



Kinetics of (TBAF + CO₂) semi-clathrate hydrate formation in the presence and absence of SDS

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Received: 3 August 2017 / Published online: 24 March 2018
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Abstract

In this communication, the impacts of adding SDS (sodium dodecyl sulfate), TBAF (tetra-*n*-butylammonium fluoride) and the mixture of SDS + TBAF on the main kinetic parameters of CO₂ hydrate formation (induction time, the quantity and rate of gas uptake, and storage capacity) were investigated. The tests were performed under stirring conditions at $T = 5\text{ }^{\circ}\text{C}$ and $P = 3.8\text{ MPa}$ in a 169 cm³ batch reactor. The results show that adding SDS with a concentration of 400 ppm, TBAF with a concentration of 1–5 wt%, and the mixture of SDS + TBAF, would increase the storage capacity of CO₂ hydrate and the quantity of gas uptake, and decrease the induction time of hydrate formation process. The addition of 5 wt% of TBAF and 400 ppm of SDS would increase the CO₂ hydrate storage capacity by 86.1% and 81.6%, respectively, compared to pure water. Investigation of the impact of SDS, TBAF and their mixture on the rate of gas uptake indicates that the mixture of SDS + TBAF does not have a significant effect on the rate of gas uptake during hydrate formation process.

Keywords Semi-clathrate hydrate · Gas hydrate · Kinetics · CO₂ · SDS · TBAF

List of symbols

P Pressure
 R Universal gas constant
 T Temperature
 V Volume of the gas phase
 Z Compressibility factor

t Time
 w Water

Subscripts

0 Conditions of the cell at time $t = 0$
 i Counter

1 Introduction

According to the Paris Agreement on Climate Change (2015), 195 United Nations members states agreed to reduce their carbon output as soon as possible (UNFCCC 2015).¹ CO₂, one of the main human-produced greenhouse gases, is a by-product of energy related industries (especially power plants) (Bhattacharjee et al. 2015). The quantity of CO₂ in the atmosphere has increased considerably in recent decades. Therefore, the capture and sequestration (storage) of CO₂ have become a priority within energy research. Chemical and physical absorption and chemical adsorption on zeolite are common ways to separate CO₂ from gas mixtures (Herzog et al. 1997; Kohl and Nielsen 1997; Kuramochi et al. 2012; Peng and Zhuang 2012; Riemer 1996). These technologies are generally expensive and thus finding an energy efficient method to capture CO₂ molecules is necessary. One of new and promising methods to separate CO₂ from flue/industrial gases is using gas hydrate technology.

Edited Xiu-Qin Zhu

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Gas hydrates or clathrate hydrates are ice-like non-stoichiometric crystalline inclusion compounds that are formed by enclathration of some guest molecules of certain sizes (such as methane, CO₂ and hydrogen sulfide.) into a three-dimensional network of hydrogen-bonded water (host) molecules (Kang and Lee 2010; Sloan 2011; Sloan and Koh 2008). Due to high gas and energy storage capacity of gas hydrates and their potential for separation processes, great attention has been paid to the positive applications of this technology (such as natural gas storage and transportation, gas separation, energy storage, water desalination, refrigeration systems, and so on (Adisasmito et al. 1991; Chatti et al. 2005; Eslamimanesh et al. 2012; Javanmardi and Moshfeghian 2003; Ji et al. 2001; Li et al. 2012; Ohgaki et al. 1996; Xu and Ge 2011; Tanii 1994), in recent years. However, high pressure/low temperature dissociation conditions, long induction time, and slow kinetic rate of hydrate growth are the major problems with using gas hydrates in gas industries (Babaei et al. 2015; Mohammadi et al. 2014a; Zhang et al. 2008). Therefore, moderating the thermodynamic conditions and promoting the kinetics of gas hydrate formation are essential to benefit the positive applications of this technology and thus reliable design of hydrate-based industries. The moderating of thermodynamic conditions of gas hydrate formation has been the objective of many research studies in recent decades (Delahaye et al. 2006; Jager et al. 1999; Lu et al. 2009; Manteghian et al. 2013; Papadimitriou et al. 2011; Strobel et al. 2006; Sun et al. 2010; Zhang and Wu 2010; Zhang et al. 2006, 2009; Zhao et al. 2008).

In 1940, Fowler et al. discovered a new structure of the hydrates, which is formed by tetra-*n*-butylammonium salts (Fowler et al. 1940). Because in these structures some water lattice sites are replaced by the guest molecules (anions), they are called semi-clathrates. In semi-clathrates formed by tetra-*n*-butylammonium salts, tetra-*n*-butylammonium chains occupy the large cages and the small cages remain vacant or partially occupied with water molecules or small gas molecules (Bonamico et al. 1962; Fowler et al. 1940; Hughes 2008; Komarov et al. 2007; Makino et al. 2009; McMullan et al. 1963; Mohammadi et al. 2013, 2014b). Mohammadi and coworkers have widely investigated the thermodynamic conditions of gas hydrate formation in the presence of some semi-clathrate formers such as tetra-*n*-butylammonium fluoride (TBAF), tetra-*n*-butylammonium chloride (TBAC), and tetra-*n*-butylammonium bromide (TBAB) (Belandria et al. 2011, 2012; Mohammadi et al. 2013, 2014b; Mohammadi et al. 2012; Mohammadi and Richon 2009). They found that the presence of studied semi-clathrate formers moderates the thermodynamics of gas hydrate formation dramatically (Belandria et al. 2011, 2012; Mohammadi et al. 2013, 2014b, 2012; Mohammadi and Richon 2009).

Despite a large number of studies undertaken on the thermodynamics of semi-clathrate hydrates, few attempts have been made to investigate the kinetics of this type of hydrates (Fan et al. 2011; Ye et al. 2014).

In recent years, the kinetic parameters of clathrate hydrate formation (such as induction time, the quantity of gas uptake and growth rate) in the presence of different additives have been studied by many researchers (Arjang et al. 2013; Bi et al. 2009; Dashti et al. 2015; Farhang et al. 2014; Fazlali et al. 2013; Ganji et al. 2007a, b; Kang and Lee 2010; Kumar et al. 2013; Lirio et al. 2013; Manteghian et al. 2013; Mohammadi et al. 2014a; Ricaurte et al. 2014; Rogers et al. 2007; Roosta et al. 2015; Sabil et al. 2010; Torré et al. 2011; Zhang et al. 2004, 2007). Mohammadi and coworkers studied the impact of sodium dodecyl sulfate and silver nanoparticles on the kinetic parameters of CO₂ clathrate hydrate formation (Mohammadi et al. 2014a). Their results show that simultaneous utilization of SDS and silver nanoparticles increases the hydrate formation rate, storage capacity and the quantity of gas uptake during hydrate formation considerably (Mohammadi et al. 2014a). Kang et al. investigated the kinetic behavior of CO₂ hydrate formation in porous media in the presence of SDS. They showed that adding SDS increases the initial CO₂ hydrate formation rate, compared to pure water. The investigation of Kumar and coworkers (Kumar et al. 2013) on the impact of different additives (Tween-80, dodecyltrimethylammonium chloride (DTACI), and SDS) on CO₂ hydrate formation kinetics show that SDS is probably the most effective among their studied additives (Kumar et al. 2013). Although, the kinetics of CO₂ “clathrate” hydrate formation in the presence of surfactants have been studied by some researchers, in recent years, the kinetics of CO₂ hydrate formation in the presence of “semi-clathrate” formers (that moderate the thermodynamics of gas hydrate formation noticeably) requires more attention.

In the present study, the impacts of SDS, TBAF, and the mixture of SDS + TBAF on the induction time, the quantity of gas uptake, the hydrate growth rate, and the storage capacity of CO₂ hydrate formation process were investigated.

2 Experimental

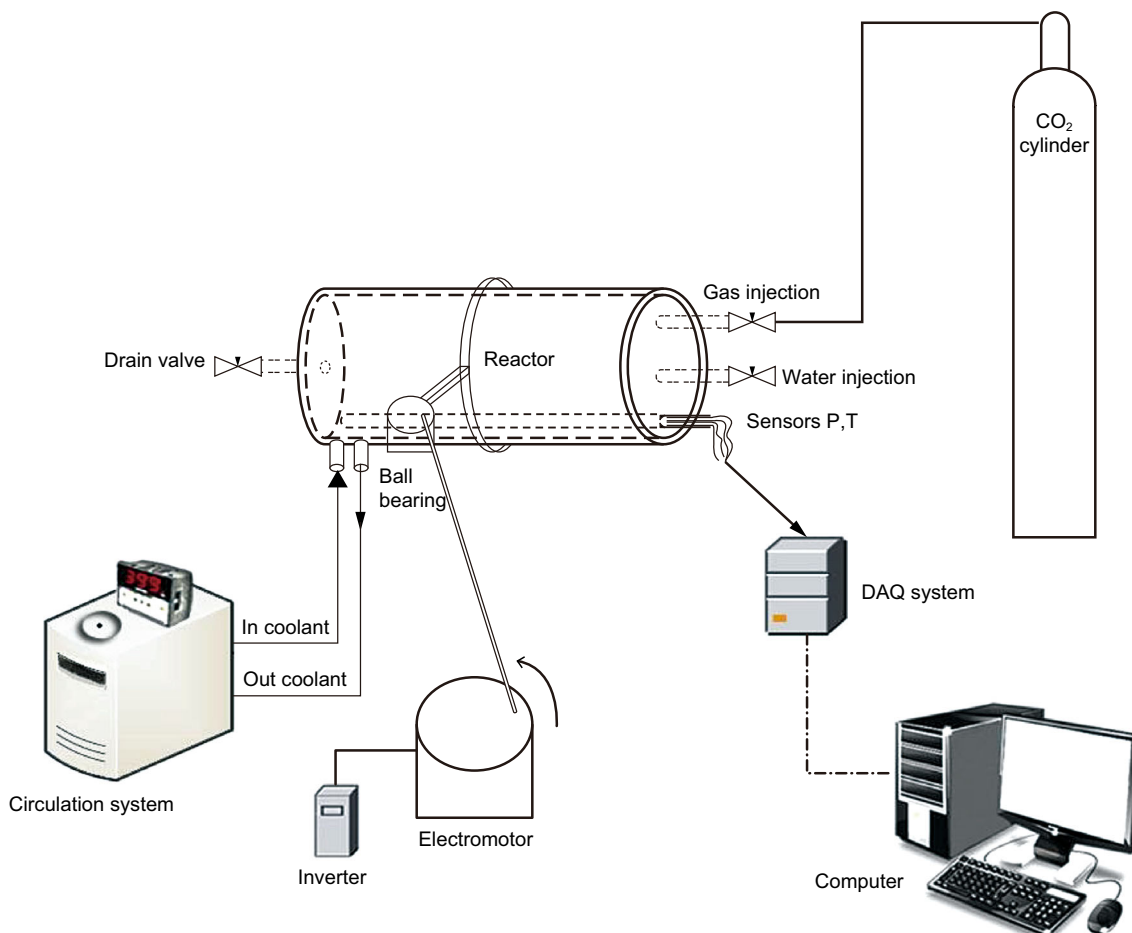
2.1 Materials and apparatus

The purities and suppliers of the materials used in this work are reported in Table 1.

The experimental apparatus is fully described elsewhere (Mohammadi et al. 2014a). Figure 1 shows the schematic picture of the apparatus. Briefly, the hydrate formation reactor with an effective volume of 169 cm³, is a jacketed

Table 1 Purities and suppliers of the materials used in this work

Chemical	Supplier	Purity
SDS	Daejung Chemical & Metal Co. Ltd. (Korea)	98 wt%
CO ₂	Sepehr gas (Iran)	99.99 mol%
TBAF	Merck (Germany)	97 mol%

**Fig. 1** Schematic illustration of the experimental apparatus used in this study

stainless steel cell. For appropriate mixing of the gas, aqueous solution and hydrate, an electric motor is used to rock the reactor. The stirring rate of the reactor is 10 rpm.

2.2 Procedure

Experiments were carried out at the Central Laboratory of Gas Conversions at the University of Bojnord, Iran. At first, the cell was washed with distilled water. To ensure that all parts of the set up are free of air, inner parts were evacuated with a vacuum pump. 50 cm³ of prepared solution was loaded into the cell at room temperature and atmospheric pressure. Then, the temperature of the reactor was set to the desired temperature of 5 °C. To achieve the desired pressure (3.8 MPa), the cell was charged with CO₂.

After the reactor was pressurized with CO₂, the electric motor was turned on with a speed of 10 rpm. The cell pressure decreased continuously due to hydrate formation until reaching a steady state condition. During the experiments, the cell temperature and pressure were recorded by the digital acquisition (DAQ) system.

3 Results and discussion

The phase equilibrium conditions for hydrate-containing systems of TBAF have been studied by some researchers. Mohammadi and coworkers (Mohammadi et al. 2013) and Li and coworkers (Li et al. 2010) determined the semi-clathrate hydrate phase equilibria of water + TBAF (2, 4,

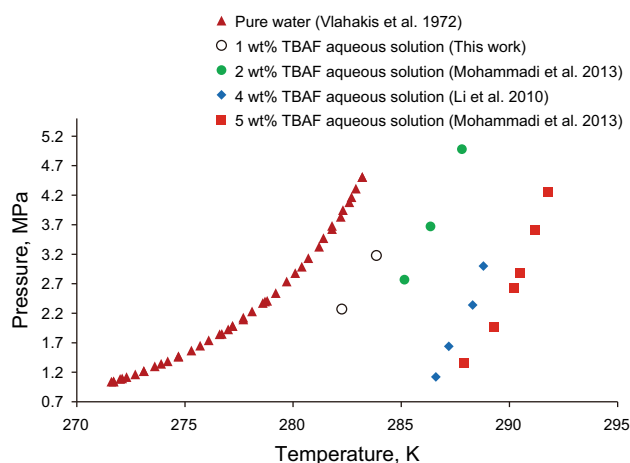


Fig. 2 Semi-clathrate hydrate phase equilibria of carbon dioxide + TBAF + water systems

and 5 wt%) + CO₂ systems. In this study, we measured the phase equilibrium conditions for 1 wt% of TBAF. The results of the measurements are shown in Fig. 2.

3.1 Quantity and rate of gas uptake

The impact of adding TBAF, SDS, and the mixture of TBAF + SDS on the quantity of CO₂ uptake, induction time, and rate of gas uptake during CO₂ hydrate formation were investigated, as mentioned earlier (Mohammadi et al. 2014a). The kinetics of hydrate formation was studied in a stirred batch reactor at the temperature of 5 °C and the pressure of 3.8 MPa, as pointed out earlier. Aqueous solutions of (a) TBAF with concentrations of 0, 1, 4, and 5 wt%, (b) SDS with concentrations of 0 and 400 ppm, and (c) SDS 400 ppm + TBAF (0–4) wt% were prepared, in order to investigate the impacts of SDS, TBAF, and SDS + TBAF on the kinetics of CO₂ hydrate formation.

The quantity of gas uptake during CO₂ hydrate formation process can be calculated by employing the real gas law (Eq. (1)) (Mohammadi et al. 2014a; Smith et al. 2001).

$$\Delta n_{\text{CO}_2} = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t} \quad (1)$$

where P is the pressure; T represents the temperature; V stands for the volume of the gas inside the reactor; Z is the gas compressibility factor; R represents the universal gas constant; and subscripts 0 and t stand for conditions of the cell at time $t = 0$ and time t , respectively.

The quantities of CO₂ uptake during hydrate formation for the systems of CO₂ + water and CO₂ + water + TBAF (1, 4, and 5 wt%) are depicted in Fig. 3. As shown in this Fig. 3, adding aqueous solution of TBAF (1, 4, and 5 wt%) increases the quantities of CO₂ uptake within 60 min of hydrate formation experiments, compared

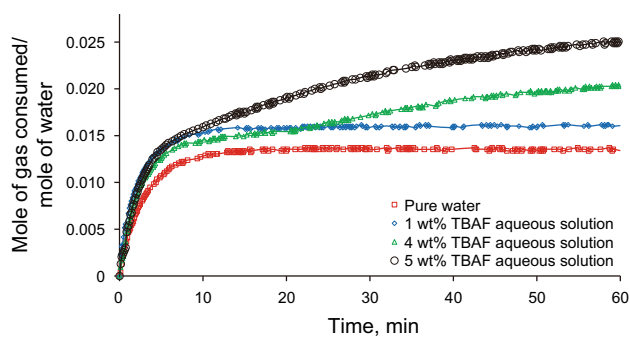


Fig. 3 The quantities of CO₂ uptake during hydrate formation in the absence and the presence of TBAF with various concentrations at an initial pressure of 3.8 MPa and temperature of 5 °C

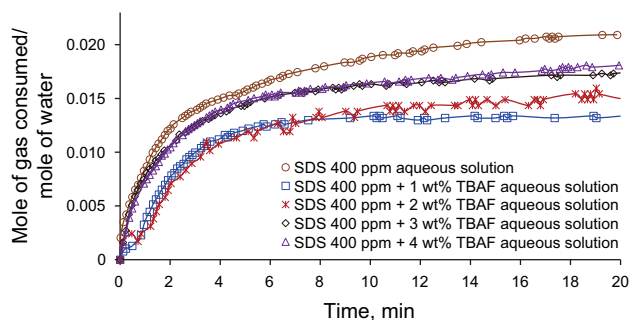


Fig. 4 The quantities of CO₂ uptake during hydrate formation in the presence of SDS 400 ppm and the various concentrations of TBAF at an initial pressure of 3.8 MPa and temperature of 5 °C

to pure water and the quantity of gas uptake during hydrate formation is proportional to the concentration of TBAF.

The maximum quantity of CO₂ uptake was obtained for 5 wt% TBAF aqueous solution. At $t = 60$ min, the quantity of CO₂ consumption per mole of feed water for this solution was found to be 0.1382 mol compared to pure water having 0.0742 mol. This means that adding 5 wt% of TBAF increases the quantity of CO₂ uptake 86%, compared to pure water. By increasing the concentration of TBAF from 1 to 5 wt%, the thermodynamics of hydrate formation are moderated (Mohammadi et al. 2013). Therefore, the driving force of CO₂ hydrate formation increases. Increasing the driving force of hydrate formation process increases the quantity of gas uptake.

Figure 4 illustrates the quantity of CO₂ uptake per mole of water during hydrate formation process in the presence of SDS (400 ppm) and the various concentrations of TBAF at an initial pressure of 3.8 MPa and temperature of 5 °C. As shown in Fig. 4, simultaneous utilization of SDS (400 ppm) and TBAF (1–4 wt%) decreases the quantity of gas uptake within 20 min of hydrate formation experiments, compared to the system of CO₂ + SDS (400 ppm) + water. In other words, adding TBAF (with concentration of (1–4 wt%) to aqueous solution of SDS

(with concentration of 400 ppm) results in a negative effect on the quantity of gas uptake during hydrate formation.

A likely reason for this phenomenon is as follows: The strong interaction between the ions of Na⁺ (released from SDS) and F⁻ (in the lattice structure of semi-clathrate hydrates) results in a negative effect on the stability of semi-clathrate lattice structure and consequently, the quantity of trapped gases will be decreased.

As shown in Fig. 4, by increasing the concentration of TBAF from 1 to 4 wt% at constant concentration of SDS (400 ppm), the quantity of CO₂ uptake during hydrate formation process increases. By increasing the concentration of TBAF (from 1 to 4 wt%) at constant concentration of SDS (400 ppm), the quantity of Na⁺ per mole of F⁻ decreases. Therefore, the negative effect of Na⁺ on the stability of semi-clathrate hydrate lattice decreases and consequently, the quantity of gas consumption would increase.

Figures 5, 6 and 7 depict the impact of adding SDS on the quantity of CO₂ uptake during hydrate formation process. Figure 5 shows the impact of SDS on the quantity of CO₂ consumption in the absence of TBAF. As shown in this figure, adding SDS increases the quantity of gas uptake during hydrate formation. SDS increases the solubility of CO₂ in water by decreasing the surface tension of water molecules at the gas–liquid interface.

The impact of SDS on the quantity of CO₂ uptake during hydrate formation in the presence of 1 wt% TBAF at an initial pressure of 3.8 MPa and temperature of 5 °C is illustrated in Fig. 6. As shown in this figure, at low concentration of TBAF, the presence of SDS -by decreasing the stability of semi-clathrate lattice- causes a negative effect on the quantity of gas uptake during hydrate formation process.

Figure 7 depicts the impact of SDS on the quantity of CO₂ uptake during hydrate formation in the presence of 4 wt% of TBAF. As illustrated in this figure, at this

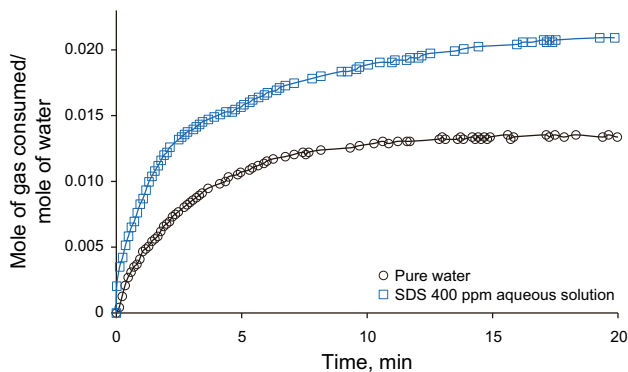


Fig. 5 The impact of adding SDS on the quantity of CO₂ uptake during hydrate formation at an initial pressure of 3.8 MPa and temperature of 5 °C

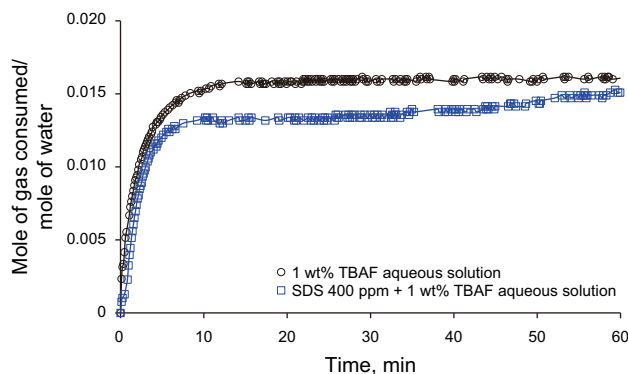


Fig. 6 The impact of SDS on the quantity of CO₂ uptake during hydrate formation in the presence of 1 wt% TBAF aqueous solution at an initial pressure of 3.8 MPa and temperature of 5 °C

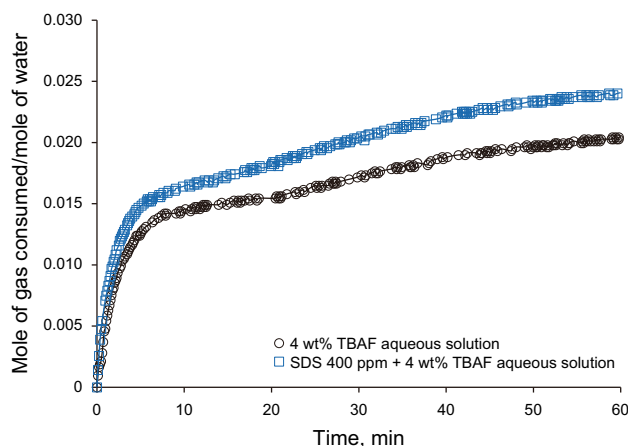


Fig. 7 The impact of SDS on the quantity of CO₂ uptake during hydrate formation in the presence of 4 wt% TBAF aqueous solution, at an initial pressure of 3.8 MPa and temperature of 5 °C

concentration of TBAF, the presence of SDS has a positive effect on the quantity of gas uptake during hydrate formation process. At this concentration of TBAF, the quantity of Na⁺ per mole of F⁻ decreases, compared to 1 wt% aqueous solution of TBAF. Therefore, the negative effect of Na⁺ on the stability of semi-clathrate lattice decreases. On the other hand, SDS decreases the surface tension of water molecules. Therefore, the quantity of CO₂ consumption in the presence of SDS is higher than that of in the absence of SDS.

Equation (2) was employed to calculate the rate of gas uptake, $r(t)$, during hydrate formation process (Mohammadi et al. 2014a):

$$r(t) = \frac{n_{CO_2,i-1} - n_{CO_2,i+1}}{(t_{i+1} - t_{i-1})n_{w0}} \tag{2}$$

where $n_{CO_2,i-1}$ and $n_{CO_2,i+1}$ are, respectively, the mole number of CO₂ in the gas phase at t_{i-1} and t_{i+1} ; and n_{w0} is the initial mole number of water.

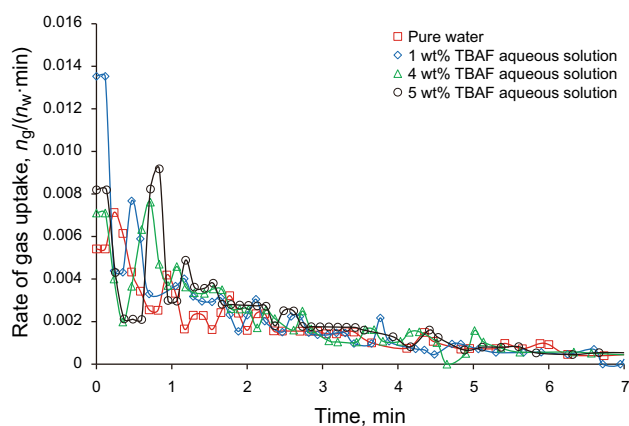


Fig. 8 The rate of CO₂ uptake during hydrate formation in the presence of TBAF aqueous solution with different concentrations, at an initial pressure of 3.8 MPa and temperature of 5 °C

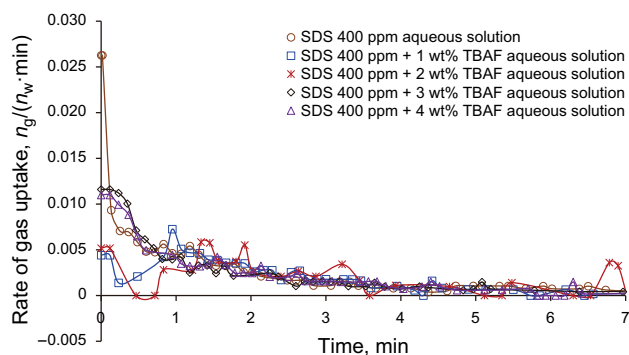


Fig. 9 The rate of CO₂ uptake during hydrate formation in the presence of SDS 400 ppm and TBAF aqueous solution with different concentrations, at an initial pressure of 3.8 MPa and temperature of 5 °C

Figures 8 and 9, respectively, show the impacts of different concentrations of TBAF on the rate of CO₂ consumption in the absence and the presence of SDS (with concentration of 400 ppm). As shown in these figures (Figs. 8, 9), the time range of rapid CO₂ consumption for the systems of CO₂ + water and CO₂ + TBAF + water was 0–5 min. This time range was 0–3 min for the systems of CO₂ + SDS + water, and CO₂ + SDS + TBAF + water. The rate of gas consumption tended to a very small value, after these time periods. As shown in these figures, the addition of TBAF does not have a significant effect on increasing the gas consumption rate.

The impact of SDS (with concentration of 400 ppm) on the rate of CO₂ uptake during hydrate formation process is illustrated in Figs. 10, 11 and 12. It can be seen that, adding SDS with concentration of 400 ppm does not have a significant effect on increasing the gas consumption rate.

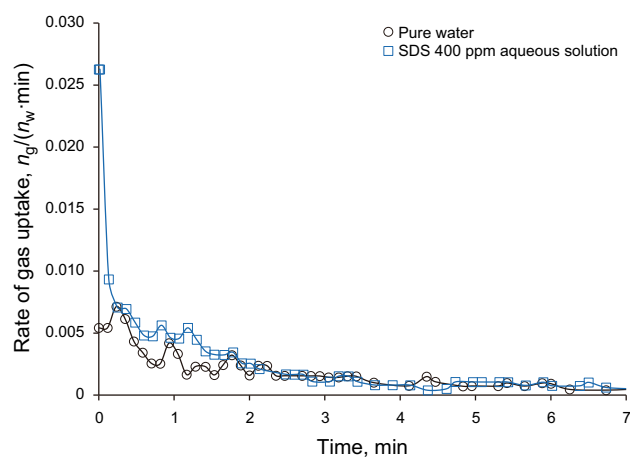


Fig. 10 The impact of SDS on the rate of CO₂ uptake during hydrate formation at an initial pressure of 3.8 MPa and temperature of 5 °C

3.2 Impact of SDS and TBAF on induction time and storage capacity of CO₂

Figure 13 depicts the induction time of CO₂ hydrate formation for the systems of CO₂ + water, CO₂ + TBAF + water, CO₂ + SDS + water, and CO₂ + SDS + TBAF + water. The numerical data of induction times are given in Table 2. In this study, the induction time is defined as the time from introducing the gas to the cell to the time of initial formation of hydrate. As shown in Fig. 13 and Table 2, all the tested additives decrease the induction time of hydrate formation. Adding SDS decreases the induction time of CO₂ hydrate formation considerably. The induction time of CO₂ hydrate formation in the presence of 400 ppm SDS is 0.4 min, while this value is 73 min for the system of CO₂ + water. Adding 5 wt% TBAF decreases the induction time of CO₂ hydrate formation noticeably, compared to pure water. The induction time of hydrate formation for the system of CO₂ + 5 wt% TBAF + water is 0.9 min at initial pressure of 3.8 MPa and temperature of 5 °C. SDS improves the induction time of hydrate formation process by decreasing the surface tension of water molecules and TBAF and by increasing the driving force of CO₂ hydrate formation.

Figure 14 shows the impacts of adding SDS, TBAF, and the mixture of SDS + TBAF on storage capacity of CO₂ within 60 min of experiments of the hydrate formation at an initial pressure of 3.8 MPa and temperature of 5 °C. The numerical data of storage capacities are given in Table 3. As shown in Fig. 14 and Table 3, all the tested additives increased the storage capacity of CO₂ in the process of hydrate formation, compared to pure water.

The storage capacity of CO₂ hydrate for 5 wt% TBAF aqueous solution was 60.6 v/v, compared to pure water

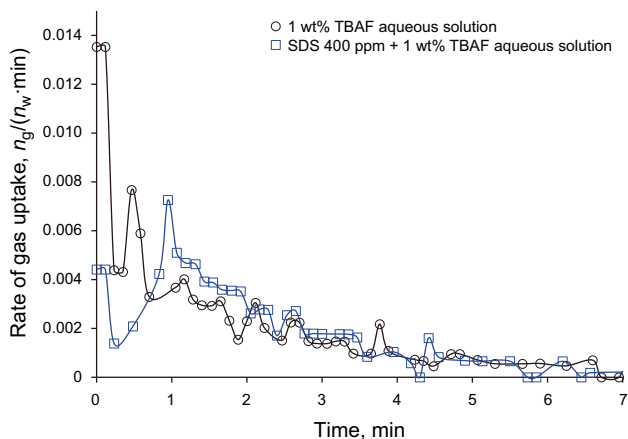


Fig. 11 The impact of SDS on the rate of CO₂ uptake during hydrate formation in the presence of 1 wt% TBAF aqueous solution, at an initial pressure of 3.8 MPa and temperature of 5 °C

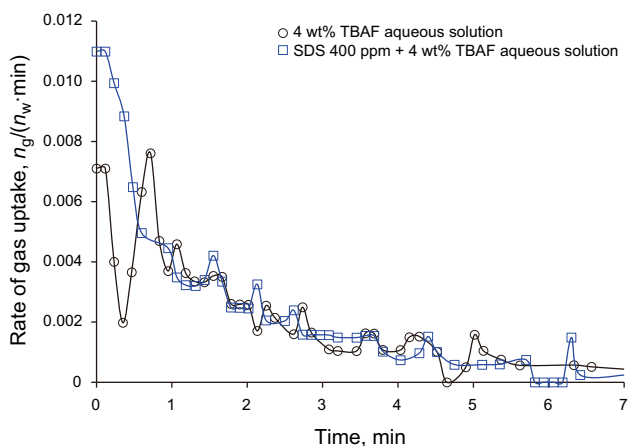


Fig. 12 The impact of SDS on the rate of CO₂ uptake during hydrate formation in the presence of 4 wt% TBAF aqueous solution, at an initial pressure of 3.8 MPa and temperature of 5 °C

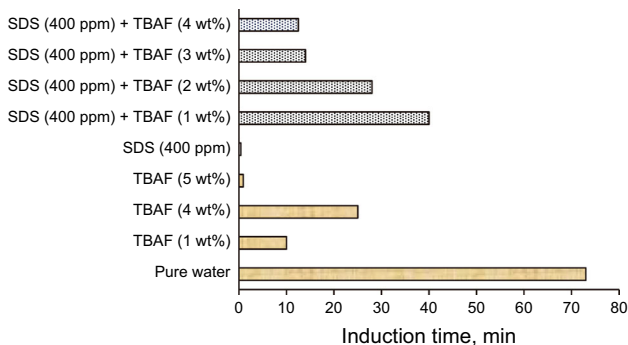


Fig. 13 The induction time of (CO₂ + TBAF) hydrate formation in the presence of SDS at an initial pressure of 3.8 MPa and temperature of 5 °C

Table 2 The induction time of CO₂ hydrate formation or (CO₂ + TBAF) hydrate formation in the absence and the presence of SDS at an initial pressure of 3.8 MPa and temperature of 5 °C

System	<i>t</i> _{ind} , min
CO ₂ + water	73
CO ₂ + TBAF (1 wt%) + water	10
CO ₂ + TBAF (4 wt%) + water	25
CO ₂ + TBAF (5 wt%) + water	0.9
CO ₂ + SDS (400 ppm) + water	0.4
CO ₂ + SDS (400 ppm) + TBAF (1 wt%) + water	40
CO ₂ + SDS (400 ppm) + TBAF (2 wt%) + water	28
CO ₂ + SDS (400 ppm) + TBAF (3 wt%) + water	14
CO ₂ + SDS (400 ppm) + TBAF (4 wt%) + water	12.5

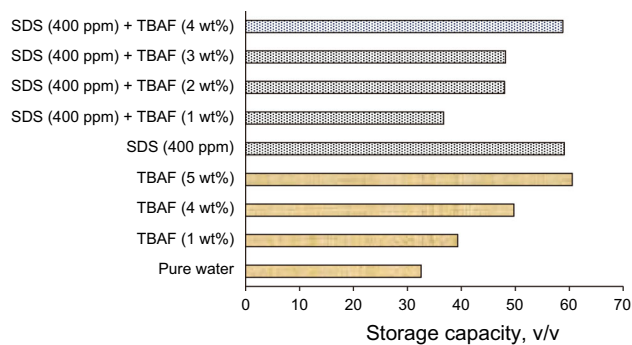


Fig. 14 The impact of SDS, TBAF, and the mixture of SDS + TBAF on storage capacity of CO₂ in the process of hydrate formation at an initial pressure of 3.8 MPa and temperature of 5 °C

with 32.5 v/v. This means that adding TBAF with 5 wt% increases the storage capacity of CO₂ hydrate 86.1%, compared to pure water. TBAF increased the storage capacity of CO₂ hydrate formation by moderating the hydrate formation conditions.

The storage capacity of CO₂ hydrate for aqueous solution of SDS with concentration of 400 ppm was 59.1 v/v. This means that adding 400 ppm SDS increases the storage capacity of CO₂ hydrate 81.6%, compared to pure water. SDS improves the storage capacity of CO₂ hydrate by decreasing the surface tension of water molecules.

4 Conclusions

In this study, the impacts of adding SDS, TBAF, and the mixture of SDS + TBAF on induction time, storage capacity, and the quantity and rate of gas uptake during CO₂ hydrate formation were investigated. Our main conclusions can be summarized as follows:

Table 3 Impacts of SDS, TBAF, and the mixture of SDS + TBAF on the storage capacity of CO₂ and initial rate of CO₂ uptake in the process of hydrate formation at an initial pressure of 3.8 MPa and temperature of 5 °C

Additive	Storage capacity, V/V	Initial rate of CO ₂ uptake × 100, n _g /(n _w -min)
Pure water	32.5	0.54
TBAF (1 wt%)	39.3	1.35
TBAF (4 wt%)	49.7	0.71
TBAF (5 wt%)	60.6	0.82
SDS (400 ppm)	59.1	1.67
SDS (400 ppm) + TBAF (1 wt%)	36.7	0.44
SDS (400 ppm) + TBAF (2 wt%)	48.0	0.52
SDS (400 ppm) + TBAF (3 wt%)	48.2	1.10
SDS (400 ppm) + TBAF (4 wt%)	58.8	1.16

- (1) The results show that adding SDS (400 ppm) and TBAF (5 wt%) increases the storage capacity of CO₂ hydrate and decreases the induction time of hydrate formation considerably.
- (2) Adding TBAF increases the quantity of CO₂ uptake within 60 min of hydrate formation experiments, compared to pure water and the quantity of gas uptake during hydrate formation is proportional to the concentration of TBAF.
- (3) Adding 400 ppm SDS at low concentration of TBAF (1 wt%), presents a negative effect on the quantity of gas uptake during hydrate formation process. By increasing the concentration of TBAF, the negative effect of SDS decreases.
- (4) Finally, adding SDS and TBAF at tested conditions does not have a significant effect on increasing the rate of gas consumption.

Acknowledgements The financial support from the Iran National Science Foundation is greatly appreciated.

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