## CHAPTER 6

NUCLEATION CONTROL AND GROWTH KINETICS

<table>
<thead>
<tr>
<th>Contents</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>83</td>
</tr>
<tr>
<td>6.2 Observations and discussion</td>
<td>84</td>
</tr>
<tr>
<td>6.2.1 Effect of concentration of feed (NH₄Cl) solution</td>
<td>84</td>
</tr>
<tr>
<td>6.2.2 Effect of gel density</td>
<td>85</td>
</tr>
<tr>
<td>6.2.3 Effect of pH of gels</td>
<td>86</td>
</tr>
<tr>
<td>6.2.4 Effect of aging of gels</td>
<td>87</td>
</tr>
<tr>
<td>6.2.5 Effect of temperature</td>
<td>87</td>
</tr>
<tr>
<td>6.3 Temperature dependence of growth kinetics</td>
<td>88</td>
</tr>
<tr>
<td>6.4 Concentration programming</td>
<td>90</td>
</tr>
<tr>
<td>6.5 Growth by electrolysis</td>
<td>91</td>
</tr>
<tr>
<td>6.6 Conclusions</td>
<td>95</td>
</tr>
<tr>
<td>References</td>
<td>97</td>
</tr>
<tr>
<td>Captions of figures</td>
<td>99</td>
</tr>
</tbody>
</table>
6.1 Introduction

The problem of nucleation is of great importance in practical operation, since the crystal which grows in any particular gel system compete with other crystals for solute. This competition limits their size and perfection and it is obviously desirable to suppress nucleation until, ideally only one crystal grows in a predetermined location. The available techniques have not yet reached this level of perfection.

The suppression of nucleation is the principle function of the gel, but it is apparent that the degree of suppression ordinary obtained is insufficient for many of crystals one wishes to grow. Though ionic diffusion is slowed by the soft three-dimensional gel frame work, this suppression of reaction-rate is still larger than the one required for liquid nucleation. Hence, nucleation control in a gel medium remains one of the serious problem for a crystal grower. It may be envisaged that the potential nuclei are physically enclosed in gel cells of a varying size and varying degree of communication with neighbouring cell. Gel cell size is (influenced by gel density, gel age\(^1\), pH of gel\(^2\), temperature\(^3\), etc. Hence nucleation control can be achieved to some extent by varying these parameters. Other conventional methods such as neutral gel technique\(^4\),
seeding\textsuperscript{1}), addition of impurities\textsuperscript{5,6}) have also been employed by some crystal growers.

Recently, the growth of single crystals in silica gel media under the influence of an externally applied electric field has drawn the attention of many crystal growers and is under modification in several laboratories\textsuperscript{7,8}). Magnetic and electric fields have been used in liquid-solid growth\textsuperscript{9}) and theory of accelerated under constant electric field has been developed by Mysels\textsuperscript{10}), Lamm\textsuperscript{11}) and Simand and Ling Yang\textsuperscript{12}). Influence of different gel parameters, temperature, concentration programme, replacement programme, etc. on nucleation and growth of AHT crystals are discussed in this chapter. A study of nucleation and growth of AHT crystals under an external uniform electric field is also reported in this chapter.

6.2 Observations and Discussion

6.2.1 Effect of concentration of feed (NH\textsubscript{4}Cl) solution

To study the effect of concentration of feed solutions, gels of same pH and density were prepared. Feed solutions of different concentrations ranging from 1.0 M to 5.0 M were added over the set gels.
The variation of nucleation density with concentration of feed solutions is shown in Fig. 6.1. This indicates that the nucleation density increases at higher concentration because of the enhanced availability of ammonium ions. It is observed that the higher concentration of feed solutions give rise to hollow and dendritic crystals. This may be due to an increase in the supersaturation at higher concentrations of the feed solution. Figs. 6.2 (a, b, c) illustrate AHT crystals growing in test tubes at different concentrations of feed solution and Figs. 6.3 (a, b, c) show typical AHT crystals grown at different concentrations.

6.2.2 Effect of gel density

The gels of various densities were obtained by mixing sodium metasilicate of sp.gr. 1.04 to 1.07 gm cm\(^{-3}\) with 1.0 M tartaric acid, keeping the gel pH constant at 4.0. It was observed that the transparency of the gel decreases as the gel density increases. Fig. 6.4 illustrates a plot of nucleation density versus gel density.

A greater gel density implies a smaller pore size and poor communication among the pores and thereby the nucleation density is decreased\(^{13}\). The increase in the gel density also increases the contamination of the
crystal with silica gel and therefore affects their quality and shape. A gel density of the range 1.05 to 1.06 gm cm$^{-3}$ gives translucent crystals. Thus a gel density of 1.04 gm cm$^{-3}$ is the optimum value for the growth of well defined single crystals of AHT. Figs. 6.5 (a,b,c) show a crystal growing in gels of three different densities.

6.2.3 Effect of pH of gels

The pH values of the gels were varied from 2 to 10 by addition of tartaric acid of various concentrations. It is observed that as the pH increases, the transparency of gel decreases. The crystals growing at higher pH values are opaque and poorly defined. This is due to the contamination of crystals by silica gel because as the pH increases the box-like network structure of the gel changes to a loosely bound platelet structure without cross linkages and the cellular nature become less distinct. Fig. 6.6 shows that the nucleation density decreases with increasing pH which may be due to improper formation of cells at higher gel pHs. Figs. 6.7 (a, b, c) show the crystals growing in gels of three different pH values and Figs. 6.8 (a, b, c) illustrate some typical AHT crystals of different morphologies.
6.2.4 Effect of aging of gels

To investigate the effect of gel ageing, gels were allowed to age for various periods before adding the feed solution. Fig. 6.9 is a plot of the age of the gels versus the nucleation density. As shown by Henisch and Dennis\(^5\) gel aging reduces the cell size and consequently the rate of diffusion of ions into the gel. It should be noted that the gel aging has no pronounced effect on the size or the quality of the crystals. Further aging of gels does not favour the growth of AHT crystals. Typical AHT crystals growing with gel aged for three different periods are shown in Fig. 6.10.

6.2.5 Effect of temperature

The temperature has considerable influence on reaction and diffusion. Influence of temperature on nucleation and growth of cuprous chloride has been studied by Armington and O'Connor\(^\text{14}\). It is easy to investigate that there should be an optimum temperature for nucleation. As the temperature increases, the free energy of formation of critical nucleus increases but the degree of supersaturation diminishes\(^\text{15}\). Single tube experiments were carried out in a constant temperature range 25° to 40°C. The variation in temperature showed
that more crystals grow at lower temperature than at higher temperature. The decrease in nucleation density at higher temperature is due to the fact that an increase in temperature causes an increase in the aqueous solubility of AHT. Thus the size of grown crystals at higher temperature is smaller than that at low temperature.

6.3 Temperature dependence of growth kinetics

In order to determine the temperature dependence of the growth kinetics of AHT needle crystals, growth experiments were conducted at various temperature ranges from 25°C to 40°C. A parabolic relation between the length of the needle crystals and the time of growth in the gel was usually found as shown in Fig. 6.11. Figs. 6.12 and 6.13 show the square of the length of the needle crystals plotted against the time of growth in the above temperature range for three different concentrations of NH₄Cl. It can be clearly seen that the linear relations are obtained. The growth rate constant 'k' determined from three results and are given in Table 6.1.

It is evident from the Table 6.1 that the highest growth rate is achieved at 25°C owing to the minimum in the aqueous solubility of AHT at this temperature.
**Table 6.1**

**Effect of growth temperature on growth rate constant**

<table>
<thead>
<tr>
<th>Obs.</th>
<th>Growth Temperature in °C</th>
<th>Growth rate constant $k$ ($cm^2 h^{-1}$) for different concentration of feed (NH$_4$Cl) solution</th>
<th>1.5 M</th>
<th>2.0 M</th>
<th>2.5 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>25</td>
<td>0.021</td>
<td>0.112</td>
<td>0.125</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>30</td>
<td>0.020</td>
<td>0.098</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>35</td>
<td>0.018</td>
<td>0.075</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>40</td>
<td>0.006</td>
<td>0.010</td>
<td>0.098</td>
<td></td>
</tr>
</tbody>
</table>
the gel aging time or the growth temperature can be expressed by the specific mathematical function:

\[ r^2 = kt \]  

(1)

where \( r \) is the length of the needle crystal, \( t \) is the growth period and \( k(\text{mm}^2 \text{h}^{-1}) \) is the growth rate constant. It has been shown that parabolic kinetics are characteristic of a one-dimensional diffusion-controlled process. Fig. 6.14 shows a plot of the rate constant \( k \) against the three concentrations of \( \text{NH}_4\text{Cl} \) solution and Fig. 6.15 illustrates curves of \( k \) against three growth temperatures. The results reported here agree with those obtained by Henisch et al. in a kinetic study of ionic crystals grown in gels.

6.4 Concentration Programming

In this procedure, 25 ml of 0.25 M \( \text{NH}_4\text{Cl} \) solution was placed over the gel. The strength of this feed solution was increased at the rate of 0.25 M per every 48 hrs. by removing 20 ml of the above feed solution and replacing it by an equal amount of more concentrated \( \text{NH}_4\text{Cl} \) feed solution. Initially, up to 0.75 M, no nucleation was observed but at 1.0 M concentration, nucleation began. The
nutrient concentrations were systematically increased up to 2.50 M. This resulted in a few nucleation centers which acted as sinks and used in the establishment of a radial diffusion pattern that substantially reduced the reagent concentration in the neighboring locations and hence the formation of additional nuclei was inhibited. On increasing the concentration, the existing crystals grew faster and non-competitively, so that their quality was correspondingly good. Figs. 6.16(a) and 6.16(b) show crystals growing without and with concentration programming respectively.

6.5 Growth by electrolysis

Another method for growth, employing an electrolytic technique was used. The crystallization apparatus used in the present study is an electrolytic cell of length 20 cm. and diameter 2.5 cm. as shown in Fig. 6.17. Procedure for preparation of gels are same as described earlier. However, data relating to electrolytic growth is as under:

1. Specific gravity of sodium metal silicate solution: 1.04 gm cm$^{-3}$
2. Concentration of feed solution ($\text{NH}_4\text{Cl}$): 1.5 M
3. Concentration of tartaric acid solution : 2.0 M
4. pH of the gel : 5
5. Mean experimental temperature : 27°C

The gels were transferred to the electrolyte cell and were allowed to set. Over the set gel 1.50 M NH₄Cl solution was poured. Care was taken to ensure that no air bubbles existed between the electrodes and solution. A suitable d.c. voltage was applied between two carbon electrodes acting as anode and cathode. The current in the circuit was measured by means of a sensitive milliammeter (mA).

After 24-36 hrs a large number of nucleation centers of AHT appeared inside the gel column. In the beginning itself, nucleations were deep inside the gel column, unlike in non-electrolytic, the two layers methods, where crystals nucleated at the interface. As the time elapsed the length of AHT crystals increased but growth ceased after 12-15 days. The experimental details and growth parameters are summarized in Table 6.2.

Under electric field NH₄⁺ and (HCOOH)⁻ ions move in opposite direction. NH₄⁺ ions are repelled
Table 6.2
Growth parameter for growing AHT crystals

<table>
<thead>
<tr>
<th>Gel pH</th>
<th>Age of gel in hrs.</th>
<th>Concentration in M.</th>
<th>Current in mA</th>
<th>Size of AHT crystals in cm.</th>
<th>Period of crystallization in days</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>72</td>
<td>1.5</td>
<td>0.05</td>
<td>1.75</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>1.5</td>
<td>0.10</td>
<td>1.95</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>1.5</td>
<td>0.30</td>
<td>2.23</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>1.5</td>
<td>0.50</td>
<td>2.51</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>1.5</td>
<td>0.70</td>
<td>2.70</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>1.5</td>
<td>0.90</td>
<td>3.00</td>
<td>6</td>
</tr>
</tbody>
</table>
from anode and attracted by cathode where a supemetastable state is formed. The ionic velocity is accelerated to a value adequate for the formatic single crystals. A chemical inhomogeneity also influences the medium which changes the structure and natural growth system. In other words, an anisotropic electric field of diffusion is produced under electric field. The diffusion by Simand and Ling Yang, Lamm, Mysels and Keuman and Bach anticipate accelerated diffusion region:

\[ D_e = D_0 + \frac{u^2 E}{2k} \]

where \( u \) is the product of ionic mobility and \( c \) the intensity of the electric field and \( k \) a constant. \((NH_4)^+ \) and \((HCOOH)^- \) ions drift in certain directions under the action of electric field as an AHT crystal is formed inside the gel region, which yields AHT crystals and is conjectured as being due to accelerated diffusion. In Fig. 6.16 some typical crystals grown by electrolysis are illustrated. It has been shown that an electric field affects the growth of crystals.
The crystals require a shorter time to attain maximum size.

A suitable and definite control over the growth rate and nucleation centers formation is exercised.

The crystal quality was unaffected by the electric field.

6.6 Conclusions

1. The nucleation control can be achieved by altering a variety of gel parameters such as gel aging time, gel density, gel pH and feed solution concentration.

2. Large transparent single crystals of AHT can be obtained at pH 5 with low density gels.

3. Gel aging usually tends to reduce the growth rate of needle crystals.

4. The feed solution concentration has a significant effect on the type of crystals formed.

5. The nucleation density increases with the feed solution concentration.
6. An increase in the temperature reduces the number of nucleation centers.

7. The highest growth rate is achieved at 25°C, the growth rate decreases above and below this temperature.

8. By concentration programme, the size and quality of crystals can be improved.

9. Although the period of crystallization is considerably reduced by applying an externally applied uniform electric field, the quality of the crystals is unaffected.

10. Crystal growth in gels is a one-dimensional diffusion-controlled process.
References

1. H. K. Henisch : "Crystal Growth in Gels"  
The Pennsylvania State  
University Press, Pennsylvania,  
USA (1960).


<table>
<thead>
<tr>
<th></th>
<th>Authors</th>
<th>Journal/Publication Details</th>
</tr>
</thead>
</table>
Captions of figures

Fig. 6.1  Nucleation density (N) versus concentration of feed (NH4Cl) solutions for four specific gravity of gels.

Figs. 6.2 Crystals growing at three concentrations of feed solution: (a) 1.0 M, (b) 3.0 M and (c) 5.0 M.

Figs. 6.3 Typical Aat crystals grown at three concentrations of feed solution: (a) 1.0 M, (b) 3.0 M and (c) 5.0 M.

Fig. 6.4 Nucleation density (N) versus gel density (gm.cm\(^{-3}\)) for eight different NH4Cl solutions.

Figs. 6.5 Crystals growing at three different gel densities: (a) 1.03, (b) 1.04 and (c) 1.06 gm cm\(^{-3}\).

Fig. 6.6 Nucleation density (N) versus the pH of gel solutions for three concentrations of NH4Cl solutions.
Figs. 6.7 Crystals grow at three pH values of gel solutions: (a) pH 4, (b) pH 5 and (c) pH 6.

Figs. 6.8 Typical AHT crystals grown at three pH values of gel solutions: (a) pH 2, (b) pH 4, and (c) pH 6.

Fig. 6.9 Nucleation density (N) versus gel aging time for three concentrations of NH₄Cl solutions.

Figs. 6.10 Crystals growing at three gel aging periods: (a) 48 hrs, (b) 110 hrs and (c) 180 hrs.

Fig. 6.11 Plots of the length of needle crystals versus time of growth for three concentrations of NH₄Cl solutions.

Fig. 6.12 Plots of the square of the needle length versus time of growth at 25°C for three different temperatures.

Fig. 6.13 Plots of the square of needle length versus time of growth at 40°C for three different concentrations of NH₄Cl solution.
Fig. 6.14 Plots of the growth rate constant \( k \) against temperatures for various feed solutions.

Fig. 6.15 Plots of growth rate constant \( k \) against the feed solution concentrations for three growth temperatures.

Figs. 6.16 (a, b) Crystals growing (a) without and (b) with concentration programming.

Fig. 6.17 Electrolytic growth of AHT crystals in silica gel.

Fig. 6.18 Typical AHT crystals grown by applying an external electric field.
Fig. 6.4

Fig. 6.5
Fig. 6.9

Fig. 6.10
Fig. 6.14

Fig. 6.15

Fig. 6.16