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

IV. Formation of the Crystal of $MgNH_4PO_4 \cdot 6H_2O$ and its Minimum Ion Concentration

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In the previous paper, the authors[1] have pointed out that the minimum concentrations of the components of the crystal will be necessary for its formation. In this paper, the authors have studied the minimum ion concentration needed for the formation of $MgNH_4PO_4 \cdot 6H_2O$.

Popoff and Neuman[2] have microscopically observed how the rate of addition, and the temperature at which addition should be made, etc., influence the shape and size of the generated crystals, in mixing of barium chloride with potassium sulfate. The authors have also observed under a microscope the size and shape of the crystal of $MgNH_4PO_4 \cdot 6H_2O$ in combination of the components of the struvite from the canned foods at various temperatures and have discovered the minimum concentration of the components necessary for the formation of the crystal.

Experimental method

Solutions A and B were prepared for the experiment. Solution A is magnesia mixture which was prepared as well as in the previous paper[3].

Solution A was diluted with water to make from 0.4 Mol to 0.0001 Mol on the basis of the quantity of magnesium sulfate in the solutions. Solution B is sodium phosphate solution, from which various concentrations of the solution were prepared from 0.4 Mol to 0.005 Mol. Each 10 cc of A and B solutions of the same concentration were mixed separatedly in Petri-dishes at room temperature (19° ~ 20°C) and 40°C. There were two mixing rates: instant and 2 minutes. Then the conditions of crystals formed by the mixing were compared in reference to the differences of the concentration of the solution, temperatures and mixing rates. When the mixing was completed, the solution in the dish was stirred by moving the dish by hand. Each 0.05 cc of the mixed solution was taken onto the slide glass by pipette, and the size of the formed crystals was measured under the microscope by micrometer. The number of the formed crystals was also measured on the counting chamber of Thoma's haemacytometer by counting three divisions having definite area.

Experimental results

The results obtained are shown in Tables 1 and 2.

Table 1. In the case of mixing A and B

Concentration of the solution	0.4 Mol		0.2 Mol		0.1 Mol		0.05 Mol	
Adding time	Instant	2 minutes	Instant	2 minutes	Instant	2 minutes	Instant	2 minutes
Number of crystals (per 1 cc)	56×10^4	60×10^4	24×10^4	24×10^4	56×10^4	60×10^4	24×10^4	8×10^4
Size of crystals (μ)	18×1.3	63×2.5	14×2.5	25×2.5	120×2.5	126×2.5	92×1.5	330×1.3
State of crystals	A B	A B	A	A	A	A′	B	A′B

Note: Signs which are described in this table show the states of the formed
A=arborescent B=broad blanches C=columnar crystal D=columnar crystal

Table 2. In the case of mixing A and B solutions at temperature of 40°C

Concentration of the solution	0.4 Mol	0.2 Mol	0.1 Mol	0.05 Mol	0.02 Mol	0.01 Mol	0.005 Mol
Adding time	Instant	Instant	Instant	Instant	Instant	Instant	Instant
Number of crystals (per 1 cc)	200×10^4	160×10^4	160×10^4	16×10^4	10×10^4	——	80×10^4
Size of crystals (μ)	26×2.6	26×4.0	50×2.6	50×3.1	82×1.2	120×1.2	8.2×1.3
State of crystals	C B	C B	C B	C	C	D	D

Note: Signs which are described in this table show the states of the formed crystals as follows.
B=broad blanches C=columnar crystal
D=columnar crystal separated

(1) *The difference of conditions of the crystal formed by different concentrations of the solutions*

As seen in Table 1 and 2, in the range of 0.02 Mol and 0.0025 Mol, the more diluted the solution is, the more regular is the form of the crystals. Above 0.05 Mol, the form of the crystal was irregular, and the crystals of needle shape gathered into arborescent colonies like frost that is found on the window glass on cold days.

The more diluted the solution is, the less is the number of crystals. Visible sized crystals are formed by mixing of A and B solutions having each above 0.01 Mol in which case the mixture contains 0.0122 % of Mg.

solutions at room temperature (19°~20°C)

0.02 Mol		0.01 Mol		0.005 Mol	0.0025 Mol	0.001 Mol	0.0005 Mol	0.0001 Mol
Instant	2 minutes	Instant	2 minutes	Instant	Instant	Instant	Instant	Instant
32×10^4	10×10^4	24×10^4	14×10^4	10×10^4	8×10^4	12×10^4	16×10^4	4×10^4
54×1.3	239×1.3	59×0.9	63×1.0	40×2.2	24×7.6	37×2.7	57×3.8	1.3×1.0
C B	D	D	D	C E	C E	C E	E	E

crystals as follows.
separated E=amorphous A′=rather large arborescent B′=rather large broad blanches

(2) Difference of conditions of the crystals obtained by different mixing rate

When each 10 cc of A solution is poured into each sample of B solution instantly or in 2 minutes, the size and form of the crystals varied by the mixing rate (mixing time) as shown in Table 1.

The shapes of the crystals in the instantly mixed solution are irregular and the sizes are small. But the forms of the crystals in the slowly (2 minutes) mixed solution are regular and the sizes are large. The difference of the influence upon the form and size of the crystals by the different rate of the mixing remarkably appeared in the concentration of each solution A and B when their make-up was above 0.01 Mol.

(3) Difference of conditions of the crystals obtained under different temperatures

As seen in Tables 1 and 2, the size and shape of crystals formed at room temperature (19° ~ 20°C) or at 40°C are different. The form of the crystals formed at 40°C seems to be more regular and more compact than the crystals formed at room temperature, even from the same concentration of both solutions. The former showed no arborescent crystals unlike the latter. And the crystals formed at room temperature are inseparably connected with each other. They give an impression of coarseness.

Summary

The authors have studied the factors influencing the size and shape of the crystals of $MgNH_4PO_4\cdot6H_2O$, when the chemical components of the crystal, magnesia mixture solution (magnesium sulfate and ammonia water), (A solution) and sodium phosphate solution, (B solution) are mixed in the same concentration in the range between 0.0001

Mol and 0.4 Mol at different temperatures (room temperature and 40°C) and at different mixing rates (instantly and during 2 minutes).

The visible crystals are formed by mixing of the two solutions above 0.01 Mol. The amount of Mg in the mixed solution yielding the visible crystals was 0.0122 %. The crystals which were formed by mixing of the two solutions above 0.05 Mol, have irregular forms which look like arborescent colonies of needle crystals. The crystals which were formed by mixing of the two solutions below 0.01 Mol are invisible and microscopic.

The crystals which were formed by instant mixing of the solutions have more irregular shape and are smaller than those crystals which were formed in two minutes mixture. The mixing rate exerts scarcely any influence upon the difference of the size and form of the crystals in the case of diluted solutions below 0.01 Mol.

The shapes of the crystals which are formed at 40°C are more regular than those at room temperature (19° ~ 20°C).

Literature cited

1) Tanikawa, E. *et al.* (1956). *Bull. Fac. Fish., Hokkaido Univ.* 7 (3), 247-251.

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3) Tanikawa, E. *et al.* (1957). *Bull. Fac. Fish., Hokkaido Univ.* 7 (4), 300-305.