TABLE I

VIBRATION FREQUENCIES IN CM.$^{-1}$

	H_3NOH^+			D_3NOD^+			
	freq.	int.	width	freq.	int.	width	q
a	..	..	...	2980	1	50	...
b	3630	3	60	2620	3	100	1.385
c	3470	7	270	2520	7	110	1.377
d	3240	4	70	2360	5	70	1.373
e	..	..	...	2230	4	40	...
f	2960	5	100	2150	4	60	1.377
g	2700	2	80	2035	2	50	1.327
h	2000?	0	120	1430	0	60	...
i	1618	3	50	1195	2	30	1.354
k	1519	3	40	1138	3	40	1.335
l	1197	2	50	880	2	30	1.360
m	1005	10	...	987	8	...	1.018

The bands *b* and *c* overlap. Error of frequency *m*: ±1 cm.$^{-1}$.

Ananthakrishnan. The bands *b*, *c*, *d*, and *i* are to be attributed to the solvent. One has to assume, however, that the stretching and bending vibrations of the hydroxyl group are covered by *c* and *i*.

If the hydroxyl vibrations are disregarded and the hydroxyl group considered a mechanical unit, a simplified model of the symmetry C_{3v} is obtained. The bands *f* and *g* represent the totally symmetric and degenerate NH stretching vibrations, *k* and *l* the corresponding bending vibrations. Line *m* is known to represent the vibration of the NH_3 group against the OH group.

The correlations of the lines of the light and heavy compounds are based on the fact that $1 < q < \sqrt{2}$, and on the intensities. No arbitrary choice is left in the correlations.

Band *h* of the light compound, 2000 cm.$^{-1}$, appeared only on one spectrum and is uncertain. No correlation with 1430 cm.$^{-1}$ of the heavy substance is suggested. The latter frequency also appeared only on one heavily exposed spectrum; it might be due to the small amount of HOD present in the solution. The weak band *a* probably corresponds to a vibration of D_2HNOD^+. The low intensity of this band and the absence of any water band of higher frequency indicate that only little hydrogen was present.

In the case of bromoform,[4] the appearance of an entirely new line in the spectrum of the deuterium compound could be explained without any doubt by accidental degeneracy. A similar explanation will be expected for band *e*. The last column of Table I indicates that this band must be due to the combination of a hydrogen frequency with the frequency $m = 987$ cm.$^{-1}$ since otherwise the accidental degeneracy would occur also in the light compound. The combination $i + m = 2182$, and a fundamental of approximately the same frequency can be made responsible for the bands *e* and *f* of the heavy compound. No other combination furnishes a satisfactory representation of the data. This interpretation supports the assumption that band *i* is produced not only by water but also by the hydroxyl group of the hydroxylammonium ion.

Summary

The Raman spectra of the light and heavy hydroxylammonium ions have been measured and interpreted.

[4] O. Redlich and W. Stricks, *Sits. Ber. Akad. Wiss. Wien.*, IIb, **146**, 77 (1936), or *Monatsh.*, **67**, 213 (1936).

PULLMAN, WASHINGTON RECEIVED MARCH 6, 1945

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY, WASHINGTON, D. C.]

Habit Modification of Ammonium Dihydrogen Phosphate Crystals during Growth from Solution

BY HARRY J. KOLB AND JOSEPH J. COMER

Introduction

Adsorption at the crystal–solution interface is far from the stage in development which adsorption at the gas–solid interface has reached. It appeared desirable to make further investigations which might lead to more information on this type of adsorption. Previous investigations of adsorption at the crystal–solution interface with subsequent modification in crystal habit have been excellently reviewed by W. G. France,[1] who has made most of the contributions to the field in this country. But because of the lack of knowledge as to the mechanism of the crystal modifications, due in a large part to the relative complexity of concentrated ionic solution chemistry in general, a survey was made for crystals whose structures are well-known and might yield interesting data in adsorption studies. Ammonium dihydrogen phosphate was selected with others, primarily because of its relatively simple crystal habit under normal conditions. Experiments have now been completed on the growth of this crystal in the presence of foreign metal ions.

Experimental

Ammonium dihydrogen phosphate crystals were grown in a large water-bath, the temperature of which could be maintained constant to ±0.1°. Eight stainless steel tanks were placed on two aluminum trays in the bath. Each tank was filled with ammonium dihydrogen phosphate solution and the thermostat then set at the saturation

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[1] Alexander, "Colloid Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, Vol. 5, p. 443.

temperature of the solution. The foreign cations were added to the tanks as nitrates or chlorides. (It had been observed that nitrate and chloride ions did not noticeably influence the habit of the ammonium dihydrogen phosphate crystal.) Seed crystals were approximately 1 sq. cm. in the z-plane and 2 cm. along the z-axis for the general tests; dimensions of the seeds were 6 sq. cm. by 8 cm. for the concentration *vs.* tapering studies with aluminum, chromic, and stannic ions. Seeds were suspended in the tanks at the ends of Lucite rods. The trays were then rocked mechanically, and the growth of the crystals proceeded by manual reduction of the bath temperature at the rate of 0.2° per day.

The experimental data were often complicated by failure of the foreign ions to remain in solution at the high phosphate concentrations involved in the growing process. By adjusting the pH with phosphoric acid, the metal phosphate precipitate could sometimes be avoided. (Phosphoric acid had also been observed to produce no measurable tapering effect on the habit of the crystals.) In several cases which appeared to give promise of good adsorption data, it was impossible to prevent the entire lot of foreign cation from precipitating as one of the insoluble phosphates.

Experimental Results

The natural crystal habit of ammonium dihydrogen phosphate is shown in Fig. 1a. The shape is that of a second order prism in combination with a second order bipyramid; the angles between the prism sides and pyramidal faces are 45°. The growth of the crystal from the supersaturated solution proceeds normally along the z-axis with the deposition of the salt on the pyramidal faces.

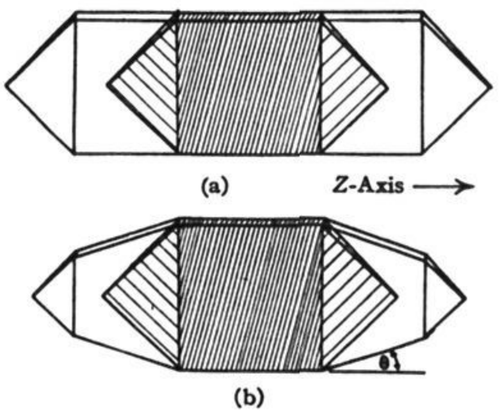

Fig. 1.—Crystal habit of ammonium dihydrogen phosphate: (a) normal, (b) tapered by cation adsorption. Shaded areas denote original seeds.

When certain foreign cations are added to the ammonium dihydrogen phosphate solution, the prism sides of a growing crystal taper toward the z-axis, and if the crystal is removed from the solution before the four sides meet, the pyramids can be observed at the end of the tapered crystal. The diagram of a tapered crystal, where addition of cations to the solution has influenced the habit, is shown in Fig. 1b.

Figure 2 shows several of the tapered crystals which have been cut perpendicular to the z-axis at the midpoint of the crystal. The discarded halves of these crystals are mirror images of those shown in the photograph. The two crystals grown in solutions containing Tl^+ and Ba^{++} were not tapered but were included in the photograph for comparison with tapered crystals.

The foreign cations which were added to the ammonium dihydrogen phosphate solution are listed as follows: Sn^{++++}, Au^{+++}, Be^{++}, Fe^{+++}, Al^{+++}, Cr^{+++}, Ti^{++++}, Hg^{++}, Cu^{++}, Zn^{++}, Pb^{++}, Ni^{++}, Ag^+, Ca^{++}, Ba^{++}, Tl^+, K^+, and Na^+. Those cations which produced tapered sides are listed in Table I. All the remaining cations which had no effect on the crystal were added in quantities of 2 g./liter. Cations of zirconium nitrate and thorium nitrate formed such extremely insoluble precipitates with constituents of the phosphate solution that they have been omitted from the above list. Co^{++} did not exist because of the formation and stability of $Co(NH_3)_6{}^{+++}$, even in acid solution. The angle, θ,

TABLE I

CATIONS WHICH TAPERED SIDES OF $NH_4H_2PO_4$ CRYSTALS

Cations which produced tapered sides	Moles/liter of ion added	θ
Sn^{++++}	4.4×10^{-5}	.7
Cr^{+++}	1.8×10^{-3}	16
Fe^{+++}	1.8×10^{-3}	6.5
Ti^{++++}	2.0×10^{-3}	4
Au^{+++}	2.0×10^{-3}	2
Al^{+++}	4.0×10^{-3}	2
Be^{++}	1.1×10^{-2}	7

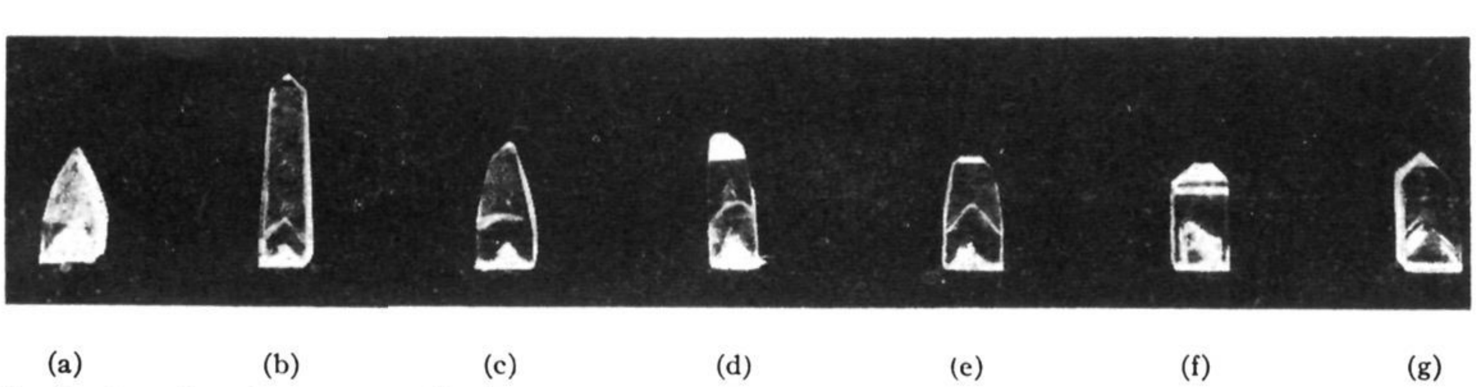
(a) (b) (c) (d) (e) (f) (g)

Fig. 2.—Tapering of ammonium dihydrogen phosphate crystals by the addition of metal ions to solution: (a) Sn^{++++}, 0.02 g./l.; (b) Sn^{++++}, 0.003 g./l.; (c) Ti^{++++}, 1.0 g./l.; (d) Ti^{++++}, 0.1 g./l.; (e) Be^{++}, 0.1 g./l.; (f) Tl^+, 2.0 g./l.; (g) Ba^{++}, 2.0 g./l.

called the degree of tapering in Table I, is shown in Fig. 1b. Ti^{++++} might have been replaced by TiO^{++} in Table I, but since evidence as to the exact nature of the ions is lacking in our case, it seemed justifiable to list them all uniformly.

Concentration *vs.* degree of tapering studies were conducted for aluminum, chromic and stannic ions at approximately 40°. The data for each ionic type have been graphed as an isotherm in Fig. 3. The experimental details for these data will be reported later.[2]

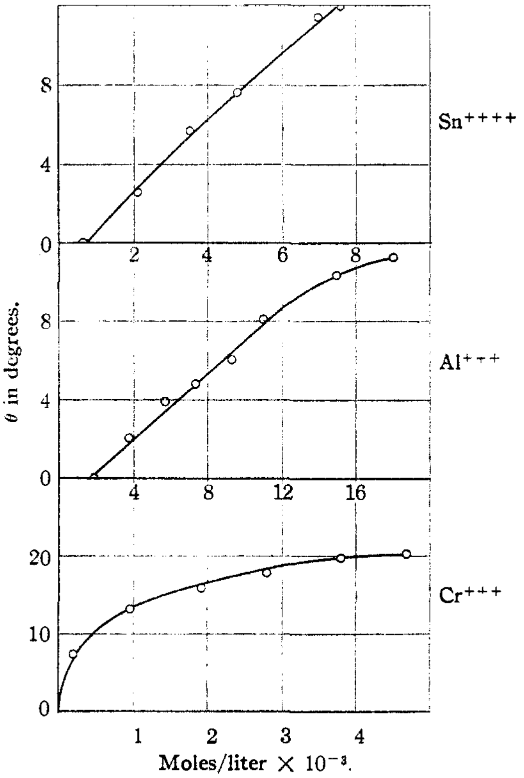

Fig. 3.—Tapering of ammonium dihydrogen phosphate crystals *vs.* concentration of metal ions.

Discussion

The adsorption of the metal ions is thought to produce the tapering in the crystal and is presumably caused by attraction of the ions in the crystal lattice. If the reader will refer to the list of cations tested (in the experimental part), he will note that the ions have been listed in order of increasing solubility product of the hydroxide. Furthermore, the cations which produce crystal tapering head this list. This insoluble hydroxide correlation is pointed out because of the scarcity of data on metal phosphate solubility. It is assumed, however, that correlation of the K_{sp}s of the phosphate, hydrogen phosphate, or dihydrogen phosphate and adsorption would be more appropriate if these K_{sp} values existed. It seems reasonable to assume, however, that there should be some similarity between a list of metal phosphate and metal hydroxide solubility products even though the similarity may be qualitative only. The ions producing the tapered crystal are also those of higher charge and smaller radius. However, one would expect to find a general correlation between increasing charge and decreasing radius and decreasing solubility products of hydroxides and phosphates. Stannic ion, which heads the K_{sp} list, does produce more tapering than any of the other ions at a given concentration, but a rearrangement of several of the other cations in the list (see Table I), is necessary before a true relationship exists between amount of tapering and the cations at the same concentration. One would not expect a sharp break between the metal ions which do and do not cause tapering. However, there is an apparent break because of the limited solubilities of most of the ions below titanic ion in the ammonium dihydrogen phosphate solution. During the experimentation, it was found that auric chloride just reached the concentration necessary to produce measurable tapering as the metal ions started to precipitate. The other metal ions at the head of the list and in Table I also precipitated during the experimental runs but not before the ionic concentrations became high enough to cause appreciable tapering. Whenever the precipitation started, no further addition of metal ions could increase the angle of tapering.

Further evidence to support the adsorption theory can be obtained from the crystal structure of ammonium dihydrogen phosphate,[3] whose space group is $D_{2d}^{12}(V_d^{12})$ [Schoenflies]. Table II gives the reticular densities of the crystal planes using the area per phosphate in the *z*-plane as the unit area. It is obvious that the prism sides [(100) and (010) planes] contain the highest phosphate reticular density whereas the *z*-plane (001) has the least phosphate reticular density. The pyramidal faces [(101) and (011) planes] have alternate phosphate and ammonium layers, with the phosphate reticular density of alternate layers between the values of the prism sides and *z*-plane (001). Adsorption should be greatest

TABLE II

RETICULAR DENSITIES OF $NH_4H_2PO_4$ PLANES

Plane	$H_2PO_4^-$ per unit area	NH_4^+ per unit area
001	1	1
002	1	1
010	2	2
020	2	2
100	2	2
200	2	2
101	$\sqrt{2}$	0
202	0	$\sqrt{2}$
011	$\sqrt{2}$	0
022	0	$\sqrt{2}$

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(2) To be published.

(3) Hassel, *Z. Elektrochem.*, **31**, 523 (1925); Hendricks, *Am. J. Sci.*, **14**, 269 (1927); West, *Z. Krist.*, **74**, 306 (1930).

on the prism sides where the phosphate surface density is always greater than on the pyramidal faces. However, one would expect the greater surface density of the prism sides to extend their influence slightly beyond the intersections of the (100) and (010) planes with the (101) and (011) planes, respectively. Thus this extension effect could very easily account for the tapering phenomenon observed in experiment.

Figure 4 represents a submicroscopic picture of a crystal and illustrates how the adsorption on the prism sides might cause tapering. Since the metal ion adsorption is strongest at the sides and along the (100) and (101) intersections, it is necessary for the growth of successive layers to deposit at a slight distance in from the intersection of the (101) plane with the (100) plane. Hence the submicroscopic picture would be step-like as shown in Fig. 4. Macroscopically the minute steps would be unnoticed and the adsorption would give a smooth tapered effect. The greater the concentration of the metal ions, the more these ions will hinder the deposition of the crystal constituents and hence the steeper the step-like formation will become.

Eventually the metal ion concentration will become large enough to inhibit the growth normal to the (101) and (011) planes. This was actually verified by experiments with stannic and chromic ions. At high concentrations of the metal ions, growth has been completely inhibited on seed crystals for a 5° temperature drop (with constant agitation). Eventually the solutions became so supersaturated that the salt deposited in fine "snow flurries." Dissolution of the seed did not occur at any time during these experimental runs. This fact verified the supersaturation effect since adsorption could inhibit crystal growth but did not inhibit the dissolving process. These inhibited crystals grew normally when removed to another saturated solution free of the metal ions.

The pyramidal planes of the crystal are occupied by alternate layers of positive and negative ions, whereas the planes which make up the prism sides consist of equal quantities of both positive and negative ions. Hence if the charge in a crystal plane were the major attraction for the metal ions, the pyramidal faces would be expected to show maximum adsorption. Inhibition of the crystal growth would probably then take place before tapering. But occurrence of the reverse effect lends support to the above explanation for tapering of the ammonium dihydrogen phosphate crystals.

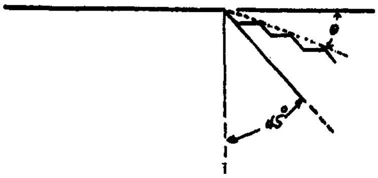

Fig. 4.—Diagram to illustrate how step-like growth on (101) and (011) planes could give the observed tapering of ammonium dihydrogen phosphate crystal.

The isotherms in Fig. 3 are represented by the formula

$$\theta = am_{+}/(1 + bm_{+}) \qquad (1)$$

where θ is angle of tapering, m_{+} is moles per liter of metal ion, and a, b are constants. It will be noted that these isotherms are similar to the adsorption isotherms for monolayers at gas–solid interfaces. But it has been found that the degree of tapering depends not only on the type of ions and concentration of the ions but also on the agitation and temperature drop. The investigation of all these effects for several metal ions is being completed, and a more thorough discussion of equation (1) will follow.[2] However, the curves in Fig. 3 have been included in this paper to illustrate the very pronounced differences in the degree of tapering for different ionic types at a given concentration and to indicate their similarity to other adsorption isotherms.

Summary

1. Experimental data on the habit modification of ammonium dihydrogen phosphate crystals by various metal ions are reported.

2. The habit modification is explained by adsorption of foreign metal ions on the crystal surface, and it is suggested that the degree of tapering may be correlated with the solubility product of the metal hydroxide.

3. Reticular densities of the ammonium dihydrogen phosphate crystal planes are presented to illustrate the compatibility of the adsorption theory with the crystal structure.

4. Quantitative data for the habit modification of the ammonium dihydrogen phosphate crystal over a range of concentrations of aluminum, chromic and stannic ions are reported.

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