

The formation of compacted hydrate shell is one of the most important reasons that hinder the rapid and successive hydrate formation, and the study on the formation characteristics of hydrate film is an important way to reveal the influence mechanism of SDS on hydrate formation. According to our previous hydrate film growth research [7] and comparison with literature [8], as shown in Fig. 1, we speculate that the differences in film formation characteristics and hydrate crystal structure may be an important reason for the influence of SDS on hydrate formation and different promoting effects.

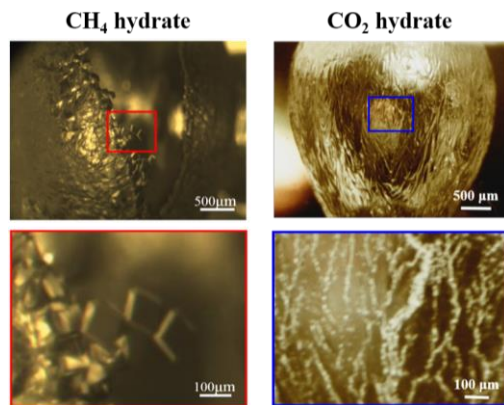


Fig. 1 Comparison of the morphology of CH₄ hydrate [7] and CO₂ hydrate film [8]

To explore the specific controlling factors and influence mechanism of SDS on the hydrate formation process, in this study, the effects of SDS surfactant cooling on the formation characteristics of hydrate film were studied from mesoscopic to molecular scale by combining with optical microscope and Raman spectrum. The results obtained in this study are of great significance to guide the selection of the SDS concentration to promote the formation of CH₄ hydrate and have insights for the modification of SDS or other surfactants accelerating CO₂ hydrate formation.

2. EXPERIMENTAL SECTION

2.1 Materials

CH₄ gas with a purity of 99.99% was supplied by the Beijing Beifen Gas Industry Corporation, China. Sodium dodecyl sulfate (SDS, analytical reagent) was purchased from Beijing Reagents Corporation. Deionized water with a conductivity less than 10 was used.

2.2 Experimental apparatus and procedures

The experimental apparatus is shown in Fig. 2. A high-pressure optical cell was used for gas bubbling and

hydrate formation. Briefly, the volume of the cell is 10 mL and the maximum operating pressure is 20 MPa. The needle at the bottom of the cell was used for bubbling. An optical microscope was used for recording the morphology changes of hydrate bubbles. A Raman spectrometer was used to measure Raman spectrum changes. A microscope attached to the Raman spectrometer was used for the comparative analysis of hydrate morphology. The Raman spectrum of the hydrate was collected by a HORIBA XploRA Raman system. 1800 grooves/mm grating 532 nm wavelength laser was employed. More information about the apparatus was detailed in previous studies [7, 9, 10].

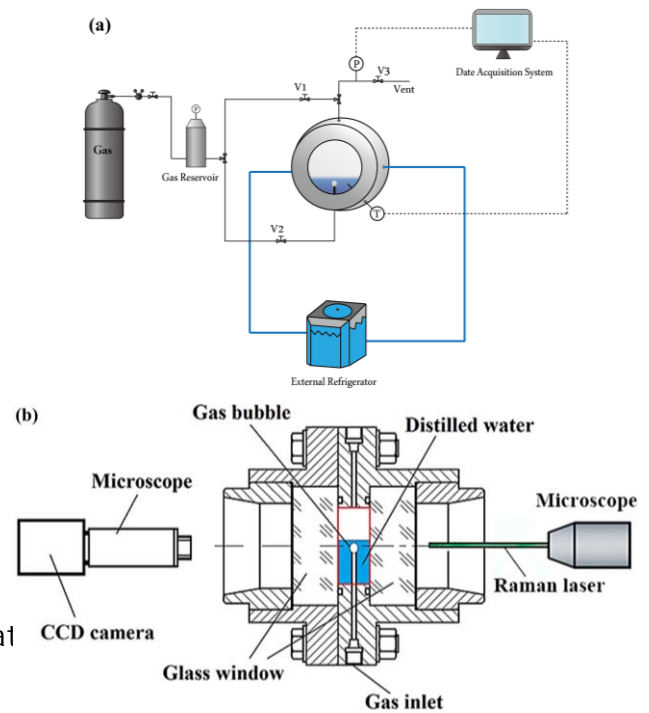


Fig 2 Schematic diagram of the experimental apparatus (a) for bubbling and hydrate formation and (b) of the high-pressure optical cell with optical microscope recording and Raman measuring.

After the cleaning of the cell, 2 mL SDS solutions with different concentrations were loaded, the system temperature was cooled to 6.74 K and kept constant. Then the cell was vacuumed. CH₄ gas was injected to a pressure much higher than the hydrate equilibrium pressure for the acceleration of hydrate nucleation. After the hydrate formation at the gas-liquid interface, the system was depressurized to dissociate hydrate. Subsequently, CH₄ gas was injected through valve 1 to target pressure for hydrate formation at the bulk gas-liquid interface. Then, the valve 1 was closed and the valve 2 and the valve 3 were simultaneous

controlled for bubbling. As soon as the gas bubble touched the hydrate layer, the hydrate film on the suspended bubble grew. After the formation of hydrate film on the bubble, the optical microscope recording and Raman spectrum measurement start.

3. RESULTS AND DISCUSSION

3.1. Morphological evolution characteristics of CH₄ hydrate film under the competition of SDS concentration and subcooling

Fig. 3 shows the effect of varied SDS solution concentrations on the formation of CH₄ hydrate under the conditions of 3.2 MPa pressure, 0.8 K subcooling, where t_0 represents the time lateral hydrate film growth completing. The initial film morphology of CH₄ hydrate was found to be obviously rougher with the addition of

25 ppm SDS, which is a reflection of the increased initial film thickness and uneven hydrate surface. That is, SDS solution in low concentration can also influence the hydrate formation to a certain extent. However, with the extension of growth time, the morphology of hydrate film became similar to that in pure water system. For the CH₄ hydrate formed with 50 ppm SDS solution, the hydrate particles formed on the gas bubble-water interface kept moving during the whole experimental process, and the complete hydrate film could not be achieved. Since the continuous renewal of the gas-liquid interface is significantly conducive to the successive hydrate formation, it can be inferred that there is a critical SDS concentration that the formation of CH₄ hydrate could be obviously promoted only above the critical point.

Table 1. Experimental conditions and results for CH₄ hydrate film formations at various SDS concentration and pressure

Runs	Temperature (K)	Pressure (MPa)	Subcooling (K)	SDS concentration (ppm)	Agglomeration or not
1	274.65	3.2	0.8	0	Yes
2		3.2	0.8	25	Yes
3		3.2	0.8	50	No
4		3.8	2.4	0	Yes
5		3.8	2.4	50	Yes
6		3.8	2.4	100	Yes
7		3.6	1.9	100	No
8		5.2	5.4	0	Yes
9		5.2	5.4	50	Yes

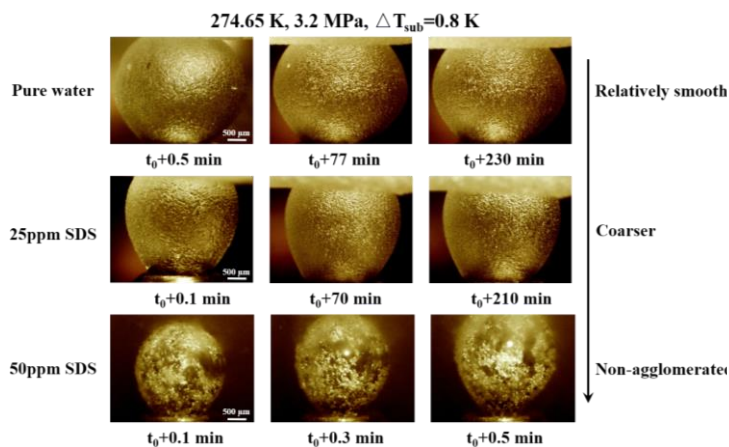


Fig. 3. Formation and evolution characteristics of CH₄ hydrate film at 0.8 K subcooling and different SDS concentrations.

As the subcooling reaching 2.4 K after the hydrate formation pressure increased slightly (from 3.2 MPa to 3.8 MPa), the morphology and its evolution of CH₄

hydrate film formed by SDS solution is presented in Fig. 4a. It can be found that the small increase in the hydrate formation driving force with the same 50 ppm SDS solution, however, directly inhibits the non-aggregated phenomenon. Nevertheless, the concentration of 50 ppm SDS under this driving force can still change the morphology of the hydrate film and lead the hydrate particles accumulated on the film to be coarser. In addition, it can be inferred, from the downward growth of the interface hydrate at time $t_0 + 270$ min in Fig. 4a and the comparison with the film morphology in pure water system, that SDS promoted the hydrate growth and delayed the aging of the film. However, the hydrate growth seemed to mainly depend on the thickening growth of hydrate film to aqueous phase. We consider that the significant change of hydrate morphology with the increase of subcooling could be mainly attributed to the change in dominance due to the competition between driving force and SDS concentration on hydrate

formation. Although the raised driving force for hydrate formation was also conducive to hydrate growth, it is inferior compared to that of hydrate growth with uninterrupted renewal of gas-liquid interface as shown in Fig. 2.

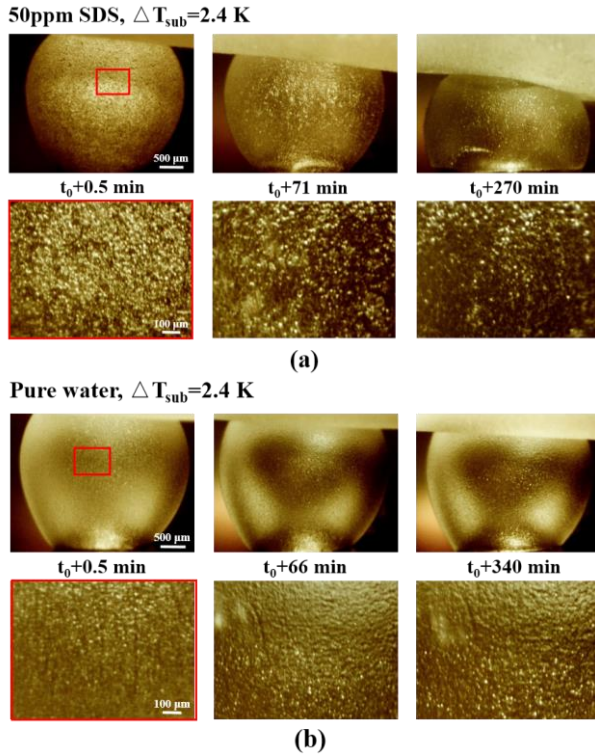


Fig. 4. Comparison of CH_4 hydrate film morphologies formed in 50 ppm SDS solution and pure water system at 2.4 K subcooling.

To enhance the competitiveness of SDS, we further increased SDS concentration, as presented in Fig. 5a. The further increase of SDS concentration led to the initial hydrate particles being fine, while still strengthened the hydrate growth. The influence of driving force on hydrate formation remained dominant under this SDS concentration condition. After the subcooling was reduced to 1.9 K, the mobile and non-aggregated phenomenon of CH_4 hydrate particles on the gas-liquid interface appeared again, indicating that the concentration of 100 ppm SDS exceeds the critical condition for SDS dominating CH_4 hydrate growth under this driving force condition. It will significantly enhance the sustainable growth ability of CH_4 hydrate.

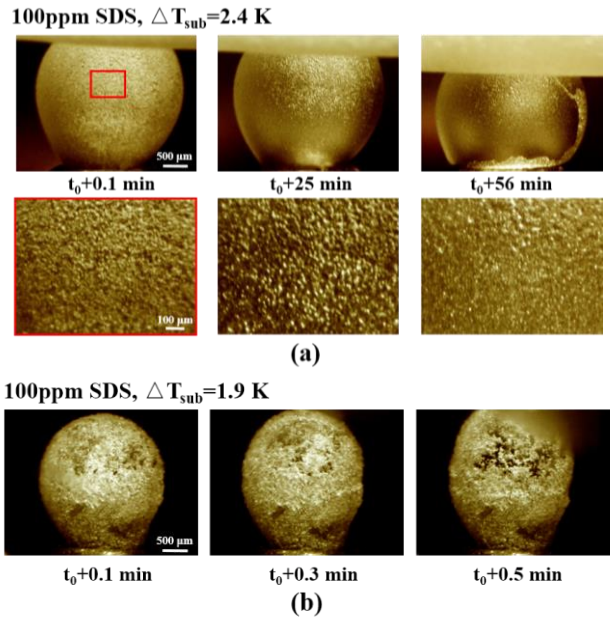


Fig. 5. Morphology characteristics of CH_4 hydrate film in 100 ppm SDS solution under different subcooling conditions.

3.2. Response characteristics of Raman spectra to its initial CH_4 hydrate film morphology

Fig. 6 illustrates the initial Raman spectra of CH_4 hydrate and its corresponding hydrate film morphology under several different pressures and SDS concentrations. According to the Raman peak of CH_4 hydrate, the addition of 50 ppm SDS significantly increased the initial hydrate film thickness for the subcooling of 2.4 K. 50 ppm SDS solution can also increase the initial thickness of CH_4 hydrate film at relatively high subcooling of 5.4 K, but its enhancement amplitude is significantly weaker than that of 2.4 K. This phenomenon was consistent with the conclusion of hydrate morphology change.

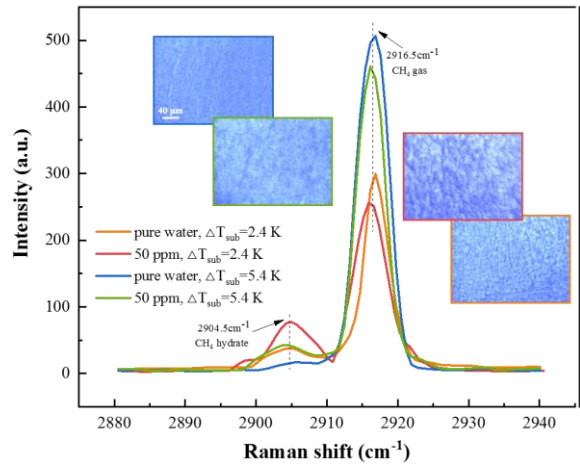


Fig. 6. Initial Raman spectra of CH_4 hydrate and its corresponding hydrate film morphology under several different pressures and SDS concentrations.

4. CONCLUSION

In this study, the effects of SDS and subcooling on the formation and evolution of CH₄ hydrate film were investigated from mesoscopic to molecular scale by combining with optical microscope and Raman spectrum. The experimental results showed that a competitive mechanism between subcooling and SDS concentration on the CH₄ hydrate formation may exist, which could dominate the growth mode of CH₄ hydrate. In case of the influence of subcooling being greater, a complete CH₄ hydrate film was formed. Once SDS concentration dominates hydrate growth, a non-aggregated CH₄ hydrate film can be formed, which ensures the continuable renewal of gas-liquid interface and is conducive for continuous hydrate growth. The critical concentrations of SDS varied with different subcooling conditions so that only if the SDS concentration exceeded the critical point can the formation of CH₄ hydrate be obviously accelerated. For low subcooling, only a small amount of SDS was required to obviously promote the growth of CH₄ hydrate. Although CH₄ hydrate film could not present the non-aggregated state when subcooling dominated hydrate formation, SDS can also promote the growth of hydrate to a certain extent. We consider whether SDS can significantly promote hydrate formation depends on the comprehensive influence of single hydrate crystal configuration of hydrate film, hydrate film growth rate and the concentration-related overall adsorption ability of SDS.

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