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THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS

VII. The formation of the separated microscopical crystal and its incipient growth

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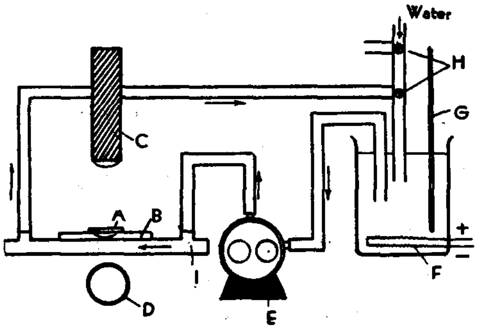
In the previous papers of this series,1)2,3) the authors have reported investigations on the various conditions influencing the crystallization and the growth of crystals in Petri-dishes or test tubes. In those experiments, the state of crystals as they approached the final condition could be only observed. Therefore it was impossible to discuss all stages except only the final state of the crystals as they were formed in the test tube or Petri-dish. In this paper the authors record their investigation of various factors influencing the crystallization and the growing process of the same separated crystal under a microscope.

During the cooling process of the mixed solution, the velocity of the growth and the variation of the size of the crystals were observed under a microscope.

1. The velocity of growth of the crystals as influenced by the cooling velocity of the true solution

1) Experimental method

Each 0.01 Mol solutions of magnesia mixture (A solution) and sodium phosphate (B solution) were prepared as described in paper III1). Each 0.1 *cc* of B solution was taken onto a hole glass which was kept at 75°∼80 °C by a small hot-water tank shown as Fig. 1, and then 0.1 *cc* of A solution was added and mixed.



Note: A = cover glass, B = hole glass,
C = microscope, D = mirror,
E = gear-pump, F = heater,
G = thermometer, H = stop cock,
I = small hot-water tank

Fig. 1. An apparatus for regulating the temperature of a hole glass

Next, water of various definite temperatures was made to circulate through the tank and the hole glass was kept at definite temperature. Thus the cooling velocity was changed at will. The condition of crystallization and the growing velocity at various velocities of cooling were observed.

2) Experimental results

At various cooling temperatures, the mean growing velocity of *c* axis and *a* axis indicated in Fig. 2 at the difference of

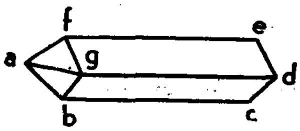


Fig. 2. Name of the crystalline axis
$\overline{bf}=\overline{ce}=a$ axis $\overline{ad}=c$ axis

10 °C, $\bar{L}=\frac{L_1-L_0}{t}$ (μ/min.), in the cooling process was calculated from the growth of the crystal, L_1-L_0; the results are shown as Table 1. Here, L_0 is the initial length of the axis of the crystal; L_1, is the length of the axis of the grown crystal after t minutes; t is the time necessary to lower the temperature by 10 °C.

Table 1. Mean growing velocities of the crystals at various temperatures differing by 10 °C (μ/min.)

Temperature	Above 70° C	70°→60°	60°→50°	50°→40°	40°→30°	30°→20°
c axis ($\overline{ad}$)	3.25	3.14	2.48	5.35	1.85	0.91
a axis ($\overline{bf}$)	0	0.63	0.41	1.84	0.14	0.08

The cooling velocity is manifested by the equation: $\bar{\theta}=\Delta\theta/\Delta t$ (°C/min.).

Here, θ (°C) is the descending of temperature in t minutes. The relations between $\bar{\theta}$ and $\bar{L}$ are shown as Tables 1, 2 and Fig. 3.

As seen in Table 1, the mean growing velocity for the difference of 10 °C at various temperatures within the range of 20° ~ 70 °C at various temperature was maximum at the range of 40° ~ 50°C for *c* axis and *a* axis.

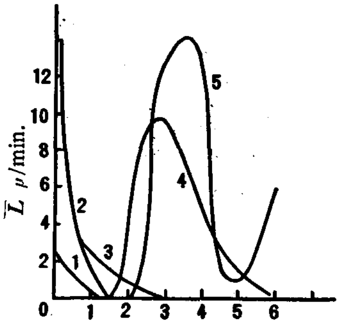


Fig. 3. Relation between the values of $\bar{\theta}$ and $\bar{L}$

As seen in Table 2, when 0.01 Mol solutions each of A and B were mixed at 75° ~ 80 °C, and then the temperature of the mixed solution was made to fall, the amorphous minute crystals generated above 70° ~ 80 °C. But microcrystals (10~20×5~10μ) which can be found under a microscope by crystal surface and shape of the crystals generated at 60° ~ 70 °C. At temperatures below 50 °C visible crystals can be observed. This fact agreed with the result described in the previous paper, Report III1), which was obtained in the combination of the component ions in test tubes. Especially, the crystals formed in the range of 50° ~ 30 °C are larger than those at other temperatures. This fact agreed with the thought of the authors to call this range the **"Zone of the formation of large crystals"**. The relation between the cooling velocity and the mean growing velocity varied with the range of the difference of the temperature. Above 60 °C, the relation was not remarkable, but in the range of 40° ~ 50 °C and 40° ~ 30 °C the relation was remarkably found. When the velocity of cooling was small, the growing velocity of the crystals was found to be large.

Table 2. Relation between the cooling velocity ($\bar{\theta}$) and the mean growing velocity of the crystals ($\bar{L}$)

Range of temperature	Sample No.	Cooling velocity (°C/min.)	Mean growing velocity (μ/min.)	
			c axis	*a* axis
Above 70°C	Tr - 12	6.0	6.2	0
	Tr - 10	5.0	1.3	0
	Tr - 11	5.0	1.1	0
	Tr - 8	3.5	12.3	0
	Tr - 2	2.3	1.9	0
	Tr - 6	2.0	0	0
70° ~ 60°C	Tr - 12	5.9	0.65	——
	Tr - 11	5.0	1.1	——
	Tr - 8	2.6	9.4	——
	Tr - 9	2.3	5.5	1.8
	Tr - 2	2.3	3.2	0.6
	Tr - 6	2.0	0.6	——
	Tr - 5	1.7	0.8	0.4
	Tr - 1	1.5	3.2	0.65
60° ~ 50°C	Tr - 8	2.3	0.8	0.8
	Tr - 6	2.1	0.7	0.3
	Tr - 4	2.0	6.1	0.0
	Tr - 5	1.4	0.0	0.0
	Tr - 2	1.3	2.7	1.3
	Tr - 7	0.9	0.9	0.3
50° ~ 40°C	Tr - 5	1.0	0.7	0.0
	Tr - 7	0.7	4.0	0.3
	Tr - 2	0.6	1.9	0.7
	Tr - 8	0.5	12.0	0.7
	Tr - 12	0.01	8.2	0.9
40° ~ 30°C	Tr - 8	0.8	1.2	0.0
	Tr - 1	0.4	1.1	0.0
	Tr - 2	0.2	1.0	0.5
	Tr - 12	0.1	2.9	0.0
30° ~ 20°C	Tr - 8	0.8	0.7	0.2
	Tr - 1	0.3	0.6	0.0
	Tr - 5	0.2	0.9	0.0
	Tr - 12	0.1	0.3	0.0

2. The velocity of growth of the crystals in 0.01% pepton solution

1) *Sample and experimental method*

A and B solutions were prepared as stated above. Ten *cc* of B solution was taken into a test tube and pepton was added and heated at 60 °C to dissolve. Thus B′ solution was prepared to contain 0.02% of pepton. Following the same method as above stated, solutions A and B′ were mixed in equal quantities, the mean growing velocity $\bar{L}$ (μ/min.) was obtained for the range of the temperatures. The mixed solution of A and B′ contained 0.01% of pepton.

2) *Experimental results*

The mean growing velocities ($\bar{L}=\frac{L_1-L_0}{t}$) for *c* axis in the respective range of the temperature for differences of 10 °C are shown in Table 3.

Table 3. Mean growing velocity of the crystals in the pepton solution (μ/min.)

Temperature	Above 70°C	70°→60°	60°→50°	50°→40°	40°→30°	30°→20°
c axis ($\overline{ad}$)	0.5	1.1	1.3	2.6	0.9	0.5
a axis ($\overline{bf}$)	0.3	0.3	0.3	0.5	0.4	0.2

As seen in Table 3, the mean growing velocity of the crystals is maximum in the range of 40° ~ 50 °C as was the case also in the true solution. However, the mean growing velocity was half of that in the true solution. This fact is considered to support the results reported in previous paper VI[4], that the crystallization is slow in solutions to which gelatine, pepton, agar had been added.

The velocity of growth of the crystal was reported as different according to the axis of the crystal, *i.e.* it is anisotropic, in the previous article. It was suggested that the growing velocity of *c* axis of the crystal is 5 times that of *a* axis in the true solution. However, in the pepton solution, the growing velocity of *c* axis of the crystal was about 3.5 times that of *a* axis.

In both solutions, long and thin pillar crystal (*triclinic system*) occurs, but the breadth is somewhat larger in the true solution than in the pepton solution.

3. The influence of the concentration of ammonium ion upon the formation of the crystals

In this article the influence of the ion concentration of ammonium upon the shape and the size of the crystals which were formed in the glass tubes or in the canned foods were observed.

1) *Experimental method*

Each 0.01 Mol solution of magnesia mixture (A′ solution) containing no ammonium and sodium phosphate solution (B solution) was prepared according to the method described in paper III[1]. Also 0.056% ammonia solution (C solution) was prepared. As in the experiment above described, 0.1 *cc* of B solution was put onto a hole glass kept at 70° ~ 80 °C. Then 0.1 *cc* of a mixture of A′ solution and C solution (to 5 *cc* of A′ solution 0.1, 0.2 and 0.5 *cc* of C solution were respectively added) was poured onto the hole glass and the solutions were mixed in the hole. The shape and size of the crystals formed at a cooling velocity of 1°C/min. were observed.

2) *Experimental results*

Results obtained are shown in Table 4.

Table 4. Crystallizing state of the crystal of $MgNH_4PO_4 \cdot 6H_2O$ as influenced by the concentration of ammonia

Sample	Concentration of NH_4^+			States of the crystals
	In A′ solution	In C solution	In the mixed solution (A′. B. C.)	
1	0.0081 %	0.00055 %	0.0087 %	60×50 (μ) amorphous
2	0.0081 %	0.0011 %	0.0092 %	60×50 (″) amorphous 34×9 (″) crystals having surface
3	0.0081 %	0.0025 %	0.01 %	38×3 (″) crystals having surface

As seen in Table 4, in the concentration of ammonium ion below 0.0092% crystals having regular shape did not occur, and only amorphous crystals generated. In other words, for the crystallization of the crystals having regular shape in the presence of 0.0122% of Mg, it was found that concentration above 0.0092% of ammonium ion is needed. When the concentration of ammonium ion is less than the equivalent amount of Mg, no crystal having regular shape generates. In this case, the molecule of NH_4Cl or NH_4OH was supposed to be entirely dissociated.

As Mg is contained in canned crab meat to the amount of about 0.01%, upon the basis of results above stated, then should be about 0.0092% of ammonium ion.

In the juice of canned crab meat 0.010~0.035% of ammonium is contained, so the crystals having regular shape will be formed as a matter of course.

Discussion

The crystallization of the crystal of $MgNH_4PO_4 \cdot 6H_2O$ is influenced by the concentration of the chemical constituents and the keeping temperature.

As seen in the second paper of this series[5], the solubility of the crystal was maximum at 50° ~ 65 °C, and that the solubility become less below or above a boundary of

50 °C. Therefore, the crystallization is considered to begin from 70° ~ 80 °C. The size of the crystal formed at 70° ~ 80 °C is too small to identify its shape and surface. The crystallization of micro-crystals having easily observable shape and surface occurs at 60° ~ 70 °C. But, the crystallization of visible crystals occurs below 50 °C.

In the process of cooling of canned foods, it is considered to be difficult to crystallize out at 70° ~ 80 °C because at that range of temperature the solubility of the crystal is small, and time required to pass the range of the temperatures is short, and the juice of canned foods contains high molecular substances (*e.g.* protein and its decomposed products). With the progress of the cooling process, small crystals formed at about 70 °C grow according to the decrease in the solubility.

The mean growing velccity for the range of 10 °C at various temperatures is remarkably large at the range of 30° and 50 °C. This agreed with **"Zone of the formation of large crystals"** described in paper III[1]. In this experiment, the formed crystals which were initially amorphous, were clearly demonstrated not to become large even after storing time. This fact is interesting, since it agrees with the result described in the previous paper[3] that is that the small crystals which have been formed by rapid cooling did not become large even if the storing conditions were good.

As important factors influencing the size of the formed crystals, there are the velocity of cooling at the time of the generation of the crystals at 70° ~ 80 °C and the ion concetration of ammonia.

Summary

Various factors exerting influence upon the crystallization and the growth of the crystals during the cooling process, *viz.*, the variation of the temperatures (cooling velocity) and the concentration of the mixed matters, were observed continuously and directly under a microscope.

In the process of cooling of the canned foods, the crystallization of the amorphous crystals usually begins at 70° ~ 80 °C. This will be understood to occur because the solubility of the crystal is the minimum. The crystallizing temperature of the microcrystal ($10 \sim 20 \times 5 \sim 10\mu$) having regular surface and shape was found to be 60° ~ 70 °C. The mean growing velocity of the crystal was ascertained to be maximum at 50°~40°C and 40° ~ 30 °C according to the calculation for the range of 10 °C. This fact agreed with that the authors have called the range of 50° ~ 30 °C **"Zone of the formation of large crystals"**.

According to the characteristics of the solution, the growing velocity of the crystal is different. The growing velocity in pepton solution is smaller than that in the true solution.

From the fact that the growing velocity is different from the crystalline axis, the

anisotropic character of the crystal was recognized. The ratio of the growing velocity in c axis to a axis was observed to be about 5. But it was 3.5 in the pepton solution. The relation between the cooling velocity ($\varDelta\theta/\varDelta t$) and the mean growing velocity of the crystal is kept constant in the range of 30° and 50 °C. If the velocity of cooling is small, the growing velocity of the crystal is large, and if the velocity of cooling is large, the growing velocity of the crystal is small.

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