Synthetic Zeolites: Growth of Larger Single Crystals

Abstract. *Synthetic zeolites 4A, P, and X were grown in acrylic gel to a size suitable for study of single crystals by x-ray diffraction.*

Crystallographic studies of synthetic zeolites have been impeded by the lack of sufficiently large crystals. When the zeolites are prepared by the usual methods, they normally grow to 5 to 10 μ in size. For single-crystal x-ray diffraction work, a size of at least 50 to 100 μ is required. We have grown synthetic zeolites of such size by a method described by Henisch, Dennis, and Hanoka (*1*); it is illustrated by the following example.

A gel was formed by dissolving, in a Waring blendor, 5 g of Carbopol 934 (*2*) in 100 cm^3 of 1*N* sodium hydroxide solution. A portion of the gel was poured into a ½-inch (12.5-mm) diameter Tygon tube bent to an O-shape (Fig. 1). Aqueous slurries of sodium disilicate nonahydrate and sodium aluminate were poured into opposite ends of the tube, leaving a 30-cm long interdiffusion path through the Carbopol gel. The tube was pinched at both ends by means of hose clamps, sealed with a soldering iron, and placed in a water bath kept at 80° to 90°C. After about 2 weeks, the tube was cut into sections and their contents were washed into a 2-liter beaker; water was added to make the total volume about 1.5 liters. The slurry was stirred for from 30 minutes to 1 hour and allowed to settle before the supernatant was decanted. The procedure was repeated two or three times until only crystalline aluminosilicate was left.

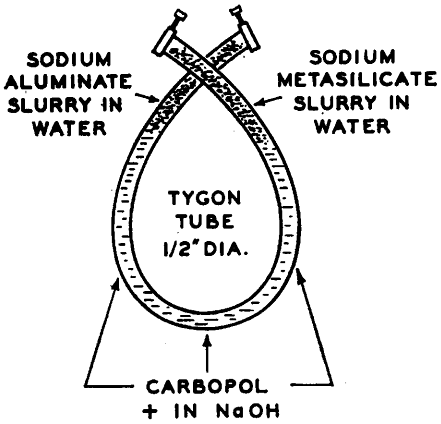

Fig. 1. Gel tube used for preparation of zeolitic crystals.

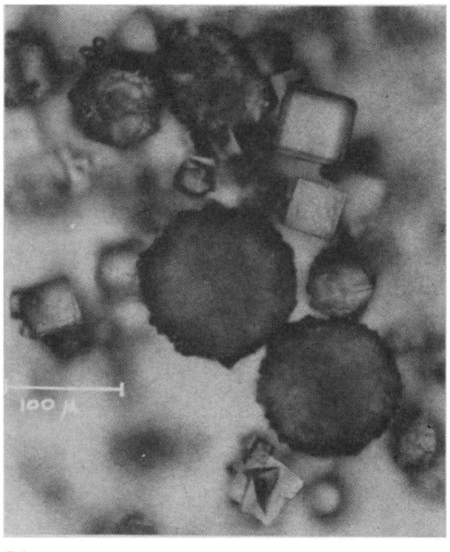

Fig. 2. Barrer species P spherulites and Linde-4A cubes grown in Carbopol gel.

The crystals were examined by optical microscope and by x-ray diffraction methods. Figure 2 shows 110-μ spherulites of Barrer species P and 60-μ cubes of Linde-4A molecular sieve. Hexagonal prisms of gibbsite, 250 μ in diameter and smaller, were also observed in the same batch but do not appear. The largest single 4A crystal that we have yet obtained was 75 μ in size. X-ray diffraction, single-crystal, rotation patterns show sharp reflections characteristic of an excellent single crystal. Acrylamide gel was tried without success, probably because the gel decomposed in the caustic medium.

Other crystallizations were carried out in Carbopol gel, with pyrex glass used instead of Tygon tubes. Three definite zones were identified, each of which contained the zeolitic species expected from the local composition. The 4A crystals in the aluminate-rich zone were numerous and small, probably because of the reaction between solution and glass silica. Faujasite crystals in the middle zone were well-formed octahedra up to 40 μ in size. Polyhedra of Barrer species P up to 150 μ in size were found in the silica-rich zone, but one could not determine whether they were single or twinned crystals.

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2. Soluble acrylic acid polymer; B. F. Goodrich Chemicals Co.
3. Obtained by D. Olson, Central Research Division, Mobil Oil Corp.

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Clathrate Hydrates of Some Amines

Abstract. *A crystallographic study of some alkylamine hydrates establishes that these are polyhedral clathrate hydrates. While the simpler alkylamines form hydrates with water structures related to those of the gas hydrates or the alkylonium salt hydrates, the diethylamine and* tert-*butylamine hydrates have water frameworks forming cages which have not previously been observed in the clathrate hydrates.*

The simpler alkylamines form crystalline hydrates which melt between +5° and −35°C (*1*). The stoichiometry of some of these has led to the suggestion (*2*) that they are clathrate hydrates with water framework structures based on or derived from those found in the gas hydrates or alkylonium salt hydrates. In order to obtain structural evidence concerning the nature of interactions between the amine and water, we have examined the x-ray diffraction data of nine of these hydrates and have carried out complete crystal-structure determinations on two of them. Our results support the inclusion of these compounds in the general class of polyhedral clathrate hydrates and reveal novel geometrical features of water frameworks not previously observed.

The hydrates of ethylamine and dimethylamine (m.p. −7.5° and −16.9°C, respectively) have cubic lattices of dimensions and symmetry which are characteristic of the 12-Å cubic gas hydrates such as $6Cl_2 \cdot 46H_2O$ (*3*). The trimethylamine, *n*-propylamine, and isopropylamine hydrates (m.p. 5.3°, −13.5°, and −4.2°C, respectively) crystallize in hexagonal structures similar in dimensions and symmetry to that of the pseudohexagonal alkylonium salt hydrate $(iso\text{-}C_5H_{11})_4N^+ \cdot F^- \cdot 38H_2O$ (*4*). In these hydrates, the amine molecules appear to enter the water frameworks of the gas hydrates without disrupting their basic structural patterns. Other amine hydrates examined include two hydrates of diethylamine (m.p. −6.6° and −7.0°C), one of *tert*-butylamine (m.p. −1°C), and a second hydrate of *n*-propylamine (incongruently melting). Since these have crystal lattices which are basically dissimilar to those of the clathrate hydrates generally known, complete structure analyses have been carried out on two of them, namely $(C_2H_5)_2NH \cdot 8.67H_2O$ which is orthorhombic, and $(CH_3)_3CNH_2 \cdot 9.75H_2O$ which is cubic. Both these structures are polyhedral clathrate hy-

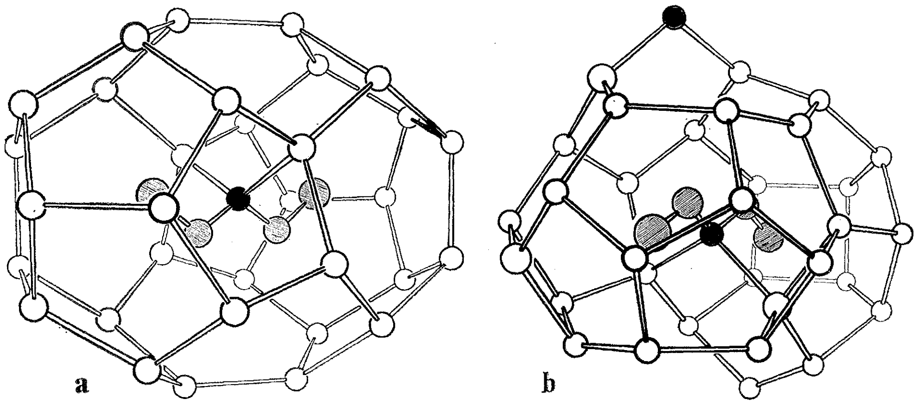

Fig. 1. The polyhedral water cages containing hydrogen-bonded diethylamine molecules in $(C_2H_5)_2NH \cdot 8\frac{2}{3}H_2O$. The shaded circles represent the diethylamine atoms, and the open circles are the hydrogen-bonded water oxygens. Each nitrogen atom (full shading) is hydrogen-bonded to two water molecules. (a) The 18-hedra with its hydrogen-bonded "guest"; (b) the irregular cage, which has three square, eight pentagonal, and six hexagonal faces if the nitrogen atoms are included as vertices.

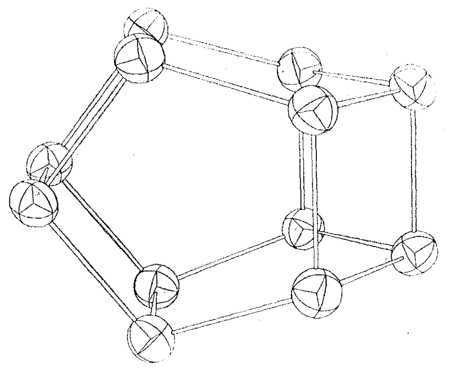

Fig. 2. The 8-hedra in $(CH_3)_3CNH_2 \cdot 9\frac{3}{4}H_2O$. The ellipsoids indicate the thermal motion of the 12 oxygen atoms which are hydrogen-bonded to form this polyhedron with four square and four pentagonal faces. These polyhedra are empty in this structure.

drates, although the familiar $H_{40}O_{20}$ pentagonal dodecahedron, which characterizes the gas hydrates, appears in neither.

The hydrogen-bonded water framework in $12(C_2H_5)_2NH \cdot 104H_2O$ contains two-dimensional networks of face-sharing 18-hedra (we use numerical prefixes to indicate the number of faces on a polyhedron) which have 12 pentagonal and 6 hexagonal faces and 32 oxygen vertices. These networks are linked by additional water molecules, thereby forming "irregular" cages having quadrilateral, pentagonal, and hexagonal faces [compare the structure of $4(n\text{-}C_4H_9)_3S^+F^- \cdot 92H_2O$, where networks of face-sharing pentagonal 12-hedra are interlayered with irregular cages (*5*)]. The diethylamine molecules are enclosed within these cages, with the >NH groups forming hydrogen-bond bridges between oxygen vertices of the water framework. These two cages and their enclosed H-bonded guests are shown (Fig. 1, a and b).

In $16(CH_3)_3CNH_2 \cdot 156H_2O$, the water framework is a three-dimensional space-filling arrangement of 8-hedra and 17-hedra, with cubic symmetry and a 19-Å periodicity. The 8-hedra have four square faces and four pentagonal faces (Fig. 2). The 17-hedra have three heptagonal, two hexagonal, nine pentagonal, and three square faces and 30 oxygen vertices. The amine molecules are located within the 17-hedra as nonbonded guests (Fig. 3, a and b), and the 8-hedra are vacant. This is, therefore, a gas-hydrate-type structure with a geometry which will accommodate guest molecules somewhat larger than those which form the cubic 17-Å gas hydrates, as for example $8(CH_3)_3CH \cdot 136H_2O$ (*6*).

The influence of the amine molecules on the stability and geometry of the water framework which encloses them presents an interesting problem. On the basis of our data, we could suppose that secondary amines act as hydrogen-bonded guests because of their capacity to form two bonds, one as acceptor and one as donor. This enables them to bridge a polyhedral void without seriously disturbing the proton distribution and geometry of the water structure. For a tertiary amine, where the alkyl groups provide more effective shielding of the nitrogen atom, the nonbonded behavior typical of a hydrocarbon guest might be expected. This is supported by the stoichiometric and crystal data for trimethylamine hydrate. The role of the primary amines in these extensively hydrogen-bonded systems may be more subtle. Their unsymmetrical hydrogen-bond function, with potential for two donor and one acceptor bonds, would be difficult to incorporate in the water structure, where there must be competition for the fourfold coordinated framework sites.

However, the evidence (see *6*) that the size of the 16-hedra in the 17-Å cubic hydrate structure is a limiting factor in the formation of gas hydrates from hydrocarbon and halogenated hydrocarbons suggests that the *tert*-butylamine molecules are contributing an additional stabilization factor to the formation of this new cubic gas hydrate.

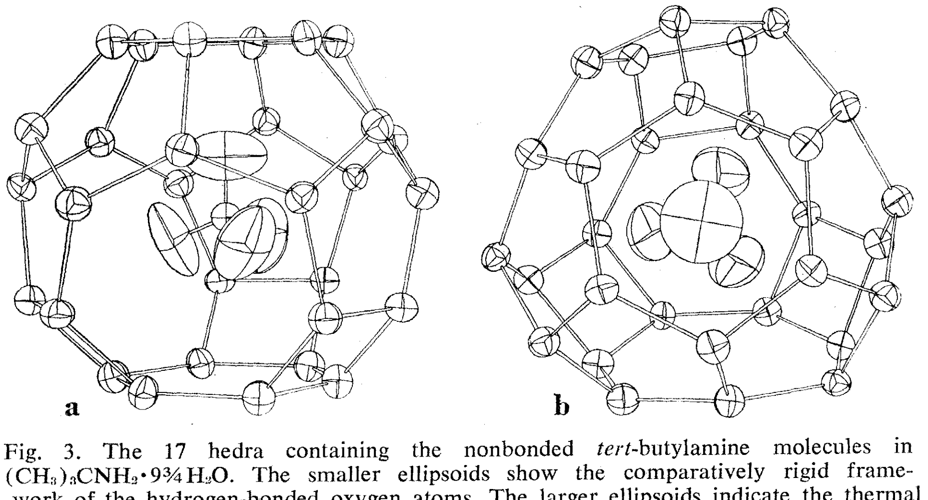

Fig. 3. The 17 hedra containing the nonbonded *tert*-butylamine molecules in $(CH_3)_3CNH_2 \cdot 9\frac{3}{4}H_2O$. The smaller ellipsoids show the comparatively rigid framework of the hydrogen-bonded oxygen atoms. The larger ellipsoids indicate the thermal motion of the guest molecules which appear to be behaving as restricted rotors. (a) General view of the polyhedron approximately normal to its threefold axis, through a heptagonal face, showing the central carbon atoms of the *tert*-butylamine molecule, with the C-N bond vertical. (b) View of the polyhedron approximately down its threefold symmetry axis, where the C-N bond of the guest molecule lies.

It is also conspicuous that, among the nine amine hydrates which we have so far examined, not one has been discovered with the 17-Å cubic structure, which is invariably found with hydrophobic guest molecules containing three to five carbon or halogen atoms.

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7. Supported by the Office of Saline Water, U.S. Department of the Interior, grant 14-01-0001-394. One of us (T.H.J.) expresses his thanks to the NASA for a research fellowship.

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Zinc Retention in Rabbits: Effect of Previous Diet

Abstract. *The retention of orally administered zinc-65 was influenced by the previous diet. Zinc-deficient rabbits fed a diet containing 25 parts of zinc per million incorporated naturally in soybean protein still retained 58 percent of an oral dose of zinc-65 16 days after the dose was given, while rabbits fed the same diet supplemented with zinc (54 parts per million) as zinc oxide retained only 14 percent. The weight gain and the appearance of the animals fed these two diets were different.*

The determination of gamma radiations emitted from the whole animal permits study of the absorption and retention of some major elements. The uptake and retention of orally administered Zn^{65} by four mammalian species was studied by Richmond *et al.* (*1*). The slopes of curves prepared by Furchner and Richmond (*2*) in their studies of the effects of excess dietary zinc were different. These variations were explained as being caused by differences in the species of the animals under study or by excess zinc in their diets. We studied the retention of Zn as it relates to nutritional, dietary zinc deficiency of rabbits during a period before administration of an oral dose of Zn^{65}.

The availability of dietary zinc to animals is in part dependent on the availabilities, for absorption, of zinc from various proteins. Proteins from soybeans, sesame seeds, and cotton seeds contain zinc in a form that apparently cannot be used by animals. Soybean protein has been studied most extensively in this respect (*3*). The evidence indicates that phytic acid present renders the zinc unavailable for absorption. Thus total analysis of the amount of zinc present in food is not a clear index of the amount of zinc absorbed by the body.

Ten weanling, New Zealand white rabbits (average weight, 795 grams) were randomly separated into two groups. One group was fed a low-zinc diet; the other was fed a high-zinc diet. We prepared the low-zinc diet by mixing dried beet pulp, 75 percent; soybean oil meal, 16 percent; cerelose, 2 percent; corn oil, 1 percent; and minerals other than zinc. The concentration of Zn determined by spectrographic analysis was 25 parts per million. In the preparation of the high-zinc diet (54 parts of zinc per million), ZnO was added to the above mixture. The calcium concentration of both diets was made extremely high so that the zinc deficiency would be more easily produced (*4*).

The criteria for judging zinc deficiency were arbitrary since the National Research Council has not determined the amount of zinc required by rabbits; therefore only reduced weight gain and general appearance could be used as signs of deficiency. The two groups of rabbits were fed their respective rations until their weights were definitely different. At this time each rabbit was given an oral dose of Zn^{65}. The dose was administered in a pellet to which radioactive zinc chloride had been added. The specific activity of the dried pellets (25,000 to 50,000 count/min) was determined with a sodium iodide crystal at a distance approximating that to the stomach of a rabbit arranged as it would have been at the outset of the experiment. For counting, an RIDL multichannel analyzer, model 3412, was used. The best geometry was obtained when the rabbit was secured with tape to a wooden frame that had a hole into which the animal's head could be placed. The specific activity of the animals was counted approximately 15 minutes after the dose was administered, this time being designated 0 hours. The specific activity was then counted at 6, 12, 24, and 48 hours, and then after each consecutive 48-hour period until 384 hours had passed. The percentage of Zn^{65} retained was determined and calculated at uniform geometry for all rabbits for each of the counting periods.

Gains in body weight for the two groups were noticeable at 2 days, the difference being greatest at 34 days. For the 34-day period, the rabbits fed the low-zinc ration gained 40 percent less weight than the other group. After the 5th day, the hair of the group fed the low-zinc diet was short and rough, being different from

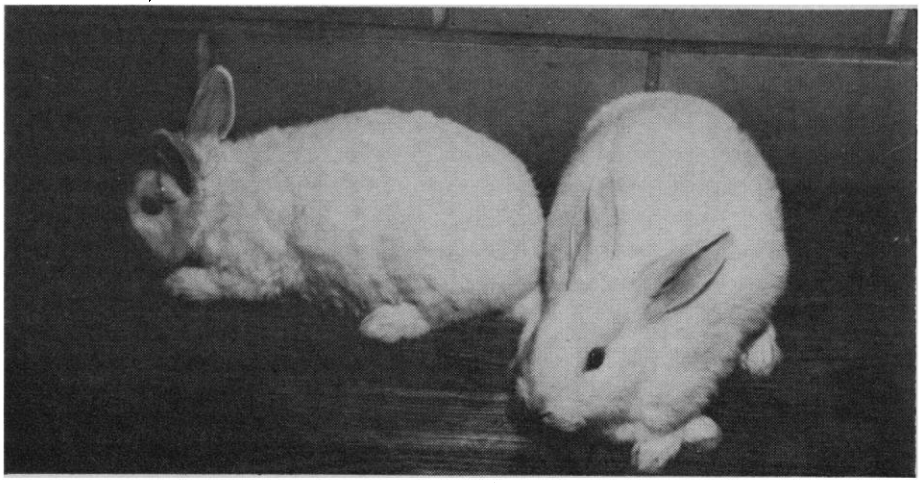

Fig. 1. Rabbits receiving diets differing in available zinc. On the left is the animal fed the low-zinc diet; on the right is that fed the high-zinc diet.