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Author(s)	TANIKAWA, Eiichi; NAGASAWA, Yoshio; SUGIYAMA, Takashi
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THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS

II. Solubility of struvite formed in canned sea foods and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals synthesized in laboratory

Eiichi TANIKAWA, Yoshio NAGASAWA and Takashi SUGIYAMA
Faculty of Fisheries, Hokkaido University

The solubility of a solid in solvents is influenced by many factors, *e.g.*, by temperature or the nature of the solvent, etc. If other conditions are kept constant, the solubility of a solid depends on the temperature. As saturated solutions involve respective amounts of the solute in equilibrium to temperature, the solid crystallizes out with the evaporation of the solvent or the lowering of temperature of the solution and this crystallizing continues until the solution reaches equilibrium with the solubility at a given temperature. The pH of the solution also influences the solubility of the solid.

The authors have studied the solubility of struvite formed in canned crab and that of crystals of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ synthesized in the laboratory, at various temperatures and pH values.

1. Solubility of crystals at various temperatures

(1) *Sample*

Two kinds of samples were employed as follows.

- (a) Struvite crystals (particles) of about 1.3~5.0 mm in size which were found in canned crab.
- (b) Synthesized crystals of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ which were prepared in the authors' laboratory

(2) *Experimental method*

An apparatus that is shown in Fig. 1 was employed for the experiment. Each 0.1 g of the samples was put into 100 cc of redistilled water in a large test tube (160 cc volume) which was kept in water in a thermostat within a temperature difference of $\pm 0.2^\circ\text{C}$. After stirring the solvent containing crystal for 30 minutes at each of the given temperatures, the authors took 50 cc of the filtrate with a pipette as soon as the dissolved solution had been

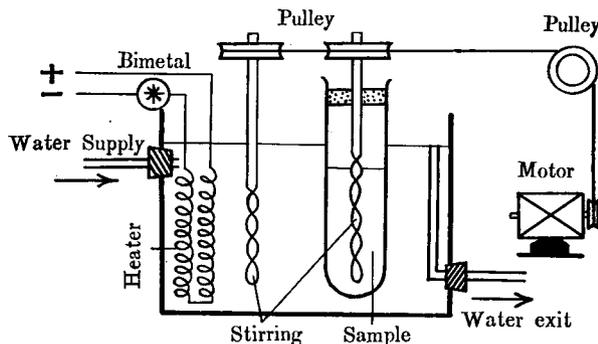


Fig. 1. Apparatus employed for estimating the solubility of the crystals

filtered through a filter paper (Toyo Filter Paper Co. No. 5) in a hot water jacket funnel of the same temperature as the above-described thermostat.

The amount of Mg in the filtrate was measured as follows: Mg in the solution was precipitated as oxine compound by addition of 2 cc of 95 % alcoholic solution of 2 % 8-hydroxyquinoline. The precipitate obtained was dissolved with HCl, to which N/10 KBrO₃ had been added. The excess quantity of KBrO₃ was titrated back with N/10 Na₂S₂O₃. The solubility of the crystal was calculated from the measured amount of Mg.

The reason that the stirring time was 30 minutes in this experiment was that there is no difference whether the stirring time is 30, 60, 90 minutes or 24 hours. That is to say, the solubility was known to reach equilibrium by stirring of 30 minutes.

(3) Experimental results

The range of the temperature at which solubilities were estimated was from 20° to 85°C. The range of the temperature for the crystal synthesized in the laboratory was from 0° to 100°C.

The variations of the solubilities of both kinds of crystals at various temperatures are shown as Tables 1 and 2. The results in Tables 1 and 2 are shown as Figs. 2 and 3.

As seen in these figures, there was some difference in the solubilities of struvite formed in canned crab and those of the synthesized crystal. The solubility of the former is largest at about 65°C, and decreased with the heightening or lowering of the temperature. The solubility of the latter is the largest at 40°~50°C, and it decreased with the heightening or lowering of the temperature. The difference of the solubilities of both crystals seems to be due to the density or to the size of the crystal. However, the solubilities of the two kinds of crystals are small at various temperatures.

At any rate, the solubility of the crystal is the largest at 40°~65°C, and decreases

Table 1. Solubility of struvite at various temperatures

Measuring temp. (°C)	20	25	30	35	40	50	55	60	65	75	85
The amount of magnesium (%)	—	0.025	0.030	0.05	0.072	0.110	0.180	0.210	0.220	0.110	0.072
Solubility of the struvite (%)	—	0.28	0.33	0.57	0.78	1.20	2.00	2.30	2.40	1.20	0.79

Table 2. Solubility of the synthesized crystal of MgNH₄PO₄·6H₂O at various temperatures

Measuring temp. (°C)	0	10	20	30	40	50	60	70	80	90	100
The amount of magnesium (%)	0.109	0.131	0.182	0.248	0.306	0.306	0.270	0.282	0.210	0.168	0.080
Solubility of crystal synthesized (%)	1.09	1.32	1.84	2.51	3.09	3.09	2.73	2.85	2.12	1.70	0.81

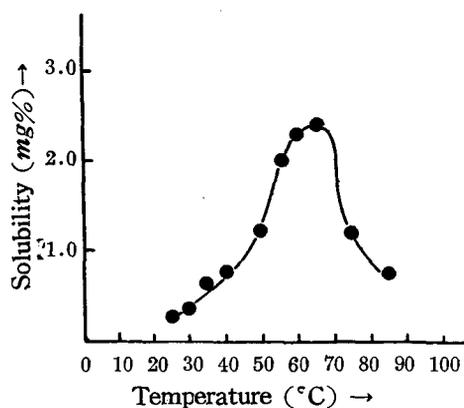


Fig. 2. Solubility of the struvite at various temperatures

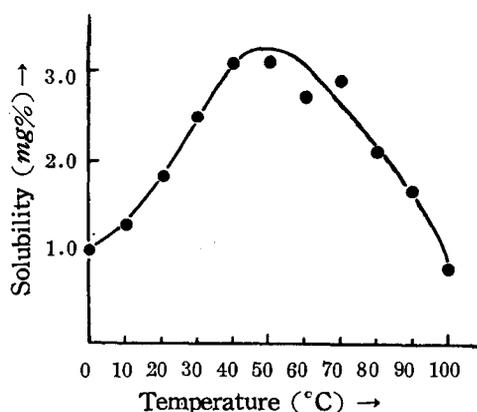


Fig. 3. Solubility of the synthesized crystal of $MgNH_4PO_4 \cdot 6H_2O$ at various temperatures

with the heightening or lowering of temperature. The solubilities of chemical compounds decrease generally with lowering of temperature and increase with heightening of temperature. In this experiment, the solubility decreased with heightening of temperature, so these results were considered to be due to some reason. Accordingly the authors have repeated the experiment two or three times, but the same results were obtained.

2. Variation in the proportion of the insoluble part of the crystal at various temperatures

The authors have ascertained futhermore the variation of the solubilities of synthesized crystal by measuring the amount of magnesium in the insoluble part of the crystal on the filter paper which was treated by the same method as previously described at various temperatures.

The variation in the proportion of the insoluble part of the crystal was manifested by the ratio (%) of the amount of magnesium in insoluble part of the crystal to the total amount of magnesium in the crystal employed.

Table 3. Variation in the proportions of insoluble part of the synthesized crystal at various temperatures

Measuring temp. (°C)	0	10	20	30	40	50	60	70	80	90	100
The amount of total magnesium (mg)	55.9	50.2	62.7	50.2	55.3	42.4	56.9	59.2	62.1	52.5	58.3
The amount of insoluble magnesium (mg)	54.8	48.9	60.9	47.7	52.2	39.3	39.3	56.4	60.1	50.9	57.5
Insoluble Mg Total Mg × 100	98.1	97.5	97.2	95.0	94.4	92.7	94.6	95.2	96.8	97.2	98.7

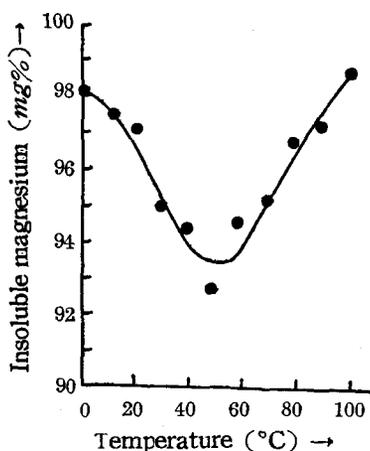


Fig. II-4. Changes in the amounts of insoluble magnesium in various temperatures

remarkably.

The authors have calculated the difference of the solubility at various ranges of temperatures from Table 2, as shown in Table 4.

Table 4 The difference of the solubility at each range of temperatures

Range of temperatures (°C)	100° ↓ 90°	90° ↓ 80°	80° ↓ 70°	70° ↓ 60°	60° ↓ 50°	50° ↓ 40°	40° ↓ 30°	30° ↓ 20°	20° ↓ 10°	10° ↓ 0°
The difference of the solubility	+0.91	+0.42	+0.73	-0.12 (?)	+0.36	0	-0.18	-0.67	-0.52	-0.23

(Note) In this table + shows increasing of the solubility with the lowering of the temperature, and - shows decreasing.

The difference of the solubility of the crystal which occurs by lowering of temperature from the upper limit temperature in each range of the temperatures, increased until 50°C and decreased below 50°. This is because the maximum solubility is at about 50°C.

As above stated, the solubility decreased above 50°C. That is to say, the crystallization becomes easy. However, the shape of the crystal crystallized out above 50°C was amorphous and it was needle-shape below 50°C. (Ref. the next report). Considering the crystallization below 50°C, the differences of the solubilities between 30°~20°C and 20°~10°C were large being largest at from 30° to 20°C. That is to say, in this latter range the crystallization is the easiest.

3. The difference of the solubilities due to the hydrogen ion concentration of the solvent

Many investigations¹⁾ have shown that the struvite obtained from the canned sea foods

is easily dissolved by acids and then is soluble in gastric juice, so it is harmless for human beings. The authors have observed the variation of the solubilities of struvite formed in canned crab and the synthesized crystal at various pH values.

(1) *Experimental method*

The pH values of the solution in which crystals were to be dissolved were adjusted by Walpole's buffer solution²⁾ (acetic acid-acetate solution: pH 3.0~5.6) and Palitzsch's buffer solution³⁾ (boric acid-borate solution: pH 6.7~9.0). The temperature at which the solubilities at various values of pH were estimated was 30°C. The method of estimation was the same as that described above in Articles 1 and 2.

(2) *Experimental results*

The experimental results concerned with the influence of pH of solvent upon the solubility of the crystals are shown in Tables 5, 6 and Figs. 5, 6.

Table 5. Solubility of the struvite in solvents of various pH values

pH	3.0	3.2	3.6	3.8	4.0	4.2	4.6	5.0	5.4	6.7	7.0	7.6	8.0	8.5	9.0
The amount of magnesium(%)	2.4	1.9	1.9	0.59	0.59	0.44	—	0.35	—	0.43	0.39	0.29	0.07	0.04	0.02
Solubility of struvite (%)	26	20	20	6.5	6.5	4.8	—	3.9	—	4.7	4.2	3.2	0.8	0.5	0.2

Table 6. Solubility of the synthesized crystal of $MgNH_4PO_4 \cdot 6H_2O$ in solvents of various pH values

pH	3.0	3.5	4.0	4.5	5.0	5.5	6.0	7.0	7.5	8.0
The amount of magnesium (%)	3.2	3.5	0.49	0.40	0.40	0.24	0.59	—	0.11	0.08
Solubility of crystal synthesized (%)	35	39	5.3	4.4	4.4	2.4	6.0	—	1.2	0.9

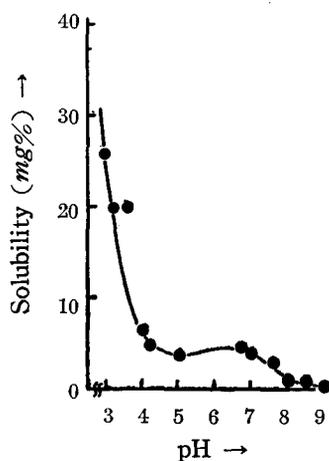


Fig. 5. Solubility of the struvite in solvents of various pH values

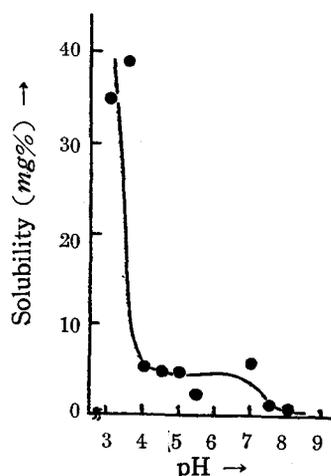


Fig. 6. Solubility of the synthesized crystal of $MgNH_4PO_4 \cdot 6H_2O$ in solvents of various pH values

As seen in Figs. 5 and 6, the solubility varies with the pH of the solvent. The solubility is comparatively larger in acidic side beyond pH 4.0, and smaller in alkali side beyond the same value of pH. That is to say, the solid crystallizes easily in alkali side beyond pH 4.0.

Summary

The solubilities of the struvite formed in canned crab and the synthesized crystal of $MgNH_4PO_4 \cdot 6H_2O$ are the largest at 65°C (struvite) and 50°~40°C (synthesized crystal). The solubility decreased with heightening above or lowering below those temperatures. The crystallization was easy below 50°C and the crystals formed were needle-shape. But the crystals formed above 50°C were amorphous. The easiest crystallization occurs within the range of 30°→20°C owing to the remarkable difference of the solubility. The solubility of the crystal becomes smaller with the increasing of pH value (alkali side beyond pH 4.0).

That is to say, if the juice of the content of canned sea foods is in alkali side beyond pH 4.0, the crystal will be easily formed.

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