



# Enhanced formation of methane hydrate using a novel synthesized anionic surfactant for application in storage and transportation of natural gas



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## ABSTRACT

Storage and transportation of natural gas in the form of hydrate attract interest in recent times as a huge amount of gas can be accumulated within a small volume of solid hydrate. In the present study, a novel surfactant synthesized from castor oil is used as gas hydrate promoter with a significant increase in formation rate, reduction of induction time and higher gas storage capacity, which is desirable for storage and transportation of natural gas in the form of hydrate. The study includes characterization of the synthesized natural surfactant and its effect on storage capacity, kinetics, and rate of formation of hydrate at different concentrations. A higher storage capacity of 96% of the theoretical maximum value was obtained for the system with 9000 ppm concentration of the surfactant. Hydrate formation follows first-order kinetics with a higher kinetic rate at higher concentration of surfactant. This indicates feasibility to use the naturally derived surfactant to increase the storage capacity and transportation efficiency of natural gas.

## 1. Introduction

Worldwide consumption of natural gas is increasing significantly because of its manifold benefits including low greenhouse gas emissions, highly efficient form of energy, and relatively reduced capital costs. However, the consumption of natural gas is significantly affected by the poor supply and storage. The efficient and effective transportation of natural gas from producing regions to consumption regions requires an extensive and elaborated transportation system. Recently, transportation and storage of natural gas in the form of hydrates draw attention due to the high gas content per volume of hydrate, environmental friendly and its non-explosive nature posing no safety risk to humans as well [1–3].

Natural gas hydrates are ice-like crystalline solids which are formed from water and low molecular weight hydrocarbon gases and noble gases [4]. Methane is the simplest hydrocarbon that forms hydrate and the primary component of natural gas. Hydrates are formed through the hydrogen bonding of the water that forms a cage and gas molecules are trapped within these cages through weak van der Waals forces under high pressure and low temperature [5]. The structure of the hydrates varies depending upon the molecular size of the guest molecules and can be classified as the cubic structure I, II and hexagonal structure H. sI hydrates are the most frequently encountered hydrates in nature which contains small hydrocarbons like methane and ethane gas. sII and sH contain larger guest molecules like isobutane, cyclopentane, neohexane

etc. [4]. Methane hydrates are reported in the literature from back in the late 1930s. Contradictory to today's perspective, it was seen more of a problem than as the solution [6]. One volume of hydrate can convert itself to 180 vol of gas and 0.8 vol of water at standard conditions [7]. The modern era has seen it as the potential source for gas storage and transportation. But this potential is undermined by the slow formation rate of gas, saturation of growth of hydrates after a certain limit [8, 9].

Recent studies revealed that the storage of natural gas as solidified hydrates (SNG) has remarkable potential to store multi-fold volumes of natural gas with a safe and environment friendly way [10–12]. The specific advantages of SNG technology include highly condensed mode of storage with relatively high energy content, moderate temperature and pressure conditions, use of low concentration of promoter and easy recovery of gas [13]. Anionic surfactants have pronounced effect in increasing the rate of hydrate formation from natural gas. The promoting effect of hydrate formation have been reported by several authors in presence of different anionic surfactants, such as linear alkyl benzene sulfonate (LABS), dodecylbenzene sulfonic acid (DBSA), sodium oleate (SO), lithium dodecyl sulfate (LDS), sodium dodecyl sulfonate (SDSN), sodium dodecyl benzene sulfonate (SDBS) and other sodium alkyl sulfates [14–16]. Adding anionic and non-ionic surfactants increase the hydrate formation rate significantly by improving the kinetic rate of hydrate formation [17, 18]. The promoting effects of different surfactants on gas hydrate formation have been reviewed by Kumar et al. [19]. Ganji et al. [20] has studied the storage capacity of

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the water with the addition of the anionic surfactants sodium dodecyl sulphate (SDS), cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and linear alkyl benzene sulfonate (LABS) and they found that in presence of above surfactants the storage capacity of the water increased dramatically. Lin et al. particularly studied the effect of SDS on the stability and kinetics of hydrates and observed the maximum storage capacity at a concentration of 650 ppm [21]. Zhong and Rogers made an investigation on ethane hydrate formation in the presence of SDS above critical micellar concentration and reported that lowest induction time was obtained at 242 ppm of SDS concentration along with the achievement of 86% storage capacity within 3 h [22]. Sun et al. studied the influence of anionic and non-ionic surfactants and found that the effect of anionic is higher than non-ionic in terms of storage capacity and use of cyclic paraffin could potentially reduce the induction time [18]. Okutani et al. made an extensive observation upon the use of SDS, sodium tetradecyl sulphate (STS) and sodium hexadecyl sulfate (SHS) with increasing alkyl chains [23]. It was observed that, the increase in alkyl chain reduced water solubility which negatively affected the hydrate formation rate in SHS and hydrate growth above aqueous phase accounted for a major portion of total hydrate formation with the use of SDS and STS.

The enhanced formation of gas hydrates in presence of anionic surfactant is mainly because of increased solubility of gas molecules in aqueous phase [22, 24]. In pure water system with low gas solubility, hydrates are commonly formed at the interface of gas and water and subsequently form a barrier between gas and water phase. In presence of surfactants, the solubility of the gas in water increases and finer hydrate particles are formed with pure water, which leads to enhanced storage capacity. This can be attributed to the micelle formation in the solution above the CMC of the surfactant as micellar solutions amend the formation mechanism and increase gas hydrate formation rate. The micelle formation in bulk water phase is improved by adding surfactants with higher surface active properties. Micelle effect was supported by many researchers as the main promotion mechanism in the presence of surfactants [21–22; 25–27]. However, this hypothesis has been criticized by several authors as micelles could not be formed below the Kraft point temperature [28–32]. Capillary effect was another proposed mechanism of promoting effects of surfactant and was accepted by various researchers [33–34]. Wang et al. also studied this capillary effect mechanism in detail and observed the contact angles of various surfactants on the reactor sidewall as this could also affect the hydrate growth [16]. Another mechanism of increased solubility of methane gas in surfactant solution is due to formation of foam as proposed by Farajzadeh et al. [35–36]. Foam can significantly accelerate nuclei process, and the larger interface area of gas liquid provides more nucleation sites, which enhances the growth of hydrates [37]. The use of the synthetic surfactants is a cause of concern because of their unhygienic nature [38, 39]. Most of the synthetic surfactants are based on slowly degradable compounds and their degradation can sometimes lead to the risk to the environment and the human beings. The cost of these surfactants is additionally a bottleneck that can affect the whole scenario and thus the idea to use naturally derived surfactants came into existence [40]. A wide variety of surfactants are developed from natural oil like jatropha oil, castor oil, palm oil, sunflower and other vegetable resources as reported in literature [41–44]. Babu et al. reported that anionic ester sulfonate surfactant synthesized from castor oil shows an ultra-low interfacial tension (IFT) with enhanced micellization [42]. Kumar et al. also derived an anionic surfactant from jatropha oil, which shows efficient IFT reduction and micelle formation in aqueous solution thermodynamically [45]. These surfactants have the good potential to replace the synthetic surfactants in terms of performance and economic feasibility. These surfactants are considered to have low toxicity, environmental friendly and stable at extreme conditions of temperature, pH, and salinity [46]. Very few literature are available on the use of natural surfactant as a tool to enhance the hydrate formation rate and storage capacity of gas in the form of hydrates.

In view of importance of natural surfactants with their efficient surface active properties, in the present study an anionic surfactant synthesized from castor oil has been used for enhanced formation of gas hydrates. The suitability of the surfactant has been confirmed by its physicochemical properties in aqueous solution. A detailed experimental study has been carried out on thermodynamic phase stability of methane hydrate in the presence of the surfactant. The hydrate formation kinetics, induction time, and the storage capacity have also been investigated.

## 2. Experimental

### 2.1. Materials used

In the present study a novel surfactant synthesized from castor oil was used to improve the hydrate formation rate. The surfactant, sodium methyl ester sulfonate (SMES) was prepared by the reaction between ricinoleic acid methyl ester, the main component of castor oil and chlorosulfonic acid in an alkaline medium. The details are provided in our earlier paper [47]. Sulfonated functional group (S=O) and other groups present in SMES have been recognised by FTIR analysis as shown in Table 1. The proposed chemical reaction for the preparation of SMES surfactant is shown in Fig. 1.

For gas hydrate formation study, experiments were done with methane having purity of 99.99% (procured from Chemtron Science Laboratory, Navi Mumbai, India), distilled water and the above synthesized natural surfactant.

### 2.2. Gas hydrate apparatus

The gas hydrate autoclave i.e. used in all the experiments, was designed by the Vinci Technologies, as shown in Fig. 2. This autoclave is used to study the thermodynamic and kinetic studies of gas hydrates formation and dissociation behaviour. The volume of the cell is 250 cm<sup>3</sup> and the pressure rating of the cell is up to 20.68 MPa. A thermostatic bath having a mixture of 25% ethylene glycol and water is used to control the temperature of the cell. A thermocouple (PT100) and a pressure transducer are employed to measure the temperature and pressure of the cell respectively. This thermocouple can read the temperature in the range of 263.15K–333.15K with an accuracy of 0.1 K. Cell is equipped with a magnetic stirrer for the agitation of the samples up to the speed of 1000 RPM. The booster pump is used to increase the inside pressure of the cell by injecting the gas. The whole setup is connected to a computer for the monitoring of the whole process.

### 2.3. Procedure

The surfactant with different concentrations i.e. 3000 ppm, 5000 ppm, 7000 ppm and 9000 ppm were mixed with the distilled water (120 cm<sup>3</sup>) to prepare the samples. The solubility of surfactant in water is significantly influenced by temperature. Particularly at low temperature precipitation of surfactant may take place. However, since all the experiments were conducted under continuous stirring we have assumed no precipitation of surfactant. Each sample was poured into the cell at ambient conditions. The gas was charged into the cell at the

**Table 1**  
Functional groups present in the IR spectra of the SMES surfactant.

Wavenumbers (cm <sup>-1</sup> )	Mode of Vibration	Functional Group
2955–2873	C-H symmetrical mode of -CH <sub>3</sub> group	-CH <sub>3</sub> methyl group
1455	C-H asymmetrical bending	-C-H alkane group
3267	-OH stretching	H-OH of water
1158	S=O stretching vibration	S=O of sulfonate
667–619	= C-H bending	= C-H of alkene

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