Reports

Growth of Oxalic Acid Single Crystals from Solution: Solvent Effects on Crystal Habit

Abstract. *Single crystals of oxalic acid dihydrate are difficult to grow from pure water solution, but good single crystals of the material may be obtained by growth from mixtures of acetone and water. The solvent markedly affects the crystal habit. Crystals grown in mixtures of acetone and water develop the prismatic habit, while those grown in water alone develop the tabular or equant habit. The forms {001}, {110}, and {101} predominate in all cases. Single crystals of anhydrous oxalic acid may also be grown from solution in glacial acetic acid, although specimens more than 2 centimeters in length are difficult to produce.*

The work described here was initiated in the hope of producing oxalate single crystals of high purity and stoichiometric composition for use in coulometric determinations (anodic oxidation of the oxalate ion) of the value of the Faraday (*1*). Initially we attempted to grow good single crystals of sodium oxalate, potassium oxalate, potassium binoxalate, and ammonium oxalate from water solution, but we were not successful. We therefore turned our attention to the growth of oxalic acid crystals. The availability of improved equipment for crystal growth and for temperature control provided the opportunity for extensive experimentation.

Anhydrous oxalic acid is dimorphous (*2*). The α-phase (I) is orthorhombic, space group P*cab*. Crystals are dipyramidal in shape with {111} as well as smaller {100}, {001}, and {012} forms. The β-phase (II) is monoclinic with space group $P2_1/c$, and tends to have a prismatic habit.

Oxalic acid dihydrate is monoclinic (*2, 3*) with space group $P2_1/n$. When crystallized from water the habit is tabular with {001} as well as {101} and {110} the predominating forms.

For most of the work reported here we employed temperature-programming methods and conducted the experiments in large crystal baths similar to those described previously (*4*) but modified to accommodate solvents whose high vapor pressure and solvent action precluded the simple polymethylmethacrylate covers used with aqueous solutions.

Figure 1 shows the bath with the modified lid assembly. Two mercury seals (Fig. 2) enclose the growth jar, which is placed within a water thermostat. The lid of the growth jar is made of pyrex glass and has an outer vertical flange as does the growth jar itself. The flanges dip into a pool of mercury contained in a circular trench machined directly into the bakelite lid which covers the surrounding water jacket. A stirrer, the control heaters, and the temperature-sensing probes are placed in the water jacket. The outer mercury seal and the seal at the rotating shaft combine to enclose solutions completely in glass except for the mercury itself, which must be inert toward the solvents employed.

The reversing motor for rotating the crystal tree is attached to and supported by an aluminum yoke which rests on four metal posts fastened to the bakelite lid. A lucite spacer is bolted to the underside of the yoke, then bonded to the glass lid (*5*), to make the rotation mechanism and the lid an integral unit for convenience in assembly.

The aluminum yoke acts as a centering device in placing the flanged lid in the mercury trough and also prevents load being directly applied to the glass lid or the crystal growth jar. Since the growth chamber is completely sealed, it may become necessary (particularly with highly volatile solvents such as acetone) to relieve inside pressure and prevent mercury from overflowing the trough. A short length of small-diameter Teflon tubing, threaded through the mercury seal, maintains the necessary equalized pressure without serious evaporation taking place.

Of many nonaqueous solvents considered for the crystallization of oxalic acid from solution, the majority proved impractical because of insufficient solubility or chemical reaction with the solute. For example, anhydrous oxalic acid is actually reported to crystallize from its solution in sulfuric acid (*6*). However, at the sulfuric acid concentrations required to produce anhydrous oxalic acid as the stable crystallizing phase, decomposition of the solute became pronounced.

Optically clear and well-developed crystals separated in the form of monoclinic prisms from a supersaturated solution of anhydrous oxalic acid in *p*-dioxane. However, the crystals were shown to be a solvate. On exposure to air they disintegrated rapidly to leave a powdery residue.

Anhydrous oxalic acid may be crystallized from its solution in anhydrous acetone. A slow reaction results, however, as can be directly observed by the development of a yellow color in the solution, turning brown on standing for a few days. This is believed to result from an acid-catalyzed condensa-

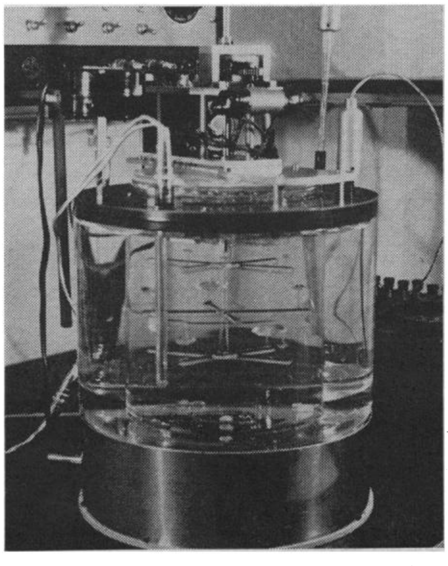


Fig. 1. Equipment for growing crystals from solutions in volatile solvents.

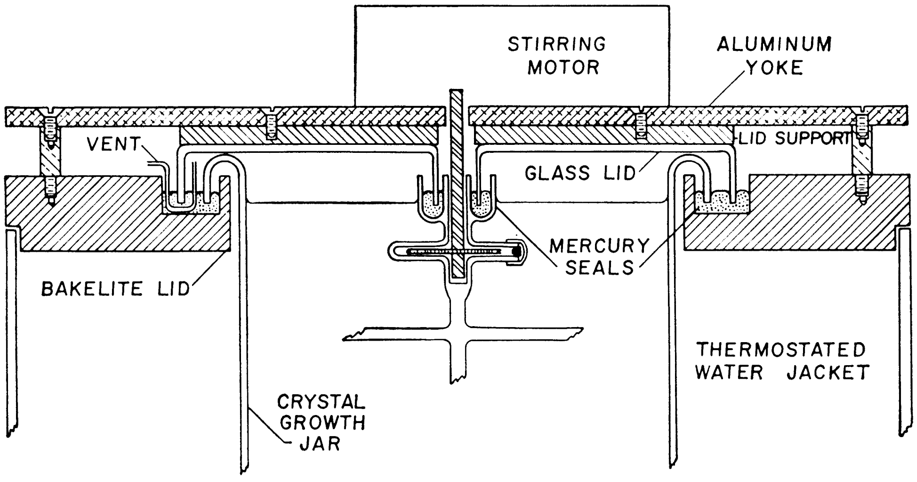
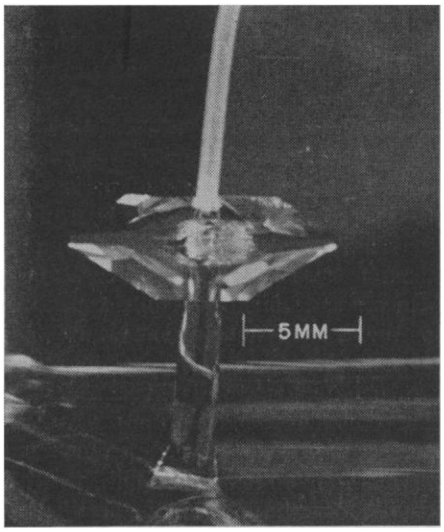


Fig. 2. Section of the sealing cover for the crystal-growth assembly.



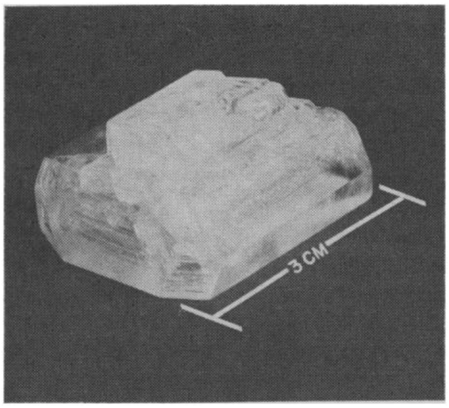


Fig. 3 (left). Anhydrous oxalic acid, α-phase, growing from solution in glacial acetic acid. Fig. 4 (above). Oxalic acid dihydrate crystal grown from water solution.

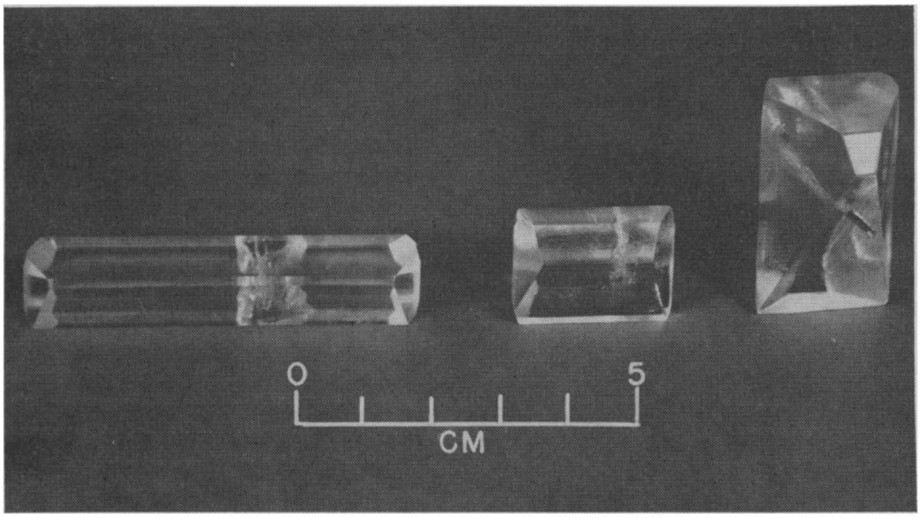
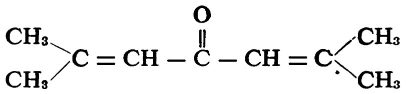


Fig. 5. Single crystals of oxalic acid dihydrate. (Left) Prismatic habit resulting from growth of the crystal from solution in 93 percent acetone, 7 percent water. (Center) Prismatic habit developed in a crystal grown from solution in 75 percent acetone, 25 percent water. (Right) Pinacoidal habit resulting from seed growth in a mixture of acetone and water followed by growth from water solution.

tion (*7*) in which the yellow compound phorone (2,6-dimethyl-2,5-heptadiene-4-one) is formed:



$$(CH_3)_2C=CH-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2$$

Crystals of oxalic acid retain a considerable quantity of this impurity. The addition of water to the solution inhibits the reaction, but the concentrations of water required give rise to the separation of oxalic acid dihydrate as the stable crystallizing phase.

The starting materials used in this investigation were of the highest purity that can be obtained commercially, usually being the analytical reagent grade. Where anhydrous oxalic acid was used it was prepared by vacuum sublimation of oxalic acid dihydrate at temperatures not exceeding 60°C.

Clear, well-developed single crystals of anhydrous oxalic acid were grown from solution in glacial acetic acid. Seed crystals were grown in small crystallizing dishes at temperatures from 45° to 55°C by evaporation of the solvent. When the seeds were of a size convenient for handling (2 to 3 mm in diameter), they were drilled with a single hole (denture burrs of the inverted-cone type serve well) and mounted on single glass pins of a crystal tree.

In accordance with procedures previously described (*4*), the tree and its load of seed crystals were planted in the growth chamber, the solution temperature being slightly above that corresponding to saturation so that the seeds would dissolve a little and misoriented crystallites, which might otherwise lead to polycrystalline growth, would disappear from the surfaces. Beginning usually at temperatures in the range 50° to 55°C, the temperature of the system was slowly lowered (0.015°C per day) to induce and maintain supersaturation as the crystals grew. Figure 3 shows one crystal in an intermediate stage of growth. The crystal shows the habit of the α-phase, with {111}, {100}, and {001} extant.

In this system difficulty was encountered in obtaining single crystals larger than two centimeters in length. Indications that the presence of a small amount of water in the solution would facilitate the growth of the anhydrous phase led to an investigation of phase relationships in the oxalic acid–acetic acid–water system (*8*). Although this study revealed that the anhydrous acid was the stable crystallizing phase in water concentrations up to 5 percent by weight at 50°C, no attempts were made to exploit this information in the growth of large single crystals.

We have been unable to grow good single crystals of oxalic acid dihydrate from pure water solution despite careful attention to detail and rigorous control of temperature and temperature-programming. Seed crystals were prepared in conventional fashion by evaporation of water solvent, then planted in the larger growth chambers and grown by temperature drops not in excess of 0.015°C per day. Experiments were conducted at temperatures near 30°C and near 55°C, but there was no obvious advantage in either temperature region. The crystal shown in Fig. 4 is typical of the specimens we obtained. Polycrystalline growth and inclusions of mother liquor are characteristic of such crystals.

Seed crystals which were prepared by solvent evaporation from solutions in acetone-water mixtures, then grown further from water solution by temperature-programming (linear temperature drop of 0.015°C per day in the temperature range from 42° to 35°C), gave single crystal specimens of greatly improved quality. The crystal at the right in Fig. 5 is typical. Resting on the basal plane in the photograph, the crystal shows the predominance of {001}, {101}, and {110} forms in habit.

From the standpoint of optical clarity, freedom from mother liquor inclusions, and well-developed habit, the best single crystals of oxalic acid dihydrate were grown from solution in acetone-water mixtures by the temperature-dropping technique. Seeds were prepared in a solvent consisting of 75 percent acetone and 25 percent water, with the temperature being in the range from 35° to 30°C. Single crystals of the dihydrate were then grown from solutions in (i) 75 percent acetone and 25 percent water, and (ii) 93 percent acetone and 7 percent water; the latter was prepared by dissolving the dihydrate acid in essentially anhydrous acetone. Resultant typical crystals are shown in Fig. 5. The crystal in the center was grown from the solution with the higher water content; the one at the left, at the lower water concentration.

The three crystals in Fig. 5 are oriented identically with {001} parallel to the surface on which they are placed and [010] in the plane of the picture. Prismatic habit is characteristic of crystals grown from acetone-water mixtures. Growth on {110} is most rapid, with an observable difference in the growth rate on these surfaces in different acetone-water mixtures. The prismatic habit in both cases is defined by {001}, {110}, and {101}. The crystal grown from water solution (Fig. 5, right) shows more rapid growth on {001} and {101}, and again the {001}, {110}, and {101} forms predominate.

The crystals of oxalic acid dihydrate grown from acetone-water mixture are considered to be the best in quality of any produced in this investigation. Portions of several specimens were analyzed by a precise coulometric titration for acidic hydrogen (*9*) to give a stoichiometric composition on this basis of 99.985 percent (standard deviation, 0.001 percent). Flame photometric analyses for lithium and sodium and spectrographic analyses for other alkali, alkaline-earth, and heavy metals indicated the presence of the following impurities: lithium, less than 1 part per million; sodium, 38 to 40 ppm; potassium, less than 1 ppm; rubidium, less than 1 ppm; magnesium, less than 1 ppm; iron, less than 1 ppm; and silicon, less than 1 ppm. Other elements were not detected. The sodium content, accounting for approximately two-thirds of the deviation from stoichiometric composition as based on the titration for acidic hydrogen, does not differ significantly from that contained in the starting material. No explanation of this indicated retention of sodium is apparent at the present time.

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10. We acknowledge the contributions made at early stages in this investigation by Robert Gaither. Appreciation is expressed to Avery T. Horton for his assistance and to George Marinenko for performing the coulometric analyses.

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Clay- and Carbonate-Accumulation Rates in Three South Atlantic Deep-Sea Cores

Abstract. *Three South Atlantic deep sea cores have been dated by the carbon-14 technique, and rates of accumulation of clay and calcium carbonate have been determined. The highest eupelagic clay rates for the Atlantic found to date are in the Argentine Basin, and the lowest are on the Mid-Atlantic Ridge.*

The rates of accumulation of both clay and calcium carbonate components of deep-sea sediments have been determined for a large number of locations in the north and equatorial Atlantic by the method of radiocarbon dating and paleontologic correlation (*1*). Although a few radiocarbon dates exist for the sediments around Antarctica, the sediments in the South Atlantic have not been dated by the radiocarbon technique.

This report includes rates of accumulation for three cores raised by the Lamont Geological Observatory, one from the Argentine Basin (V15-142), one from the Mid-Atlantic Ridge (V16-36), and one from the Walvis Ridge (V12-66). The last two are high carbonate cores (about 90 percent $CaCO_3$), and the usual method of carbon-14 assay of the carbonate was followed. The Argentine Basin sediments are all very low in calcium carbonate but significantly high in organic carbon (about 0.8 percent) so that dates were obtained on the organic matter. There may be some uncertainty about the amount of fossil carbon represented. Because of the homogeneous appearance of these cores down their lengths, the density and calcium carbonate content determined on