

Zhen PAN, Yi WU, Liyan SHANG, Li ZHOU, Zhien ZHANG

Progress in use of surfactant in nearly static conditions in natural gas hydrate formation

© Higher Education Press 2020

Abstract Natural gas hydrate is an alternative energy source with a great potential for development. The addition of surfactants has been found to have practical implications on the acceleration of hydrate formation in the industrial sector. In this paper, the mechanisms of different surfactants that have been reported to promote hydrate formation are summarized. Besides, the factors influencing surfactant-promoted hydrate formation, including the type, concentration, and structure of the surfactant, are also described. Moreover, the effects of surfactants on the formation of hydrate in pure water, brine, porous media, and systems containing multiple surfactants are discussed. The synergistic or inhibitory effects of the combinations of these additives are also analyzed. Furthermore, the process of establishing kinetic and thermodynamic models to simulate the factors affecting the formation of hydrate in surfactant-containing solutions is illustrated and summarized.

Keywords gas hydrate, kinetic hydrate promoter, compounding, model, surfactant, mechanism

1 Introduction

Natural gas hydrate, which is also known as combustible ice, is a nonstoichiometric compound with an appearance

similar to that of ice crystals [1]. When water molecules and methane are subjected to high-pressure and low-temperature conditions, the water molecules capture gas molecules by forming a cage structure bridged by hydrogen bonds. As the cage structure continues to grow, the two further aggregate into gas hydrates [2–6]. Natural gas hydrate is one of the most abundant clean energy sources in the world, which has a higher energy storage capacity than direct energy sources such as petroleum. One cubic meter of natural gas hydrate can contain up to approximately 170 m³ of methane gas [7,8]. In recent years, natural gas hydrate has been used for natural gas storage and transportation, saving a great deal of money. Additionally, natural gas hydrate has shown a superior technical potential compared to liquefied natural gas (LNG) [9,10]. At the same time, the water and carbon dioxide produced by the combustion of natural gas hydrate are relatively less polluted to the atmospheric environment than those produced by other energy sources [11]. Therefore, increased research into natural gas hydrate could be of great significance for solving energy problems and achieving sustainable development [12,13].

As petroleum reserves continue to decrease, new commercially viable energy sources are being sought for. The emergence of natural gas hydrate could provide a new direction for the energy industry. It can be applied in many industrial fields such as seawater desalination, gas storage and transportation, refrigeration, and the selective separation of gases [14]. Therefore, natural gas hydrate should be rationally developed and utilized to achieve the sustainable development of natural resources.

At present, the storage and transportation of natural gas hydrate are being extensively investigated by scholars. The natural gas hydrate storage and transportation technology has developed rapidly in recent years. The huge gas storage capacity and mild gas storage conditions of natural gas hydrate facilitate its industrial production, which has good application prospects. Because hydrate forms slowly under natural conditions and is difficult to mine, the development of methods to increase the rate of hydrate formation is key

Received Sept. 29, 2019; accepted Feb. 26, 2020; online Jul. 31, 2020

Zhen PAN, Yi WU
College of Petroleum Engineering, Liaoning Shihua University, Fushun 113001, China

Liyan SHANG (✉), Li ZHOU
College of Chemical Engineering and Environmental Engineering,
Liaoning Shihua University, Fushun 113001, China
E-mail: lyshang2011@126.com

Zhien ZHANG
William G. Lowrie Department of Chemical and Biomolecular
Engineering, The Ohio State University, Columbus, OH 43210, USA

to current hydrate storage and transportation problems [15]. The formation process of natural gas hydrate for industrial application is mainly in a condition of strong forced convection in order to efficiently form it, where the influences of fluid flow may be of primary factor. The main difficulties in the preparation of natural gas hydrate in the laboratory are the slow formation rate and the poor stability of gas hydrate [16]. The nucleation process of natural gas hydrate is stochastic [17]. The hydrate forms preferentially at the gas-water interface; the formed hydrate film slows the diffusion of the hydrocarbon gas, thereby hindering further hydrate formation [18]. Accordingly, various methods for destroying hydrate films and accelerating hydrate nucleation have been proposed, including both physical acceleration methods and chemical methods involving the addition of an active agent. Experimental results have shown that the existing physical methods, including stirring [19] and spraying [20], have higher requirements than chemical methods in terms of the experimental equipment required, and various technical and safety problems associated with these methods remain to be solved. The use of a reactor incorporating stirring or water spraying was found to increase the production cost of the test device, complicating the process and reducing the total hydrate formation to some extent. In contrast, the addition of a surfactant is an effective and convenient method for forming natural gas hydrate using a relatively simplified apparatus [21]. Reducing the operating costs of the natural gas hydrate formation process is beneficial in terms of achieving a sustainable development strategy [22]. The addition of a low concentration of surfactant can reduce the duration of the hydrate induction period. Some surfactants may increase the hydrate nucleation rate and the gas storage capacity of the hydrate, making the gas hydrate more efficient and safer for storage and transportation, respectively. The development of surfactants that can reduce equipment pollution and economic loss caused by foam generated from hydrate dissociation is also highly desired [23,24].

Therefore, to develop efficient natural gas resource storage and transportation strategies, potential surfactants for gas hydrate applications should be studied systematically and in depth. At the same time, research into the similarities and differences among the reaction mechanisms of different surfactants is of great practical significance. In this paper, the works focusing on the formation of hydrates in surfactants in nearly static conditions were reviewed, and the reaction mechanisms, types, structures, concentrations, and electrical properties of the various surfactants used in the hydrate formation systems were analyzed. Besides, differences in the carbon chain lengths and electrical properties of the surfactants were discussed. Moreover, the use of surfactants in systems containing pure water, brine, other additives, and porous media was considered, along with other complex systems. Furthermore, kinetic and thermodynamic models for predicting

the growth of hydrate in surfactant-containing systems were summarized.

2 Effect of the surfactant hydrate reaction mechanism

In pure water, the formation and accumulation of natural gas hydrate is a long and complicated process. In a stationary (non-stirred) system, the water solubility of the gas molecules is limited, resulting in a high gas concentration at the interface, which in turn causes the hydrate to form preferentially at the interface and ultimately hinders hydrate formation [25,26]. This hydrate layer hinders the further progress of the reaction, limiting hydrate production. The effect of various reaction parameters on the formation of hydrate in stirred pure water systems was reported by Zhang et al. [27]. When the temperature of the system dropped to a certain value, the hydrate formed rapidly (Fig. 1). Low temperature is a necessary condition for the formation of hydrates. When a surfactant is added, the surfactant molecules can aggregate to form micelles, biofilms, or complicated multilayered structures in the liquid phase, which in turn promote the formation of hydrates. The mechanism of hydrate formation has been thoroughly studied. However, controversy remains regarding the mechanism of the formation of natural gas hydrate in the presence of various surfactants.

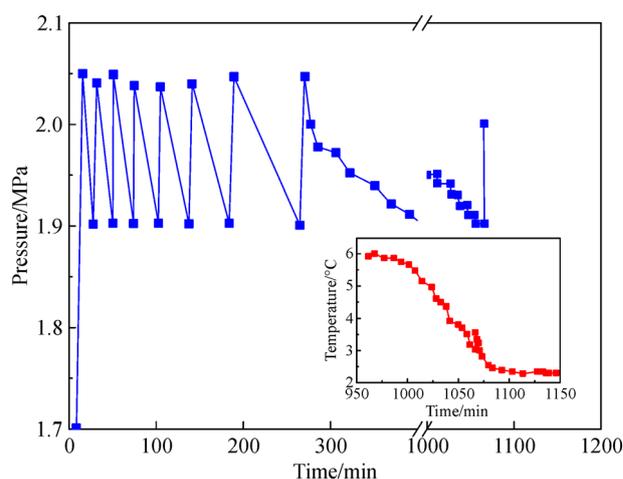


Fig. 1 Variation of pressure and temperature with time in the formation of hydrate in 3.5°C pure water (adapted with permission from Ref. [27]).

Initially, scientists could only speculate on the mechanism of hydrate formation. In 1993, Kalogerakis et al. [28] reported that the presence of surfactants strongly affected the gas solubility and hydrate formation rate, and the hydrate particles formed in the presence of different surfactants had different characteristics. In 2012, Lo and coworkers [29] drew similar conclusions, suggesting that

the adsorption of surfactants on the surface of hydrates promotes further hydrate formation by reducing the interfacial tension of the hydrates as well as increasing the dissolution of gas molecules. In 2013, Tang et al. [30] reported that surfactants accelerate the growth rate of hydrates via solubilization effects.

Mel'nikov et al. [31] proposed another point of view in 1998. They suggested that laboratory-generated hydrate crystals were not dense membranes, but instead migrated from the aqueous phase to the wall of the vertical reactor, where they grew by capillary force to maintain gas-water contact within the hydrate layer. In 2010, Tajima et al. [32] used a digital camera to observe the morphology of the hydrate formed in the presence of a surfactant, which was rough and uneven. They asserted that the hydrate film was relatively loose. The presence of surfactants caused the surface of the film to collapse, allowing continuous contact between the gas and the solution and thus accelerating the continuous formation of hydrate. However, their experiments were carried out using a spiral agitator, and the renewal of the hydrate layer was greatly affected by the agitation, leading to dynamic interface in the study. Okutani et al. [33] specifically examined the morphology of hydrates formed in surfactant-containing systems in order to verify crystal growth. They found that a hydrate layer consisting of dendritic material was formed on the surface of the solution. The dendritic structure does not directly indicate that the capillary force accelerates the rate of hydrate formation. When the hydrate is formed, the water molecules are forced and aggregate along specific channels. To more intuitively illustrate the capillary action in the solution, in 2017, Asaoka et al. [34] added colored water into the reaction vessel for observation of the surfactant. As shown in Fig. 2, they claimed that the height of the hydrate was consistent with the level reached by the water due to capillary action. Since the hydrate system was contained in a closed reactor environment, this phenomenon was unlikely to occur without a surfactant, which

confirmed the fact that the main driving force for the growth of the hydrate in the vertical direction was the capillary force. To account for growth in the horizontal direction, they proposed various potential mechanisms such as concentration diffusion, micelle formation, and the deposition of sodium dodecyl sulfate (SDS) crystal deposition.

Zhong and Rogers [35] and Irvin et al. [36] proposed another mechanism for the role of SDS for gas hydrate formation in 2000. They reported that the surfactant SDS could promote the formation of hydrates via the formation of micelles in the reaction solution. The presence of micelles would accelerate the dissolution of the gas molecules enclosed in the micelles, with water molecules condensing on the surface of the micelles. As the number of micelles increased, hydrates would be formed in a cage structure and uniformly deposited at the bottom of the reactor, as depicted in Fig. 3. Zhang et al. [37] reported that the surfactant could form a cluster structure in the solution that could enclose low-solubility gas molecules in the hydrophobic groups and evenly distribute the hydrophilic groups. By reducing the surface tension of the solution, the surfactant could increase the solubility of the gas molecules, thereby accelerating the progress of the reaction. Bhattacharjee et al. [38] found that the formation of micelles not only improved the solubility of the gas but also played a role in rapidly increasing the nucleation of the hydrate.

Di Profio et al. [39] held the opposite view regarding the ability of the surfactant SDS to form micelles in hydrate formation. They believed that it was impossible for micelles to form in the solution under the hydrate formation conditions, and reported that no significant drop in the critical micelle concentration (CMC) value occurred in the hydrate formation experiment. Zhang et al. [40] pointed out that SDS micellization could not occur below the normal Krafft point. Therefore, even in a high-pressure methane environment, no SDS micelles would be

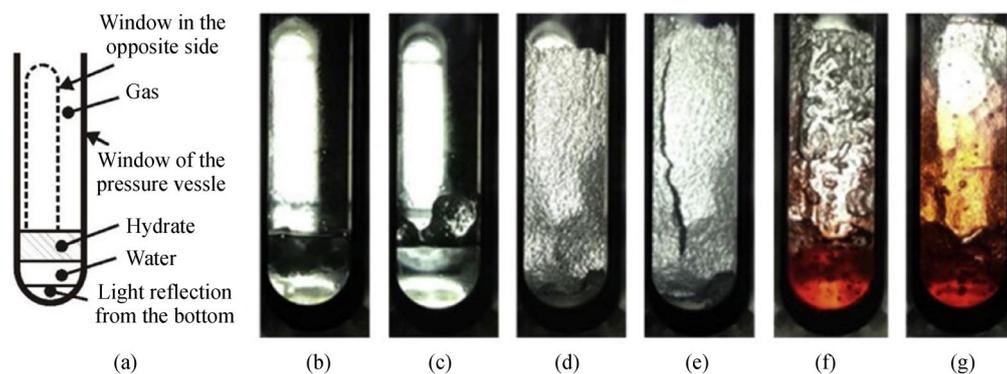


Fig. 2 Growth behavior of hydrates on the glass wall as seen from the side (adapted with permission from Ref. [34]). (a) schematic view of the view from the window. Elapsed time after gas injection: (b) 1 min, (c) 90 min, (d) 164 min, (e) 192 min, (f) 195 min, and (g) 200 min.

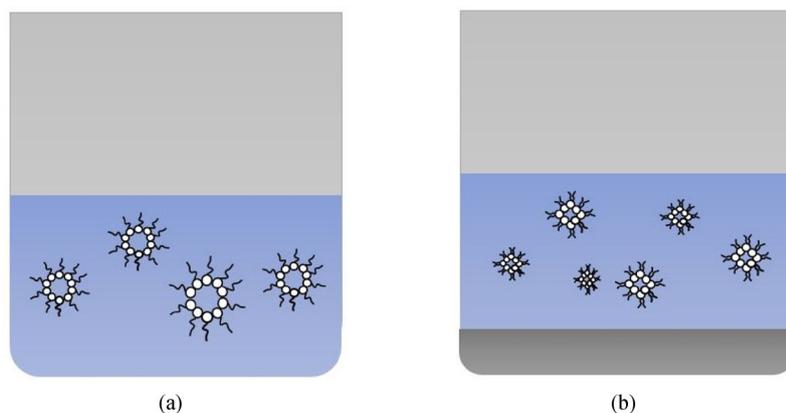


Fig. 3 Micellar system.
(a) Before hydrate formation; (b) after hydrate formation.

present in the aqueous phase. Instead, they asserted that SDS promoted the formation of gas hydrates by reducing the energy hindrance in the nucleation process by adsorbing onto the hydrate core. In contrast, Choudhary et al. [41] noted that the Krafft point temperatures reported in the literature were typically measured at atmospheric pressure, and thus were not applicable to the environment of the surfactant in hydrate formation experiments and could not be used to determine whether micelles were formed under these conditions. Thus, the possibility of micelle generation in the gas hydrate formation process could not be ruled out.

In view of the above information, surfactants are able to increase the production rate of hydrates mainly via a reduction in the tension between the water-air interface that allows the gas to diffuse more easily into the aqueous phase, although it remains unclear whether this reduction results from altered gas solubility, capillary forces, or the formation of micelles. It remains unclear why high rates of hydrate formation are always maintained in static systems containing SDS. According to experimental results using different surfactants, surfactants can influence the rate of hydrate formation via multiple mechanisms. The effects of surfactants on the substances in the reactor can be divided into vertical effects and horizontal effects. In addition to surface tension at the gas-water interface, multiple forces, including capillary forces, van der Waals forces, and micelle forces, may exist between the gas and water molecules.

In the reaction system, two or more interactions have resulted in the different nucleation modes for the hydrate. Taking a single hydrate molecule as an example, in the horizontal direction, the interactions consist of surface tension (mainly at the liquid surface), hydrogen bonding, and van der Waals forces. In the vertical direction, they include gravity, buoyancy, and capillary forces. As for the direction of the micellar forces to which the hydrate molecules are subjected, the current research has not yet determined, and further judgments need to be made

according to the specific experimental conditions. Furthermore, dynamic processes related to capillary action can be captured directly using digital devices, but the effects of micellar agglomeration and intermolecular forces are difficult to observe visually. Most research into the potential role of micelles has been inferred from other measurable physical quantities and experimental phenomena. In future, the microscopic phenomena of hydrate formation should be further studied to provide data supporting the various mechanisms above.

Some researchers gradually began to infer the fundamental reaction mechanism of surfactants through experimental phenomena. Meng et al. [42] analyzed the measured critical micelle concentration in different surfactants and proposed reaction mechanisms for hydrate formation. They concluded that the mechanism by which polyoxy ethylene lauryl ether (AEO) and dodecyl trimethylammonium bromide (DTAB) promoted hydrate formation was mainly related to micelles. In the presence of AEO and DTAB, the hydrate was concentrated at the bottom of the reactor and formed gradually with the further diffusion of gas into the solution. However, images of the reaction captured using a high-speed camera showed that the solution in the reaction system flowed upward along with the hydrate void. This mode of flow indicated that SDS used as a surfactant acts by capillary action to shorten the induction period of the reaction and promote the formation of hydrates. Qin et al. [43] selected a representative anionic surfactant, SDS, in the gas hydrate formation experiments. The induction time and production rate of methane hydrate formation in systems containing 10 mmol/L or 0.3 mmol/L SDS were analyzed, and the critical micelle concentration of SDS at 8°C was measured using the surface tension method. The results showed that when the concentration of the surfactant exceeded its CMC of 2.5 mmol/L, its hydrate promoting effect was gradually strengthened.

Unlike in the study by Meng et al. [42], the above analysis of the effect of SDS is based on the assumption

that the Krafft point temperature in the SDS system is 8°C. Concentrations above and below the critical micelle concentration were selected. However, the temperature of the reactor during the test is quite different from the Krafft point temperature, and the effect of this difference on the formation of the hydrate cannot be ignored. The hydrate formation process is an exothermic process, and the resulting temperature change will affect the solubility of the surfactant and gas in the solution to some extent. Since the hydrate is formed under low-temperature and high-pressure conditions, the temperature change caused by the formation of the hydrate has little effect on the temperature of the overall system, and changes in the mechanism due to the fact that sharp fluctuations in the temperature can be discarded. At the same time, the rate of hydrate formation is also affected by the temperature, pressure, and concentration of the active agent. We believe that the actual Krafft point temperature should be measured more accurately irrespective of whether surfactant SDS exerts a micelle force or whether the Krafft point temperature can be used as a basis for judging the formation of micelles. If the Krafft points obtained under the relevant experimental conditions are not far apart, there may be no micelles in the SDS solution. The new methods such as microscopic observation techniques and molecular simulations can be used to analyze the mechanism by which surfactants promote hydrate formation in the future, which in turn could provide new practical methods for engineering applications.

3 Effect of surfactants in different reaction systems

Many researchers are interested in the application of

surfactants to promote the formation of hydrates, which can be used for the mass storage and safe transportation of natural gas. Others have focused on the transportation of natural gas via pipelines. In this context, surfactants have been used to achieve smooth operation, transport along long-distance pipelines, and reduce the formation of foaming [44,45]. In this review, the rate of hydrate formation using a surfactant as promoters for the former application is focused on. Natural gas hydrates formation via a slow process under natural conditions, typically requires more than 20 h [46]. In recent years, various additives have been reported to improve the formation rates and gas content of gas hydrates, including natural gas hydrate [47]. Many types of surfactants are available with a wide variety of properties. Therefore, in this section, different type of hydrate promoters are presented.

3.1 Effects of surfactants on hydrate formation in pure water

Surfactants are generally amphiphilic, with a hydrophilic group at one end and a hydrophobic group at the other; these two moieties are connected by a covalent bond [48]. The surfactants can be located at the surface of the solution, which affects its surface properties [49]. The formation of hydrates occurs via contact between gas molecules and water molecules. Hydrates are initially formed at specific locations at the gas-liquid-solid interface where there is direct contact between the natural gas, solution, and wall, and then gradually grow toward the gas-liquid interface and continue to grow upward along the wall, eventually forming a gas hydrate layer as exhibited in Fig. 4. As the gas molecules continue to enter the water layer where they are incorporated into natural gas hydrate molecules, it becomes more difficult for further gas

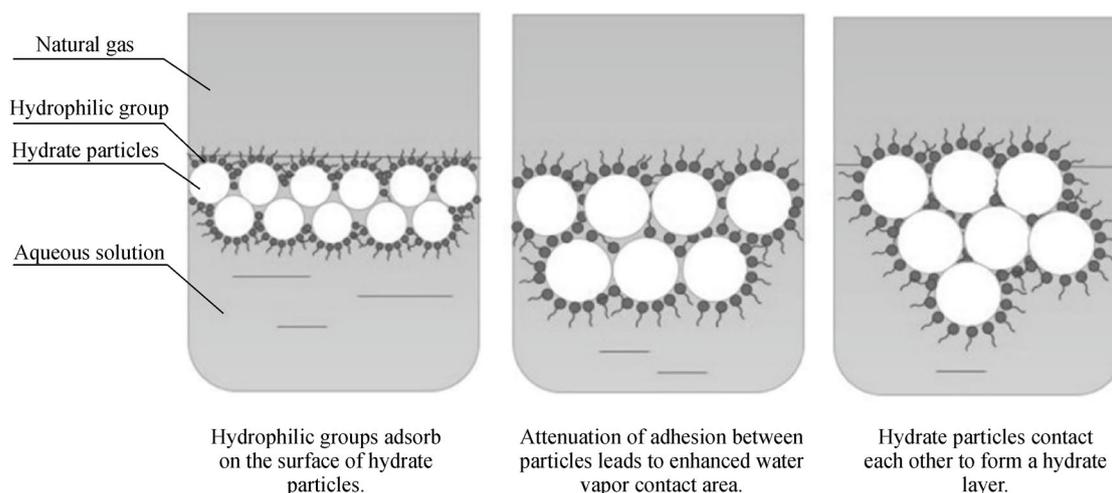


Fig. 4 Process of adsorption of surfactants on surfaces of hydrate particles permission (adapted with from Ref. [51]).

molecules to cross the gas-water interface, resulting in an unsatisfactory rate of hydrate formation in a pure water environment [50,51]. The addition of a chemical agent such as a surfactant can change the state of the gas-water interface to facilitate the entry of gas molecules, which in turn accelerates the formation of hydrates.

3.1.1 Effect of surfactant type

Surfactants can be classified as anionic, cationic, or nonionic based on their electrical properties [52,53]. Each class of surfactants plays different roles in promoting the formation of hydrates [54]. However, all types of surfactants have effects on the hydrate storage capacity and formation rate. Table 1 summarizes previous studies involving the use of different surfactants in hydrate formation. Meng et al. [42] used the anionic surfactant SDS, cationic surfactant DTAB, and nonionic surfactant AEO as examples. The molecular structures of the three surfactants are displayed in Fig. 5. SDS was found to have the best hydrate-promoting performance, and demonstrated great advantages in increasing the gas content and shortening the induction time compared to those of the other two surfactants. Zhou et al. [55] used the surfactants SDBS (anionic), CTAB (cationic), and P123 (nonionic) to enhance the formation of gas hydrates, and CTAB exhibited the best promotion performance. Karaaslan and Parlaktuna [56] studied the anionic surfactant LABSA, cationic ETHOXALATE, and nonionic DAM, and found that the anionic surfactant LABSA had accelerated hydrate formation under all tested experimental concentrations. They also confirmed that poly(vinyl alcohol) (PVA) and polyoxyethylene(5) nonylphenyl ether (Igepal-520) promoted the formation of hydrates [57].

According to previous experimental studies, the hydrate promotion of anionic surfactants are better than other active agents. The effect of surfactants on the formation of natural gas hydrates may be related to their charge. Ionic surfactants contain terminal groups that can be ionized and obtain a positive or negative charge in the presence of water molecules in a pure aqueous solution. A hydrated ion H_3O^+ (or OH^-) is also formed in the ionization of the surfactant, enhancing the activity of the solution itself. When natural gas molecules enter the liquid layer, natural gas hydrates are more likely to form in the acidic (or basic) solution than in neutral pure water. However, for nonionic surfactants, the molecules themselves cannot become charged. The influence of the ionic force on hydrate formation is subtle; it is very difficult to identify precisely the effect of the large-scale use of surfactants in synthesizing hydrates. However, the understanding of the effect of surfactant charge could be further developed and applied in the selection of surfactants. Complex and versatile physicochemical reactions occur in the formation of hydrates. Most current research assumes that anionic surfactants have the best effect in terms of hydrate

promotion, but there are only few potential mechanisms to explain this phenomenon.

Additionally, due to the difference in molecular structure, the same type of surfactants has different effects on hydrate formation. Wang et al. [58] studied three anionic surfactants, SDS, SDSN, and SDBS, which have the same carbon chain but different head groups. SDSN and SDS shortened the induction time of the reaction, and their hydrate formation was basically completed within 40 min. However, several hours were required using the same concentration of SDBS. This study demonstrated that the hydrate-promoting effect of surfactants is closely related to the molecular structure of surfactants. Okutani et al. [59] compared three surfactants with the same head group, sodium tetradecyl sulfate (STS), sodium hexadecyl sulfate (SHS), and SDS. SDS, which has the shortest alkyl chain, exhibited the fastest hydrate formation rate at a concentration of 0.1 wt%, and achieved the highest gas content. STS achieved similar results to those of SDS at a lower concentration of 0.01 wt%. SHS, which has the longest carbon chain, had a weaker effect on the rate of hydrate formation. Daimaru et al. [60] studied the effects of three analogous surfactants with different carbon chain lengths, C4, C12 (SDS), and C18. The rate of hydrate formation increased using all three of these anionic surfactants, of which, C4 had the greatest acceleration effect, increasing the hydrate production rate 5-fold compared to the case of the surfactant-free solution. Zhao et al. [61] observed the formation of hydrates in three alkyl polyglycolide (APG)-based surfactants, APG06, APG0810, and APG1214, as shown in Fig. 6. As the length of the carbon chain increased, the effect of the surfactant on the formation of hydrates was also enhanced. APG06 had the shortest carbon chain, which allowed the hydrate to form a monomolecular film at the gas-liquid interface. This film hindered the continued growth of the hydrate crystals and reduced the rate of hydrate formation or even stopped the reaction.

The different relationships between the carbon chain length and the hydrate promotion effect observed for anionic and nonionic surfactants can be attributed to differences in the hydrate formation mechanism. The nonionic surfactant APG forms micelles in the reaction system via the aggregation of the carbon chains of the APG molecules. As the carbon chain increases, the formation time of micelles increases. The increased micelle concentration enhances the contact between water molecules and the gas molecules, accelerating hydrate formation. For sodium sulfate-based anionic surfactants, the reaction system mainly relies on the capillary force; the solution is drawn upward along the wall of the reaction vessel, which accelerates the contact of water molecules with gas molecules and preferentially generates hydrates at the three-phase gas-liquid-solid junction. No micelles are present in the solution system, and excessively long carbon chains may directly hinder the effect of the capillary

Table 1 Summary of different types surfactants on hydrate formation

Number	Surfactant	Type	Concentration range/(wt%)	Conclusion	Reference
1	APG	nonionic	0–0.16	Among them, at higher concentrations (0.08–0.16 wt%), the formation rate of hydrate in APG solution was very fast, the induction time was shortened to about 15min, and the induction time at 0.02 wt% in SDBS system was 25–30 min	[54]
	SDBS	anionic	0–0.2		
2	SDS	anionic	0.01, 0.02, 0.05, 0.07, 0.09, 0.12	All three reduced the phase equilibrium point and induction time of the hydrate	[77]
	CTAB	cationic	0.02, 0.03, 0.05, 0.07, 0.09		
	P123	nonionic	0.01, 0.03, 0.05, 0.09		
3	SDS	anionic	0.03, 0.05, 0.1	SDS effectively accelerated the rate of hydrate formation at three concentrations. LABS increased the rate of hydrate formation at 0.05 wt% and 0.1 wt%, but decreased at 0.03 wt%. In addition, CTAB and ENP promoted the hydrate formation at 0.01 wt%, and weaken at 0.03 and 0.05 wt%	[72]
	LABS	anionic			
	CTAB	cationic			
	ENP	nonionic			
4	SDS	anionic	0.03, 0.05	Compared to pure water, the induction time of hydrate formation in the presence of surfactant was reduced.	[106]
	HTABr	cationic	0.03, 0.05, 0.07		
	Brij-58	nonionic	0.03, 0.05, 0.07		
5	PVP	nonionic	0.005, 0.01	PVP showed a dual effect of promoting and inhibiting hydrate nucleation in the test	[68]
6	SDS	anionic	0.008, 0.0125, 0.1, 0.2, 0.4	SDS at 0.1 wt% or above was quite effective for increasing hydrate formation rate and gas conversion rate. STS was less effective to promot hydrate formation	[59]
	STS	anionic	0.0007, 0.0035, 0.01, 0.04, 0.06		
	SHS	anionic	0.0003, 0.001, 0.002, 0.004, 0.016		
7	LABSA	anionic	0.005, 0.01, 0.1, 1	With the addition of LABSA, the rate of hydrate formation increased; low concentrations of ETHOXALATE also increased the rate of hydrate formation. DAM has the weakest promotion ability of the three	[56]
	DAM	cationic			
	ETHOXALATE	nonionic			
8	Aerosol-OT/AOT	anionic	0.038	According to the analysis of infrared spectrum, SDS had obvious acceleration effect on hydrate formation, and CPC had no effect on its formation	[53]
	SDS	anionic			
	CPC	cationic			
9	SDS	anionic	0.5	Upon addition of the surfactant, a higher hydrate density was obtained and hydrate formation was accelerated	[6]
	PEG400	cationic			
10	SDS	anionic	0.05, 0.07, 0.09, 0.11	As the amount of surfactant increased, the rate of hydrate formation increased and the induction time decreased. The effect of anionic SDS on hydrate formation rate was the most significant, and cation HTABr had the greatest influence on induction time	[52]
	HTABr	cationic			
	Tritonx-405	nonionic			
11	SDS	anionic	0.1–0.4	When using SDS and SDSN, all reaction times were reduced to less than 40 min. While using SDBS, it took several hours to achieve pressure balance	[58]
	SDSN	anionic			
	SDBS	anionic			
12	SDS	anionic	0, 0.1, 0.2, 0.3	The addition of DTAC had little effect on the formation of methane hydrate. SDS, DAH and DN ₂ Cl had obvious promoting effects on methane hydrate formation. SDS had a higher hydrate formation rate than the other two, but at 0.1 and 0.2 wt%, DN ₂ Cl had a better methane uptake than SDS	[78]
	DAH	cationic			
	DTAC	cationic			
	DN ₂ Cl	nonionic			

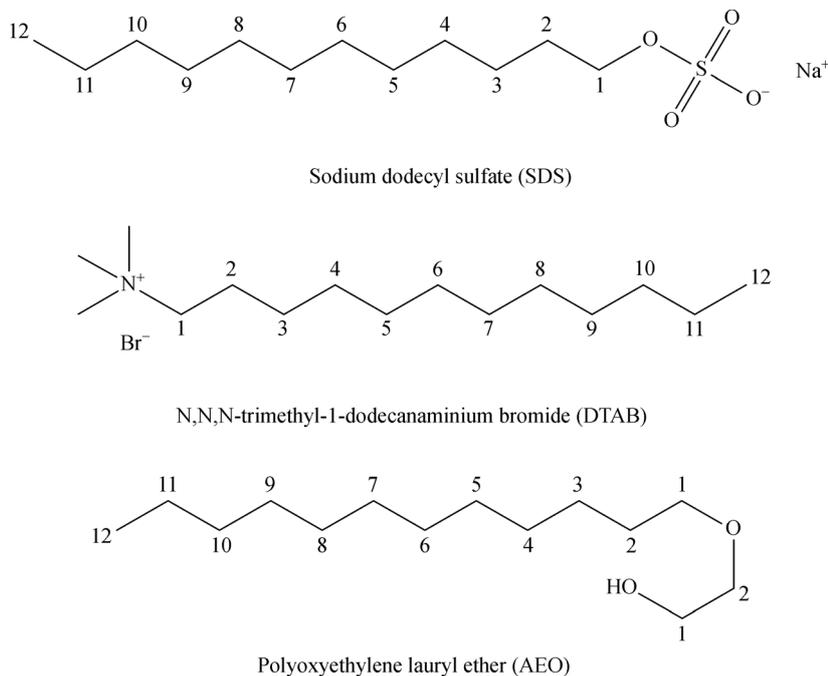


Fig. 5 Molecular structures of three surfactants.

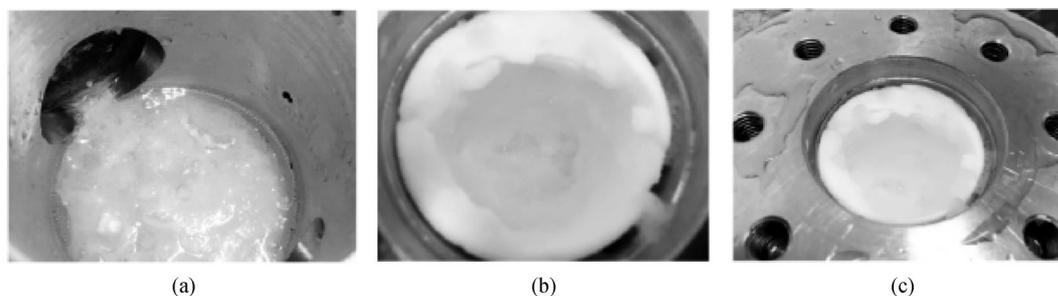


Fig. 6 Hydrate formation in (a) APG06, (b) APG0810, and (c) APG1214 aqueous solutions (adapted with permission from Ref. [61]).

force. Therefore, compared to sulfate-based surfactants with longer alkyl groups, such as C12, C18, the surfactant with the short C4 carbon chain showed the most obvious enhancement of hydrate formation.

3.1.2 Effect of surfactant concentration

The measurement of the effect of the concentration of the surfactant is relatively straightforward compared to the evaluation of the effects of other parameters [62]. In addition to ionic (cationic or anionic) and nonionic surfactants, the fluorocarbon surfactant Intechem-01 (FC-01) [63], gemini surfactants Dowfax 8390 [64], Dowfax C6L and Dowfax 2A1 [65], and castor-oil-derived sodium (ricinoleic acid) methyl ester sulfonate (SMES) [14], have also been studied. Surfactants based on a wide variety of structures are available, and have great performance differences which affect various aspects of the formation

of natural gas hydrates to different degrees. When a surfactant is combined with the other additive, hydrate formation can occur under multiple macroscopic conditions, such as induction time and virtual hydration number.

Khokhar et al. [66] used 0.1% PVP solution as a promoter in an investigation of the gas storage capacity of hydrates. They found that the storage capacity of the resulting hydrate was greater than that of the hydrate synthesized in PVP-free conditions (pure water). On this basis, Liu et al. [67] used 99.9% pure PVP and investigated the formation of hydrates in PVP solutions with mass fractions of 0%, 0.5%, and 1%. The pressure and temperature changes in the reactor were recorded in real-time using a magnetically coupled stirring device. The results indicated that the optimal PVP solution had a mass fraction between 0 and 1%; such a solution could accelerate the formation of hydrates without changing the thermal conditions. Interestingly, in an experiment and

simulation conducted by Ke et al. [68], PVP played a dual role, both inhibiting and promoting the hydrate nucleation rate. They hypothesized that the occurrence of this dual role may be due to the change in the degree of subcooling of the reaction system, which in turn changes the docking orientation of PVP. However, this assumption required further verification. The maximum hydrate-promoting effect occurred at a specific surfactant concentration. As the surfactant concentration is increased above this value, the accumulation of excess surfactant in the solution may hinder hydrate formation, leading to a decreased rate of hydrate formation. With increasing PVP concentration, the position of each phase in the solution system changed, decreasing the recognition ability of the surfactant molecule, which reduced the formation rate or even caused destruction of formed hydrate. Scholars try to study the optimal concentration range of surfactants. Depending on the experimental conditions, the concentration can be roughly divided into low concentration, medium concentration, and high concentration regions, and the effects of the active agents can be studied in each concentration region.

ZareNezhad et al. [69] used the effective diffusion coefficient to evaluate the hydrate growth process. At an SDS concentration of 0.05 wt%, the effective diffusion coefficient and conversion rate of the gas molecules were high. This demonstrated that 0.05 wt% was the optimal concentration for the synthesis of the hydrate. The R^2 obtained from the measurement was 0.983, further indicating that the measurement method was accurate [70]. Ganji et al. [71,72] prepared SDS solutions in the laboratory at concentrations of 0.03, 0.05, and 0.1 wt%, respectively. As shown in Fig. 7, at an SDS concentration of 0.05 wt%, the rate of formation of the hydrate was more than 35 times greater than that of the SDS-free solution, and the induction time was effectively shortened, with the hydrate reaching a stable state in approximately 1 h.

However, at 0.03 wt%, the hydrate formation rate was faster, but the induction time was longer than that at 0.05 wt%.

Notably, the optimum concentration of SDS in the above studies differed. The optimum concentration in the former was 0.05 wt%, while in the latter the hydrate formation rate at 0.03 wt% was considered most desirable. In this regard, this is due to the different experimental conditions used. The formation of hydrates is mainly affected by temperature and pressure. When hydrate formation is studied under different experimental conditions, the conclusions will inevitably differ. In actual engineering production, the use of surfactants can increase the rate of hydrate formation, enabling the storage and transportation of natural gas. The environmental conditions of the natural gas should be analyzed in detail to determine the optimal active agent concentration and treatment scheme.

In addition to common ionic and nonionic surfactants, researchers have explored novel surfactants with special properties, as shown in Table 1. Surfactant APG [73] is known as a “green surfactant,” and has attracted extensive research interest. In Ref. [61], the optimum hydrate formation rate was observed at an APG0810 concentration of 1500 mg/L, while APG0810 concentrations higher than 2500 mg/L led to prolonged induction and slowed hydrate formation. Shi et al. [74] investigated the fluorocarbon surfactant FC-01. The new active agent exhibited a high surface activity, which effectively reduced the interfacial tension, and was chemically stable. As shown in Fig. 8, the lowest surface tension achieved using FC-01 was 17.1 mN/m at 25°C and a mass fraction of 0.08%, while the minimum surface tension of SDS was 34 mN/m. These results demonstrated that FC-01 promoted hydrate formation more effectively at the same concentration.

Sun et al. [75,76] discussed the formation of hydrates in several different reaction systems consisting of stirred pure water, the anionic surfactant SDS, and the nonionic

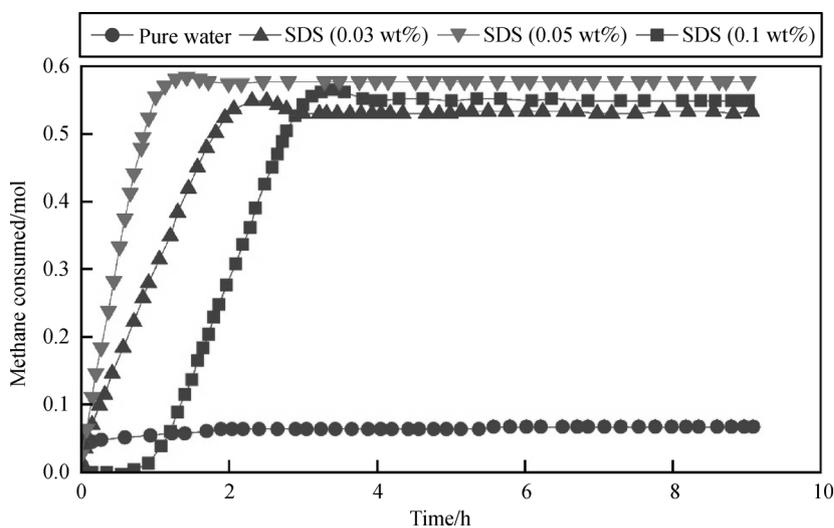


Fig. 7 Storage capacity of methane hydrate with and without SDS (adapted with permission from Ref. [71]).

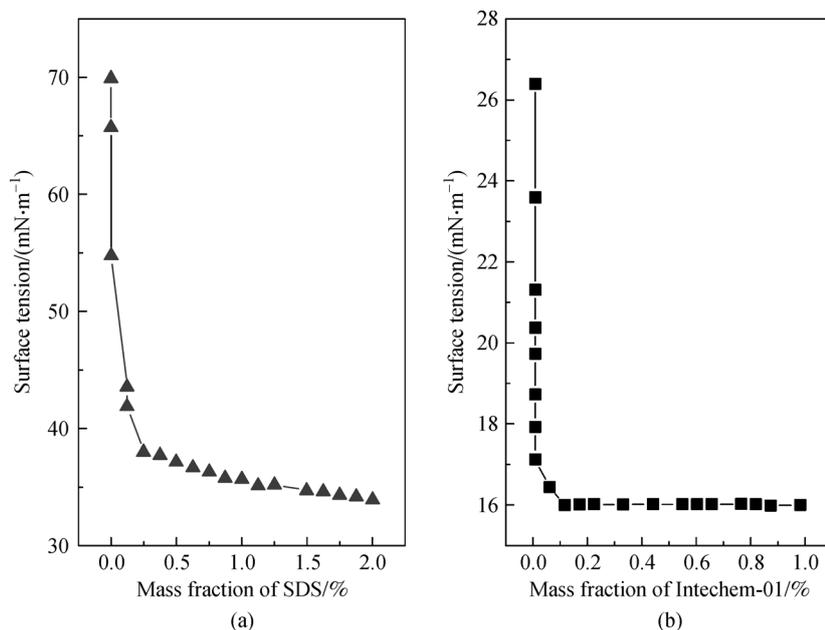


Fig. 8 Surface tension at the same concentration at 25°C. (a) Pure SDS solution; (b) pure Intechem-01 solution (adapted with permission from Ref. [74]).

surfactant diphosphoglycerate (DPG). Compared to those of the hydrates formed using agitation systems, the effective diffusion coefficient and gas molecule conversion rates were found to be high in DPG. However, the main effect of SDS was to shorten the induction time. When the two surfactants were combined, the induction time was also shortened, but the hydrate generated had a lower gas storage capacity than that of SDS. Zhou et al. [77] experimentally studied the effects of surfactants SDBS, CTAB, and P123 on hydrate formation. SDBS was found to have the greatest promotion effect at 700 mg/kg. The effect was comparable to those of CTAB at 300 mg/kg or P123 at 500 mg/kg. Du et al. [78] compared surfactants in terms of their effect on the induction time, hydrate synthesis rate, and hydrate gas content. The addition of dodecyl trimethylammonium chloride (DTAC) had little effect on the formation of methane hydrate, while SDS, dodecyl amine hydrochloride (DAH), and N-dodecylpropane-1,3-diamine hydrochloride (DN₂Cl) significantly promoted methane hydrate formation.

Some natural gas reservoirs in the natural environment consist of multiple strata. New surfactants have been used in various fields in recent years, and the surfactants available for hydrate research have also gradually become more diverse. Studies of chemical agents that promote hydrate formation are not limited to ionic or nonionic surfactants. Storage and transportation technology should be incorporated with this new knowledge regarding the characteristics and effects of surfactants on hydrates in order to develop new ideas and directions for natural gas exploitation.

3.2 Effects of surfactants on hydrate formation in brine

Generally, the main role of the surfactant is to reduce the surface tension of the liquid surface so that gas molecules can easily enter the solution to accelerate the reaction, which changes the morphology of hydrate formation and provides conditions for continuous chain reactions. Most salts dissociate into their ionic components in water, which reduces the solubility of gas molecules in aqueous solution and increases the tendency of gas molecules to be adsorbed in the hydrate cavity [79].

Eastman et al. [80] studied the growth of methane hydrate in 0–10 wt% NaCl solution in the presence of the surfactants sodium dodecyl sulfate, potassium lauryl sulfate, and sodium laurate. As the salt concentration was increased, the conversion rate of the hydrates and the rate of total hydrate formation for all the surfactants used in the experiment decreased significantly. Zhang et al. [81] performed hydrate formation experiments in SDS solutions containing NaCl with the mass fractions 0%, 0.5%, 2%, and 3.5% respectively. They reported that NaCl enhanced the reduction of the surface tension of the gas and liquid by SDS. The surface tension reduction effectively accelerated the nucleation process of the hydrate and shortened the induction time. Delroisse et al. [82] studied the addition of NaCl to the cationic surfactant DA 50. The adsorption of the surfactant at the gas-water interface increased in the presence of NaCl, accelerating the formation of the hydrate.

According to the findings of the above researchers, salt compounds can promote the formation of hydrates at low

concentrations. The salt concentration can be analyzed as a function of the surfactant concentration. As the concentration of salt increases, the promotion of hydrate formation by the surfactant is enhanced [83]. After the ionic compound is dissolved, free positive and negative charges are formed in the aqueous solution, which affects the activity of the aqueous solution. Therefore, further studies of salts dissolved in water should be conducted, including experiments on salts that dissociate in aqueous solution.

3.3 Effects of surfactants compound with porous media

The addition of surfactants accelerates hydrate formation. However, hydrate dissociation produces foam, which limits the application of surfactants. Researchers have found that combining porous media and surfactants can simultaneously improve heat transfer and mass transfer conditions in the reaction and increase the rate of hydrate formation [84]. In nature, hydrates are mainly located in sea sediments. The environmental conditions in these sediments are complex, and differ from those in the formation of natural gas hydrates in free surface [85]. The pore structure of the sediment has similarities with porous media. Studies of hydrate formation in porous media have demonstrated that their porosity provides a larger nucleation area for hydrates, and they can transmit and release the reaction heat to the outside effectively, improving the heat transfer conditions in the reaction. In the absence of surfactants, the formation of hydrates is limited by mass transfer, and hydrates form preferentially at the gas-water interface, preventing contact between the gas and water [36]. Therefore, the addition of a surfactant can effectively improve the mass transfer conditions in the reaction by reducing the surface tension of the liquid and reducing the gas-liquid mass transfer resistance. Thus, it is of practical significance to explore the effects of combined use of surfactants and porous media in hydrate formation [86,87].

In the analysis of samples obtained from the natural hydrate layers, more than 90% of the hydrates are located in the voids of the rock mass [88]. First, researchers analyzed the formation of hydrates in porous media systems [89]. Cha et al. [90] proposed that water molecules could adsorb on the pore surfaces of porous media, and that the probability of contact between gas and water molecules was improved. Based on theoretical analysis, Xu et al. [91] used nanoscale silica gel for phase equilibrium experiments. Porous media of 20.872 μm partial size were found to accelerate the rate of hydrate formation. The above studies proved that different types of porous media could be used, and when they had appropriate size conditions, they all exhibited a promoting effect on hydrate formation.

Dicharry et al. [92] found that in porous silica gels with pore sizes of 30 nm and 100 nm, the use of surfactants had a positive effect on the kinetics and productivity of hydrate

formation. Nesterov et al. [93] added the nonionic surfactant nonylphenol ethoxylate (AF-9-12) or alumina powder to shorten the hydrate induction period from 105 min in pure water to a minimum of 30 min. When both the surfactant and the alumina powder were used, the induction period was further shortened to less than 20 min. Liu et al. [94] added alumina and silica with particle sizes of 1, 2, and 6 nm to a SDS system. Better gas absorption was observed using alumina than silica in the dissolution and induction phases, while the gas absorption in the growth phase was larger using silica. Alumina and silica are of small particle sizes, which can shorten the induction time and accelerate the synthesis of hydrates during hydrate formation. They had a synergistic effect with the surfactant and influenced the nucleation of the hydrate. The main factor associated with this phenomenon was their particle size. Nano particles provide a favorable area for the nucleation of hydrates. Mohammadi et al. [95] studied the effect of silver nanoparticles and 0.05 wt% of SDS on the hydrate system. They found that additive-containing systems consumed more gas than the pure water system, which confirmed that both additives accelerated hydrate formation. Moraveji et al. [97] studied the solubility of methane in solutions containing SDS and nanoparticles. When the mass fraction of the nanoparticles was 1%, the solubility of methane increased, which indicated that both the rate of hydrate formation and the gas storage capacity were increased. In addition, Hosseini et al. [16] found that the addition of few-layer graphene nanosheets to an SDS solution not only shortened the induction time and increased the gas storage capacity, but also played a role in improving the stability of hydrates. Wang et al. [98] reached the same conclusion in a study involving polystyrene nanospheres (PSNS) and SDS.

Rogers et al. [99] found that sodium montmorillonite, a common swelling clay in marine sediments, preferentially adsorbed biosurfactants and promoted hydrate formation. In contrast, the surface properties of kaolin were not conducive to the formation of hydrates. Liu et al. [100] prepared a mixed solutions of SDS and Fe_3O_4 that could be used as a promoter for hydrate formation. As shown in Fig. 9, for a given concentration, the SDS/ Fe_3O_4 induction period was shorter than that of the SDS-only solution, with the induction of SDS/ Fe_3O_4 being reduced to less than 10 min after mixing. Smaller porous particles resulted in an increased reaction rate, which was further increased by the synergistic effect of the surfactant.

The research reported clearly demonstrates that the gas hydrate formation rate and gas content are affected by both porous media and surfactants. In addition to the types of surfactants and their concentrations, the influence of surfactants on hydrate formation is also closely related to the ambient pressure and temperature. The addition of porous media increases the complexity of the reaction system. The surface properties of porous media are diverse

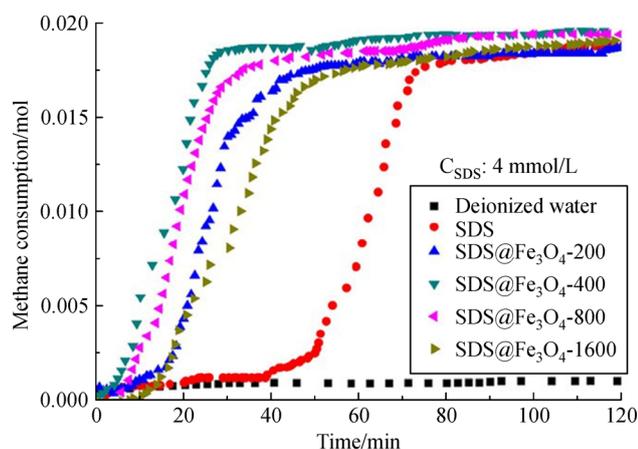


Fig. 9 Methane consumption during hydrate formation using an SDS/ Fe_3O_4 solution for a fixed 4 mmol/L SDS and different Fe_3O_4 concentrations, 200, 400, 800, and 1600 mg/L respectively (adapted with permission from Ref. [100]).

and can affect multiple factors such as the surface energy, porosity, and wetting angle during hydrate formation. Therefore, it is also a relatively complicated process to study the combination of porous media with other additives. The above experimental results demonstrate that the rate of hydrate formation in the porous media/surfactant systems is synergistically enhanced by the two additives. The promotion effect also shows that the combination of surfactants with other additives can further affect the accumulation of natural gas hydrate, which has a practical significance for real-world storage and transportation applications.

3.4 Hydrate formation in complex systems

Studies have shown that surfactants, salts, and porous media can accelerate nucleation in the formation of hydrates. On this basis, research is being conducted on the use of surfactants in conjunction with other additives. Some researchers have reported that the use of a single surfactant has a limited effect on the promotion of hydrate formation compared to the use of multi-component systems. Surfactants can be combined in a specific proportion to achieve a synergistic hydrate production enhancement. Table 2 lists the effect of the combining a surfactant with a substance on the formation of hydrates under different conditions.

In view of the good hydrate-promoting effect of SDS, scientists have attempted to combine SDS with various additives and surfactants to further accelerate the formation of hydrates and increase their gas storage density. Zhang et al. [63] used the platinum plate method of surface tension measurement to study the combination of two different types of surfactants, FC-01 and SDS. The surface tension exhibited a parabolic tendency, with the minimum surface tension being observed at FC-01 mass fractions of 0.6 to 0.7. They also compared the lowest surface tension of the SDS/FC-01 with the experimental data for FC-01 reported by Shi et al. [74]. As shown in Fig. 10, the use of both surfactants was found to be superior to the single surfactant under the same condition.

Tetrahydrofuran (THF) is often used to reduce the residual pressure [101]. SDS is used to increase the gas storage and reaction rate of natural gas hydrates.

Table 2 Summary of hydrate formation in complex systems

Number	Compounding	Conclusion	References
1	SDS + quartz sand + NaCl (50, 100, 200 mmol)	The combination of porous media and surfactants had a positive effect on hydrate formation kinetics and hydrate formation. When the NaCl concentration was 50 mmol, the methane consumption was higher than that of pure water	[11]
2	T40, T40/T80 (1:1), T40/T80 (4:1)	Surfactant T40 had a more pronounced effect in promoting hydrate nucleation and shortening induction time compared to the compound system	[37]
3	SDS (0.01, 0.05, 0.1, 0.15 wt%) + 3 mol% THF	The addition of THF further increased the rate of hydrate formation, shortened the induction time, and the gas consumption could be more than twice	[102]
4	SDS (0.005, 0.05 wt%) + 5 mol% THF	The solution system after the addition of THF had a faster nucleation rate and a higher gas storage capacity	[103]
5	propanone + SDS	The rate of hydrate formation was not significantly affected when the acetone concentration was less than 0.03 mol, but the rate of formation of hydrate was increased at high concentrations	[105]
6	THF, SDS + THF, SDBS + THF	The addition of an anionic surfactant increased the rate of hydrate formation. In contrast, the rate of formation of hydrates in THF + SDBS was much better than that of THF + SDS	[104]
7	TBAB + SDS	The addition of 0.15 wt% SDS to the 20 wt% TBAB system increased the gas consumption rate to 177%	[107]
8	TBAB + SDS + silica sand	The amount of methane absorbed in the TBAB + SDS system was higher than in other systems, indicating that the two surfactants produced a synergistic effect. In addition, it had good hydrate kinetics in porous media	[108]

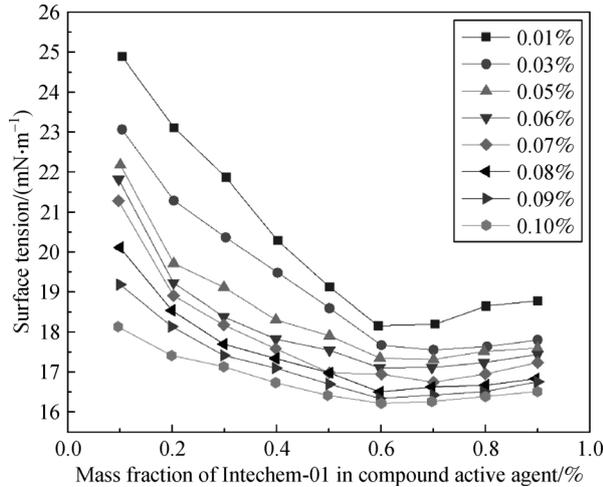


Fig. 10 Surface tension of mixtures of surfactants SDS and FC-01 at different concentration ratios at 30°C (adapted with permission from Ref. [74]).

Researchers have attempted to combine these two accelerators to achieve a synergistic effect. Kakati et al. [102] added 3 mol % THF to an aqueous solution of SDS and used the mixed solution as an effective accelerator for natural gas hydrate storage. SDS had little effect on the pressure and temperature of the hydrate formation system. When THF was added, the formation pressure of the hydrate was lowered. Figure 11 specifically illustrates the advantages of THF in accelerating hydrate nucleation. The rate of hydrate formation after the addition of THF was significantly higher than that in the absence of THF. Lirio et al. [103] experimentally demonstrated that when 0.05 wt % of SDS was added along with 5 mol% of THF, a faster nucleation rate and a higher gas storage capacity were

achieved compared with a single accelerator. Cai [104] added THF to both 0.03 wt% SDS and 0.05 wt% SDBS systems to accelerate hydrate formation. In addition, Partoon and Javanmardi [105] studied a system in which acetone and SDS were added. In this system, high acetone concentrations increased the rate of hydrate formation, but reduced the methane absorption capacity of the hydrate.

However, some researchers have also reported that the rate of hydrate formation in systems containing a combination of surfactants is lower than that in the single-surfactant system. For example, Zhang et al. [37] conducted experiments using Tween-40 (T40), T40:T80 (1:1) and T40:T80 (4:1) with three concentrations of Tween solution to study the effect on the induction time. When the concentration of the surfactant exceeded that of CMC, the surfactant in the aqueous solution was converted into micelles. Most of the gas molecules combined with water molecules to form a cluster structure, which accelerated the nucleation of the hydrate. At the same time, they also compared the three solution environments and found that the pure T40 solution more significantly promoted hydrate nucleation and shortened the induction time. Fazlali et al. [106] studied the kinetics and thermodynamic effects of a mixture of SDS, hexadecyl trimethyl ammonium bromide (HTABr), and polyoxyethylene(20)cetyl ether (Brij-58) on methane hydrate formation. The type of surfactant or surfactant mixture used in the tests had little effect on the thermodynamic changes in the formation of hydrates. The effect of SDS on the rate of hydrate formation was greater than that of the mixture. The compound surfactant did not exhibit the expected synergistic acceleration effect, but instead, the single surfactant had a more obvious influence on the hydrate synthesis.

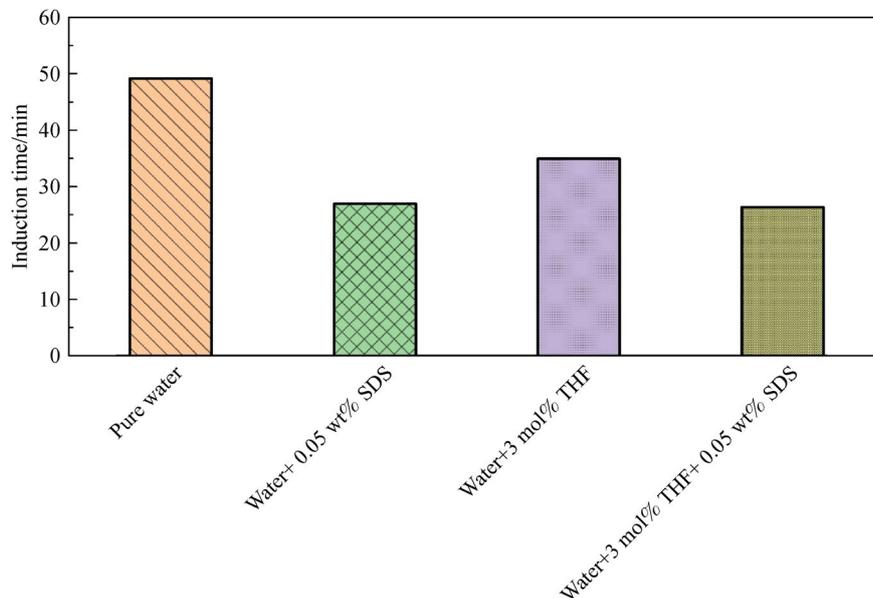


Fig. 11 Induction time after addition of different concentrations of SDS and THF (adapted with permission from Ref. [102]).

Based on the above results, it indicates that the surfactant reaction mechanisms are different. Surfactant mixtures may affect both the capillary action and micellar action in a hydrate-forming system. They also affect the experimental procedures of hydrate formation, and both effects may occur in mixtures. Renault-Crispo and Servio [107] studied the effect of the thermodynamic promoter tetrabutylammonium bromide (TBAB) and the kinetic promoter SDS on a methane hydrate system. They found that the binding capacity of methane in a water-gas system increased when the appropriate concentrations of SDS and TBAB were added. The systems with mixed surfactants and porous media have been widely reported for the gas hydrate formation [108].

When two surfactants with the same reaction mechanism are mixed, they exhibit an additive effect on hydrate formation. When their reaction mechanisms are different, the concentrations of the two surfactants become the dominant factor. This situation is more complicated than when both surfactants have the same mechanism. There may exist a critical concentration that allows the two active agents to act synergistically and achieve optimal results. There are also conditions in which a mixture of surfactants is disadvantageous for hydrate formation, that is, compounding surfactants in high concentration suppress the hydration formation rate. A single variable should be selected for in-depth analysis of the different systems.

In addition, due to the difference between hydrophilic and lipophilic surfactants, for the further application of surfactants, the following application-type recommendations are proposed. Among them, surfactants with poor foaming properties (such as SDS) can be used in the process of static hydrate preparation; lipophilic surfactants (such as T40) are mainly used in the field of pipeline transportation with rich oil content. For different surfactants, further research is still needed for specific scenarios.

4 Evaluation of surfactant effects in theoretical modeling of hydrate generation reactions

Experimental studies can be used to study the use of surfactants to promote hydrates. However, due to the complex environmental conditions in the experimental system, there may inevitably exist some errors in the results. Thus, researchers are attempting to develop novel models for the dynamic and thermodynamic simulations.

Choudhary et al. [41] used molecular dynamics simulations to visually describe the molecular mechanisms responsible for the effects of SDS on methane hydrate formation.

They chose hydrate formation conditions similar to those used in the laboratory, and introduced the parameter F_4 in Eq. (1) as a criterion for hydrate formation.

$$F_4 = \frac{1}{n} \sum_{i=1}^n \cos 3\varphi_i. \quad (1)$$

The F_4 reflects the hydrate nucleation and rate of growth over time. The system was simulated at 270 K and 10 MPa, the F_4 parameter value of the pure gas hydrate was maintained at approximately 0.7, and the F_4 parameter value of the liquid water was about -0.04 .

Mainusch et al. [109] developed a thermodynamic model based on the models proposed by Pieroen [110] and Moshfeghian and Maddor [111]. The model was used to predict the formation temperature of methane hydrate in a mixture of acetone and water. In the model, the effects of pressure and concentration on the hydrate formation enthalpy were considered, as expressed in Eq. (2).

$$\ln a_w = \frac{\Delta H}{nR} \left(\frac{1}{T} - \frac{1}{T^0} \right). \quad (2)$$

By fitting the vapor-liquid equilibria (VLE) data of the acetone and water system, the activity expression of water is written as

$$\ln \gamma_w = 1.656 \left(1 + \frac{1.656x_w}{1.900x_a} \right)^{-2}. \quad (3)$$

In the simulation results, at acetone mole fractions of less than 0.5%, the equilibrium pressure was reduced after hydrate formation, and the appearance of the hydrate was further improved at the acetone concentration above 0.5%, inhibition was observed. Based on the error of the parameter fitting, the model was demonstrated to have good predictive ability.

Zhang et al. [112] assumed that hydrate nucleation and crystallization occurred only in the liquid film where the gas was in contact with the solution, and used a diffusion reaction kinetics model to analyze the hydrate growth process. It was concluded that SDS not only reduced the interfacial tension between the hydrate and the liquid, but also increased the nucleation and growth rate of the hydrate by increasing the total specific surface area of hydrate particles and the area of the two-phase interface.

In 2013, Karimi and coworkers [113] used SDS, SDBS, and Triton X-100 (TX-100) surfactants for hydrate formation and obtained the kinetic equation for the hydrate, as expressed in Eq. (4).

$$r_f = - \left(\frac{dn}{dt} \right) = ak_f RT \ln \frac{f_g}{f_{eq}}. \quad (4)$$

They refined the previous model and established the new expression [114], as expressed in Eq. (5).

$$\frac{n_{ci}}{n_{cf}} = \frac{\frac{P_0}{Z_0} - \frac{P_i}{Z_i}}{\frac{P_0}{Z_0} - \frac{P_f}{Z_f}} = \left[\frac{t_i}{t_k} \exp \left(1 - \frac{t_i}{t_k} \right) \right]^{\frac{-A_r}{RT}}, \quad (5)$$

where t_k and $-A_p/(RT)$ are the dynamic model parameters. The absolute value of the slope, $|A_p/(RT)|$, can be regarded as a rate constant that can be used to determine the effects of the stirring rate, pressure, and temperature in the reactor, as well as the effect of the additive concentration on the kinetics of hydrate nucleation. Kinetic measurements of hydrate formation in the presence and absence of the surfactant T40 were also conducted. The change in the surfactant concentration is related to the kinetic factors of hydrate formation.

The simulation results were consistent with the experimental ones, which confirmed the rationality of the model. In another paper, the same authors found that SDS and T-40 could promote hydrate formation, and SDS had a better performance [115]. However, limitations in the use of models remain, such as the use of relatively simple model parameters, leading to less accurate fitting. In future studies, both experimental and simulation studies should be performed simultaneously in the same experimental environments. Their results could be compared and discussed to improve the numerical model and verify the experimental data.

5 Conclusions and outlook

To provide an in-depth discussion of hydrates and their applications, this paper summarized the mechanisms of various surfactants that have been reported to promote hydrate formation. It also discussed the various factors affecting the process of hydrate formation by surfactants and introduced mathematical models of the kinetics and thermodynamics of surfactant-promoted hydrate formation.

Researchers dispute whether SDS forms micelles in the hydrate formation process. Different classes of surfactants exhibit different relationships between their ability to promote hydrate formation and their carbon chain structures. Some researchers have reported that the longer carbon chains enhance the formation of hydrates, while others have come to the opposite conclusion.

To further understand the properties of hydrates and promote research of surfactants in the field of natural gas, the following future research directions are suggested:

The mechanism by which surfactants promote hydrate formation remains unclear. In the literature, two mechanisms have been proposed, i.e, capillary force and micelle formation. The capillary phenomenon can be observed using a high-speed camera, but the development of a method to visually confirm the micelle shape requires further research.

Seabed sediments in which natural hydrate formation occurs contain complex and diverse ion species, as well as mineral layers with pore structures similar to those of some porous media. Porous media and salt similar to those in

natural sediments conditions could be applied in conjunction to enhance the formation of hydrates. The effects of Na^+ , Mg^{2+} , and other ions should be experimentally studied, and the experimental results should be used to provide theoretical support and references for industrial natural gas hydrate storage and transportation.

Parameters such as the induction time, gas storage density, and methane absorption should be used to evaluate the performance of hydrate formation methods. In addition, the foaming properties of surfactants also have a certain effect on their practical applications. In the future, research can be conducted for specific application scenarios.

It is critical to improve existing kinetic or thermodynamic models used to simulate the hydrate formation process. It is particularly important to analyze which surfactant parameters most strongly affect hydrate formation, further optimize existing models, and establish more practical and efficient mathematical models.

Acknowledgements This work was supported by the Doctoral Research Start-up Fund Project of Liaoning Province, China (No. 2019-BS-159).

Notations

n	Oxygen-oxygen logarithm of water molecules
a	Activity
ΔH	Enthalpy of formation of a hydrate/J
T	Hydrate formation temperature in the presence of an inhibitor/K
T_0	Hydrate formation temperature of pure water/K
R	Universal gas constant
x	Mole fraction

Greek letters

φ	Twist angle between the farthest O-H vectors of the two water molecules
-----------	---

Subscripts

w	Water
a	Acetone

References

1. Semenov M Y, Ivanova I K, Koryakina V V. Peculiarities of natural gas hydrate formation from ice in reactors under high pressure. IOP Conference Series: Earth and Environmental Science, 2018, 193: 012061
2. Bhade P, Phirani J. Effect of geological layers on hydrate dissociation in natural gas hydrate reservoirs. Journal of Natural Gas Science and Engineering, 2015, 26: 1549–1560
3. Ding L, Shi B, Liu Y, Song S, Wang W, Wu H, Gong J. Rheology of natural gas hydrate slurry: effect of hydrate agglomeration and deposition. Fuel, 2019, 239: 126–137

4. Kumar A, Bhattacharjee G, Kulkarni B D, Kumar R. Role of surfactants in promoting gas hydrate formation. *Industrial & Engineering Chemistry Research*, 2015, 54(49): 12217–12232
5. Pan Z, Liu Z, Zhang Z, Shang L, Ma S. Effect of silica sand size and saturation on methane hydrate formation in the presence of SDS. *Journal of Natural Gas Science and Engineering*, 2018, 56: 266–280
6. Pan Z, Wang Z, Zhang Z, Ma G, Zhang L, Huang Y. Natural gas hydrate formation dynamics in a diesel water-in-oil emulsion system. *Petroleum Science and Technology*, 2018, 36(20): 1649–1656
7. Sloan E D Jr. Fundamental principles and applications of natural gas hydrates. *Nature*, 2003, 426(6964): 353–359
8. Yang Y, He Y, Zheng Q. An analysis of the key safety technologies for natural gas hydrate exploitation. *Advances in Geo-Energy Research*, 2017, 1(2): 100–104
9. Koryakina V V, Ivanova I K, Semenov M E. Oil emulsions as medium of natural gas hydrate formation. *IOP Conference Series: Earth and Environmental Science*, 2018, 193: 012035
10. Wang Z, Ma G, Shang L, Zhang L. Effect of a nonionic surfactant on the formation of natural gas hydrate in a diesel emulsion system. *Petroleum Science and Technology*, 2018, 36(23): 2017–2023
11. Sun X, Liu D, Chang D, Wang W, Pan Z. Analysis of natural gas hydrate formation in sodium dodecyl sulfate and quartz sand complex system under saline environment. *Petroleum Science and Technology*, 2018, 36(14): 1073–1079
12. Koh D Y, Kang H, Lee J W, Park Y, Kim S J, Lee J, Lee J Y, Lee H. Energy-efficient natural gas hydrate production using gas exchange. *Applied Energy*, 2016, 162: 114–130
13. Makogon Y F. Natural gas hydrates—a promising source of energy. *Journal of Natural Gas Science and Engineering*, 2010, 2(1): 49–59
14. Chaturvedi E, Prasad N, Mandal A. Enhanced formation of methane hydrate using a novel synthesized anionic surfactant for application in storage and transportation of natural gas. *Journal of Natural Gas Science and Engineering*, 2018, 56: 246–257
15. Sloan E D. Clathrate hydrates: the other common solid water phase. *Industrial & Engineering Chemistry Research*, 2000, 39(9): 3123–3129
16. Hosseini M, Ghozatloo A, Shariaty-Niassar M. Effect of CVD graphene on hydrate formation of natural gas. *Journal of Nanostructure in Chemistry*, 2015, 5(2): 219–226
17. Khodaverdiloo K R, Erfani A, Peyvandi K, Varaminian F. Synergetic effects of polyacrylamide and nonionic surfactants on preventing gas hydrate formation. *Journal of Natural Gas Science and Engineering*, 2016, 30: 343–349
18. Fan S, Yang L, Lang X, et al. Kinetics and thermal analysis of methane hydrate formation in aluminum foam. *Chemical Engineering Science*, 2012, 82: 185–193
19. Vysniauskas A, Bishnoi P R. A kinetic study of methane hydrate formation. *Chemical Engineering Science*, 1983, 38(7): 1061–1072
20. Ohmura R, Kashiwazaki S, Shiota S, Tsuji H, Mori Y H. Structure-I and structure-H hydrate formation using water spraying. *Energy & Fuels*, 2002, 16(5): 1141–1147
21. Kuhs W F, Staykova D K, Salamatin A N. Formation of methane hydrate from polydisperse ice powders. *Journal of Physical Chemistry B*, 2006, 110(26): 13283–13295
22. Kezirian M T, Phoenix S L. Natural gas hydrates to enable the safe, sustainable, and economical production of offshore petroleum reserves. In: *Offshore Technology Conference*, Houston TX, USA, 2018
23. Wang F, Guo G, Luo S J, Guo R B. Preparation of $-\text{SO}_3^-$ -coated nanopromoters for methane hydrate formation: effects of the existence pattern of $-\text{SO}_3^-$ groups on the promotion efficiency. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, 2017, 5(6): 2640–2648
24. Song Y M, Wang F, Guo G, Luo S J, Guo R B. Amphiphilic-polymer-coated carbon nanotubes as promoters for methane hydrate formation. *ACS Sustainable Chemistry & Engineering*, 2017, 5(10): 9271–9278
25. Link D D, Ladner E P, Elseni H A, Taylor C E. Formation and dissociation studies for optimizing the uptake of methane by methane hydrates. *Fluid Phase Equilibria*, 2003, 211(1): 1–10
26. Israelachvili J N, McGuiggan P M. Forces between surfaces in liquids. *Science*, 1988, 241(4867): 795–800
27. Zhang P, Wu Q, Mu C, Chen X. Nucleation mechanisms of CO_2 hydrate reflected by gas solubility. *Scientific Reports*, 2018, 8(1): 10441–10452
28. Kalogerakis N, Jamaluddin A K M, Dholabhai P D, Bishnoi P R. Effect of surfactants on hydrate formation kinetics. In: *SPE International Symposium on Oilfield Chemistry*, New Orleans, LA, LSA, 1993
29. Lo C, Zhang J, Somasundaran P, Lee J W. Investigations of surfactant effects on gas hydrate formation via infrared spectroscopy. *Journal of Colloid and Interface Science*, 2012, 376(1): 173–176
30. Tang J, Zeng D, Wang C, Chen Y, He L, Cai N. Study on the influence of SDS and THF on hydrate-based gas separation performance. *Chemical Engineering Research & Design*, 2013, 91(9): 1777–1782
31. Mel'nikov V P, Nesterov A N, Feklistov V V. Formation of gas hydrates in the presence of additives consisting of surface-active substances. *Chemistry in the Interests of Sustainable Development*, 1998, 6: 97–102 (in Russian)
32. Tajima H, Kiyono F, Yamasaki A. Direct observation of the effect of sodium dodecyl sulfate (SDS) on the gas hydrate formation process in a static mixer. *Energy & Fuels*, 2010, 24(1): 432–438
33. Okutani K, Kuwabara Y, Mori Y H. Surfactant effects on hydrate formation in an unstirred gas/liquid system: amendments to the previous study using HFC-32 and sodium dodecyl sulfate. *Chemical Engineering Science*, 2007, 62(14): 3858–3860
34. Asaoka T, Ikeda K. Observation of the growth characteristics of gas hydrate in the quiescent-type formation method using surfactant. *Journal of Crystal Growth*, 2017, 478: 1–8
35. Zhong Y, Rogers R E. Surfactant effects on gas hydrate formation. *Chemical Engineering Science*, 2000, 55(19): 4175–4187
36. Irvin G, Li S, Simmons B, John V, McPHERSON G A R Y, Max M, Pellenbarg R. Control of gas hydrate formation using surfactant systems: underlying concepts and new applications. *Annals of the New York Academy of Sciences*, 2000, 912(1): 515–526
37. Zhang B, Wu Q, Sun D. Effect of surfactant Tween on induction

- time of gas hydrate formation. *Journal of China University of Mining and Technology*, 2008, 18(1): 18–21
38. Bhattacharjee G, Kushwaha O S, Kumar A, Khan M Y, Patel J N, Kumar R. Effects of micellization on growth kinetics of methane hydrate. *Industrial & Engineering Chemistry Research*, 2017, 56(13): 3687–3698
 39. Di Profio P, Arca S, Germani R, Savelli G. Surfactant promoting effects on clathrate hydrate formation: are micelles really involved? *Chemical Engineering Science*, 2005, 60(15): 4141–4145
 40. Zhang J S, Lee S, Lee J W. Does SDS micellize under methane hydrate-forming conditions below the normal Krafft point? *Journal of Colloid and Interface Science*, 2007, 315(1): 313–318
 41. Choudhary N, Hande V R, Roy S, Chakrabarty S, Kumar R. Effect of sodium dodecyl sulfate surfactant on methane hydrate formation: a molecular dynamics study. *Journal of Physical Chemistry B*, 2018, 122(25): 6536–6542
 42. Meng H, Guo R, Wang F, Luo S, Xu H. Effect of different surfactants on methane hydrate formation. *Renewable Energy Resources*, 2017, 3: 329–336 (in Chinese)
 43. Qin X, Wu Q, Zhang B. Effect of sodium dodecyl sulfate on the process of methane hydrate formation. *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2006, 69(7): 519–523
 44. Koh C A, Westacott R E, Zhang W, Hirachand K, Creek J L, Soper A K. Mechanisms of gas hydrate formation and inhibition. *Fluid Phase Equilibria*, 2002: 143–151
 45. Wu M, Wang S, Liu H. A study on inhibitors for the prevention of hydrate formation in gas transmission pipeline. *Journal of Natural Gas Chemistry*, 2007, 16(1): 81–85
 46. Chong Z R, Yang S H B, Babu P, Linga P, Li X S. Review of natural gas hydrates as an energy resource: prospects and challenges. *Applied Energy*, 2016, 162: 1633–1652
 47. Karaaslan U, Uluneye E, Parlaktuna M. Effect of an anionic surfactant on different type of hydrate structures. *Journal of Petroleum Science Engineering*, 2002, 35(1–2): 49–57
 48. Liu Z, Song Y, Liu W, Lang C, Zhao J, Li Y. Formation of methane hydrate in oil-water emulsion governed by the hydrophilic and hydrophobic properties of non-ionic surfactants. *Energy & Fuels*, 2019, 33(6): 5777–5784
 49. Mankowich A M. Physicochemical properties of surfactants. *Industrial & Engineering Chemistry*, 1953, 45(12): 2759–2766
 50. Wang L, Wang S L, Kang T T. Surfactant effect of promoting research on hydrate formation. *Advanced Materials Research*, 2015, 1092–1093: 220–225
 51. Xie Y, Yang L, Liu D, Meng Y. Research in surfactant effect on promoting gas hydrates formation. *Journal of Refrigeration*, 2016, 3: 35–41 (in Chinese)
 52. keshavarz Moraveji M, Ghaffarkhah A, Sadeghi A. Effect of three representative surfactants on methane hydrate formation rate and induction time. *Egyptian Journal of Petroleum*, 2017, 26(2): 331–339
 53. Rauh F, Pfeiffer J, Mizaikoff B. Infrared spectroscopy on the role of surfactants during methane hydrate formation. *RSC Advances*, 2017, 7(62): 39109–39117
 54. Zhang C S, Fan S S, Liang D Q, Guo K H. Effect of additives on formation of natural gas hydrate. *Fuel*, 2004, 83(16): 2115–2121
 55. Zhou S D, Yu Y S, Zhang X P, Wang S L, Zhang G Z. Investigation on the effect of surfactant on surface tension of liquids for gas hydrate formation. *Natural Gas Chemical Industry*, 2013, 38: 42–45
 56. Karaaslan U, Parlaktuna M. Surfactants as hydrate promoters? *Energy & Fuels*, 2000, 14(5): 1103–1107
 57. Karaaslan U, Parlaktuna M. Promotion effect of polymers and surfactants on hydrate formation rate. *Energy & Fuels*, 2002, 16(6): 1413–1416
 58. Wang F, Jia Z Z, Luo S J, Fu S F, Wang L, Shi X S, Wang C S, Guo R B. Effects of different anionic surfactants on methane hydrate formation. *Chemical Engineering Science*, 2015, 137: 896–903
 59. Okutani K, Kuwabara Y, Mori Y H. Surfactant effects on hydrate formation in an unstirred gas/liquid system: an experimental study using methane and sodium alkyl sulfates. *Chemical Engineering Science*, 2008, 63(1): 183–194
 60. Daimaru T, Yamasaki A, Yanagisawa Y. Effect of surfactant carbon chain length on hydrate formation kinetics. *Journal of Petroleum Science Engineering*, 2007, 56(1–3): 89–96
 61. Zhao J L, Ma G Y, Pan Z. Influences of alkyl polyglucoside on formation of methane hydrate. *Chemical Engineering (China)*, 2018, 9: 17–22 (in Chinese)
 62. Posteraro D, Ivall J, Maric M, Servio P. New insights into the effect of polyvinylpyrrolidone (PVP) concentration on methane hydrate growth. 2. Liquid phase methane mole fraction. *Chemical Engineering Science*, 2015, 126: 91–98
 63. Zhang L, Zhang X, Wang S, Zhou S, Wang L. Effect of composite surfactant on surface tension of gas hydrate formation liquid. *Petrochemical Technology*, 2013, 42: 1224–1228 (in Chinese)
 64. Verrett J, Servio P. Evaluating surfactants and their effect on methane mole fraction during hydrate growth. *Industrial & Engineering Chemistry Research*, 2012, 51(40): 13144–13149
 65. Salako O, Lo C, Couzis A, Somasundaran P, Lee J W. Adsorption of Gemini surfactants onto clathrate hydrates. *Journal of Colloid and Interface Science*, 2013, 412: 1–6
 66. Khokhar A A, Gudmundsson J S, Sloan E D. Gas storage in structure H hydrates. *Fluid Phase Equilibria*, 1998, 150–151: 383–392
 67. Liu J, Ma G Y, Pan Z, Shang L Y, Yang F, Tan F Z. Experiment on formation and decomposition of methane hydrate. *Chemical Engineering*, 2015, 43: 35–40 (in Chinese)
 68. Ke W, Svartaas T M, Kvaløy J T, Kosberg B R. Inhibition–promotion: dual effects of polyvinylpyrrolidone (PVP) on structure-II hydrate nucleation. *Energy & Fuels*, 2016, 30(9): 7646–7655
 69. ZareNezhad B, Mottahedin M, Varaminian F. Effects of process variables on the initial gas hydrate formation rate: the case of ethane hydrate formation in the absence or presence of SDS kinetic promoter. *Journal of Molecular Liquids*, 2014, 198: 57–62
 70. ZareNezhad B, Mottahedin M, Varaminian F. Experimental and theoretical investigations on the enhancement of methane gas hydrate formation rate by using the kinetic additives. *Petroleum Science and Technology*, 2015, 33(8): 857–864
 71. Ganji H, Manteghian H M, Rahimi Mofrad. Effect of mixed compounds on methane hydrate formation and dissociation rates and storage capacity. *Fuel Processing Technology*, 2007, 88(9): 891–895

72. Ganji H, Manteghian M, Sadaghiani zadeh K, Omidkhan M R, Rahimi Mofrad H. Effect of different surfactants on methane hydrate formation rate, stability and storage capacity. *Fuel*, 2007, 86(3): 434–441
73. ZareNezhad B, Varaminian F. A unified approach for description of gas hydrate formation kinetics in the presence of kinetic promoters in gas hydrate converters. *Energy Conversion and Management*, 2013, 73: 144–149
74. Shi Q, Wang S, Yu H, Zhao S. Study on surfactivity of natural gas hydrate solution. *Natural Gas Chemical Industry*, 2011, 36(4): 17–20 (in Chinese)
75. Sun Z, Wang R, Ma R, Guo K, Fan S. Natural gas storage in hydrates with the presence of promoters. *Energy Conversion and Management*, 2003, 44(17): 2733–2742
76. Sun Z G, Ma R, Wang R Z, Guo K H, Fa S S. Experimental studying of additives effects on gas in hydrates. *Energy & Fuels*, 2003, 17(5): 1180–1185
77. Zhou S D, Wang S L, Zhang G Z. Effect of different surfactants on gas hydrate formation. *Advanced Materials Research*, 2013, 645: 146–149
78. Du J, Li H, Wang L. Effects of ionic surfactants on methane hydrate formation kinetics in a static system. *Advanced Powder Technology*, 2014, 25(4): 1227–1233
79. Jiménez-Ángeles F, Firoozabadi A. Hydrophobic hydration and the effect of NaCl salt in the adsorption of hydrocarbons and surfactants on clathrate hydrates. *ACS Central Science*, 2018, 4(7): 820–831
80. Eastman M J. Surfactant enhanced methane hydrate growth in quiescent sodium chloride solutions. Dissertation for the Master's Degree. Irvine: University of California, Irvine, 2016
81. Zhang Q, Wu Q, Zhang H. Effect of propane and NaCl-SDS solution on nucleation process of mine gas hydrate. *Journal of Chemistry*, 2017: 1059109
82. Delroisse H, Torrè J P, Dicharry C. Effect of a hydrophilic cationic surfactant on cyclopentane hydrate crystal growth at the water/cyclopentane interface. *Crystal Growth & Design*, 2017, 17(10): 5098–5107
83. Ma S, Pan Z, Li P, Wu Y, Li B, Kang J, Zhang Z. Experimental study on preparation of natural gas hydrate by crystallization. *China Petroleum Processing and Petrochemical Technology*, 2017, 19(1): 106–113 (in Chinese)
84. Abdi-Khanghah M, Adelizadeh M, Naserzadeh Z, Barati H. Methane hydrate formation in the presence of ZnO nanoparticle and SDS: application to transportation and storage. *Journal of Natural Gas Science and Engineering*, 2018, 54: 120–130
85. Cui Y, Lu C, Wu M, Peng Y, Yao Y, Luo W. Review of exploration and production technology of natural gas hydrate. *Advances in Geo-Energy Research*, 2018, (1): 53–62
86. Rezaei E, Manteghian M, Tamaddondar M. Kinetic study of ethylene hydrate formation in presence of graphene oxide and sodium dodecyl sulfate. *Journal of Petroleum Science Engineering*, 2016, 147: 857–863
87. Kakati H, Mandal A, Laik S. Promoting effect of Al₂O₃/ZnO-based nanofluids stabilized by SDS surfactant on CH₄+ C₂H₆+ C₃H₈ hydrate formation. *Journal of Industrial and Engineering Chemistry*, 2016, 35: 357–368
88. Palodkar A V, Jana A K. Fundamental of swapping phenomena in naturally occurring gas hydrates. *Scientific Reports*, 2018, 8(1): 16563
89. Yousif M H, Abass H H, Selim M S, Sloan E D. Experimental and theoretical investigation of methane-gas-hydrate dissociation in porous media. *SPE Reservoir Engineering*, 1991, 6(1): 69–76
90. Cha S B, Ouar H, Wildeman T R, Sloan E D. A third-surface effect on hydrate formation. *Journal of Physical Chemistry*, 1988, 92(23): 6492–6494
91. Xu Z, Zhou Z, Du P, Cheng X. Effects of nano-silica on hydration properties of tricalcium silicate. *Construction & Building Materials*, 2016, 125: 1169–1177
92. Dicharry C, Duchateau C, Asbaï H, Broseta D, Torrè J P. Carbon dioxide gas hydrate crystallization in porous silica gel particles partially saturated with a surfactant solution. *Chemical Engineering Science*, 2013, 98: 88–97
93. Nesterov A N, Reshetnikov A M, Manakov A Y, Adamova T P. Synergistic effect of combination of surfactant and oxide powder on enhancement of gas hydrates nucleation. *Journal of Energy Chemistry*, 2017, 26(4): 808–814
94. Liu Z, Pan Z, Zhang Z, Liu P, Shang L, Li B. Effect of porous media and sodium dodecyl sulphate complex system on methane hydrate formation. *Energy & Fuels*, 2018, 32(5): 5736–5749
95. Mohammadi A, Manteghian M, Haghtalab A, Mohammadi A H, Rahmati-Abkenar M. Kinetic study of carbon dioxide hydrate formation in presence of silver nanoparticles and SDS. *Chemical Engineering Journal*, 2014, 237: 387–395
96. Mohammadi A. Effect of SDS, silver nanoparticles, and SDS plus silver nanoparticles on methane hydrate semicompletion time. *Petroleum Science and Technology*, 2017, 35(15): 1542–1548
97. Moraveji M K, Golkaram M, Davarnejad R. Effect of CuO nanoparticle on dissolution of methane in water. *Journal of Molecular Liquids*, 2013, 180: 45–50
98. Wang F, Luo S J, Fu S F, Jia Z Z, Dai M, Wang C S, Guo R B. Methane hydrate formation with surfactants fixed on the surface of polystyrene nanospheres. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, 2015, 3(16): 8316–8323
99. Rogers R, Zhang G, Dearman J, Woods C. Investigations into surfactant/gas hydrate relationship. *Journal of Petroleum Science Engineering*, 2007, 56(1–3): 82–88
100. Liu G Q, Wang F, Luo S J, Xu D Y, Guo R B. Enhanced methane hydrate formation with SDS-coated Fe₃O₄ nanoparticles as promoters. *Journal of Molecular Liquids*, 2017, 230: 315–321
101. de Deugd R M, Jager M D, de Swaan Arons J. Mixed hydrates of methane and water-soluble hydrocarbons modeling of empirical results. *AIChE Journal*, 2001, 47(3): 693–704
102. Kakati H, Mandal A, Laik S. Effect of SDS/THF on thermodynamic and kinetic properties of formation of hydrate from a mixture of gases (CH₄+ C₂H₆+ C₃H₈) for storing gas as hydrate. *Journal of Energy Chemistry*, 2016, 25(3): 409–417
103. Lirio C F D S, Pessoa F L P, Uller A M C. Storage capacity of carbon dioxide hydrates in the presence of sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF). *Chemical Engineering Science*, 2013, 96: 118–123
104. Cai J, Xu C G, Chen Z Y, Li X S. Recovery of methane from coal-

- bed methane gas mixture via hydrate-based methane separation method by adding anionic surfactants. *Energy Sources. Part A, Recovery, Utilization, and Environmental Effects*, 2018, 40(9): 1019–1026
105. Partoon B, Javanmardi J. Effect of mixed thermodynamic and kinetic hydrate promoters on methane hydrate phase boundary and formation kinetics. *Journal of Chemical & Engineering Data*, 2013, 58(3): 501–509
106. Fazlali A, Kazemi S A, Keshavarz-Moraveji M, Mohammadi A H. Impact of different surfactants and their mixtures on methane-hydrate formation. *Energy Technology (Weinheim)*, 2013, 1(8): 471–477
107. Renault-Crispo J S, Servio P. Methane gas hydrate kinetics with mixtures of sodium dodecyl sulphate and tetrabutylammonium bromide. *Canadian Journal of Chemical Engineering*, 2018, 96(7): 1620–1626
108. Mech D, Sangwai J. Investigations on the formation kinetics of semicathrate hydrate of methane in an aqueous solution of tetra-n-butyl ammonium bromide and sodium dodecyl sulfate in porous media. *Energy Sources. Part A, Recovery, Utilization, and Environmental Effects*, 2018, 40(20): 2415–2422
109. Mainusch S, Peters C J, de Swaan Arons J, Javanmardi J, Moshfeghian M. Experimental determination and modeling of methane hydrates in mixtures of acetone and water. *Journal of Chemical & Engineering Data*, 1997, 42(5): 948–950
110. Pieroen P A. Gas hydrates—approximate relations between heat of formation, composition and equilibrium temperature lowering by “inhibitors”. *Recueil des Travaux Chimiques des Pays-Bas*, 2010, 74: 995–1002
111. Moshfeghian M, Maddox R N. Method predicts hydrates for high-pressure gas streams. *Oil & Gas Journal*, 1993, 91(35): 78
112. Zhang J S, Lee S, Lee J W. Kinetics of methane hydrate formation from SDS solution. *Industrial & Engineering Chemistry Research*, 2007, 46(19): 6353–6359
113. Karimi R, Varaminian F, Izadpanah A A, Mohammadi A H. Effects of different surfactants on the kinetics of ethane-hydrate formation: experimental and modeling studies. *Energy Technology (Weinheim)*, 2013, 1(9): 530–536
114. Karimi R, Varaminian F, Izadpanah A A. Study of ethane hydrate formation kinetics using the chemical affinity model with and without presence of surfactants. *Journal of Non-Equilibrium Thermodynamics*, 2014, 39(4): 219–229
115. Karimi R, Varaminian F, Izadpanah A A, Mohammadi A H. Effects of two surfactants sodium dodecyl sulfate (SDS) and polyoxyethylene (20) sorbitan monopalmitate (Tween^(R)40) on ethane hydrate formation kinetics: experimental and modeling studies. *Journal of Natural Gas Science and Engineering*, 2014, 21: 193–200