Habit Modifications of Sucrose Crystals

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INTRODUCTION

Casual inspection of most crops of crystals, including sugar, usually suggests a rather uniform appearance in shape. More careful scrutiny, though, (or better, measurement to discriminate subjective differences due to size) reveals this to be not exactly so. Differences are accentuated when the crystals are grown under non-uniform conditions. This is especially pronounced when the batch is developed without stirring, such as on a microscope slide. The variations persist even when the syrup is seeded; for now the non-uniformity of the seed stock is superimposed upon other variations in growth conditions. In fact, subtle differences occur in the best grown single crystals. Certainly, Kucharenko's (6) specimens are some of the best known of these, yet they exhibit variations in the dimensionless shape factor $\frac{area^3}{Vol^2} \sim \frac{(cm^2)^3}{Vol^2} \sim \frac{cm^6}{g^2}$ of as much as 6 units about the average of 69.93 ± 1.64 cm^6/g^2.

However, even more pronounced than these differences which may be considered minor and due to variations in seed and growth stabilities, is the influence of impurities. The best known examples of these are the influences of raffinose and dextran on the shape of sucrose crystals but there are many others.

RAFFINOSE

This is probably the most carefully studied of sucrose crystal modifiers. It has been considered in detail by Hungerford and Nees (4), Vavrinecz (18), and Mantovani (7), amongst many others, and the needle like form produced

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in its presence is well known to all sugar men. This enlongated shape results from the preferential adsorption of raffinose especially on the girdle faces of the crystal where fructose-fructose interactions seem likely (13). This impedes their rate of advance and hence areal enlargement. This stereospecific adsorption has been demonstrated chromatographically (16). Smyth (13), as well as Mantovani (8) and Kelly and Mak (7), have pointed out the conformation of molecular structure of adsorbant and crystal structure of adsorbate in this and other cases and this plausibly accounts in part for the stereospecific interaction.

Incidentally, this partial chemical and structural similarity raises the question whether or not raffinose might not act as a heterogeneous nucleating agent for sucrose crystallization and vice versa. When first tried this was found to be so, but after recrystallizing the seed stock and working in effectively sterile conditions to avoid the sugar dust ever present in any sugar labroatory, it was found ineffective. The disregistry in crystal lattice dimensions is just too great!

Since raffinose occurs throughout a doped crystal and not superficially on the surface, as do many other impurities, one would expect some distortion of the basic sucrose lattice structure on account of the difference in overall molecular size and structure (15). However, this could not be found in a careful x-ray examination (17) of a single crystal of sucrose containing 0.3% raffinose. This had been grown from a syrup containing 5 g. raffinose per 100 g. water. The difference calculated for straightforward substitutional incorporation of this amount of raffinose is less than 0.005Å, which was beyond the limit of detection of the equipment available. Neither could the powder x-ray methods available be expected to reveal this small amount of impurity, so that the question still remains open (15). Essentially the same conclusion was reached by Robinson (10), in Brisbane, who examined in the same way a crystal grown in the presence of dextran.

Sketchy phase rule work on the sucrose-raffinose-water

systems suggests than any raffinose co-crystallized with sucrose under ordinary equilibrium conditions would be in the form of the pentahydrate. However, no evidence for this could be found from moisture determinations and differential thermal analysis behavior. But again, the effects can be estimated to be at the limit of sensitivity of these methods so that improved or other devises will be necessary to answer this intriguing question more definitively.

Another interesting thing about sucrose-raffinose syrups- Sarig and Mullin (11) have recently reported that crystal habit modifiers frequently caused a considerable reduction in size of crystal slurries when gently agitated. The following account illustrates this to apply for raffinose containing slurries; probably as a result of attrition and recrystallization. This hypothesis is indicated by results with NaCl and different habit modifiers: That is, salt, which normally crystallizes as cubes, comes down as octahedra in the presence of urea and as fragile dendrites when even small amounts of ferrocyanide ion are present. The relative reduction is much greater in this case than with the control or added urea.

Original coarse granulated	10% through 40 mesh
Tumbled 3 days in saturated syrup	15% " " "
Same + 5 g. raffinose/100 water	30% " " "
Fine granulated	1.4% through 100 mesh
Tumbled 3 days	5.6% " " "
Same + raffinose	9.7% " " "

DEXTRAN

Dextran as impurity causes as much concern in the cane segment of the industry as does raffinose in the beet. It causes elongation c-wise, just as rafinose extends the crystal along the b-axis. This is probably the result of preferential adsorption on the polar faces but this has not been specifically demonstrated. Dextran is particularly obnoxious because it increases the viscosity of syrups tremendously along with the other problems of modified crystals. It can be destroyed enzymatically (5) and so can raffinose and starch; although much of the latter can be more effectively removed by good clarification. After all, this step is as important in purifying sugar by removal of impurities as

is the crystallization itself where sucrose is separated from impurity.

OTHER CASES

The effect of many other substances on the shape of sucrose crystals has been investigated by many technologists (2, 3, 12) in addition to those already cited. In most instances, though, their influence is not as marked as that of the polysaccharides already mentioned. Prisms, triangles, plates, pyramids, twins and other forms are not uncommon but the causative agents have not always been identified. This is important to know should efforts be intended to alleviate the effects of these agents.

A special case reported by Sutherland (14) in 1969 is the development of elongated crystals by cyclic dissolution and growth. The change occurs because dissolution is diffusion controlled and the same for all facts whereas growth is not.

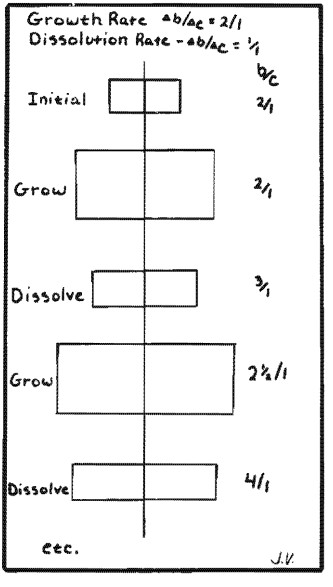

Figure 1. Repeated growth and dissolution of a crystal-idealized.

Along somewhat similar lines and suggested by a procedure utilized by Accorsi and Mantovani (1) to determine the rates of growth of different faces, one can visibly demonstrate crystal form modification by preventing growth of

different faces with a coat of varnish. This may have to be refurbished periodically to reduce distortion by overlap, etc.

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