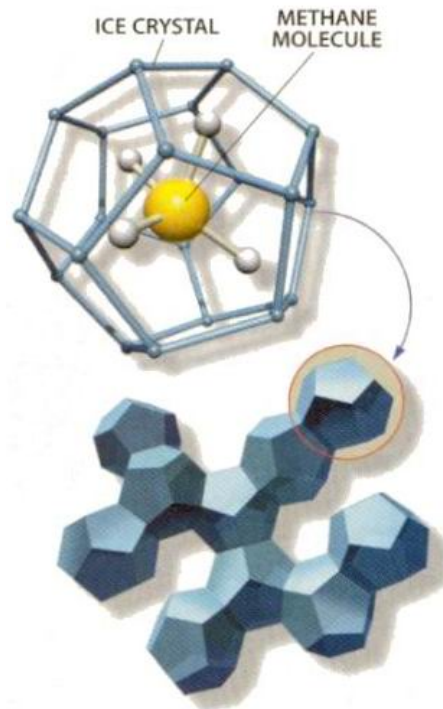


GAS HYDRATE MORPHOLOGIES



Diploma Thesis

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ABSTRACT

The Gas hydrate Crystal structure II (sII), has been studied using a technique for growing single crystals in a simple laboratory setup .The experiments were carried out in model systems of miscible fluids. The structure II crystals were grown from solutions containing water and Tetrahydrofuran (THF).Uninhibited growth of the single crystals showed a gradual but distinctive changes in the morphology from regular planar crystals to very thin planar with dendrites , as the degree of supercooling increases.Stoichiometric ratios also influenced the crystal shape. THF-poor system showed thin crystals in contrast to THF Rich system which produced relatively thicker crystals. The application of thermodynamic inhibitors (methanol) shows a marked changed in structure (from needlelike shape to irregular tiny thin crystal) as compared to the uninhibited crystal at the same conditions. The single crystals also showed changes in shape (from thick crystals to thin crystals) with the application of PVCap inhibitors with decreasing thickness as inhibitor concentration is increased.

CHAPTER 1 Introduction

1.0 Background

Multiphase transport of produced hydrocarbons over long distances is very often plagued by the problem of hydrate formation, which in the worst case can lead to plugging and production loss. Over the last few years, some efforts have been targeted towards finding ways to ‘live with’ hydrates in a system instead of trying to completely avoid them. Such efforts tend to focus on finding ways-by using chemicals or other means to produce slurry of hydrate particles in an oil and/or water carrying fluid. There is a large need to know more about the actual particle morphologies that can be formed in such slurries, in order to be better able to explain and predict flow behaviour and slurry rheology.

Structure II is formed when THF which is a miscible liquid is completely mixed with water with a hydrate dissociation point of 4.4°C. We shall study the crystal growth of Tetrahydrofuran (THF) hydrate as analogue to the gas hydrate, which normally forms in pipelines, flowlines, production risers, orifices and valves.

Another important practical application in the morphological study of single hydrate crystals is that it helps in the identification of structures of several sea floor hydrate deposits by visual means Sassen and MacDonald (1994) in their studies discovered and

characterized several hydrate deposits in the sea floor in the Gulf of Mexico. Even though such deposits are usually an agglomeration of many intergrowing crystals, it is still possible to identify characteristic angles from broken-off pieces or protrusions from the surface. These angles can be related to the major faces seen in sII hydrates and thereby give an indication of the structure.

1.1 Hydrates in General

Hydrates belong to a larger class of compounds known as clathrates, inclusion compounds which is based on three-dimensional ice-like framework of hydrogen-bonded water molecules, which were first discovered around the eighteenth century. It was German scientist Hammerschmidt (1934) who discovered that what had previously been assumed to be ice plugs in natural gas pipelines were actually natural gas hydrates. His pioneering work initiated many attempts to develop procedure to prevent formation of hydrates in industrial systems, starting with the Hammerschmidt equation for calculating needed amounts of anti-freezes like methanol or Glycols.

Hydrates are crystalline compounds similar to ice in which a guest molecule is trapped in cavities or cages built from Hydrogen-bonded water molecules. The lattice which is built by these water molecules is not stable without the inclusion of the guest molecules in the cavities. The extra van der Waals forces added from the guest are required to stabilize the structure. The guest molecules do not form chemical interactions with the host lattice indicating that no chemical bonding is involved.

Smaller hydrocarbon methane, ethane, propane and iso-butane can fit into the cavities in the hydrate structure, whereas normal-butane and larger molecules are too big to occupy the two different structures so-called structure I(sI) and structure II(sII) which are most

Common. However, larger molecules may fit into the newly discovered structure H (sH) (Ripmeester et al., 1987, Mehta and Sloan, 1994), which was not studied in this work.

1.2 Crystallography of Hydrates

The water molecule cavities which are the building blocks of sI and sII hydrates come in three different sizes. One is the pentagonal dodecahedron, or the 5^{12} cavity, consisting of 20 water molecules, arranged in 12 pentagonal “rings” (the shorthand name, being 5^{12}) which fit together to form the cavity. The next, consisting slightly bigger cavity, is the tetrakaidecahedron, consisting of 12 pentagonal rings plus 2 hexagonal ones $5^{12}6^2$. The largest cavity is the hexakaidecahedron which contains 12 pentagonal rings, but with an additional 4 hexagonal ones ($5^{12}6^4$).

Figure 1 shows a schematic representation of these cavity structures. The H-bonds between neighboring water molecules are approximately 2.8 Å in length. Combining 5^{12} cavities with $5^{12}6^2$ cavities results in the so-called structure I hydrate lattice, while a combination of 5^{12} cavities with $5^{12}6^4$ cavities results in the so-called structure II hydrate lattice. Both of these structures, with their cubic unit cells are illustrated in Figure 1. Structure I is a body-centered cubic structure, with a unit cell size of 12 Å. Structure II is a face-centered cubic structure, and the unit cell has a dimension of 17.3 Å. (Larsen, 1997)

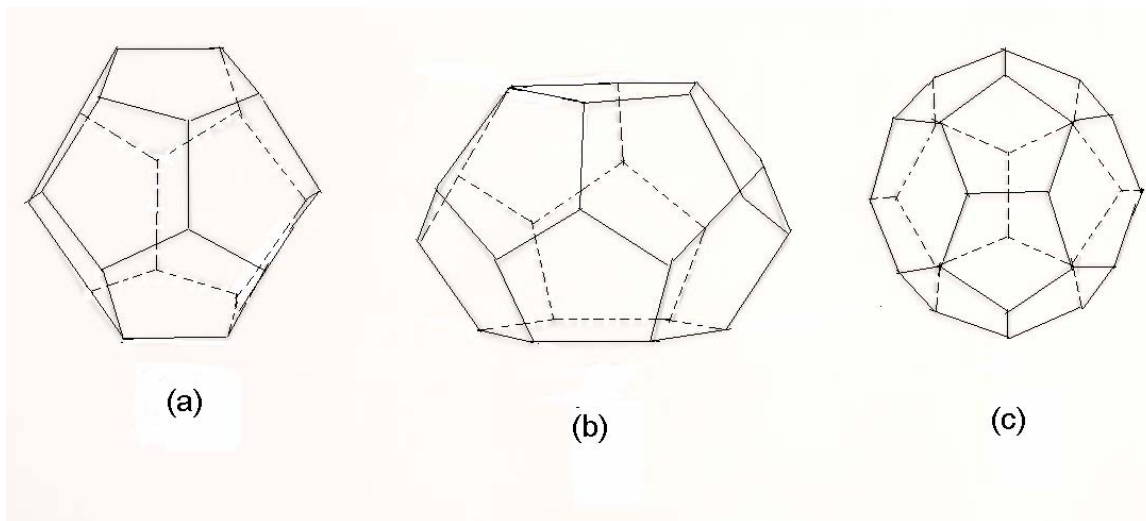


Figure 1: The three different cavities of sI and sII hydrates

(a) 5^{12} (b) $5^{12}6^2$ (c) $5^{12}6^4$ Source: (Larsen, 1997)

Normally, the smaller hydrate-forming components (e.g. methane, ethane) tend to form sI hydrates, while larger molecules like propane, i-butane form sII. However, there are numerous examples contrary to this, as e.g. N_2 and O_2 are known to stabilize sII. Another example is that a system rich in methane will form sII with only 0.5 mol% propane in the mixture, as propane is too large for the large cavities of sI (Larsen, 1997).

The stability of the hydrate requires a certain amount of filling, or degree of occupancy of the cavities, but all the cavities need not be filled by the guest molecules. Hence hydrates are non-stoichiometric compounds, where it is difficult to determine a priori the exact ratios between guests and water molecules. The ideal stoichiometric formulas for the two structures are:

sI: $6X.2Y.46H_2O$

sII: $8X.16Y.136H_2O$

Where X and Y refer to the large and small cavities respectively. In practice, there will almost always be less guest molecules present than what is predicted by the above expressions (Sloan, 1998).

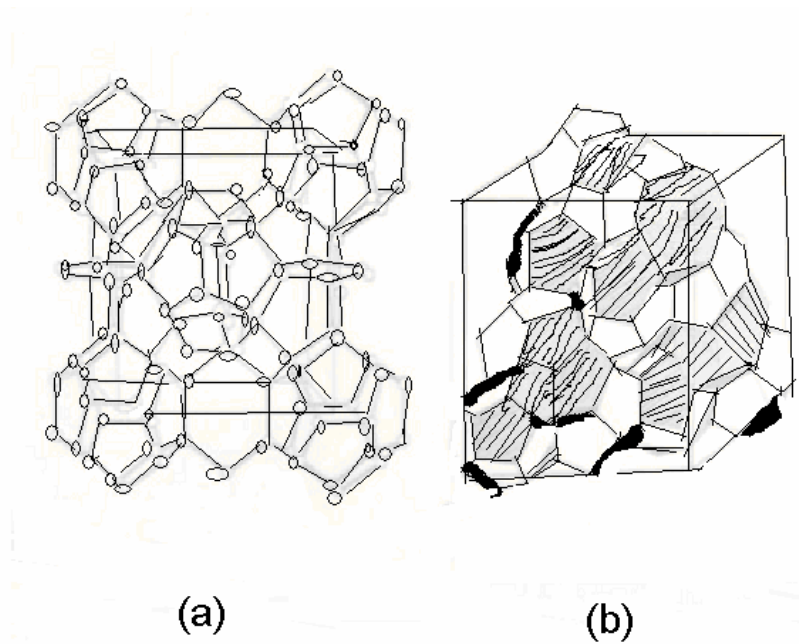


Figure 2: Unit cells of hydrate structures Source: Sloan (1990)

1.3 Hydrate Thermodynamics

The thermodynamics of hydrates have been studied extensively since HammerSchmidt's (1934) discovery, and are now at the stage where accurate predictions of e.g. stability and composition are good enough for practical industrial application. If the composition of a transported fluid in a pipeline is known it is very easy to predict the pressure and

temperature conditions at which hydrates may exist with the aid of computer programs (based on the theory set forth by van der Waals and Platteuw in 1959). These programs can also predict with a reasonable degree of accuracy the amount of inhibitors which need to be added to meet specific criteria of supercooling or overpressure in a system.

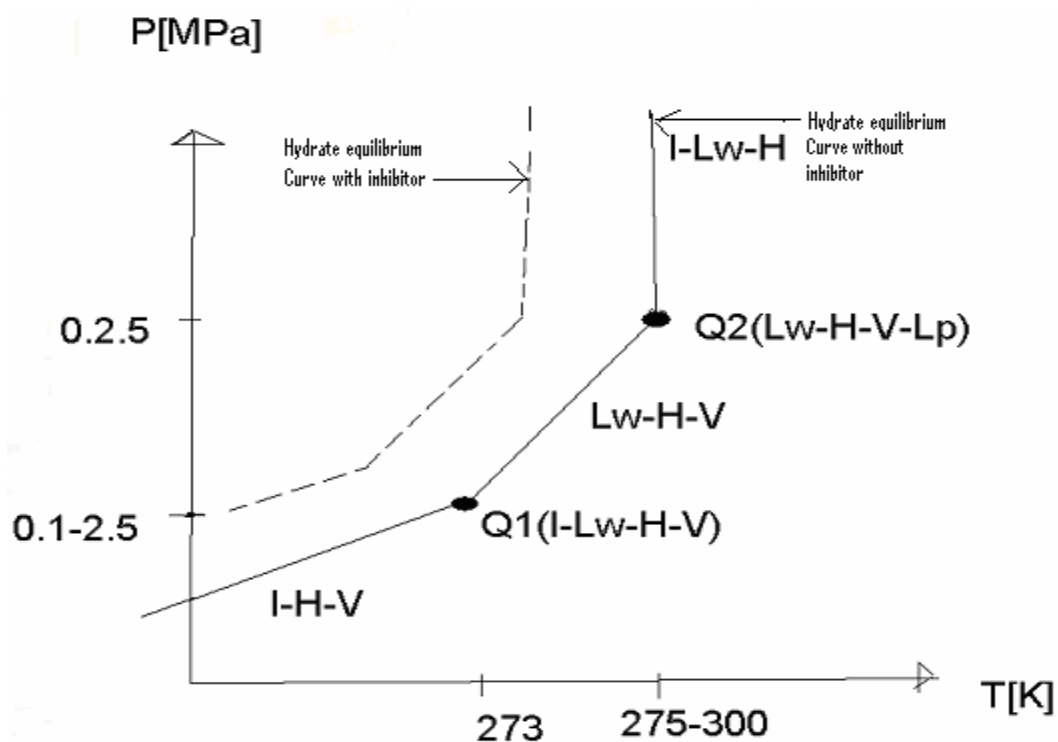


Figure 3: Pressure –temperature behaviour for a hydrate system (Sloan, 1998)

Hydrates are stable to the left of the solid equilibrium line.

I, Lw, H and V represent Ice, liquid water, Hydrate and Vapour respectively.

The Q1 is the quadruple point temperature (where all four-phases coexist) which is close to 273K for all hydrate formers though the quadruple pressure varies.

The Lw-H-V line has pressure –temperature conditions of the most interest in natural gas systems.

I-H-V line, which has a lower slope than the Lw-H-V line, is a problem due to ice formation because the temperature is less than 273K. The I-Lw-H line rises vertically from the quadruple point with very large pressure changes for small temperature changes, as typified by incompressible phases and no upper point were found. The pressures and temperatures of the Lw-H-V and I-H-V lines mark the limits to hydrate formation. To the right of both lines (both with inhibitor and without inhibitor) hydrate cannot form and the system will contain only fluids, while hydrate formation will occur to the left of Lw-H-V and I-H-V. Since ice and hydrates both cause flow problems, a gas pipeline heuristic is made to keep the system temperature above the ice point and to the right of the Lw–H-V line (Sloan, 1998).

Figure 3 illustrates the generic pressure-temperature behaviour of a hydrate-forming system, with the solid line signifying the stability boundary for hydrates. Upon warming, hydrate will melt at the temperature given by this line, and they cannot exist to the right of the line, i.e. at higher temperatures or lower pressures. However, there is usually a very significant metastable effect for hydrate formation, such that moving from the right of the line in Figure 3 and into the hydrate stability region does not necessary mean that hydrates will be formed. There are many good examples of systems which have been sitting well inside this region for long periods without having hydrates appear. The barrier against nucleation of the first hydrates is large enough to often require vigorous stirring, nucleation promoting surfaces or other ‘non-thermodynamic’ factors to initiate the process of hydrate growth. The dotted line see Figure 3 also shows (i.e. the broken lines) what will happen if a thermodynamic inhibitor is added to the system-the equilibrium existence line for hydrates will be shifted towards the left, towards lower temperature and higher pressures, giving a larger P-T region in which to operate without hydrate problems. The most common of these inhibitors are methanol (MeOH) and different glycols. They work as “anti-freezes” in the system. The mechanism through

which these alcohols work is thought to be twofold. First they form hydrogen bonds with water using their OH-groups, and secondly they tend to cluster water molecules around their hydrocarbon ends. Both of these effects will make water less available for the kind of structuring which is needed to form hydrates. The main disadvantage of using these compounds is that they are required in large amounts-sometimes as much as 40-50wt% of the liquid water phases in the system. This creates huge demands on limited space and logistics requirements for e.g. offshore platforms.

1.4 Hydrates Kinetics

Hydrate kinetics is still under investigation and is not very well understood. Most research conducted in the past dealt with the study of assemblages of many crystals (Makogon, 1974). Though there have been many efforts to carry out more research into this area one area of particular interest as far as my study is concerned is the study done by Smelik and King (1997) which investigated growth of single hydrate crystals in a high-pressure gas experiment set-up. Another advantage of the study of single hydrate crystals is that it can evaluate or help in the determination of actual morphologies of the single hydrate crystal. Therefore the study of single hydrates crystal becomes more useful in contrast to study of assemblages of many crystals which does not focus on the morphology according to work done by (Makogon, 1974). The single hydrate crystal has a constant crystallographic orientation and its lattice is continuous.

1.5 Industrial Challenges

Gas hydrates have been studied because of the serious problems they present in natural gas systems. Hydrates forms plugs to block entire pipelines, as well as cause problems in valves, separators and other processing equipment. Plugs or other hydrate occurrences are difficult and expensive to remove, as they require that the system be brought outside the hydrate stability region through pressure reductions, temperature increases, chemical additions, or that the hydrate actually be removed mechanically.

According to Englezos (1993) 5-8% of capital costs in new plants for offshore development or onshore processing may be due to the need for hydrate control and

countermeasures. Disruptions of normal operation are costly, but there is also the factor of significant hazards in connection with hydrate removal (Lysne et al., 1995), e.g. as illustrated in Figure 4, where a hydrate plug can become a projectile in the pipeline may result in serious injury and in some cases fatalities. To minimize risk of injury a double sided depressurization is recommended though it's more expensive to carry out this method.

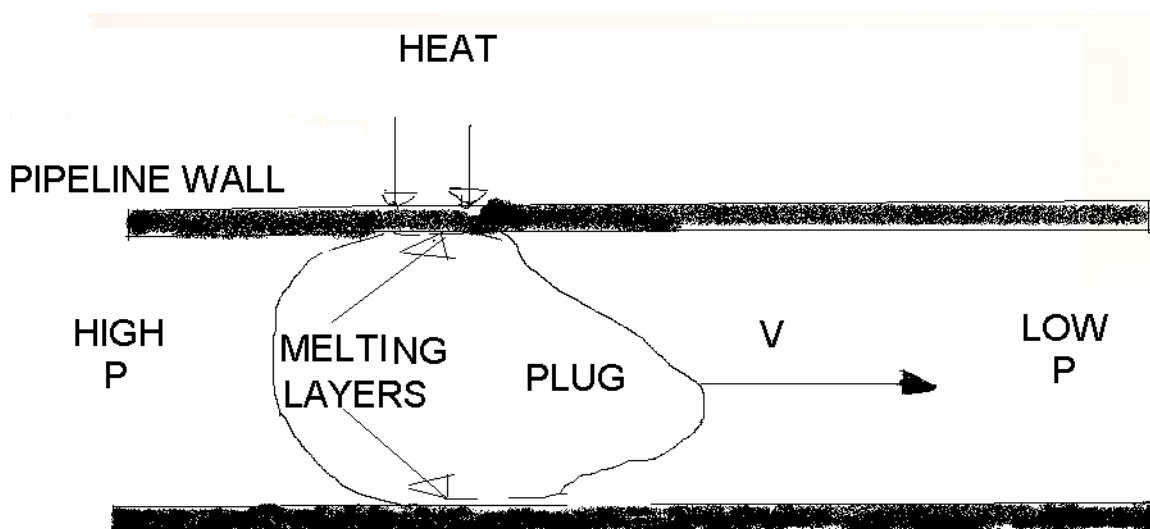


Figure 4: Hydrate projectiles from One-sided depressurization to melt a plug. (Sloan, 1998)

One sided depressurization to melt a plug may result in a high mass, high velocity projectile (Hydrate projectiles). In order to reduce overpressure in the pipe both ends of the pipe must be depressurized in such as way that one side does not have a significantly higher pressure than the other side. Depressurization can be achieved isothermally, by reducing the pressure very slowly. When the pressure is reduced, sensible heat is supplied from the surroundings to both the hydrate interface and vapour phase. The dissociation of the Hydrate start as the temperature remains constant. Another method of depressurization is by isenthalpic means that is rapid pressure reduction without heat transfer. This method is known as Joule-Thomson expansion. The pressure reduction

would make the gas expand further into the hydrate region. The rapid isenthalpic expansion alone would promote the hydrate formation by cooling the gas. The latter method is therefore not very effective in controlling the hydrate formation. (Sloan, 1998) There is therefore a significant need to look for new inhibitors which are very effective at much lower concentrations. It also is becoming more difficult and costly to remove hydrate in the traditional manner. Thus it is recommended to avoid hydrate formation before they even appear.

1.6 Inhibitors

Though the efficiency of inhibitors has been highlighted, there are also the problems of the traditional thermodynamics inhibitor approach, and it should be clear that the need to look for reasonably cheap inhibitors which will work with the same efficiency at low concentrations is essential. Other characteristics which would be useful are cheaper prices, inert behaviour with respect to other components and being environmentally friendly and regenerable after use. These inhibitors are grouped into two as follows

- Anti-agglomerates
- Kinetic inhibitors

The anti-agglomerates are surface-active agents which are intended to stop individual particles of hydrates from agglomerating (forming a cluster) and creating large masses which allow the hydrate to form, but keep them in a transportable form, such that e.g. pipeline operations are not severely affected. This is mainly achieved through the formation of relatively stable water-in-oil emulsions. Some problems encountered by this efforts in this field so far, are adverse effects on viscosity, the need for a hydrocarbon liquid phase to be present, and also a limited capability to handle water-rich fluid systems. Work in this field was started by Behar and coworkers, as reported in e.g. Behar et al. (1994).

The principle behind kinetic inhibitors is to find substances that interfere with the growth process of hydrates, and prevent hydrate particles from becoming large enough to bring about problem of possible plugging. Therefore through adsorption of these substances on the crystal surface rapid hydrate growth is considerably slowed down. The absorption of these kinetic inhibitors by the system as it's continually nucleates new particles and as such try to extend the period before sudden growth in the system occurs. This means that the free water residence time is lessened than the time until a given fluid volume will have run out of its supply of inhibitors. Thus the pipeline transport time is increased ensuring that it is out of hydrate forming conditions before massive growth is started. (Sloan 1998)

1.6.1 Kinetic inhibition in nature

Kinetic inhibition has been found to occur in nature, a similar phenomenon is found in polar fish. These fish can survive sea temperature of -2°C meaning that their body fluids remain liquid at those conditions. However it is because of their highly developed specialized proteins in their blood which tend to adsorb to the ice crystals and thereby interfering with the growth process, very much like the processes which will be described in this work. There have been unsuccessful attempts to use the same polar fish inhibitors molecules on hydrates (Edwards, 1994). PVCap chemical would be used in this thesis work though the working principles are similar to the fish anti-freeze.

1.7 Hydrates as a Resource

Naturally occurring gas hydrates (structure I) have received considerable attention over the last 15 years, ever since researchers began to realize their great abundance.

The Polar Regions and deep –ocean is believed to contain considerable amount of methane which represent a possible energy resource. Though the technology has not yet been developed to economically extract the methane, the known and natural hydrate formations represent very huge potential energy reserves, estimated at $1027 - 1034 \text{ m}^3$ of methane according to (e.g., Holder et al.1984; Kvenvolden 1994).

1.7.1 Environmental Concerns

It has been suggested that hydrates may influence atmospheric CH₄ and CO₂ levels as gas is either released or absorbed by hydrates (Macdonald 1990; Nisbet 1992). The atmospheric cycling of methane and CO₂ is thought to have influenced climate conditions and the advance and retreat of glaciations throughout geologic time. It is estimated that methane has a greenhouse effect twenty times larger than carbon dioxide on a molecule per molecule basis. Thus a small rise in sea temperature may be enough to melt off a significant layer of methane hydrates, and thereby initiate warming effects.

1.7.2 Hydrates as gas storage reservoirs

There have been some suggestions for the practical utilization of hydrates as solid gas storage reservoirs. This has been proposed for stationary storage as well as for transport situations. As hydrate can concentrate methane by a factor of 164 compared to standard temperature and pressure, it is a very promising adventure. One main competitor to such proposed scheme is the use of liquid natural gas (LNG) which concentrates the gas at higher rate. Transport of LNG requires much specialized equipment, however, and one recent proposal by Gudmundsson and Børrehaug (1996) indicates that transport of gas as hydrate might compete with LNG. One of their important points is that hydrate can be stored at temperatures above its decomposition temperature as long as ice freezes on the surface and coats the hydrate particles. Their proposed procedure is still under development.

1.8 Crystallization Theory

In addition to hydrate phenomena, this thesis requires some familiarity with some basic crystal growth. Myerson and Ginde (1993) give an overview of crystal growth mechanisms, from which Figure 5 has been taken. This illustrates how crystal growth is thought to progress layer by layer, each new layer in sequence eventually covering the entire crystal face. The process of filling

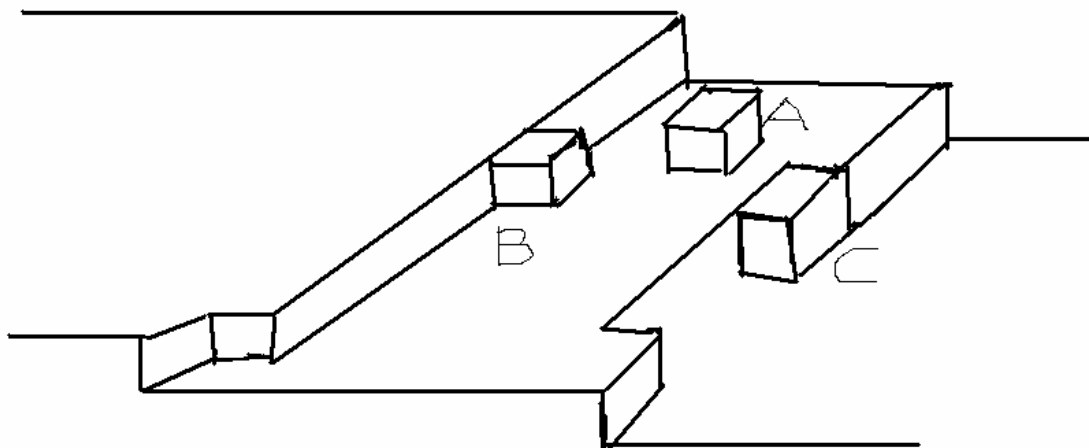


Figure 5: Crystal growth process. Source: Myerson and Ginde (1993).

Out these layers is illustrated by three different possible mechanisms. “A” signifies a new building block attaching to the middle of a terrace on the crystal surface, “B” shows attachment to a step, i.e. on the progressing front of a new layer, and in “C” a new building block has found its place in a so-called kink site. These different sites are distinguished by the number of chemical bonds which are formed between the existing crystals surface and the new building block. At “A” the only interaction is with the force-field below the new particle, at “B” twice as many bonds can be formed by the addition of few force field at the back, and at “C” three force-field combine to keep the new force-field at the back, and at “C” three force-fields combine to keep the new part of the crystal immobile in its place. Energetically, “C” is better than “B” which in turn is better than “A” in terms of incorporating new material into the crystal. (Larsen, 1997)

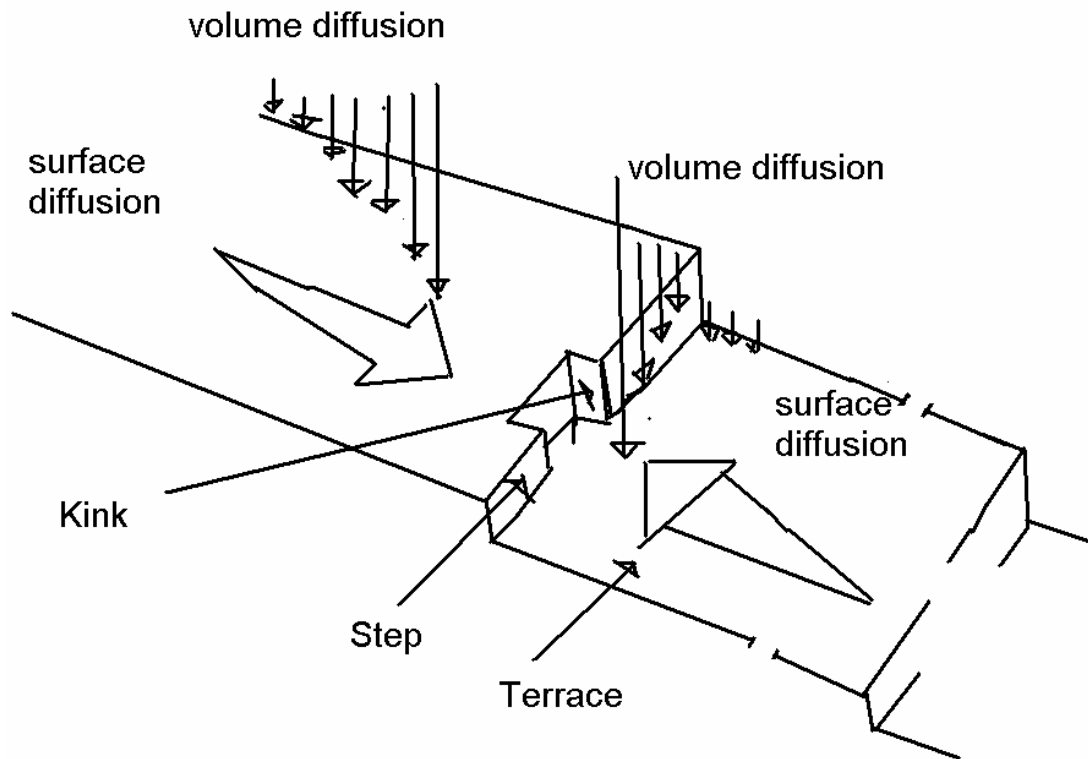


Figure 6: Diffusion processes for crystal growth. Source: Klug (1993)

Figure 6 shows one additional aspect which must be taken into account. New building materials first have to diffuse to the surface from the bulk solution, and once they reach the surface, diffuse along it to suitable site of the types described above. In reality this is of course not a simple process, as it will involve some material desorbing and going from the surface into the bulk as well, but under growth conditions, the average diffusion direction is from the bulk, to the surface and to the preferred growth sites. The mechanism responsible for creating these steps in the first place (crystal lattice dislocations or surface nucleation); will be discussed in connection with the experimental results. The above picture of crystal growth can also be used to look at what might happen with impurities (as our kinetic inhibitors will be PVCap), in the system. So even if instead of crystal building block we substitute one of our inhibitor molecules, the mechanism of surface attachment will still be the same as above.

1.9 Justification for the Present Work

This study was carried out by eliminating as many complicating factors as possible. Thus the experimental setup was aimed at using very simple experimental method in the final set-up. The investigation was aimed at studying the basic phenomena at work with single crystals chosen as the focus of the experiments. The visual observation of the phenomena of single crystals gained primary importance. Thus such an investigation is needed to act as a starting point before any of the involved phenomena could be understood and linked to larger and more complex real-life systems.

CHAPTER 2

2.0 The hydrate-forming systems

The sII hydrates was the focus of my investigation. This is because sII is the most frequent which is mostly identified in practical applications in pipeline transport sII will rather form in preference to sI even in the water-gas system with a relatively small amount of propane. sH is not investigated in this work, however, there are indications that sH may be a significant problem structure in transport systems with certain heavy hydrocarbon components. (Mehta, 1995).

In selecting the hydrate formers three properties were the main considerations.

- Forming hydrates at easily attainable laboratory temperatures at atmospheric pressure
- Complete miscibility in water
- They should be expected to form a specific structure.

To reduce the numbers of parameters the experiments at this stage was carried out in simple systems. In Practical situations there are two phases (gas and Liquid) however our situation has only one phase due to the miscibility of THF and water however results produced has been satisfactory.

2.1 Structure II Hydrate: THF and Water

Tetrahydrofuran (THF) was chosen as a structure II hydrate former. Hydrates formed from the melt have an equilibrium dissociation of 4.4 °C at atmospheric pressure (Erva, 1956). THF is a liquid below 65°C and is completely miscible with water in all proportions. The molecule, C_4H_8O is large enough 5.9Å diameter (von Stackelberg and Meinhold, 1954) to only fit into the large cavities of sII hydrates. Though irritating no extreme precautions are needed in its handling or storage.

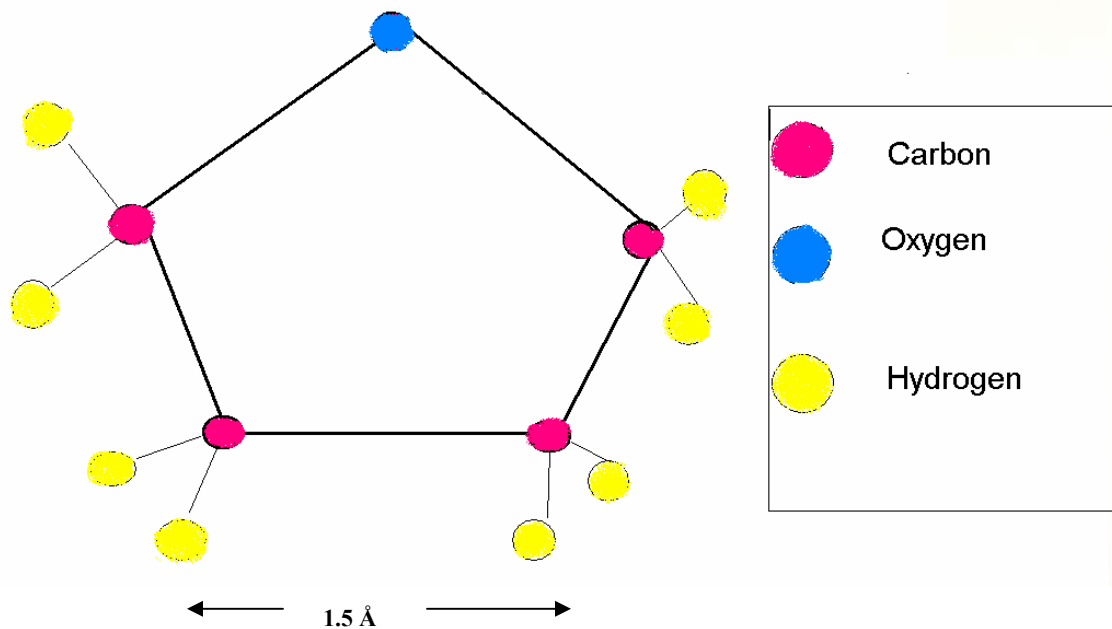


Figure 7: The THF molecule.

Length scale is only approximate.

Figure 7 shows a schematic representation of a THF molecule, and Table 1.0 sums up some of its physical and chemical properties. High grade (spectrophotometric grade) 99.5wt% THF without inhibitor was used in our experiments.

When the experiments were started it was assumed the degree of filling of cavities were close to 100%. Thus it became simple in the calculation and preparation of solutions containing THF and water in the correct ratio corresponding to a “stoichiometric” hydrate. The sII hydrates contains 17 water molecules per large guest (i.e. THF molecule). This work out to be 19wt% THF in the solution (weight percentages were most often used, as sample preparation was simply done by weighing). This corresponds to 21vol% THF, in the solution, or 5.56 mol%.

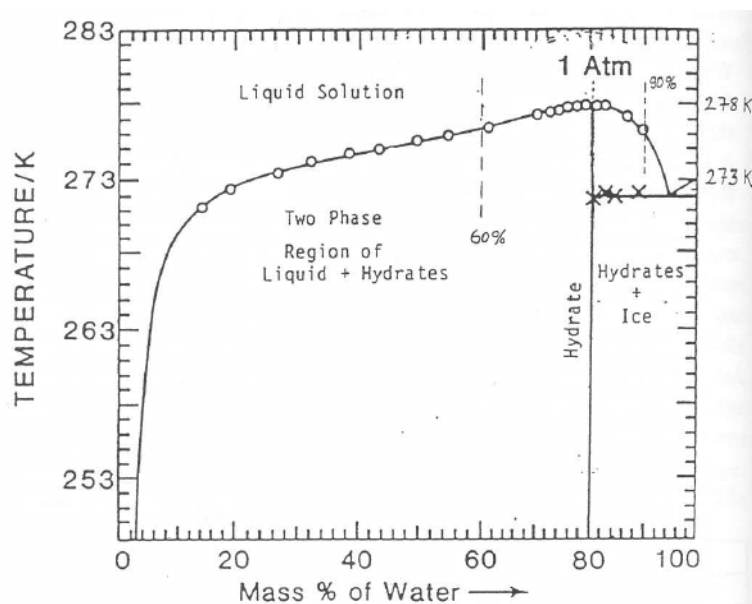


Figure 8: A partial phase diagram for the THF –water system

Source : (Larsen, 1997)

Property	Value
Molecular formula	C ₄ H ₈ O
Molecular weight	72.106g/mol
Boiling point	65- 67 °C
Melting point	-108 °C
Equilibrium hydrate dissociation temperature	4.4 °C
Hydrate structure formed	sII
Density	889kg/m ³
Viscosity	0.48cP(O °C)
Vapour pressure	143mmHg (20 °C)

Table 1: Some physical and chemical properties of tetrahydrofuran

In the experiments conducted, the THF single hydrates were observed to be less dense than the experimental solution, i.e. they would float if break off from the pipette. The density of the stoichiometric solution is about 976kg/m^3 , and 100% occupancy of the large cavities gives the hydrate a density of 971kg/m^3 . The degree of filling, assuming that the small cavities stay empty, will therefore result in floating hydrate for structure II.

THF SINGLE CRYSTALS

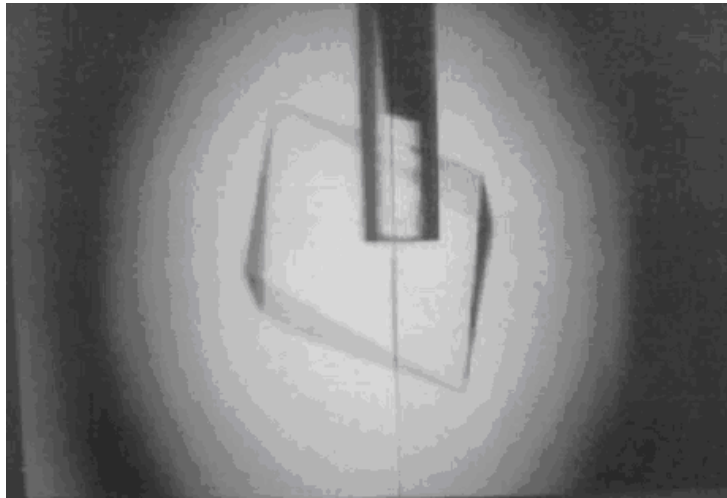


Figure 9: sII THF hydrate single crystal. Grown at stoichiometric conditions, at $\Delta T=1.4\text{K}$. Scale: outer diameter of pipette end is 1.6mm. Source: (Larsen, 1997)

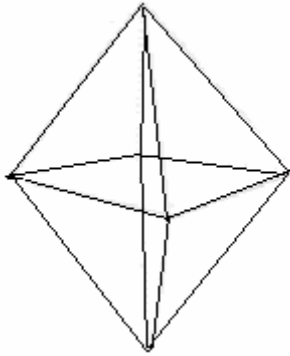


Figure 10: Octahedral Crystal shape (cubic shape)

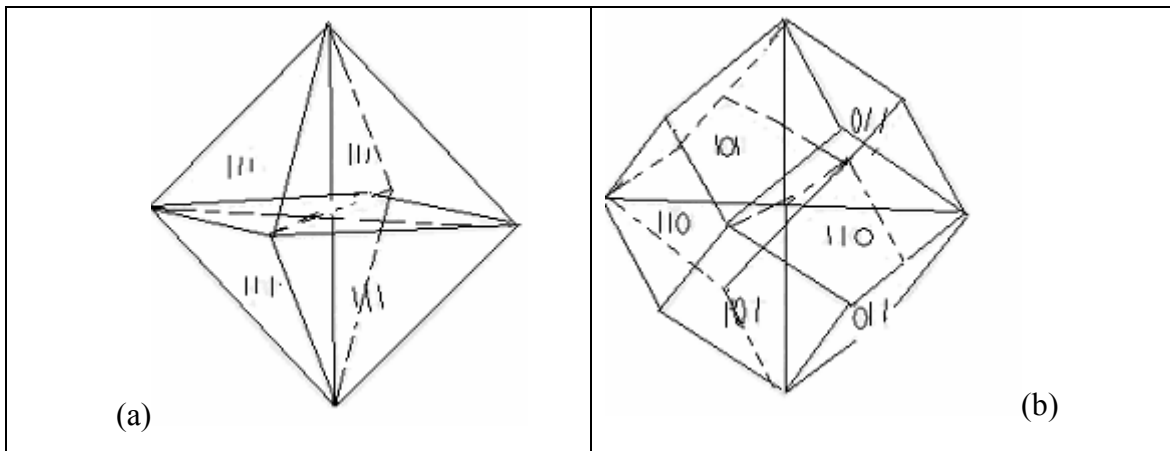


Figure 11: octahedral crystal in (a) and Dodecahedral crystal in (b) showing the planes
Source: Philips, 1951



Figure 12: Conceptual view of octahedron emerging from cubic building blocks.
Source: Philips (1951)

2.2 Kinetic Inhibitors

The three most common kinetic inhibitors used in controlling hydrates formation are poly(vinyl pyrrolidone)(PVP), poly(vinyl caprolactum (PVCap) and terpolymer of vinyl pyrrolidone, vinyl dimethylaminoethylmethacrylate(Abbreviated name: VC-713). These molecules all have carbon backbone chains with amide linkages to the pendant groups of different types. The polymer molecules have their mechanical properties (viscosity, diffusivity) decided by the backbone, while the pendant groups are responsible for specific functional properties (adsorption, etc). However, PVCap was chosen as kinetic inhibitor for this study. The structure may help in understanding the mechanism of inhibition.

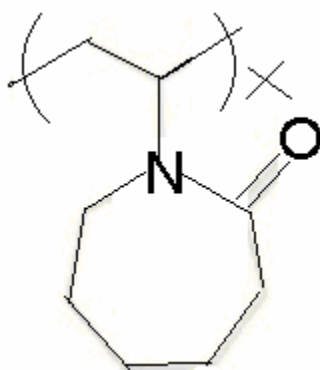


Figure 13: PVCap inhibitor molecule

Figure 14: shows a schematic representation of the PVCap polymer molecule. The bonding angles between the molecules prevent them from all lying in the same plane, as indicated in Figure 14: For the different variations of PVCap used in this work, more is known about molecular weights and chain lengths than for the other kinetic inhibitors. The molecules which were used varied from around 1000g/mol to about

30,000g/mol in molecular weight. In terms of pendant groups, this corresponds to chains containing from 7 to 200 pendants, or a maximum backbone length of 17Å to 500Å. Most of the information about polymer molecular weights was provided by Dr Brittan at the University of Akron, using vapour pressure osmometry (VPO) and gel permeation chromatography (GPC) techniques. PVCap in aqueous solution has a relatively low cloud point (temperature at which it falls out of solution) in the range of 31 °C to 36 °C at 0.5 wt% concentration, depending on the molecular weight. It is, however, readily re-dissolved if the temperature is lowered below this point again. Most of the PVCaps used in this work were obtained from the industrial manufacturer BASF. (Larsen, 1997)

2.3 Thermodynamic inhibitors

Chemical inhibition is typically implemented with thermodynamic inhibitors, such as methanol and mono- ethylene and triethylene glycol. These inhibitors have the ability to shift hydrate equilibrium conditions toward higher pressures and lower temperatures. As a consequence, the operating condition is no longer in the hydrate stable region. However, a large quantity of inhibitor is usually required, especially for severe conditions. The demand for a large volume of thermodynamic inhibitor creates logistic problems and safety concerns for the handling, transportation and storage of these chemicals. Methanol was used in this study. It is relatively cheaper and effective. The amount of methanol to be injected in the pipe to prevent or inhibit hydrate formation is given by Hammerschmidt (1939) equation

$$\Delta T = 2,335W / (100M - MW) \dots \dots \dots (1)$$

Where

ΔT = hydrate depression, °F,

M = molecular weight of the alcohol or glycol, and

W = weight per cent of the inhibitor in the liquid.

An improved version of the Hammerschmidt equation according to Nielson and Bucklin (1983) which is valid over wider range in concentration is given in equation 2

$$\Delta T = -129.6 \ln(1 - x_{\text{MeOH}}) \dots\dots\dots (2)$$

Where ΔT is in $^{\circ}\text{F}$, x is mole fraction

2.4 Crystal Growth

2.1.1 Fundamental morphology

In stoichiometric solutions without inhibitors (i.e. growth from the melt), the morphology (shape and structure) of the THF were identified as belonging to the isometric system, i.e. their axes are at right angles to each other. The initial discoveries of the octahedral sII single hydrate crystal morphology, and the growth change to plates associated with small amounts of inhibitors were made by T.Makogon and reported in his thesis (1997) at the Colorado School of Mines. The Thesis work is aimed by reproducing these initial results, and then extended to give a more in-depth explanation and discussion of the observed phenomena. In this work, most the experiments performed dealt with effects of kinetics inhibitors as well as that of thermodynamic inhibitors on the morphology of the Single crystals. The main growth phenomena therefore were studied in at least all experiments for each case. The supercooling range (cooling below the hydrate dissociation point 4.4°C) was 1.4 to 6.9K. Most of the experiments were performed at the assumed stoichiometric ratios though off-stoichiometric experiments for sII were also examined. No morphological descriptions of hydrate single from controlled growth were readily available in the literature at the beginning of this work.

2.1.2 Growth Mechanisms

The growth mechanisms are concerned about the gradual or stepwise growth of the crystals. Some work has been done by (Klug, 1993). This suggests that the surface of the growing THF is molecularly somewhat rough, and that the growth mechanism for the crystals is the creation and propagation of steps on the faces. Figures 14 and 15 give a conceptual picture of the processes involved in the different growth mechanisms. Screw dislocations appear when part of the crystal is displaced one or more repeating distances along an axis, giving rise to a spiraling self-repeating step around the axis. Surface nucleation, or the birth/spread model of crystal growth views the 2-dimensional nucleation of 'islands' of supercritical size as the limiting factor for creating steps. Once the step is created, the propagation mechanism for a layer is the same in the two models. The birth and spread model needs a new nucleation event to start the next layer.

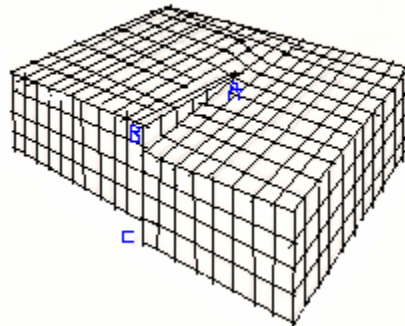


Figure 14: Screw dislocation on a crystal surface.

**From A to B, the crystal structure has been shifted one repeat unit, giving a self-repeating spiral step.
Source : (Myerson and Ginde, 1993)**

Birth and spread mechanism for crystal growth. Surface nucleation is needed to create steps (Mullin, 1993).

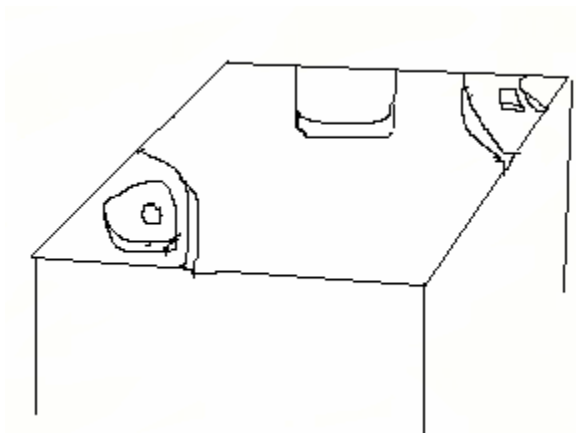


Figure 15: Growth mechanisms for hydrates.

Without specifying the step-creating mechanism; it illustrates the process of diffusion to and incorporation into the crystal.

Source: Sloan (1997).

2.5 Local concentration and stoichiometry

Most of the experiments were performed at a stoichiometric ratio for the respective systems, assuming full occupancy of the THF molecules in the large cavities of the structure. If the solution composition is different from the crystal composition, layers of the excess component can be expected to build up close to the surface, and due to the refractive index differences between water and THF, will be visible to observation. The stoichiometric ratio of 19wt% THF did indeed showed clearly less visible layers than ratios of more or less than 19wt% THF both of which had quite visible layers emerging.

The composition of THF hydrate is growth rate dependent. Higher growth rates give less cavity filling, which can be studied by mapping the decomposition

temperature (Larsen, 1997). No such effects were taken into account in this work, as since the influence is expected to be small at the moderate growth rate variations.

CHAPTER 3

3.0 Experimental equipment and procedure

The basic experimental setup was built and first used by Makogon (1997) who started the study of the phenomena single hydrate crystals growth. In addition to the main apparatus, Chemicals and other materials were used to examine certain phenomena in smaller numbers of experiments. This will be described in the latter chapters in the results and conclusion part of this thesis.

3.1 Main Growth Cells

The main experimental setup was very simple, designed for a basic visual study of single crystal growth, with direct observation of the crystal behaviour at macroscopic levels. The cells can be used to study single hydrates growth for both sI and sII experiments.

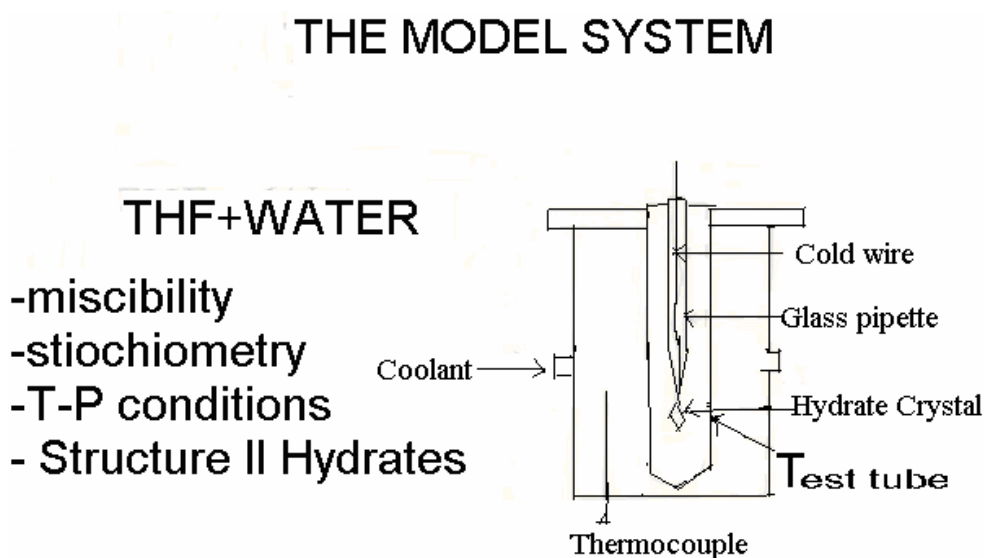


Figure 16: Main growth cell.

Original figure is due to Makogon (1997).

Figure 16 shows a schematic of the cell used for the main experiments. The apparatus consisted of a Transparent Plexiglas cooling jacket through which water and ethylene glycol coolant was circulated through insulated lines to the cell to obtain the desired experimental temperature. The temperature range for the experiment was between 263K to 277K. The relatively large volume of the coolant of about 3 litres maintained constant temperature in the cell and temperature stability was good. The temperature of the cell was measured using Metrix TH 3050 Thermocouple. Inside the bath were four Pyrex glass test tube (about 65 ml volumes each, and 2.5cm inner diameter). The experimental solution was contained in the test tubes. Glass pipettes (approximately 1mm inner tip) extended into the solution from rubber caps. The pipettes were open to the atmosphere at the top, and to the bulk solution at the bottom. The prepared experimental solutions were poured gently in the test tubes at a temperature above the hydrate dissociation temperature. The cooler was then set to the desired temperature for the experiment. The volume of the coolant was controlled by adjusting a screw cap fitted along the flowlines near the cell. A constant difference in Temperature (about 0.3K) between the cooler set temperature and the measured temperature at a copper –constantan thermocouple in the cooling jacket was taken into account. The temperature controlled within ± 0.1 K. The test tubes were carefully stirred and screwed –capped when the solution was poured in, and then left to equilibrate for about 10 minutes after the thermocouple sitting next to the test tubes in the cooling jacket indicated that the desired temperature had been attained.

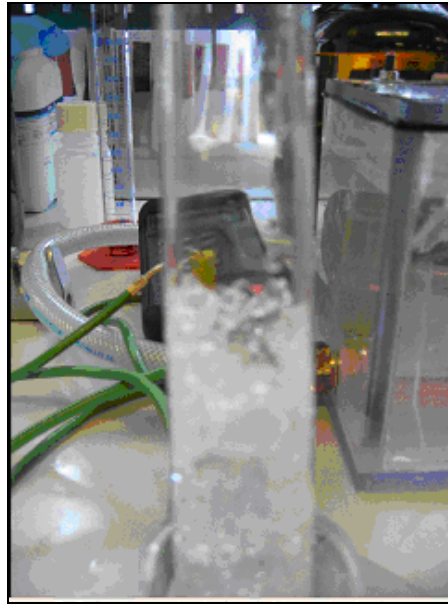


Figure 17: The coolant and the test tube for growing the hydrates.

Source: Multiphase Flow Lab SINTEF

3.2 Methodology

The experimental solutions were prepared in beakers by weighing the different components in the correct amounts. Both PVCap and methanol inhibitor solutions were prepared by a standard procedure to ensure identical conditions between batches. Stock aqueous solutions were prepared by measuring the correct amount of dried polymer into a beaker, and adding water to get the correct concentration. These solutions were then sealed and vigorously stirred before being used. The stock solutions were diluted to the desired concentration for each specific experiment. In general, stock solutions were not kept for longer than one week, after which fresh solutions were prepared. Stock solutions were not added to the THF and the diluting water until just before being poured into the test tubes. All the concentrations of inhibitor reported in this work are in wt%, based only on the amount of water in the experimental solution. If percentages based on the total amount of liquid in the system are needed, Inhibitor wt% in sII experiments needs to be multiplied by a factor of 0.8.

- Nucleation and start of the crystal growth was achieved by the use of thin metal wires inside the pipettes. The wires had previously been cooled in liquid nitrogen and sometimes just ice water though the former was more efficient. The wires were then carefully and quickly dropped into the pipettes, keeping the tips at a desired distance from the pipette end. This procedure was able to create enough transient local supercooling, as well as suitable surface, to immediately nucleate a large number of crystals on and around the wire. With time these crystals grew throughout the pipette and into the bulk solution, single crystals appeared in most times. The process were repeated with new pipettes for which new cold wires would quickly be inserted if for instance crystal aggregates grew out to be replaced. The whole process was repeated to get a consistent results for the single hydrate formed. To study the effect of inhibitors, the same procedure was repeated using THF with various concentrations for PVCap and methanol inhibitor to compare its effects on crystals with the uninhibited system (THF with only water). After each crystal growth photographs of it were immediately taken with the an Olympus digital 7.1 MP camera.

Similarly, different stoichiometric ratios effects were also performed using the same procedure as already explained. The whole experimental setup was placed inside a powerful fume hood. In most of the experiments, the growth of the crystal was captured on an Olympus digital camera mounted on a Tripod stand. The instruments and materials used were:

- HAAKE F3 Coolant
- Metrix TH 3050 Thermocouple
- an Olympus digital 7.1 MP camera
- a Tripod stand
- Safety goggles
- Hand gloves
- Methanol

- PVCap inhibitor
- Beakers and Test tubes
- Measuring cylinder

. The volumes of the containing vessels had volumes ranging from 0.5 to 2.5 liters. The bottles placed closed to the cooling jacket, to allow magnetically driven stir-bars to be used inside the experimental solutions.

3.3 Experimental Errors

The possible errors that might have occurred in my experiments were temperatures measurements, weights measurements, and inhibitor effects on the volume as well as few water droplets that might have remained in the test tubes after rinsing.

The absolute error in temperature measurements was estimated at $\pm 0.1\text{K}$, based on calibration with different mercury thermometers, and on the observed minor fluctuations in the displayed temperature. The error estimates for inhibitor contents are based on no water evaporating from the stock solutions (verified by occasional weighing). From these, an absolute maximum error in amounts weighed was estimated at $\pm 0.005\text{g}$. For the THF/water ratio, this will give a negligible deviation from the desired value. It results in a possible error of $\pm 0.25\%$ in the assumed inhibitor concentration in stock solution. After dilution into the experimental solution, this means that the error in assumed inhibitor amounts is less than 1% of the total amount of inhibitor.

Another source of error is introduced by the possibility of water droplets being left in the test tube from rinsing and cleaning procedures. This amount would certainly be less than 1ml, and thus could influence the stoichiometric ratio by no more than -2%. The inhibitor concentration may then be a maximum of 3% lower than the assumed value. For the inhibitor amounts, the error will be small, at $\pm 3\%$ of the total mass of inhibitor).

CHAPTER 4 Experimental results

4.0 Crystals formed from uninhibited system

Different supercooling temperatures were applied to observe the effect on the shapes of the single crystals growth from the THF/Water system.

Less supercooling produced regular but thicker crystals whilst more supercooling produces thin crystals with dendrites.

Table of results			
Experiment 1			
THF+ water =normal mixture			
Test	Temp/°C	supercooling	Shape of Crystals
1	3.00	1.4	plate crystals
2	2.50	1.9	plate clear crystals
3	2.00	2.4	plate crystals
4	1.50	2.9	planar crystals
5	1.00	3.4	planar crystals
6	0.50	3.9	planar crystals
7	0.00	4.4	thin hexagonal planar transparent, small units
8	-0.50	4.9	thin hexagonal planar transparent, small units
9	-1.00	5.4	thin planar transparent, small units
10	-1.50	5.9	thinner planar transparent, smaller units
11	-2.00	6.4	Thinner planar hexagonal, some needle like
12	-2.50	6.9	Thinner planar hexagonal, some dendrites

Table 2: The gradual change in crystal shape with varying supercooling Temperatures

From Table 2 the single crystal appears thinner for higher supercooling (lower temperatures) relatively thicker and coarser at lower supercooling (higher temperatures). See Appendix B for elaborate description of the Crystals at all the different supercooling temperatures.

The Table xx in Appendix B shows the sketches of the single crystals grown from the uninhibited solution at all the different supercooling temperatures.

The crystals generated between supercooling range (4.4-6.9K) were relatively thinner and some had dendrites though the crystals formed were fairly regular and exhibited the same overall shape. The crystals formed in the intermediate supercooling range (2.9-3.9K) were also thin and a little rougher and also showed overall similar shape. With the supercooling range (low supercooling) approaching the dissociation temperature of the hydrate .i.e. (1.4-2.4K) the crystals developed was regular but relatively thicker and rough. Thus the greater the amount of supercooling the crystals become thinner and dendrites develops. This trend according to (Larsen, 1997) agrees well with previous established patterns from the crystal growth literature for instance that of Murowchick and Barnes (1987).

4.1 Crystals from Off-stoichiometric experiments

After looking at the supercooling effects on shapes at normal Stoichiometric conditions, different stoichiometric ratios solutions were prepared to identify the effects on the shapes of the crystals. THF was increased by a factor of 2 to its stoichiometric value (19%) to make a THF –rich systems. Crystals formed from this gave 2-dimensional hexagonal plates and the crystals formed were relatively thicker. Rough sketch of the crystals is shown below in Figure 18(photograph taken for this crystal was not clear) hence the sketch was provided to illustrate the growth of the crystal. For the THF –poor system (i.e. THF was reduced by a factor of two), the crystals formed from this was similarly a 2-dimensional

hexagonal plate, however the plates were thin and flaky as captured by the camera in figure 20.

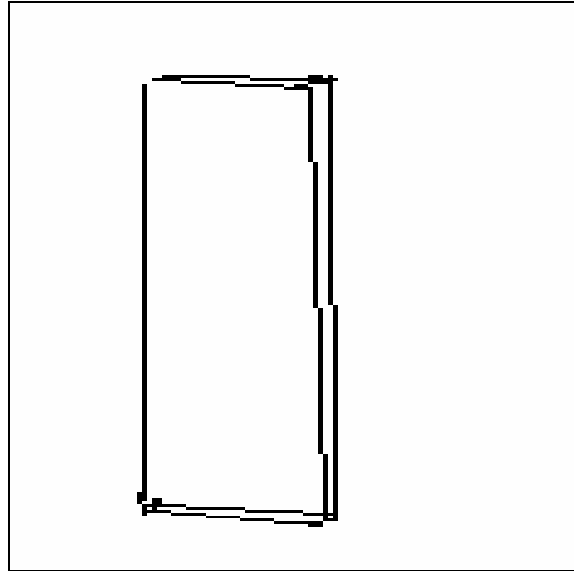


Figure 18: Sketch of Planar growth in THF-rich system (60wt %).

$\Delta T=2.8K$ Pipette end is 1.6mm|



Figure 19: photo of crystal growth in THF-rich system (60wt %).

$\Delta T=2.8K$ Pipette end is 1.6mm

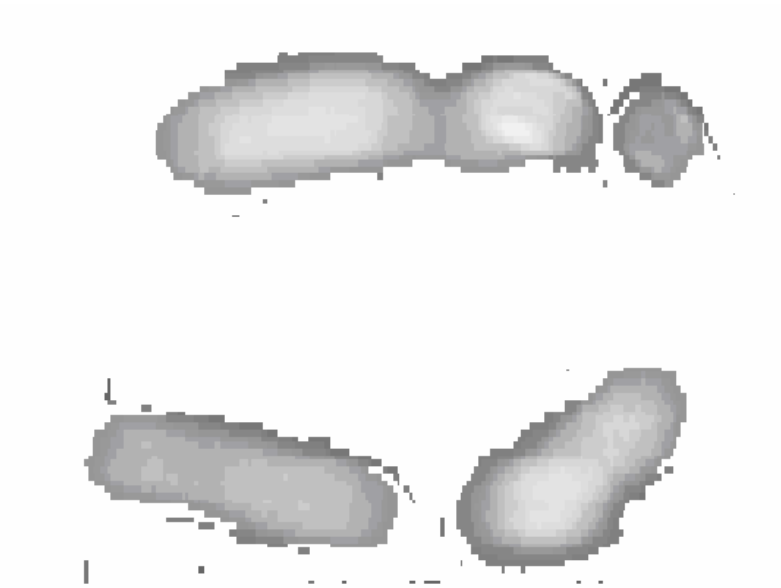


Figure 20: Planar growth THF-poor system (90wt%water)
 $\Delta T=2.8K$ Pipette end is 1.6mm

The Crystal developed in the off stoichiometric systems generally took longer time to appear than normal stoichiometric ones at the same conditions of supercooling probably due to a required orientation of the THF and water at the correct proportions. Again the growth rate of the THF-poor system was slower than that of THF-rich systems. Therefore the crystal shapes was dependant on the stoichiometric ratio of the THF-water systems.

4.2 Inhibitor effects on *STRUCTURE II* crystals

This was the third factor that was applied to study the effects of inhibitors on crystal shapes of sII hydrates. Though several inhibitors were available PVCap was used in these experiments to study the morphological changes in the sII crystals. All the solutions were at normal stoichiometric ratios. Generally the supercooling range was between 1.4 -5.9K however higher supercooling was applied to study thermodynamic inhibitor effects as it

would be explained in the next subsection .Figure 21 below shows the crystal growth at a concentration of 0.05wt% PVCap at temperature of 0 °C ($\Delta T=4.4K$).

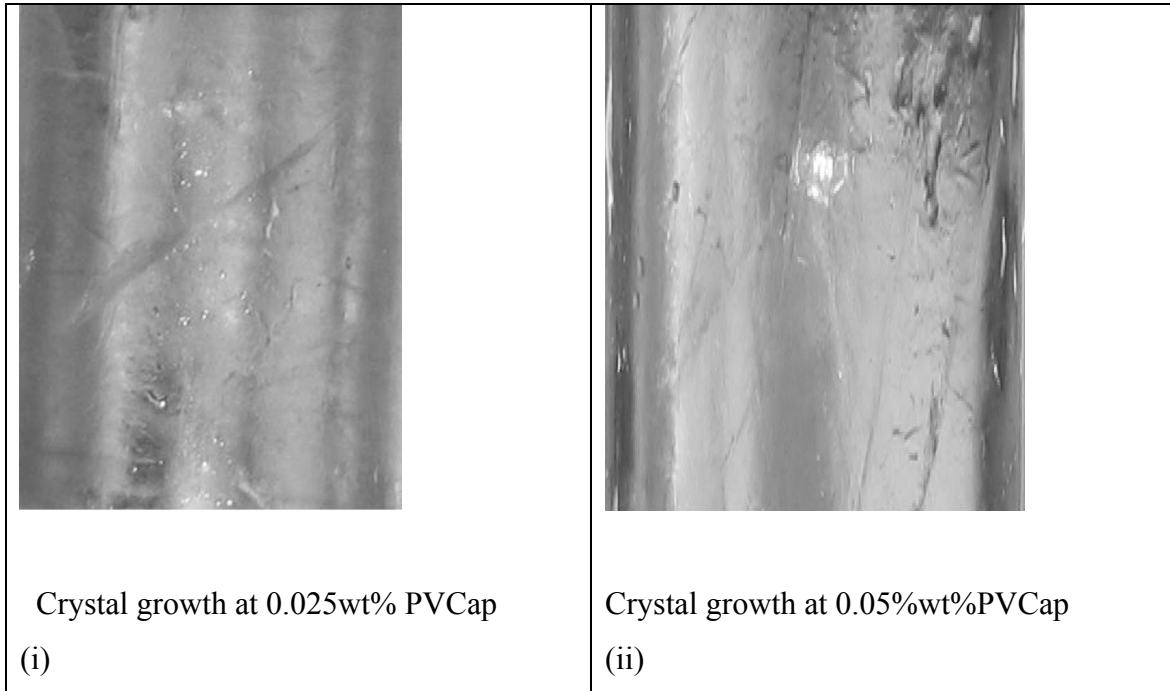


Figure 21: Crystal growths at different concentrations at same $\Delta T=4.4K$

Scale x2

As the concentration of the inhibitor increases the crystals become thinner and flatter as seen in Figure 21(ii). Since the concentration of PVCap (see Figure 21(ii)) is higher than that of Figure 21(i) the hydrates in the lower concentration of PVCap will form relatively more crystals and a little thicker crystal than the one in the higher concentration of PVCap.

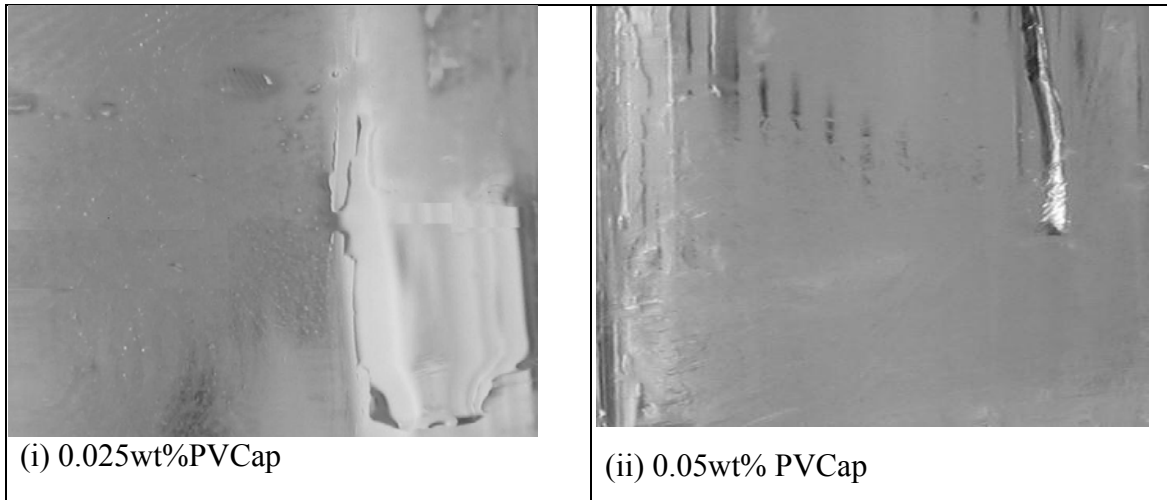


Figure 22: Crystal Growth at different concentrations at same $\Delta T=6.4K$

Scale is approximately X2

Pipette end is 1.6mm

The higher concentrations of PVCap produce a thinner and flaky. It appears more supercooling produces crystals with dendrites and is relatively thinner. Again cooling the solution further from $0^{\circ}C$ to $-2^{\circ}C$ ($6.4K$) Figure 22 produces significant changes of the crystals shapes than less supercooling (ΔT at $4.4K$). At the same concentration with different supercooling temperatures, (Figure 21(i) and Figure 22 (i)) it was observed that more crystals is produced with more relatively thicker crystals at a lower temperature ($\Delta T=6.4K$) than at higher temperature at $\Delta T=4.4K$. With higher concentration of inhibitors. (Figure 21(ii) and Figure 22(ii)) of $0.05\%wt$ PVCap the temperature effect is not so much felt probably due to the predominate effect of the pendant group of the polymer on all sides the crystals of the hydrate despite the increase in supercooling.

4.2.1 Thermodynamic inhibitor effects on structure II Crystals.

The other type of inhibitor that was used to observe the crystal shapes was methanol a volatile non viscous liquid. More amount of methanol concentration was required to produce visible effects in the crystal shapes of the sII hydrate. At 25%vol some crystal were formed at 0°C then at 50% crystals was formed at -10 °C however 75%vol could not produce any crystals it was completely inhibited in conformity with the Hammerschmidt equation.

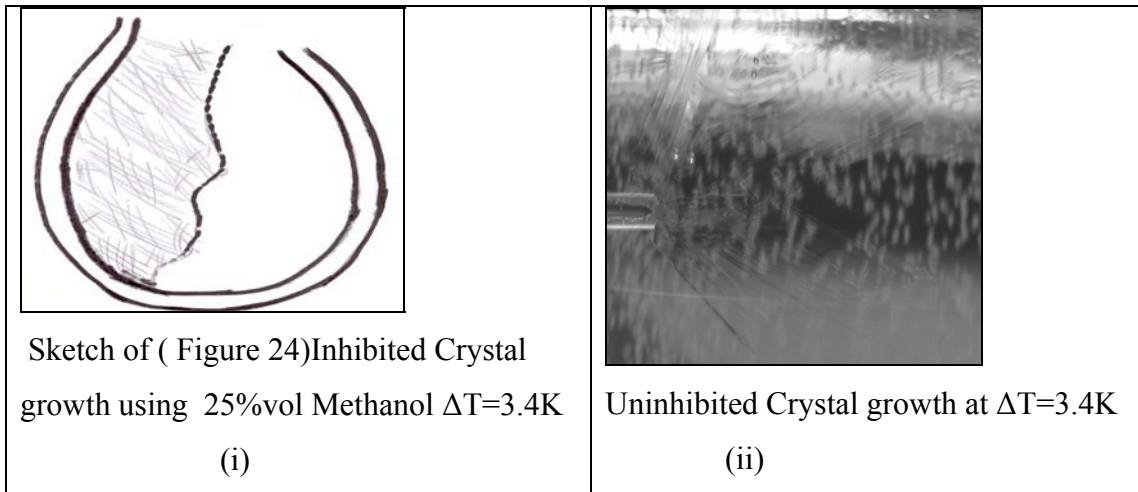


Figure 23: Crystal Growth at two different conditions at the same temperature.

Pipette end is 1.6mm

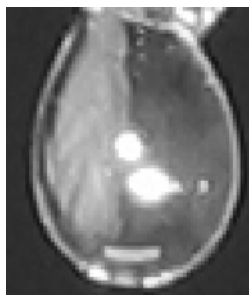


Figure 24: Photo of the Inhibited Crystal growth using Methanol $\Delta T=3.4K$

The application of the thermodynamic inhibitor results in hydrogen bonding between the OH-groups of methanol and the water molecules thereby clustering around the hydrocarbon end and therefore making water less available for the kind of structuring which is needed to form hydrates. Methanol is required in large amount to achieve inhibition. In this experiment as shown by Figure 4.7 or 4.8 it is apparent that the crystal shape has changed significantly as a result of the presence of the inhibitor changing the shape from needle and spiky shapes to very thin and small crystals.

CHAPTER 5 Discussions of Results

The results provides some intriguing points to think about and determine ways based on logical and sound scientific analysis to explain the observed behaviour.

First the results from the uninhibited single crystal growth shows a gradual morphological change in the single hydrate crystal from a less supercooling (ΔT 1.4K) to the highest supercooling temperature ($\Delta T=6.9K$). As already displayed in the experimental results in Table 2 it could be observed that the supercooling range of (1.4-2.4K) produced regularly shaped clear platelets. Then in the intermediate supercooling range of (2.9-3.9K) the crystals become less regular in shape and more planar and flatter. Then at the highest supercooling range of (4.4-6.9K), the crystals become very thin and with some developing dendrites. The morphological change in the single crystals become more prominent suggesting that more supercooling has greater effect of the crystals shape than less supercooling. See Appendix for all the morphological changes of the Single crystals at all the different supercooling range.

In order to understand these observed phenomena we have to look back at our experiment set up concerning the crystal growth in the cell. In the cell when the crystals were developing the major factor at play is that the hydrate crystallization process is an exothermic (heat releasing) process that releases relatively large amounts of heat at higher supercooling (High ΔT) consequently heat conduction from the face of the crystals take more time than the vertices and edges which have smaller surface area than the surface of the crystals. As a result of this the vertices will grow faster than the surfaces giving rise to structural changes in the shape as observed in the Table 2. Since the edges of the crystals are closer to the test tube wall than the surface heat transfer is faster than the heat transfer from the surfaces. This phenomenon explains why more supercooling release more energy and consequently more heat transfer leading to growth at the edges outgrowing the surface of crystals. The high supercooling results in higher growth rate

hence more morphological changes in shape of the hydrate crystal. Therefore the higher supercooling gives thinner and flatter and smaller crystals than low supercooling.

For the next part of experiments regarding the stoichiometric effects, results indicated that shapes of crystals are also dependent on stoichiometric ratios. Concerning off-stoichiometric ratios, the THF-rich systems crystals formed were thicker than the THF-poor water system (Which were flaky). The most likely explanation to these observed trend maybe that for the different diffusivities of water with respect to THF and THF with respect to water. Since water is less bulky in size than THF at the molecular level at a particular temperature.

In case of THF poor system since the layer of excess component is water the THF (more bulky) will diffuse through water more slowly (slow rate of formation) thus confirming the thin shape observed in Figure 20. However in the case of THF rich solutions more THF is present thus diffusion of the water molecule (less bulky) through THF is faster and thus more thickening is observed as seen in Figure 18 by the sketch. Therefore the shapes are influenced by the relative diffusivities of the two components THF and water.

Finally, taking a look at the morphological differences due to inhibitors and increasing inhibitor concentration. The kinetic inhibitors (PVCap) have affinity to bond to the surface of the hydrate crystal thus interfering with further growth so that if more inhibitors are added (i.e. increased concentration) then a barrier is established against mass transfer of either water or THF to the surface of the hydrate crystal. This is illustrated and supported by Figure 22(i) which has a lower inhibitor concentration and therefore produced relatively thicker crystals than what is observed at Figure 22(ii) which has higher concentration and thus produced crystals are thinner and smaller. The observed shape of the crystals is also due to the fact that the edges and vertices tend to be less affected by the inhibitor (less contact area) thus making the edges outgrow the surface of the hydrate crystal.

Concluding, regarding the methanol inhibitor (thermodynamic) the mechanism of inhibition is the hydrogen bond between the methanol and water (making water less available) after occupying the hydrate cavity this rather disturbs and resists the formation of the hydrate crystals by not having the perfect orientation for hydrate formation. The figure 23 (sketch of figure 24) shows that the addition of methanol inhibitor causes a change in shape from needle-crystals in the uninhibited crystal growth to a very thin and flat crystal in the methanol inhibited growth at the same temperature of supercooling.

CHAPTER 6 Conclusions and Recommendations

6.1 Conclusions

The Uninhibited growth of the single hydrate (II) crystals showed gradual but distinctive changes in the morphology from regular planar crystals to a very thin planar with dendrites as the degree of supercooling increases. Stoichiometric ratios also influenced the crystal shape. THF- poor system showed thin crystals in contrast to THF rich system which produced relatively thicker crystals. The application of thermodynamic inhibitors (methanol) shows a marked changed in structure (from needlelike shape to irregular tiny thin crystal) as compared to the uninhibited crystal at the same conditions. The single crystals also showed changes in shape (from thick crystals to thin crystals) with the application of PVCap inhibitors with marked reduction in thickness as inhibitor concentration is increased.

6.2 Suggestions for Further work

The study focus exclusively on Structure II hydrates. Perhaps in future it will be useful to research into sI and sH. Since the experiments were carried out at atmospheric pressure, high pressure system can be used (as carried out by Smelik)to ascertain the reliability and its application to real life systems .Then also powerful camera with high magnification can be used to study further at the microscopic levels to complement the macroscopic level study by visual means.

Nomenclature

Å = Armstrong units

Kg= Kilogram

L= litres

Mol =mole

M= meter

wt% = Percentage weight

X =large cavities

Y= Small cavities

I= Ice

Lw = liquid water

H = Hydrate

V= Vapour

Q1= Quadruple point (lower)

Q2 = Quadruple point (upper)

K = Temperature in Kelvin

T = Temperature

P = Pressure

T = Temperature

°C = Temperature in degree Celsius

W = Weight

MW= molecular weight

°F = degree Fahrenheit

ln = natural logarithm

x = mole fraction

ml = milliliters

LNG= Liquid natural gas

atm= Atmosphere

Cp = centipoises

mmHg =millimetres of mercury

m³ =cubic metres

ΔT = degree of supercooling

Poly (vinyl pyrrolidone) = PVP

Poly (vinyl Caprolactum) =PVCap

THF= Tetrahydrofuran

sII = Structure II

sI = Structure I

sH = Structure H

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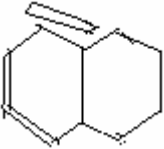
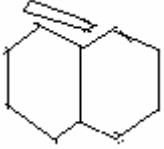
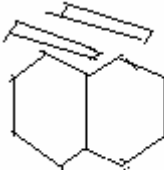
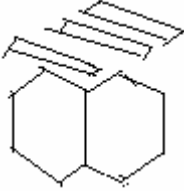
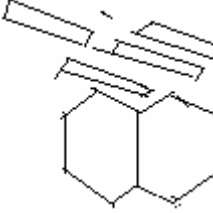
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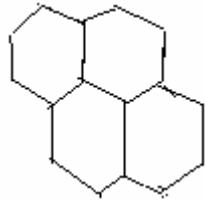
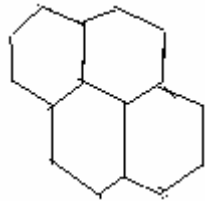
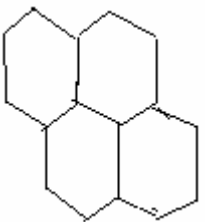
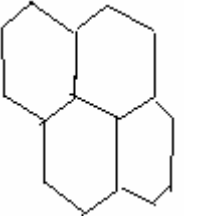
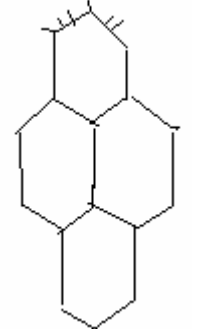
Von Stackelberg M., Meinhold, 1954, Z.EleKtrochem. vol.58, p40

Appendix

Table of results			
Expeiment 1			
THF+ water =normal mixture			
Test	Temp/°C	supercooling	Shape of Crystals
1	3.00	1.4	plate crystals
2	2.50	1.9	plate clear crystals
3	2.00	2.4	plate crystals
4	1.50	2.9	planar crystals
5	1.00	3.4	planar crystals
6	0.50	3.9	planar crystals
7	0.00	4.4	thin hexagonal planar transparent,small units
8	-0.50	4.9	thin hexagonal planar transparent,small units
9	-1.00	5.4	thin planar transparent,small units
10	-1.50	5.9	thinner planar transparent, smaller units
11	-2.00	6.4	Thinner planar hexagonal, some needle like
12	-2.50	6.9	Thinner planar hexagonal, some dendrites

Table3: Results of shapes of crystals at different degrees of supercooling.

TEST	TEMP/ o	Supercooling/K	Shape	Description
1	3.0	1.4		Regular plate crystals
2	2.5	1.9		Regular clear crystals platelets
3	2.0	2.4		Regular crystal platelets
4	1.5	2.9		Planar crystal platelets
5	1.0	3.4		Planar crystals platelets

6	0.5	3.9		Planar hexagonal crystals
7	0.0	4.4		Thin planar small hexagonal crystals
8	-0.5	4.9		Thin planar transparent small hexagonal crystals
9	-1.0	5.4		Thin planar transparent small hexagonal crystals
10	-1.5	5.9		Planar hexagonal(more slender) with few needle-like protrusions

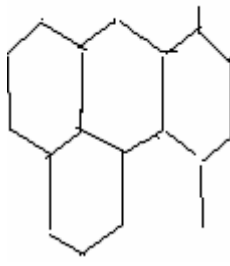
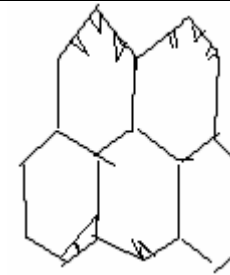
11	-2.0	6.4		Planar and very thin hexagonal crystal with needlelike protrusions
12	-2.5	6.9		Very thin planar hexagonal with dendrites

Table 4: showing all the shapes of single crystals at the varying degrees of supercooling.