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Surfactant effect on the kinetics of mixed hydrogen/propane hydrate formation for hydrogen storage as clathrates

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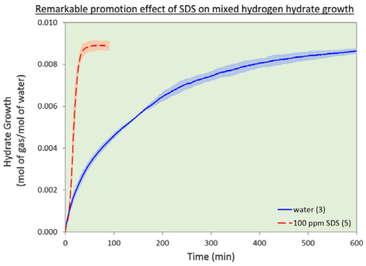
HIGHLIGHTS

- Anionic SDS surfactant effect on the formation of H_2/Propane mixed hydrates in STR.
- Observation of a distinct two step hydrate growth mechanism using SDS surfactant.
- Significant improvement in the rate of mixed hydrate formation using surfactant.
- t_{90} Reduced from 5.6 h to 0.4 h using SDS surfactant (at concentration ≥ 100 ppm).

GRAPHICAL ABSTRACT



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ABSTRACT

Effect of sodium dodecyl sulfate (SDS) surfactant on the kinetics of mixed hydrogen/propane hydrates was studied extensively in a stirred tank reactor. SDS concentration was varied in the range of 5–1000 ppm and its effect on the kinetics of the mixed hydrogen hydrate formation was observed. Anionic SDS surfactant drastically improved the rate of mixed hydrate formation due to which the hydrate formation time reduced significantly. The time required for 90% completion of the hydrate formation reduced from 334.2 (± 27.7) min (water without any surfactant) to just 25.5 (± 1.8) min in presence of SDS surfactant at concentrations greater than or equal to 100 ppm. The presence of SDS resulted in a distinct two step hydrate growth mechanism. Hydrate growth behavior similar to control (water) experiments was observed from nucleation till certain time (deflection time) beyond which the surfactant exhibited its property and increased the rate of hydrate formation resulting in faster completion of mixed hydrogen hydrate formation.

1. Introduction

Gas hydrates or clathrate hydrates are inclusion compounds wherein guest gas species are enclosed in cages formed by host water. Entrapped gas molecules interact with host water cages only through physical bonds. Clathrate hydrates can form any of the classical structures namely sI, sII and sH or semi-clathrates depending upon the size and nature of guest entities. These compounds are found to be non-stoichiometric implying that the number of guest molecules occupying hydrate cages (cage occupancy) may vary for the same standard hydrate structure formed using fixed number of water molecules (Davidson, 1973; Englezos, 1993; Sloan and Koh, 2008). 46, 136 and 34 molecules of water are reported to form unit structures of sI, sII and sH hydrate, respectively. sI structure consists of two dodecahedron (5^{12}) cages and six tetrakaidecahedron ($5^{12}6^{2}$) cages, sII structure are made of sixteen dodecahedron (5^{12}) cages and eight hexakaidecahedron ($5^{12}6^{4}$) cages), the largest size sH hydrates are having three dodecahedron (5^{12}) cages, two irregular dodecahedrons ($4^{3}5^{6}6^{3}$) cages and one icosahedron ($5^{12}6^{8}$) cage.

Gas hydrates once considered being a nuisance causing plugs in oil and gas pipelines have been proven to be useful in many practical applications (Englezos and Lee, 2005; Sloan, 2003). Selective nature of

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certain gas molecules to form hydrates in specific ranges of temperature and pressure conditions paved way for application of hydrates in gas separation (Babu et al., 2013a,b; Kang and Lee, 2000; Li et al., 2011; Linga et al., 2007a). Gas hydrates due to their inclusive nature and high volumetric density find prominent usage in gas storage and transport applications. It has been reported that approximately 163 m^3 of methane could be stored in just 1 m^3 of hydrates. Other significant advantages of clathrates include being environment friendly and possess no safety risk due to their non-explosive nature. Storing hydrogen in the form of hydrates at moderate temperature and pressure conditions with addition of small concentration of promoter makes it a promising candidate for stationary hydrogen storage applications (Frankcombe and Kroes, 2007; Ozaki et al., 2014; Struzhkin et al., 2007; Veluswamy et al., 2014b). Other novel applications of gas hydrates are in the areas of desalination (Cai et al., 2014; Kang 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).

Pure hydrogen hydrates form only at extremely high pressures (in the order of GPa) at ambient temperature which restricts their practical application. Addition of certain low concentration of thermodynamic promoter molecules reduces the mixed hydrogen hydrate formation pressure substantially thereby making it favorable for storing hydrogen in the form of hydrates (Du et al., 2012; Duarte et al., 2008; Florusse et al., 2004; Hashimoto et al., 2008; Lee et al., 2005; Trueba et al., 2011; Tsuda et al., 2009). However, the hydrogen storage capacity gets lowered in comparison to pure hydrogen hydrates due to the added promoter molecules occupying hydrate cages. Major challenges hindering the commercial implementation of hydrates in hydrogen storage application are - low hydro gen storage capacity due to the presence of promoters, the slow rate of hydrate formation (Trueba et al., 2012, Veluswamy and Linga, 2013; Veluswamy et al., 2014a) and the possible hydrogen diffusion reported to be observed through the hydrate cages (Alavi and Ripmeester, 2007; Frankcombe and Kroes, 2007; Okuchi et al., 2007). Different methods to improve the hydrogen storage capacity in hydrates have also been reported (Grim et al., 2012; Kumar et al., 2013b; Lu et al., 2012). However, only few efforts have been put forth in improving the rate of mixed hydrogen hydrate formation. Preparation of mixed hydrogen hydrates starting from mixture of ice and pure promoter hydrates with or without the porous media support had resulted in increased hydrogen uptake and faster rates of hydrate formation (Lu et al., 2012; Saha and Deng, 2010; Sugahara et al., 2009). However, the energy requirement for such a process was quite high; it was also difficult to achieve higher hydrogen uptake/release and improved formation rates during repeated cycles of hydrogen enclathration. Surfactant molecules have been demonstrated to increase the rate of hydrate formation in many natural gas systems like methane and CO_2 without affecting thermodynamic conditions of hydrate formation i.e., no change in the hydrate phase equilibrium (Kalogerakis et al., 1993; Karaaslan and Parlaktuna, 2000; Verrett et al., 2012; Verrett and Servio, 2012; Watanabe et al., 2005a; Zhong and Rogers, 2000). Thus surfactants are often referred as “kinetic promoters” as they help in increasing the rate of hydrate formation and resulting in faster gas uptake.

The mechanism by which surfactants promote hydrate formation has been highly debated. Zhong and Rogers (2000) studied quiescent systems containing ethane/water and natural gas/water along with sodium dodecyl sulphate (SDS) surfactant. They report critical micelle concentration (CMC) for SDS surfactant beyond which micelles solubilized with hydrocarbon gases initiate a subsurface and result in 700 fold increase in the rate of hydrate formation compared to the system without any added surfactant. However, the micelle formation mechanism resulting in increased rate of hydrate formation was disputed by the study conducted by Di Profio et al. (2005) because they did not observe any micelle formation under similar hydrate formation conditions using SDS, other anionic and cationic surfactants. Another work by Di Profio et al. (2006) conducted using sodium oleate and dodecyl benzene sulfonic acid surfactants resulted in a pronounced decrease in methane hydrate formation rate at concentrations above CMC compared to experiments conducted below CMC. Further studies (Watanabe et al., 2005a; Zhang et al., 2007a) also report that micelle formation of SDS under hydrate formation conditions would not be possible.

Some studies report that SDS surfactant causes a capillary suction resulting in the growth of hydrate front in upward direction on the reactor walls resulting in improved rates compared to the hydrate film growth occurring at the liquid–gas interface in experiments conducted with water devoid of the surfactant (Gayet et al., 2005; Yoslim et al., 2010). Few studies also report SDS adsorption on hydrates and discuss the effect of adsorption in influencing the hydrate formation kinetics (Lo et al., 2010; Zhang et al., 2007b, 2008).

Surfactants have been reported to improve the rate of hydrate formation in fixed bed reactor configurations (Dicharry et al., 2013; Kang and Lee, 2010; Kumar et al., 2013a). Experiments have also been conducted to study the effect of surfactants in promoting hydrate formation in stirred tank reactor (Ganji et al., 2007; Lee et al., 2009; Lin et al., 2004; Verrett et al., 2012). These studies compare the performance of different surfactants for specific gas–liquid systems in order to determine the optimal concentration of the surfactant in achieving the fastest gas uptake due to the increased rate of hydrate formation.

The present study investigates the effect of SDS surfactant in improving the kinetics of mixed hydrogen/propane hydrate formation. Our recent work (Veluswamy et al., 2014c) on the formation kinetics of mixed hydrogen/propane hydrates using hydrogen/propane ((90.5/9.5 mol%) gas mixture showed that it took almost 10–14 h for hydrate formation to be complete (reach a steady state or no further gas consumption due to hydrate formation) despite performing the experiments at 8.5 MPa (7 MPa driving force) and 274.2 K. The highest hydrogen uptake (0.32 wt% on atomic basis) was achieved under these experimental conditions. This showed the sluggish nature of mixed hydogen/propane hydrate formation. In an attempt to improve the rate of mixed hydrogen/propane hydrate formation, a well-known kinetic promoter, anionic SDS surfactant was added in different concentrations and its effect on the formation of mixed hydrogen hydrates was studied. The reason for choosing SDS surfactant is that it is known to be the best performing kinetic promoter for different hydrocarbon-water systems in the literature. This study also presents visual observations of the mixed hydrogen/propane hydrate crystals recorded during the conduction of experiments. To the best of our knowledge, there are no studies conducted so far to increase the rate of mixed hydrogen hydrate formation starting from aqueous solution or water emphasizing the importance of the present study.

2. Experimental section

2.1. Materials

Gas cylinder having hydrogen/propane (90.5/9.5 mol%) purchased from SOXAL Private Ltd was used in experiments. Accuracy of ± 1% in composition of gas mixtures was guaranteed by the supplier. Distilled water from a conventional apparatus for making distilling water was used in the experiments. Sodium dodecyl sulphate (biotechnology grade) having 99.0% purity purchased from Amresco was used in experiments.

2.2. Experimental apparatus

Detailed description of the setup employed for conduction of experiments is available in Babu et al. (2014b). Schematic of the