

### 3.3. CRYSTALLIZATION

The solid organic compounds obtained as a result of organic reactions are generally not pure. Purification of these organic chemical compounds containing impurities is usually carried out by crystallization from suitable solvent or solvent mixtures. However, direct crystallization process can not be applied to crude products with excess impurities. Because some impurities reduce the rate of crystallization, they can even prevent crystal formation completely, so that a considerable amount of matter can be lost. For this reason, pre-purification processes such as extraction or distillation should be applied before crystallization.

#### 3.3.1. Crystallization Process

The purification of solids by crystallization are based on different solubility characteristics in the appropriate solvent or solvent mixture. The phases of the crystallization process are as follows:

1. Solubility of the impure substance in the appropriate solvent at the boiling point or near the boiling point.
2. Separation of hot solution from undissolved matter or dust by filtration.
3. Providing crystallization of the dissolved substance by cooling the hot solution.
4. Filtration of the crystals from the solvent phase and drying

After drying the resulting crystals are checked for their purity based on their melting point, if not pure, recrystallized with solvent. This process is called **recrystallization**. This process is continued until the melting point is fixed.

The separation of impurities by crystallization is as follows:

For example; the impurity in substance A is substance B (It is generally assumed that there is about 5% impurity in one substance). The solubility of A and B in a selected solvent and at a certain temperature is  $S_A$  and  $S_B$ . In this case, 3 possibilities can be mentioned;

1. The impurity may be highly soluble from the substance to be purified.  $S_B > S_A$
2. The impurity may be slightly soluble from the substance to be purified.  $S_A > S_B$
3. Their resolutions may be equal.  $S_A = S_B$

As can be seen, in the first possibility it may be obtain pure substance A by crystallization, in which case the impurity will remain in the main solution.

FOR EXAMPLE: Solubility of 100 g of a substance A in a 100 ml of a suitable solvent at 15°C is  $S_A = 10 \text{ g} / 100 \text{ ml}$  and  $S_B = 5 \text{ g} / 100 \text{ ml}$ . If this substance is purified by crystallization technique;

In 100 g, there is 5 g of impurity (B) and 95 g of substance A. Whole substance B is dissolved at 15°C in 100 ml of solvent, 10 g of A is dissolved; according to this, 85 g of substance A can be crystallized purely.

### 3.3.2. Properties of Crystallization Solvent

1. The substance to be purified should be solved a lot at high temperature, little at low temperature
2. It should give the well-formed crystals of the substance to be purified.
3. It should be readily separable from the crystals of the substance to be purified and boiling point should be low.
4. It should not react with the substance to be purified
5. It should not be volatile, flammable and toxic, should be easy to find.

Some of the most commonly used solvents in crystallization are: Water, ether, acetone, chloroform, methanol, carbon tetrachloride, ethyl acetate, ethanol, benzene, petroleum ether etc. Heating in the presence of flammable solvents such as ether, acetone, methanol, ethanol, ethyl acetate, benzene, petroleum ether should not be carried out in the naked flame, water bath should be used. The most commonly used solvents and properties in the crystallization process are shown in the following table:

Solvent	B.P.	Properties
Distilled water	100	Used wherever convenient
Diethyl ether	35	Flammable
Acetone	56	Flammable
Chloroform	61	Nonflammable, steamy toxic poisonous
Methanol (99 %)	64.7	Flammable, toxic
Carbon tetrachloride	77	Nonflammable, steamy toxic poisonous
Ethyl acetate	78	Flammable
Methanol (Technical, 95 %)	77.8	Flammable
Ethanol	78	Flammable
Petroleum ether	40-60	Flammable
Acetic acid	118	Pungent

Since the ether is too volatile, it climbs up the sides of the beaker, therefore it should not be used as much as possible in crystallization processes. In addition, the material remains as residue in the bottom of the beaker because the ether volatilizes in a short time. Carbon sulfur also should not be used as much as possible because it forms low flash point mixtures in air.

The choice of solvent in crystallization is usually determined experimentally. Practically, if 0.1 g of the substance is dissolved in 1 ml of solvent without heating or 0.1 g of the substance is not dissolved by heating with 3 ml of solvent, it is not suitable.

If the substance to be crystallized dissolves easily in one solvent and poorly in another, pairs of solvents can be used for a good crystallization operation. However, these two solvents must be

intermiscible. For this, the substance is first dissolved in the solvent in which it is dissolved a lot and then the solvent in which the substance is poorly dissolved is added little by little as hot. When slight turbidity occurs, little of the first solvent is added and it is allowed to crystallize in the cold. Alcohol-water, benzene-petroleum ether, acetone-petroleum ether are among the most commonly used solvent pairs. Theoretically, two properties are used in solvent selection;

1. A substance is very soluble in the solvent where its chemical and physical properties are similar.
2. A polar substance dissolves more in a polar solvent than in an apolar solvent. Polar compounds are very soluble in water. Especially if they have hydrogen bond, their solubility in water increases even more. For organic structures containing carboxylic acid, alcohol, amine and amide, the solubility in water is high. Besides, the salts of the organic substances are easily soluble in water. All hydrocarbons and alkyl halides are insoluble in water. Nonpolar solvents, such as ether, benzene, dissolve most of the nonionic compounds. In general, as the fragment of hydrocarbons increases in organic compounds, that is, as the number of C increases, their solubility in water decreases and their solubility in nonpolar solvents increases. As the molecular weight increases, the solubility in water decreases. Nevertheless, there are exceptions. For example, the nonsubstituted amides are less soluble in water than the substituted amides. Because an association occurs in nonsubstituted amides *via* hydrogen bridges, so that case reduces the solubility in water. Thus, the addition of halogen into the structure is another effect that reduces the solubility in water. Water, formic acid, acetic acid, methanol for polar solvents; benzene, acetone, chloroform for apolar solvents give examples.

### **3.3.3. Crystallization Techniques**

A suitable solvent for the chemical compound is found and the solution is heated until the boiling point is reached. The boiling solution should be filtered rapidly before being allowed to cool. For this, it is usually used pleated filter paper and a funnel with a large short neck. The large and short neck prevents the formation of crystals by cooling down the solution and difficulties in filtration by clogging. No crystals remain on the filter paper with a good filtration. The filtered solution is covered with a watch glass and allowed to cool. The size of the crystals formed depends on the cooling process. Rapid cooling provides small crystal formation; slow cooling provides large crystal formation. Large crystals contain significant amounts of solvents. Small crystals may adsorb more impurities because the unit surface volume will increase. For this reason, cooling should usually be done in the middle heat. The resulting crystals are filtered through flat filter paper or vacuum using a Buchner Funnel. Drying process can be carried out in the open air, under the melting point, in the fixed incubator or vacuum desiccator.

### 3.3.4. Difficulties in Crystallization

1. Decolorization: The crude product may contain color impurities. Because the crystals can adsorb these impurities, colored and dirty crystals are obtained. They can be removed by using substances that are capable of adsorbing impurities such as activated charcoal. A small amount of activated charcoal up to 1-2% of the weight of the crude product is added and boiled. The charcoal with high adsorption power usually adsorbs easily the large molecular impurities and removes the color of the solution. Activated charcoal should not be used in excess, otherwise it will be also absorbed the main substance and the efficiency will be reduced. The solution can be separated from the activated charcoal by filtration.
2. Crystallization difficulty and separation in oil-form: If the substance separates in oil-form (this may be due to rapid cooling or concentrating solution), it is dissolved by heating. Then the single-phase clear solution is cooled slowly or the cooling solution is stirred vigorously to prevent separation in oil-form, so that, even if the oil particles are formed, they are prevented from clustering and crystallization is provided. Sometimes crystallization does not start from saturated solutions, in which case the following steps are carried out to initiate crystallization;
  - Adding the seed crystal
  - Scratching with glass rod
  - Cooling down to very low temperatures
  - Volatilizing a little bit of solvent in the solution

### 3.3.5. Filtration Process in the Crystallization

The process applied to separate the liquid phase from the solid phase in a mixture is called filtration. Filtration is a very demanding process, since purification by good crystallization depends on perfect filtration. Filtering during crystallization is usually carried out twice:

- The filtration of the prepared hot solution before crystallization,
- The crystals are filtered out from the main solution, after the crystallization is completed.

#### 1. The filtration of the prepared hot solution before crystallization:

Heat loss should be avoided as much as possible during the filtration of hot solutions. Otherwise, crystals form on the filter paper and funnel pipe in order to the solubility declines as a result of decrease the temperature, so filtration becomes more difficult. For prevent cooling should be filtered quickly, heated the funnel and filter paper to the boiling solution temperature, and prevented evaporation as much as possible. To achieve these conditions, flow pipe cut funnel and pleated filter paper are used. The funnel, which has filter paper soaked with solvent on it by covering with the watch glass, is placed on a beaker with some pure solvent in it, and the beaker is heated down. Then the pure solvent in the beaker is transferred to another beaker and immediately filtered into the same beaker. The funnel heating process can also be carried out using the solution itself to be filtered, or it can also

be heated by placing on the solution in the beaker or Erlenmeyer flask. Thus, the funnel heats up as it functions as a condenser, after that, the solution is immediately filtered by the funnel heated.

2. The crystals are filtered out from the main solution, after the crystallization is completed:

The process of filtering out from the main solution of the crystals is always done by applying vacuum, not by ordinary filtration. The vacuum is provided by a tromp fitted to the tap. The vacuum pump should not be used in this process because the solvent evaporates in order that the vapor pressure of the filtrate is high and increases the vapor pressure by dissolving in the oil of vacuum pump. Vacuum accelerates filtration as well as separates completely the crystals from the main solution. Buchner Funnel and Nuche Erlenmeyer flask are used if many substances are dissolved. After the filter paper is cut according to the funnel and placed in the funnel, first vacuum is made by operating the tromp, then the substance to be filtered is started to be poured into the funnel. Slow suction in the filtration process is more effective than rapid suction because very thin grains eluate onto the filter paper at rapid suction, which reduces the permeability of the paper. Because of the filtration, some main solution holds on to the crystals, which remain on the filter paper, in this case it is removed by washing with a small amount of pure solvent. As soon as the solvent dripping to Nuche Erlenmeyer finishes, the vacuum is cut off. The rest of the funnel is placed on the watch glass together with the filter paper by the aid of a forceps, or the funnel is turned upside down on the watch glass and the crystals are blown onto a watch glass by attaching a rubber hose to the pipe part of the funnel.

Glass filters (Gooch crucible) made by sintering glass powders at the filter part are used in the filtration of solvents to be reacted with filter paper (for concentrated acidic or basic substances). As they are expensive materials, special care should be taken in their use, no excess vacuum should be made and chromic acid solution should be used as a cleaner. Instead of the porcelain Buchner Funnel, perforated porcelain plated filters are used in the filtration of small amount of substance.