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Morphology of Cyclopentane Hydrates in Saline Water

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Abstract

This effort focuses on morphology of cyclopentane hydrates formed from pure and saline water. Different brine solutions of Na₂SO₄, NaCl, NaCl-MgCl₂, or NaCl-KCl-MgCl₂ are considered at different concentrations and subcoolings. Especially, a small close reactor cell was used under a microscope with neither agitation nor seeds. Results show that the CPH crystals morphology is approximately comparable at the same subcooling, while the size of the individual crystals drops significantly with increasing of subcooling, regardless the type of salts and their concentrations.

Keywords: Clathrates; Cyclopentane Hydrates; Crystallization; Brine; Morphology.

1. Introduction

Cyclopentane hydrates (CPH) morphology is crucial in CPH-based desalination, or water treatment, applications since this affect strongly the desalting process and of course the equipment design. A few studies on the CPH morphology exist in literature [1–5]. Usually, only small glass vessels (about 4ml) are used. Moreover, they present an horizontal interface, no agitation, the system only consider NaCl and is seeded [1,2]. Therefore, this new effort examines other saline systems, under different concentrations, to study CPH morphology (NaCl, NaCl-

MgCl₂, NaCl-KCl-MgCl₂, and Na₂SO₄). Each time, three different subcoolings are used. A non-mixing small reactor cell (1.2ml) is used, without agitation, nor seed. Moreover, note that the geometry of the system presents a vertical interface between liquid water and cyclopentane, making the set-up easy to observe under a microscope.

2. Experimental observations

Chemicals utilized (Cyclopentane, NaCl, KCl, MgCl₂, and Na₂SO₄) were all provided by Sigma-Aldrich [6,7]. The schematic of reactor system and experimental protocol was well described by Ho-van et al [8]. The microscope is employed to observe and record the CPH crystallization, mainly at the interface between water and CP liquid. Photos of the individual hydrate crystals are taken for classification and comparison.

Effects of electrolytes and initial subcooling on the CPH morphology are illustrated in Figure 1. Three different initial subcoolings are considered in pure water and in presence of six different brine solutions (2.5°C, 3.5°C and 4.3°C). Note that, in presence of salts, the subcooling does not remain the same during the hydrate formation. Indeed, the CPH generation process excludes the salts. Hence the salinity of the brine increases along with the crystallization. Therefore, since the temperature is kept constant, only the initial subcooling is chosen for each experiment.

All pictures of individual crystals have been taken at the end of each experiment (after days), when the crystal growth has ended. In this figure, the grain boundaries are delineated in black. First, individual crystals' size at lower subcooling (2.5°C) is systematically bigger than that at higher subcoolings (3.5°C or 4.3°C). At 4.3°C initial subcooling, the approximate size 0.02–0.3mm, while the size is 0.05–0.5mm at 3.5°C, and 0.1–0.9mm at 2.5°C. This is similar to the observations of Sakemoto et al [1] and Kishimoto *et al.* [2]. Moreover, lower initial subcooling leads to polygons (2.5°C), while at higher subcoolings the smaller crystals take the form of

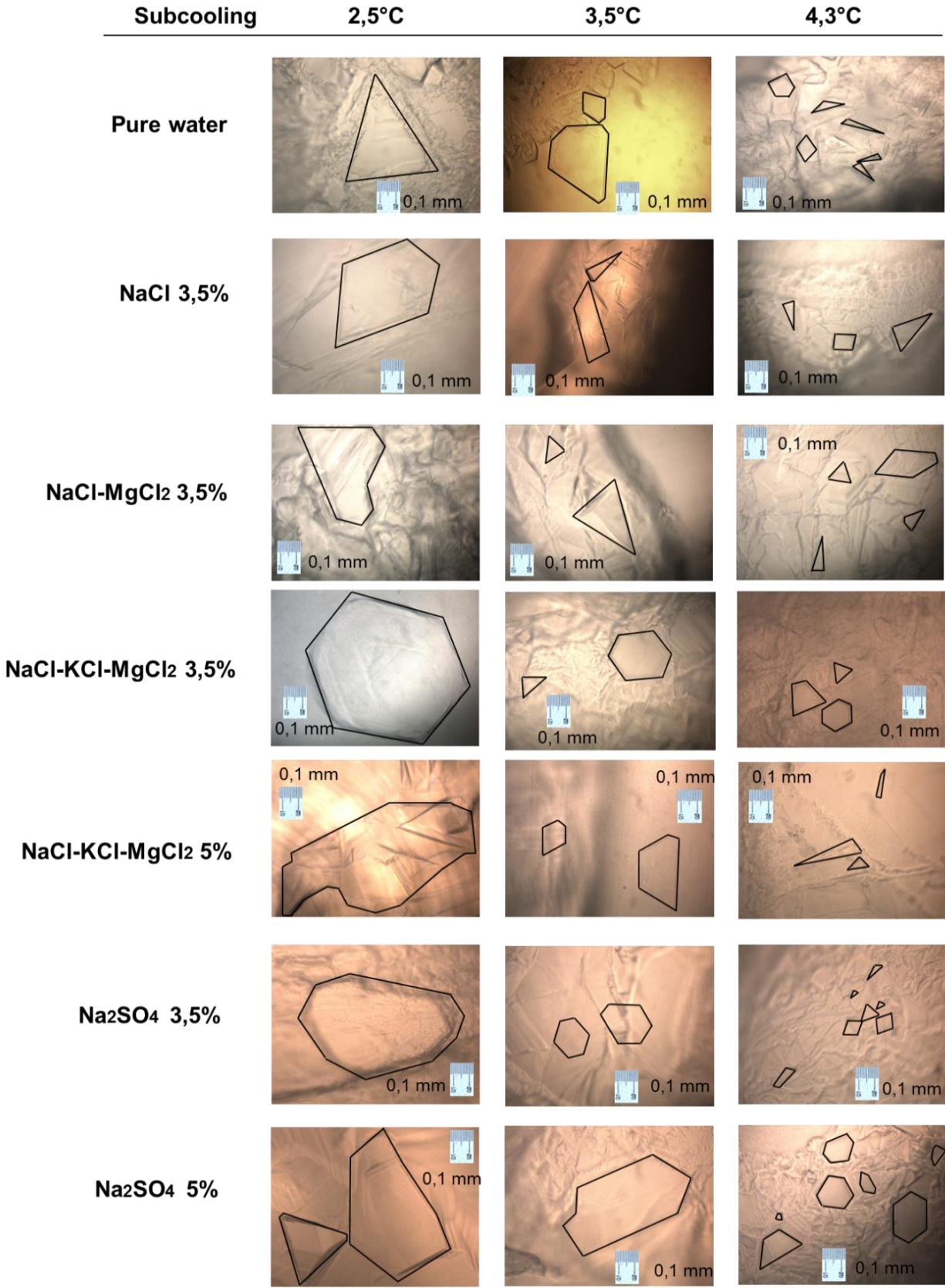


Figure 1. Morphology of individual CPH crystals under different subcoolings in brine

slender polygons (3.5°C), or sword-like shapes (4.3°C). This expected observation can be attributed to the higher crystallization rate at high driving force, leading to a reduction in the crystals size, as described in detail elsewhere [1–4,9].

However, note that, in these experiments, only 2D pictures are taken. Therefore, all photos are just planar sections of 3D crystals. Hence, sword-like shapes observed can be a slice of bigger cubic CPH crystals. Nevertheless, observations are consistent with literature [1,2], and a better-suited system would be needed to acquire more precise data on CPH morphology.

Second, it is important to notice that the size of CPH crystals is usually the same for all systems at same initial subcooling. Therefore, the kind of salt is not a significant factor to discuss the crystals' shape in the system. Only the effect of subcooling is relevant. Again, this observation agree well with literature [1,2].

Finally, the hydrate crystals in the water phase (right) are likely to form with a bigger size compared with those in the CP phase (left), as seen in Figure 2. Indeed, there is a quick growth toward the CP phase and a slower growth rate into the water phase. Ho-Van et al. [8] observed this phenomenon, took videos, and measured the interface growth speed. In the CP phase the individual crystals are more difficult to detect and seemingly stick together as a polycrystalline layer because of their very small size. Many channels and capillaries, which are supposed to be the ways for water and CP migration, can also be seen on the hydrate structure surface.

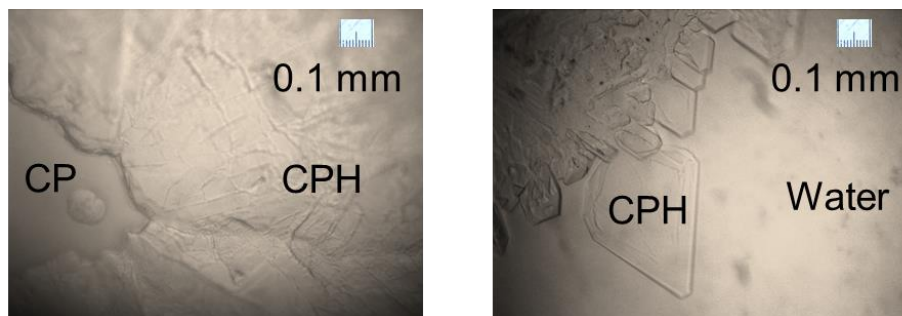


Figure 2. Crystals shape in the CP (left) and water (right) phases at initial subcooling of 3.5°C

3. Conclusion

Results show that the salt concentration does not influence significantly the crystal morphology. However, the subcooling is an essential parameter for all tested systems. Obviously, the size of individual crystals decreases with increasing of subcooling. This points out that subcooling might be used as the only parameter for the morphology classification of individual CPH crystals in such system (no agitation, with salts). Also, bigger crystals have been found in the water phase rather than in the liquid cyclopentane phase, due to the difference in the transport mechanism.

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