# Decomposition of Methane Hydrate in the Presence of Sodium Dodecyl Sulfate

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**Abstract**. Presented work is devoted to the study of the process of decomposition of methane hydrate obtained in the presence of sodium dodecyl sulfate. It was found that the rate of dissociation increases with temperature and surfactant concentration increasing. It was found that free gas volume inside the reactor plays important role in the process of methane hydrate formation and influences on kinetics of hydrate formation and methane concentration in produced hydrate. It has been suggested that the decrease in the gas content in the resulting hydrate is associated with a decrease in the cooling efficiency with a larger reactor load and a decrease in the area of the effective cooling surface of the reactor walls and the formation of a hydrate on the reactor walls that reduces heat exchange between the remaining liquid phase and the refrigerant.

## 1. Introduction

Gas hydrates are inclusion compounds in which gas molecules are enclosed in crystalline cells consisting of water molecules joined by hydrogen bonds. Gas hydrates can be formed and stably exist in a wide range of pressures and temperatures (for methane from $2 \times 10^{-8}$ to $2 \times 10^{3}$ MPa at a temperature of 70 to 350K) [1].

In nature, hydrates are found mainly near the surface of the earth in those regions where the temperature and pressure correspond to the conditions of their formation. If the temperature and pressure do not match the conditions required for the existence of the hydrate, then the hydrate becomes unstable. For this reason, for example, it is rather difficult to study the deposits of methane hydrate, because when it is delivered to the surface the temperature increases and the pressure decreases that leads to the decomposition of the hydrate.

A great interest in methane in the form of gas hydrate is mainly caused by huge resource of gas hydrates and their wide distribution in the earth's crust (in the cryolithozone) and in the world oceans. The extraction of methane from natural hydrates has a clearly expressed practical meaning: the extraction of natural gas as a fuel. The first estimation for permafrost areas in 1977 gave a value of 37 trillion $m^3$ — for the USSR and 57 trillion $m^3$ — for the world in total [2]. To date, several hundreds of gas-hydrate deposits have been identified in the world. Only for the North American continent, according to the US Department of Geological Survey, gas resources in gas hydrate deposits identified by seismic sounding and deep drilling with core sampling and a full range of geophysical studies exceed 9,000 trillion $m^3$.

In recent years, one of the main areas of research and development related to methane (natural gas) hydrate is the storage of methane (natural gas) in gas hydrate state. Methane hydrate allows storing the gas in compact form and safe conditions. One volume of hydrate contains about 160 volumes of methane [1]. In addition, methane hydrate is interesting from the point of view of methane

transportation. Particular interest is bounded with the idea of dividing the delivered hydrate into methane and pure water (without impurities), which can be used for cooking or backed into the hydrate production cycle. Hydrate transport is also important for areas with poorly developed oil and gas infrastructure. Speaking about methane hydrate as an option for storing and transporting energy, it is important to note the effect of self-preservation of gas hydrate — the slow decomposition of the hydrate at negative temperatures due to the coating of its surface with a film of ice [3]. Due to this effect, natural gas hydrate can be in a metastable state for a fairly long time (up to a day) at atmospheric pressure and temperature of $-20\,°C$ [4], whereas, according to the phase diagram of methane hydrate, at atmospheric pressure for stability of methane hydrate, temperature should be lower than $-80\,°C$.

The use of hydrate technology for gas storage and transportation has several advantages. Hydrate technology does not presuppose the use of cryogenic temperatures in contrast to the storage of natural gas in a liquefied state, however, more carriers will be needed to use hydrate technology because of the lower density of natural gas to the same volume, which leads to an increase in transportation costs. Even so, the additional transportation costs will be balanced by the cost of production and storage reduced with respect to the technology of liquefying natural gas, thanks to the low temperature of gas storage in the hydrate state. Thus, the technology of natural gas storage in a hydrate state wins about 20% of the cost of using it in comparison with liquefaction in the case of production in the amount of up to 1.5 million tons per year and a transportation range of 1—6 thousand km [5]. In particular, it says that transportation of natural gas in gas hydrate state may be more preferable for APEC region if Russian Far East is considered as natural gas source.

One of the main problems in natural gas storage in hydrate state is the slow rate of hydrate formation. Scientists from all over the world have made efforts to find the solutions of this problem, such as the development of new designs of reactors that ensure maximum contact of the gas-water phases or the introduction of additives to the system that enhance the kinetics of formation of gas hydrates [6—8]. These additives are commonly known as kinetic promoters and they represent usually surface-active agents. Sodium dodecyl sulfate (SDS) is one of such surface-active agents that can be used for accelerating the process of hydrate formation [9—10]. At the same time the process of dissociation of gas hydrate obtained in the presence of SDS is also important from practical point of view. This work represents the study of the process of decomposition of methane hydrate obtained in the presence of SDS in order to determine the storage and transport conditions for methane in such hydrate state.

## 2. Materials and methods

Methane was used with a purity of 99.6% (Moscow Gas Processing Plant). To intensify the hydrate formation process, solutions of sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) manufactured by PanReacApplyChem with a purity of 95% was used.

In the first series of experiments, a steel cylindrical reactor with internal volume of 300 ml with cooling jacket was used to produce methane hydrate. The pressure in the reactor was measured by an AIR-10N pressure transducer with an accuracy of 0.01 bar, the temperature was measured by thermocouple with an accuracy of $0.1\,°C$. The temperature during hydrate formation experiments was maintained with the help of LOIP FT liquid cryo-thermostat, the accuracy of keeping the temperature was $0.5\,°C$. Data received from the sensors were transmitted to the computer. Scheme of laboratory plant for studying the kinetics of the methane hydrate decomposition process is shown in figure 1.
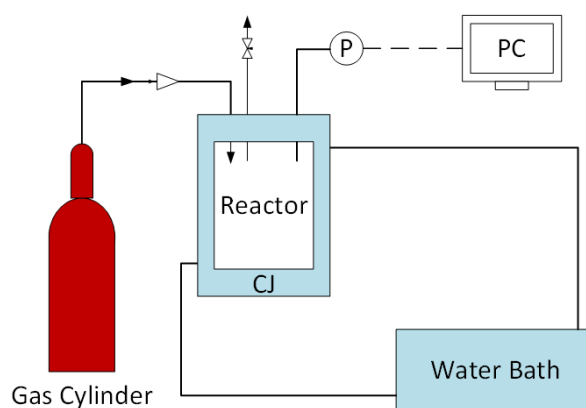
**Figure 1.** Schematic of the tank reactor setup for hydrate formation and decomposition in the first series of experiments.

The SDS aqueous solutions with concentrations of 0.1, 1 and 10 wt% were prepared and loaded into the reactor. In each experiment 150 cm$^3$ of distilled water was used. Reactor was sealed, a temperature was adjusted by cryostat in order to attain the desired experimental temperature (270 K). The vessel was flushed with pure methane gas by repeating rapid pressurization (1 MPa) and depressurization cycles. Then the reactor was pressurized with the pure methane gas up to the pre determined experimental pressure of 5.0 MPa thus providing sufficient driving force for hydrate formation. As soon as the desired experimental pressure was reached, the stirrer was turned on at 200 rpm to provide enough agitation of reaction medium to facilitate rapid formation of hydrate. After 3 hours, the reactor was cooled to –10 and kept in this state for 1 hour, then the residual pressure was discharged, the temperature was raised to –5 ℃,–3 ℃, –1 ℃ and the pressure increase in the reactor was measured.

In the second series of experiments, the methane content in the hydrate was measured as a function of the volume of the liquid. The reaction was carried out in a 500 ml cylindrical reactor with cooling jacket. In this series of experiments the reactor was filled by different amount of SDS aqueous solution: 100, 200, 300 and 400 cm$^3$.
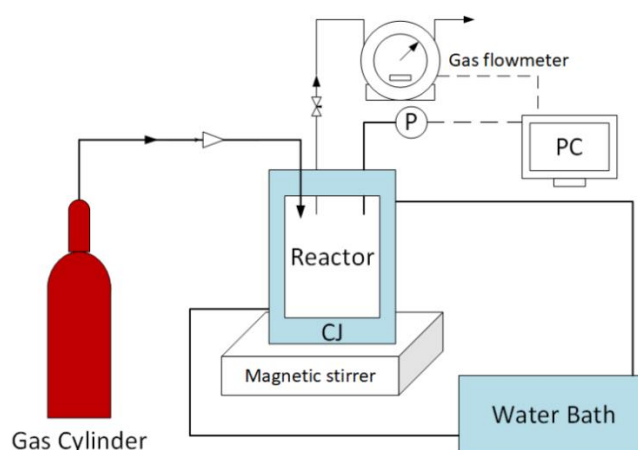


**Figure 2.** Schematic of the tank reactor setup for hydrate formation and decomposition in the second series of experiments

In all experiments the same solution of 0.1 wt% of SDS was used. Other hydrate formation conditions of these experiments were the same as in the first series of experiments. Hydrate decomposition was studied with the help of gas flow meter Ritter TGO. Scheme of laboratory plant for second series of experiments is shown in figure 2.

## 3. Results and discussion

*3.1 Dependence of the rate of methane hydrate decomposition on temperature and concentration of surfactants*

Pressure growth curves in the reactor during the decomposition of methane hydrate at different temperatures and surfactant concentrations are shown in figure 3 (left). It can be seen that the hydrate obtained in the presence of aqueous solution of SDS with concentration of 0.1% at temperatures of –3 ° C and –5 ° C practically does not decompose. The decomposition for this hydrate is only observed at temperature of –1 ℃. Methane hydrate obtained in the presence of aqueous solution of SDS with concentration of 1% does not decompose at temperature of –5 °C, at a temperature of –3 ° C there is slight increase in pressure in the reactor is observed, and at temperature of –1 ℃ the pressure increased up to 1 MPa after 2 hours. The decomposition of methane hydrate obtained in the presence of a aqueous solution of SDS with concentration of 10% is observed already at temperature of –5 ℃ as can be seen from figure 3 (right)
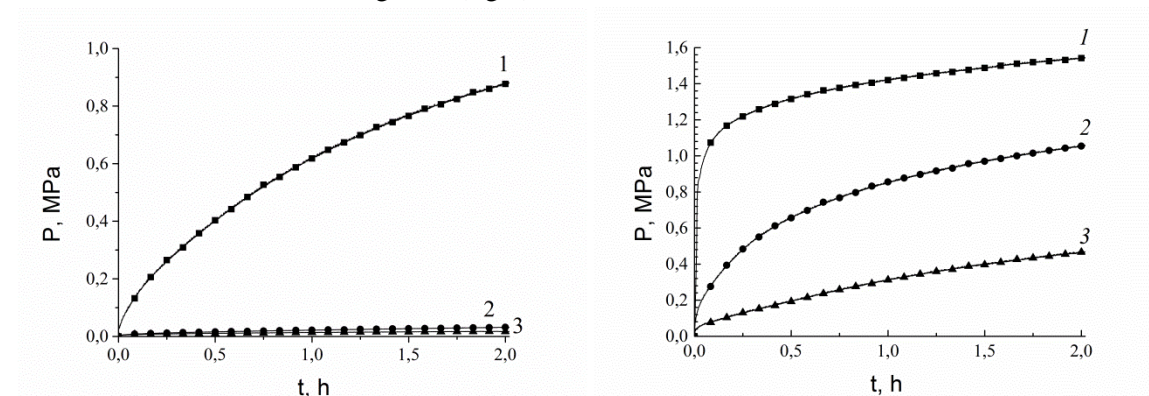


**Figure 3.** Growth of pressure in the reactor during the decomposition of methane hydrate for a concentration of 0.1 wt% (left) and 10 wt% (right), temperatures: *1 — –1 °C, 2 — –3 °C, 3 — –5 ℃.*

The comparison of experimental data says that with SDS concentration increasing the hydrate becomes less stable. This is due to the fact that at a higher SDS concentration, the hydrate contains more methane and so it is less stable. The highest decomposition rate is observed at SDS concentration of 10% and temperature of –1 ℃. At temperature of –5 ℃ and concentrations of 0.1% and 1%, dissociation was almost not observed during 2 hours.

**Table 1**. The rate of dissociation ($cm^3$/min) of methane hydrate at various temperatures and SDS concentrations

|            | –1 °C | –3 °C | –5 °C |
|------------|-------|-------|-------|
| 0,1 wt%.   | 40,36 | 1,84  | 0     |
| 1 wt%.     | 46,96 | 3,04  | 0,61  |
| 10 wt%     | 76,51 | 53,36 | 23,82 |

Table 1 shows the decomposition rates of methane hydrate ($cm^3$/min) that were determined from pressure grows in experiments with different SDS concentrations and temperatures. It can be seen that with an increase in the SDS concentration and temperature, the rate of dissociation increases substantially.

*3.2. Dependence of the methane content in the hydrate on volume of the liquid phase within the reactor*

In the second series of experiments, hydrate formation was studied by feeding methane to the reactor and maintaining a constant pressure of 50 ± 2 bar for different initial volumes of the liquid phase. The

SDS concentration in the initial solution was the same (0.1%). Results of this series of experiments are shown in table 2.

Results of experiments show that the methane concentration in hydrate decreases with increase in the amount of the solution loaded into the reactor. This is bounded with insufficient cooling efficiency (that was the same in all experiments) with increased loading. Moreover, the increase of the amount of the solution loaded into the reactor leads to the decreasing of surface of reactor walls that is in gas phase. At the same time, our experimental study showed that surface of reactor walls situated in gas phase is more active than the surface located in liquid phase. This statement is confirmed by figure 4 showing that hydrate inside the reactor produced predominantly on the surface of reactor walls. Even at the lowest loading the all surface inside the reactor was covered by methane hydrate crystals. It says that free gas volume inside the reactor plays important role in the process of methane hydrate formation and influences on kinetics and methane concentration in produced hydrate.

**Table 2.** The methane content in the hydrate as a function of the volume of the liquid phase inside the reactor (with internal volume of 500 ml)

| Volume of liquid (SDS aqueous solution) loaded into the reactor, $cm^3$ | Methane volume obtained after dissociation, $cm^3$ | Concentration of methane in obtained hydrate, $cm^3$ of methane per 100 $cm^3$ of solution |
|---|---|---|
| 0.1 | 18,5 | 18,5 |
| 0.2 | 35,1 | 17,6 |
| 0.3 | 45,3 | 15,1 |
| 0.4 | 50,3 | 12,6 |

## 4. Conclusion

The study of dissociation of methane hydrate obtained at various temperatures and SDS concentrations showed that the rate of dissociation increases with temperature and SDS concentration increasing. Methane hydrate obtained in the presence of SDS with concentration of 0.1%, begins to dissociate at temperature of –3 ℃ with a rate of 1.84 $cm^3$/min. The methane hydrate obtained in the presence of SDS with concentration of 1% dissociates with rates of 46.96 $cm^3$/min, 3.04 $cm^3$/min and 0.61 $cm^3$/min at temperatures of 1 ℃, –3 ℃ and –5 ℃ respectively.



**Figure 4.** The image of 500 ml reactor with methane hydrate obtained from 100 $cm^3$ aqueous SDS solution (0.1%).

Methane hydrate obtained in the presence of SDS with concentration of 10% dissociates intensively already at a temperature of −5 ℃ with a rate of 23.82 cm$^3$/min. Based on the results of hydrate dissociation, it can be concluded that the most optimal concentration of sodium dodecyl sulfate in aqueous solution is the concentration of 0.1%, because at this concentration the intensive hydrate formation is achieved while the methane hydrate is stable at a temperature of −5 ℃ and lower. During the study of the effect of the initial volume of liquid loaded into the reactor (volume of gas phase) on the methane content in the produced hydrate, it was found that the maximum specific methane content is achieved with the smallest volume of loaded aqueous solution. It was bounded with the fact that surface of reactor walls situated in gas phase is more active in hydrate formation process than the surface located in liquid phase.

## 5. References

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