In addition, they presented that the anion type of ionic liquids could be effective as an inhibitor and they showed that tetrafluoroborate ionic liquids act as a kinetic inhibitor so that its performance is better than the other ionic liquids [46,47]. Villano and Kelland [45] showed that 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM[BF<sub>4</sub>]) are the weak kinetic inhibitors when they are applied to prevent the synthetic natural gas hydrate formation in the range of 0.5–1 wt.%. Also, they noted that these ionic liquids were good synergists in the presence of the commercial kinetic inhibitors such as Luvicap 55W and RE5131 HIO. The equilibrium conditions of methane hydrate formation in the presence of the ionic liquids, based on dialkylimidazolium and tetraalkylammonium cations, were investigated by Li et al. [31]. Also, Tumba et al. [44] studied methane and carbon dioxide hydrates in the presence of tributylmethylphosphonium methylsulfate. Their investigations indicated that tributylmethylphosphonium

methylsulfate prevents the formation of the CO<sub>2</sub> and CH<sub>4</sub> hydrates. The effect of 1-ethyl-3-methyl imidazolium cation of ionic liquids was investigated for CO<sub>2</sub> hydrate formation by Makino et al. [32]. They measured the induction times of hydrate formation for the CO<sub>2</sub> + ionic liquid + water systems and showed that the induction times of these systems are shorter than the water + CO<sub>2</sub> system. Indeed, these ionic liquids with 0.10 mol% can be used as the kinetic hydrate promoters. Keshavarz et al. (2013) studied experimentally the effect of aqueous solutions of the three ionic liquids containing 1-butyl-3-methylimidazolium tetrafluoroborate (0.10, 0.15 and 0.20 mass fraction), 1-butyl-3-methylimidazolium dicyanamide (0.10 mass fraction), and tetraethyl-ammonium chloride (0.10 mass fraction) on the methane hydrate formation.

In this work, the induction time and the rate of gas consumption of methane hydrate in the presence of imidazolium based aqueous ionic liquid solutions are measured using a high pressure reactor. The ionic liquids used in this work are 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][MeSO<sub>4</sub>]), 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO<sub>4</sub>]), 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO<sub>4</sub>]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([OH-



**Fig. 1.** Schematic of the experimental apparatus for measuring gas hydrate dissociation conditions. V<sub>1</sub>, V<sub>2</sub>, V<sub>3</sub>, V<sub>4</sub>, valve; M, magnetic stirrer; T, platinum resistance thermometer for temperature; P, pressure transducer.

Download English Version:

<https://daneshyari.com/en/article/5411191>

Download Persian Version:

<https://daneshyari.com/article/5411191>

[Daneshyari.com](https://daneshyari.com)