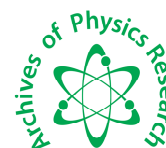




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The roles of gel medium and gelling solution in the growth of the crystals: A case study of calcium levo-tartrate

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ABSTRACT

The growth of calcium tartrate crystals by gel method is well reported and hence considered here for the case study. An attempt has been made for the first time to address the question whether the sodium metasilicate (SMS) solution has any role, or gelling solution has any role in the growth of crystals and up to which limit the thin gel can grow the desired compound crystals. In this regard, several experiments were carried out; first, the direct reaction between calcium chloride and levo tartaric acid failed produce calcium tartarate precipitates but the addition of SMS resulted in to calcium tartarate precipitates; second, to investigate the role of gel pH and gel density, the pH of gelling solution comprised of SMS and levo tartaric acid was varied from 5.35 to 2.5 and calcium chloride supernatant solution was poured on the gel and it was found that the thin gels could not support the growth of crystals firmly; and third, as sodium hydroxide is produced in the gelling process, sodium hydroxide was added in the aqueous mixtures of calcium chloride and levo tartaric acid and precipitates of calcium levo tartrate were obtained. It was found that at low pH values, the thin gel produced the crystalline mass at the bottom of the growth vessel, but to grow good quality crystals firm gel was required, which could be obtained at sufficiently higher pH values. The SMS and NaOH solutions triggered calcium levo tartrate precipitations, but to set gel the SMS solution of proper pH was needed. The confirmations of the formation of calcium levo tartrate crystals, calcium levo tartrate precipitates and crystalline mass were carried out by powder XRD and FT – IR spectroscopy. The possible mechanism of SMS solution and SMS gel in the formation of crystals, crystalline mass and precipitates has been discussed.

Keywords: Gel Growth; Powder X – Ray diffraction; FT - IR.

INTRODUCTION

The growth of crystals from gel is the simplest technique under ambient conditions. This technique is well suited for the crystal growth of compounds which are sparingly soluble and decompose at fairly low temperature. In the gel growth, interestingly, the gel acts as a three dimensional crucible which supports the crystals; supplies the nutrients for the growth through its porous medium and at the same time it allows the growth without exerting major forces on it. By carefully selecting the gel density, pH of the gelling solution and the concentration of the reactants; good quality single crystals can be grown at room temperatures. This technique is well explored by numerous workers and described in detail [1-3] whereas; several authors [3-5] have suggested improvements and modifications in this technique. A modified gel growth technique has also been proposed for the growth of micro – crystals, in which the gel droplet is set on glass slide, protected under glass cover-slip and placed in the petri – dish having suitable reacting solution to diffuse into the gel for the growth of micro-crystals; which facilitated the *in situ* observations

under microscope [6]. Moreover, a growth of calcium tartrate crystals was reported in the filament network of fungi *Aspergillus niger*, which mimicked the gel [7]. Calcium tartrate crystals in pure and doped forms have been grown by several researchers [1-3, 7-12]. A careful survey of literature available on the gel growth of crystals over the period of last three decades a plenty of detailed discussion is available on the mechanism of gel growth of various crystals and effect of various growth parameters, however, so far the knowledge of the present authors is concern no detailed study is available on the role sodium metasilicate(SMS) solution and SMS gelling solution in crystal growth. The present authors feels that the gel is not only providing porous and physically conductive medium for the nucleation and growth of crystals through constant supply of nutrients from its polymeric porous network but it is also expected to participate chemically to form nucleation of the crystals and their further growth. In the present investigation, calcium levo tartrate crystals are taken as hallmark to investigate the role of SMS solution, the role of pH of gelling solution and further the role of NaOH solution produced during gelling.

MATERIALS AND METHODS

For the precipitation study equal volumes of aqueous solutions of 1 M calcium chloride and 1 M levo tartaric acid were mixed and stirred well using magnetic stirrer. No precipitations were obtained. This experiment was repeated at different temperatures up to 70 °C, but no precipitation was observed as a result of direct reaction.

The same experiment was repeated by adding 2 ml, 1 M SMS solution to the mixture of 9 ml, 1 M calcium chloride and 9 ml, 1 M levo tartaric acid and white precipitates were obtained, which were further characterized. At an ambient temperature, different amount of SMS solution was added in the mixture of calcium chloride and levo tartaric acid solutions under rigorous stirring by keeping the total volume of the mixture constant 20 ml, the pH of the mixture was also measured and precipitates were observed at the bottom of the test tube. Table 1 gives the composition of the solutions with pH value.

Table 1: Composition of the solution with pH

Contents	Value of pH
10 ml CaCl ₂ + 10 ml C ₄ H ₆ O ₆ + 0 ml SMS	1.09
9.5 ml CaCl ₂ + 9.5 ml C ₄ H ₆ O ₆ + 1 ml SMS	1.24
9 ml CaCl ₂ + 9 ml C ₄ H ₆ O ₆ + 2 ml SMS	1.30
8.5 ml CaCl ₂ + 8.5 ml C ₄ H ₆ O ₆ + 3 ml SMS	1.35
7.5 ml CaCl ₂ + 7.5 ml C ₄ H ₆ O ₆ + 5 ml SMS	1.5

For crystal growth in the sodium metasilicate gel, glass test – tubes of 25 mm diameter and 150 mm length were used for crystallization. SMS solution of specific gravity 1.06 was mixed with 1M levo tartaric acid solution in such a way that the pH values of the mixture (gelling solution) could be varied from 5.35 to as low as 2.5. The mixtures were poured in the respective test tubes and allowed to set the gel. The supernatant solution of 1M CaCl₂ was poured carefully on set gels. The nucleation of crystals started within 24 hours and complete crystal growth took place within 20 to 25 days.

In the last experiment, an aqueous solution of 2 ml, 1 M NaOH was added to the mixture contain 9 ml, 1 M calcium chloride and 9 ml, 1 M levo tartaric acid and stirred well. White precipitates were obtained which were recovered after filtration.

The dimensions of the grown crystals were measured by travelling microscope having least capacity of measurement of 0.01 cm.

2.2. Characterization

Crystalline samples as well as precipitates were characterized by powder XRD using Philips X’PERT MPD system with Cu K_α radiation. The data were analyzed by computer software powder X. The FT – IR spectra were recorded by using Nicolet (Thermo Scientific) - 6700 set up in the range from 400 cm⁻¹ to 4000 cm⁻¹ in KBr medium.

RESULTS AND DISCUSSION

Considerable amount of discussion has been made on the growth of calcium tartrate crystals [1]. It has been found that as the pH of the mixture of SMS solution and tartaric acid, i.e., the gelling solution, decreases, the gelation time

increases rapidly and for certain low values of pH the gel does not form [12]. Recently, the roles of different parameters in the gel growth have been reported for crystals such as neodymium tartrate [13], potassium dihydrogen tartrate [14].

In the present study, for understanding the growth of crystals in the gel medium, several experiments have been conducted.

The mixing of aqueous solutions calcium chloride and levo tartaric acid did not exhibit any direct reaction and no precipitation was observed. Further, the attempt was made by adding sodium metasilicate solution in to the mixture of calcium chloride and levo tartaric acid and precipitates were observed. Figure 1 shows the precipitates at the bottom of the test tube for 9 ml calcium chloride, 9 ml levo - tartaric acid and 2 ml SMS. These precipitates were filtered, washed with distilled water and air dried for powder XRD studies.



Fig. 1: Calcium levo - tartrate precipitates



Fig.2: Calcium levo – tartrate crystals at 4.5 pH



Fig. 3: Calcium levo – tartrate crystalline mass at 2.8 pH

It is well established fact that the pH of the gelling solution and the gel density as well as gelling time is closely related. As the pH increased, the gel was found to be thick and the gel setting time was smaller. In the case of pH ranging from 3.2 to 5.35, the gels were quite firm and the growth of crystals took place within the gel. Figure 2 shows the growth of prismatic single crystals of calcium levo tartrate for 4.5 pH. At this pH value the gel was adequately firm to facilitate the crystal growth. The pH of the resulting solution determines the course and polymerization rate [3]. The pore size distribution changes the nature of the gel, i.e., hard gel is having smaller average pore sizes and the soft gel is having larger average pore sizes [1]. The diffusion of molecules of supernatant solution takes place into the gel through the pores available in the gel. Therefore, a tuning is required between the pore size distribution and diffusing molecular dimensions to get maximum diffusion for growth of crystals. It was observed that the gelling solutions having pH below 3.0 did not set into gel form even after one month. When calcium chloride solution was added in the gelling solution of pH 2.8, small calcium levo tartrate crystalline mass was found to be grown at the bottom of the test tubes, which is shown in Figure 3. Figure 4 (a) shows the histogram for average length of the grown crystals for different pH values, whereas Figure 4 (b) is the histogram for average breadth of the grown crystals for different pH values. From these histograms, one can see that the maximum dimension (length and breadth) of grown crystals is observed at 4.5 pH. This indicates that at this pH the pore size dimensions are suitable for the passage of maximum number of supernatant solution molecules to the nucleation sites to grow larger crystals. At higher pH values, the harder gel having smaller average pore size imposing constraints on crystals, which reduces the growing crystal dimensions; whereas, at the lower pH values the dimensions of the grown crystals are again small, which may be due to large pore sizes bringing more competition

during passage of the nutrient molecules to the growth sites. The single crystals were gently removed from the gel, washed with distilled water and air dried before powdering for powder XRD studies.

From above discussion, a conclusion can be drawn that for the precipitation the presence of SMS solution is necessary, however, for the growth of good quality single crystals SMS gel of appropriate density is needed. One can further consider that the SMS gel serves two purposes; first, it facilitates the reaction between two aqueous solutions which otherwise not possible directly by stirring or heating; and secondly, the SMS gel provides the conducive environment for the nucleation and growth of crystals by providing nutrients through its porous structure.

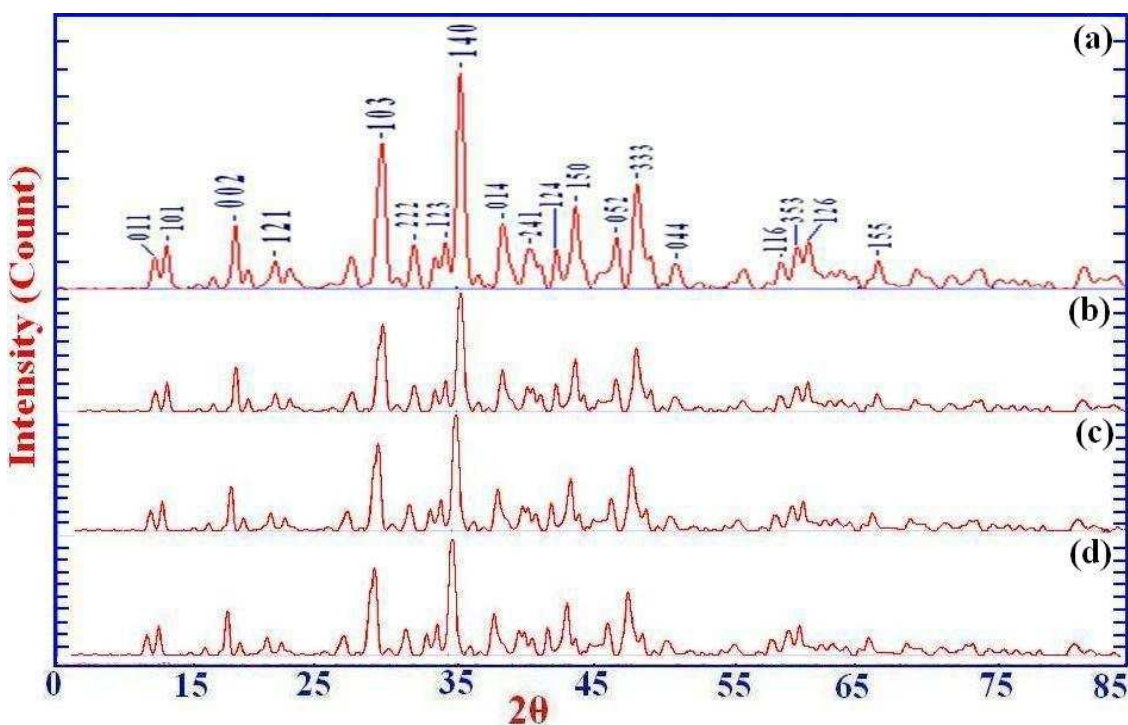
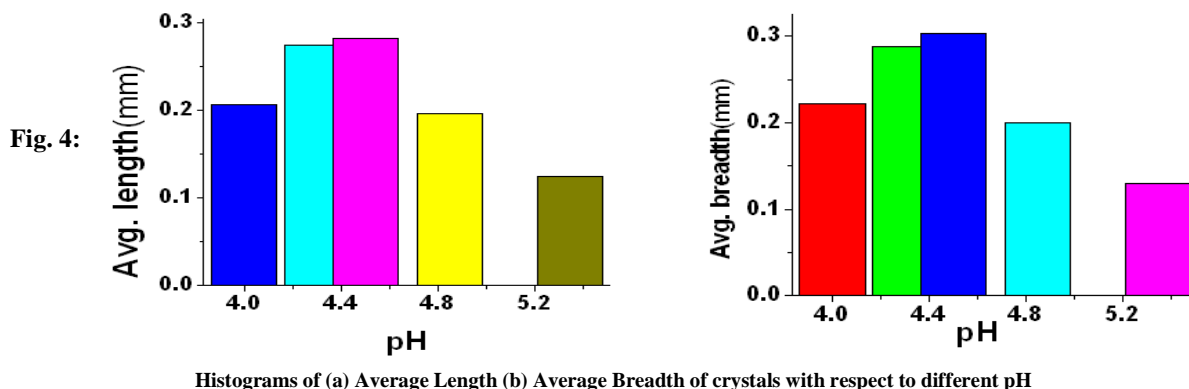
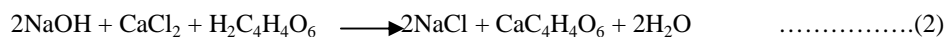


Fig. 5: Powder XRD patterns of calcium tartrate (a) crystals (b) crystalline mass (c) precipitates obtained by the mixing of SMS, CaCl₂ and l- tartaric acid and (d) precipitates obtained from the mixture of NaOH, CaCl₂ and tartaric acid.

Further, the mechanism by which SMS facilitates the nucleation of the crystal was investigated. When SMS is dissolved in water, monosilicic acid is produced in accordance with the dynamic equilibrium. Expected reaction is,



This NaOH is expected to produce precipitates of calcium tartrate by the following reaction,



To verify this reaction the mixture containing equal amount of solutions of calcium chloride and tartaric acid were mixed with NaOH solution and precipitates were observed. The observed precipitates were filtered, air dried and characterized by powder XRD.

3.2. Powder X – Ray Diffraction Study

The powder XRD pattern of calcium levo tartrate crystals grown at 4.5pH is shown in Figure 5 (a). The data have been analyzed and the unit cell parameters are found to be a=9.2164 Å, b=10.5462 Å, and c=9.6233 Å, which are compiled in Table 2. This corresponds to the unit cell parameters reported earlier [11, 15].

Table 2: Unit cell parameters of calcium tartrate crystals and precipitates

Sample	Crystal System: Orthorhombic		
	a (Å)	b (Å)	c (Å)
Calcium Levo tartrate Crystals	9.2164	10.5462	9.6233
Calcium Levo tartrate Crystalline mass	9.2164	10.5462	9.6233
Calcium Levo tartrate precipitates using SMS solution	9.2194	10.5675	9.6487
Calcium Levo tartrate precipitates using NaOH solution	9.2175	10.5640	9.6452

The powder XRD pattern of crystalline mass obtained at the bottom of the test tube for the pH value 2.8 is shown in Figure 5 (b). From Table 2 one can notice that the unit cell parameters are found to be the same as that of the calcium levo tartrate crystals. It suggests that the soft watery gel has allowed the growth of crystalline mass of calcium levo tartrate at the bottom of the test tube.

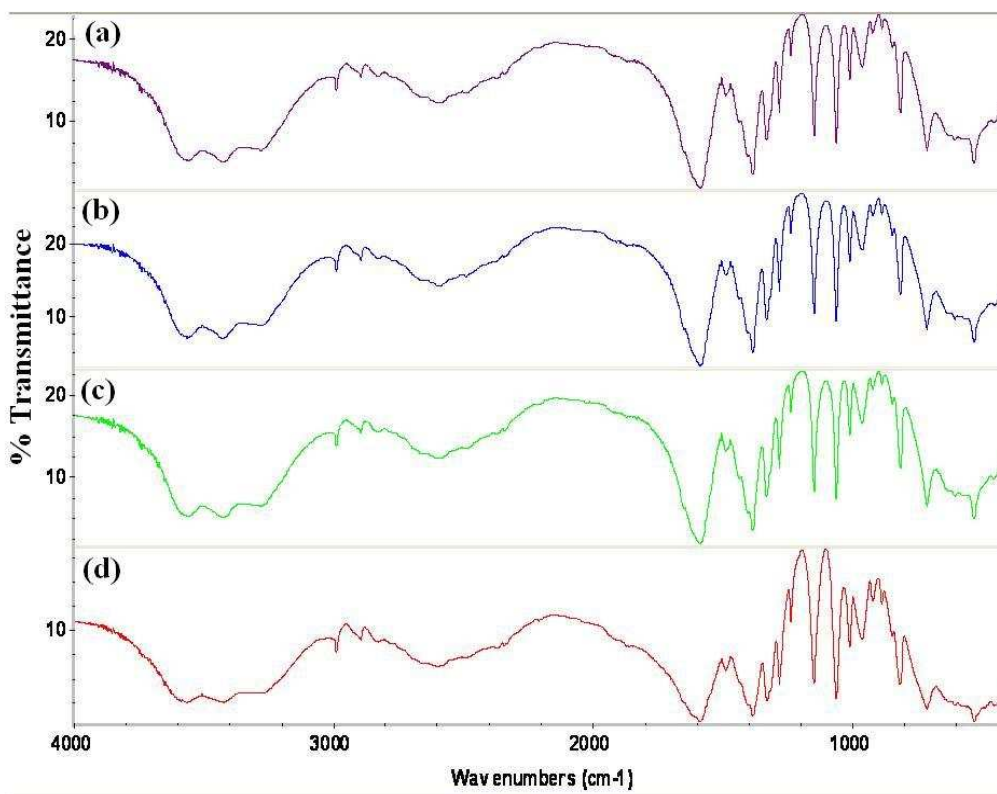


Fig. 6: FT – IR spectra of calcium tartrate (a) crystals (b) crystalline mass (c) precipitates obtained by the mixing of SMS, CaCl₂ and 1-tartaric acid and (d) precipitates obtained from the mixture of NaOH, CaCl₂ and Tartaric acid

The powder XRD pattern of the precipitates obtained by adding 2 ml SMS solution having specific gravity 1.06 to 9 ml, 1 M calcium chloride and 9 ml 1 M levo tartaric acid solutions is exhibited in figure 5 (c). The unit cell parameters values are given in Table 2, which is found to be the same as that of the calcium levo tartrate crystals. It

can be argued that for the growth of good quality crystals, the proper density of gel is required, however, for the precipitation only the mixing of SMS solution into reactants is needed. In other words, the addition of SMS solution in the two non-reacting mixtures facilitates the precipitation.

The powder XRD pattern of the precipitates obtained on adding 2 ml, 1 M NaOH to the mixture containing equal amount of solutions of 9 ml, 1 M calcium chloride and 9 ml, 1 M tartaric acid is given in Figure 5 (d). The calculated unit – cell parameters are given in Table 2, which correspond to that of the calcium levo tartrate. This confirms the above mentioned hypothesis that sodium hydroxide produced due to the dissolution of sodium metasilicate in water, is responsible for triggering precipitation of calcium levo tartrate.

3.3. FT – IR Study

The FTIR spectra of the grown calcium levo tartrate crystals at pH 4.5, crystalline mass collected from the bottom of the test tube at pH 2.8 and precipitates obtained by adding SMS solution into the mixture of calcium chloride and levo tartaric acid solutions are shown in figures 6 (a), 6 (b) and 6(c), respectively. Figure 6 (d) represents the FTIR spectrum of precipitates obtained from the mixture of calcium chloride, levo tartaric acid and sodium hydroxide. It can be noticed that the FTIR spectra shown in Figures 6 (a), 6 (b), 6 (c) and 6 (d) are nearly the same. The tartrate ion consists of two halves, each consisting of a carboxyl group, a tetrahedral carbon and hydroxyl oxygen. These two halves are connected through C – C bond with each other. Therefore, the stretching vibrations of hydroxyl group and C – H groups are expected. Also, a free tartrate ion has two hydroxyl groups, which may give rise to two bands of stretching vibrations of the hydroxyl group [16].

The FTIR spectra are recorded in the wavenumber range 400 – 4000 cm^{-1} . The strong absorption bands within 3600 cm^{-1} – 3400 cm^{-1} are due to O – H stretching mode. The absorptions within 2990 cm^{-1} - 2850 cm^{-1} are due to C – H stretching mode. The bands around 1588 cm^{-1} and 1490 cm^{-1} are attributed to the C=O stretch of carbonyl group. The strong peak around 1385 cm^{-1} is assigned to C = O symmetric + δ (O – C = O) mode [16-19], while for the same absorption the C – O stretching is assigned by the other workers [6, 7, 10]. As these vibrations overlap, therefore, not identified separately. The absorption around 1330 cm^{-1} is due the C – O stretching. The absorption at 1282 cm^{-1} is due to C – H bending. The peak around 1148 cm^{-1} is due to C – H vibrational modes. The peaks of various intensities at 1061 cm^{-1} and 1011 cm^{-1} are due to out of plane O – H deformation and C – O stretching vibrations, respectively. The absorptions between 817 cm^{-1} and 534 cm^{-1} are due to calcium–oxygen bonding. The FTIR spectra obtained in the present study is similar to the IR spectrum of calcium tartrate crystals reported earlier [7, 11, 15]. From the FT – IR spectra the presence of O –H, C = O, C – O and Ca – O bonds are confirmed in all samples, i.e. calcium levo tartrate crystals, crystalline mass and precipitates.

CONCLUSION

The role of gelling solution pH on the growth of calcium levo tartrate crystals was investigated in the pH ranging from 5.35 to 2.5. The pH influences the polymerization process in the gel formation and the pore size of the gel allows the movement of reacting molecules to form a nucleation and subsequently the growth of the crystals. Good quality, large numbers of prismatic and transparent crystals were grown for pH 4.5, which suggested that appropriate gel density and pore size distribution facilitated the maximum growth. The gel was not set for the pH values below 3.0 and the solution remained watery. In the case of watery type gel solution the crystalline mass was formed at the bottom of the test tube. The role of SMS solution in the gel formation was confirmed as the gel density varied with pH of the solution. The role of SMS solution in the precipitation of calcium levo tartrate was also confirmed. The NaOH solution, generally produced by dissolving SMS solution in water, resulted in precipitates of calcium levo tartrate. The powder XRD and FT-IR spectroscopy confirmed that all the three, i.e., crystals, crystalline mass and precipitates, were of calcium levo tartrate. From this study it can be concluded that the SMS gel not only facilitates the nucleation and subsequently the growth of crystals but plays important role in forming a compound, which is not possible by reacting two solutions directly.

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