

Effect of Different Kinds of Hydrate Promoters on the Kinetics of Methane Hydrate Formation in Methane-Water-Oil System

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ABSTRACT: *In this work, the effect of hydrate promoters on methane hydrate formation in a methane-water-oil system with different initial water cuts from 20 vol% to 100 vol% were studied. For comparison, four promoters based on different promotion mechanisms, sodium dodecyl sulfate (SDS), L-leucine (L-l), tetrabutylammonium bromide (TBAB), and polysorbate 80 (Tween 80) were used. The experimental results show that four hydrate promoters did inhibit the nucleation of methane hydrate in 100 vol% water cut system, but the growth kinetic of methane hydrate was effectively improved compared with the system without a hydrate promoter. The induction time decreased with the increase of initial water cut under the same concentration of hydrate promoter for the methane-water-oil system, and the total methane consumption used for hydrate formation gradually increased with increasing initial water cut (except Tween80). But the current results also show significant improvement in normalized gas consumption per unit of water content with the increase of oil phase volume fraction that upon addition of oil phase the methane dissolution and mass transfer rate in the methane-water-oil system improve further, meaning that the formation rate of methane hydrate is enhanced. Because of the emulsifying property of Tween 80, the emulsion structure of the systems within Tween 80 hindered the hydrate growth process to some extent. Out of the four hydrate promoters used in this study, SDS was found to be most effective in enhancing the formation kinetic of methane hydrate as well as reducing the induction time in the methane-water-oil system under similar conditions.*

KEYWORDS: *Methane hydrate; Hydrate promoter; Induction time; Formation kinetic; Methane-water-oil system.*

INTRODUCTION

Gas hydrates are three-dimensional ice-like crystalline compounds, often found in nature. There are several necessary conditions for hydrate formation: (1) host water

molecules, (2) suitable guest molecules (methane, ethane, propane, carbon oxide, hydrogen sulfide, and so on), (3) suitable high pressure and lower the temperature typically

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in the vicinity of the freezing point of ice [1,2,3]. Since 1930's, gas hydrates have paid more attention, because they can cause blockage in the multiphase petroleum transport pipelines under the deep sea [4]. But later on, realized as a potential energy resource when they show in large chunks in the natural environment. The global estimates on the amount of energy (methane) trapped within natural gas hydrate deposits would be twice that of all fossil fuel reserves available worldwide [5].

However, several problems, such as the slow growth and low storage capacity during the hydrate formation process, are not conducive to the industrial application of hydrates in natural gas storage and transportation [6]. In order to enhance the kinetics of the hydrate formation process starting from bulk water or water-gas surface, the chemical additives commonly referred to as "promoters" have been proposed. Surfactants including anionic, cationic, and non-ionic ones have been reported to promote gas hydrate formation effectively. The first study on the effect of surfactant on the mechanism and kinetics of gas hydrate formation was investigated by *Melnikov et al* [7]. *Kalogerakis et al.* [8] studied Sodium Dodecyl Sulfate (SDS) and other three non-ionic surfactants in influencing the kinetics of methane hydrate formation and demonstrated that SDS had a pronounced effect in increasing the rate of hydrate formation. *Zhong & Rogers* [9] confirmed the remarkable promoting effect of SDS on gas hydrate formation, that is, the rate of gas hydrate formation in a quiescent system could be increased by 700 times. *Lin et al.* [10] investigated the effect of SDS on the formation and dissociation kinetics behavior of methane hydrate, with an emphasis below ice point. They found that a maximum storage capacity of 170 V/V could be achieved at 650 ppm. *Du et al.* [11] reported an experimental study of the kinetics of methane hydrate formation in the presence of ionic surfactants with equal carbon chain lengths, such as SDS, dodecylamine hydrochloride (DAH), dodecyltrimethylammonium chloride (DTAC) and N-dodecylpropane-1,3-diamine hydrochloride (DN₂Cl). It was found that the addition of DTAC had little effect on methane hydrate formation whereas SDS, DAH, and DN₂Cl had pronounced promoting effects. *Wang et al.* [12] investigated the effect of three anionic surfactants with the same carbon chain but different head groups, including dodecyl sulfonate (SDSN), SDS, and sodium dodecylbenzene sulfonate (SDBS) on methane hydrate formation. They found the concentrations of SDSN

and SDS did not show an obvious influence on the promotion effect of methane hydrate formation, while the concentration of SDBS significantly affected the promotion effect because of the micelle effect. *Moraveji et al.* [13] studied the effect of three different classes of surfactants involving anionic (SDS), cationic (hexadecyl trimethyl ammonium bromide (HTABr)), and non-ionic (poly oxy ethylene octyl phenyl ether (TritonX-405)) on methane hydrate formation process and found SDS is more significant than the others.

In addition, amino acids as a new class of hydrate promoters also draw lots of attention, because they can shorten the induction time and quicken the kinetics of hydrate formation without the appearance of foam during the dissociation stage [14]. *Liu et al.* [15] studied the promotion effect of selected natural amino acids on the kinetics of methane hydrate formation and reported a high methane uptake of 143 mg methane/g of solution in presence of 0.5 wt% L-leucine (L-I). *Chen et al.* [16] studied the mechanism of L-I in promoting methane hydrate formation using molecular dynamic simulation. The simulation results show that the hydrophobic group of L-I molecule can be adsorbed by the hydrate interface and disturbed the local water structure near the hydrate surface, which contributed to rapid gas mass transfer rate and promoted the growth of methane hydrate.

Besides the study on the hydrate promoters, the absorption-hydration hybrid method using the oil-water system has received extensive attention recently [17]. The oil phase can be used as the absorbent for natural gas. The oil-water system not only enhances the contact between the gas phase and water phase but also effectively improves the gas storage capacity. There are lots of studies about the induction time and hydrate formation kinetic in pure water, and many researchers also found that some hydrate promoters can inhibit the hydrate nucleation [18-21]. But hydrate nucleation and growth in the water-oil system may not be the same as the pure water, in view of the differences in the heat and mass transfer. *Chen et al.* [22] determined the metastable boundary conditions of water-in-oil emulsions in the hydrate formation region and developed a thermodynamic model. *Ma et al.* [23] studied the hydrate formation kinetics and gas-hydrate equilibrium for a simulated catalytic cracking gas in the water-in-oil emulsion and found that the hydrate formation rate can be enhanced in the water-in-oil emulsion compared to pure water. *Li et al.* [24] investigated the effects of agitation rates, average water droplet diameters at 30 vol% water cut, and

temperatures of 269.15-277.15 K on the induction time and hydrate formation rate. The results show that the induction time initially decreased as the agitation rate increased and then increased at a higher agitation rate, and the hydrate formation rate increased with the increasing agitation rate and decreasing the average diameter and temperature. *Chen et al.* [25] found that subcooling is the major factor that affects induction time in oil-dominated dispersed systems and subcooling of 4 K can be seen as an inflection point.

However, few studies have been conducted on the effect of hydrate promoters on the kinetics of methane hydrate formation in the water-oil system. Therefore, the present work is mainly aimed to study the influence of different kinds of hydrate promoters upon the methane hydrate formation kinetic behaviors in methane-water-oil systems with different initial water cuts from 20 vol% to 100 vol%.

EXPERIMENTAL SECTION

Materials

The methane gas used in the present work was compressed methane gas with high-purity grade (99.995%), purchased from Qingdao Heli Gas Co. Ltd. The deionized water used was prepared by twice distilling in our laboratory with conductivity less than 10^{-4} S·m⁻¹. To eliminate the impact of resin and asphaltene compositions in crude oil, diesel oil with a freezing point of 253.2 K is adopted as the oil phase in this paper. And the composition of diesel oil determined by the use of a crude oil boiling point distillation system is presented in Table 1. The hydrate promoters under test included SDS (99.5% pure), L-1 (98% pure), tetrabutylammonium bromide (TBAB) (99.0% pure), and polysorbate 80 (Tween 80) (pharmaceutical pure) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. and used without further purification. The chemical structures of the mentioned promoters are shown in Fig.1.

Apparatus and procedure

Fig. 1 shows the schematic of the experimental apparatus. The most important parts of the apparatus are a transparent sapphire cell with a diameter of 2.54 cm and an effective volume of 60 cm³, and a steel-made blind cell with an effective volume of 150 cm³. The designed

Table 1: The composition of diesel oil.

component	mol%	wt%
Heptanes	0.50	1.05
Octanes	0.50	0.92
Nonanes	2.81	4.60
Decanes	7.74	11.40
Undecanes	8.74	11.73
Dodecanes	9.95	12.24
Tridecanes	8.74	9.94
Tetradecanes	6.53	6.90
Pentadecanes	4.92	4.86
Hexadecanes	4.72	4.37
Heptadecanes	5.33	4.64
Octadecanes	6.83	5.63
Eicosanes	14.47	10.74
Tetracosanes	15.78	9.77
Octacosanes plus	2.41	1.28
Total	100.00	100.00

maximum pressure of the sapphire and blind cells are 15 MPa and 25 MPa, respectively. A calibrated Heise pressure gauge and differential pressure transducers are used to measure the system pressure with a precision of ± 0.01 MPa. The system temperature is controlled by a humidity chamber with a precision of ± 0.1 K, and the temperature sensor used is a secondary platinum resistance thermometer Pt100.

Before the experiment, the sapphire cell was washed with distilled water and dried, and then loaded with 10 mL of the prepared oil-water mixture. Subsequently, the sapphire cell was installed and connected to the blind cell. These two cells were then purged through vacuuming, replacing with methane, and vacuuming in turn. Afterward, the top valve of the sapphire cell was closed and the blind cell was charged with methane until the desired pressure was achieved. The air bath was set to the experimental temperature. Thereafter, when the sapphire cell system achieved the given temperature and kept at least 1.0 h, the top valve of the sapphire cell was opened, letting the low-temperature methane into the sapphire cell. When the pressure of the sapphire cell reached the specified value, the stop valve was closed again. The stirrer was turned

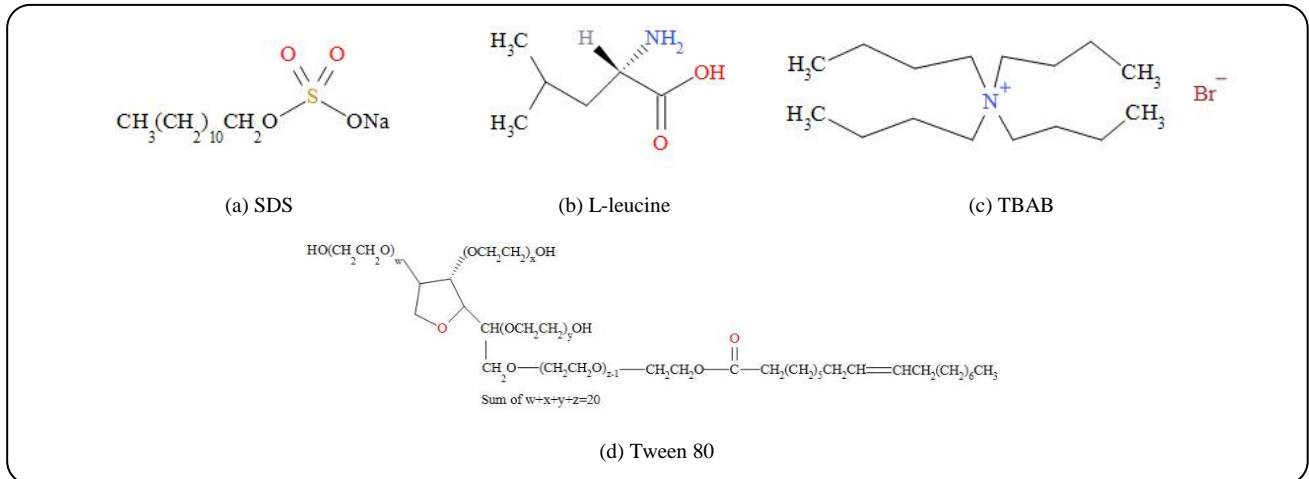


Fig. 1: Chemical structures of four hydrate promoters.

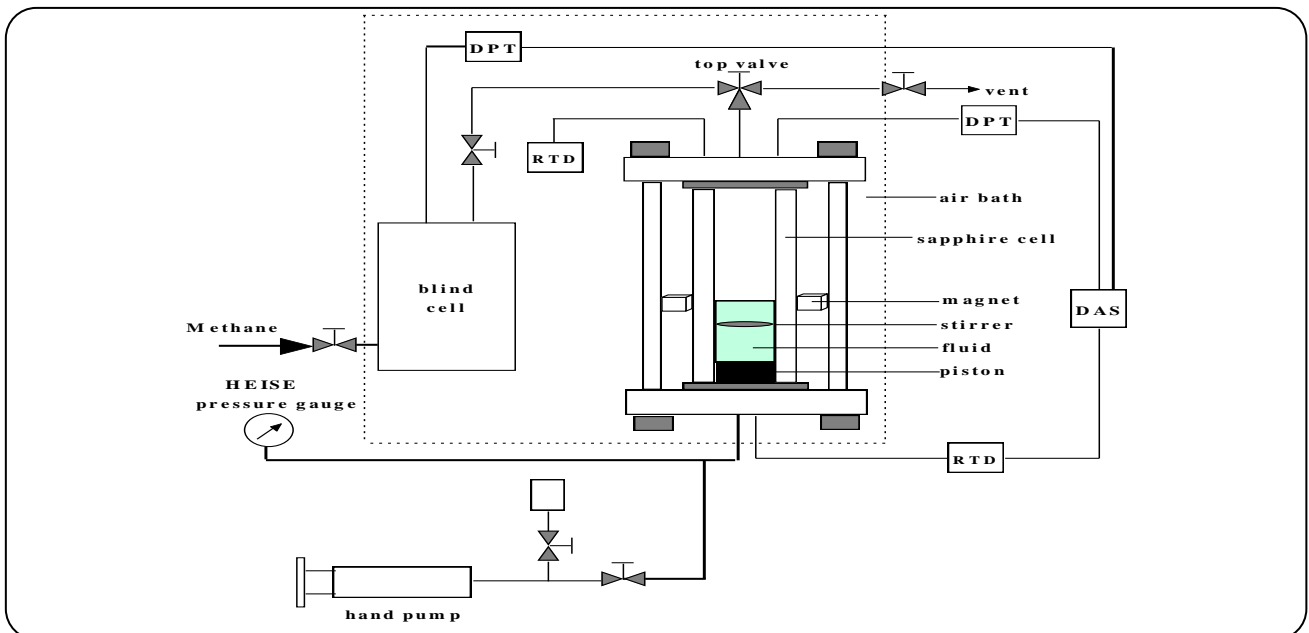


Fig. 2: Schematic diagram of the experimental apparatus.

on with the stirring speed of 60 rpm. The system pressure dropped rapidly to a stable value, which means that the methane gas reached the dissolved equilibrium in the diesel oil. And then this stable stage may be kept for a period until the gas hydrate forms in the system. The time from the injection of methane to the appearance of gas hydrate determined by the naked eye was defined as the induction time. The pressure variation with the time was recorded by the computer. After 1.0 h from the beginning of the hydrate formation, the experiment was manually stopped and the temperature of the air bath was set to 298.2 K. In this work, the temperature and initial pressure of all the experiments were performed at 276.2 K and 7.00 MPa.

Data analysis

It was reported that the solubility of methane in pure water is much less than that in the oil by several orders of magnitude [26]. Therefore, the solubility of methane in water was neglected in this work. The methane solubility in oil, S , is defined as,

$$S = \frac{n_g}{n_g + n_o} \quad (1)$$

Where n_g represents the methane moles dissolved in the oil, and n_o is the mole number of diesel oil. The methane

solubility S can be determined by gas-liquid equilibrium calculation using the Patel-Teja equation of state [27]. So, Eq. (1) can be rewritten:

$$n_g = \frac{S n_o}{1 - S} \quad (2)$$

The mole number of diesel oil is determined by:

$$n_o = \frac{m_o}{M_o} \quad (3)$$

where m_o represents the mass of diesel oil measured in the experiment, and M_o is the molecular weight of diesel oil.

When the methane hydrate appears, the total mole number of methane gas in the sapphire cell contains the residual gas phase and is dissolved in the diesel oil,

$$n_1 = \frac{P_1 V_g}{Z_1 R T} + \frac{S_1 n_o}{1 - S_1} \quad (4)$$

Where P_1 , T , V_g , and R denote the system pressure at the beginning of hydrate formation, system temperature, gas phase volume in the sapphire cell, and the universal gas constant. Z_1 and S_1 represent the gas compressibility factor and methane gas solubility in the oil at P_1 and T . The gas compressibility is calculated by the Peng-Robinson Equation of State (PR EOS) [28].

With the formation of methane hydrate in the cell, the gas molecules transfer from the gas phase to the hydrate phase, resulting in the pressure drop. Therefore, the gas mole number at time t including the residual gas phase and in the oil can be calculated by

$$n_t = \frac{P_t V_g}{Z_t R T} + \frac{S_t n_o}{1 - S_t} \quad (5)$$

Where P_t , Z_t , and S_t are the pressure at time t , compressibility factor at P_t and T , and methane solubility in the diesel oil at P_t and T , and the unit of time is min in this study. Thus, the mole number for the gas hydrate formation can be calculated by Eq. (4) and Eq. (5),

$$\Delta n = n_1 - n_t \quad (6)$$

RESULTS and DISCUSSION

Induction time and gas consumption in the water-oil system

The induction time is an important parameter for assessing the performance of hydrate promoters and

can be measured by both visual observation and pressure drop profile methods [29]. The induction times of hydrate formation in this paper were determined by visual observation. Considering the randomness of hydrate nucleation, each experiment was repeatedly carried out three times and the average value and standard deviation were calculated. n_{15} , n_{30} , and n_{50} were defined as the gas consumption when the times were 15 min, 30 min, and 50 min after the appearance of methane hydrate in the methane-water-oil system, respectively. Table 2 shows the values of induction time and n_{15} , n_{30} , and n_{50} at different experiments.

As shown in Table 2, the induction time showed a trend of decrease with increasing initial water cut, in which the induction time varied from 12.25 min to 4.75 min. Four hydrate promoters did inhibit the nucleation of methane hydrate in 100 vol% water cut system, and the induction times were longer than the system without a promoter. But compared with the water-oil system at a given initial water cut, the induction time could be shorted considerably by adding hydrate promoters except Tween 80. For example, when methane hydrate formed in 0.05% SDS solution, the induction times reduced to only 9.42 min, 8.08 min, and 5.58 min for 20 vol%, 50 vol%, and 80 vol%, respectively. The phenomenon suggested that the addition of SDS, L-1, and TBAB can significantly promote the hydrate formation in the water-oil system. The obvious difference between methane hydrate formation was ascribed to the promoting mechanism of hydrate promoter. Firstly, some surfactants (SDS/Tween80) can effectively reduce the gas-liquid interface tension and then increase the solubility of gas at the gas-liquid interface, resulting in the rapid formation of methane hydrate [9, 30]. Secondly, formed porous methane hydrate can improve the transfer of methane during the hydrate formation process. But for the system in the presence of Tween 80, there is an obvious difference, showing that the induction times prolong to 80.65 min, 27.17 min, and 20.28 min for 20 vol%, 50 vol%, and 80 vol%, respectively. Because of the emulsifying property of Tween 80, the water-oil system exhibits the stable emulsion characteristic under agitation effect, hindering the hydrate formation.

Effect of oil phase on the kinetics of Methane hydrate formation

Fig. 3 shows the pressure and gas consumption with time in the methane-water-oil system without promoter addition.

Table 2: Induction time and gas consumption of methane hydrate formation with different promoter solutions at 276.2 K and initial pressure of 7.00 MPa.

No.	Watercut (vol%)	Promoter	Induction time (min)		Gas consumption (mmol)		
			Av ^a	Sd ^b	n_{15}	n_{30}	n_{50}
1	20	-	12.25	2.15	2.8615	3.8425	4.8528
2	50	-	11.50	2.05	7.4126	9.8965	10.0529
3	80	-	10.15	1.01	10.7241	13.0487	15.0563
5	100	-	4.75	0.80	11.7222	14.7188	16.4172
6	20	0.05%SDS	9.42	1.20	10.3847	12.0562	15.6895
7	50	0.05%SDS	8.08	1.15	19.1652	31.7524	43.3208
8	80	0.05%SDS	5.58	0.88	37.8125	51.1367	57.6247
9	100	0.05%SDS	4.25	1.38	45.8086	66.0895	74.7828
10	20	0.5%L-1	11.17	1.05	4.6412	5.7625	7.0968
11	50	0.5%L-1	9.37	0.75	5.6231	7.4632	12.5021
12	80	0.5%L-1	5.25	0.90	6.6785	11.3124	29.7105
13	100	0.5%L-1	5.05	1.50	13.2851	19.7250	33.8285
14	20	1.0%TBAB	10.34	2.55	3.9114	4.5627	5.5468
15	50	1.0%TBAB	10.12	2.20	9.6354	19.2789	22.3617
16	80	1.0%TBAB	8.75	1.38	9.7258	24.2057	31.7804
17	100	1.0%TBAB	7.25	1.44	11.0025	26.7563	38.0627
18	20	1.0%Tween80	80.65	5.23	1.6425	2.7125	3.5680
19	50	1.0%Tween80	27.17	3.88	1.3837	2.7718	2.1384
20	80	1.0%Tween80	20.28	3.05	9.9785	12.3068	13.6842
21	100	1.0%Tween80	6.25	1.75	15.7599	22.5526	22.7807

a) Av: average value; b) Sd: standard deviation

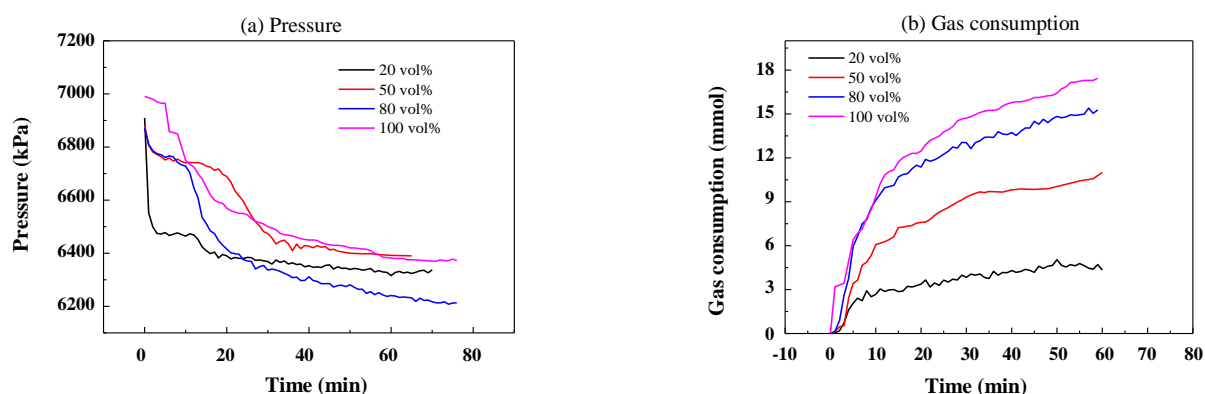


Fig. 3: The pressure and gas consumption as a function of time for four initial watercut systems without promoter at 276.15 K and 7.0 MPa.

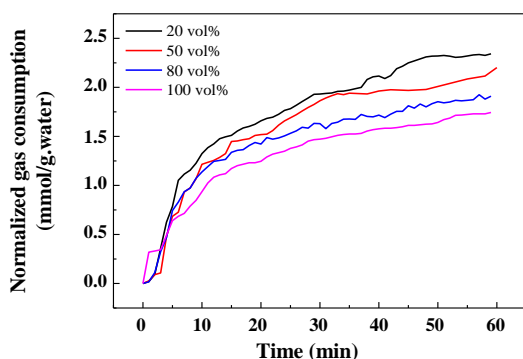


Fig. 4: Normalized gas consumption per water content for four initial water cut systems without promoter at 276.2 K and 7.0 MPa.

It can be seen from Fig. 3(a) that the whole hydrate formation process at four different water cuts systems exhibits a similar extent, consisting of two obvious stages: gas absorption equilibrium and methane hydrate formation. During the hydrate growth period, a rapid pressure decrease was observed as the gas was consumed. The more the gas molecules consume, the faster the hydrates grow. Therefore, it can be found that from Fig. 3(b), the hydrate formation rate increases with the increase of water cut in the water-oil system. For example, the methane consumptions are 2.8615 mmol, 7.4126 mmol, 10.7241 mmol, and 11.7222 mmol for four initial water cuts systems without hydrate promoter addition when the hydrate forms 15 min later. This phenomenon can be contributed that the greater water cut can provide a larger contact area between gas and water similar to the studies by *Mu et al* [31].

The normalized gas consumption per water content for four initial water cut systems was calculated and presented in Fig 4. As shown in Fig. 3 and Fig. 4, the variation of normalized gas consumption is different from the gas consumption and normalized gas consumption increases with decreasing initial water cut at the same time. Upon the addition of the oil phase, the methane dissolution and mass transfer rate in the methane-water-oil system improves further, meaning that the formation rate of methane hydrate is enhanced to some extent. For example, the normalized gas consumption was 1.9325 mmol/g, 1.8632 mmol/g, 1.6305 mmol/g, and 1.4718 mmol/g for the initial water cuts from 20 vol% to 100 vol%.

Effect of Initial Watercut on the Kinetic Behavior of Hydrate Formation

Fig. 5 gives the gas consumption with four kinds of

hydrate promoters at four initial water cuts, and the detailed gas consumption at different stages were shown in Table 2. As can be seen from Fig. 4, the gas consumption increase with increasing water-cut and SDS exhibits the most significant promoting effect for methane formation. n_{50} for a system with 0.05% SDS, were 15.6895 mmol, 43.3208 mmol, 57.6247 mmol, and 74.7828 mmol with increasing water-cut. But the promoting effect of L-1 and TBAB obviously decreased. n_{15} , n_{30} , and n_{50} of L-1 and TBAB were lower than SDS. For example, n_{50} of L-1 were just 7.0968 mmol, 12.5021 mmol, 29.7105 mmol, and 33.8285 mmol for initial water cuts from 20 vol% to 100 vol%. But it appears different trend for Tween 80, the gas consumption rate followed roughly the order of

$$100 \text{ vol\%} > 80 \text{ vol\%} > 20 \text{ vol\%} > 50 \text{ vol\%}.$$

Effect of Promoter Type on the Kinetic Behavior of Hydrate Formation

Fig.6 shows the evolution of the methane consumption during the hydrate growth period at different water cuts systems, which can also be seen in Table 1. As can be seen from Fig. 6, all four hydrate promoters can effectively promote the methane hydrate formation in 100 vol% system compared to the system without a hydrate promoter. For example, the gas consumption at 50 min was 74.7828 mmol, 33.8285 mmol, 38.0627 mmol, 22.7807 mmol, and 16.4172 mmol for the systems within 0.05% SDS, 0.5% L-1, 1.0% TBAB, 1.0% Tween80 and without hydrate promoter, respectively. Meanwhile, SDS has the best promotion effect for methane hydrate formation than other hydrate promoters, meaning the higher methane consumption at the same experimental time. It is noteworthy that n_{15} , n_{30} , and n_{50} for SDS were three times higher than that obtained in the system without hydrate promoters. For example, n_{15} , n_{30} , and n_{50} of a system with 20 vol% can reach up to 37.8125 mmol, 50.1367 mmol, and 57.6247 mmol. However, Tween80 does not exhibit an obvious promotion effect for the methane hydrate formation in the water-oil system, and even shows an inhibition effect in the 20 vol% system. n_{15} , n_{30} , and n_{50} in the 20 vol% system with Tween 80 were just 1.6425 mmol, 2.7125 mmol, and 3.5680 mmol, approximately 1/3 lower than that of the water-oil system with no promoter addition. This phenomenon can be attributed to the different formation mechanisms of different hydrate promoters. Because of the emulsifying properties of Tween80, the

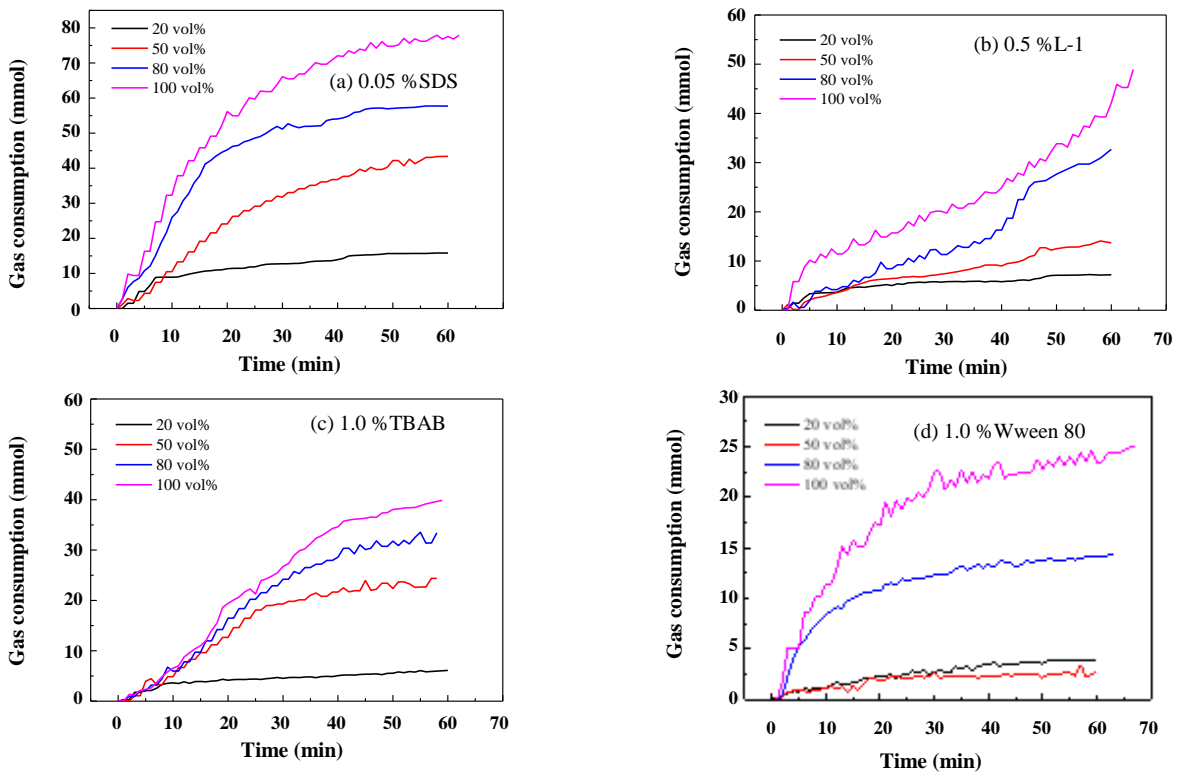


Fig. 5: Cumulative methane uptake as a function of time in the presence of different kinds of hydrate promoters at three initial water cuts.

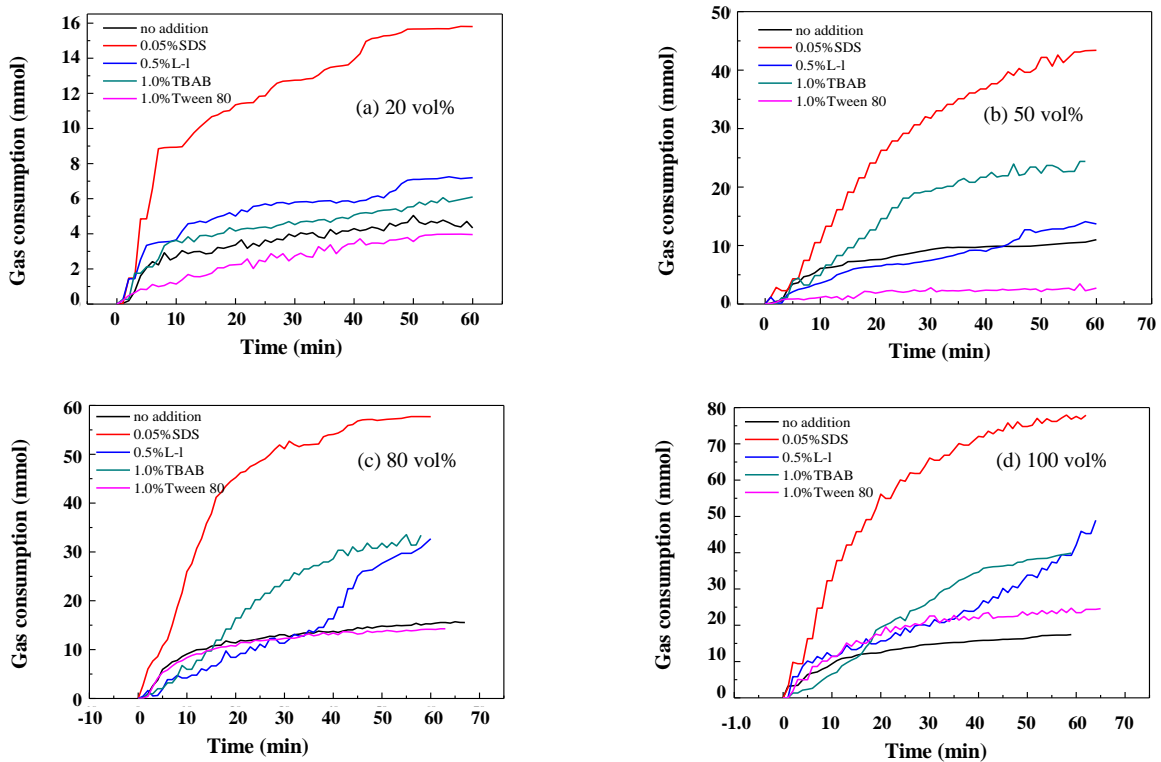


Fig. 6: The evolution of the methane consumption during the hydrate growth period at three initial water cuts.

the methane-water-oil system presents obvious structure characteristics of oil-in-water emulsion or water-in-oil emulsion. The hydrate formation needs to break the existing emulsion structure, so Tween80 has an inhibition effect on the hydrate formation process to some extent.

CONCLUSIONS

The promotion effects of different kinds of hydrate promoters (SDS, L-I, TBAB, and Tween 80) on methane hydrate formation in a methane-water-oil system with three initial water cuts from 20 vol% to 100 vol% were studied in the present work. All four hydrate promoters were found to inhibit the nucleation of hydrate in 100 vol% system, but the growth kinetic of methane hydrate was effectively improved compared with the system with no addition. For the water-oil system, the induction time decreased with the increase of initial water cut under the same concentration of hydrate promoter. Different from the variation of total gas consumption with the initial water cut, the normalized gas consumption per unit of water content increased with increasing oil phase volume fraction. In addition, the hydrate promoters expect Tween 80 can significantly improve the hydrate formation process in the water-oil system. In general, SDS exhibits the most significant promotion effect for methane hydrate formation in the methane-water-oil system than the others.

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