CHAPTER 7

CRYSTAL HABIT AND MORPHOLOGY

CONTENTS PAGES

7.1 Introduction

Habit of a crystal is defined as its overall external shape which results from different rates of growth of its faces. During the process of crystallization, one set of faces may be induced to grow faster than others or growth of another set may be retarded. Crystals of same substance grown by different methods may be completely dissimilar in appearance eventhough they belong to same crystal system. Crystal habit is mostly described in qualitative terms such as platy, cubic, octahedral, prismatic, prismatic pyramidal, needle-like, dendritic, lamellar, etc.

Crystal habits and habit modifications of a variety of crystals, grown under different conditions and also by different methods, are described by Buckley[1], Mullin[2], Elwell and Scheel[3], Burton et al[4], Chernov[5], Hartman[6], Kern[7] and many others. Today possible morphologies of crystals are drawn by a computer in a matter of minitues, provided its structure is known. Despite remarkable advances in this field, the study of crystal morphology and habit is not outdated, because habit plays a vital role in the growth of large high quality crystals. Now-a-days crystal grower is more interested in finding explanations for habit modifications in synthetic crystals. This chapter deals with the habit modification and the influence of gel parameters on morphology of RHT crystals.

7.2 Influence of Growth Conditions on Habit

The habit of crystal is determined by the slowest growing faces. For the equilibrium form of the crystal, these faces have the lowest surface energy, but it is apparent that crystal habit is governed by kinetic rather than equilibrium considerations[8]. A number of factors such as degree of supersaturation, type of the solvent, pH of the gel media, presence of impurities, etc. affect the habit of a crystal. Kern[7] showed that in a number of experiments many ionic crystals change their habit when supersaturation exceeds a certain critical value. Wells[9] observed that a change in solvent results in a change of the crystal habit. Many times pH of gels has considerable influence on growth rate of crystals which ultimately changes the crystal habit[10,11]. Habit modifications are also observed when significant changes in growth temperature, and occurrence, since increase in temperature fastens the growth rate[12-14]. The most common cause of habit changes is the presence of impurity in the crystallizing solution[15]. Habit modification by impurities is a surface phenomenon. Impurity molecules or ions are attracted by various faces of the crystal and physically absorbed or chemisorbed on the surface. In this way, available sites for surface nucleation or solute deposition are reduced and growth on that particular face is retarded. It is observed that only very small traces (0.01 %) are significant to produce habit changes. This means many observed crystal habits may be caused by unsuspected impurity effects.

7.3 Results

In the present investigation, crystals with different habits are obtained at different depths in the growing test tubes and at different growth conditions. The morphology of the grown crystal is affected mainly by the concentration of feed solution and the pH of the system. Three types of morphologies of RHT crystals are observed namely (i) Orthorhombic disphenoidal crystals, (ii) Tetrahedral disphenoidal crystals, and (iii) Prismatic needle crystals.

7.3.1 Orthorhombic Disphenoidal Crystals

In this category rod-like orthorhombic crystals are obtained. High concentrations of RbCl feed solution at pH between 3 and 5 (Figure 7.1(a) gave rise to a rod-like orthorhombic disphenoidal type of crystals as shown in Figure 7.1(b). The usual region of crystal growth in the test tube is clearly seen from Figure 7.1(a). The morphology of this type of crystals is depicted in Figure7.1(c). Most of them are fairly transparent.

7.3.2 Tetrahedral Disphenoidal Crystals

Usually, the nucleation of this

type of crystal is initiated just below the gel solution interface and also at the extreme bottom of the glass test tube. The usual regions of crystal growth in test tube is clearly illustrated in Figure 7.2(a). This type of crystals are shown in Figure 7.2(b). The morphology of this type of crystal is schematically shown in Figure 7.2(c). The inclusion of gels take place in this type of crystals without affecting their morphology. Due to this inclusion transparency of the crystals reduces.

7.3.3 Prismatic Needle Crystals

The nucleation of this type of crystals initiates just below the gel-solution interface extended upto bottom, depending on the feed--solution concentration. They start growing from a bunch of nuclei with the diffusion of feed solution into the gel. With lapse of time, the thickness of the crystal increases, fast growth rate is observed along c-direction which is the growth direction of RHT of different habits. The growth of needle is due to the presence of diffusion field around the tips of the needle and the crystals grow into the supersaturated solution whereas the sides of the crystals are in contact with a largely exhausted solution. The prismatic needle crystals growing into glass test tube is shown in Figure 7.3(a). Some of the typical prismatic-needle crystals are illustrated in Figure 7.3(b). Schematic representation of the morphology of these crystals is depicted in Figure 7.3(c). The crystals are quite transparent.

It is pertient to mention that c-axis happens to be the growth axis of RHT crystals. Hence, whenever, isolated crystals are growing, irrespective of their orientation with respect to the vertical axis of the test tube, they always grow along c-axis. In many cases the growth axis of isolated crystals are normal to each other.

7.4 Influence of Gel pH

The effect of gel pH on the morphology of the grown crystals is studied by keeping all other gel parameters constant. Effect of gel pH is studied and summarised as follows :

pH range between 3 and 5 gave rise

to rod-like orthorhombic disphenoidal crystals. At pH > 6 prismatic needle crystals are observed and pH < 3 is responsible for the formation of disphenoidal tetrahedral crystals.

7.5 Effect of Concentration of Feed Solution

The effect of concentration of feed solution (RbCl) on the morphology and size of the grown crystals is studied bykeeping all other parameters constant and varying the concentration of feed solution. It is observed that increasing the concentration of feed solution increases linear growth along growth axis for prismatic needle and orthorhombic disphenoidal crystals. Needle crystals are translucent and geometrically well-defined. Disphenoidal crystals increase in size with the increase of concentration of feed solution.

7.6 Discussion

Crystal habit is governed by the interaction between surface and the diffusion field. Once the habit is established, the diffusion field around it will orient itself to confirm the crystal symmetry and tend to maintain it.

The parameters such as concentration of feed solution, pH of gel, impurities in the solvent, gel ageing, temperature, etc. have considerable influence the crystal morphology. In a steady state of concentration gradients, diffusion rate also becomes steady which favour the growth of well defined crystals. However, slower growth rate along one direction results in the growth of rod-like disphenoidal crystals. Faster growth rate along c-axis i.e. growth direction results in the growth of prismatic needle crystals. In a moderate supersaturation of feed solutions, crystals continue to develop as a disphenoidal tetrahedral crystals.

7.7 Conclusions

1. Red-like orthorhombic and tetrahedral disphenoidal crystals are obtained under different growth conditions.

2. Transparent prismatic needle RHT crystals are obtained.

3. The growth rate along c-axis for needle and orthorhombic disphenoidal crystals increases with increasing concentration of feed solution.

4. Generally, crystals are transparent but due to gel inclusion opaque crystals are resulted.

5. Restricted amount of gel inclusion takes place in tetrahedral disphenoidal crystals.

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Captions of the figures

Figure 7.1(a)	RHT orthorhombic disphenoidal crystals growing in silica gel medium.
Figure 7.1(b)	Some of the typical orthorhombic disphenoidal crystals.
Figure 7.1(c)	Schematic representation of the morphology of orthorhombic disphenoidal crystals.
Figure 7.2(a)	RHT tetrahedral disphenoidal crystals growing in silica gel medium.
Figure 7.2(b)	Some of the typical tetrahedral disphenoidal crystals.
Figure 7.2(c)	Schematic representation of the morphology of tetrahedral disphenoidal crystals.
Figure 7.3(a)	RHT prismatic needle crystals growing in silica gel medium.
Figure 7.3(b)	Some of the typical prismatic needle crystals.
Figure 7.3(c)	Schematic representation morphology of prismatic needle crystals.

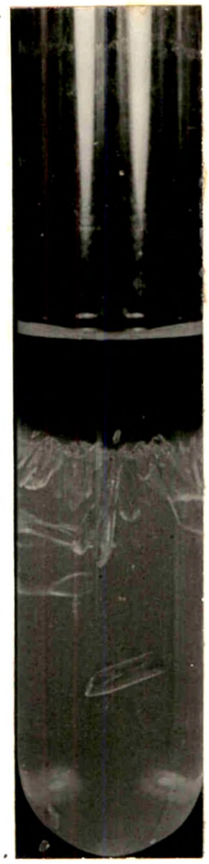

Fig. 7.1(a)

Fig. 7.1(c)

Fig. 7.1(b)

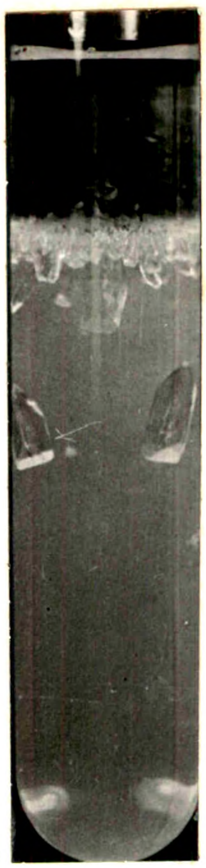

Fig. 7.2(a)

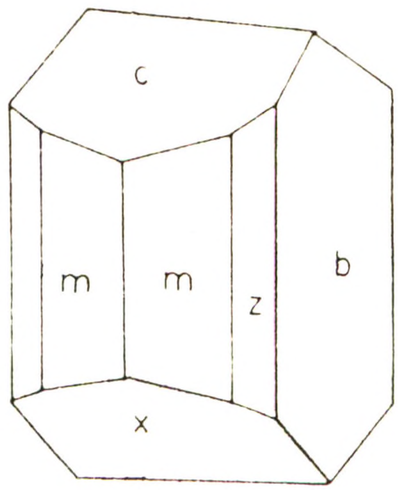

Fig. 7.2(c)

Fig. 7.2(b)

Fig. 7.3(a)

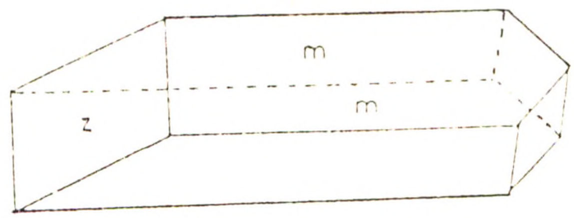

Fig. 7.3(c)

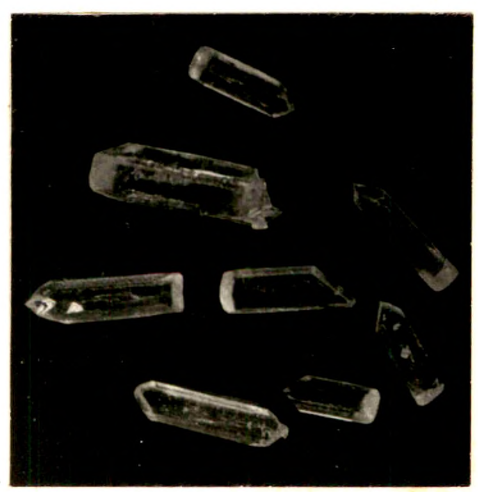

Fig. 7.3(b)