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Influence of cationic and non-ionic surfactants on the kinetics of mixed hydrogen/tetrahydrofuran hydrates

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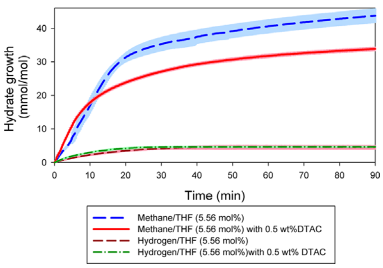
HIGHLIGHTS

- Cationic and non-ionic surfactant effect on the formation of H_2/THF mixed hydrates.
- Presence of THF retards the kinetic promotion effect of surfactants for hydrate formation.
- Surfactant effect on mixed THF hydrate formation is characteristic of the guest gas.
- Surfactant did not influence the dissociation kinetics of H_2/THF mixed hydrates.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the kinetics of mixed hydrogen/tetrahydrofuran (THF) hydrate formation in presence of cationic dodecyl trimethylammonium chloride (DTAC) surfactant and non-ionic Tween-20 (Polysorbate 20) surfactant was evaluated. Stoichiometric concentration of 5.6 mol% THF solution with varying surfactant concentrations from 0.01 wt% to 1 wt% were experimented and their effect on the mixed hydrogen/THF hydrate formation was studied. Marginal improvement in the mixed hydrogen/THF hydrate formation rates were observed for both the chosen surfactants with maximum of about 20% increase using 0.5 wt% DTAC and 0.1 wt% Tween-20. Decomposition kinetics of mixed hydrogen/THF hydrates using thermal stimulation ($\Delta T = 20$ K) with and without stirring showed that stirring improved the decomposition kinetics with t_{90} of 22.2($\pm$0.8) min in comparison to t_{90} of 29.1($\pm$0.6) min for the experiments conducted without stirring. The presence of surfactant did not significantly affect the decomposition kinetics for experiments conducted both with and without stirring. Methane/THF mixed hydrate formation under similar experimental conditions studied show that the presence of 0.5 wt% DTAC surfactant resulted in reduction of hydrate formation rates by approximately 20%. The effect of surfactant in presence of THF characteristically differs depending upon the guest gas and the system under investigation.

1. Introduction

Hydrogen storage in the form of clathrate hydrates is relatively a new and promising method for storing the cleanest energy carrier gas (Strobel et al., 2009a, 2007; Struzhkin et al., 2007; Veluswamy et al., 2014b). Storing hydrogen in hydrates is the most environmental friendly method requiring only water and very low concentrations of promoter molecules (typically less than 6 mol%). Easy recovery of molecular hydrogen and recyclability of promoter and water without significant loss for successive storage cycles is possible by this method. Further added benefits include the non-explosive nature of hydrates which is a safe option for storing the flammable hydrogen gas.

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These characteristic advantages of the clathrate based hydrogen storage process makes it attractive and a viable option to store hydrogen compared to the conventional hydrogen storage methods (compression and liquefaction) and sorption (physisorption and chemisorption) based hydrogen storage.

Clathrate hydrates are caged inclusion compounds in which guest gas species are enclosed in cages formed by host water molecules (Davidson, 1973; Englezos, 1993; Sloan and Koh, 2008). The mode of interaction between encaged gas and host water molecules is through physical bonds. Another notable feature of clathrate hydrates is that they are non-stoichiometric in nature. This means that the cage occupancy (number of guest gas molecules occupying hydrate cages) may vary for the same standard hydrate structure formed depending on the guest gas species and conditions of hydrate formation. High volumetric storage capacity of gas is possible in clathrate hydrates. 1 m^3 of solid methane hydrate is equivalent to 163 m^3 of methane at STP. Similar high volumetric storage capacity has been demonstrated to be observed in other pure natural gas hydrates. This is a key attribute for gas hydrates in gas storage and transport applications. Other applications of gas hydrates are in gas separation (Babu et al., 2013a; Kang and Lee, 2000; Linga et al., 2007a, b, 2010; Link et al., 2003; Torré et al., 2012), desalination (Babu et al., 2014; Cai et al., 2014; Park et al., 2011; Sun et al., 2004) and cold storage (Shi and Zhang, 2013; Xie et al., 2010; Zhang and Ma, 2012).

Hydrogen molecule having the diameter of 2.28 Å was initially assumed to be too small to stabilize the water cages to form hydrates. The possibility of storing hydrogen in the form of clathrate hydrates was first reported by Vos et al. (1993). Despite the smallest size, hydrogen forms a classical sII structure with sixteen dodecahedron (5^{12}) cages and eight hexakaidecahedron ($5^{12}6^{4}$) cages) made of 136 water molecules at very high pressures between 0.75 and 3.1 GPa and temperature of 295 K. A salient feature of hydrogen hydrates compared to other hydrate forming guest molecules is the multiple occupancy of hydrogen molecule in both small and large cages (Chen et al., 2009; Lee et al., 2005; Lokshin et al., 2004; Mao et al., 2002). However, pure hydrogen hydrates require extremely high pressures (in the order of few GPa) at moderate temperatures which might be too difficult to be used for commercial applications. Hydrogen hydrate formation pressure substantially lowers when promoter molecules (in low concentrations) are added making it feasible for storing hydrogen in the form of hydrates at moderate temperature conditions applicable for commercial storage. However, there is a substantial reduction in the hydrogen storage capacity due to the promoter molecules occupying most of the large cages in hydrate structure limiting the hydrogen stored in hydrates. Mixed hydrogen hydrates with structures like sII, sH, semiclathrates and sI have been reported to form with different promoter molecules or compounds (Du et al., 2012; Duarte et al., 2009; Grim et al., 2012; Trueba et al., 2011). Strobel et al. (2007) computed maximum theoretical hydrogen storage capacities possible in different hydrate structures like sI, sII, sH, semi-clathrates and sVI with the assumption of single hydrogen molecule occupancy in 5^{12} small cages and multiple hydrogen occupancy in medium and large cages of hydrate structures (only hydrogen was assumed to occupy all hydrate cages). The storage capacities computed by such assumption are 7.2 wt%, 4.1 wt%, 3.8 wt%, 3.7 wt% and 3.3 wt% for sVI, sH, sII, semiclathrate and sI structures respectively. Though theoretical calculations show high hydrogen capacities for different hydrate structures, experimentally high storage capacities were reported for sII hydrates compared to other hydrate structures under moderate conditions of temperature and pressure as summarized in the recent review by Veluswamy et al. (2014b).

There are several literature works on THF/hydrogen hydrates spanning thermodynamic, kinetic, molecular characterization and morphological observations (Nagai et al., 2008; Ogata et al., 2008; Strobel et al., 2009b, 2009c; Sugahara et al., 2009; Veluswamy et al., 2014c). Florusse et al. (2004) reported a drastic reduction in hydrogen hydrate forming pressures with the addition of THF as promoter at 5 MPa and 279.6 K. The highest storage capacity of 4.03 wt% was reported by Lee et al. (2005) formed using 0.15 mol% THF at 12 MPa and 270 K. However, such a storage capacity could not be reproduced and demonstrated by other researchers. Sugahara et al. (2009) reported 3.4 wt% storage capacity formed using 0.5 mol% THF at 60 MPa and 255 K. Most of these mixed hydrogen/THF hydrates were formed starting from ice/THF hydrates at subzero temperatures and high pressure. So far in the literature, THF is the best promoter reported for storing hydrogen as clathrate hydrates. However, forming mixed hydrogen/THF hydrates at these conditions demand high energy requirement in addition to the associated problem of the recyclability of solid ice/THF for successive hydrate formation cycles. Macroscopic kinetic studies on mixed hydrogen/THF hydrates starting from aqueous solution highlight the challenges in forming mixed hydrogen/THF hydrates including the difficulty in forming hydrates even at very high driving force; longer time for hydrate formation due to slower kinetics and low hydrogen storage capacities achieved (Nagai et al., 2008; Trueba et al., 2012; 2013; Veluswamy et al., 2014a, 2015; Veluswamy and Linga, 2013).

The present study attempts to improve the kinetics of mixed hydrogen/THF hydrates using surfactants starting from the aqueous solution. Surfactants, typically at low concentrations have been proven to promote the natural gas hydrate formation rates significantly thereby considerably reducing the time taken for the completion of hydrate formation (Di Profio et al., 2005; Karaaslan and Parlaktuna, 2000; Watanabe et al., 2005; Zhang et al., 2007; Zhong and Rogers, 2000). Surfactants when used at low concentrations act as “kinetic promoters” as they improve the kinetics of hydrate formation. Surfactants are also known to change the morphology of hydrate crystal formation (Lim et al., 2013; Yoslim et al., 2010; Zhong and Rogers, 2000). Our previous study showed the superior performance of sodium dodecyl sulfate surfactant in improving the kinetics of mixed hydrogen/propane hydrates with distinct two stage growth steps when used in concentrations of 0.0005–0.1 wt% (Veluswamy et al., 2015). The time required to achieve 90% (t_{90}) of the gas uptake reduced from 334.2($\pm$27.7) min to 25.5($\pm$1.8) min with the addition of 0.01 wt % or higher concentration of SDS surfactant. However, despite the improved kinetics, the storage capacity of molecular hydrogen in hydrogen/propane mixed hydrates remains low due to increased propane occupying hydrate cages at the conditions of hydrate formation. To the best of our knowledge there have been no studies reported so far investigating the surfactant effect on mixed hydrogen hydrates using liquid promoters. Well studied anionic sodium dodecyl sulfate surfactant that effectively improved the rates of methane and CO_2 hydrate formation, did not promote mixed hydrogen/THF hydrate formation (Veluswamy and Linga, 2013). Hence, we selected two other categories of surfactant—a cationic surfactant (Dodecyl trimethylammonium chloride) and a non-ionic surfactant (Tween-20) to investigate the kinetics of mixed hydrogen/THF hydrate formation.

Dodecyl trimethylammonium chloride (DTAC) surfactant was shown to reduce the induction time and improve separation factor of CO_2 hydrate formation in presence of tetrabutyl ammonium bromide (Li et al., 2010). Du et al. (2014) studied the effect of DTAC (0–0.03 wt%) on methane gas hydrate kinetics in a static system at conditions of 274 K and 15 MPa. Thus being extensively studied cationic surfactant for promoting the kinetics of gas hydrate formation, DTAC was chosen in the present study. Lee et al. (2009) performed sulfur hexafluoride (SF_6) hydrate formation experiments at 276.2 K and 0.78 MPa, with addition of