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Experimental study of CO_2 hydrate formation kinetics with and without kinetic and thermodynamic promoters

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Abstract. In this work, an experimental study of CO_2 hydrate formation kinetics was undertaken. The effects of stirring rate and initial pressure on the hydrate formation rate were investigated. The results showed that a stirring rate of 600 rpm was optimum for increasing the CO_2 hydrate formation rate, especially at lower temperatures. The effects of additives on the hydrate formation rate were also investigated. Three surfactants: Sodium Dodecyl Sulfate (SDS), Dodecyl Trimethyl Ammonium Bromide (DTAB) and Triton X-100 (TX-100), were tested. DTAB and TX-100 were new surfactants for investigation into CO_2 hydrate formation kinetics. SDS and DTAB did not significantly affect the hydrate formation rate at concentrations of 300 and 500 ppm, whereas SDS increased, and DTAB insignificantly decreased the hydrate formation rate at 1000 ppm. Furthermore, TX-100 negligibly decreased the hydrate formation rate at 300 and 500 ppm, but significantly decreased the rate at 1000 ppm. In contrast, the application of thermodynamic additives, tetrahydrofuran (THF) and tetra-*n*-butyl ammonium bromide (TBAB), at low concentrations, increased the hydrate formation rate, and these additives affected the rate of hydrate formation in a manner similar to kinetic promoters.

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1. Introduction

Gas hydrates, or clathrate hydrates, are crystalline solid compounds, whose properties and stability depend on the conditions of pressure and temperature. These hydrates are composed of host water and certain guest gas molecules under appropriate pressure and temperature conditions. The gas molecules are trapped inside the cavity of cages composed of the hydrogen-bonded water molecules. Based on the molecular size of the encaged (guest) molecules, these clathrate hydrates are classified into three main structures: I, II and H. Gas hydrates can be utilized to achieve various industrial goals, such as gas storage, cool storage, gas transportation, or the separation of gas mixtures [1,2]. Some critical problems, such as slow hydrate formation rates, unreacted interstitial water and high pressure operating conditions, hinder these industrial goals [3]. Consequently, methods that increase the formation rate of the hydrates and methods that allow depressurization of the gas hydrates have both been considered.

Among the gases capable of forming hydrates, CO_2 is important and plays a crucial role. The separation of CO_2 from the combustion of fossil fuels is important because carbon dioxide contributes significantly to global warming. Therefore, the formation of CO_2 hydrate has been investigated as a method for the separation of CO_2 from the atmosphere [4].

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In addition, the formation of CO_2 hydrate has been applied to water desalinization. CO_2 hydrate slurry can also be used as a Phase Change Material (PCM) in secondary refrigeration and cool storage because of its high dissociation enthalpy [5].

The high rate and low pressure of CO_2 hydrate formation are important for industrial purposes. The most straightforward method of increasing the hydrate formation rate is to mix the gas and liquid-water phases using mechanical methods, including the bubbling of gas through water, stirring and spraying water in a continuous gas phase [6]. These methods, however, consume a significant amount of power. One way to overcome this problem is to promote the hydrate formation rate by the addition of kinetic promoters (mainly surfactants) to the liquid-water phase. The effects of surfactants have been extensively investigated, with respect to methane and other light hydrocarbon hydrates [7-13], whereas few investigations into the effects of surfactants on the kinetics of CO_2 hydrate formation have been reported. Furthermore, thermodynamic additives, such as tetrahydrofuran (THF) and tetra-*n*-butyl ammonium bromide (TBAB), have been used to decrease the equilibrium pressure of hydrate formation [14]. However, few investigations into the effects of these additives (thermodynamic additives) on the kinetics of CO_2 hydrate formation have been published, and no investigations into the effects of THF and TBAB at low concentrations have been reported. THF can form hydrate with water molecules under atmospheric conditions (THF hydrates). In addition, it can form gas hydrate with gas molecules, such as methane, ethane and CO_2. THF molecules cannot occupy any of the sI cavities, but can occupy large cavities sII hydrate. So, THF decreases the gas hydrate formation pressure in a gas-THF-water system. It also reduces the induction time, because the nucleation process is increased in the presence of THF. TBAB forms two types of semiclathrate hydrate with water molecules under atmospheric conditions and at near room temperature (crystal types A and B). It also influences the thermodynamics of gas hydrates. In fact, THF and TBAB are the additive thermodynamics for hydrate formation with gas molecules [15-17].

Zhang et al. (2010) [18] investigated the use of SDS to promote the formation of CO_2 hydrate, and they found that SDS was not effective. Sabil et al. (2010) [19] reported kinetic data for the formation of single and mixed carbon dioxide-tetrahydrofuran hydrates. Linga et al. (2007) [20] investigated gas hydrate formation for hydrogen/carbon dioxide and nitrogen/carbon dioxide with THF and reported that THF, at a concentration of 1 mol%, reduces the induction time and the rate of hydrate growth. Li et al. (2009) [21] investigated the capture of CO_2 from a binary mixture of (CO_2+N_2) via formation of hydrate in a 5 wt% TBAB solution. They found that TBAB increased the hydrate formation rate and enriched the level of CO_2 in the hydrate phase.

Unfortunately, only a limited number of investigations into the effects of additives on the kinetic behavior of CO_2 hydrate are available in the literature. Therefore, the aim of this study is to investigate the effects of thermodynamic additives (THF and TBAB) at low concentrations and surfactants (SDS, DTAB and TX-100) at different concentrations, on the kinetic behavior of CO_2 hydrate. In addition, the effects of two other parameters have been determined: the stirring rate and the initial pressure (driving force). The highest rate of CO_2 hydrate formation in a stirred tank reactor and the effects of different parameters on the CO_2 hydrate formation rate were also determined.

2. Experimental

2.1. Materials

Carbon dioxide with purity of 99.99% was supplied by Technical Gas Services. It was used to form hydrate with de-ionized water. The surfactants utilized in the experiments were Sodium Dodecyl Sulfate (SDS) as an anionic surfactant with the chemical formula $C_{12}H_{25}NaO_4S$ (Merck, Germany), dodecyl trimethyl ammonium bromide (DTAB) as a cationic surfactant with the chemical formula $C_{15}H_{34}BrN$ (Merck, Germany) and Triton X-100 (TX-100) as a non-ionic surfactant with the chemical formula $C_{14}H_{21}(C_2H_4O)_nOH$ (Merck, Germany). In addition, two thermodynamic additives were used in the experiments: tetrahydrofuran (THF) with the chemical formula C_4H_8O (Merck, Germany), and tetra-*n*-butyl ammonium bromide (TBAB) with chemical formula $C_{16}H_{36}BrN$ (Merck, Germany). The additives were weighed with a balance that was accurate to 0.1 mg for the preparation of aqueous solutions at the required concentrations (information about the test materials is presented in Table 1).

2.2. Apparatus

The schematic diagram of the set-up used for the experiments is shown in Figure 1. The apparatus consisted of a cylindrical high-pressure stainless steel cell with a capacity of 600 cm^3. The cell was equipped with a four-blade mixer and could operate at pressures up to 10 MPa and in the temperature range of 253.15-373.15 K. Water/ethylene glycol coolant was circulated through the interlayer of the cell, and the temperature of the cell was adjusted with a controllable circulator. The cell was enclosed with insulation. The cooling system was also equipped with a controllable circulator and coolant bath. The temperature was measured using a PT100 thermometer (Pro-Temp Controls, Santa Ana, California, United States) with an uncertainty of

Table 1. Test materials used for experiments.

Component	Chemical formula	Purity	Supplier
Carbon dioxide	CO_2	99.99%	Technical gas services
SDS	$C_{12}H_{25}NaO_4S$	$\geq$ 98 %	Merck, Germany
DTAB	$C_{15}H_{34}BrN$	$\geq$ 97 %	Merck, Germany
TX-100	$C_{14}H_{21}(C_2H_4O)nOH$	$\geq$ 98 %	Merck, Germany
THF	C_4H_8O	$\geq$ 99.9 %	Merck, Germany
TBAB	$C_{16}H_{36}BrN$	$\geq$ 99 %	Merck, Germany
Water	H_2O		Deionized-distilled

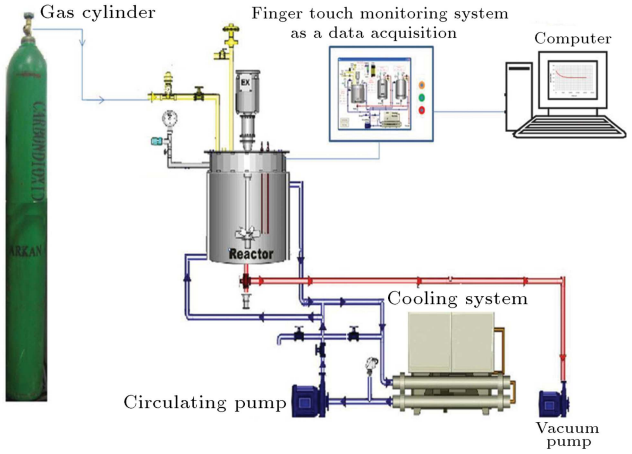

Figure 1. Experimental setup and hydrate formation apparatus.

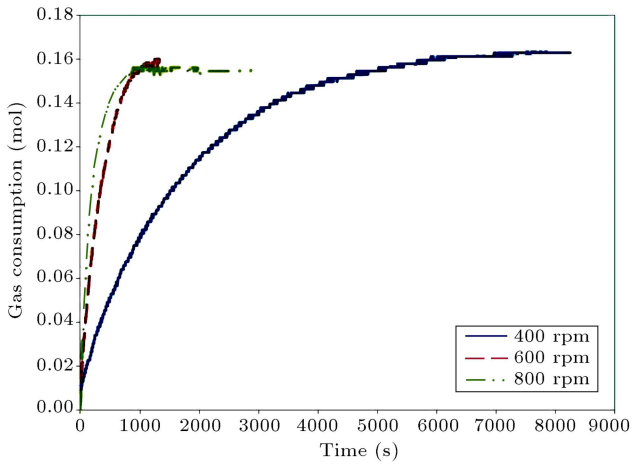

Figure 2. The effect of stirrer speed on CO_2 hydrate formation rate at temperature 274.2 K.

±0.1 K. The cell pressure was measured using a BD-Sensors-Str.1 pressure transmitter with an uncertainty of ±0.1 bar. The system was also connected to a computer that recorded the pressure and temperature of the cell as a function of time.

2.3. Experimental procedure

Prior to all experiments, the cell was washed and rinsed three times with de-ionized water. The hydrate formation cell was evacuated using a vacuum pump. The cell was subsequently charged with 300 cc of distilled water or an aqueous solution of the additive with a predetermined concentration for each experiment. All experiments were performed at constant temperatures. The cell was pressurized to approximately 0.3 MPa below the equilibrium pressure of hydrate formation. The coolant bath was turned on and the cell was allowed to reach the desired temperature for the formation of the hydrate. When the operating temperature was stable, gas was slowly charged into the cell, and the system was allowed to reach a supersaturated condition. The reactor was then pressurized to the desired experimental pressure with gas from the cylinder. The mixer was started at the desired stirring rate, and the temperature and pressure were recorded during the hydrate formation process. Each experiment was continued until a constant pressure was reached at least for 1 h. In addition, each experiment was repeated two or three times.

3. Results and discussion

3.1. Effects of stirring rate

Stirring is a straightforward way to mix gas and liquid water phases and increase the hydrate formation rate. Two questions should be addressed: (1) Do the same effects of stirring rate occur at different temperatures? (2) What are the effective and optimum conditions for increasing the hydrate formation rate? To answer these two questions, CO_2 hydrate was initially formed at 2.24 MPa and 274.2 K (stirring rates were 400, 600 and 800 rpm). Figure 2 represents a plot of gas consumption as a function of time at different stirring rates. The gas consumption rate reflects the hydrate formation rate. The results showed that an increase in stirring rate from 400 rpm to 600 or 800 rpm considerably increased the hydrate formation rate. The increase in the hydrate formation rate, when the stirring rate was increased from 600 rpm to 800 rpm, was not as pronounced. As shown in Figure 3, similar results were obtained at 275.2 K. Thus, 600 rpm was the optimum stirring rate at these two temperatures.

Similar experiments were performed at 276.2 K

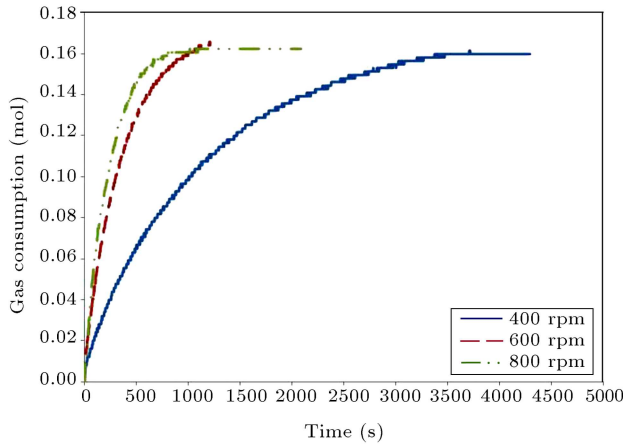

Figure 3. The effect of stirrer speed on CO_2 hydrate formation rate at temperature 275.2 K.

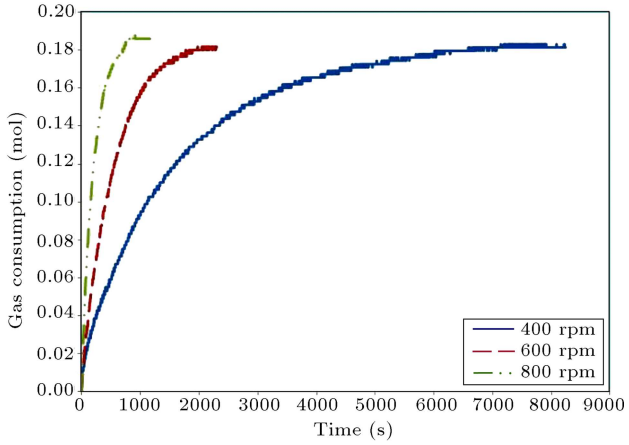

Figure 4. The effect of stirrer speed on CO_2 hydrate formation rate at temperature 276.2 K.

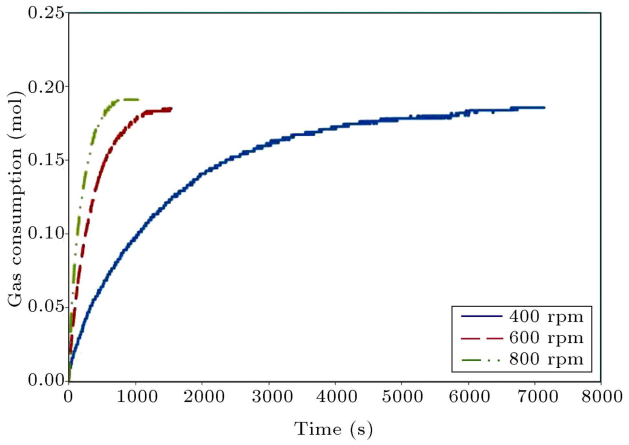

Figure 5. The effect of stirrer speed on CO_2 hydrate formation rate at temperature 277.2 K.

and 277.2 K. Figures 4 and 5 show that the hydrate formation rate increased when the stirring rate was increased from 400 rpm to 600 or 800 rpm. Furthermore, variations in the hydrate formation rate were greater than variations observed at lower temperatures, such as 274.2 K and 275.2 K, when the stirring rate was changed from 600 rpm to 800 rpm. Table 2 shows the driving force and initial hydrate formation rate for these experiments at different temperatures and initial pressures. The driving forces were the same in all of the experiments. The results show that a stirring rate of 600 rpm was optimum for increasing the CO_2 hydrate formation rate, especially at low temperatures. Also, these results can be compared with the experimental results of Hao et al. (2008) [22] for methane hydrate formation in a stirring rate from 320 rpm to 800 rpm. They showed that a stirring rate of 320 rpm was optimum for increasing the methane hydrate formation rate. So, the optimum stirring rate for CO_2 hydrate formation is more than for methane hydrate formation.

Table 2. Experimental results for the effect of stirrer speed on CO_2 hydrate formation rate.

T_{exp} (k)	$P_{initial}$ (MPa)	Driving force (MPa)	Initial hydrate formation rate, R_0 (moles/min)
Stirrer speed = 400 rpm			
274.2	2.24	0.90	0.0222
275.2	2.38	0.86	0.0245
276.2	2.64	0.92	0.0218
277.2	2.81	0.91	0.0183
Stirrer speed = 600 rpm			
274.2	2.23	0.89	0.0353
275.2	2.40	0.88	0.0408
276.2	2.64	0.92	0.0262
277.2	2.80	0.91	0.0453
Stirrer speed = 800 rpm			
274.2	2.21	0.87	0.0429
275.2	2.40	0.87	0.0448
276.2	2.66	0.94	0.0565
277.2	2.82	0.94	0.0679

3.2. Effects of initial pressure

Different experiments were performed to investigate the effects of initial pressure on the hydrate formation rate at a stirring rate of 800 rpm. Figures 6 shows the effect of different initial pressures on the CO_2 hydrate formation rate at 275.2 K. An increase in initial pressure from 2.17 MPa to 3.30 MPa resulted in a significant increase in the hydrate formation rate. Similar experiments were performed at 276.2 and 277.2 K, and the results are shown in Figures 7 and 8, respectively. The initial hydrate formation rates at different initial pressures are presented in Table 3. The initial hydrate formation rate increased as the initial pressure was increased. The higher initial pressure increases the driving force (i.e., the difference between the initial pressure and the equilibrium pressure),

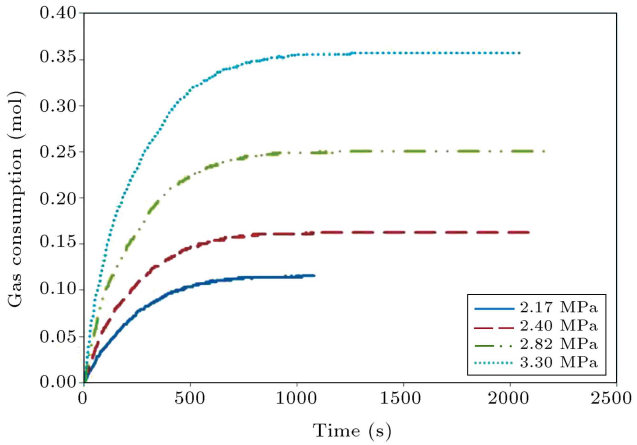

Figure 6. The effect of initial pressure on CO_2 hydrate formation rate at temperature 275.2 K.

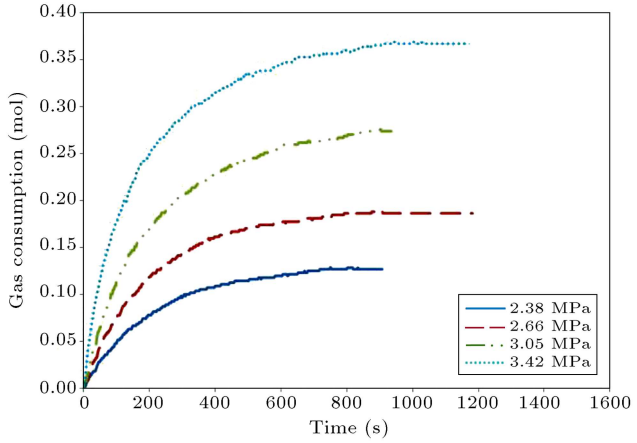

Figure 7. The effect of initial pressure on CO_2 hydrate formation rate at temperature 276.2 K.

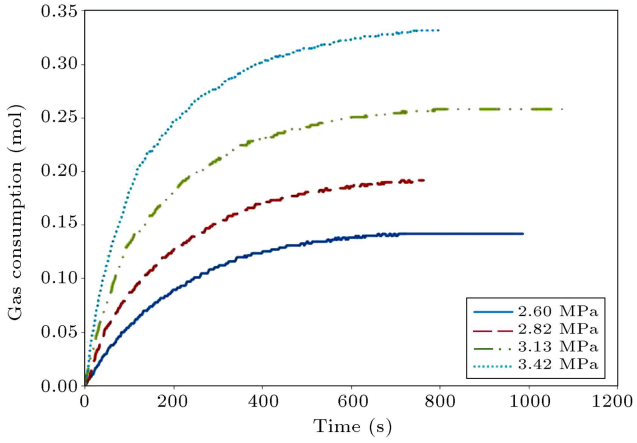

Figure 8. The effect of initial pressure on CO_2 hydrate formation rate at temperature 277.2 K.

which, consequently, increased the hydrate formation rate. In other work by Kang and Lee (2010) [23], the initial hydrate formation rate for CO_2 hydrate in porous media and without mixing was between 0.0660 - 0.1563 (moles/h at 275.2 K), but, in this work, it is higher. So, the effect of mixing is more than porous media.

Table 3. Experimental results for the effect of initial pressure on CO_2 hydrate formation.

T_{exp} (k)	$P_{initial}$ (MPa)	Driving force (MPa)	Initial hydrate formation rate, R_0 (moles/min)
275.2	2.17	0.64	0.0233
275.2	2.40	0.87	0.0448
275.2	2.82	1.27	0.0729
275.2	3.30	1.66	0.1169
276.2	2.38	0.67	0.0364
276.2	2.66	0.94	0.0565
276.2	3.05	1.32	0.0782
276.2	3.42	1.65	0.1588
277.2	2.60	0.72	0.0385
277.2	2.82	0.94	0.0679
277.2	3.13	1.20	0.1043
277.2	3.42	1.47	0.1582

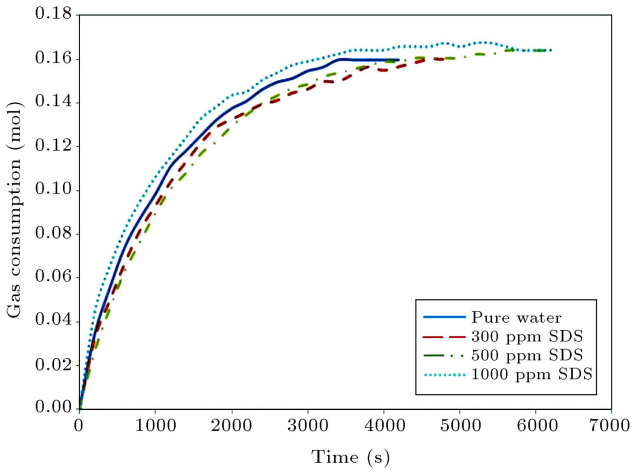

Figure 9. CO_2 hydrate formation rate with and without SDS at temperature 275.2 K.

3.3. Effects of surfactants

Sodium Dodecyl Sulfate (SDS), Dodecyl Trimethyl Ammonium Bromide (DTAB) and Triton X-100 (TX-100) were used to investigate the effects of surfactants on the kinetics of CO_2 hydrate formation at a stirring rate of 400 rpm. Figure 9 represents the effect of Sodium Dodecyl Sulfate (SDS) on CO_2 hydrate formation rate at 275.2 K and at SDS concentrations of 300, 500 and 1000 ppm. At concentrations of 300 and 500 ppm, SDS did not effectively increase the CO_2 hydrate formation rate. As shown in Table 4, the initial rate of hydrate formation was lower at these two concentrations than the initial hydrate formation rate with pure water; a SDS concentration of 1000 ppm

Table 4. Experimental results for the effect of surfactants on CO_2 hydrate formation.

Concentration of additive (ppm)	T_{exp} (k)	$P_{initial}$ (MPa)	Driving force (MPa)	Initial hydrate formation rate, R_0 (moles/min)
Not additive				
	275.2	2.38	0.86	0.0245
SDS				
300	275.2	2.38	0.86	0.0163
500	275.2	2.40	0.88	0.0164
1000	275.2	2.40	0.88	0.0448
TX-100				
300	275.2	2.40	0.88	0.0246
500	275.2	2.38	0.86	0.0245
1000	275.2	2.39	0.87	0.0164
DTAB				
300	275.2	2.40	0.88	0.0286
500	275.2	2.44	0.92	0.0248
1000	275.2	2.38	0.84	0.0244

increased the hydrate formation rate, but the increase was slight. Thus, no significant effect of SDS on hydrate formation rate was observed. The mechanism of surfactants such as SDS is not well understood. Surfactants reduce the interfacial tension between gas and liquid and also increase the nucleation rate by decreasing the interfacial tension between hydrate and liquid. In addition, SDS enhances the crystal growth rate of hydrate by increasing the surface area of hydrate particles, and enhances the area of the gas-liquid interfacial. SDS also increases gas solubility in aqueous solution [24]. There may be several factors involved in enhancing the hydrate formation rate with gas molecules such as light hydrocarbons, but, the main reason for promoting the effect of SDS on the hydrate formation rate of light hydrocarbons is possibly due to the adsorption of DS^- on the hydrate crystals. In fact, DS^- adsorbs on crystal hydrate and forms a monolayer. The headgroups of DS^- attach onto the surface of the hydrate crystal and the tail of it is towards the aqueous phase. Surfactant tails orient parallel to each other and form hydrophobic microdomains on the crystals of hydrate. The hydrophobic molecules, such as methane, can be entrapped in hydrophobic microdomains [25-27]. So, the methane hydrate formation rate is enhanced with SDS, but CO_2 molecules are hardly entrapped because of the hydrophilic molecules. In addition, anions such as carbonate or bicarbonate compete with DS^- for adsorption on the hydrate crystals [18]. Thus, the effect of SDS on the CO_2 hydrate formation rate may not be considerable because of competitive adsorption between CO_2 and DS^- on the crystal surfaces. To investigate the effects of cationic and non-ionic

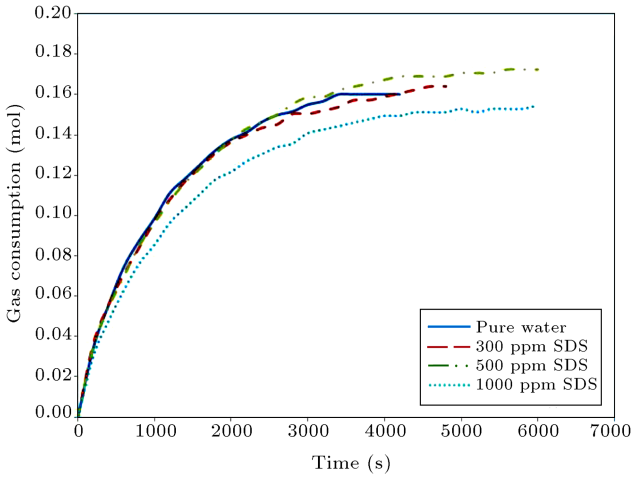

Figure 10. CO_2 hydrate formation rate with and without DTAB at temperature 275.2 K.

surfactants, similar experiments were performed using DTAB as a cationic surfactant and TX-100 as a non-ionic surfactant. As shown in Figure 10, DTAB was not effective at concentrations of 300 and 500 ppm. At a concentration of 1000 ppm, DTAB reduced the CO_2 hydrate formation rate. The results of TX-100 are shown in Figure 11. Concentrations of 300 and 500 ppm decreased the CO_2 hydrate formation rate, although the degree of this reduction was not substantial. At a TX-100 concentration of 1000 ppm, the CO_2 hydrate formation rate decreased significantly. Therefore, the effects of the cationic and non-ionic surfactants at concentrations of 300 and 500 ppm were approximately the same as SDS. Table 4 confirms these results. Also, Kang et al. showed that there is an

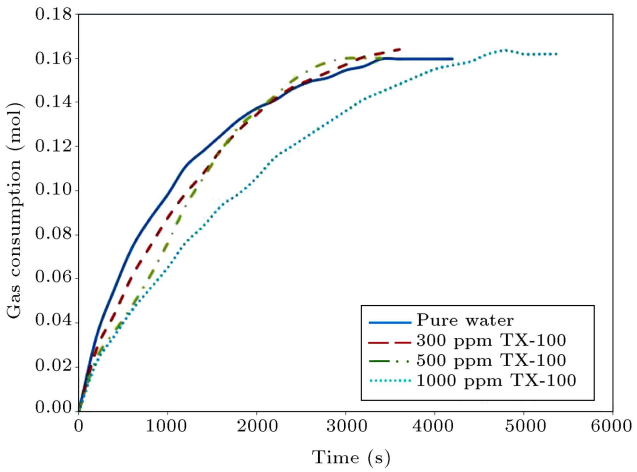

Figure 11. CO_2 hydrate formation rate with and without TX-100 at temperature 275.2 K.

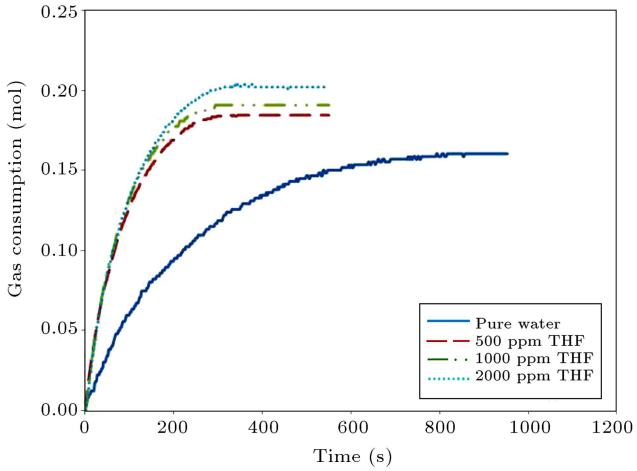

Figure 12. CO_2 hydrate formation rate with and without THF at temperature 275.2 K and very low concentrations.

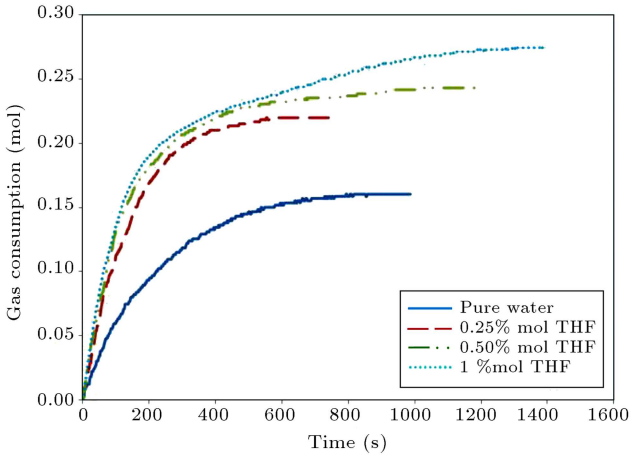

Figure 13. CO_2 hydrate formation rate with and without THF at temperature 275.2 K and low concentrations.

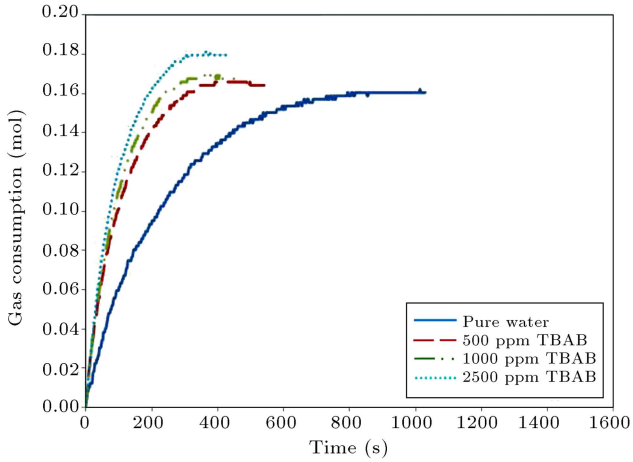

Figure 14. CO_2 hydrate formation rate with and without TBAB at temperature 275.2 K and very low concentrations.

optimum value for added SDS concentration. So, an excess amount of SDS decreases the hydrate formation rate [23].

3.4. Effects of thermodynamic additives

Thermodynamic additives, such as THF and TBAB, significantly reduce the pressure of hydrate formation. THF forms sII hydrate and TBAB forms semiclathrate hydrate with water [18]. The hydrate formation kinetics and thermodynamics of these additives at high concentrations have been investigated. In this work, the effects of these additives at low concentrations were investigated. The first set of experiments was performed with THF. THF concentrations of 500, 1000 and 2000 ppm were examined at 275.2 K and at a stirring rate of 800 rpm. The results in Figure 12 show that, at these concentrations (i.e., very low concentrations), the hydrate formation rate increases considerably. Furthermore, the effects of THF were similar to those of kinetic additives because of the increased hydrate formation rate, whereas the surfactants were not effective. Experiments using THF were also performed at higher concentrations. These concentrations were 0.25, 0.50 and 1 mol% (10,000, 20,000 and 40,000 ppm). These concentrations are low in comparison with the concentration of 5.56 mol% that represents a stoichiometric ratio of THF for sII hydrate formation. The results shown in Figure 13 indicate that the hydrate formation rate also increased at these concentrations. Table 5 shows that, at very low concentrations of THF (500, 1000 and 2000 ppm), the initial hydrate formation rate is greater than the rate at higher concentrations of THF (0.25, 0.50 and 1 mol%). Therefore, THF at very low concentrations was more effective than at higher concentrations, even though the driving force (difference between initial pressure and equilibrium pressure) was greater at higher concentrations. Experiments for TBAB were performed at concentrations of 500, 1000 and 2500 ppm. Figure 14 shows the

Table 5. Experimental results for the effect of thermodynamic additives on CO_2 hydrate formation rate.

Concentration of additive (ppm)	T_{exp} (k)	$P_{initial}$ (MPa)	Driving force (MPa)	Initial hydrate formation rate, R_0 (moles/min)
Not additive				
	275.2	2.40	0.87	0.0448
THF				
500	275.2	2.41	1.00	0.1158
1000	275.2	2.40	1.04	0.1154
2000	275.2	2.40	1.11	0.1116
10000	275.2	2.40	1.22	0.0805
20000	275.2	2.40	1.37	0.0961
40000	275.2	2.41	1.59	0.1040
TBAB				
500	275.2	2.40	0.88	0.0883
1000	275.2	2.40	0.90	0.0922
2500	275.2	2.41	0.97	0.1002

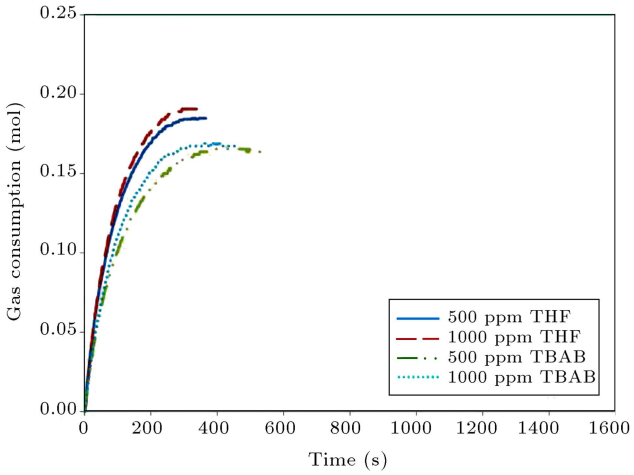

Figure 15. Comparison between THF and TBAB on CO_2 hydrate formation rate.

results and indicates that the hydrate formation rate is increased at these concentrations. Table 5 shows that the initial hydrate formation rate with an aqueous solution of TBAB is greater than that with pure water. Therefore, TBAB, like THF, shows effects similar to those of kinetic additives. Figure 15 compares the hydrate formation rate for THF and TBAB. The figure shows that the increase in the hydrate formation rate is greater for THF. Table 5 also confirms that the initial hydrate formation rate for THF is greater than that for TBAB. Different experiments for CO_2 hydrate formation showed that the highest rate of CO_2 hydrate formation in a stirred tank reactor was observed for an aqueous solution of THF and that hydrate formation was completed in 300 s at very low concentrations of THF.

4. Conclusions

The rates of hydrate formation at temperatures of 274.2, 275.2, 276.2 and 277.2 K were increased when the stirring rate was increased from 400 rpm to 600 or 800 rpm. The results indicated that a stirring rate of 600 rpm was optimum for increasing the CO_2 hydrate formation rate, especially at lower temperatures. The effects of the initial pressure were studied, and the hydrate formation rate increased at higher initial pressures. Also, the effects of additives were investigated. DTAB and TX-100 were new surfactants for investigation into CO_2 hydrate formation kinetics. SDS and DTAB at concentrations of 300 and 500 ppm did not effectively increase the CO_2 hydrate formation rate. However, SDS increased and DTAB negligibly decreased the hydrate formation rate at concentrations of 1000 ppm. TX-100 decreased the hydrate formation rate negligibly at concentrations of 300 and 500 ppm, but decreased the rate considerably at 1000 ppm. The thermodynamic additives, THF and TBAB, increased the hydrate formation rate at all concentrations. The effect of THF was greater than that of TBAB. Interestingly, the thermodynamic additives increased the CO_2 hydrate formation rate, but the surfactants decreased or, at several concentrations, increased negligibly.

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