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# Anti-agglomerant performance of surfactants evaluated in cyclopentane hydrate and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> gas hydrate systems.

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## Abstract

The risk of gas hydrate formation and plugging of oil and gas production pipelines is one of the main concerns of flow assurance engineers. The use of anti-agglomerants (AAs) is increasingly regarded as a robust and economical option to prevent hydrate blockage. Indeed, their performances are a priori independent of the subcooling, and their minimal concentration (several wt% in the water phase) for an efficient protection is much lower than those of thermodynamic hydrate inhibitors (e.g. methanol or glycols, which require several dozen wt%).

The main objective of this work was to evaluate and compare the AA performance of surfactants of different affinity in cyclopentane (CP) hydrate and gas (methane – propane mixture) hydrate systems. The study was performed with two surfactants: Noranium<sup>®</sup> DA 50 and Inipol<sup>®</sup> AH 81, which are respectively water-soluble and dispersible in water. Their AA performance was evaluated and compared without or with 4 wt% NaCl. A comparative study of the effect of the surfactants on the water/CP interfacial activity was carried out by surface pressure measurements. The impact of the surfactants on hydrate formation and morphology was observed by microscopic observations at the water/CP interface. Lastly, the AA performance of DA 50 and AH 81, was evaluated at the macroscopic scale in a batch reactor under agitation. The experiments in reactor were performed in oil-dominated systems (70 vol%) with CP as the oil phase in the CP hydrate system, and n-octane in the gas hydrate one.

Measurements of interfacial tension (IFT) were performed with a drop tensiometer on a CP drop in an aqueous phase. They allowed to determinate the surface pressure,  $\Pi (= \gamma_0 - \gamma)$ , which is the difference between the IFT of a system without surfactant ( $\gamma_0$ ) and the IFT of the system with surfactant ( $\gamma$ ). Experiments were conducted with a concentration of 0.01 wt% AA because IFT was too low at higher surfactant concentration with NaCl to achieve measurements. Adding NaCl affected the interfacial activity of DA 50 with a significant increasing of  $\Pi$ , whereas with AH 81,  $\Pi$  value remained constant.

The microscopic observations at the water/CP interface showed that spectacular changes in the hydrate growth pattern and morphology were observed between DA 50 without NaCl and DA 50 + 4 wt% NaCl. In the former case, smooth and striated plates separated by wrinkled areas formed. In the latter case, small pyramidal crystals with the vertex pointing to the CP phase covered the whole interface, suggesting hydrate crystals were CP-wettable. With AH 81, large pyramidal crystals grew with the vertex pointing to the CP phase and then sank into the water phase underneath the water/CP interface. Such a behavior reflected a modification of the hydrate wettability, and thus suggested changes in the configuration of the AA molecules adsorbed on the hydrate surface. The observed unusual formation of individual crystals with AH 81 and DA 50 in the presence of NaCl may have an interesting effect on the AA performance of these surfactants.

The AA performance of the surfactants was evaluated by torque measurements in a batch agitated reactor. Without surfactant and with or without salt, a “catastrophic” hydrate crystallization occurred, that led to the complete blockage of the agitator. In the presence of DA 50, the systems without NaCl showed poor AA performance: a peak of torque occurred in both CP and gas hydrate systems. The addition of NaCl had a benefic effect on the torque signal, which means a better AA performance of DA 50. The microscopic observation of final CP hydrate particles showed without NaCl, large particles ( $\approx 700 \mu\text{m}$ ) composed of several crystals aggregated, whereas with 4 wt% NaCl the crystals were very small ( $\approx 70 \mu\text{m}$ ) and not agglomerated. AH 81 showed the opposite behavior: without NaCl, it presented a good AA performance, and in the presence of NaCl, its performance decreased. The observation of CP hydrate particles formed with AH 81, showed large agglomerated particles. The fact the particles did not dispersed into the

CP phase suggested that they were water-wettable. The results obtained with both CP and gas hydrates are consistent with each other, and torque measurements reported with both surfactants suggest different ways of actions in their ability to disperse hydrates into the oil phase. DA 50 with NaCl allows the formation of oil-wettable hydrate particles preventing their agglomeration. On the other hand, with AH 81, the hydrate particles remain water-wettable but the adsorbed AH 81 molecules prevent/limit the formation of strong capillary bridges between them.