Direct Observation of the Effect of Sodium Dodecyl Sulfate (SDS) on the HCFC-22 Hydrate Formation in a Static Mixer

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Direct observation of the formation behavior of HCFC-22 hydrate in a Kenics type static mixer was conducted focusing on the effect of an addition of a surfactant, sodium dodecyl sulfate (SDS). The formation pattern of the hydrate was changed by the SDS addition from "slurry" to "plug," and a continuous cycle of hydrate film formation and bubble escape was observed. The hydrate formation rate was increased about 10-fold by the addition of SDS (1000 ppm).

Gas hydrates (hydrates, hereafter) are inclusion compounds with cage-like structures composed of hydrogen-bonded water molecules. Several applications of hydrates have been proposed in environmental and energy fields, including gas storage, separation, and transportation. To make these applications viable, an effective hydrate formation process with a high formation rate and low power consumption will be required. Hydrate formation is usually carried out in a stirred-tank-type reactor, where hydrates form at the bubble surface of the guest gas dispersed in the water-phase. Once the hydrate is formed, however, the further formation would be blocked by the hydrate film hindering the direct contact of gas-phase and water-phase. For the continuous formation of hydrate, the hydrate film should be removed by vigorous stirring, which may increase the power consumption of the process. Another method for promoting hydrate formation would be using kinetic promoters. Zhong and Rogers[1] first reported a dramatic increase in the hydrate formation rate by a surfactant, sodium dodecyl sulfate (SDS). A number of reports on the promotion effect of the surfactants have been published after that;[2] however, mechanism of the effect of surfactants on the hydrate formation was not thoroughly clarified.

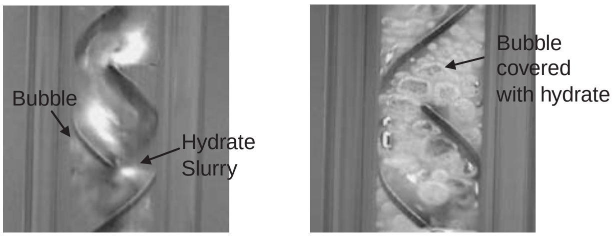
This study attempts to elucidate the effect of SDS addition through the direct observations of hydrate formation in a static mixer. The static mixer is a motionless mixing device composed of mixing elements inserted in a straight empty pipe, which has been successfully applied to the hydrate formation process by the present authors.[3] In this study, a transparent Pyrex-glass tube was used as a housing pipe, which enables a direct observation of the formation behavior of hydrates in the mixer. Details of the experimental system were described elsewhere.[3b] The mixer was set vertically, and water (or SDS solution) was first filled in the mixer. Flow of the guest gas (HCFC-22) was introduced from the bottom side through a nozzle (2-mm inner diameter). Hydrate was formed at the interface of the gas bubbles and water during the ascending of the bubbles. Unreacted gas was ventilated from the top of the mixer, and the outlet and inlet gas flow rates were monitored by mass flow meters to determine the hydrate formation rate.

Figure 1 shows snapshots of two distinct patters of hydrate formation, "hydrate slurry" and "hydrate plug," observed in the Kenics type static mixer without SDS. The hydrate slurry (Figure 1a) was mainly formed under higher temperature and lower pressure conditions. Hydrate film was initially formed at the bubble surface, and then the film was removed (shedding) from the surface and dispersed in water phase as small hydrate particles. No plugging of the reactor was observed in such cases. The hydrate plug (Figure 1b) was observed under lower temperature and higher pressure conditions, which are more favorable for the hydrate formation. The bubbles were quickly covered with hydrate film, and trapped in the hydrate shell. Then, the bubbles covered with the hydrate film agglomerated to form the hydrate plug, which eventually plugged in the mixer. The apparent gas uptake rate for the case with the hydrate plug formation was higher than that for the case with the hydrate slurry formation.

The addition of SDS in the water phase (1000 ppm) changed the hydrate formation pattern. Figure 2 shows the time variation of the hydrate formation under the same condition as the case of Figure 1b, under which the hydrate slurry was formed without SDS. At the initial stage up to 20 s after the gas uptake was started, the hydrate film was formed at the bubble surface, and the film was removed to form the hydrate slurry (Figure 2a). After 40 s, the bubbles covered with hydrate film started to agglomerate to form the hydrate plug as shown in Figure 2b. The trapped gas bubbles, however, escaped from the shell by breaking the hydrate film (Figure 2c). The escaping bubbles of HCFC-22 into the water phase were quickly re-covered with the hydrate film, but the trapped gas re-escaped from the shell. This hydrate formation-bubble escaping cycle continued for a while, and the size of bubbles was reduced with time. The hydrate shells remaining after the escape of bubbles were agglomerated in the mixer. Finally, the gas phase was almost completely convert-

(a) Hydrate "slurry" formation (b) Hydrate "plug" formation

Figure 1. Snapshots of two typical formation patterns of HCFC-22 hydrate in a Kenics type static mixer without SDS. (a) Temperature = 283 K, (b) 280 K. Other conditions are common: gas flow rate = 198 mL/min; pressure = 0.40 MPa. Elapsed time after starting hydrate formation = (a) 95 s, (b) 50 s.



(a) Hydrate slurry formation (b) Bubble agglomeration

(c) Escape of trapped gas (d) Hydrate particle agglomeration

Figure 2. Snapshots of HCFC-22 hydrate formation with 1000 ppm SDS aqueous solution in a Kenics type static mixer. Inlet flow rate of HCFC-22 gas was 198 mL/min, pressure 0.40 MPa, Temperature = 283 K. Elapsed time after the hydrate formation started = (a) 20 s, (b) 40 s, (c) 50 s, (d) 60 s.

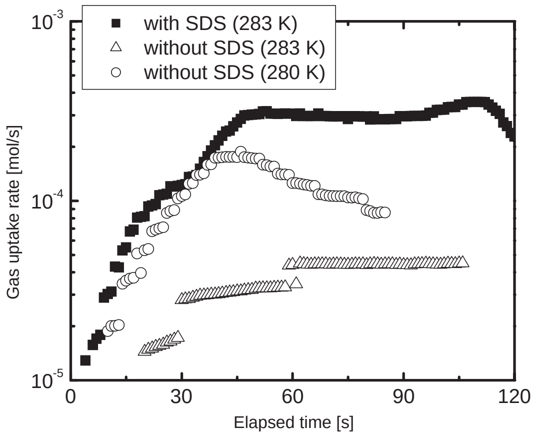


Figure 3. Time variation of the gas uptake during the hydrate formation.

ed into the hydrate phase (Figure 2d). Similar behavior was observed for the lower-temperature conditions at 278 K with the same pressure.

The gas uptake rates of HCFC-22 during the hydrate formation were plotted against the elapsed time in Figure 3. Since the solubility of HCFC-22 in water is extremely low, the apparent gas uptake rate can be regarded as the hydrate formation rate.

The hydrate formation rates at 283 K and 0.4 MPa increased with time at the initial stage up to 40 s, which corresponds to the transition of the hydrate slurry formation to the hydrate plug formation as shown in Figures 2a and 2b. The formation rate became almost constant after that, which corresponds to the continuous cycle of hydrate formation-bubble escaping. The formation rate was accelerated about ten-fold by the addition of SDS compared with the case without SDS under the same temperature and pressure, under which the hydrate slurry was formed. The initial hydrate formation rate with SDS at 283 K and 0.4 MPa was almost equivalent to that without SDS at 280 K and 0.4 MPa. However, decline of the formation rate was observed for the case without SDS after about 40 s. This decline corresponds to the plugging of the mixer by the agglomerated hydrate plug.

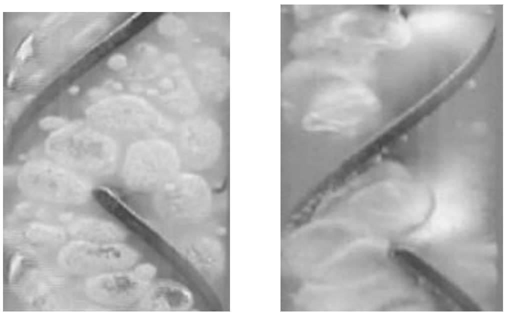


Figure 4. Surface of the gas bubbles covered with the hydrate film formed with SDS (left) and without SDS (right). Conditions are same as those in Figure 2.

The above effects of the SDS addition could be attributed to a morphology change of the hydrate film. The hydrate film formed with SDS addition seems to be composed of a number of small crystals of hydrate, while hydrate film with smoother surface was formed without SDS as shown in Figure 4. It is considered that the surface hydrate film would be more loosely packed or even porous when formed with SDS, which would provide direct contact paths for the gas phase and the aqueous phase. As a result, the hydrate formation rate would be accelerated by the addition of SDS. The loosely packing would also reduce the mechanical strength of the hydrate film, which enabled the gas bubbles to be escaped from the hydrate shell by breaking the film more easily. The morphology change would be due to the adsorption of SDS molecules[4] on the bubble surface, with which the continuous growth of the hydrate crystals on the bubble surface to form the hydrate film with smooth surface would be retarded.

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