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# USE OF MICROSCOPIC OBSERVATIONS OF CYCLOPENTANE HYDRATE CRYSTAL MORPHOLOGY AND GROWTH PATTERN TO ESTIMATE THE ANTI-AGGLOMERANT CAPACITY OF SURFACTANTS

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## INTRODUCTION

Subsea production of oil and gas is always faced with the risk of pipeline blockage by natural gas hydrate plugs. Anti-agglomerants (AAs) are chemicals, usually surfactants, which can be used to prevent such a risk. They enable the hydrates to form as a transportable slurry of particles dispersed in the oil phase. AAs are tested for performance in stirred vessels, rocking cells and flow loops usually at high pressure. Cyclopentane (CP) hydrates, which have the same structure (sII) as natural gas hydrates, form at atmospheric pressure, and therefore have been widely used for a quick evaluation of the performance of AAs.

The objective of the present work was to find out if microscopic observations of hydrate formation at a quiescent water/CP interface might be a method for obtaining valuable indicators as regards the anti-agglomeration capacity of a surfactant. For the ten different surfactants used in this study, the morphology and wettability of the hydrate crystals and the AA performance (evaluated by torque measurements) were determined on CP hydrates. For some of them, the experiments were also performed with CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> hydrates at high pressure. In addition, the influence of some experimental parameters such as the presence of salt (NaCl) and the composition of the oil phase on the hydrate crystal morphology and AA performance were investigated for some of the surfactants studied.

## EXPERIMENTAL CONDITIONS

**Materials:** Cyclopentane (CP) ; Gas mixture of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> (84/16 (mol%/mol%)) ; n-octane (n-C8) ; n-dodecane (n-C12) ; Deionized water ; Salt (NaCl)

**Anti-agglomerants:** Noranium® DA 50, Inipol® AH 81, Noranium® CES 80, Noranium® M2C, and Noranium® M2SH were provided by Arkema ; BzC12, TMDACI, TMDAHS, and CES Br were provided by Sigma Aldrich ; IND is a reference AA of the market.

### Experimental conditions:

CP hydrates: Subcooling:  $\Delta T_{sub} = 6 \text{ }^\circ\text{C}$  ;  $P = P_{atm}$  ; Oil phase: CP, CP/n-C8 or CP/n-C12

Microscopic observations: 0.1 wt% of AA ; 0 or 4 wt% of NaCl

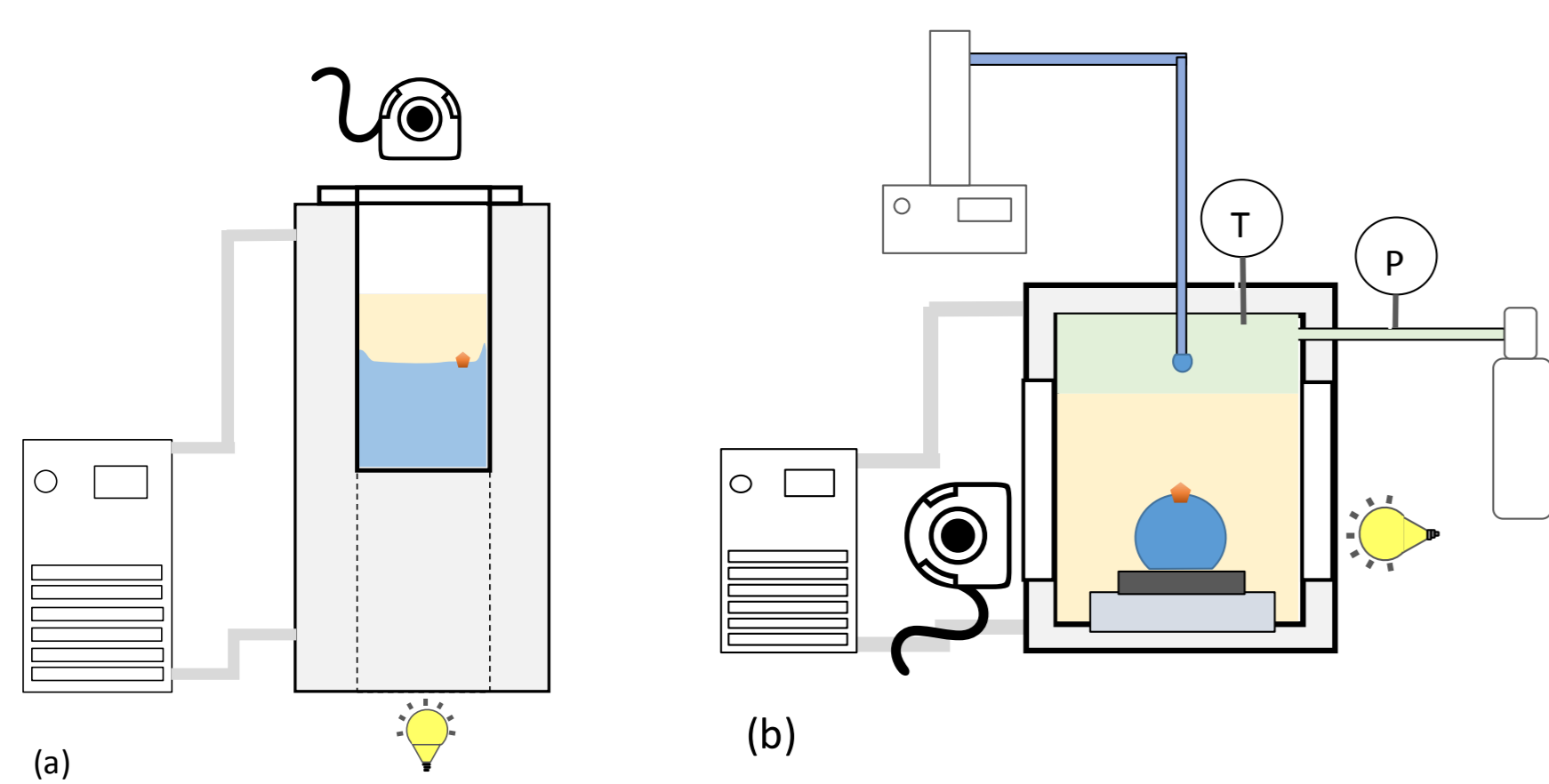
CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> hydrates:  $\Delta T_{sub} \approx 10 \text{ }^\circ\text{C}$  ;  $P = 70 \text{ bar}$  ; Oil phase: n-C8

AA performances: 1 wt% of AA ; 0 or 4 wt% of NaCl ; Watercut: 30 vol% ;  $N = 200 \text{ rpm}$

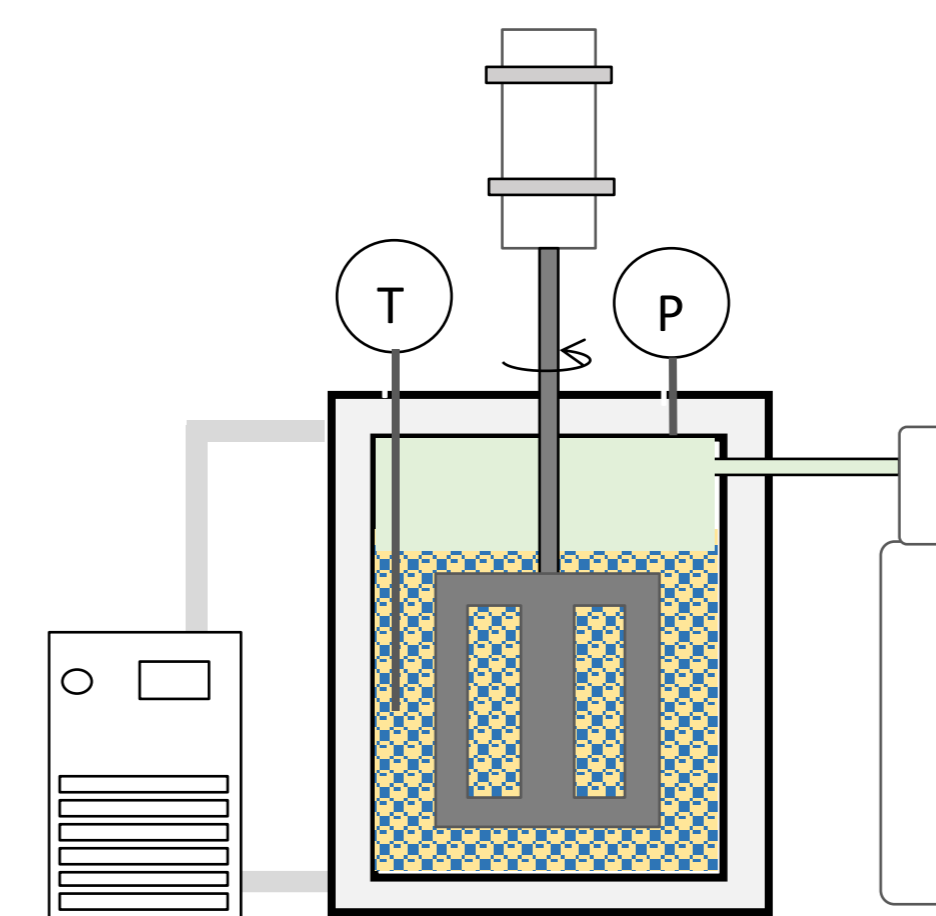
### Apparatus:

For the microscopic observations:

For the AA performances:



**Figure 1:** Experimental setups used for the microscopic observations of hydrate formation: a) for CP hydrates, and b) for CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> hydrates.



**Figure 2:** Experimental setup used for the evaluation of anti-agglomeration performance.

## RESULTS AND DISCUSSION

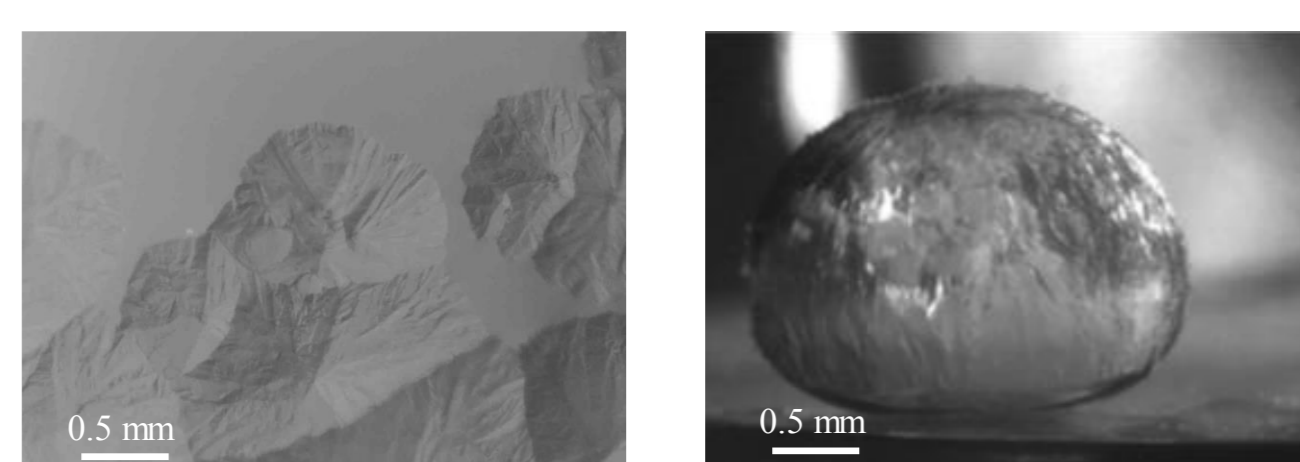
### CP hydrates

### CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> hydrates

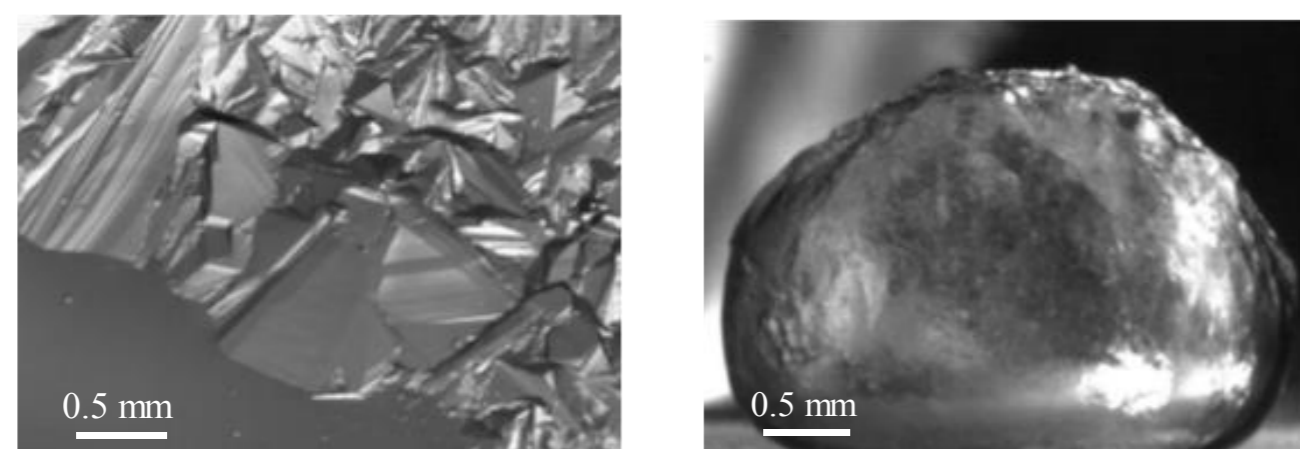
### CP hydrates

### CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> hydrates

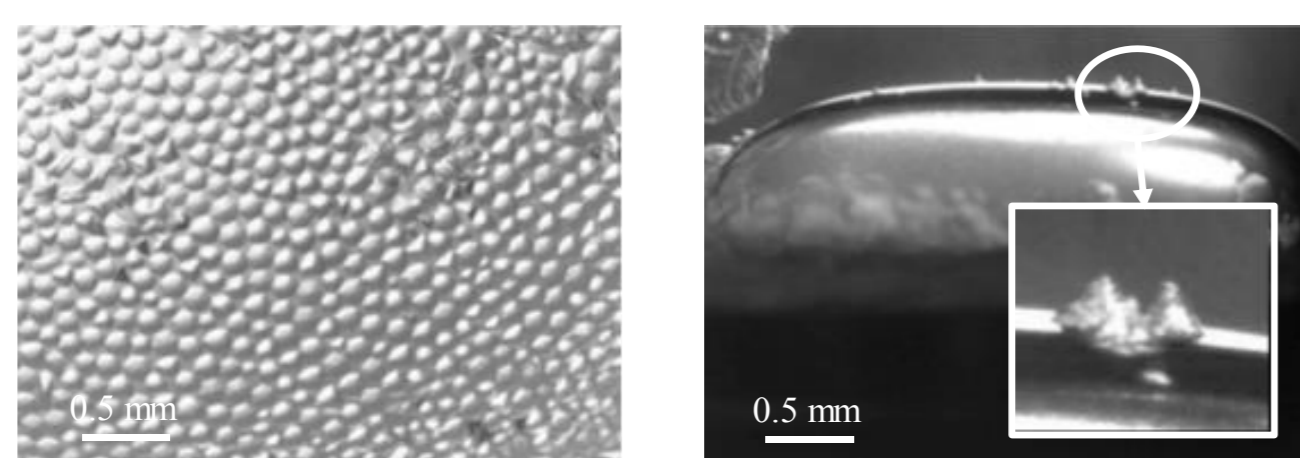
Without surfactant



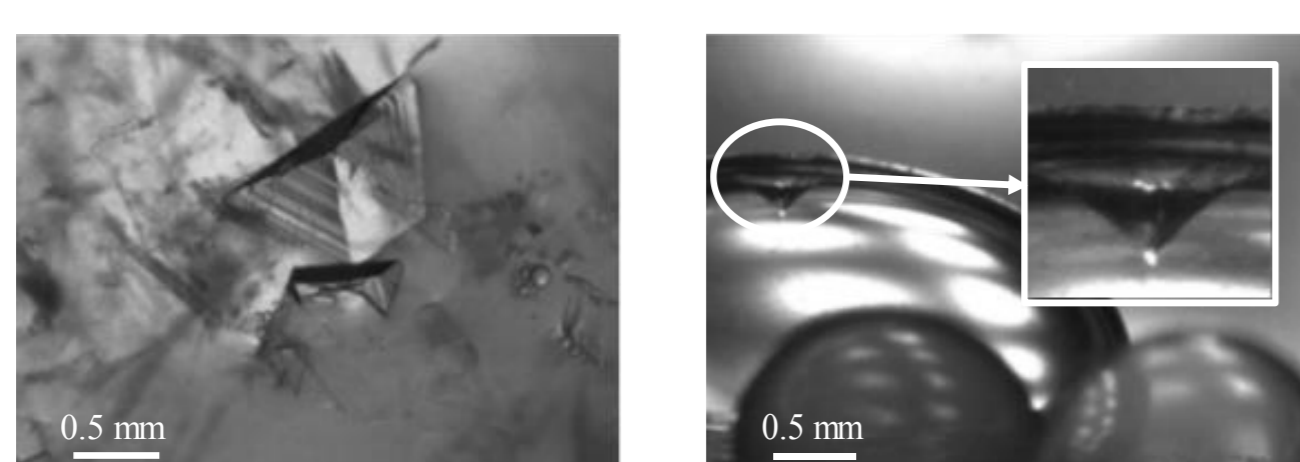
DA 50



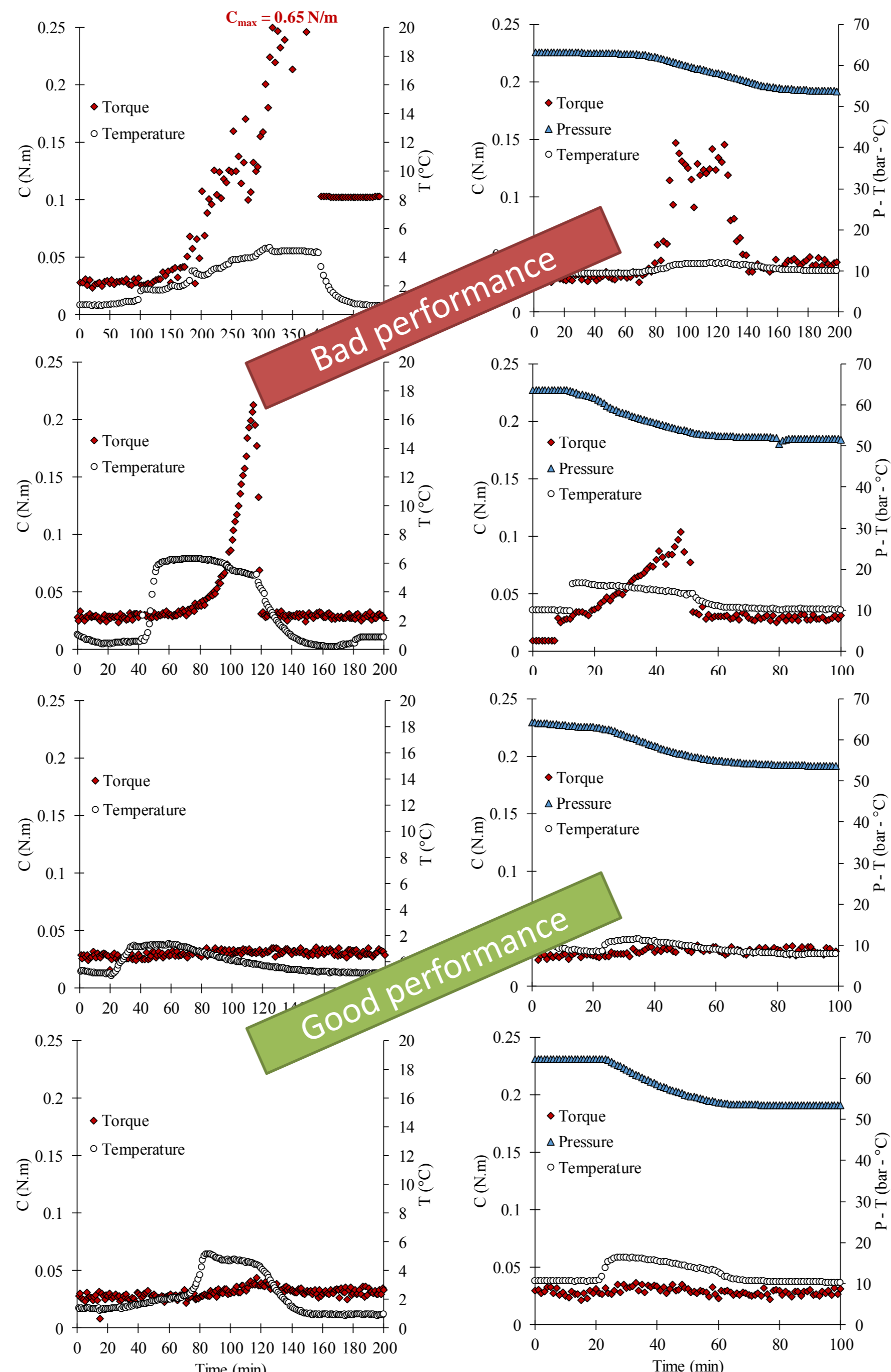
DA 50 + 4wt% NaCl



AH 81



**Figure 3:** Microscopic observations of CP-hydrate and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub>-hydrate crystals at the water/oil interface.



**Figure 4:** Torque (C), pressure (P) and temperature (T) vs. time.

Figures 3 and 4 show typical results obtained with the different surfactants studied.

**“Bad performance”** means the torque C significantly increased during the hydrate formation experiment. Large (>1000 μm) CP-hydrate particles, *wetted by the water phase*, were observed at the end of the experiment.

**“Good performance”** means C remained almost constant during the hydrate formation experiment.

- All the surfactants (IND, CES 80, M2SH) that induced the formation of *individual* hydrate crystals at the water/CP interface and that changed hydrate crystals from *water-wet* to *oil-wet* crystals showed good AA performance.
- Some surfactants (AH 81, TMDAHS) that induced the formation of *individual* hydrate crystals at the water/CP interface but did not change the wetting of the crystals showed good AA performance. These surfactants sufficiently decreased the water/oil interfacial tension to drastically reduce the capillary adhesion between the hydrate particles.
- A surfactant can show bad AA performance for a system composition and good performance for a different composition (e.g. DA 50, and DA 50 + 4 wt% NaCl (see Figure 3 and 4)).
- The nature of the counterion of the surfactant molecule may drastically change the AA performance. As an example, CES 80 and CES Br have a different counterion: ethylsulfate for CES 80 and bromide for CES Br. The former surfactant showed good AA performance, whereas the latter showed bad performance.

## CONCLUSIONS

The similarities between the shapes of the CP-hydrate crystals and the CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub>-hydrate crystals formed at the water/oil interface (Figure 3) and between the AA performance of the surfactants for both hydrate systems (Figure 4) show that the CP hydrates are interesting analogs for sII gas hydrates for evaluation of the antiagglomeration potential of a surfactant. The experimental results obtained with the ten different surfactants and the different conditions used in this study suggest the following correlation: the surfactant that induces the formation of individual hydrate crystals at the water/CP interface that have poor tendency to agglomerate to each other exhibits good AA performance. Therefore, the microscopic observation of the morphology and growth pattern of CP-hydrate crystals formed at a quiescent water/CP interface might be envisaged as a simple and rapid way to assess if a surface-active molecule has anti-agglomeration capacity on sII gas hydrates.