

# Experimental Investigation toward the Kinetic Study of Methane Hydrate Formation in the Presence of THF+SDS

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**ABSTRACT:** In this study, the effect of the mixture of two types of promoters including THF and SDS as well as the effect of temperature and pressure was studied on the methane hydrate formation. In order to investigate the effect of promoters, the induction time, as well as the amount of water, converted to the hydrate was reported; moreover, the percent of methane hydrate was calculated as results. According to the results obtained from experimentation, by adding SDS as surfactant the induction time decreases significantly in the presence of 0.243 mL THF. The results showed that for the condition where initial pressure was 40 bar and SDS concentration was chosen to be 1500 ppm the induction time decreases 59.5%. Also, the results declared that with the increase in the initial pressure the values of the induction time decline. For those that the initial pressure was set at 50 bar and the aqueous solution contains 250 ppm SDS the rate of hydrate formation was observed to be higher than those lower SDS concentrations were used. Furthermore for the condition where the initial pressure was set on 40 bars and the concentration of SDS was chosen to be 1500 ppm the rate of hydrate formation was found to be the maximum value. Finally, the results of experimentation and modeling showed that for the condition where initial pressure was chosen 50 bar the apparent rate constant of hydrate formation was maximum, for the solution with 250 ppm SDS. Also, this parameter would be 80% much higher than those of pure water was used at beginning of the hydrate crystals growth.

**KEYWORDS:** Methane hydrate; Sodium dodecyl sulfate; Tetra hydro furan; Kinetics and modeling of hydrate formation.

## INTRODUCTION

As one of the non-stoichiometric compounds that can enclose gaseous materials in their microscopic structure, clathrate is mentioned in which water molecules are situated in the especial state to form a hollow structure by means of the hydrogen bond. These cage-like structures are able to encapsulate various molecules with suitable sizes such as methane [1]. It has been reported in different researches that in spite of the negative effect of clathrate

in petroleum and gas processing, there are large numbers of beneficial applications that have been noticed in early researches including gas storage, water desalination, gas separation process, carbon dioxide capture, and heat transfer processes [1-11].

The storage capacity of gas hydrates are determined by knowing data on the kinetics of hydrate formation in the presence of various types of promoters. There are wide

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ranges of studies that have been focused on the effects of kinetics promoters on gas hydrate formation. *Lirio et al.* studied the effect of SDS and THF as new promoters in order to assess CO<sub>2</sub> hydrate storage capacity. The results of their experimentation exhibited that by adding SDS to the solution, the induction time for hydrate formation declines because of synergy between THF and SDS [12]. *Partoon et al.* researched in order to investigate the effect of the kinetic promoter of SDS on the phase behavior and kinetics of methane hydrate formation. They concluded that SDS in the presence of a certain amount of propanone, (as a thermodynamics promoter) the rate of hydrate formation as well as the storage capacity increases significantly [13]. Also, *Veluswamy et al.* investigated the kinetics hydrates formation of hydrogen/THF for hydrogen storage applications. The results of their experiments showed that induction time was not affected by adding the promoter to the solution [14]. *Lu et al.* showed that 2.9 mol% TBAB or THF made the hydrate formation pressures of systems nearly identical. They also studied the effects of DTAC and TBAB as well as the initial pressures on the hydrate induction time. Therefore, they concluded that CO<sub>2</sub> separation efficiency is maximum when 2.80 mol% DTAC is used [15]. *Li et al.* also did different researches and showed that TBAB, TBAC, and TBAF enhance the hydrate stability and this property increases with the enhancement in the concentrations of TBAB, TBAC, and TBAF. Finally they found that the phase equilibrium pressure of mixture in which TBAF was used as a promoter is lower than that of others at the constant temperature.

*Li et al.* investigated the effect of TBAB and cyclopentane on hydrate formation. they observed that gas uptake at 4 MPa and 274.65 K was due to the replacement of TBAB cation with cyclopentane [16]. In addition *Link et al.* did research and observed the positive impact of SDS as a surfactant on the rate of hydrates formation and gas uptake [17].

*Tang et al.* studied the impact of SDS and THF on the rate of hydrate formation within a hydrate-based gas separation process. Their experimentation exhibited that SDS increases the rate of hydrate formation and reduces induction time while THF enhances the gas separation efficiency [18]. *Daraboina et al.* also observed the high performance of gas separation from flue gas during hydrate formation by using two different promoters including THF and cyclopentane in comparison to the

condition where individual promoter used. Their results posit that hydrate formation from both promoters system has higher dissociation temperatures [19].

*Lee et al.* investigated the phase equilibrium behavior of different mixtures including CH<sub>4</sub>+THF, CO<sub>2</sub>+THF, CH<sub>4</sub>+CO<sub>2</sub>, and CH<sub>4</sub>+CO<sub>2</sub>+THF at different pressures, temperatures, and concentrations. Their findings also exhibited that by adding THF the dissociation boundary happens at lower pressures and higher temperatures. Their results also showed that the mixture of THF, CH<sub>4</sub>+CO<sub>2</sub> forms s(II) hydrate structure [20]. *Kang et al.* reported their results for equilibrium condition for and mixed hydrate formation of CO<sub>2</sub>, N<sub>2</sub> in presence of THF as a promoter. They also reported that by adding a small amount of THF the dissociation condition occurred at higher temperatures and lower pressures [21]. *Zhong et al.* also reported similar findings at the condition where hydrate formed from a mixture of CO<sub>2</sub> and CH<sub>4</sub> [22].

*Roosta et al.* investigated the kinetics of methane hydrate formation in the presence of various promoters including SDS, THF, and TBAB at a condition where pressure and concentration were chosen to be relatively low. They found that by adding the mixture of SDS, THF, and TBAB the methane hydrate formation rate enhanced significantly. *Li et al.* and *Zhong et al.* investigated the thermodynamics effect of THF and SDS for the methane gas purification from coal mine gas as well as coal-bed methane. They found that the combination of SDS and THF increases the methane separation efficiency from mentioned gas fields [23, 24]. Also, *Sun et al.* researched in order to study the separation of methane from coal-bed methane gas by using hydrate of TBAB in presence of SDS. Their results showed that by adding SDS and TBAB the gas separation efficiency enhances while the induction time of hydrate formation declines.

According to the results of previous scholars, it can be concluded that the studies regarding the kinetics of methane hydrate formation in the presence of promoters including THF and SDS for storage and transportation are rare and require thorough investigations. Therefore, in this research, the effect of mentioned promoters as well as temperature and pressure has been studied, and finally, the results of experimentation and optimum condition were reported. In addition, the apparent rate constant of hydrate formation was calculated by using mathematical modeling at different concentrations of SDS in presence of THF.

**Table 1: The chemicals, (with detailed specification), were used for experimentations.**

Name	Source	Chemical formula	Molecular weight (g/mol)	Purity
Methane	Technical Gas Services, United Arab Emirates	CH <sub>4</sub>	16.04	99.9%
Sodium dodecyl sulfate (SDS)	Merck Co. Germany	NaC <sub>12</sub> H <sub>25</sub> SO <sub>4</sub>	288.37	95%
Tetra hydro furan (THF)	Merck Co. Germany	C <sub>4</sub> H <sub>8</sub> O	72.11	99.9%

## EXPERIMENTAL SECTION

### materials

In this research two types of different promoters including Sodium Dodecyl Sulfate (SDS) with a purity of 95%, and Tetra Hydro Furan (THF) with high purity of 99.9% were purchased from Merck Co. Germany. Also, methane with a purity of 99.9% was purchased from Technical Gas Services, United Arab Emirates, (The specifications of all chemicals are presented in Table 1) Moreover, it should be noted that deionized water was used for washing the glassware and preparing solutions in all the experiments.

### Experimental apparatus

The schematic diagram of the apparatus that was used in this research is shown in Fig.1a. As it has been in previous researches, the gas hydrates are formed at a condition where pressure is high and the temperature is kept at low values [23, 24]. Thus, the reactor of hydrate formation must be designed in order to tolerate high-pressure conditions and low temperatures. Fig.1b shows the reactor of methane hydrate formation in which the walls of the reactor are made of stainless steel. In addition, for entering and exiting the gas from the reactor as well as charging

the reactor with solution, two pairs of valves are inserted at top of the reactor and one below with a high-pressure bearing of 6000 psi. Moreover, the main part of the reactor is a jacketed cylindrical cell, (for controlling temperature), which has been made of stainless steel with a maximum working pressure of 2200 Psi. The internal volume of the reactor was chosen to be 390 mL and the temperature of the solution inside the reactor was controlled with a temperature bath connected to the jacket of the reactor. Two thermometers, (Pt 100), were inserted into the reactor for measuring the temperatures in order to estimate temperature difference in and outside of the reactor, (the temperature difference was estimated to be less than 0.1 °C). For controlling the temperature of reactor cooled

water is injected into the reactor's jacket after passing through the thermal bath circulator model RM6, LAUDA Co. (Fig.1c). The pressure inside the reactor was measured with a pressure transducer (type 26-600G, up to 16 MPa). The uncertainty of pressure measurement was estimated to be less than 7.5 psi, calculated by comparing of those measured with deadweight balance (Desgranges and Huot, model 520). Moreover, in order to record the temperature and pressure, in-house software was used with interval times of 20 s. It has been mentioned in previous efforts that with the increase of turbulences more gas molecules are dissolved inside the aqueous solution leading to an enhanced mass transfer rate [25]. Thus in this research, a stirrer was used to increase mass transfer rate and accelerate hydrate crystals formation inside the reactor.

### Experimental method

In order to carry out experimentation the reactor is evacuated to 0.15 psi for 2 hr, during this time the system was flushed with the hydrate forming gas. Afterward, 100 mL of the desired aqueous solution, with a certain amount of THF and SDS, was injected into the reactor. The temperature of the reactor was set at 2 °C. For the next part of the experiment, the pressure of the reactor increased by introducing methane gas that was supplied from gas storage (Fig.1a). The gas was injected into the reactor until the pressure reaches the desirable values, (50 and 40 bar). After injection of methane gas, the solution was stirred with the speed of 800 rpm. Finally, in order to determine the time needed for hydrate formation and its rate, the pressure, and temperature of the reactor were recorded at different time intervals. The temperature was monitored by using an electrical sensor at different times and the pressures were measured by using a pneumatic digital pressure indicator. The amount of methane consumption during the hydrate formation process was estimated by using the precise equation of state which is explained in the modeling section.

In this research the moles of methane consumption, (in form of hydrate) was calculated by means of following equation:

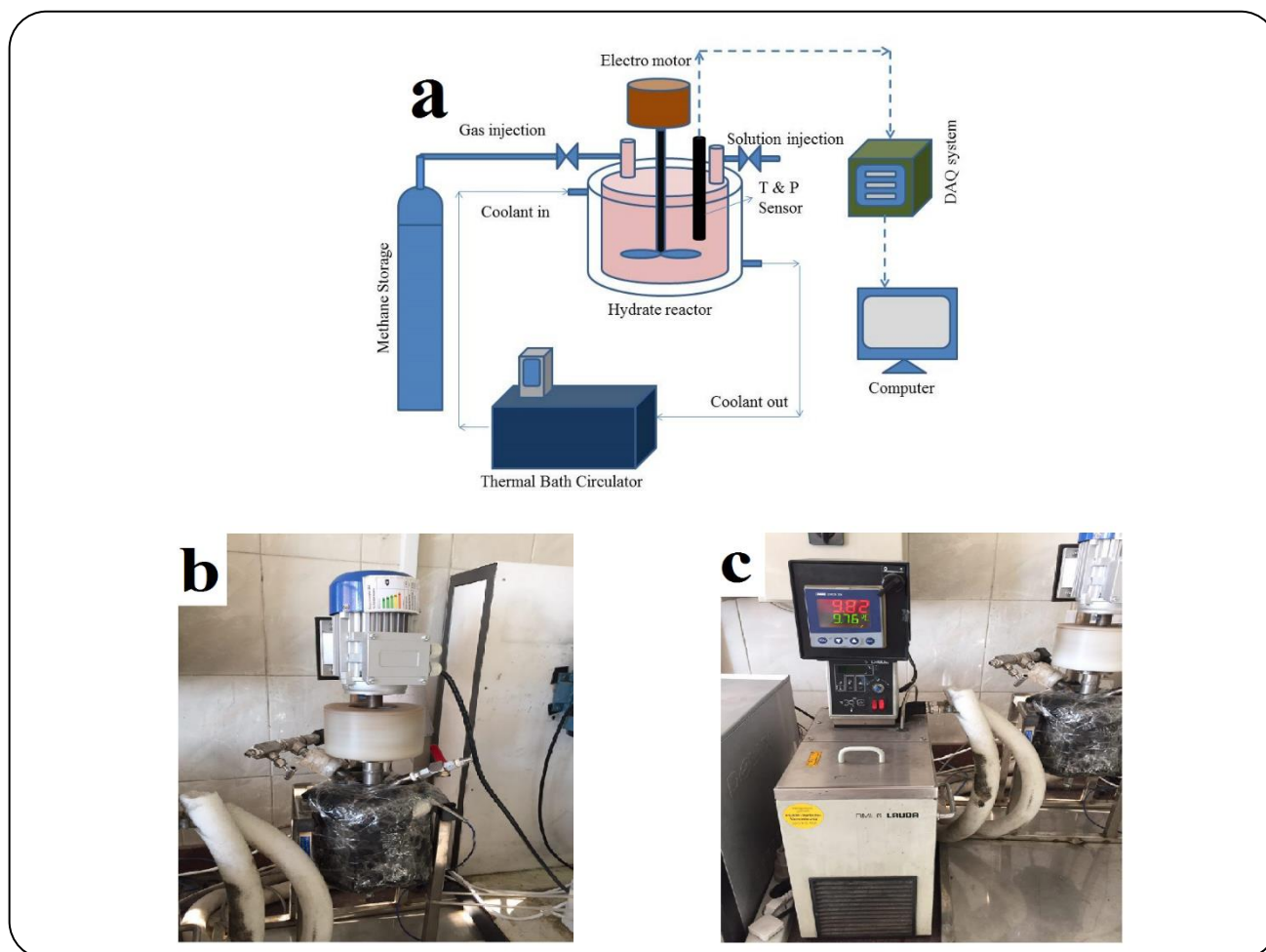


Fig. 1: a) schematic of apparatus used in this research, b) the reactor was used for hydrate formation, c) thermal circulator bath used for controlling temperature.

$$\Delta n_{CH_4} = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t} \quad (1)$$

Where  $\Delta n_{CH_4}$  is moles of methane consumed during hydrate formation,  $P$  is the pressure of reactor,  $T$  is the temperature of the reactor,  $V$  is volume of gas (equal to 290 mL), also the subscript 0 and t refer to the initial condition and any time during hydrate formation respectively. Moreover, in this equation  $Z$  is the compressibility factor that was calculated by means of the cubic Peng-Robinson equation of state. The value of  $Z$  at any time was calculated by solving Eq. (2) by Computer Program provided in MATLAB R2009a:

$$Z^3 - (B - 1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2)$$

$$(AB - B^2 - B^3) = 0$$

Where  $A$  and  $B$  are calculated as follow:

$$A = \frac{(a\alpha)P}{(RT)^2} \quad (3)$$

$$B = \frac{bP}{RT} \quad (4)$$

Also the value of  $a$ ,  $b$  and  $\alpha$  are calculated by using Eq. (5) to (10) which are presented in Table 2 as a function of methane critical temperature ( $T_c$ ) and pressure ( $P_c$ ) as well acentric factor ( $\omega$ ). It should be noted that three different values might be obtained for compressibility factors that the greatest one can be used in Eq. (1) due to the fact that this equation is used for the gas phase.

### Modeling

This research also for estimating methane hydrate growth rate in the presence of a mixture of both THF

**Table 2: Equations for calculating compressibility factor based on Peng-Robinson EoS.**

Equation	Number
$a = 0.45724 \frac{R^2 T_c^2}{P_c^2}$	(5)
$b = 0.07780 \frac{R T_c}{P_c}$	(6)
$\alpha = (1 + m(1 - Tr^{0.5}))^2$	(7)
$m = 0.3746 + 1.5423\omega - 0.2699\omega^2$	(8)
$T_c = 190.56 \text{ K}$ , for methane gas	(9)
$P_c = 45.99 \text{ bar}$ , for methane gas	(10)
$\omega = 0.45724$ , for methane gas	(11)

and SDS as kinetics promoter, the proposed model of Engelzos and Bishnoi was employed, which is as follows:

$$R_i(t) = -\frac{dn_H}{dt} = K_{app} (f^g - f^{eq})_i \quad (12)$$

Where,  $R_i(t)$  is the hydrate growth rate at any time;  $n_H$  is the moles of methane consumed at a certain time;  $K_{app}$  is the apparent rate constant of hydrate formation;  $f^g$  is the fugacity of methane in the gas phase which have been calculated by Peng-Robinson equation of state, (Eq.(13)), finally  $f^{eq}$  (the fugacity of methane at the equilibrium conditions) was calculated from the equilibrium condition by using Eq.(13) [26].

$$\ln\left(\frac{f^g}{P}\right) = Z - 1 - \ln(Z - B) - \quad (13)$$

$$\frac{A}{2\sqrt{2}B} \ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right)$$

In Eq. (13) the values of  $A$  and  $B$  were calculated from Eqs. (3) and (4) and the value of compressibility factor was calculated from Eq. (2).

The rate of hydrate formation at any time can be calculated by the following equation:

$$R_i(t) = \frac{n_{CH_4,i-1} - n_{CH_4,i+1}}{t_{i+1} - t_{i-1}} \quad (14)$$

Where,  $n_{CH_4,i-1}$  and  $n_{CH_4,i+1}$  are the moles of methane in the gas phase at times of  $t_{i-1}$  and  $t_{i+1}$ , respectively. Also, the apparent rate constant of methane hydrate formation is defined as:

$$\frac{1}{K_{app}} = \frac{1}{k_g} + \frac{1}{k_d} \quad (15)$$

Where  $k_g$  are The growth constant of hydrate crystals, and  $k_d$  are mass transfer coefficient in liquid phases. According to the results of *Pahlavanzadeh et al.* [27] the following assumption is taken into consideration for calculating the mass transfer coefficient. Due to the agitation which have been applied during hydrate the mass transfer resistance in the liquid phase can be neglected, and, therefore the apparent rate constant of hydrate formation can be calculated as follow:

$$K_{app} = k_g \quad (16)$$

Accordingly, the apparent rate constant of hydrate formation in this model can be considered a suitable parameter for comparing the growth rates of hydrate crystals at the condition where different SDS concentrations were chosen.

Finally, in order to calculate the amount of water hydrate conversion the following equation was used:

$$\text{Water Hydrate Conversion} = \frac{M \cdot \Delta n_{CH_4}}{n_{w_0}} \quad (17)$$

In this equation,  $M$  is hydrate number which is equal to 5.75 for I morphology of methane hydrate and  $\Delta n_{CH_4}$  is the number of methane moles that has been converted to hydrate, (which can be calculated by using the pressure drop and EoS), and  $n_{w_0}$  is the initial amount of water moles.

## RESULTS AND DISCUSSION

In this research, the kinetics of methane hydrate formation was studied by means of pressure and temperature diagram vs. time of hydrate formation. For comparing different condition where the various concentration of SDS was used, the induction time for hydrate crystals was studied, (the induction time refer to the condition where first crystals of hydrate are formed, at this condition the methane molecules are encapsulated in cage like structure of water molecules). Fig. 2 represents the pressure of reactor vs. time condition where various concentrations of SDS are used with initial pressure of 40 bar. In this figure the concentration of THF was set at 0.243 Vol%. The results of this figure shows that total pressure of reactor decreases significantly after passing through the certain time, after 2 hr the pressure of reactor

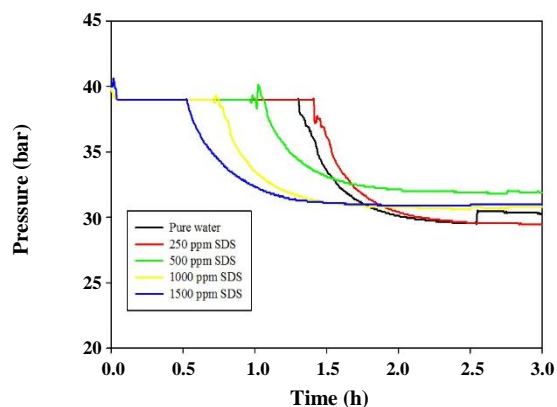


Fig. 2: Pressure vs. time for different concentrations of SDS in presence of 0.243 mL THF with an initial pressure of 40 bar.

decreases insignificantly declaring a lower rate of hydrate formation. Moreover, as it is clear from this figure, the pressure of the reactor decrease by introducing methane gas to the reactor that is due to the dissolving of gas molecules in the aqueous solution. In addition, the results posit that with the increase of SDS concentration the hydrate crystals formation occurred faster.

Fig. 3 shows the temperature of the reactor at different times where various concentrations of SDS were used. In this figure, the initial pressure of the reactor was set at 40 bar. The concentration of THF was also set at 0.243 Vol%. As it is obvious from this figure, the temperature of the reactor drops from 8 °C to 2.3 °C due to the high temperature of methane gas which has been introduced from gas storage, with higher temperature. According to these results, the temperature of the reactor increases significantly at the condition where the pressure of the reactor decreases significantly. It has been mentioned in previous efforts that the hydrate formation of gases is exothermic which means heat is produced during hydrate crystals formation [23, 27]. The results of this figure also declare that with the increase of SDS concentration the increase in temperature was faster showing hydrate crystals formation. Also for those where the SDS concentration was set at 250 ppm the change in temperature was found to be higher than 60 min.

Table 3 shows the initial temperature and pressure as well as induction time for those where the different concentration of SDS was used. The results of this table were obtained at the condition where 0.243 mL THF was added to the aqueous solution. According to this table, with the increase of SDS concentration the induction time

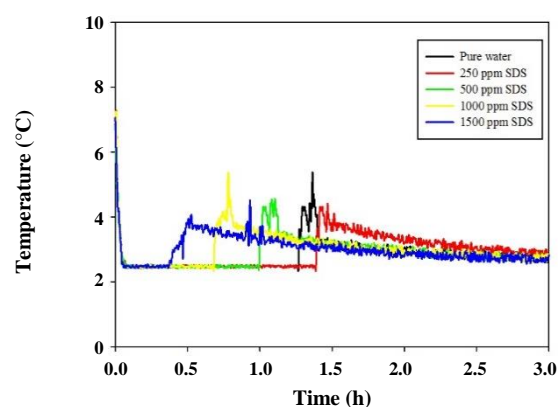


Fig. 3: Temperature vs. time for different concentrations of SDS in presence of 0.243 mL THF with an initial pressure of 40 bar.

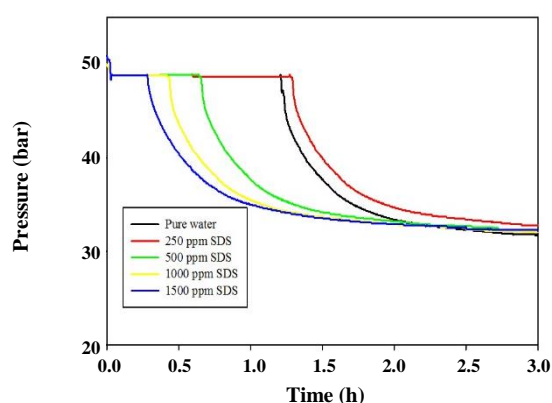
decreases declaring positive effect of SDS in hydrate crystals formation. These results exhibit that with the increase in SDS concentration from 250 ppm to 1000 ppm the induction time decrease about 62%. Moreover, it is evident that for the experiment where SDS concentration was chosen to be 250 ppm the induction time increase slightly showing the negative effect of low SDS concentration in an aqueous solution.

Fig 4 also shows the pressure of reactor vs. time at a condition where various concentrations of SDS are used with an initial pressure of 50 bar. For this condition, the concentration of THF was set at 0.243 Vol%. The findings presented in this figure exhibits that total pressure of reactor decreases significantly after passing through the certain time, ranging from 20 min to 90 min based on various SDS concentrations. In addition, it is obvious from this figure that the pressure of the reactor decreases below 50 bar due to the dissolving of methane gas molecules in the mixture of SDS+THF+water. According to the results presented in this figure, the pressure of the reactor decreases insignificantly after passing through 120 min showing a lower rate of hydrate formation [27]. Moreover, with the increase of SDS concentration the hydrate crystals formed at the lower time declaring high effect of SDS concentration on the rate of methane hydrate formation; although, the time needed for hydrate formation in pure water is lower than solution containing 250 ppm SDS.

The results presented in Fig. 5 show the temperature of the reactor at various times where SDS was used with concentrations of 250, 500, 1000, and 1500 ppm. In this figure also the initial pressure of the reactor was set at 50 bar

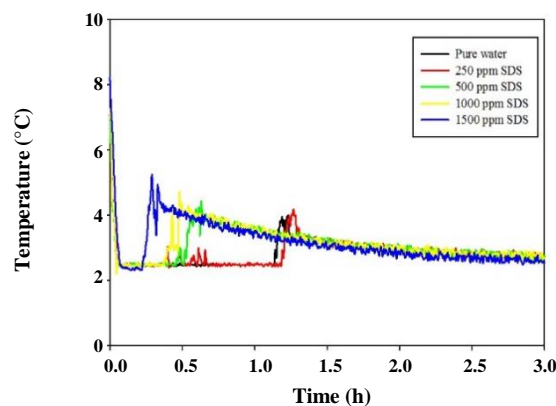
**Table 3: Induction time for methane hydrate formation at different concentration of SDS in presence of 0.243 mL THF with initial pressure of 40 bar.**

SDS concentration (ppm)	Initial pressure (bar)	Temperature (K)	Induction time (min)
0	40.0	275.6	79
250	39.8	275.6	84
500	40.0	275.6	64
1000	40.6	275.7	45
1500	40.0	275.5	32

**Fig. 4: Pressure vs. time for different concentration of SDS in presence of 0.243 mL THF with an initial pressure of 50 bar.**

and 0.243 mL THF was added to the solutions. The results exhibited in this figure show that the temperature of the reactor drops from 8 °C to 2.3 °C similar to those presented in Fig. 3. The reason for the temperature drop is due to high the temperature of methane gas which is introducing to the reactor. Moreover, it is also clear that the temperature of the reactor increases significantly at the condition where the pressure of the reactor decreases significantly. The results of this figure also exhibit that with the increase of SDS concentration in the aqueous solution the sudden increase in temperature was faster. Consequently, for the solution containing 250 ppm SDS the change in temperature was found about 75 min.

The results presented in Table 4 also show the initial temperature and pressure as well as induction time for those where the different concentration of SDS was used and the initial pressure was set at 50 bar. The results of this table were obtained at the condition where THF concentration was set at 0.243 Vol%. According to these results, with the increase of SDS concentration, the induction time decreases declaring positive effect of SDS in hydrate

**Fig. 5: Temperature vs. time for different concentrations of SDS in presence of 0.243 ml THF with an initial pressure of 50 bar.**

crystals formation, (similar to those where obtained at an initial pressure of 40 bar). These results exhibit that with the increase in SDS concentration from 250 ppm to 1000 ppm the induction time decrease about 78%. According to the data presented in Tables 2 and 3, it can be concluded that for those experiments where the initial pressure was set at 50 bar the induction time decrease significantly at the same SDS concentration. With the increase in initial pressure from 40 to 50 bar, the induction time decreases 47% for 1500 ppm SDS.

### Methane hydrate formation

Fig.6 shows the results of methane hydrate formation vs. time at a condition where the various concentration of SDS in presence of THF was used and the initial pressure of the reactor was set at 40 bar. As it is evident from this figure at the first times of hydrate formation methane gas consumption is low and after a period of time, the methane consumption increases significantly. The results of this figure also represent that with the increase of time the amounts of methane consumption change insignificantly

**Table 4: Induction time for methane hydrate formation at different concentration of SDS in presence of 0.243 mL THF with initial pressure of 50 bar.**

SDS concentration (ppm)	Initial pressure (bar)	Temperature (K)	Induction time (min)
0	49.8	275.7	72
250	50.0	275.7	77
500	50.0	275.6	39
1000	50.0	275.7	25
1500	50.9	275.5	17

**Table 5: Percent of hydrate formation and moles of consumed methane at different concentration of SDS in presence of 0.243 ml THF with an initial pressure of 40 bar.**

SDS concentrations (ppm)	Initial pressure (bar)	Temperature (K)	Moles of methane consumed at first 30 min	Final percent of water converted to hydrate (%)
0	40.0	275.5	0.00902	0.97
250	39.7	275.6	0.00854	0.90
500	39.8	275.6	0.00756	0.78
1000	40.0	275.6	0.00869	0.86
1500	40.6	275.7	0.00864	0.91

after about 60 min declaring no hydrate formation and a lower rate of methane consumption. Moreover, it is clear from this figure that at the condition where pure water was used for hydrate formation the consumption of methane is higher than that SDS+THF was used as promoters. Consequently, this results in exhibits that at the condition where 500 ppm SDS was used, the amounts of methane consumption was minimum declaring a lower amount of formed hydrate. It is concluded from this figure that SDS in presence of THF has a negative effect on methane storage as hydrate at the condition where the initial pressure was set at 40 bar.

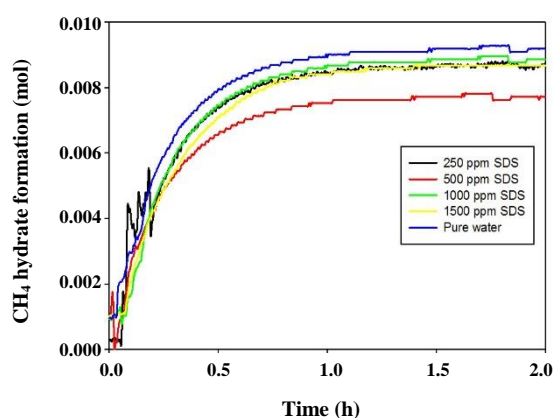
Table 5 shows the final percent of water converted to hydrate and methane consumption for the first 60 min of hydrate formation at the condition where different SDS concentrations were used and the initial pressure was set at 40 bar. As it is evident from the results presented in this table that for those contains 250 ppm SDS the final percent of water converted to hydrate would be 0.90%. In addition, for those solutions contain 500 ppm SDS the final percent of water converted to hydrate is minimum, (equal to 0.78%). Also for the condition where the initial pressure was set at 40 bar and the pure water was used, the moles of methane consumed at the first 60 min is maximum and equals 0.00902 moles.

Fig. 7 also exhibits the results of methane hydrate formation vs. time at a condition where the various concentration of SDS was used and the initial pressure of the reactor was set at 50 bar. It is obvious from data presented in this figure that methane gas consumption is low at the first times of hydrate formation and after a certain period of time the methane consumption increases significantly similar to the results of Fig. 6. The results of this figure also show that with the increase of time the amounts of methane consumption change insignificantly after about 60 min declaring a lower rate of methane consumption. In addition, it is clear from this figure that at the condition where the aqueous solution containing 250 ppm SDS and 0.243 mL THF the consumption of methane is higher than other solutions. On the other hand, for those where SDS concentration was 1500 ppm the methane consumption was minimum value. Consequently, these results posit that at the condition where 250 ppm SDS was used, the amounts of methane consumption were maximumly declaring a higher amount of hydrate formation and by adding more SDS to the solution the value of methane consumption declines significantly. It is concluded from this figure that the solution containing 250 ppm SDS in presence of THF has a positive effect on methane storage as hydrate at the condition where the initial pressure was set at 50 bar.



**Table 6: Percent of hydrate formation and moles of consumed methane at different concentration of SDS in presence of 0.243 mL THF with initial pressure of 50 bar.**

SDS concentrations (ppm)	Initial pressure (bar)	Temperature (K)	Moles of methane consumed at first 30 min	Final percent of water converted to hydrate (%)
0	49.8	275.7	0.00725	0.81
250	50.0	275.7	0.01077	1.21
500	50.0	275.6	0.00680	0.78
1000	50.0	275.7	0.00707	0.82
1500	50.9	275.5	0.00669	0.76

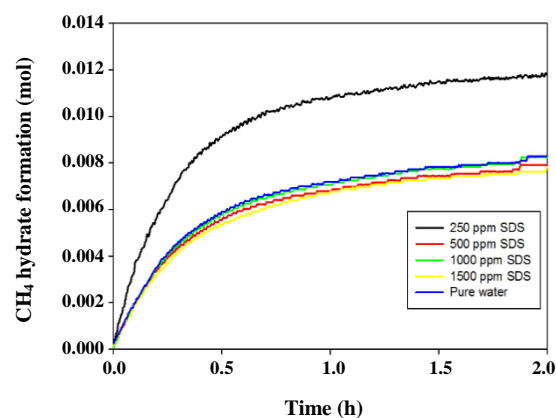


**Fig. 6: Methane hydrate formation vs. time for different concentrations of SDS in presence of 0.243 mL THF with an initial pressure of 40 bar.**

Table 6 also presents the final percent of water converted to hydrate and methane consumption for the first 60 min of hydrate formation at the condition where various SDS concentrations were used and the initial pressure was set at 50 bar. As it is evident from the results presented in this table that for those contains 250, 500, and 1000 ppm SDS the final percent of water converted to hydrate would be 1.21%, 0.78%, and 0.82%, respectively. In addition, for those solutions contain 1500 ppm SDS the final percent of water converted to hydrate is 0.76%. Also for the condition where the initial pressure was set at 50 bar and the solution with 250 ppm SDS was used, the moles of methane consumed at the first 60 min is maximum and equals 0.01077 moles.

#### Apparent rate constant

The apparent rate constant of hydrate formation vs. time is plotted in Fig.8 at the condition where initial pressure of the reactor was set at 40 bar. The values of the apparent rate constant are calculated by using Eq. (12). According



**Fig. 7: Methane hydrate formation vs. time for different concentrations of SDS in presence of 0.243 mL THF with an initial pressure of 50 bar.**

to the results presented in this figure, the values of the apparent rate constant of hydrate formation is high at the beginning of the hydrate crystals formation and after a period of time it reaches the constant value. In addition, for those solutions where 500, 1000 ppm, and pure water was used the constant rate of hydrate formation at the beginning of methane, consumption is similar. On the other hand, the constant rate of methane formation for the solution contains 1500 ppm SDS is much higher than other after 60 min of hydrate formation.

Also, the apparent rate constant of hydrate formation vs. time is plotted in Fig.9 at the condition where the initial pressure of the reactor was set at 50 bar. According to these results, the values of the apparent rate constant of hydrate formation are high at the beginning of the hydrate crystals formation and after a period of time, it reaches a constant value similar to those presented in Fig.8. Moreover, for the solution contains 250 ppm SDS the constant rate of hydrate formation at the beginning of methane consumption is much higher declaring a positive effect

of SDS in the presence of THF. On the other hand, the constant rate of methane formation, (for the solution contains 1500 ppm SDS), is lower than others after 60 min of hydrate formation.

In this research, the highest maximum apparent rate constants are obtained for systems containing water, 0.243 mL THF, and various concentrations of SDS. The maximum apparent rate constant declines with the increment of SDS concentration. With the increase of SDS concentration at initial pressures of 40 and 50 bar, the formation of more stable hydrate nuclei has resulted at the end of the nucleation stage. Hence, at the beginning of the hydrate growth stage, a larger amount of hydrate is formed with higher growth rates. Since the presence of SDS and THF increases the kinetics of hydrate formation it can be concluded that more nucleation sites are the main reason for more methane consumption. According to the results presented in Figs. 8 and 9 the maximum values of the apparent rate constant are shown at the beginning of the hydrate growth stage. For the purpose of comparing the effect of SDS concentration understudy on the growth rate of methane hydrate formation, an average value of apparent rate constant within the first 5 min of the hydrate growth stage is estimated, (the maximum apparent rate constant). The maximum of apparent rate constants are presented in Fig. 12 for the hydrate formation process in the presence of SDS and THF at the condition where initial pressure was chosen 40 and 50 bar. As it can be seen in Fig. 10, the highest average apparent rate constant was obtained for the system of 250 ppm SDS in the presence of THF at the condition where the initial pressure of the reactor was chosen to be 40 bar and the lowest value of the average apparent rate, the constant was observed for the system 1000 ppm SDS with the initial pressure of 50 bar. The main reason for this trend is that in the presence of SDS in the hydrate the growth stage is attributed to the reduction in the interfacial tension between hydrate and liquid and, consequently, enhancement in the mass transfer. Therefore, the combination of both mass transfer enhancement, in the presence of SDS, and larger numbers of nuclei at the beginning of the hydrate growth in the presence of THF increases the overall growth rate of methane hydrate formation, as it has been in previous researches adding THF to the hydrate formation increases the numbers of nuclei for hydrate crystal growth [18, 20].

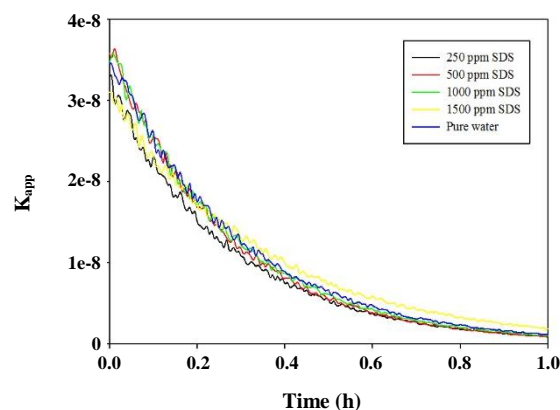


Fig. 8: Apparent rate constant vs. time for different concentration of SDS in presence of 0.243 mL THF with initial pressure of 40 bar.

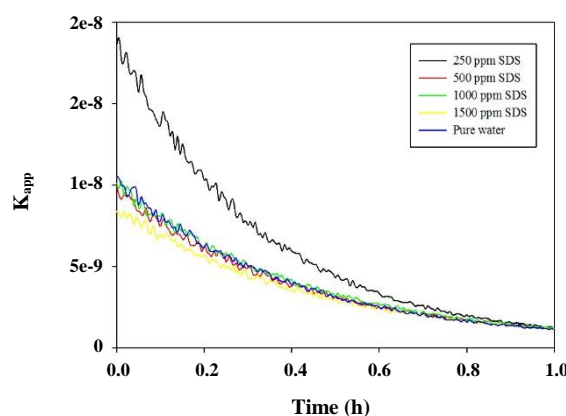


Fig. 9: Apparent rate constant vs. time for different concentrations of SDS in presence of 0.243 mL THF with an initial pressure of 50 bar.

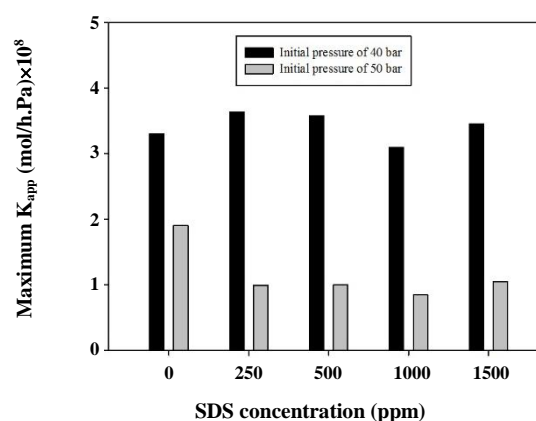


Fig. 10: Maximum apparent constant rate vs. different concentrations of SDS in presence of 0.243 mL THF with an initial pressure of 40 and 50 bar.

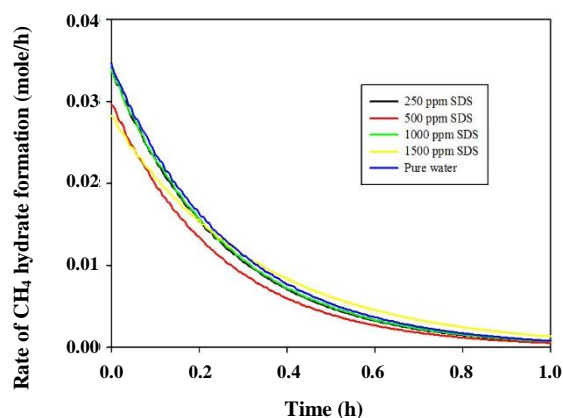


Fig. 11: Methane hydrate formation rate vs. time for different concentrations of SDS in presence of 0.243 ml THF with an initial pressure of 40 bar.

#### Rate of methane consumption

Fig.11 represents the plot of methane consumption rate vs. time for hydrate formation at the condition where the initial pressure was set at 40 bar. As it can be concluded from this figure, the rate of methane consumption at the beginning of hydrate formation is high and decreases with the increases of time. The main reason for decreasing the rate of methane consumption is attributed to the driving force, (the fugacity difference of methane gas at gas-liquid interface and bulk), for gas molecules diffusion through the crystal structures of the hydrate. In addition, it is evident that with the increase of time near to 60 min the rate of methane consumption approaches to 0 and for the condition where solution contains 1500 ppm SDS the methane hydrate formation reach to the equilibrium condition later. On the other hands, when the solution contains 500 ppm SDS the rate of methane, consumption is higher and the system reaches equilibrium condition faster.

Also, Fig.12 shows the plot of methane consumption rate vs. time for hydrate formation at the condition where the initial pressure was set at 50 bar and various SDS concentrations were used. As it can be seen from this figure, the rate of methane consumption at the beginning of hydrate formation is high and decreases with the increases of time similar to the results presented in Fig.11. Also, these results show that with the increase of time near to 60 min the rate of methane consumption approaches to 0 and for the condition where solution contains 250 ppm SDS the methane consumption rate is higher than other solution and it declines with the increase of time.

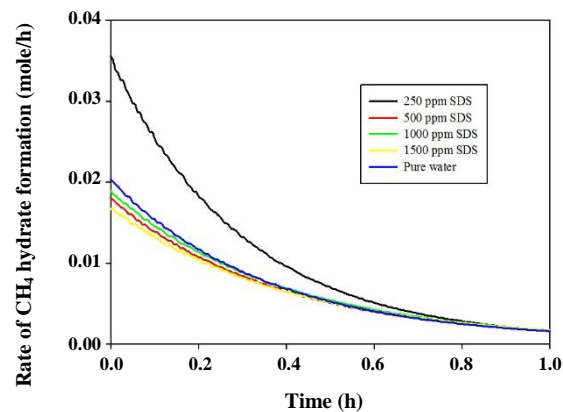


Fig. 12: Methane hydrate formation rate vs. time for different concentrations of SDS in presence of 0.243 ml THF with an initial pressure of 50 bar.

On the other hand, when the solution contains 1500 ppm SDS the rate of methane consumption at the beginning of hydrate formation is low and for the condition where pure water has used the rate of methane consumption is much higher than that contains 500, 1000, and 1500 ppm.

#### CONCLUSIONS

In this research, the effect of two types of promoters including THF+SDS and the effect of temperature and pressure was studied on the methane hydrate formation rate. For investigating the effect of the mixture of promoters, the induction time, as well as the amount of water converted to the hydrate, was reported. According to the findings obtained from experimentation, by adding SDS as surfactant the induction time decreases significantly in the presence of 0.243mL THF.

According to the results presented in this study it can be concluded that for the condition where initial pressure was 40 bars and SDS concentration was chosen to be 1500 ppm the induction time decreases 59.5%. Also, the results showed that with the increase in the initial pressure, the values of the induction time decline declaring a positive effect of initial pressure. For those that the initial pressure was set on 50 bar and the solution contains 250 ppm SDS the rate of hydrate formation was observed to be higher than those of lower SDS concentrations were used.

Furthermore, for the condition where the initial pressure was set on 40 bar and the concentration of SDS were chosen to be 1500 ppm the rate of hydrate formation was found to be the maximum value.

Finally, the results of experimentation and kinetics modeling showed that for the condition where initial pressure was chosen 50 bar the apparent constant rate of hydrate formation was maximum for a solution with 250 ppm SDS, in presence of 0.243 Vol% THF. Also, the value of the apparent constant rate of hydrate formation would be 80% much higher than those of pure water was used, at beginning of the hydrate crystals' growth.

#### Nomenclature

P	Pressure, Pa
V	Gas volume, m <sup>3</sup>
R	Universal gas constant, 8.314 J/mol.K
T	Temperature, K
Z	Compressibility factor
n	Moles of gases, mole
P <sub>c</sub>	Critical pressure, Pa
T <sub>c</sub>	Critical temperature, K
ω	Eccentric factor
f <sup>g</sup>	Gas fugacity, Pa
f <sup>eq</sup>	Fugacity of gas at interface or equilibrium, Pa
K <sub>app</sub>	Apparent rate constant, mole/h.Pa
R <sub>i</sub> (t)	Hydrate rate growth, mole/h
k <sub>g</sub>	Mass transfer coefficient at gas phase, mole/h.Pa
k <sub>d</sub>	Mass transfer coefficient at liquid phase, mole/h.Pa

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