



# Effect of SDS/THF on thermodynamic and kinetic properties of formation of hydrate from a mixture of gases ( $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$ ) for storing gas as hydrate

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## ABSTRACT

In this work, the effect of sodium dodecyl sulfate (SDS) and combined effect of sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF) on thermodynamic and kinetic properties of  $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$  hydrate formation have been studied. Four different concentrations of sodium dodecyl sulfate (100 ppm, 500 ppm, 1000 ppm and 1500 ppm) have been used to see its effect on phase equilibrium condition and formation kinetics. Though sodium dodecyl sulfate (SDS) does not vary the pressure–temperature condition of hydrate formation, it has a prominent favorable effect on induction time, gas consumption, storage capacity and formation rate. The addition of 3% (mol) tetrahydrofuran (THF) to water + SDS system results in large shifts in phase equilibrium boundary to lower pressure and higher temperature. It has been noticed that the addition of tetrahydrofuran further enhances the formation rate. So the mixture of sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF) can be effectively used as promoter for storing natural gas as hydrate.

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## 1. Introduction

Gas hydrates are ice like crystalline non-stoichiometric compound. When water and gas molecules are kept at high pressures and low temperatures, water molecules form cages around the gas molecules and the resulting structure is hydrate [1]. There is no chemical bonding between gas molecule and water. The gas molecule can rotate inside the cage [2]. Depending on the size and type of guest molecule all known common hydrate forms three types of structure: structure I, structure II, and structure H.

Several studies on the phase equilibrium and kinetics of gas hydrate formation and dissociation have been reported by many researchers, but most of them are on hydrate formation/dissociation in pure or binary gas mixture [3–9]. On the other hand, there are very limited experimental data of hydrate formation and dissociation conditions in ternary gas mixtures [10–14]. Natural gas is a mixture of many hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , etc.) and non-hydrocarbon gases ( $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$ , etc.). Each of these components has its own hydrate structure and hydrate equilibrium conditions. So it is important to understand how the presence of different components of natural gas influences the structural characteristics,

guest distribution, phase behavior as well as kinetics of natural gas hydrate.

Hydrate finds its use in many industrial applications like storage and transport of natural gas [15], gas separation [16],  $\text{CO}_2$  capture [17],  $\text{CO}_2$  sequestration [18], seawater desalination [19] and cold storage [20]. Among these applications of gas hydrate, storing gas in the form of hydrate gains interests in recent time due to high gas content per volume of hydrate, environmentally friendly and as well as its non-explosive nature that possesses no safety risk [21]. Despite these advantages, two main challenges regarding storing gas as hydrates are high formation pressure [12] and slow formation rate [22]. Many researchers have reported various thermodynamic promoters such as tetrahydrofuran (THF), acetone, 1,4-dioxane and quaternary ammonium salts like tetra-*n*-butylammonium bromide (TBAB) and tetra-*n*-butylammonium fluoride (TBAF) for the reduction of equilibrium pressure [12,23]. Among these, tetrahydrofuran (THF) is most commonly used to reduce formation pressure for  $\text{CH}_4$  [24],  $\text{CO}_2$  [25],  $\text{CH}_4 + \text{CO}_2$  [26] and  $\text{CO}_2 + \text{N}_2$  [27]. Kang et al. [27] studied the three phase equilibrium condition for simple and mixed hydrate of  $\text{CO}_2$ ,  $\text{N}_2$  and THF. They found that the dissociation pressure was shifted to higher temperatures and lower pressures conditions by adding small amount of THF. Similar results were also reported by Zhong et al. [26]. They studied the phase equilibrium conditions for hydrate formed from a mixture of  $\text{CO}_2$  and  $\text{CH}_4$ . Lee et al. [24] studied the phase equilibrium behavior of  $\text{CH}_4 + \text{THF}$ ,  $\text{CO}_2 + \text{THF}$ ,  $\text{CH}_4 + \text{CO}_2$  and

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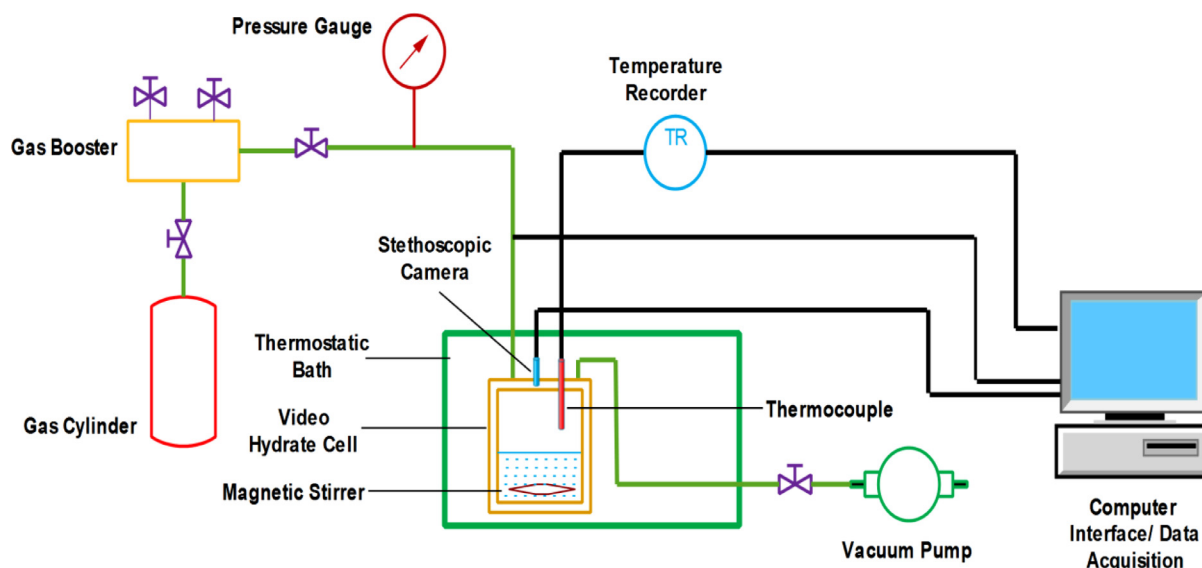


Fig. 1. Schematic diagram of the experimental setup.

$\text{CH}_4 + \text{CO}_2 + \text{THF}$  over a wide range of pressures, temperatures and concentrations. Their results also showed that addition of THF shifted the dissociation boundary to lower pressures and higher temperatures. They also reported that with THF,  $\text{CH}_4 + \text{CO}_2$  hydrate formed s(II) structure. Lee et al. [12] studied the stability conditions and guest distributions of  $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$  in presence of THF through thermodynamic and spectroscopic analysis.

Surfactants have been used widely specially sodium dodecyl sulfate (SDS) to improve the rate of hydrate formation rate without affecting the hydrate phase equilibrium [28,29]. The mechanism by which surfactant promote hydrate formation rate is still unclear. In some literatures [29–31], it was reported that formation of some micelle like structure in aqueous phase containing surfactant is responsible for enhanced kinetics of hydrate formation. However many researcher [32–35] questioned this micelle formation mechanism. They reported that surfactant micelles are not present under hydrate forming conditions. On the other hand, Gayet et al. [36] and Yoslim et al. [37] reported that surfactant prevents formation of a thin and rigid hydrate film at the liquid–gas interface. Instead, some porous fiber like crystals were formed on the reactor wall and liquid migrated from the bulk phase to porous structure due to capillary suction. Few studies also reported [38,39] surfactant adsorption on hydrate surface and its effect on hydrate forming kinetics. So, detailed molecular level study is still necessary to know the exact method of promotional effect of surfactant on the kinetic of hydrate formation.

The objective of this study is to see the effect of promoter for storing natural gas as hydrates. In this study, effect of sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF) on phase equilibrium condition and formation kinetics of  $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$  hydrate were studied. Equilibrium condition of  $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$  hydrate in SDS and SDS+THF (3% mol) was determined. Induction time, gas consumption, formation rate, water conversion and storage capacity were also calculated in SDS and SDS+THF (3% mol) to see their effect on hydrate formation kinetics.

## 2. Experimental

### 2.1. Experimental apparatus

The schematic diagram of the experimental setup is shown in Fig. 1. The setup consists of a thermo-static bath, cell, booster and

Table 1. Composition of gas mixture.

Component	Concentration (mol%)	Accuracy (%)
Propane	3.03	± 1
Ethane	7.04	± 1
Methane	balance	–

data acquisition system. The bath works with a thermostatic fluid (a mixture of 85% water and 15% glycol) to control the inside temperature of the cell with an operating temperature range from –10 to 60 °C. The bath size is about 225 × 370 × 429 mm. The cell is a stainless-steel cylinder with a capacity of 250 cm<sup>3</sup>. Maximum allowable working pressure is 20.68 MPa. The cell is equipped with a PT100 probe to measure the temperature inside the cell, the uncertainty of the measurement being ± 0.05 K. The cell pressure is measured by a pressure transducer with an accuracy of 0.1% (Full scale). A magnetic stirrer with adjustable rotation speed (up to 1000 rpm) is used to agitate the fluid inside the cell. The cell is connected to the gas cylinder through a booster to build up high pressure inside the cell. The vacuum pump seen in Fig. 1 is used to evacuate air in the cell before inserting gas. The data are recorded by a computer running an AppliLab (v6.0) software program.

### 2.2. Materials

The gas mixture used in the present study was supplied by Ultra Pure Gases (I) Pvt. Ltd. Gujarat, India. The composition of the gas mixture is given in the Table 1. SDS (purity 99.0%) and THF (purity 99.7%) were supplied by Central Drug House (P) Ltd., New Delhi, India and RANKEM, Gurgaon, India, respectively. Distilled water produced by a laboratory purification system was used in all experiments.

### 2.3. Procedure

In this work, two types of experiments have been performed: hydrate stability zone study and hydrate kinetics study. During hydrate stability zone (HSZ) study, the pressure and temperature at which hydrate is stable were measured; and in hydrate kinetics study (HKS), induction time and pressure–temperature as a function of time during hydrate formation were measured. For both types of experiments, first the cell was filled with 120 cm<sup>3</sup> of pure

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