

PRF# 57216-UNI9 Surfactant effect on Hydrate Crystallization at oil-water interface

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In this study we have developed a novel approach using visualization techniques and internal pressure measurements to understand cyclopentane clathrate hydrate formation in the presence of nonionic surfactants. The hydrate-inhibiting performance of low ($< \text{CMC}$), medium ($\approx \text{CMC}$), and high ($> \text{CMC}$) concentrations of Span 20, Span 80, Pluronic L31, and Tween 65 at 2°C on a $2 \mu\text{L}$ water droplet. Monitoring the internal pressure of the water droplet undergoing hydrate crystallization provided information on the change of interfacial tension during crystallization process. The results of this study provide information on surfactant effect on hydrate crystallization. The results have shown that,

- Two types of crystals were found: planar shell and conical crystal.
 - For plain water and surfactant concentration below CMC, the hydrate formed as a planar shell.
 - In the planar shell growth, the crystal starts to form at the nucleation point and grows towards the equator.
 - The undercooling acts as a driving force to propagate the hydrate front at the interface. The outcome is that the hydrate shell is constantly increasing in size.
 - Apparent average interfacial stress measurements reveal a constant decrease in apparent average interfacial stress values as a result of a constant decrease in available surface area for the surfactant molecules.
 - For surfactant concentrations above the CMC, the hydrate formed as a conical crystal.
 - When the conical crystal growth becomes large enough, a portion of the circumference of the cone breaks free from the droplet surface. Then the remaining solution from inside the droplet redistributes to fill and engulf the cone.
- The conical shape is induced by planar pressure from the crowding on the interface as the crystal wants to grow faster than the surfactants can get out of the way of the progressing hydrate front.
- Apparent average interfacial stress measurements showed an oscillatory behavior during cone generation and separation. There was an initial decrease in apparent average interfacial stress which results from the formation of the conical crystal and the reduction of available surface area for the surfactant molecules. Once the crystal has reached a critical size, a portion of the cone breaks free from the droplet surface. That results in a sudden increase in the available surface for the surfactant molecules. Hence, a temporary increase in the apparent average interfacial stress was observed. The oscillatory behaviour of the apparent average interfacial stress is a result of the growth and release of the hydrate cones from the surface of the droplet.
- As for the location of the surfactant molecules in the system, we believe that the majority of surfactant gets expelled from the interface and pushed into either the water or the cyclopentane. We also believe that some surfactant does get decorated or adsorbed to the exterior hydrate surface based on results of others who specifically tested adhesion among hydrate particles formed with (and in the presence of) surfactant. We do not believe that the surfactants are within the bulk hydrate structure at very significant concentrations due to the relatively large size of the surfactants compared to the guest molecules (surfactants would not make a stable hydrate).
- The hydrate morphology is not a function of the droplet curvature but only of the type and concentration of the surfactants.
- The lowest hydrate growth rate observed was $0.068 \text{ mm}^2/\text{min}$ with Tween 65_{high}, proving it to be the most effective inhibitor tested when used at concentrations above the CMC. The most influential properties associated with Tween 65 are believed to be its comparatively large molecular weight (1845 g/mol) and central HLB (10.5) close to 10, which work to preserve adsorption at the interface. The remainder of the surfactants all had lower weight and were of varying degrees more hydrophobic than Tween 65.

In this research project we have established a set of general conditions for the formation of the different types of hydrate crystals in the presence of nonionic surfactants. We have confirmed previous observations regarding formation of hollow conical crystals at high surfactant concentration and provided proof for previous hypothesis regarding oscillatory behaviour due to crowding of surfactant molecules at the interface. This work will help develop a better understanding of hydrate formation in the presence of surfactant molecules and can lead to the design of more effective, eco-friendly surfactants which will have broad applications in offshore natural gas production and seabed oil capture.

Career Impact:

This grant has allowed me to start the research program on hydrate formation and stability. We were able to develop an experimental system that will be useful to the formation of hydrates as well as the formation of other crystals. We were able to publish the results in a scientific paper and two national conferences. I have also started collaboration with Dr. Malcolm Kelland of the University of Stavanger, Norway.

Student Impact:

Three graduate students have presented this project as their MS thesis. Currently one graduate student and two undergraduate students are working on the research project.

Published Results:

This study was published in

1. Kevin Dann and Liat Rosenfeld, "Surfactant Effect on Hydrate Crystallization at the Oil–Water Interface", *Langmuir* 2018 34 (21), 6085-6094, DOI: 10.1021/acs.langmuir.8b00333.
2. Hoi Yan Ko, Kevin Dann and Liat Rosenfeld, "Studying surfactant effect on hydrate crystallization at oil-water interface using low cost integrated modular Peltier device (IMPd)", *JoVE* 2019, Accepted.

Results of the study were presented in two conferences: American Physical Society - Division of Fluid Dynamics (APS-DFD), November 2017, Denver CO and the annual AIChE meeting, October 2017, Minneapolis MN.