

Role of adsorption on the growth of barium and lead tartrate crystals in silica gels

M ABDULKHADAR* and M A ITTYACHAN

Department of Physics, University of Kerala, Kariavattom, Trivandrum 695 581

* Department of Physics, Government Arts College, Trivandrum 695 014

MS received 9 June 1979 ; revised 20 August 1979

Abstract. Barium and lead tartrate crystals were grown in silica gel by single diffusion method. At basic pH values, barium tartrate is precipitated as a white column of colloidal particles. This column appears to move down with increasing thickness. Finally crystals develop at the expense of this white column. Lead tartrate also is initially precipitated as a column of colloidal particles in the gel. On adding acetic acid or tartaric acid over the gel, this column transforms into dendrites and later into single crystals. The development of crystals from colloidal precipitate has been explained on the basis of adsorption.

Keywords. Gel growth ; barium tartrate ; lead tartrate ; adsorption ; colloidal precipitate ; dendrites.

1. Introduction

Gels can act as excellent supporting media for growth of crystals (Henisch 1973). Gels hold the specimen crystals, control nucleation and act as a medium through which the reacting nutrients can diffuse at a rate conducive for growth of crystals to proceed. Apart from these, a gel is a conglomeration of colloidal particles possessing the important surface phenomenon—adsorption (Weiser 1958 ; Tayler 1923) studies on growth of tartrates of barium and lead offer conclusive evidence for the influence of adsorption on crystal growth from gels.

2. Experimental

Experiments consist in growing tartrates of barium and lead in silica gel. The peculiar phenomenon exhibited by lead tartrate grown at acidic pH has already been reported by the authors (Abdulkhadar and Ittyachan 1977). At basic pH values an odd phenomenon is observed during growth of lead tartrate. A similar phenomenon is exhibited by barium tartrate as well.

The experiments were conducted in test tubes of 3 cm diameter and 20 cm length. Silica gel of specific gravity 1.03 was used. The pH was adjusted by titration with

1 M tartaric acid and was kept above 7. A solution of lead acetate or barium chloride (1 M) was poured over perfectly set gel. A film of white precipitate was observed at once on the gel surface.

With lead tartrate this white film grows in thickness and extends gradually down into the gel as Liesegang rings (Kurt 1954) destroying the transparency of the gel (figure 1). This white column is perfectly opaque. With barium tartrate, the observation is quite strange and interesting. The white film formed at the gel surface gradually grows thick. After attaining a certain thickness, this white band appears to move down from the gel surface, at the same time gaining more and more thickness (figure 2). The rate of shift of the white column and the rate of its gaining thickness, slacken gradually. This is represented in figure 3. During the course of shift of this white column, if nucleation occurs the nuclei start growing at the expense of this column (figure 4). As the crystals grow, the neighbouring portion of the column disappears in a spherical way, leaving a transparent spherical shell of gradually increasing radius with the crystal at the centre of the shell. If more than one nucleus occur, more such shells will be observed. The white column finally disappears completely as the crystals (spherulites in this case) reach maximum size, restoring the gel its transparency once again. In the pH range 6 to 7 periodic precipitations—Liesegang rings—were observed and they behave very similarly as before in movement and crystal formation. The observations are also similar with dilute nutrient solutions. Figure 5 shows the shift of the column with time.

On the basis of the assumption that the shift and the disappearance of the white column are dependent on pH, attempts were made to induce the above phenomenon in the case of lead tartrate. The supernatant lead acetate solution was poured out from the test tube containing the gel incorporated with lead tartrate precipitate. The tube was then cleaned with distilled water and 0.5 M to 1 M tartaric acid or acetic acid was poured into it. The white column gradually dis-

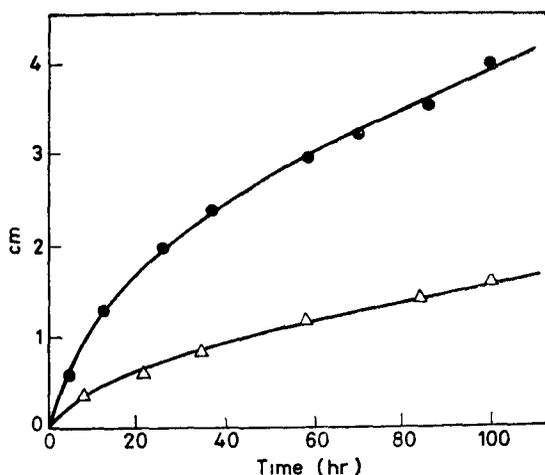


Figure 3. Time-displacement graph. Top curve—displacement of bottom surface of the band with time. Bottom curve—displacement of top surface of the band with time.

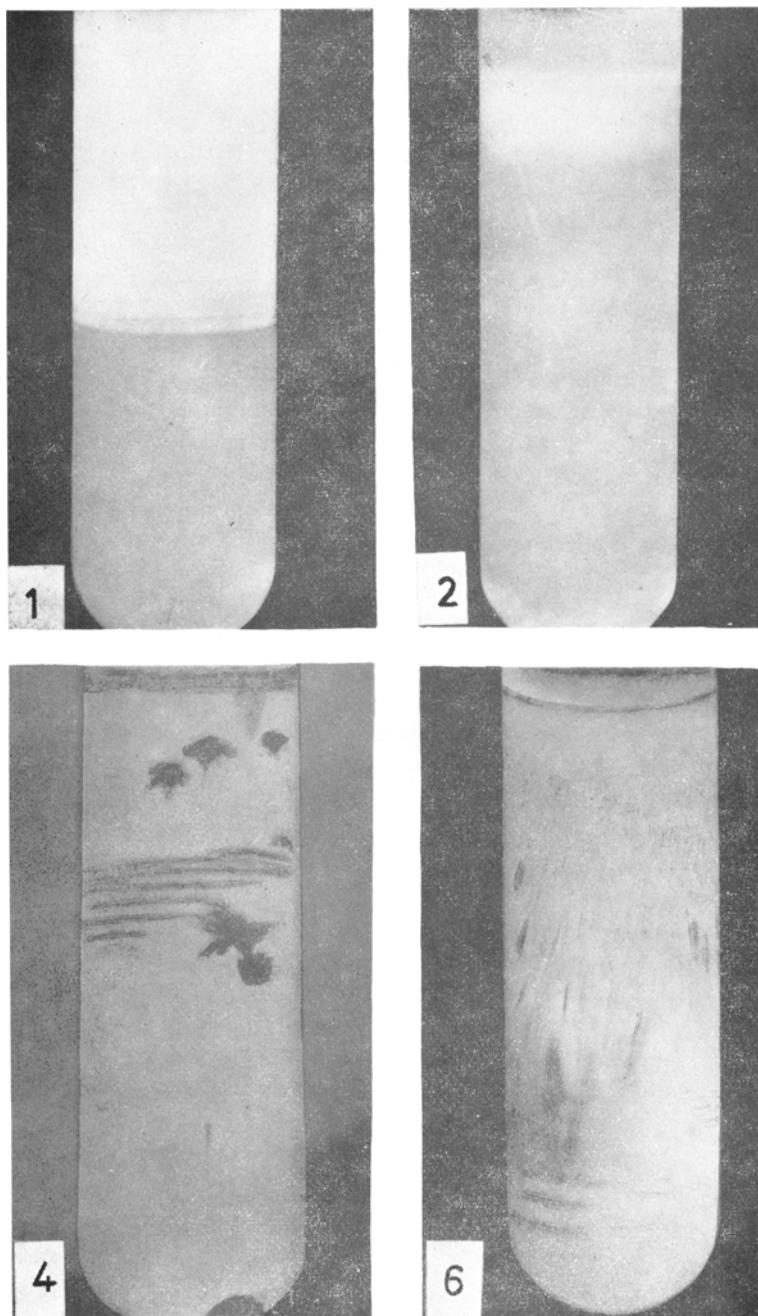


Figure 1. Lead tartrate is initially precipitated as a white column of colloidal particles. This column gradually grows in thickness, destroying the transparency of the gel.

Figure 2. Barium tartrate is precipitated as white band or rings, depending on the pH, which descend with increasing thickness.

Figure 4. Crystals develop at the expense of the band or rings of barium tartrate precipitate.

Figure 6. On adding dilute acetic acid or tartaric acid, the white column of lead tartrate precipitate gradually disappears and well-shaped dendrites grow from the gel surface downwards.

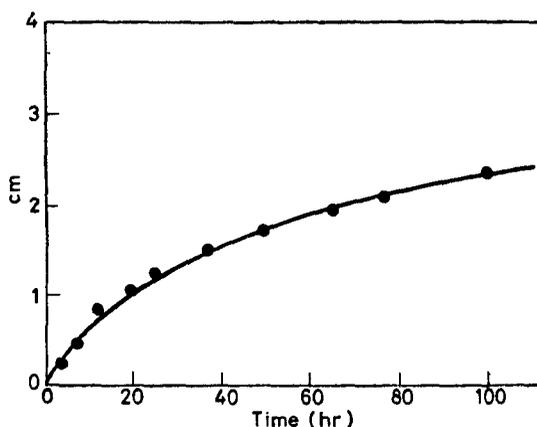
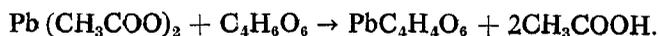
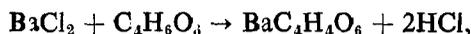


Figure 5. Graph of shift of the band of barium tartrate with time.

appears with the formation of dendrites (figure 6) which grow downwards. They attain a length almost equal to that of the white column. These dendrites later develop into single crystals (Abdulkhadar and Ittyachan 1977). Acids other than acetic and tartaric acid cannot be used since they react readily with the lead tartrate precipitate which appears as the white column.

In the above experiments, barium and lead tartrates were expected to form by the following reactions:



The experiments were conducted at room temperature which varied between 24° C and 30° C.

3. Discussion

Explanation to the above observations can be offered on the basis of adsorption and its dependence on pH (Weiser 1958). Silica gel is a polymerised form of silicic acid. Gels do possess adsorption to varying degrees. Due to the high rate of reaction of the nutrients, the product of reaction, *viz.*, barium tartrate or lead tartrate has no time for regular growth into crystals initially. So they are precipitated into a colloidal conglomeration. The colloidal particles are readily adsorbed by the gel resulting in a column of white precipitate. The reaction generates acid in both the cases. As the reaction proceeds, *i.e.*, as the top nutrient diffuses further into the gel, more and more acid is liberated. This lowers the effective pH around the reaction site. The force of adsorption decreases with decrease of pH. Two types of adsorption have to be considered: (i) adsorption of the colloidal particles by the gel, (ii) adsorption among the colloidal particles.

In barium tartrate the force of adsorption of type (i) decreases more rapidly than that of type (ii) with decrease in pH. As the top nutrient diffuses into the

gel, the top film formed initially gradually attains thickness, the material in this band being colloidal particles of barium tartrate. When a certain amount of nutrients have reacted, the amount of acid liberated will be sufficient to bring the force of adsorption of type (i) to a minimum, if not zero; hence the colloidal particles move as a band downwards where pH is large and the adsorption of type (i) is large. Simultaneously, the top nutrient diffuses further into the gel, it reacts with the nutrient in the gel and produces more colloidal particles of barium tartrate. So the thickness of the band increases. Theoretically, a band of gradually increasing thickness and moving downwards should be expected. It is experimentally observed. At the end of the reaction, the rate of reaction slackens; therefore the variation of pH is small and hence the shift of the band will be less swift. This is evident from the time-displacement graph (figure 5). As reaction proceeds, a stage will be reached when the pH is lowered to a value where the adsorption of type (ii) decreases to a minimum rendering the colloidal particles free so that they can diffuse to the growth site. Each of these particles can now act as nucleus for crystal growth. By probability a few of these nuclei grow gradually. The smaller crystals dissolve more easily than the larger ones due to the large value of surface-to-volume ratio and thus assist the larger ones to grow. That the crystals grow at the expense of the colloiddally dispersed particles is clear from the experimental observation of complete disappearance of the white column.

In lead tartrate the white column of colloidal particles remains undisrupted in course of time when left to itself, provided the pH of the gel is definitely basic. The acid produced by the chemical reaction is not sufficient to lower the pH to a value when the forces of adsorption of type (i) and type (ii) are sufficiently less so that the particles are free and diffuse to the growth site of a crystal. Because of this restriction to the motion of the particles, the nuclei, if there exist a few at any instant, cannot grow at all. When the pH is lowered by the addition of acid, the forces of adsorption of types (i) and (ii) decrease making the particles mobile and thereby assisting crystal growth. The conditions for dendritic growth are satisfied initially and hence the crystals grow as dendrites. Finally the whole of the white column disappears and well-grown dendrites result. Now the dendrites start thickening leading to their conversion to single crystals.

The above experiments conducted with agar gel do not yield any of the foregoing results. This may be because the property of adsorption is different for different gels and the adsorption of agar gel and that of the above products of reaction do not match for the exhibition of the phenomenon.

4. Conclusions

The property of adsorption of gel and the product of reaction in the gel has great and definite influence on the growth of crystals in gels, at least at certain conditions. If the product of reaction is a precipitate, then to explain any phenomenon exhibited by it, the property of adsorption should be taken into account. Like barium and lead tartrate it may also be possible to grow other more important crystals from the materials in the colloidal form.

References

- Abdulkhadar M and Ittyachan M A 1977 *J. Cryst. Growth* **39**–365
Hensich H K 1973 *Crystal growth in gels* (Pennsylvania and London : Pennsylvania State University Press)
Kurt H S 1954 *Chem. Rev.* **54** 80
Tayler W W 1923 *The chemistry of colloids* (London : Edward Arnold)
Weiser H B 1958 *A text book of colloid chemistry* (New York : John Wiley)