CHAPTER 4

Growth of d-AHT single crystals in silica gel

GROWTH OF d-AHT SINGLE CRYSTALS IN SILICA GEL

4. 1 Introduction:

The growth of single crystals of ammonium- hydrogen-d-tartrate (d-AHT) is of considerable interest in view of the fact that it exhibits piezoelctric properties and its growth morphology and other properties are relatively unknown. The importance of gel techniques and its preference to other crystal growing techniques have been emphasized in Chapter III.

d-AHT has been grown in this lab (1) using Ammonium Chloride as the feed solution. In this chapter, the performance and potentiality of the gel technique is tested in producing larger and more perfect single crystals of d-AHT using other salts as the feed solution.

A qualitative study was undertaken to determine the best ammonium halide which could promote growth and subdue dissolution, preferably zero dissolution. In gel growth, both growth and dissolution takes place simultaneously after a certain time, and until and unless one is controlled, the other gets the better hand and in this stead it was found that Ammonium Bromide was the best so far as controlling the dissolution was concerned. It should be remarked here that the habits, morphology, nucleation etc. remained more or less similar using all different types of ammonium halides.

4.2.1 Experimental Preparation of Sodium metasilicate Solution:

The solution of commercial water glass in distilled water was filtered with ordinary filter paper to separate the floating and suspended impurities. As a result transparent golden coloured solution of sodium metasilicate ((SMS solution) was obtained and could be preserved as a stock solution for quite a long time. Distilled water was added to this sodium meta-silicate solution to get a specific gravity of 1.039. For obtaining the desired specific gravity of SMS solution there are two ways viz. 1) from a prepared plot of specific gravity vs quantity of distilled water, as a ready reckoner; 2) from direct calculation. The present author had determined the specific gravity by calculation.

When this solution is mixed with any mineral or organic acid, gel formation takes place due to polymerization as described earlier (cf. Chapter III). Time required for gelation depends on a number of factors such as density and pH of gel solution, acid used for gelation, ambient temperature, etc. Gels of low density and low pH values required relatively longer time for setting. Since single crystals of d-AHT had to be prepared it was necessary to have aqueous solution of d-tartaric acid.

4.2.2 Preparation of d-tartaric acid solution (TA):

In the present work, solution of d-tartaric acid ($C_4H_4O_6$ - GR quality 99.5% pure) was prepared by dissolving it in a an appropriate amount of distilled water to give the required molar concentration as shown in Table 4.1.

TABLE 4.1

Molar concentration of TA (d-tartaric acid) in distilled water at 30 Deg C.

Sr No	Amount of TA in gms	Volume of soln. in cc	Molar concentration (M)
1.	225.135	1000	1.5
2.	300.180	1000	2.0
3.	375.225	1000	2.5
4.	450.270	1000	3.0
5.	525.315	1000	3.5

4.2.3 Preparation of Gel:

Silica gels were prepared by mixing sodium meta-silicate solution (Sp.gr 1.039) with d- tartaric acid (TA) solution having different molar concentrations, in different amounts. If in a solution of 100 cc, 20 cc of tartaric acid solution is poured into 80 cc of sodium metasilicate solution, then tartaric acid solution in the mixture is 20%. The pH of the mixture was measured by a pH-meter.

Crystallization was carried out in standard test tubes of different dimensions (2.5 cm diameter and length 22.5 cm; 3.6 cm diameter and length 20 cm).

The gel was usually set within 4 to 18 days, depending on the gel density, pH of the gel solution and the ambient temperature.

After ensuring proper gel setting, the growth experiment was started by adding the feed solution (FS) ammonium bromide (GR quality), having different concentrations varying from 1.5 M to 3.5 M, above the set gel with the help of a pipette (least count 0.1 ml).

4.2.4 **Preparation of Feed Solution:**

Solutions of ammonium bromide (NH4Br GR quality) were prepared in a similar way as d- tartaric acid solutions, of different molar concentration.

TABLE 4.2

Molar Concentration of FS (Feed solution - Ammonium bromide) in distilled water at 30 Deg C.

Sr No.	Amount of FS in gms	Volume of Soln. in cc	Molar concentration (M)
1.	97.94	1000	1.5
2.	195.88	1000	2.0
3.	244.85	1000	2.5
4.	293.82	1000	3.0
5.	342.79	1000	3.5

The drops from the pipette were allowed to fall gently along the sides of the test tube in order to prevent breaking of the surface and inner structure of the gel. The FS diffused in the gel slowly and reacted with the gel incorporated TA, forming transparent, geometrically well-defined single crystals of ammonium hydrogen d-tartrate (d-AHT) in the test tube.

The chemical reaction between these reagents was as follows:

$NH_4Br + C_4H_6O_6 \dashrightarrow NH_4HC_4H_4O_6 + HBr$

There are basically three regions in a test tube where the crystal nuclei have opportunities to grow. They are :

i) The interface between the gel and the FS, where reaction between FS and gel takes place resulting in the production of crystal nuclei. The interface is also the site where syneresis takes place (Fig. 4.1).

ii) The central part of the test tube. The FS percolates through the pores of the gel and reacts with the gel acid. The crystal nuclei begin to develop in the gel pores of the central part of the tube (Fig. 4.2).

iii) The walls and bottom of the test tube. The FS can also slip through some space between the gel and tube walls. The solution reacts with the impregnated acid in the gel, with the formation of crystal nuclei near the walls and bottom of the test tube (Fig. 4.3).

The crystals were collected from all these three regions after allowing sufficient time for nucleation and subsequent growth (6 to 8 weeks).

CAPTION TO FIGURES

Crystals growing :-

Fig. 4.1	at the interface
Fig. 4.2	in the central part of the test tube
Fig. 4.3	at the bottom & walls of the test tube

Morphology of the crystals growing in gel :-

Fig. 4.4(i)	Needle shaped
Fig. 4.4(ii)	Orthorhombic disphenoidal
Fig. 4.4(iii)	Sphenoidal

CAPTION TO FIGURES

4.1 Photograph of crystals growing at the interface in gel in a test tube showing:

a) ammonium bromide,feed solution (FS);

b) crystals in gel liquid interface, (S) sphenoidal and orthorhombic disphenoidal (ODS);

c) d-tartaric acid impregnated sodium metasilicate gel.

4.2 Photograph of crystals growing in the central part in gel in a test tube, showing :

a) ammomium bromide, feed solution (FS);

b) crystals in gel : orthorhombic disphenoidal (ODS) in the central part of test tube;

c) tartaric acid impregnated sodium metasilicate gel.

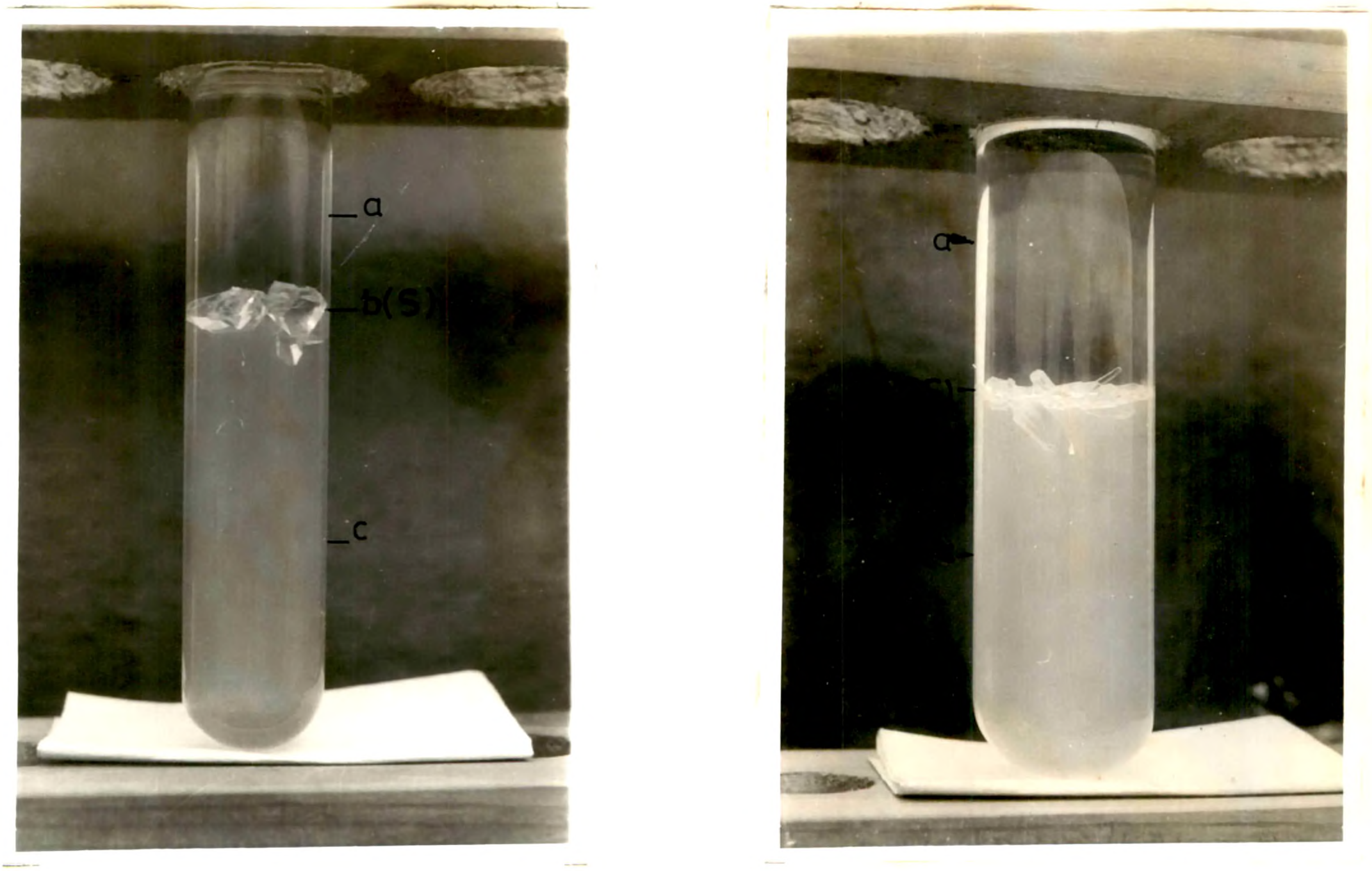


Fig 4.1

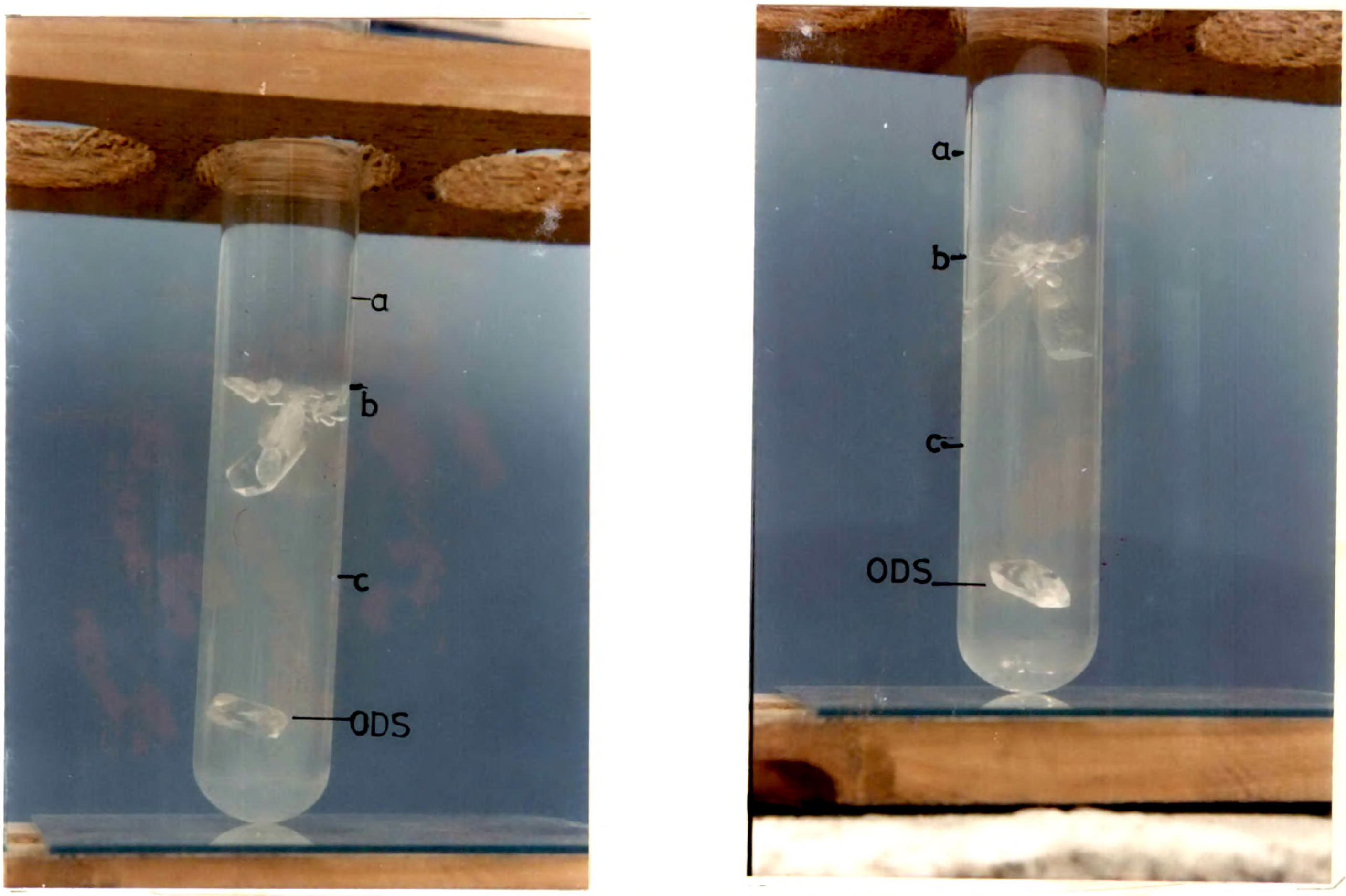


Fig 4.2

CAPTION TO FIGURES

4.3 Photograph of crystals growing at the bottom of the gel in a test tube showing

a) ammonium bromide, feed solution (FS);

b) crystals at the interface,

c) tartaric acid impregnated sodium metasilicate gel.

4.4 Photograph of d-AHT single crystals of different habits obtained by mixing TA of 2.0M concentration in sodium metasilicate of specific gravity 1.039 to form gel and 2.0M ammoniun bromide added as feed solution.

4.4(i) a) 20% TA of gel pH 2.67, needle shaped (N) crystals in gel ;

b) at the interface and (C) throughout the test tube;

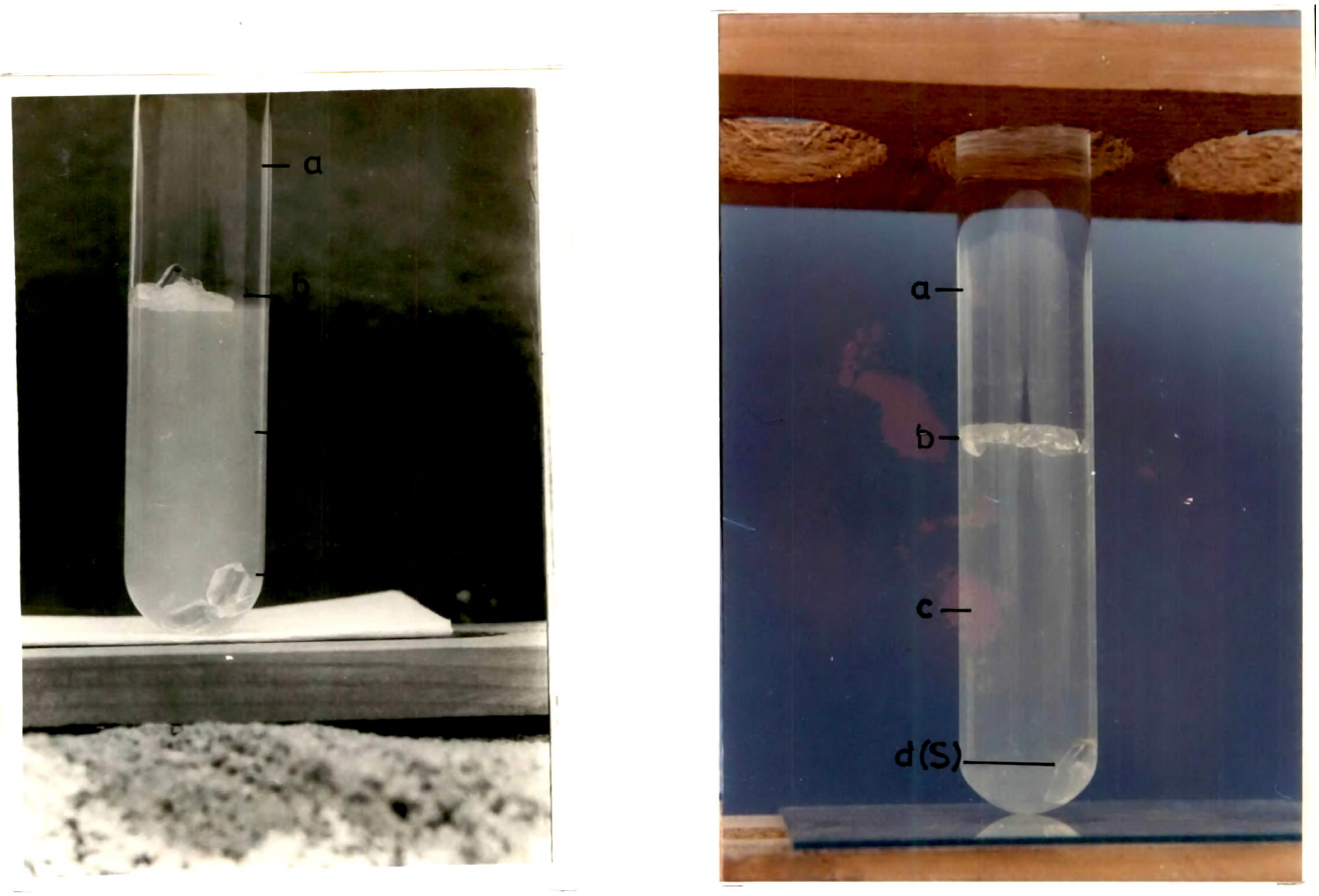


Fig 4.3

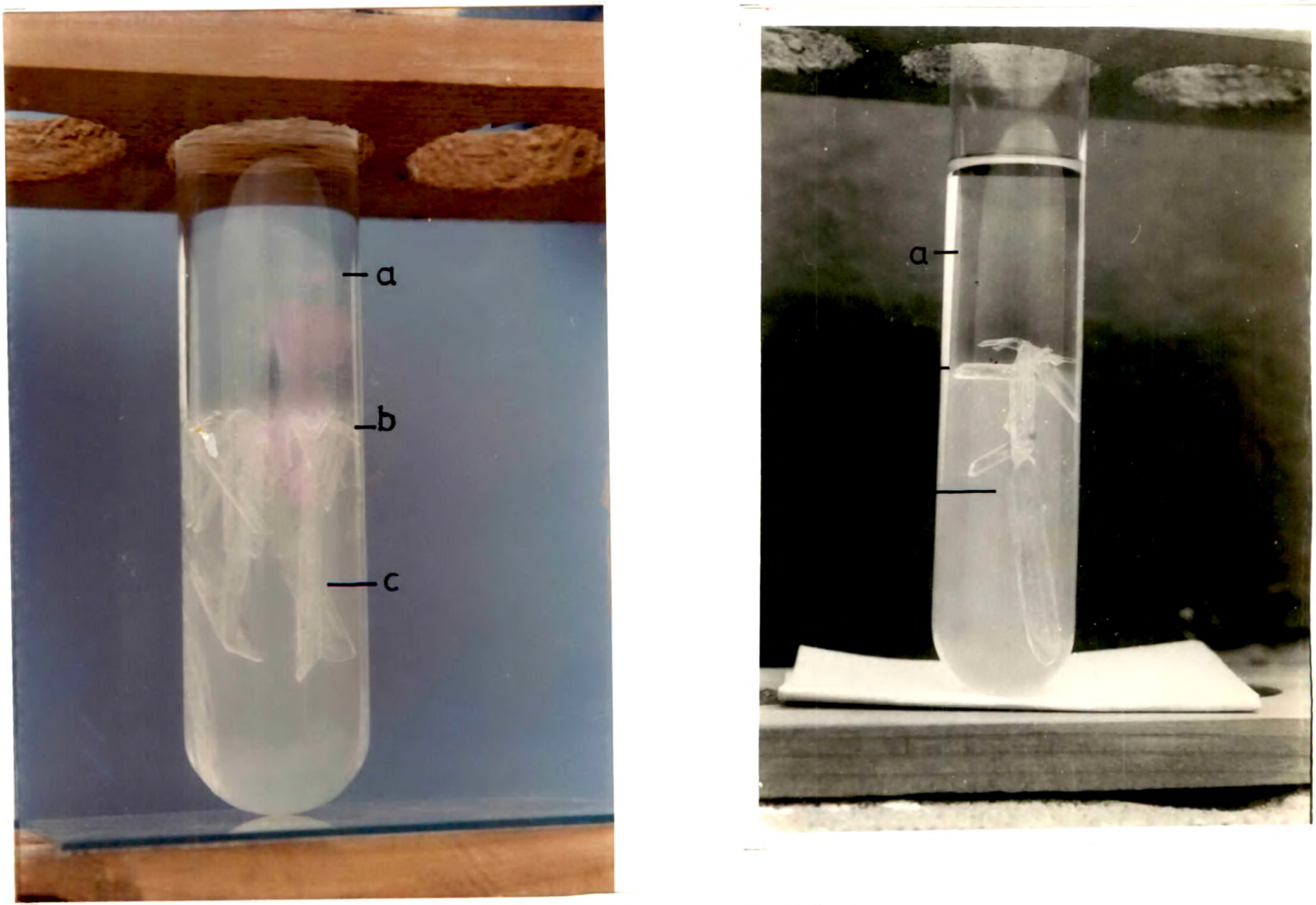


Fig 4.4(i)

4.2.5 Morphology of crystals:

A large range of concentration of reactants (tartaric acid impregnated gel and ammonium bromide) was used to determine optimum conditions for growth of good quality single crystals of d- AHT. The concentration of tartaric acid solution (TA) in SMS was varied. The gel concentration refers to the concentration of TA in it. Further, with a given concentration of TA, the quantity of TA added to SMS was also varied. This amount was indicated in percentage of the entire solution (SMS & TA). The experimental work was carried out at room temperature ranging from 29 to 34 degrees C.

For initiating growth, the minimum concentration of tartaric acid in gel was 0.5 M. Below this concentration gelation was impossible. For any molar concentration of TA in gel, 10% TA in 90% SMS forms precipitates and not gel, With 20% TA in 80% SMS, the gel formation takes place. The gel is translucent. With 30% TA, the gel becomes transparent. The pH value does not play a significant role in the formation of gel. Further, it does not affect the morphology of the growing crystal. However, it is the quantity of acid (TA) in gel which determines the habit of a crystal. It is therefore, possible to grow crystals by varying concentrations from 0.5 M to 5.099 M, which corresponds to the saturated solution of TA in water at room temperature. For lower gel concentration (between 0.5 M to 1.5 M) the quantity of TA should be more than 50% to obtain crystals of good geometrical shape.

The concentration of FS was varied from 1.5M to 3.5M. For concentration less than 1.5M, the ability of the FS to diffuse was greatly diminished thereby decreasing the probability of formation of crystal nuclei and subsequent growth. For FS concentration >3.5M, where the TA concentration in gel is less (<3.5M), the diffusion is heavy, resulting in the growth of translucent crystals. But if the concentration of TA is also 3.5 or more, good transparant crystals are obtained for the above FS concentration. Further, for the same saturated solutions of FS and TA (5.099M), good transparent crystals were obtained. The detailed observations are described below:-

There were basically three habits of the d-AHT crystals grown in silica gel. They were :

i) Needle shaped crystals (4.4.i)
ii) Orthorhombic disphenoidal crystals (4.4.ii)
iii) Sphenoidal (tetrahedral) crystals (4.4.iii)

It should be noted that only three habits mentioned above were observed for all possible combinations of different factors affecting the growth of these crystals in gels.

The name needle shaped crystals generally indicate the shape similar to that of a needle, i.e. a cylindrical shape with a pointed end. However, this is not observed by the author. In the present case, the name indicates an accelerated growth along one direction as compared to the growth along different directions, thereby thickening the needle and giving rise to many faces (i.e. more than eight faces - Fig. 4.5). The needle shaped crystals

CAPTION TO FIGURES

4.4 Photograph of d-AHT single crystals of different habits obtained by mixing TA of 2.0M concentration in sodium metasilicate of specific gravity 1.039 to form gel and 2.0M ammoniun bromide added as feed solution.

4.4(ii) a) 40% TA, of gel pH 2.45, orthorhombic disphenoidal crystals (ODS) in gel;

b) at the interface and (C) at lower part of the test tube;

4.4(iii) a) 60% TA, of gel pH 2.02 ;

b) sphenoidal crystals (S) in gel.

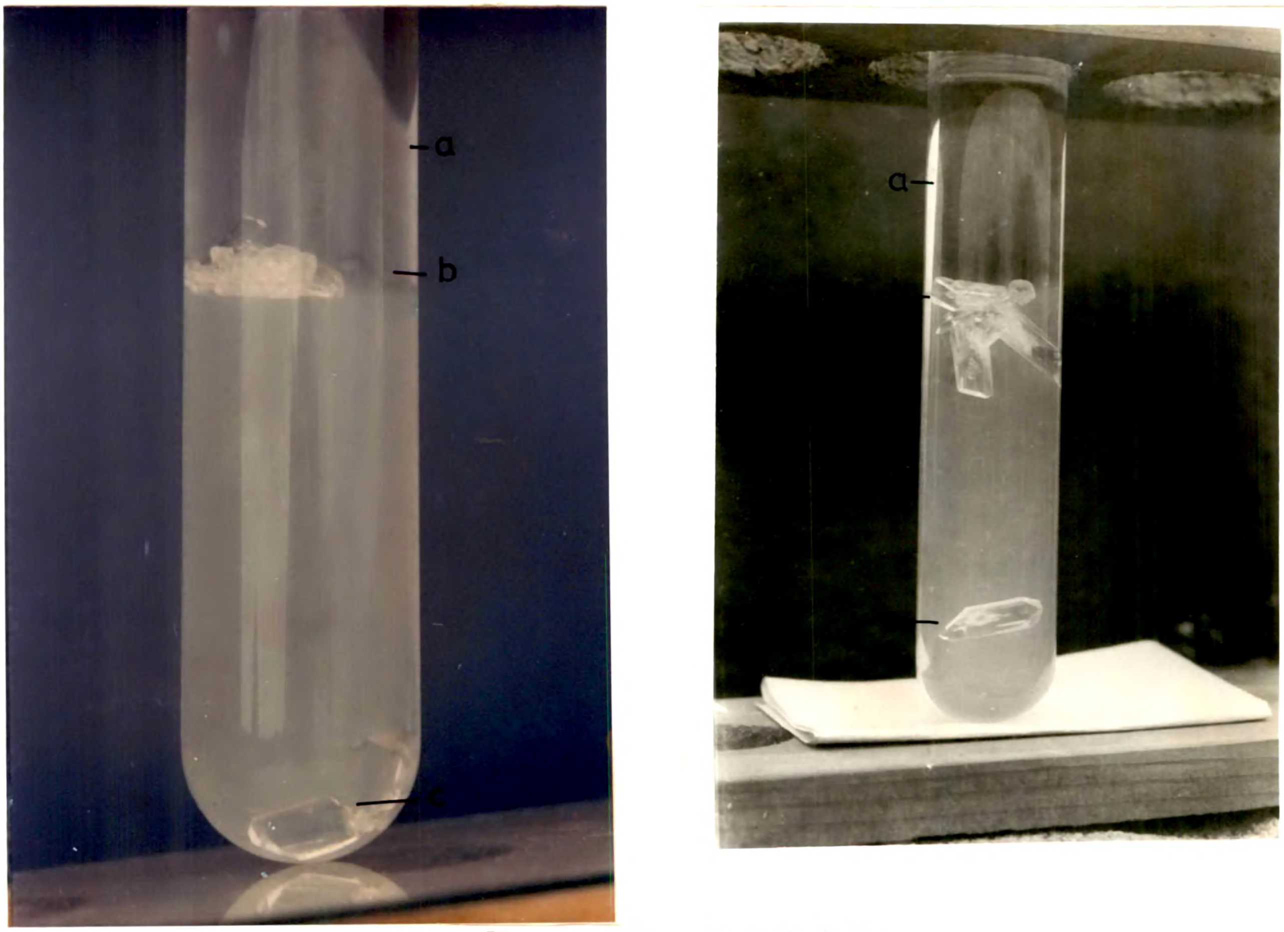


Fig 4.4(ii)

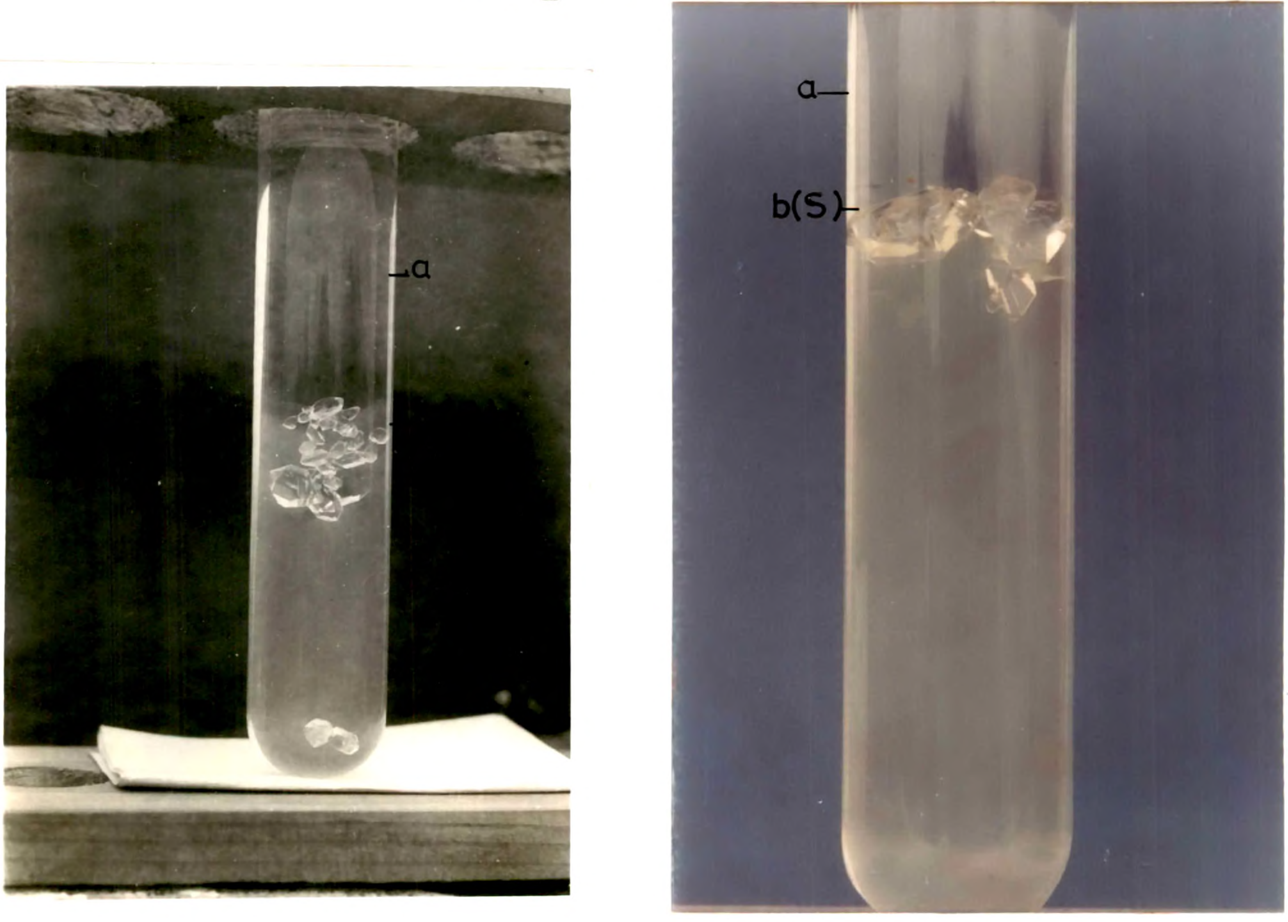


Fig 4.4(iii)

Fig. 4.5 (a) Photograph of needle shaped d-AHT crystal grown in gel.

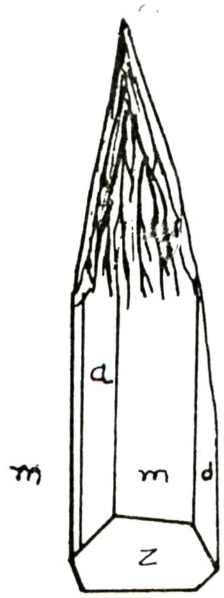


Fig. 4.5 (b)

Schematic diagram of a needle shaped crystal.

z (111)
m (110)
a (100)
d (130)

start growing from a bunch of nuclei at the interface between the gel and FS. With the timely arrival of FS, they start getting separated as fine needles. The gradual deposition of crystal material thickens the needle and also extends its growth along one direction viz. c-axis, which is the growth direction of d-AHT crystals of different habits. Further it does not normally coincide with the vertical axis of the test tube.

Many observations regarding orientation of these crystals with the vertical axis of test tube were made. There did not appear to be any preferred orientation, Fig. 4.5.

The orthorhombic disphenoidal and sphenoidal crystals were normally found at the central part and bottom part of the gel in the test tube.

The size of a face of a grown crystal depends upon the amount of feed material available to the growing crystal. This can be qualitatively connected with various parts of the test tube at which crystals of different habits were grown.

Thus when fairly large amount of FS was available, needle-shaped crystals grew. With decreasing amount the habit became orthorhombic disphenoidal. With a further drop in the availability of feed solution, only sphenoidal crystals could be obtained. This also suggests rather an elegant method to grow crystals of the desired habit. In majority of the grown crystals, c-axis happens to be the growth axis, which is inclined to the vertical. However, there are a few exceptions to this general observation.

The habit and quality of the grown crystals depend not only on the amount of material (FS) available at the site but also on the rate at which the material reaches that site. It was observed that the crystals with very high growth rate were of inferior quality and vice versa. This can be understood qualitatively. The deposit of molecules at appropriate places on a growing surface of a crystal is necessary for ordered growth. Further, some time is necessary for the molecules to settle at these places. If the rate of arrival of material on the growing surface is not commensurate with the above requirements, the crystal will be obviously of inferior quality, Fig. 4.6.

The observations were extended over a period of two months and Table 4.3 and Table 4.4 summarises the results of experiments carried out. The maximum length obtained along the growth axis [001] in the case of needle shaped and orthorhombic disphenoidal, and along [101] direction in case of sphenoidal shaped crystals are mentioned. Thus with 1.5M & 20% TA long (45 mm) needle shaped crystals were found with progressive reduction in length for orthorhombic disphenoidal and sphenoidal habits. The table indicates that with a suitable combination of conditions regarding concentration (pH) gel setting time etc., it is possible to grow crystals of desired morphology and size.

The problem of nucleation is of great importance in practical operation, since a crystal which grows in any particular gel system competes with others for solute. This competition limits their size and perfection and it is obviously desirable to

CAPTION TO FIGURES

Fig.4.6

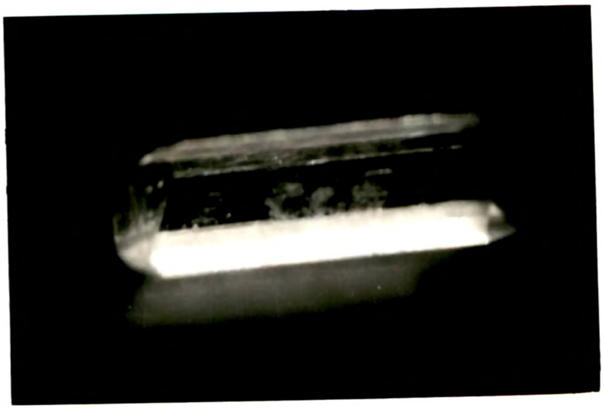
Photographs of the different

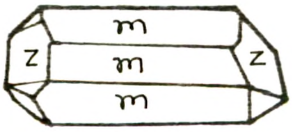
morphologies of

crystals

grown from

silica gel

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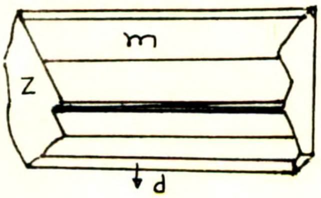
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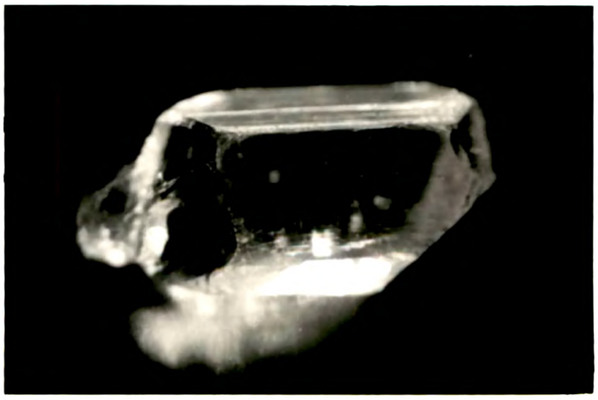

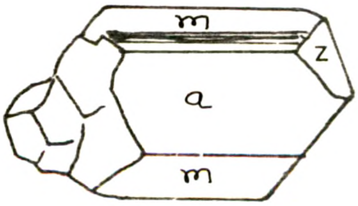
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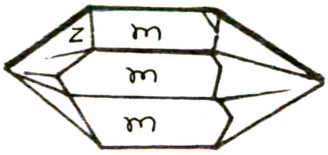
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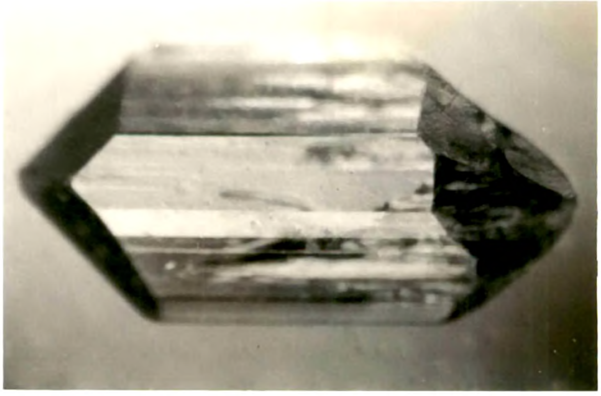

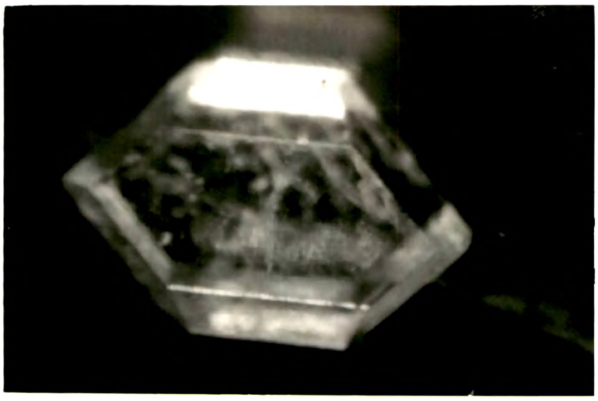

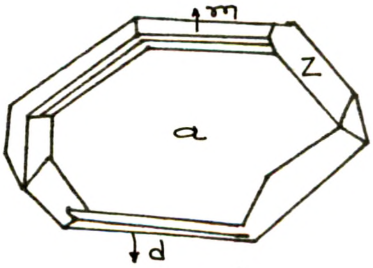
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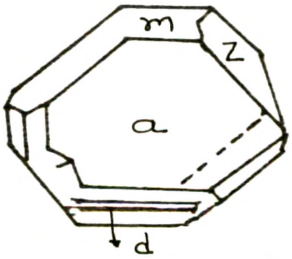
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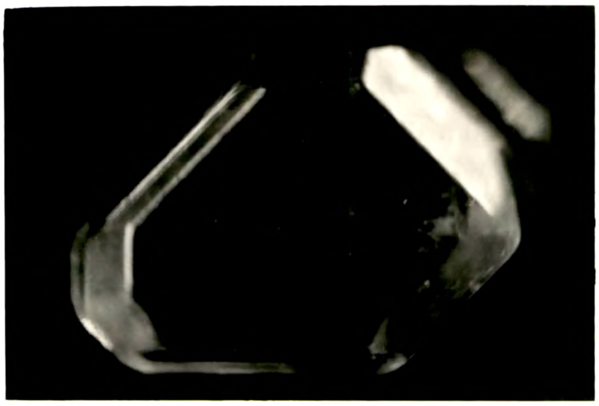

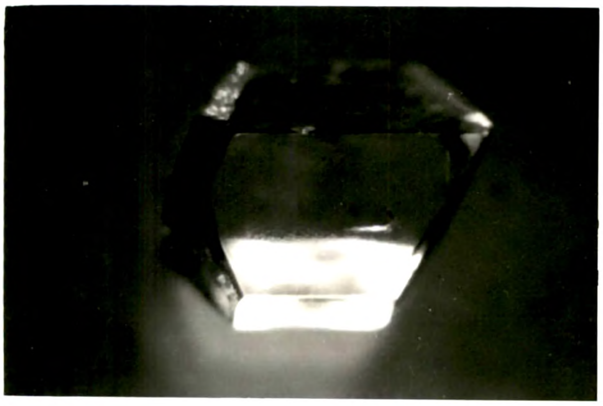

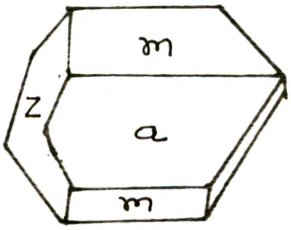
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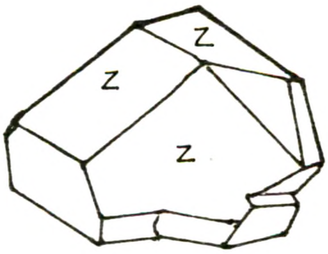
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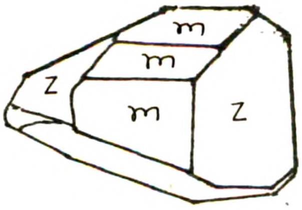
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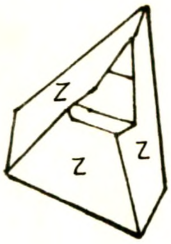
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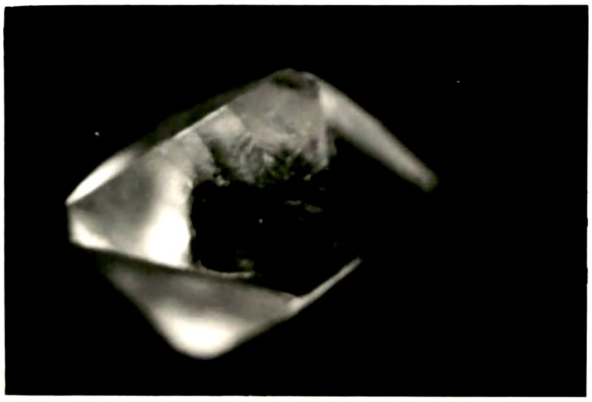

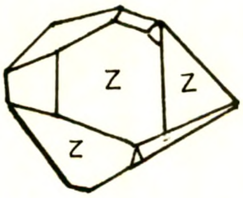
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suppress a large number of nucleations until, ideally only one crystal grows from a nucleus in a predetermined location. The author has at present taken care of this to a good extent while growing single crystals of d-AHT (Figs. 4.1 - 4.4).

Extreme care was taken to have minimum disturbance to the gel before, while and after, adding the feed solution.

Gel cell size is influenced by gel density, gel age (2), gel pH (3) and temperature (4). Hence nucleation control can be achieved to some extent by varying these parameters. In the present case, gel pH appears to have little influence on the pore-size and crystal habit. Other conventional methods such as the neutral gel technique (5) seeding (2), addition of impurities (6,7) have also been employed by some crystal growers.

Recently the growth of single crystals in silica gel media under the influence of an electric current through gel has drawn the attention of many crystal growers (8,9,10). The present author had studied the effect of electric current on d-AHT crystals growing in the gel. It was seen that the electric current retarded the growth process.

It is now well established (11,3,11) that density of sodium metasilicate solution should be taken as 1.039 gm/cu.cm for preparing a silica gel. Experiments were conducted in the laboratory by different workers to determine the appropriate density of SMS (12,13). It was found from those experiments and others carried out by the present author that the density of SMS solution should be taken as 1.039 gm/cu.cm for preparing tartaric acid impregnated gel. The setting time of a gel depends not on the concentration of TA, but on its quantity. The setting time was found to vary from 4 days to about 18 days. It was observed that with 1.5M and 60% TA, the number of days required for the setting of gel was 17. When the test tube was kept for more days, a fungus growth was observed on the gel surface, hence the period cannot be increased beyond 20 days.

While trying to assess qualitatively the formation of a gel, the gel was slightly disturbed. In order to avoid this effect, sufficient time was allowed before the FS was added.

The amount of FS and its molar concentration was fixed. This was gently added to the gel.

There are several parameters which affect the crystal growth in a gel. They are :

i) Setting time of gel;
ii) Quantity of acid in gel;
iii) Gel pH;
iv) Number of crystal nuclei.

The observations are given in Table 4.3, 4.4 and graphical plots in Figs 4.7, 4.8, 4.9, 4.14, 4.15 & 4.16.

In Fig 4.7 the straight line plot of gel setting time in days versus quantity of acid in gel, for varying concentration of acid is given. Some salient features of the plots are as follows:

TABLE 4.3

R.T. - 30°C
FS Concn. - 2 M

Data on crystal morphology, gel-pH, molar concentration of TA for fixed molar concentration of F.S.*

TA** concn.	% acid with SMS***	gel pH	gel pH / acid pH	Crystal Morphology Maximum linear growth parallel to			Gel setting time (in days)
				Needle shaped (in mm)	C-axis (001) Orthorhombic disphenoidal	(101) Sphenoidal	
1.5 M	20%	3.10	2.09	45	-	-	4
	30%	2.90	1.95	-	30	20	7
	40%	2.70	1.82	-	35	15	11
	50	2.48	1.67	-	20	25	14
	60	2.25	1.52	-	-	18	17
2.0 M	20	2.87	2.27	48	-	-	3
	30	2.67	2.11	-	28	12	7
	40	2.45	1.94	-	32	16	10
	50	2.27	1.80	-	30	24	13
	50	2.02	1.6	-	-	26	17

* F.S. Feed Solution
** T.A. Tartaric acid solution
*** S.M.S. Sodium Metasilicate Solution

..2

TABLE 4.3

R.T. - 30°C
FS Concn. - 2 M

Data on crystal morphology, gel-pH, molar concentration of TA for fixed molar concentration of F.S.*

TA** concn.	% acid with SMS***	gel pH	gel pH / acid pH	Crystal Morphology Maximum linear growth parallel to			Gel setting time (in days)
				Needle shaped (in mm)	C-axis (001) Orthorhombic disphenoidal	(101) Sphenoidal	
2.5 M	20	2.60	2.32	31	-	-	4
	30	2.45	2.18	-	18	10	7
	40	2.27	2.03	-	28	8	10
	50	2.07	1.84	-	25	18	14
	60	1.9	1.69	-	-	28	18
3.0 M	20	2.52	2.8	60	-	-	3
	30	2.39	2.65	-	24	12	7
	40	2.20	2.44	-	30	10	11
	50	1.97	2.18	-	28	8	15
	60	1.80	2	-	-	14	18
3.5 M	20	2.45	3.26	40	-	-	4
	30	2.30	3.06	-	18	9	7
	40	2.10	2.8	-	22	6	11
	50	1.85	2.46	-	28	8	14
	60	1.72	2.29	-	-	18	17

* F.S. Feed Solution
** T.A. Tartaric acid solution
*** S.M.S. Sodium Metasilicate Solution

TABLE 4.4

Data on number of d-AHT crystals in 33.27 cm^3 of gel for varying concentration of FS* and gel PH

* FS Feed Solution
** TA Tartaric Acid Solution
*** SMS Sodium Metasilicate Solution

R.T. 30°C
T.A. Conc. 2.5 M

% of TA** with SMS***	gel PH	Conc. of FS (in M)	Crystals in the test tube	Setting time (in days)
20%	2.6	1.5	7	4
		2.0	12	
		2.5	15	
		3.0	23	
		3.5	28	
30	2.45	1.5	9	7
		2.0	11	
		2.5	14	
		3.0	12	
		3.5	19	
40	2.27	1.5	10	10
		2.0	14	
		2.5	8	
		3.0	22	
		3.5	25	

..2.

TABLE 4.4

Data on number of d-AHT crystals in 33.27 cm^3 of gel for varying concentration of FS* and gel PH

* FS	Feed Solution
** TA	Tartaric Acid Solution
*** SMS	Sodium Metasilicate Solution

R.T. 30°C

T.A. Conc. 2.5 M

% of TA** with SMS**	gel PH	Conc. of FS (in M)	Crystals in the test tube	Setting time (in days)
50%	2.07	1.5	8	14
		2.0	11	
		2.5	19	
		3.0	10	
		3.5	18	
60%	1.9	1.5	6	18
		2.0	10	
		2.5	8	
		3.0	12	
		3.5	14	

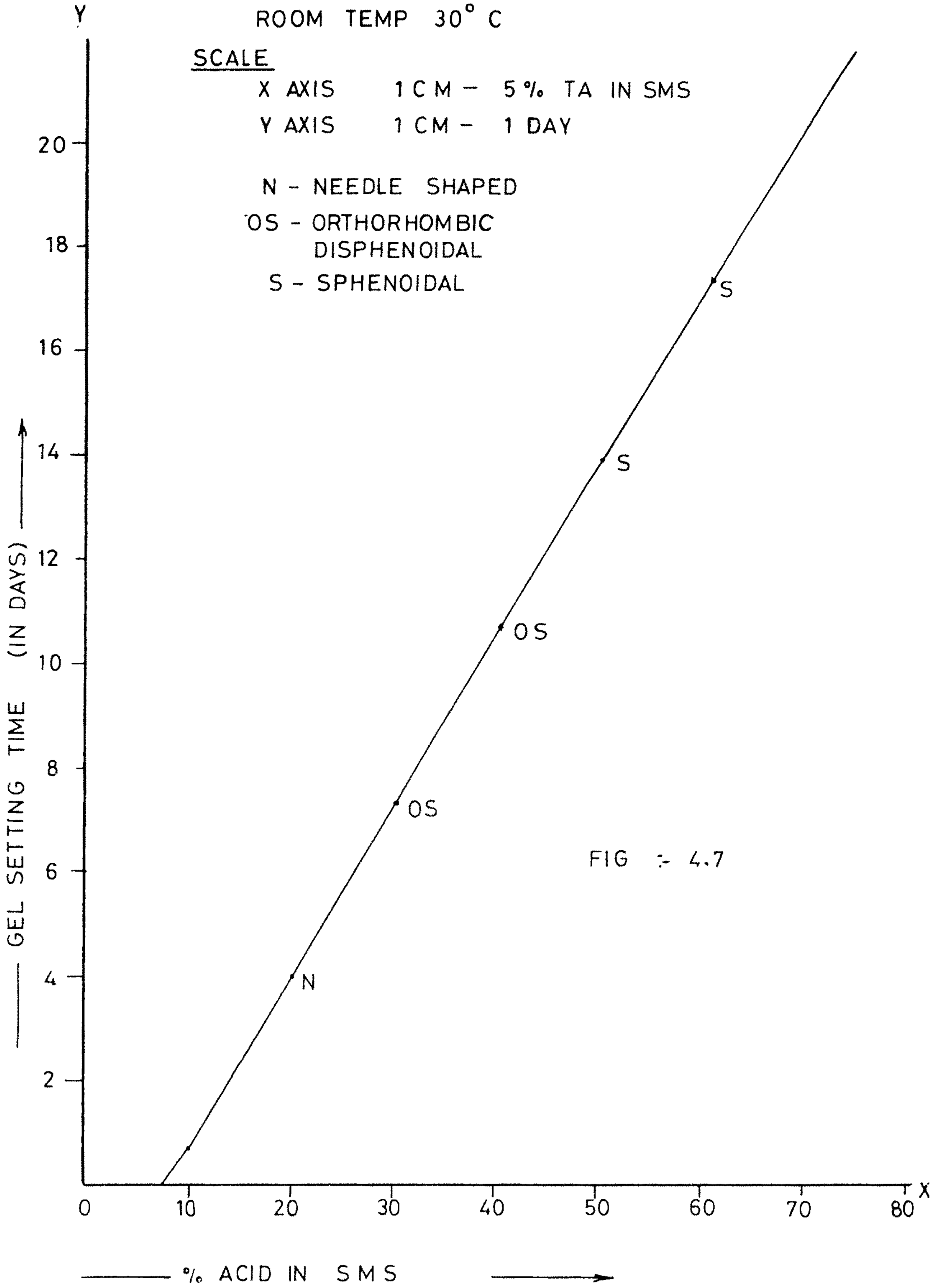


FIG :- 4.7
ROOM TEMP 30° C
SCALE
X AXIS 1 CM - 5 % TA IN SMS
Y AXIS 1 CM - 1 DAY
N - NEEDLE SHAPED
OS - ORTHORHOMBIC DISPHENOIDAL
S - SPHENOIDAL
Y
X
GEL SETTING TIME (IN DAYS)
% ACID IN SMS
0
10
20
30
40
50
60
70
80
2
4
6
8
10
12
14
16
18
20
N
OS
OS
S
S

FIG :- 4·8

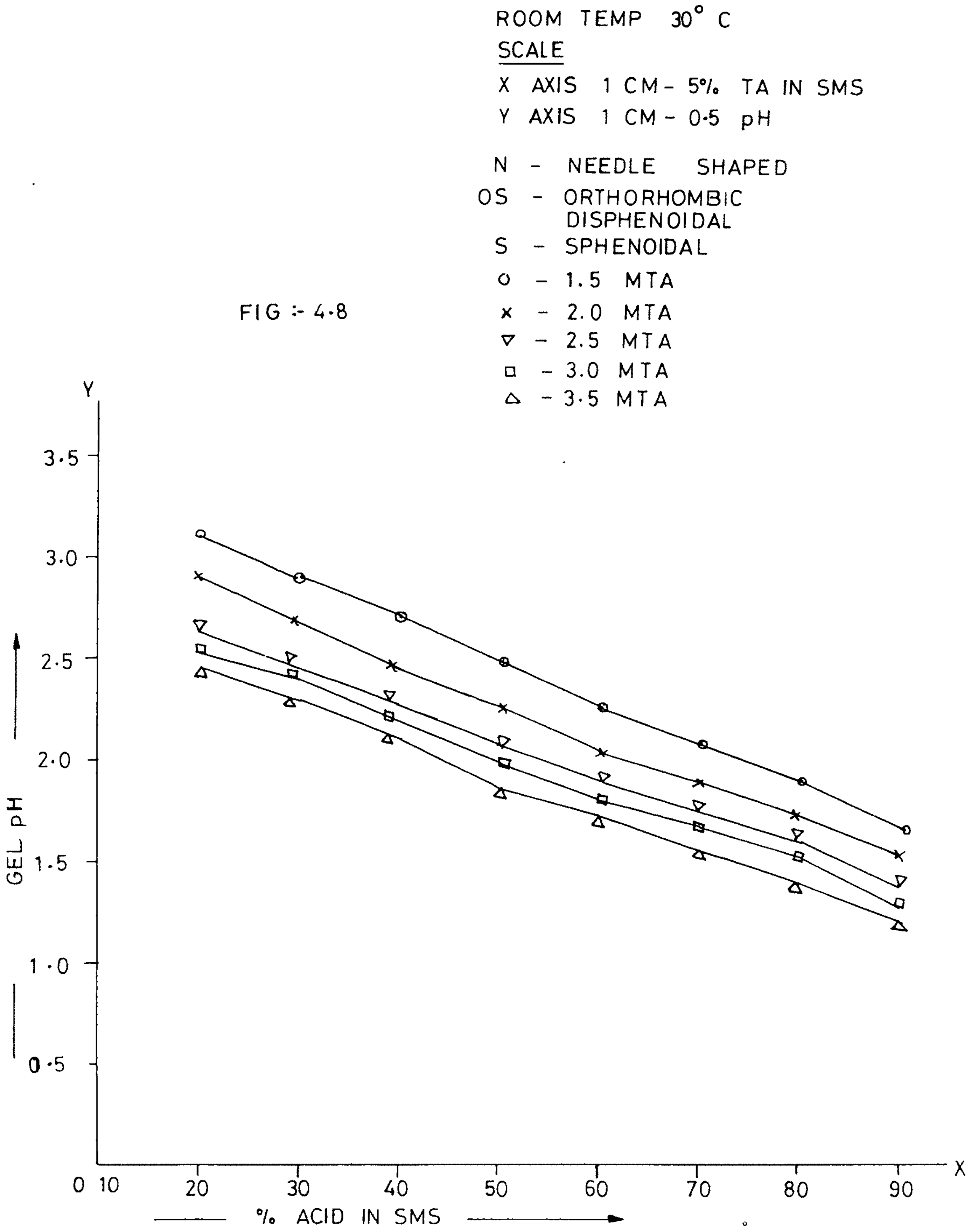
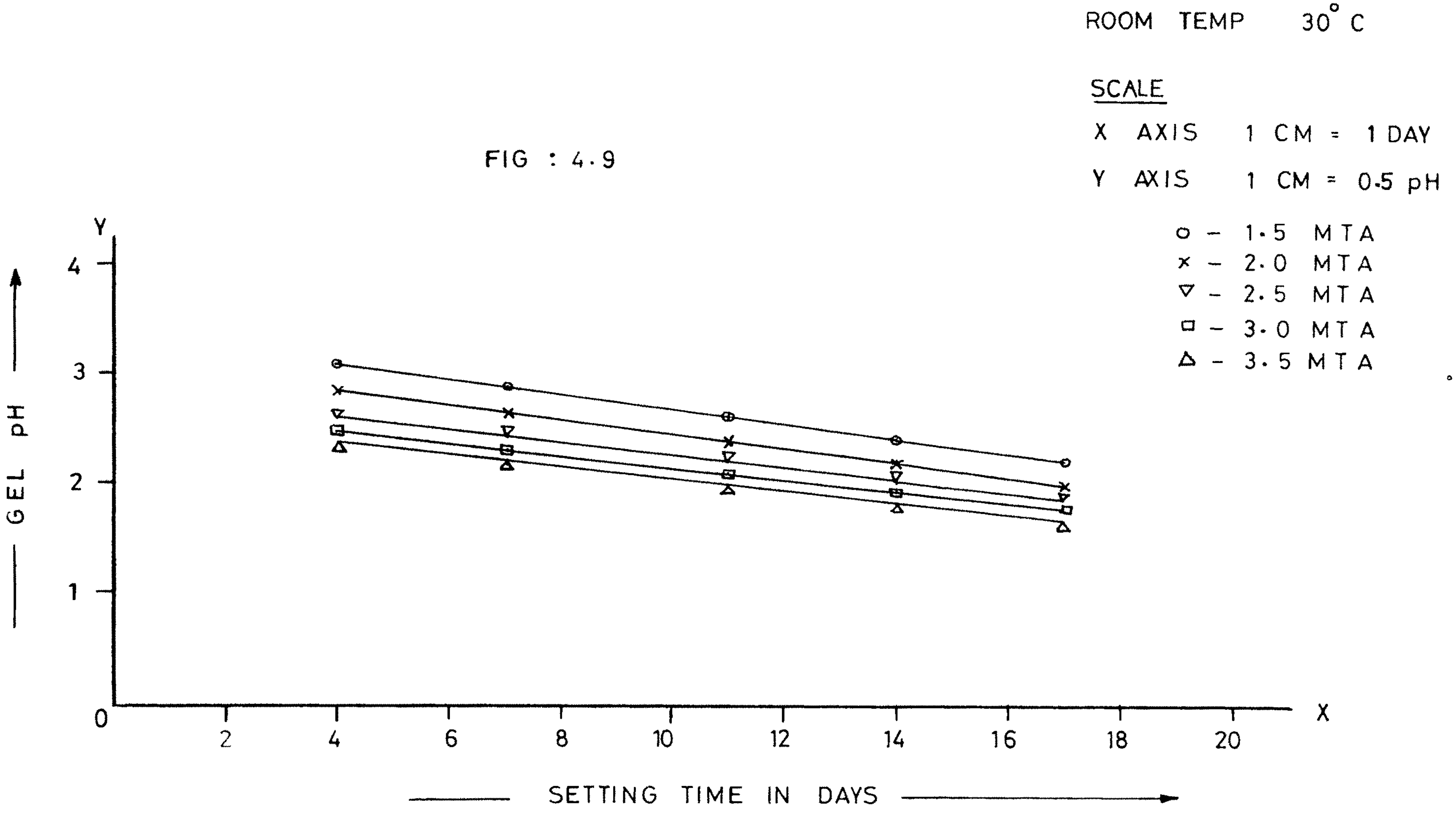

ROOM TEMP 30° C
SCALE
X AXIS 1 CM - 5% TA IN SMS
Y AXIS 1 CM - 0·5 pH
N - NEEDLE SHAPED
OS - ORTHORHOMBIC DISPHENOIDAL
S - SPHENOIDAL
○ - 1.5 MTA
× - 2.0 MTA
▽ - 2.5 MTA
□ - 3.0 MTA
△ - 3·5 MTA
Y
3·5
3·0
2·5
2·0
1·5
1·0
0·5
GEL pH
X
0
10
20
30
40
50
60
70
80
90
% ACID IN SMS

FIG : 4·9


ROOM TEMP 30° C
SCALE
X AXIS 1 CM = 1 DAY
Y AXIS 1 CM = 0·5 pH
○ – 1·5 MTA
× – 2·0 MTA
▽ – 2·5 MTA
□ – 3·0 MTA
△ – 3·5 MTA
Y
GEL pH
4
3
2
1
0
2
4
6
8
10
12
14
16
18
20
X
SETTING TIME IN DAYS

1) Needle shaped crystals were obtained at 20% quantity of acid irrespective of the molar concentration of the acid;

2) For 30% and 40% of TA in gel, only orthorhombic disphenoidal and sphenoidal crystals were obtained;

3) Sphenoidal crystals are got for 50% and 60% quantity of acid;

4) Extrapolating the line at 7.5% gel, the gel setting time is zero, which clearly indicates that only above a certain percentage, a gel can be set. A precipitate is formed instantaneously while mixing SMS and TA for producing 7.5% gel.

5) 80% TA when mixed with SMS solution produced gel after three months. Hence this observation was not shown in the graph;

6) It should be mentioned that whatever is the molar concentration of the acid (TA), in the range (1.5M - 3.5M) the setting time for the gel for a particular quantity of acid in the is fixed e.g. 20% acid in gel takes 4 days to set in all the five different concentration (1.5M, 2.0M, 2.5M,3.0M, 3.5M) of TA.

7) It is clear from the plots that gelation time varies in inverse proportion with gel pH, at a given temperature. Greater is the gelation time smaller is the gel pH and conversely (Fig 4.9).

CAPTION TO FIGURES

4.10 Same morphology of crystal in all the three regions of the test tube - interface, central part and the bottom of the test tube

CAPTION TO FIGURES

4.10 Photographs of d-AHT crystals of different morphology obtained by mixing TA of 2.5M concentration in sodium metasilicate of specific gravity 1.039 to form gel, and 2.5M ammonium bromide added ad feed solution.

4.10(i) a) 20% TA, of gel pH 2.6

b) Needle shaped crystals (N) at interface and central part of the test tube.

4.10(ii) a) 30% TA, of gel pH 2.45

b) Needle shaped (N) at interface and orthorhombic disphenoidal (ODS) crystals at bottom.

4.10(iii) a) 40% of TA, of gel pH 2.27

b) orthorhombic disphenoidal (ODS) crystals at the bottom and interface.

4.10(iv) a) 50% of TA, of gel pH 2.07

b) orthorhombic disphenoidal (ODS) and sphenoidal (S) crystals at the interface and (ODS) at the bottom of the test tube.

4.10(v) a) 60% of TA, of gel pH 1.90

b) sphenoidal (S) crystals at the interface and bottom of the test tube.

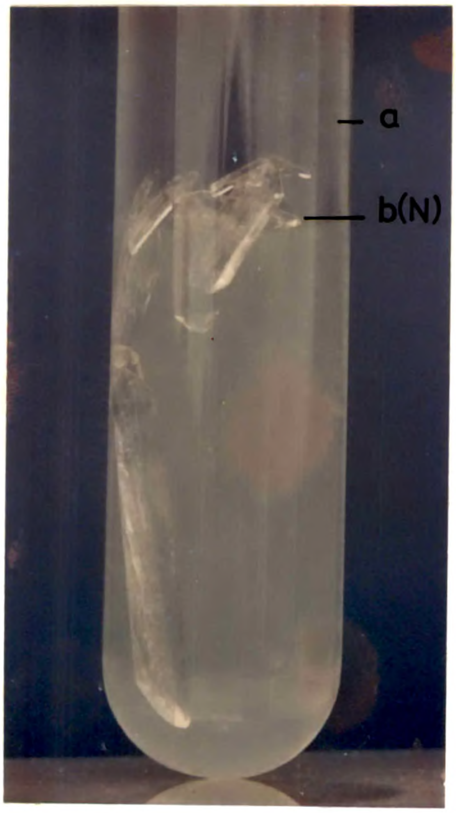


Fig 4.10(i)

Fig 4.10(ii)

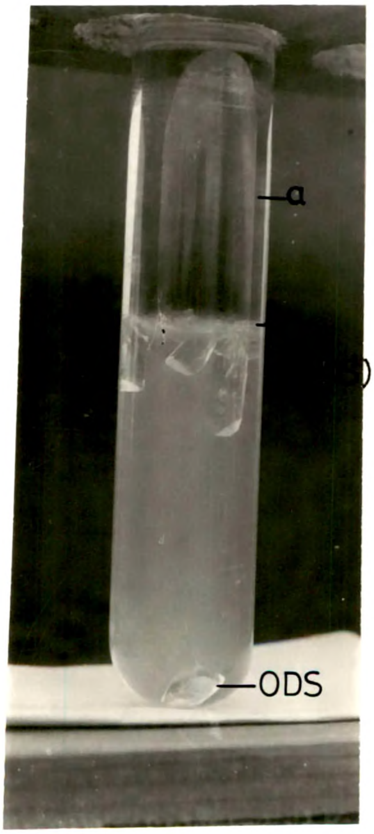


Fig 4.10(iii)

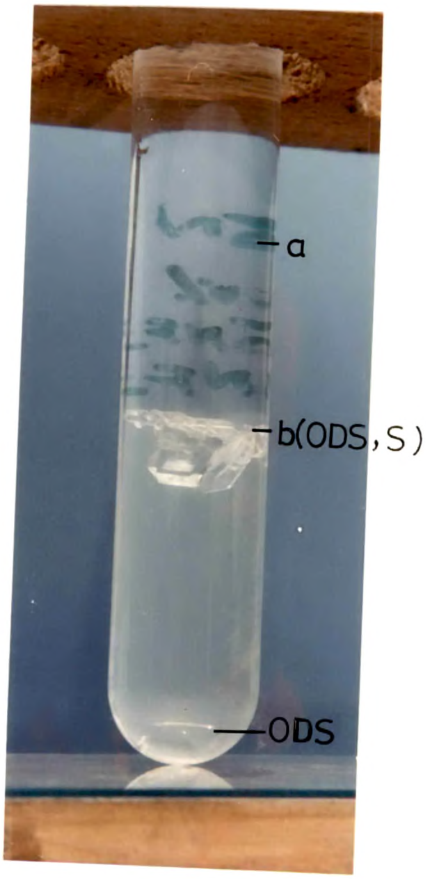


Fig 4.10(iv)

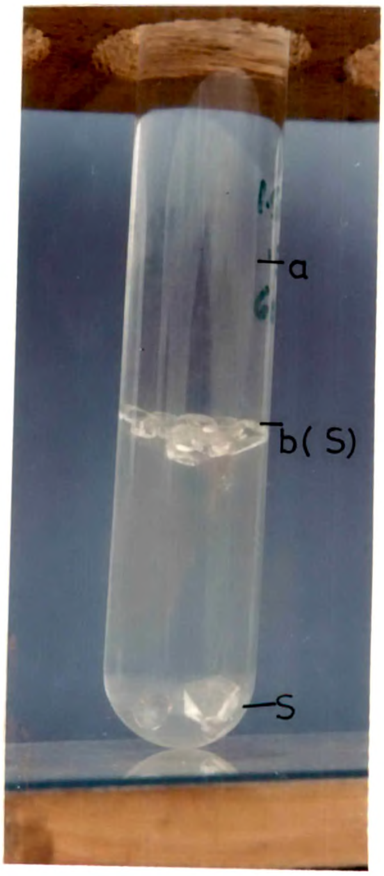


Fig 4.10(v)

8) When the FS concentration is more, the nucleation is more. Due to heavy diffusion and greater density the FS penetrates faster into the gel. (Table 4.4 - Figs. 4.14, 4.15 & 4.16).

It is rather remarkable to note that it is the quantity of acid in gel and not the gel pH which is solely responsible for the crystals habits. For a particular percentage of TA in gel, there is a constancy in the habit, in all the three regions of the test tube e.g. for 20% gel, needle shaped crystals are formed at the interface, central part and bottom of the test tube. For 60% gel, sphenoidal crystals are formed at the interface, central part, and bottom of the test tube Fig 4.10.

4.2.6 Effect of gel pH:

It is known that pH of a gel is associated with its pore-size, larger is the pore size in a gel, smaller is the pH value (2). Pore size in turn controls the intake of chemicals taking part in a reaction in a pore volume. This produces different crystallographic habits of the crystal (14). However, in the present work it is found that crystal habit is not controlled by gel pH or molar concentration of TA. Experimental observations are shown in Table 4.3 and 4.4. In all cases gel pH was determined at the time of making gel with SMS and TA. The feed solution was added on the surface of a set gel. Increase of molar concentration of an acid for a fixed quantity of TA in gel was accompanied by a decrease of gel pH. It is clear from the observation table that molar concentration and gel pH has practically no effect on crystal habits. However, the most important factor was the quantity of TA in gel which decided the crystal habits. Thus irrespective of gel pH or TA molar concentration, needle shaped crystals were obtained for 20% TA in gel, similarly orthorhombic disphenoidals were observed for 30% and 40% TA in gel, whereas sphenoids were formed for 50% and above of TA in gel.

As the pH of the gel decreases, the box-like network structure takes place (2), the diffusion of feed solution is slow (15), and the deposition of materials/molecules in regular sequence takes place. The growing faces are well developed, giving rise to equal sized faces - sphenoidal faces. This suggests that the diffusion of molecules was uniform along directions normal to the sphenoidal faces (111). This also indicates that in the case of orthorhombic disphenoidal crystals (ODS) the flow of molecules was less along directions normal to the "Z" faces (111) and more along the directions normal to prism faces (110).

4.2.7 <u>Effect of different types of feed solution on the growing crystals:</u>

The work on growth of d-AHT crystals in silica gel, mentioned above was carried out by using ammonium bromide, of different molar concentrations (1.5M, 2.0M, 2.5M, 3.0M, 3.5M) as feed solutions. Several ammonium salts can be utilised instead. The present author had made a comparative study of the effect of ammonium iodide, ammonium chloride, ammonium acetate, also as feed solutions. In all the cases, the growth (in length) and the morphology remained more or less the same, as previously described. However, the study of microstructures on the as-grown and prism faces had clearly revealed that the amount of inherent etching of the growing crystal was the least when ammonium bromide was used as FS. (Figs. 4.11). Thus ammonium bromide was the best feed solution among the ammonium halides. This is due to the fact that Bromine, being lower down in the reactivity series, the hydrobromic acid which was evolved during the reaction, as a waste product, was less reactive than hydrogen chloride, which was released while using ammonium chloride as feed solution. Ammonium iodide would have been better, but the iodide got oxidised. While in contact with the atmosphere, the ammonium iodide took a reddish brown colour which when added as FS, gave crystals having the same slightly brownish tint.

4.2.8 Effect of apparatus on size and quality of crystal:

By the same procedure as briefed earlier, gel was prepared and crystals grown in two types of specially designed apparatus (Fig. 4.12, 4.13). Agglomerates of bigger crystals were formed but because of the gel inclusions the crystals were not clear. The present observations support the conclusions drawn by G. Sperka and F.A Mautner (16) while growing Cs_2ReCl_6 in gel.

4.3 Conclusions:

The study of various gel parameters on nucleation and growth of d-AHT crystals have clearly shown that:

Fig.4.11 (a) - Photomicrograph of as-grown z-face (111) with ammonium bromide as the feed solution.

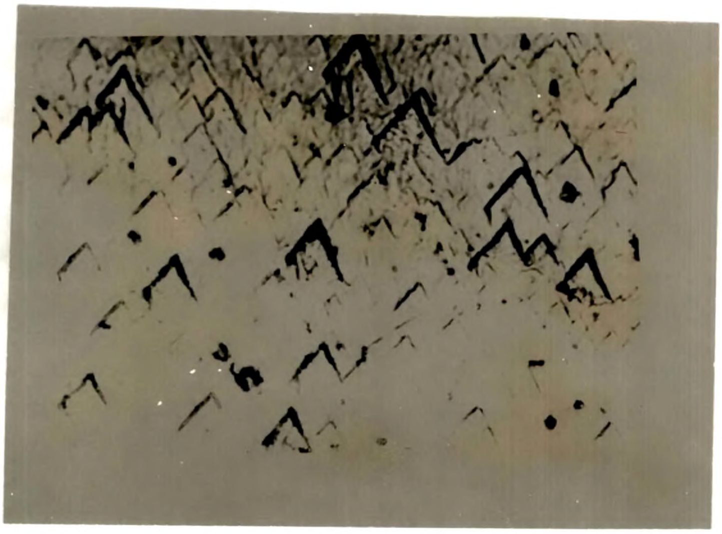


Fig.4.11 (b) - Photomicrograph showing the inherent etching of the growing crystal on the as-grown z-face (111) using ammonium chloride as feed solution.

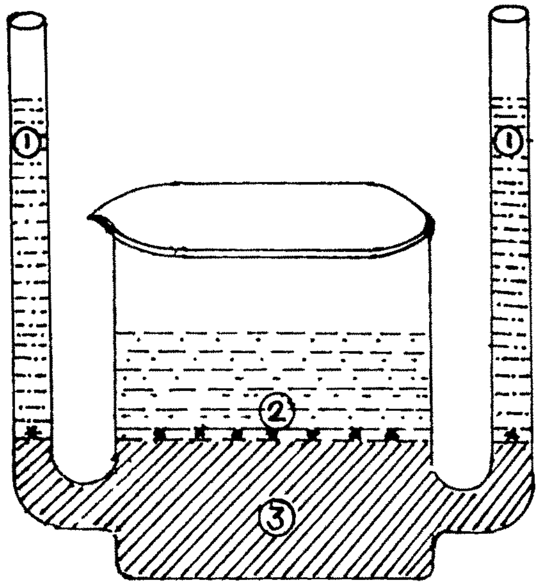


Fig. 4.12

Schematic diagram of the modified apparatus used for the growth of d-AHT single crystals.

1. Feed Solution
2. d-AHT Crystals
3. Tartaric acid impregnated gel

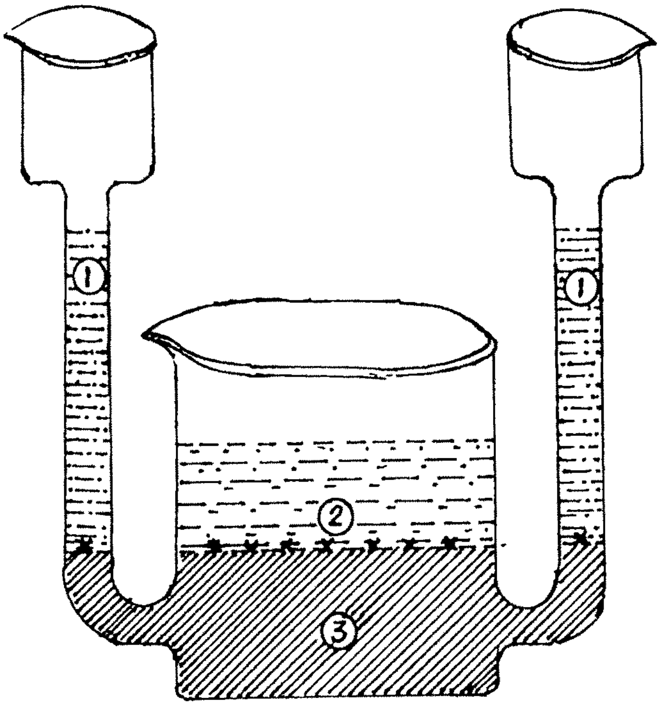


Fig. 4.13

Schematic diagram of the modified U-tube apparatus used for the growth of d-AHT single crystals.

FIG :- 4.14

ROOM TEMP 30° C

SCALE

X AXIS 1 CM - 1 DAY

Y AXIS 1 CM - 5 N CM^{-3}

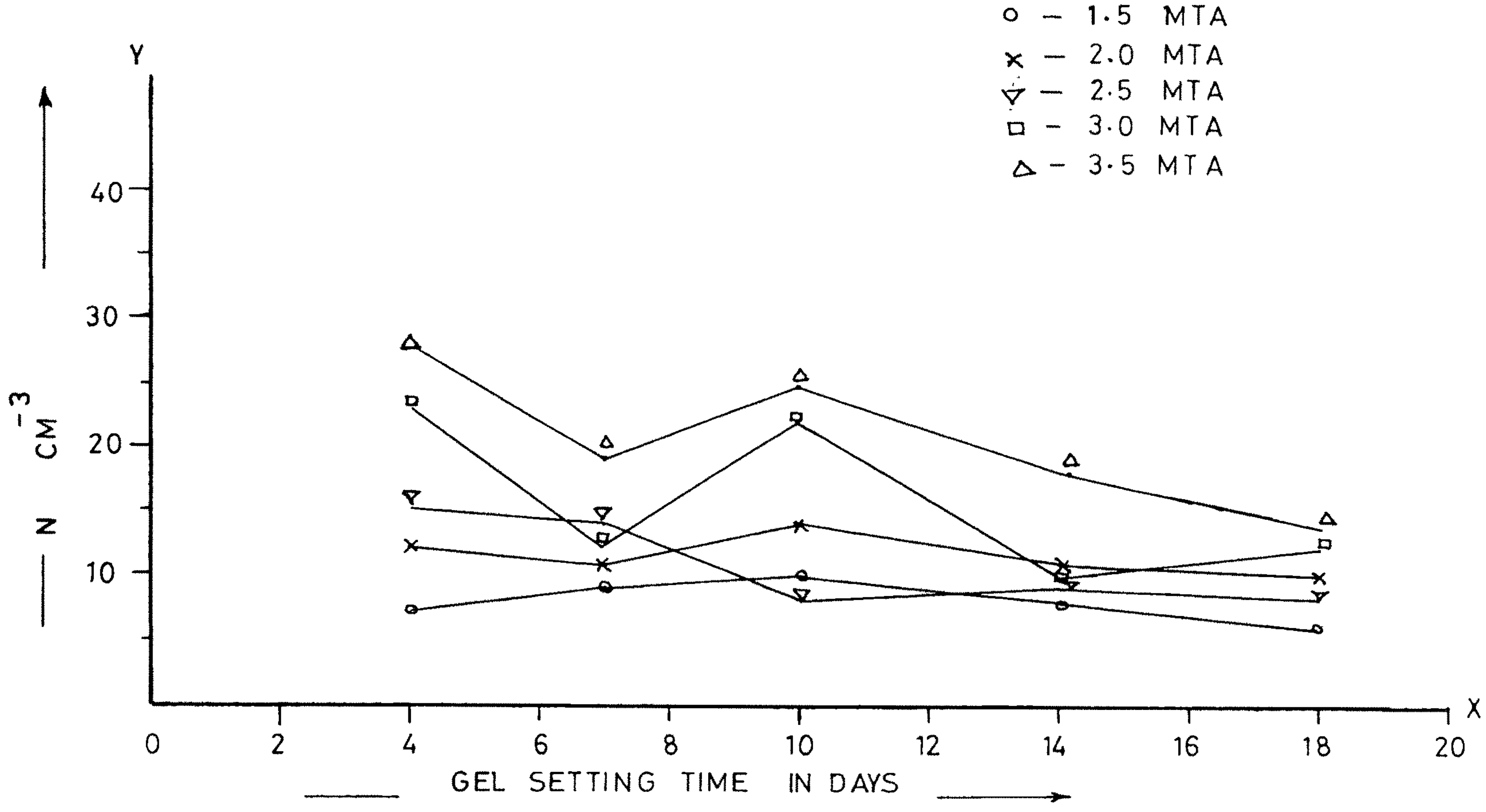


FIG : 4·15

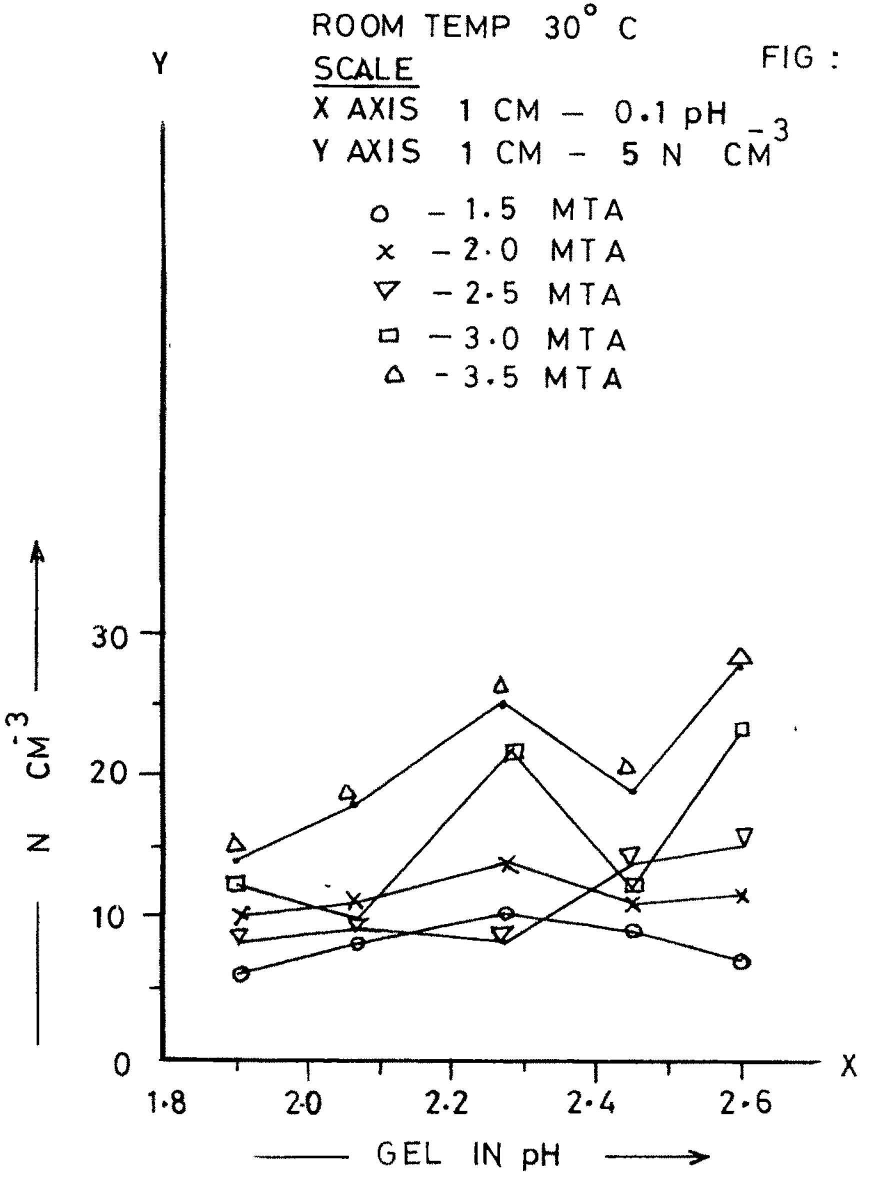
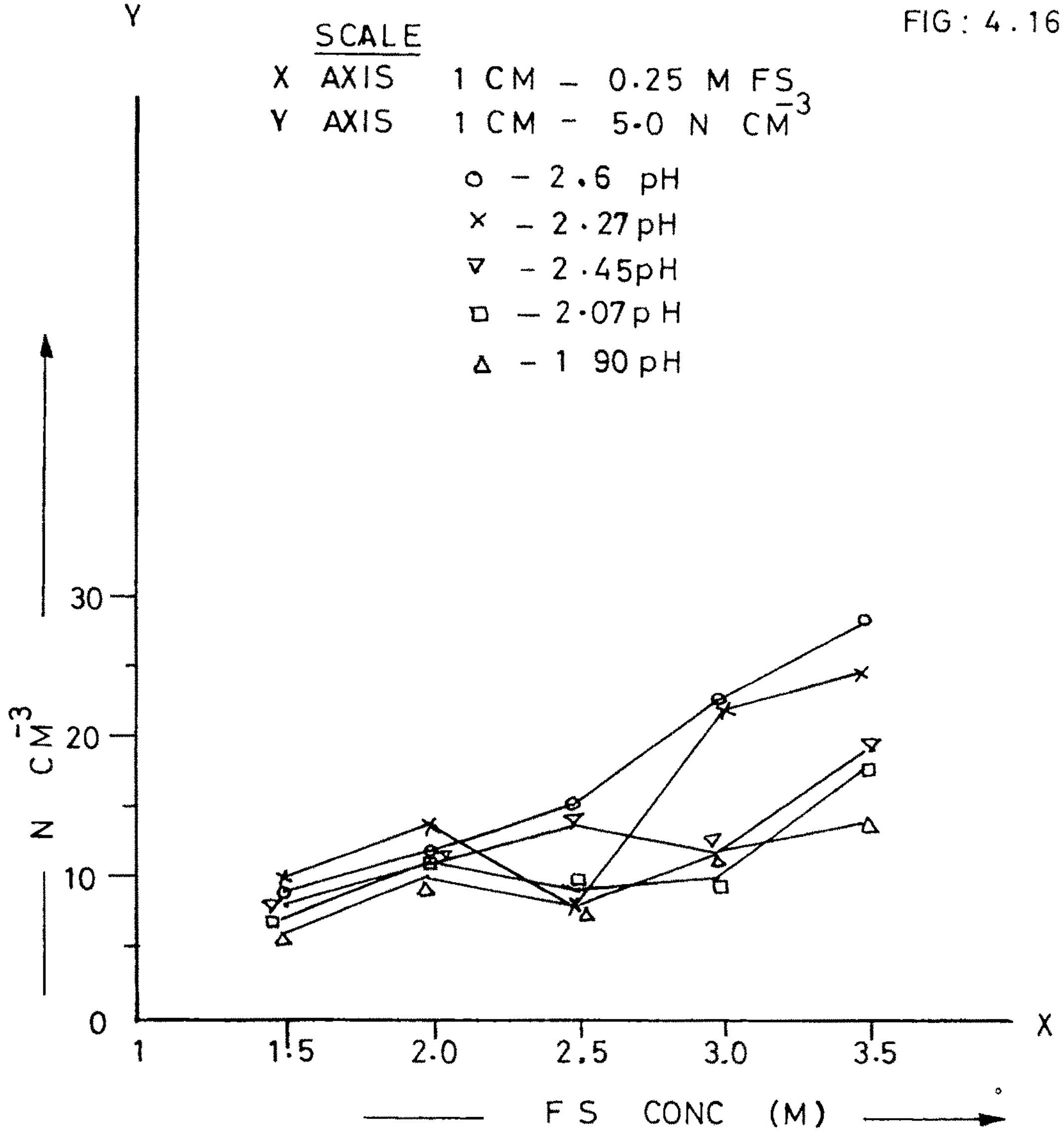


FIG : 4.16



1) Quantity of acid in gel has a dominating effect on the morphology of d-AHT crystals, whereas gel pH and acid pH do not show any significant effect.

2) For a wet and fungus free gel, the gel age does not noticeably affect crystal growth.

3) Crystal habit is independent of the FS concentration. However, for the penetration and growth of crystals, the minimum concentration of FS should be 1.5M.

4) Irrespective of the concentration of TA, the setting time for a gel for a particular quantity of acid in gel is fixed.

5) Needle shaped crystals are obtained at 20% quantity of acid in gel irrespective of the molar concentration of the acid and FS. Similarly, orthorhombic disphenoidal for 30% and 40% TA in gel, and sphenoidal crystals for 50% and 60% TA in gel.

6) For 7.5% of TA in gel and below, the setting time for gel is zero - a precipitate is formed instantaneously.

7) Gelation time varies in inverse proportion with gel pH, at a given temperature.

8) For a particular quantity of TA (acid) in gel, the same morphology is seen at the interface, central and bottom parts of the test tube.

9) Bigger crystals were obtained in the specially modified U-tube apparatus, but there were gel inclusions in all of them.

LIST OF TABLES

CAPTIONS TO FIGURES

4.1 Photograph of crystals growing at the interface in gel in a test tube showing:

a) ammonium bromide, feed solution (FS);

b) crystals in gel liquid interface, (S) sphenoidal and orthorhombic disphenoidal (ODS);

c) d-tartaric acid impregnated sodium metasilicate gel.

4.2 Photograph of crystals growing in the central part in gel in a test tube, showing:

a) ammonium bromide, feed solution (FS);

b) crystals in gel: orthorhombic disphenoidal (ODS) in the central part of the test tube;

c) tartaric acid impregnated sodium metasilicate gel.

4.3 Photograph of crystals growing at the bottom of the gel in a test tube:

a) ammonium bromide (FS)

b) crystals at the interface

c) tartaric acid impregnated sodium metasilicate gel

d) crystals in gel: orthorhombic disphenoidal (ODS) and sphenoidal (S) crystals at the bottom of the test tube.

4.4 Photographs of d-AHT single crystals of different habits obtained by mixing TA of 2.0M concentration in sodium metasilicate of specific gravity 1.039 to form gel, and 2.0M ammonium bromide added as feed solution.

4.4(i)

a) 20% TA of gel pH 2.87, needle shaped (N) crystals in gel;

b) at interface and (C) throughout the test tube;

4.4(ii)

a) 40% TA, of gel pH 2.45, orthorhombic disphenoidal crystals (ODS) in gel;

b) at the interface and (C) at lower part of the test tube;

4.4(iii)

a) 60% TA, of gel pH 2.02;

b) sphenoidal crystals (S) in gel.

4.5

a) Photograph of needle shaped d-AHT crystals grown in gel.

b) Schematic diagram of a needle shaped crystal

4.6 Different morphologies of d-AHT crystal grown in silica gel.

4.7 Plot of gel setting time (T) in days versus percentage of acid (TA) in SMS for different concentrations of TA and different crystal habits: needle shaped (N), orthorhombic disphenoidal (ODS), and sphenoidal (S).

4.8 Plot of gel pH (initial value of pH of mixture of TA + SMS) versus percentage of acid (TA) in SMS.

4.9 Plot of gel pH (initial value of pH of a mixture of TA + SMS) versus gel setting time in days (T).

4.10 Photographs of d-AHT single crystals of different morphology obtained by mixing TA of 2.5M concentration in sodium metasilicate of specific gravity 1.039 to form gel, and 2.5M ammonium bromide added as feed solution.

4.10(i)

a) 20% TA, of gel pH 2.6

b) needle shaped crystals (N) at interface and central part of the test tube.

4.10(ii)

a) 30% of TA, of gel pH 2.45

b) needle shaped (N) at interface and orthorhombic disphenoidal (ODS) crystals at bottom.

4.10(iii)

a) 40% of TA, of gel pH 2.27

b) orthorhombic disphenoidal (ODS) crystals at the bottom and interface.

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