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FULL LENGTH ARTICLE

Effect of three representative surfactants on methane hydrate formation rate and induction time

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Abstract The effects of three types of surfactants on methane hydrate formation process were investigated. Three different classes of surfactants involving anionic (sodium dodecyl sulfonate), cationic (hexadecyl trimethyl ammonium bromide) and non-ionic (poly oxy ethylene (40) octyl phenyl ether) have been used. Thermodynamics of hydrate formation, formation rate, kinetic constants and induction time in the presence of surfactants with various concentrations were analyzed. Critical micelle concentrations (CMCs) of these surfactants in water were determined by induction time measurements in various concentrations under methane hydrate formation conditions. The critical micelle concentration (CMC) at the methane hydrate formation conditions for SDS, HTABr and TritonX-405 solutions were obtained at 450, 380 and 950 ppm, respectively. The experimental results indicated that hydrate formation rate increased with the use of surfactants for all concentrations and induction time decreased. It was found that for surfactants, CMC at hydrate formation conditions was less than CMC at ambient conditions.

1. Introduction

Gas hydrates belong to a special class of solids which are called clathrates. They are molecular complexes formed from mixtures of water and low molecular weight non-polar gases at sufficiently high pressures and low temperatures [1].

There are three structures of gas hydrates involving structure I (sI), structure II (sII) and structure H (sH). Structure I is body centered cubic structure which is formed by small gas molecules. Structure II is a diamond lattice within a cubic frame and structure H is known as double hydrate, which requires a cooperative gas to stabilize the small cavities of the structure [1]. If all of the positions of the three hydrate structures are filled, the hydrate molecule will contain 85% (mol) water and 15% (mol) gas [2].

The hydrate formation mechanism in the presence of surfactant molecules is shown in Fig. 1. The cluster growth of gas and water molecules is as a precursor of hydrate nuclei formation [3]. By growing hydrate nucleus up to critical size which is a stable condition, the crystal hydrate formation will be immediately achieved [4]. Note that effective critical nuclei size is lowered by surfactant absorption which in turn results in a higher hydrate nucleation rate [5].

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Hydrate gas has the ability to store a large amount of methane [6,7]. Thus, it can be used in the field of storage and transportation of natural gas [8]. A lot of storage properties of hydrate are improved by adding surfactants to a system [2,9]. Surfactant is an amphiphilic compound which can reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids and increasing the solubility, mobility, bioavailability and subsequent biodegradation of hydrophobic or insoluble organic compounds [10].

Zhong and Rogers (2000) showed that there are a lot of problems in the natural gas storage process which are removed using micellar solutions. Karaaslan and Parlaktuna (2000) experimentally showed that the presence of an anionic surfactant such as Linear Alkyl Benzene Sulfonic Acid (LABSA) considerably increases hydrate formation rate [11].

Link et al. (2003) reported that Sodium Dodecyl Sulfate (SDS) is the most appropriate surfactant for promoting methane hydrate formation [12]. Sun et al. (2003) showed that micellar surfactant solutions increase the gas hydrate formation rate and storage capacity [13]. According to this work, the effect of an anionic surfactant (SDS) on natural gas storage in hydrates is more remarkable in comparison with the effect of a nonionic surfactant such as dodecyl polysaccharide glycoside. Cyclopentane reduces hydrate formation induction time however it did not improve the hydrate formation rate and storage capacity. Lee et al. (2009) demonstrated that addition

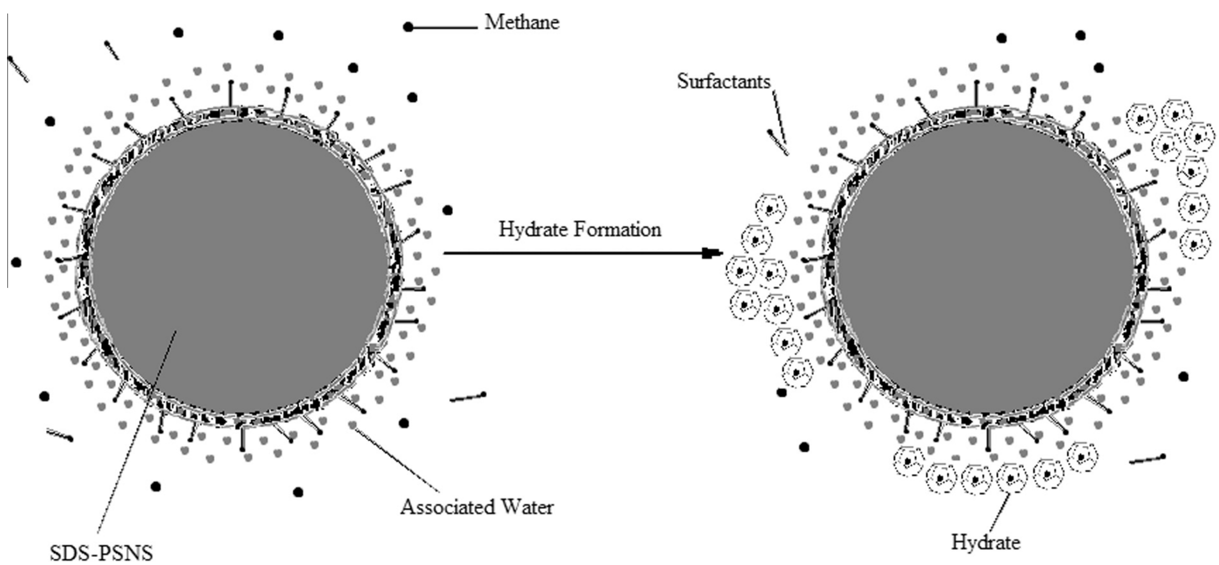

Figure 1 Hydrate formation mechanism in the presence of surfactant molecules.

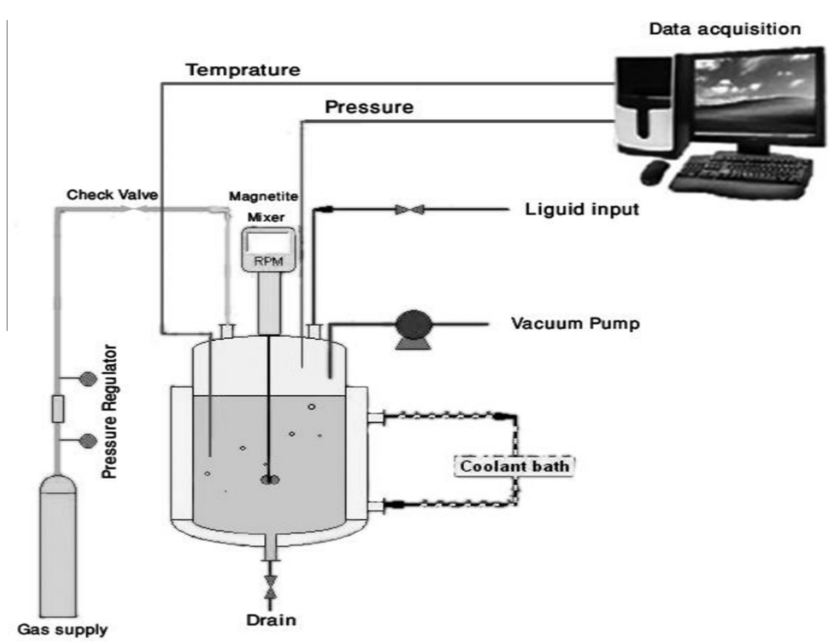

Figure 2 Schematic diagram of methane hydrate formation apparatus.

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