CHAPTER 3

GROWTH OF THIOUREA BASED ORGANIC AND SEMIORGANIC SINGLE CRYSTALS

3.1 GENERAL CONSIDERATIONS

The factors during crystal growth which affect the size of the crystals are solubility of compound in the solvent chosen for recrystallization, the number of nucleation sites, mechanical agitation to the system, and time.

The principle if this method is based on the concepts of solubility and super saturation. At a given temperature, a limited amount of a substance dissolves in a particular solvent. The amount defines the solubility at that temperature. The solubility is a function of the temperature of the solvent. In most cases, the solubility increases with temperature. If a saturated solution is prepared at a certain temperature and then cooled to a lower temperature, it contains more salt than the permitted by the solubility at the lower temperature. The same thing happens if some of the solvent is allowed to evaporate. The solution is now in the super saturated state this is a metastable state and with the slightest induction, the extra salt precipitates. If a ‘seed’ crystal is introduced into the solution, the substance precipitating from the solutions will grow around the seed crystal forming a larger single system. In the absence of a “seed” even dust particles provide a nucleus for crystal growth. A slow growth rate, prevention of multiple nucleations and good control temperature are conditions conducive to the growth of a crystal. The
actual temperature of growth, the pH of the solutions and the presence of deliberately added impurities (called activities) are additional parameters that determine the rate of growth and also the external form (morphology) of the crystal.

3.1.1 Solvent

Choose the solvent in which your compound is moderately soluble. If the solute is too soluble, this will result in small crystal size. Avoid solvents in which your compound forms supersaturated solutions. Supersaturated solutions tend to give crystals which are too small in size.

3.1.2 Nucleation

The favor sites at which crystals begin to grow will result in fewer crystals each of larger size, this is desirable. Conversely, many nucleation sites results in a smaller average crystal sites, and is not desirable. In many recrystallizations ambient dust in the laboratory provide sites of nucleation. It is important to minimize dust or other extraneous particulate matter in the crystal growing vessel. Nucleation is an important phenomenon in crystal growth and is the precursor of crystal growth and overall crystallization process. The condition of supersaturating alone is not sufficient cause for a system to being to crystallization. Before crystals can grow there must exist in the solution, a number of minute solid bodies known as centre of crystallization, seeds, nuclei (or) embryos.

In a supersaturated or super cooled the system when few atom or molecules join together to form a cluster, then the cluster are join to from a new solid phase is called nuclei. The kinetic phase change take place in four different stages. That is,
1. The development of supersaturated state, which may arise due to chemical or photo chemical reaction or the consequence of a change in temperature, pressure, tension or other chemical or physical condition.

2. The generation of minute speaks or nuclei.

3. The growth of nuclei to form particles of macroscopic dimensions or domains of the phase (crystal).

4. The relaxation processes such as agglomeration by which the texture of the new phases changes.

Nucleation may occur spontaneously or it may be induced artificially. Based on these it is classified into two types.

(1). Homogeneous nucleation

(2). Heterogeneous nucleation

The cluster \( A_i \) may be formed by the evaporation of a molecule from some cluster \( A_{i+1} \)

\[
\begin{align*}
A_{i+1} & \quad \text{K.E} \\
\leftrightarrow & \\
A_i & \quad \text{Heat}
\end{align*}
\]

The phase change take place by single molecules becoming attached to of various sizes, these processes predominated slightly over the reverse processes in which the various embryos lose single molecules. The size distribution of embryos changes with time, the numbers if the large ones increasing. There is a critical size which is in unstable equilibrium with the supersaturated vapor and solution. This is a critical nucleus, the formation of which constitutes the bottleneck of the phase change.
Once embryos achieve the critical size, there is a high probability that they will grow to macroscopic size.

\[ A_i + A_1 \rightarrow A_{i+1} \text{ [solid phase/crystal]} \]

**Nucleation Chart**

Solution [solvent + solute]

\[ \uparrow \downarrow \]

Super saturation

\[ \uparrow \downarrow \]

Monomers of the solution

\[ \uparrow \downarrow \]

Cluster [group of monomers]

\[ \uparrow \downarrow \]

Embryos [group of clusters]

\[ \uparrow \downarrow \]

Critical Nuclei [combination of many embryos]

\[ \uparrow \downarrow \]

Large nuclei

\[ \uparrow \downarrow \]

Crystal / solid phase
3.1.3 Mechanics

Mechanical disturbance of the crystal growing vessel results in smaller crystals. Let the crystals grow with a minimum of disturbance this means: Don’t try to grow crystals next to your vacuum pump, and don’t pick up the vessel every day to check on how your crystals are growing. Set up the crystal growing attempt, in a quiet, out of way place and forget about it for a week.

3.1.4 Time

This is related to mechanics. Crystals fully recognizes that patience is a virtue and will reward those who practice it.

3.1.5 Techniques

Crystal growing is an art, and there are as many variations to the basic crystal growing recipes as there are crystallographers. The recipes give below are ones which I have either tried or I have read about and reasonable.

The techniques chosen will largely depend on the chemical properties of the compound of interest. Slow Evaporation is the simplest way to grow crystals and works best for compound which are not sensitive to ambient conditions in the laboratory. Prepare solutions of the compound in a suitable solvent. The solution should be saturated or nearly saturated. Transfer the solution to a clean crystal growing dish and cover. The covering for the container should not be air tight. Aluminium foil with some holes poked in it works well, or a flat piece of glass with microscope slides used as a spacer also will do the trick. Place the container in a quiet out of the way place and
let it evaporate. This method works best where there is enough material to saturate at least a few milliliters of solvent.

### 3.3 SOLUBILITY CURVE

If a solution is represented by a point A is cooled without any loss of solvent (line ABC) spontaneous crystallization cannot occur, until conditions represented by the point C or reached.

At the point C, crystallization may be spontaneous or it may be induced by seeding agitation or mechanical shock. Further cooling to some point D may be necessary before crystallization can be induced, especially with very soluble substances, such as thiourea.

![Figure 3.1 Solubility curve](image-url)
The evaporation of solvent from the solution may also result in supersaturating. Line A B’ C’ represents and operation of this process carried out at constant temperatures. In this, penetration beyond the super solubility curves into the label zone rarely happens, as the surface from with evaporation takes place is usually supersaturated to a grater degree on this surface eventually fall into the solution and seed it.

In practice, a combination of cooling and evaporation process is adopted which represented by the curve A B” C” in the Figure 3.1.

3.4 TAUTOMERIC FORMS OF THIOUREA

Thiourea (thiocarbamide, thiocarbonyl diamide) is an organic compound, containing carbon, nitrogen, sulfur and hydrogen, with the structural formula shown in Figure 3.2. It is similar to urea, except that the sulfur atom replaces oxygen atom. The properties of urea and thiourea differ significantly because of the electronegativity difference of sulfur and oxygen. Thiourea has wide importance in organic synthesis. The terms thioureas or thiocarbamides refers to a broad class of heteroatomic compounds. Thiourea occurs in two tautomeric forms:

![Thione form and Thiol form](image)

Figure 3.2 Tautomeric forms of thiourea
It is prepared from ammonium thiocyanate but more commonly is synthesized by the reaction of hydrogen sulfide with calcium cyanamide in the presence of carbon dioxide (Mertschenk et. al. 2002).

Many thiourea derivatives are equally useful as is thiourea. N,N-substituted thioureas are generally prepared by allowing the corresponding cyanamide to react with LiAlHSH (prepared by reacting sulfur with lithium aluminum hydride, reaction shown as Figure 3.3, in the presence of HCl in anhydrous diethyl ether. (Galstukhova et al. 1970).

![Figure 3.3 Thiourea derivatives](image)

3.4.1 Importance of Thiourea

Thiourea has wide applications in industrial fields:

1. Thiourea is used in synthesis of aminothiazoles, the reaction of carbonyl compounds (alpha-halo ketones) and thiourea (Dodson & King 1945).

2. It is also used preferably in the ozonolysis to give carbonyl compounds (Gupta et.al. 1982). Dimethyl sulfide can also be used effectively as a reagent for ozonolysis, but it has an abhorrent odour and is highly volatile, whereas thiourea is odourless, solid and preferable than dimethyl sulfide.
3. It is used to reduce peroxides to the corresponding diols (Kaneko et. al. 1974). The intermediate of the reaction (an epidioxide), is reduced by thiourea to diol.

4. It is widely used to synthesize thiols from alkyl halides. The reactions proceed via the intermediate which is isothiuronium salt (Speziale 1963). It is used in preference to alkali metal sulfides as it avoids formation of dialkyl sulfides, which is a side product that hinders the action of sodium sulphide and related reagents.

5. Thioureas undergo condensation reaction with β-dicarbonyl compounds to give pyrimidines (Foster & Snyder 1963). They are considered as building blocks of pyrimidines and their derivatives. The amino group of the thiourea condenses with a carbonyl, followed by cyclisation. This cyclised structure undergoes tautomerisation and finally desulfurisation results in the formation of pyrimidine.

Thiourea also has **wide applications in commercial fields**:

1. It involves in production of flame retardant resins and accelerators for vulcanization.
2. It is a common source of sulfur for making semiconductor cadmium sulfide nanoparticle.
3. It is used as an auxiliary agent in almost all other types of copy paper.
4. A reagent for gold and silver leaching can be created by selectively oxidizing thiourea.
5. Thiourea and its derivatives are used in electroplating industry.
3.5 PREPARATION OF THIOUREA BASED ORGANIC AND SEMI ORGANIC SINGLE CRYSTALS

3.5.1 Thiourea Crystals from Aqueous Solution

The growth of thiourea single crystal was carried out from aqueous solution by solvent evaporation technique. 100 ml of saturated solution was prepared at room temperature and then filtered to remove any insoluble impurities. The saturated solutions were kept in the well cleaned beakers and the outer face was covered by perforated filter paper. The beakers were kept at room temperature. The growth period of single crystal takes two weeks.

3.5.2 Sulphuric Acid Doped Thiourea Crystals

The growth of thiourea single crystal was carried out from concentrated sulphuric acid solution by Solvent evaporation technique. 50 ml saturated solution was prepared at room temperature and then filtered to remove any insoluble impurities. The spontaneous nucleation was prevented during the filtration process. Seed crystals were prepared by isothermal condition. The saturated solutions were kept in the Petri dish and the outer face was covered by perforated transparent polythene paper or filter paper. The petri dishes were kept at the room temperature until small transparent well-shaped crystals obtained within first week and at the second week, the seed crystals and single crystals were grown in the petri dishes. The growth period of single crystal takes within 2 weeks. The grown crystals possess well defined morphology with reasonable size of about $1 \times 1 \times 0.5 \text{ cm}^3$ and $1.1 \times 1 \times 0.4 \text{ cm}^3$ along all the three crystallographic directions as shown in Figure 3.4.
3.5.3 Nitric Acid Doped Thiourea Crystals

The growth of thiourea single crystal was carried out from concentrated nitric acid solution by Solvent evaporation technique. 100 ml saturated solution was prepared at room temperature and then filtered to remove any insoluble impurities. The spontaneous nucleation was prevented during the filtration process. Seed crystals were prepared by isothermal condition. The saturated solutions were kept in the beaker and the outer face was covered by perforated transparent polythene paper or filter paper. The beakers were kept at the room temperature until small transparent well-shaped crystals obtained, within second week, the seed crystals and single crystals were grown in the beakers. The growth period of single crystal takes within 2 weeks. The grown crystals possess well defined morphology with reasonable size of about 1. 2 × 0.7 × 0.5 cm³, 1× 0.8× 0.6 cm³ along all the three crystallographic directions as shown in Figure 3.5.
3.5.4 Calcium Thiourea Nitrate (CTN) Crystals

Raw materials of calcium nitrate and Thiourea in the ratio of 1:1 were dissolved in double distilled water to prepare the aqueous solutions of CTN. The synthesized salt was obtained by evaporating the solvent.

$$\text{CaNO}_3\cdot 4\text{H}_2\text{O} + (\text{NH}_2\text{CSNH}_2) \rightarrow (\text{NH}_2\text{CSNH}_2)\cdot \text{CaNO}_3$$

The saturated solution of CTN was prepared at room temperature. Since thiourea has the coordination capacity to form different phases of metal-thiourea complexes, the mixtures of the reactants has to be stirred well to avoid co-precipitation of multiple phases. The product was purified by repeated recrystallization before it used for the crystal growth. CTN crystals were grown from aqueous solution by slow evaporation method. The crystals of CTN, which are optically transparent, are obtained after 20 days and the grown crystals possess well defined morphology with reasonable size of about $1.1 \times 0.7 \times 0.5 \text{ cm}^3$ along all the three crystallographic directions as shown in Figure 3.6.

Figure 3.5 Single crystals of nitric acid doped thiourea
3.5.5 Sodium Thiourea Chloride (NTC) Crystals

Before starting the synthesis process, repeated recrystallization processes purified the commercially available raw materials and the recrystallized salt was used for the present studies. Sodium thiourea chloride was synthesized by 1:1 ratio of high purity thiourea salt and sodium chloride. The synthesized salt of NTC was grown by the slow evaporation low temperature solution growth technique. The reaction undergoes in the following way

\[(\text{NH}_2\text{CSNH}_2) + \text{NaCl} \rightarrow (\text{NH}_2\text{CSNH}_2).\text{NaCl}\]

The saturation of NTC was obtained by dissolving the recrystallized material with continuous stirring of the solution using a magnetic stirrer. On reaching saturation, the equilibrium concentration of the solute was determined gravimetrically. The saturated solution was further purified by filtering through the filter paper provided with fine pores. The filtered solution was tightly closed with thick filter paper so that the rate of evaporation could be minimized. The solution was kept in an undisturbed
condition. Transparent optical quality single crystals were obtained after 25 days. The grown crystal is shown in Figure 3.7.

**Figure 3.7 Single crystals of sodium thiourea chloride**

### 3.5.6 Zinc Thiourea Chloride (ZTC) Crystals

The ZTC salt was synthesized using zinc chloride and thiourea in a stoichiometric ratio 1: 1. The required quantity of zinc chloride and thiourea were estimated from the following reaction:

\[
\text{ZnCl}_2 + (\text{NH}_2\text{CSNH}_2) \rightarrow \text{Zn} (\text{NH}_2\text{CSNH}_2)\text{Cl}_2
\]

The calculated amounts of the salts were dissolved in the deionized water. The purity of the synthesized salt was increased by successive recrystallization process. The growth of ZTC single crystals were carried out by low temperature solution growth technique by solvent evaporation. Optically transparent ZTC crystal has been crystallized in a period of 15 days which are as shown in Figure 3.8.
3.5.7 Zinc Thiourea Sulphate (ZTS) Crystals

By mixing equal ratio of aqueous solutions of Zinc sulphate and thiourea in the stoichiometric ratio 1: 3 the ZTS salt has been synthesized. The required quantity of Zinc sulphate and thiourea is estimated from the chemical reaction.

\[ \text{ZnSO}_4 + 3(\text{NH}_2\text{CSNH}_2) \rightarrow \text{Zn}[\{(\text{NH}_2\text{CSNH}_2)_3\}]\text{SO}_4 \]

The required weight of salts are very well dissolved in double distilled water and thoroughly stirred to avoid the co-precipitation of the salts by using a magnetic stirrer. Successive recrystallization process has been carried out to improve the purity of the synthesized salt. To avoid decomposition of the solute molecules, the mixer is heated up to 50 °C. The ZTS crystals are grown from aqueous solution by slow evaporation technique which is non-hygroscopic. Good optically transparent ZTS crystal has been crystallized with well defined faces in a period of 25 days which are as shown in Figure 3.9.
3.5.8 Potassium Thiourea Chloride (PTC) Crystals

The commercially available raw materials of potassium chloride and thiourea have taken in the ratio of 1:1 and its purity was improved by repeated recrystallization processes. The purified salt was synthesized by dissolving it in deionized water. The chemical reaction is given below:

\[
\text{KCl} + [(\text{CSNH}_2)_2] \rightarrow \text{K}[\text{CS(NH}_2)_2] \text{Cl}
\]

Since thiourea has the coordinating capacity to form different phases of metal–thiourea complexes, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. In solution growth technique, the size of a crystal depends on the solubility of the material. Successive recrystallization process has been carried out to improve the purity of the synthesized salt. The PTC crystals are grown from aqueous solution by slow evaporation technique. Optically transparent PTC crystal has been crystallized with well defined faces in a period of 20 days which are as shown in Figure 3.10.
3.5.9 Potassium Thiourea Sulphate (PTS) Crystals

By mixing equal ratio of aqueous solutions of Potassium sulphate and thiourea in the stoichiometric ratio 1:1 the PTS salt has been synthesized. The required quantity of potassium sulphate and thiourea is estimated from the chemical reaction.

\[ K_2SO_4 + (NH_2CSNH_2) \rightarrow K_2(NH_2CSNH_2)SO_4 \]

The required weight of salts are very well dissolved in double distilled water and thoroughly stirred to avoid the co-precipitation of the salts by using a magnetic stirrer. Successive recrystallization process has been carried out to improve the purity of the synthesized salt. To avoid decomposition of the solute molecules, the mixer is heated up to 50 °C. The PTS crystals are grown from aqueous solution by slow evaporation technique which is non-hygroscopic. Good optically transparent PTS crystal has been crystallized with well defined faces in a period of 25 days which are as shown in Figure 3.11.
Single crystals of thiourea based organic and semi-organic (metal complex) crystals were grown by solution growth employing slow evaporation technique at room temperature. From the saturated aqueous solution prepared using the synthesized salts of CTN, NTC, ZTC, ZTS, PTC, PTS and deionized water, the transparent colourless single crystals were grown within 3 weeks employing slow evaporation technique at room temperature and the grown crystals possess well defined morphology with reasonable size.