Effect of Sodium Dodecyl Sulphate on Gas Hydrate Formation Kinetics of Methane and Ethane Mixtures

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Abstract

In this study, the effects of sodium dodecyl sulphate (SDS) on gas hydrate formation kinetics of methane and ethane mixture has been investigated experimentally and also the thermodynamic natural path has been used for modeling of the hydrate formation rate in a constant volume process. Different mole fractions of methane 0.1, 0.2, 0.3, 0.5, 0.68 and 0.8 have been studied. All experiments have been carried out at a constant temperature of 277.15 K, approximately initial pressure of 3.6 MPa and a stirrer speed of 800 rpm, with and without the presence of SDS with concentration of 500 ppm. The results show that SDS increases the hydrate formation rate by means of decreasing the gas liquid surface tension, so that the initial rate of hydrate formation and the model kinetic parameter of A_r/RT are increased about 3 and 1.2 times, respectively. Besides, SDS transforms two-step process of methane-ethane hydrate formation to one-step of that. This surfactant also promotes the hydrate growth in the liquid phase and increases the moles of gas consumed, so that the highest amount of gas consumption for hydrate formation belongs to the mixture with 0.3 mole fraction of methane.

1. Introduction

Gas hydrate is a kind of nonstoichiometric clathrate crystals, formed from water and certain natural gas molecules at appropriate pressures and temperatures, which gas molecules are caged inside a network of water molecules linked together through hydrogen bonding. Gas hydrates occur in different structures known as structure I, II and H, which structure is stable depends mainly on the size of the guest molecules (Carroll, 2002; Sloan & Koh, 2008).

There are two opposite directions in the studying of hydrates. While the studies related to the problematic side of hydrates, such as plugging pipeline in the oil industry, are those of trying to find ways of hydrate inhibition, there are some investigations for finding some means for the promotion of hydrate formation as a new natural energy resource and a new means for natural gas storage and transport

(Karaaslan & Parlaktuna, 2000; Sun et al., 2003). But slow formation rate of natural gas hydrate has been considered to be a critical problem hindering the industrial application of gas hydrate (Ganji et al., 2007a). For solving this problem, scientists proposed for using additives such as surfactants as the strong promoters (Ganji et al., 2007a; Karaaslan & Parlaktuna, 2000; Sun et al., 2003; Zhang et al., 2004). Surfactant (surface active agent) is compound whose molecules feature both lipophilic and hydrophilic moieties, i.e., it is amphiphilic. Molecules of surfactant in water tend to aggregate to form various kinds of supramolecular structure, such as spherical and rod-like micelles, multilayer structures and complex biological membranes (Di Profio et al., 2005; Smith et al., 2004).

In recent years, researchers have reported the promotion effect of some surfactants on gas hydrate formation. Surfactant addition decreases the surface tension of the medium in

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which it is dissolved, so that it improves the gas to liquid mass transport. Improved mass transport is believed to enable a surfactant to act as a promoter of gas hydrate formation (Yoslim & Englezos, 2008). In the absence of any additive the hydrate appear as a thin film at the gas/liquid interface, while surfactant is present in the system hydrate crystals are seen in the vicinity of liquid-gas-solid line and in the vertical chamber walls (Gayet et al., 2005; Lee, 2006; Okutani et al., 2008).

Kalogerakis et al. (1993) in investigating the inhibition effects of surfactants on hydrate formation found that at some concentration these additives can promote the process. Zhong and Rogers (2000) reported that sodium dodecyl sulphate (SDS) increases the rate of ethane hydrate formation in a quiescent system by a factor greater than 700, when its concentration is higher than 242 ppm. Lang et al. (2010) have studied the methods of intensification of methane and hydrogen storage in clathrate hydrate such as using of additives.

Gas hydrate formation in general is a multicomponent and multiphase crystallization process (Carroll, 2002; Sloan & Koh, 2008). In the case of gas hydrates formed from a gas mixture, a few researches were conducted for studying the effect of surfactants on their gas hydrate formation rate. Chen et al. (2009) measured phase equilibrium conditions of pure and mixed gas hydrate in CH_4/CO_2+SDS aqueous solution, CH_4/CO_2+SDS aqueous solution+silica sand and $(CH_4+C_2H_6+C_3H_8)$ gas mixture+SDS aqueous solution systems, where SDS was added to increase the hydrate formation rate without evident effect on the equilibrium condition. Yoslim and Englezos (2008) studied the effect of one anionic surfactant on the formation/dissociation of hydrate from a gas mixture of 90.5% methane-9.5% propane at two different surfactant concentrations (645 and 2200 ppm). Their results showed that the addition of 2200 ppm of SDS was found to increase the mole consumption for hydrate formation by 4.4 times (Yoslim & Englezos, 2008). Sun et al. (2003) used an anionic surfactant, a nonionic surfactant, their

mixtures and cyclopentane to improve the hydrate formation of a synthetic natural gas (92.05% methane, 4.96% ethane, 2.99% propane) in a quiescent system. The effect of an anionic surfactant (SDS) on natural gas hydrate formation rate and storage capacity is more pronounced compared to the effect of a nonionic surfactant (DPG). Also cyclopentane could only reduce hydrate formation induction time.

In this study, the effect of SDS on the gas hydrate formation rate of methane/ethane mixtures in different compositions of methane in the mixture have been studied experimentally. Also, chemical affinity has been used for modeling of hydrate formation rate in a constant volume and constant temperature process (Garfinkle, 1999). The model kinetic parameters have been obtained and compared in two various conditions.

2. Experimental

2.1. Apparatus

The experimental data of the hydrate formation of methane-ethane gas mixtures at various mole fractions of methane and ethane were obtained by using an experimental setup. The schematic of set up is shown in Fig. 1. The reactor is a stirred batch reactor with the volume of 600 cm^3, which was capable at operating pressures between 0 to 10 MPa. To enable the heating and cooling of the system, it has equipped with a jacket and the temperature of the reactor was controlled by circulating a coolant. Setup includes cooling bath, heating electric, vacuum pump and separate two reservoirs for gas and liquid storage. The temperature is measured using PT100 thermometers with an accuracy of ±0.1 K. The cell pressure was measured using a pressure transducer with an accuracy of about ±0.1 MPa. The signals of pressure and temperature are acquired by a data acquisition system driven by a personal computer. The cell pressure and temperature data from the acquisition system are saved at specified sampling intervals on the computer hard disk.
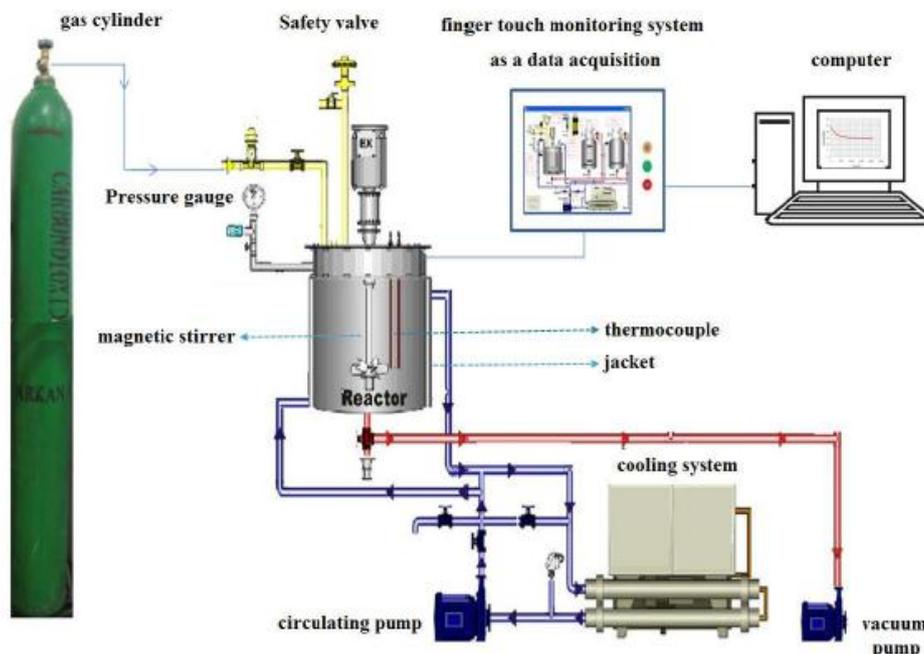
Figure 1. Experimental hydrate formation setup.

2.2. Materials

Methane and ethane (supplied by a technical gas service) with a normal purity of 99.5% were used to form gas hydrate with deionized and distilled water and sodium dodecyl sulphate (supplied by Merck, Germany) with purity of 98% and chemical formula of $C_{12}H_{25}O_4SNa$.

2.3. Procedure

First gas mixtures with experimental fraction of methane/ethane were supplied at the storage cylinder. The hydrate formation reactor was evacuated. Subsequently, 300 cm^3 of deionized and distilled water or aqueous solution of additive with concentration of 500 ppm was charged into the reactor. This concentration of additive has been reported in literature that it was optimum value to obtain the highest rate of hydrate formation of pure methane and pure ethane (Daraee et al., 2011; Ganji et al., 2007a; Ganji et al., 2007b). Therefore, the same value has been used in this work. After reactor charging, it is pressurized to about 0.05 MPa below the equilibrium pressure for the hydrate formation at the specified experimental temperature. The constant temperature bath is turned on and the reactor is allowed to reach the constant experimental temperature. When the solution attained thermal equilibrium, the reactor is pressurized to the experimental pressure by supplying gas form the cylinder. The mixing is started and data collection began. The present experiments were performed at a speed stirrer of 800 rpm and temperature of 277.15 K.

To obtain the amount of gas consumed during the hydrate formation process, the following equation was used:

$$n=PV/ZRT \qquad (1)$$

Where P, V and T are pressure, volume and temperature, respectively. Also R is the gas constant and Z is the compressibility factor obtained from Peng Robinson equation of state.

The pure methane and pure ethane both form sI hydrates, but the mixtures of CH_4-C_2H_6 may form sI, sII hydrates or both of them depending on mole fraction of CH_4 in the mixture. So different experimental points have been selected that they correlate with mixtures at 0.1, 0.2, 0.3, 0.5, 0.68 and 0.8 mole fractions methane and initial pressure of approximately 3.6 MPa, because the mixtures of 0.1, 0.2 and 0.3 C_1 initially form sI hydrates, the mixtures of 0.68 and 0.8 C_1 initially form sII hydrates and the mixture of 0.5 C_1 initially form simultaneous sI and sII hydrates at given pressure (Fig. 2) (Ballard & Sloan Jr, 2001).
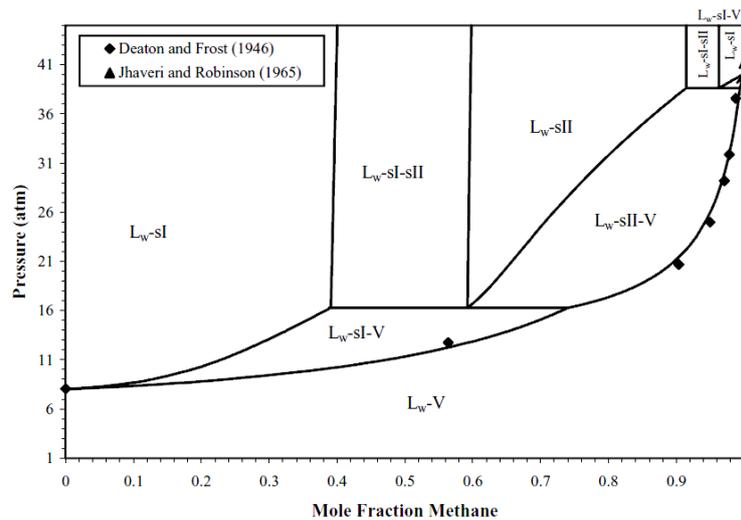
Figure 2. Pseudo-P-x diagram for methane+ethane+water system at 277.6 k (Ballard & Sloan Jr, 2001).

3. Kinetics Modeling

In the previous work, we studied kinetics of methane-ethane hydrate formation by means of thermodynamic natural path in chemical reaction kinetics (Naeiji & Varaminian, 2013). This introduces a conceptual model that defines a macroscopic driving force and uses only the initial conditions (temperature and pressure) and final conditions (equilibrium conditions). The basic idea is that there is only a unique path for each experiment and on this path decays the chemical affinity (Garfinkle, 1999).

The chemical affinity as a generalized force is defined as:

$$A_i = -RT \sum \ln(\zeta_{Q_i}) \qquad (2)$$

Where ζ_Q is a dimensionless measure of the extent of reaction and its value in hydrate formation is determined as:

$$\zeta_Q = \frac{n_A - n_i}{n_A - n_B} = \frac{\left(\frac{P_A}{Z_A}\right) - \left(\frac{P_i}{Z_i}\right)}{\left(\frac{P_A}{Z_A}\right) - \left(\frac{P_B}{Z_B}\right)} \qquad (3)$$

Where A and B is related to initial and final condition of hydrate formation, respectively, i indicates time of process and Z is the compressibility factor for gas.

By calculating extent of reaction (Eq. 3) and chemical affinity at every time (Eq. 2), the model parameters of A_r and t_k can be obtained by following equation:

$$A_i = A_r \ln[\zeta_{t_i}.\exp(1 - \zeta_{t_i})] \qquad (4)$$

Where $\zeta_{ti}=(t_i/t_k)$ and A_r is a constant of proportionality, which it denoted the affinity rate constant. The model in detail has been given in our previous work (Naeiji & Varaminian, 2013).

4. Results and Discussion

The effect of SDS on hydrate formation kinetics of methane-ethane gas mixture with initial concentrations of 0.1, 0.2, 0.3, 0.5, 0.68 and 0.8 mole fractions of methane was investigated. The gas hydrate formation rate curves against time (the variation of pressure in the hydrate formation reactor with time) in both cases of pure water and additive's aqueous solution (500 ppm) are shown in Figs. 3-8. It is obvious that SDS intensively increases the hydrate formation rate and the time to attain steady state condition is decreased in the mixtures, as it was previously found for pure methane and pure ethane in the presence of SDS (Roosta et al., 2013). Moreover, it is found that SDS hasn't any effect on structure and equilibrium condition of hydrate formation because the equilibrium pressure of hydrate formation does not change significantly in the presence of SDS.

It can be seen from Figs. 3-5 that hydrate formation process of the mixtures of 0.1, 0.2 and 0.3 mole fractions methane, which form sI hydrate, has two stages (Naeiji et al., 2014). This behavior can be discussed as follows, at the first stage, methane and ethane form sI hydrate and the end of first stage methane finishes in the gas phase, but driving force is suitable to form ethane hydrate, so the second step is more related to ethane hydrate formation. But, two stages process is not

observed in the presence of SDS. It means, SDS solution causes two-stage process of hydrate formation transforms to one stage hydrate formation by means of making changes in gas-water interface and more gas diffusion into the solution.

At high mole fractions of methane in the mixture, the P-t curve of hydrate formation has one step (Figs. 6-8). The ethane concentration in the gas phase and the fractional filling of cavities by ethane in the hydrate phase intensely decreases by decreasing pressure. So, it seems that at first, ethane tends to form sII hydrate and the mole fraction of methane increases in the gas phase. But driving force is not enough to form further methane hydrate, then the hydrate formation process is reached to its equilibrium conditions.

The obtained experimental results with and without the presence of SDS are given in Tables 1 and 2. SDS is a kinetics surfactant and it has not any effect on structure and equilibrium condition of hydrate formation, as expressed by Chen et al. (2009). But, in the presence of SDS, expected time to attain equilibrium reduces more than 0.5 times and the initial rate of hydrate formation significantly increases about 3 times compared to the system without SDS. A number of researchers have also confirmed that nucleation and growth of hydrate formation usually occurs at the gas-liquid interface (Hirai et al., 1995; Kimuro et al., 1993; Mori, 1998); therefore, it is one of the key factors to promote the hydrate formation kinetics. It has been found from the literature that some surfactants can considerably lower the gas-liquid surface tension; the air-water interfacial tension at 25

°C is lowered up to 48.56 and 25 mN/m in the presence of 500 ppm SDS and 5 ppm LAE2, respectively (Erfani & Varaminian, 2016; Khodaverdiloo et al., 2016; Khosharay, 2013). So, they help lowering the mass transfer resistant and promote hydrate formation kinetics.

It should be notice that the initial rate of hydrate formation has been determined by:

$$rate_{ini} = \frac{\Delta P}{\Delta t} = \frac{P_1 - P_2}{2000} \tag{5}$$

Where P_1 and P_2 are initial pressure of hydrate formation and after 2000 seconds, respectively.

The results of modeling for mixture of 0.1 mole fraction of CH_4 are shown in Figs. 9 and 10. The model parameters have been obtained by plotting A_i versus ln $[\zeta_{ti}.exp(1- \zeta_{ti})]$ (Fig. 9) that their values are given in Tables 1 and 2. The variation of pressure system with time during hydrate formation has been calculated using averaged A_r and t_k for each experiment. It can be seen in Fig. 10 that there is good agreement between calculated results and experimental data with average error of 0.9% at hydrate formation of methane-ethane mixtures. In the presence of SDS, the parameter of A_r/RT is increased about 1.2 times compared to without SDS. Based on the model, A_r is the affinity rate constant and it can be considered as a kinetic parameter. Thus, the process of hydrate formation is facilitated in the presence of SDS. It is in agreement in what was obtained by experimental results.

Table 1. Experimental and modeling results of gas hydrate formation kinetics in pure water.

Mixture (y_1)	Structure	Initial pressure (MPa)	Equilibrium pressure (MPa)	Time to attain equilibrium (Sec)	A_r/RT	Initial rate of hydrate formation*10^{-4} (MPa/sec)
0.1	sI	3.58	0.95	18620	0.435-	2
0.2	sI	3.45	1.21	16100	-0.606	2
0.3	sI	3.58	1.25	24600	-0.452	3
0.5	sI-sII	3.63	1.45	50800	0.365-	2
0.68	sII	3.64	1.75	44000	-0.498	2
0.8	sII	3.62	1.91	23600	-0.362	4

Table 2. Experimental and modeling results of gas hydrate formation kinetics in SDS solution.

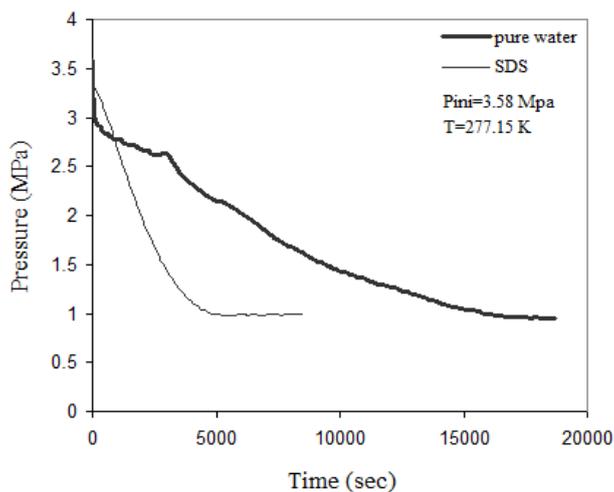| Mixture (y_1)	Structure	Initial pressure (MPa)	Equilibrium pressure (MPa)	Time to attain equilibrium (Sec)	A_r/RT	Initial rate of hydrate formation*10^{-4} (MPa/sec)
0.1	sI	3.59	1.00	8300	-0.536	7
0.2	sI	3.47	1.23	9100	0.812-	5
0.3	sI	3.74	1.20	11800	0.460-	9
0.5	sI-sII	3.68	1.50	9100	-0.445	8
0.68	sII	3.66	1.73	11700	-0.515	11
0.8	sII	3.6	1.90	27600	-0.411	10

Figure 3. Methane/Ethane hydrate formation rate with and without the presence of SDS in 0.1 mole fraction of CH_4.
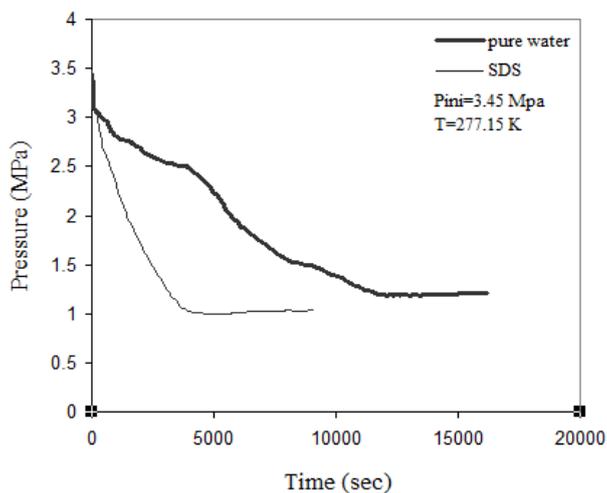

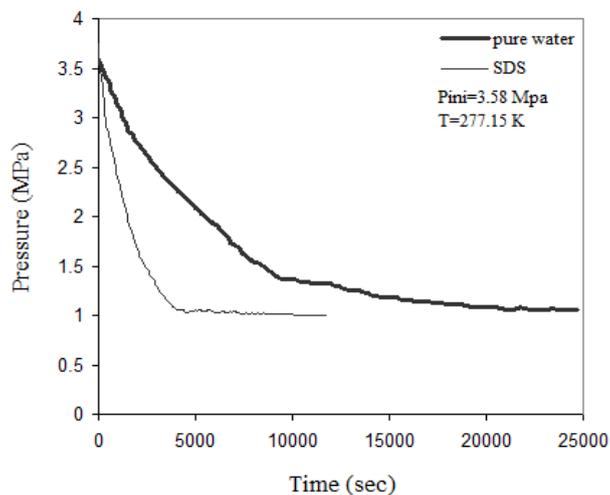**Figure 4.** Methane/Ethane hydrate formation rate with and without the presence of SDS in 0.2 mole fraction of CH_4.

Figure 5. Methane/Ethane hydrate formation rate with and without the presence of SDS in 0.3 mole fraction of CH_4.
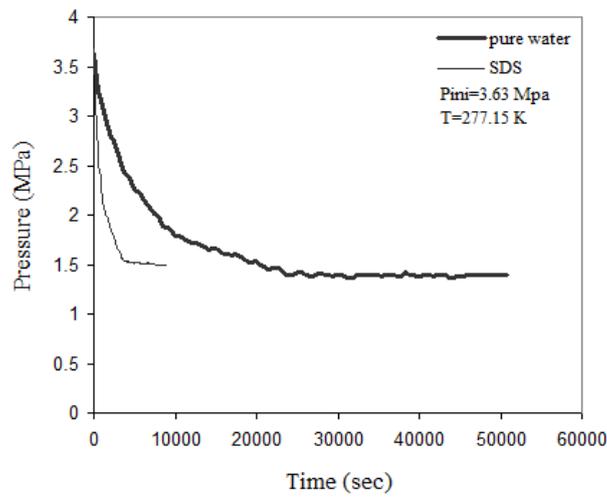
Figure 6. Methane/Ethane hydrate formation rate with and without the presence of SDS in 0.5 mole fraction of CH$_4$.
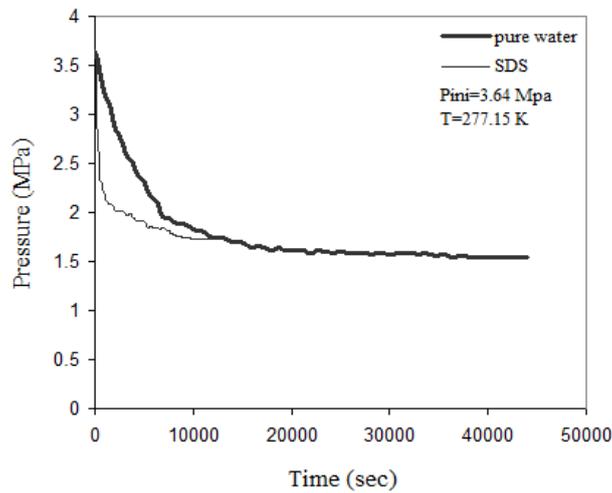

Figure 7. Methane/Ethane hydrate formation rate with and without the presence of SDS in 0.68 mole fraction of CH$_4$.
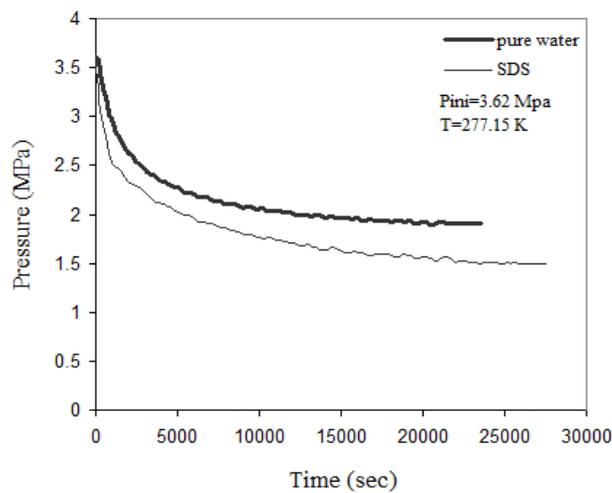

Figure 8. Methane/Ethane hydrate formation rate with and without the presence of SDS in 0.8 mole fraction of CH$_4$.
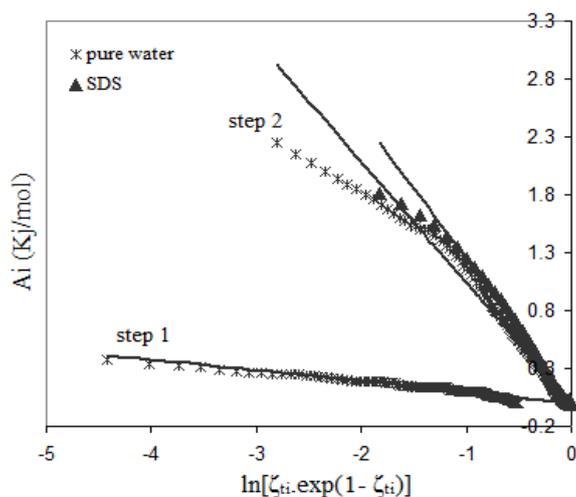
Figure 9. Affinity versus ln $[\zeta_{ti}.\exp(1-\zeta_{ti})]$ for hydrate formation with and without the presence of SDS in 0.1 mole fraction of CH_4 (step 1 and step 2 refer to first and second step of hydrate formation, respectively).
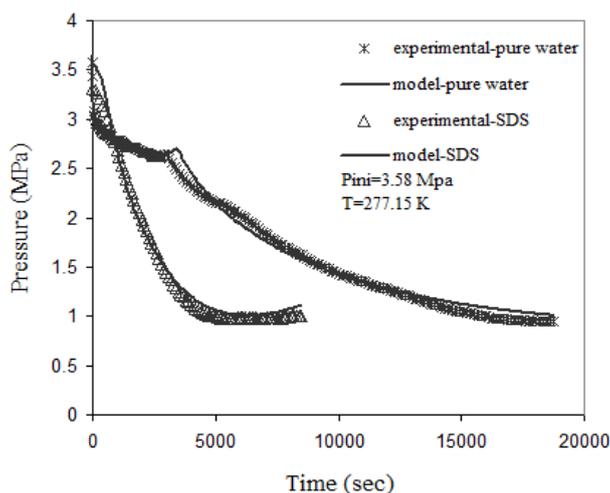

Figure 10. Experimental and calculated results for hydrate formation with and without the presence of SDS in 0.1 mole fraction of CH_4.

4. Conclusion

The effect of anionic surfactants sodium dodecyl sulphate (SDS) with a concentration of 500 ppm on hydrate formation kinetics of methane/ethane gas mixtures has been investigated experimentally and the thermodynamic natural path has also been used for modeling of the hydrate formation rate. Using surfactants the solubility of the gas in water increases and is made a higher mass transfer rate. It is found that SDS hasn't any effect on structure and equilibrium condition of hydrate formation while it can increase the methane/ethane hydrate formation rate effectively, as the initial rate of hydrate formation is increased about 3 times and the expected time to attain equilibrium reduces more than 0.5 times at the presence of SDS.

The model kinetic parameter, A_r/RT, is influenced by SDS as it is increased about 1.2 times. In the case of two-stage processes, SDS solution is also caused two-stage hydrate formation process transforms to one stage. As the final conclusion, the largest amount of gas consumption for hydrate formation was observed at the composition of 0.3 mole fraction of methane.

This surfactant has the excellent promotion effect on hydrate formation rate in total present mixtures of methane and ethane in this work.

Acknowledgements

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Nomenclature

A	Chemical affinity
A_r	Constant of proportionality
C_1	Methane
C_2	Ethane
n	Number of gas moles
P	Pressure
P_{ini}	Initial pressure
R	Universal gas constant
t	Time
t_k	Time required to obtain equilibrium conditions
T	Temperature
V	Volume
y_1	Mole fraction of methane in gas phase
Z	Compressibility factor

Greek Letters

ζ_Q	Extent of reaction based on mole
ζ_t	Extent of reaction based on time

Subscripts

A	Initial condition of hydrate formation
B	Final condition of hydrate formation
i	Index of time

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