

GROWTH AND INHIBITION PHENOMENA OF SINGLE HYDRATE CRYSTALS

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ABSTRACT

Single crystals of structure II (sII) and structure I (sI) hydrates were grown in aqueous tetrahydrofuran (THF) and ethylene oxide (EO) solutions. Normal growth habits from the melt are {111} crystallographic planes for sII, and {110} for sI. Addition of polymeric inhibitors in very small amounts changed the growth habit of sII to thin, 2-dimensional hexagonal {111} plates, and caused rapid small-scale branching of sI crystals. The highly branched sI crystals were found to still be single crystals. Higher concentrations of inhibitor were found to stop the growth of sII crystals completely. These concentrations were as low as 0.1 wt% at low supercooling. The minimum concentration needed to stop growth changed with temperature, polymer characteristics and solution agitation. Experiments showed the polymer adsorption to be practically irreversible, and an inhibition hypothesis was developed.

INTRODUCTION

Natural gas hydrates are of great interest from several different viewpoints. Historically, hydrates have been studied as a nuisance causing problems in the oil and gas industry (Englezos, 1993). Over the previous decade another motivation for study has been their role as deposits of immense energy resources in subsea sediments and subterranean permafrost (Kvenvolden, 1994). Just recently, the economics of using hydrates as a suitable storage and transport medium for natural gas have been addressed anew (Gudmundsson and Børrehaug, 1996). A comprehensive overview of hydrates is given by Sloan (1990).

This work uses model systems as an analogue to natural gas hydrates. To circumvent the need for high pressures or very low temperatures, tetrahydrofuran (THF) and ethylene oxide (EO) aqueous solutions are used to form structure II (sII) and structure I (sI) hydrates, respectively. THF and water mixed at the stoichiometric ratio for hydrates (17 water molecules per THF molecule) has a hydrate equilibrium melting point of about 4.4°C at 1 atm. pressure. For ethylene oxide at stoichiometry (23 water molecules per 3 EO molecules) the equilibrium melting temperature is about 11°C. In natural gas applications, sII is the predominant structure.

Over the past 50 years, the thermodynamics of hydrates have been studied extensively, to the point where commercially available simulation codes can predict equilibrium conditions with an accuracy good enough for most practical purposes. The kinetics of hydrate growth have not reached nearly the same level of resolution. Several groundbreaking studies have increased our understanding, but much work still remains to be done. This work takes a very basic approach, studying single crystals of the hydrate structures.

In addition to the basics of crystal growth, the main focus of this work is to study the effects of addition of inhibitors to the systems. Thermodynamic inhibitors like methanol have traditionally been used to alleviate or avoid problems with hydrates in the oil and gas industry, but the use of these can have severe implications for economy, logistics and product quality. There has therefore been a significant driving force towards finding better inhibitors which will work at much lower concentrations. There are two main classes of these inhibitors: anti-agglomerants (emulsifying agents) and kinetic inhibitors (chemicals that interfere with the growth process of the hydrate crystals). We have studied three of the best-known kinetic inhibitors in some detail. These are poly(vinylpyrrolidone) (PVP), poly(vinylcaprolactam) (PVCap) and a terpolymer of vinylpyrrolidone, vinyl caprolactam and dimethylaminoethylmethacrylate (VC-713) (Lederhos et al., 1996).

EXPERIMENTAL PROCEDURES

The growth cell used in our experiments is shown in Fig. 1. It consists of a transparent plexiglass cooling jacket for temperature control to within 0.1 K. Glass test tubes extend into this cooling chamber, and are filled with the experimental solution. The temperature is set to a predetermined level of supercooling and the solutions are left to equilibrate before proceeding. A rubber cap holds a thin glass pipette in the middle of the test tubes (open to the atmosphere at the top and to the experimental solution at the bottom). Crystal nucleation and initial growth is forced by inserting a cold wire into the pipette, creating a momentarily large local supercooling as well as a nucleation surface. The crystal growth then progresses inside the pipette, and, more often than not, nicely defined single crystals emerge into the test solution when the growth reaches the tip of the pipette. The cooling chamber has several test tubes, enabling quick transfer of crystals between uninhibited and inhibited solutions at the same temperature.

RESULTS

Uninhibited crystal growth

THF hydrate sII crystals grown from the melt (the stoichiometric solution) exhibit the {111} crystallographic planes, in the form of regular octahedra. One such crystal is shown in Fig. 2. Irregularities in form were sometimes observed, but at moderate supercooling (0-4 K) the {111} planes were always dominant. Higher supercooling resulted in skeletal crystals while still retaining the octahedral outline. Even higher supercooling (>8 K) resulted in dendritic growth of the crystals. Over the supercooling range of 0-5 K, the growth rate of these crystals was found to be exponential as a function of the supercooling.

Crystals of EO hydrate (sI) grown from the melt exhibit the {110} crystallographic planes, in the form of a dodecahedron with rhombic faces. This is the same shape as the common garnet. Fig. 3 shows one such crystal grown at a supercooling of 0.5 K. So far, no clear evidence of other crystallographic planes has been found for this system.

Crystal growth with inhibitors

For the THF hydrates, substantial changes in growth habit is observed already at very low concentrations of inhibitor in the system. For a supercooling of 1.4 K, concentrations lower than 0.1 wt% of PVP, PVCap or VC-713 all change the growth from octahedra to two-dimensional hexagonal plates. The large faces of these plates are still {111} planes, but some questions remain as to the orientation of their thin edges. The orientation of these planes is shown in Fig. 4, where an uninhibited octahedral crystal was transferred to a solution with inhibitor. The planes grow off the edges of the existing crystal, or sprout from its body, but are always parallel to the facets of the original crystal.

At slightly higher concentrations of the inhibitors PVCap and VC-713, further crystal growth is inhibited completely. At a magnification of 50x, no growth of the crystal faces could be measured over a period of more than 24 hours. This phenomenon is seen at concentrations from 0.1 wt% at 1.4 K supercooling for the best inhibitor polymers. The minimum concentration needed to achieve full inhibition depends strongly on the supercooling and to some degree also on the polymer type and molecular weight, as well as solution agitation. Fig. 5 shows one example of the dependence on supercooling. PVP does not produce complete inhibition, even at concentrations as high as 5.0 wt%.

To study the assumed adsorption of the polymers to the crystal surface, a set of experiments were conducted in which crystals which had been exposed to the no-growth solutions for periods ranging from 5 minutes to several hours were transferred back to uninhibited solutions. None of these crystals showed any further growth until at least 3 hours after being transferred back, and then only from the vertices of the original crystals, or from the interface between the crystals and the glass pipettes. The new growth quickly grew throughout the tubes and obscured any further investigation of the surface of the original crystals.

As control experiments, several tests with known non-inhibitors were performed. Polyvinyl alcohol, urea, hydroxyethylcellulose and polyacrylamide show no impact on the growth habits of the sII crystals at all. These chemicals were chosen because of their solubility in water, and in some cases for their similarity to the polymeric inhibitors in having a vinyl backbone and high hydrogen bonding capability.

EO hydrate crystals show an even more dramatic change of growth habit when a small amount of inhibitor is added to the melt. Low concentrations (0.1-0.2 wt%) produce rapid, small-scale branching of the crystals, producing spherical globules with flimsy branches. This effect was obtained only with PVCap and VC-713. Further experiments in flat capillaries on a cooled bed under a microscope revealed that the branching EO crystals are most likely still single crystals. At intermediate concentration of inhibitor, when the branching had clearly started but were still visibly faceted, the individual branches were seen to preserve a constant crystallographic orientation throughout (Fig. 6).

The EO hydrate system is still under investigation concerning the possibility of complete inhibition.

DISCUSSION

Crystal growth planes which are exhibited macroscopically are the slowest growing planes (faster-growing planes grow out of existence). Studying molecular models of the sII hydrate, it is evident that the 6-membered rings of the large cavities all lie in the {111} planes. This suggests a hypothesis for the normal growth habit, appealing to a presumed higher energy barrier against producing these rings compared to the 5-membered rings. The H-bonds between water molecules are strained more from their natural angle in forming 6-membered rings than in forming 5-membered ones. We therefore believe this process is slower, and may result in the planes containing these rings being the slowest growing. This hypothesis is strengthened when noting that 5-membered rings seem to be naturally occurring structures in water (Rahman and Stillinger, 1973). This contrasts with Smelik and King (1996) who describe a mechanism where forming of the S^{12} cages is viewed as the controlling factor. Our hypothesis does not transfer directly to the sI hydrate, but a similar argument can be made about specific {110} planes having a higher number of hexagonal rings per unit area (although not parallel to the plane) than e.g. the {100} or the {111} planes. No clear evidence for either of these hypotheses has been presented to date.

The exponential shape of the curve for growth rate vs. supercooling would indicate that the so-called Jackson α -factor is greater than 3 (Myerson, 1993), suggesting that the surface of the growing THF hydrate is molecularly smooth, and that the growth mechanism is creation and propagation of steps on the faces. We believe that surface nucleation is the most probable mechanism for this, as invoking screw dislocations as the dominating factor does not explain orientation preference and homogeneity. However, in the very few cases where other planes than {111} are seen, screw dislocations on {111} might be invoked as an explanation for speeding these planes up and exhibiting otherwise outgrown facets.

We have no completely satisfying explanation for the 2-dimensional growth at intermediate concentrations of inhibitor. The question is complicated by the fact that in some cases, the edges of these

plates have been identified as also being $\{111\}$, and this is puzzling, as it implies that some $\{111\}$ planes grow faster than others. Fundamentally there seems to be only two options to explain this, since just at an edge one expects the physical conditions in the liquid containing the crystal to be virtually identical on the two faces very close to their common edge. One possibility is an imperfection of some kind that stimulates growth on one of the faces (the thin edge), and the other is some kind of time-dependent adsorption effect for the inhibitor.

The first of these explanations has some precedent in the effect caused by stacking faults (van de Waal, 1996). Such faults would not be unexpected on the sII $\{111\}$ planes. We do not rule out this mechanism, but we are skeptical of it because of the complete lack of macroscopic morphological evidence of such faults. The second possible explanation appeals to a mechanism where a fast-growing plane pushes aside the inhibitor as it grows, quickly enough that the polymer can not reorient and find its structural fit and bond onto the leading surface. This phenomenon has some precedence also, in the effect of kinetic inhibitors on ice growth (Harrison et al., 1987). We do not feel confident in choosing one of these explanations over the other at present, and may eventually have to appeal to a combination of the two. The results indicate preferential adsorption on $\{111\}$, but this question is not completely resolved, as the crystals also only exhibit $\{111\}$ in their uninhibited state.

We believe that the complete growth inhibition is a result of polymer adsorption to the crystal surface, with the adsorbed molecules acting as barriers to further growth. When the concentration is high enough, polymer molecules will sit closer on the surface than twice the critical radius for crystal growth at the corresponding temperature, and the crystal will not be able to grow between the polymer strands. The adsorption process is fairly rapid, as no measurable growth takes place after a crystal is transferred to an inhibited solution, and the minimum no-growth concentration is probably close to the concentration needed at the surface, as the diffusivity of the polymer is much lower than any other component in the system. However, there has to be some time involved in diffusion and orientation of the inhibitor, if the latter of the above hypotheses for 2-dimensional growth is physically correct.

The tests with non-inhibitors show that it is not enough to have long molecules acting as diffusion barriers or molecules with a high capacity for H-bonding. We think that the pendant groups of our polymers are important in achieving strong adsorption. One possible explanation is that the pendants fit as pseudo-guest molecules in unfinished large cavities, with extra binding to the surface caused by H-bonds from the carbonyl groups on the pendants. There is some evidence from molecular simulations suggesting that this might happen (Makogon (1997), Carver et al. (1995)). The experiments where inhibited crystals were transferred back into uninhibited solutions, show that the adsorption is practically irreversible. Each pendant group or H-bonding site on its own probably shows equilibrium adsorption and desorption, but in the case where numerous sites along a polymer chain are engaged in this process, desorption of some of them would have little influence on the overall molecule, and these sites would be kept close to their adsorption area, and could easily re-adsorb. For the entire polymer to desorb, all the adsorption sites would have to "let loose" at the same time, an event which is statistically unlikely after a certain number of adsorption points has been achieved for each molecule. When desorption and further growth was found to occur, it happened in areas where it is easy to imagine the polymer fit to be less than perfect: at the vertices and at the interface between the crystal and the glass pipettes.

The EO hydrates grown with inhibitor have not yet been studied in as much detail as the THF system, but the preliminary results show some parallels to the sII hydrates. PVCap and VC-713 show different results than PVP, indicating that the difference in inhibition performance might be more fundamental than just a difference in degree of effectiveness. We believe that this is mainly due to the pendant group of PVP being smaller and not having the same stabilizing effect to provide strong adsorption. The dramatic small-scale branching of the EO hydrate crystals with inhibitor is somewhat similar to what is known in the crystallographic literature as spherulitic growth. However, our experiments indicate that these crystals are still single crystals with constant orientation throughout, whereas for spherulites, the orientation will be off by some degree for each new branch. We believe that this is a new phenomenon, as we have not been able to find reports of such growth in the literature, and remains a topic for further investigation.

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FIGURES

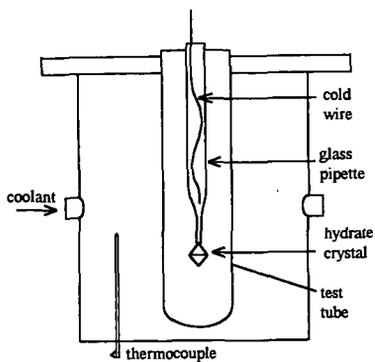


Figure 1 The experimental cell. Water or water-glycol mixtures are used as a coolant. The test tubes are ~2.5 cm outer diameter, screwcapped pyrex glass.

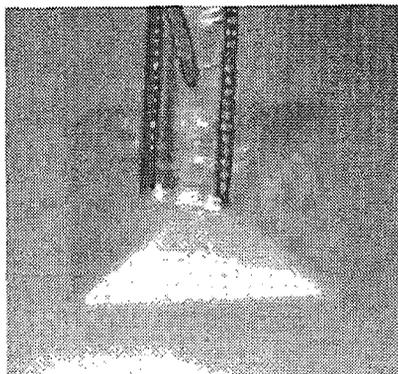


Figure 2 Octahedral s II {111} crystal of THF hydrate grown without any additives at $\Delta T = 3.4$ K. Pipette end is approximately 2 mm across.

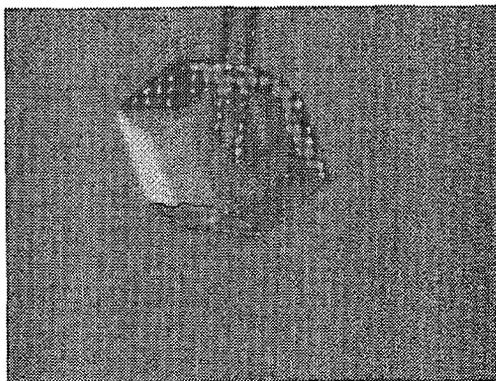


Figure 3 Dodecahedral s I {110} crystal of EO hydrate grown without any additives at $\Delta T = 0.5$ K. Pipette end is approximately 0.2 mm across.

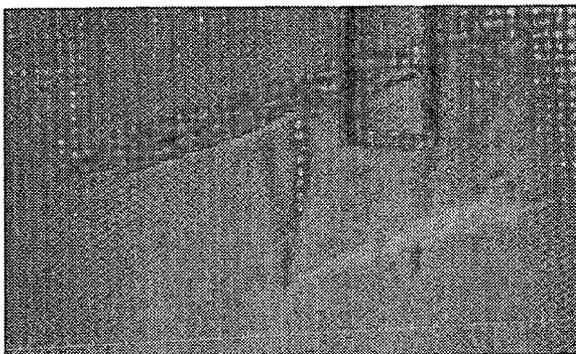


Figure 4 THF hydrate crystal growing in solution with 0.25 wt% VC-713 at $\Delta T=2$ K. Original crystal outline is seen, with the induced 2-d plates sprouting from it. Pipette end is approximately 2 mm across.

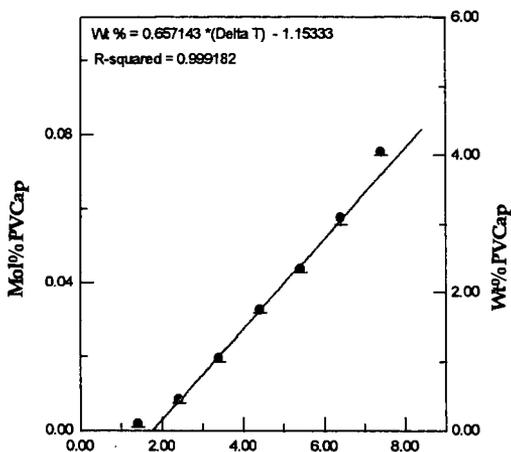


Figure 5 Complete inhibition and its dependence on supercooling. ΔT vs. concentration of inhibitor shows minimum concentration required to have complete inhibition of crystal growth. THF hydrates, sll. The inhibitor is a PVCap.



Figure 6 EO sI crystal grown in capillary at $\Delta T=0.5$ K. Intermediate concentration of inhibitor between unaffected and highly branched crystal, 0.08 wt % PVCap. Note preservation of crystallographic orientation throughout.