J. Chem. Thermodynamics 111 (2017) 7–19

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

# Investigation of the performance of biocompatible gas hydrate inhibitors via combined experimental and DFT methods

Nabila Adam Mohamed [a], Mohammad Tariq [a], Mert Atilhan [b,*], Majeda Khraisheh [a], David Rooney [c], Gregorio Garcia [d], Santiago Aparicio [d,*]

[a] Chemical Engineering Department, Qatar University, 2713 Doha, Qatar
[b] Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar
[c] School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast UKBT9 5AG, Northern Ireland, United Kingdom
[d] Department of Chemistry, University of Burgos, Spain

ARTICLE INFO

*Article history:*
Received 9 March 2016
Received in revised form 28 February 2017
Accepted 14 March 2017
Available online 18 March 2017

*Keywords:*
Gas hydrates
Ionic liquids
Thermodynamic inhibitors
Flow assurance
Phase behaviour

ABSTRACT

In this work, three ionic liquids (ILs) from the bio-compatible family of choline cations attached to anions of varying hydrophobicity namely: choline acetate (ChOAc), choline bistriflamide ($ChNtf_2$), and choline chloride (ChCl), have been tested for their gas hydrate inhibition properties for methane and a multi-component Qatari natural gas type mixture (QNG-S1). A rocking-rig assembly (RC-5) has been used to obtain the pressure-temperature (P-T) loops for the studied systems in absence/presence of inhibitors. Two concentrations of 1 and 5 wt% for the choline IL-inhibitors have been chosen which shows distinct effectiveness towards studied single and multi-component hydrate systems. Hydrate suppression temperatures ($\Delta T$) have been calculated from the obtained dissociation data for quantitative analysis of inhibition effect of ILs and its trends against pressure dependence were discussed. Further, to understand the mechanism of hydrate formation and dissociation, the imaging of a complete P-T loop for $CH_4$ + 5 wt% $ChNtf_2$ system has been performed using a borescope camera attached to gas hydrate autoclave (GHA) apparatus. Furthermore, the main features of the interaction mechanism between selected ionic liquids and hydrate structures were elucidated at the molecular level through quantum chemical calculations by using density functional theory (DFT) methods. The results on the effectiveness of bio-compatible ILs as hydrate inhibitors compared to their conventional counterparts have been proposed in the manuscript.

## 1. Introduction

Gas hydrates are crystalline solids composed of hydrogen bonded water molecules with a guest gas molecule inside of it, which forms at low temperature and high pressures, but above the freezing point of water [1–3]. These conditions often exist during gas processing. Their formation in oil and gas industry may cause pipeline blockage and leads to serious operating and safety problems [4].

The industrial solutions for the hydrates problem are widely known and their effectiveness in preventing the formation of hydrates has been extensively studied. Several methods are available to mitigate the formation of gas hydrates viz., dehydration, system heating/depressurization, and inhibition [5,6]. Generally, the most viable option to encounter this issue is by adding the inhibitors in the system. Two most commonly used inhibitors by gas and oil industries are: the classical thermodynamic inhibitors (THIs) and kinetics inhibitors (KHIs) [7–10]. The classical THIs are industries favorites, especially methanol (MeOH) and mono-ethylene glycol (MEG). Though, toxicity, corrosiveness, storage and the high cost of the huge amounts of THIs required for hydrate preventing are major drawbacks. In addition, the application of THIs requires separation and recovery units which adds more cost for their implementation. These serious operational problems particularly the corrosive nature may also reduce the lifetime of the flow-lines and process equipment [11,12]. All these environmental and economic concerns coincided with the classical inhibitors posed the intense need for pursuing novel hydrate inhibitors research. Due to the major drawbacks of THIs, more emphasis on the environmentally friendly low-dosage kinetic inhibitors (KIs) has been started to gain attention in the recent years. The drawbacks of THIs given the push to the search for environmentally benign kinetic inhibitors (KIs). KIs are effective at low dosage (>1 wt%) thereby have significant advantages in terms of cost-

---

* Corresponding authors.
*E-mail addresses:* mert.atilhan@qatar.tamu.edu (M. Atilhan), sapar@ubu.es (S. Aparicio).

http://dx.doi.org/10.1016/j.jct.2017.03.013
0021-9614/

effectiveness and economy [13]. However, the existing KIs are not economically effective under the conditions of higher pressures and large degree of sub-cooling. Therefore, there is a need to search for more effective alternatives compared to their conventional counterparts.

Recently, the hydrates inhibition researches are focusing on ionic liquids (ILs) and seeking for more environmentally friendly, biodegradable green solvents with good inhibition performance [14,15]. ILs proved to have all these desired characteristics with the ability to be designed from widespread ranges of cations and anions providing tuning properties. ILs are still new candidates for gas hydrate inhibition and are still under development. However, their tunable chemical and physical properties increase their applications and might produce effective hydrate inhibitors. The myriad range of ILs that could be designed for hydrate inhibition requires more fundamental and systematic study for their thermodynamic and kinetic behavior. Thus, the selected ILs in this study are choline based, a biocompatible cation [16], with different anions with varying hydrophobicity and are tested both in single (methane) and multi-component systems (Qatar natural gas type mixture, QNG-S1) to provide a new understanding of the current knowledge on ILs and their applicability on the hydrate prevention applications.

Qatar holds the world's third-largest proven reserves of natural gas at 885 trillion cubic feet. Since, the natural gas reservoirs are located 80 km offshore in Qatar and the production of liquefied natural gas depends on reliable flow from offshore wellheads to onshore processing facilities, flow assurance has become one of the critical challenging problems [5,17]. Thereby, it is interesting to study the effectiveness of selected choline based ILs-inhibitors towards alternative solutions to flow assurance issues in Qatari oil and gas industries.

In this present work, the applicability of choline ILs as hydrate inhibitors for methane and QNG-S1 have been studied using rocking cell (RC-5) apparatus. The obtained hydrate equilibrium data were used to calculate the hydrate suppression temperatures in order to quantify the effectiveness of ILs towards methane and QNG-S1 hydrate inhibition. The borescope camera installed in the gas hydrate autoclave (GHA) was used to capture images of the process of hydrate formation/dissociation cycles of methane in presence of a selected hydrophobic IL inhibitor to unravel the mechanism of the inhibition process. The overall results present a complete picture and suitability of tested ILs in using them as low dosage hydrate inhibitors (LDHIs) for methane and QNG-S1.

## 2. Methods

### 2.1. Materials

QNG-S1 was procured from Quality Specialty Gases, Qatar with a stated mixtures composition accuracy of 2%. Details about the various components and their relative uncertainties are furnished in Table 1. Gas compositions were checked with GCMS for the composition and the uncertainties. Methane was purchased from Buzware Scientific and Technical Gases, Qatar, with a stated purity of 99.99%. All ILs with a stated purity of ≥99% have been purchased from IoLiTec GmbH, Germany. The structure and other details of ILs are furnished in Table 2. Throughout the experiments Millipore Quality water has been used for making solutions. All the IL inhibitor solutions were prepared by weighing on Mettler Toledo, XS-105 electronic balance with a precision of ±0.00001 g

### 2.2. Experimental methods

Rocking cell assembly and gas hydrate autoclave (both from PSL Systemtechnik GmbH, Germany) have been calibrated using pure methane in water and in presence of 10 wt% methanol (AR grade) with known HLVE data to check their performances and validation. Then, Methane and QNG-S1 mixture were tested alone and in presence of various concentrations of hydrate inhibitors to obtain HLVE data. Isochoric pressure search method [18] has been used to get the HLVE data in all the apparatuses

**Table 1**
Composition of Qatar natural gas type (QNG-S1) mixture used in this work.

| Component | Composition (mole fraction) | Relative uncertainty (mole fraction %) |
|---|---|---|
| Methane | 0.84990 | 0.2 |
| Ethane | 0.05529 | 2.0 |
| Propane | 0.02008 | 2.0 |
| *iso*-Butane | 0.00401 | 2.0 |
| *n*-Butane | 0.00585 | 2.0 |
| *iso*-Pentane | 0.00169 | 5.0 |
| *n*-Pentane | 0.00147 | 5.0 |
| *n*-Octane | 0.00152 | 5.0 |
| Toluene | 0.00090 | 5.0 |
| Methyl cyclopentane | 0.00102 | 5.0 |
| Nitrogen | 0.03496 | 2.0 |
| Carbon dioxide | 0.02331 | 2.0 |

### 2.3. Rocking cell assembly (RC-5)

The RC-5 (PSL Systemtechnik GmbH, Germany), Fig. 1(a), used in this study contains five test cells. This means that five runs can be performed simultaneously. However, the only variables possible, for these simultaneous runs, can be the composition of the sample and pressure. To start a fresh experiment the test cell was removed from its platform axis after it was depressurized and the temperature sensor and pressure supply tube were disconnected. Then it was mounted on the assembling aid and the screw lid was opened with a jaw wrench. The ball casing of the test cell and the mixing ball were washed carefully for several times with distilled water, ethanol and dried then filled with the prepared test mixtures (i.e., water with/without inhibitors) as per the experimental requirement. Then the test cell was sealed properly in the same way it was opened, reinstalled to its corresponding place on the platform axis in the bath, and reconnected to the temperature sensor and pressure supply. The test procedure with this experimental set-up was started with filling each cell (with maximum volume of 40 $cm^3$) with 15 ml of ultrapure water, then pressurized it directly with the sample gas to the target pressure, as desired by each set of the experiments

Each test cell with its aqueous content was flushed, filled with tested sample gas and pressurized up to the desired/started pressure. After temperature/pressure conditions within the each test cell were stabilized, RC-5 software was started to design the whole experimental protocol. The script was edited depending on isothermal cooling method according to following steps: (a) initialization phase of the experiment was started to stabilize the RC-5 temperature to 20 °C (starting temperature) for over an hour and also to check for any possible leak. (b) The experimental phase of the run was then started by cooling the fluid inside the vessel rapidly with rate (1.8 °C/h) from 20 °C to 2 °C with an agitation of 10 rocks/min, then the system was left for 24 h at 2 °C to form hydrates. By the time hydrates were formed, as indicated by pressure drop, the ball may stop rolling, as it plugged the cell. (c) After hydrates were formed, heating process was started back to the initial temperature with very slow rate (0.18 °C/h) for complete hydrate melting. Stepwise heating method was used during the hydrate dissociation period and 12 h of intermission has been given at every 12 h for the experiments. This makes an approximate heating rate of