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Acceleration of methane hydrate nucleation by crystals of hydrated sodium dodecyl sulfate

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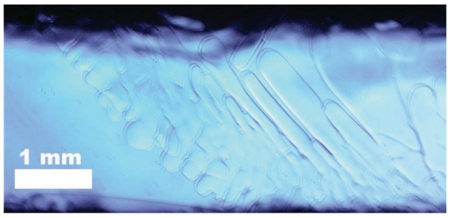
It was shown that hydrated crystals of sodium dodecyl sulfate (SDS), which precipitate from dilute SDS solutions sharply accelerate nucleation of methane gas hydrate. This finding adds significant details to the available information on the mechanisms of hydrate formation from SDS solutions and can form the basis for the development of a new class of kinetic promoters of hydrate formation.



Keywords: gas hydrate, nucleation, methane, hydrated crystals, sodium dodecyl sulfate, hydrate formation promoter, kinetic promoter.

One of the current trends in the field of gas hydrates is related to the search for substances which accelerate formation of gas hydrates from water and gas under static conditions.[1–4] These properties are characteristic of surfactants, in particular sodium dodecyl sulfate (SDS), which is the most actively examined substance in this field.[3,5–7] It is known that under static conditions, the formation of hydrate usually occurs at the gas–water interface. The resulting hydrate film blocks the mass transfer of gas to liquid and practically stops the process of hydrate formation. The degree of water to hydrate conversion is usually a few percent in this case. In the presence of a surfactant dissolved in water, the hydrate is formed in the form of a loose mass saturated with water that creeps out onto the walls of the reactor; 80–90% of the water turns into hydrate in this case. Previous reports have shown that under static conditions SDS inhibited formation of gas hydrates at low concentrations and promoted the formation of gas hydrates only at the high concentration.[6,8] Here we present new results concerning the role of SDS in methane hydrate nucleation.

The experiments were carried out using the apparatus described in detail elsewhere.[9] Typically, a sample of water or 0.1 wt% SDS solution were placed in a glass cuvette with internal dimensions of 18 × 10 × 14 mm^3 (width × thickness × height). The cuvette was inserted into a high-pressure chamber. Further, the apparatus was purged with methane (1 MPa) three times, and the required gas pressure and temperature were maintained in the chamber. The high-pressure chamber has two leucosapphire windows which permits visual observation and video registration of the processes occurring in the cuvette. More than ten experiments have been performed on methane hydrate formation from SDS aqueous solution. In all cases, the obtained results agree with each other.

In preliminary experiments, we observed that methane hydrate formation is preceded by the appearance of unknown transparent crystals obviously not being methane hydrate on the surface or in the volume of the solution. The phase diagram analysis of the SDS–water system and experiments with SDS solutions of different concentrations showed that these crystals are one of the low-water SDS hydrates, most likely a dihydrate.[6,10] The precipitation/dissolution temperature of these crystals is ~10 °C at atmospheric pressure when SDS solution concentration is 0.1 wt%.[6,10] The increased methane pressure only slightly shifts the precipitation–dissolution equilibrium temperature of hydrated SDS crystals.[11] The nucleation of methane hydrate soon after the formation of these crystals was observed in every experiment. This suggested that hydrated SDS crystals are an effective promoter of methane hydrate formation. Further, the growth of the hydrate in all cases proceeded according to the above scheme (the hydrate creeps out onto the walls of the reactor), which is common for surfactant solutions. It is interesting to note that according to published data,[12] the density of hydrated SDS crystals is ~1.2 g cm^{-3}. Apparently, they can stay on the water surface due to surface tension forces.

To confirm or refuse the hypothesis about the acceleration of methane hydrate nucleation by hydrated SDS crystals, we performed the following experiments. Hydrated SDS crystals were grown from 0.1 wt% SDS solution at 0 °C and atmospheric pressure. The crystals formed within ~12 h as almost invisible plates and needles on the surface of SDS solution. Their presence was confirmed by visual observations of sinking crystals when tapping on the apparatus [Figure 1(*a*)] and partial ‘immersion’ of the crystals into the liquid during the subsequent purging of the apparatus with methane [Figure 1(*b*),(*c*)]. We can say that the gas pressure squeezed out the crystals into the liquid. After purging, methane pressure of 3.1 MPa was set in the apparatus, which corresponds to supercooling of 1.8 °C with respect to the equilibrium curve of methane hydrate.[13] The nucleation of the hydrate occurred within 2 and 4 min in two independent experiments (Figure 2). Similar experiments were carried out at 11°C and a pressure of 9.9 MPa at the same SDS

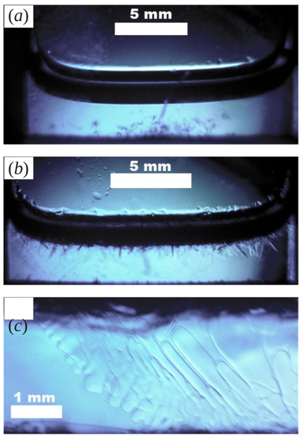


Figure 1 Crystals of hydrated SDS: (*a*) in solution at atmospheric pressure, (*b*) squeezed out into the volume of the solution when purging with methane, and (*c*) in the volume of the solution in the near-wall region of the cuvette.

concentration. The supercooling was also 1.8 °C in this case. The same supercooling value allowed us to assume that the hydrate nucleation time in this case would be the same as it was in the experiments at 0 °C. No noticeable amount of hydrated SDS crystals was formed after maintaining the SDS solution at 11 °C and atmospheric pressure for 12 h. Then the methane pressure was set at 9.9 MPa. After that, in one of the experiments, the hydrate formed after 1.5 days. In another experiment, the hydrate was not formed within a week, then the experiment was terminated. It should be noted that in the case when hydrate nucleation occurred, further growth of the hydrate proceeded with the formation of a loose mass, as described above (Figure 2). In experiments with pure water under different conditions, the hydrate was not formed during a week (then the experiments were terminated).

Thus, the obtained data show that hydrated SDS crystals precipitating from SDS solutions under suitable conditions indeed accelerate the nucleation of methane hydrate. At the same time, we did not observe a significant effect of these crystals on the process of further growth of methane hydrate. Both in the presence and in the absence of hydrated SDS crystals, the growth of hydrate occurs in the form of a loose mass extruded onto the walls of reactor. Similar considerations about the role of hydrated SDS crystals were expressed earlier.[6] In this work, this assumption is experimentally confirmed. The results obtained add significant details to our understanding of the mechanisms of the influence of SDS impurities on the processes of hydrate formation. In addition, a new class of substances has been discovered that accelerate the nucleation of gas hydrates. This may stimulate further work in this direction.

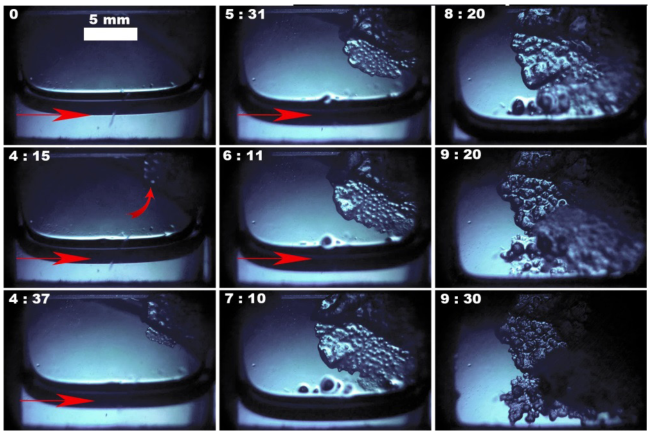


Figure 2 The process of hydrate formation from 0.1 wt% SDS solution at 0 °C under methane pressure of 3.1 MPa. Time is shown in the format min : s. The horizontal arrow marks the initial level of the solution; the bent arrow indicates the place where the hydrate mass was first observed on the cuvette wall.

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References

1 M. R. Ghaani, J. M. Schicks and N. J. English, *Appl. Sci.*, 2021, **11**, 469.
2 G. Bhattacharjee, M. N. Goh, S. E. K. Arumuganainar, Y. Zhang and P. Linga, *Energy Environ. Sci.*, 2020, **13**, 4946.
3 Z. Pan, Y. Wu, L. Shang, L. Zhou and Z. Zhang, *Front. Energy*, 2020, **14**, 463.
4 A. Yu. Manakov and A. S. Stoporev, *Russ. Chem. Rev.*, 2021, **90**, 566.
5 O. B. Kutergin, V. P. Melnikov and A. N. Nesterov, *Dokl. Akad. Nauk*, 1992, **323**, 549 (in Russian).
6 A. N. Nesterov and A. M. Reshetnikov, *J. Nat. Gas Sci. Eng.*, 2022, **99**, 104424.
7 Y. He, M.-T. Sun, C. Chen, G.-D. Zhang, K. Chao, Y. Lin and F. Wang, *J. Mater. Chem. A*, 2019, **7**, 21634.
8 B. Sowa and N. Maeda, *Energy Fuels*, 2015, **29**, 5692.
9 T. P. Adamova, A. Yu. Manakov and A. S. Stoporev, *Russ. J. Appl. Chem.*, 2019, **92**, 607 (*Zh. Prikl. Khim.*, 2019, **92**, 572).
10 H. Khan, J. M. Seddon, R. V. Law, N. J. Brooks, E. Robles, J. T. Cabral and O. Ces, *J. Colloid Interface Sci.*, 2019, **538**, 75.
11 J. S. Zhang, S. Lee and J. W. Lee, *J. Colloid Interface Sci.*, 2007, **315**, 313.
12 L. A. Smith, R. B. Hammond, K. J. Roberts, D. Machin and G. McLeod, *J. Mol. Struct.*, 2000, **554**, 173.
13 E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases*, 3rd edn., CRC Press, Boca Raton, FL, 2008.

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