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參展科別 **化學**

作品名稱 **The change in NaCl crystals from cubic to octahedral～Sodium polyacrylate stabilizes the {111} face of Miller indices～**

得獎獎項 **大會獎：一等獎**

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關鍵詞 **NaCl, crystal, octahedral**

作者照片

Abstract

When adding 2% or 4% sodium polyacrylate as habit modifier, standard milky-white octahedral NaCl crystals grew gradually in saturated NaCl solution on the bottom of the container. [1] [2] Sodium polyacrylate is well known as a highly water-absorbable polymer with many carboxylate anions. In the case of low concentration (0.01%, 0.02%, 0.05%, 0.1% and 0.5%) sodium polyacrylate many small or microscopic crystals whose shapes were nearly octahedrons and had {111} faces were observed with an optical microscope on the bottoms of the solution containers. In low concentration sodium polyacrylate, octahedral NaCl crystals made up of electrostatically unstable {111} faces grew similarly to crystals in high concentrations of 2% or 4% NaCl. Therefore, by adding sodium polyacrylate to saturated NaCl solution, cleaved rock salt crystals in this sol were observed to find out whether or not a change in crystal morphology from cuboids of {100} faces to octahedrons of {111} faces would occur. Regardless of the sodium polyacrylate concentrations of 0.01%, 0.02%, 0.05%, 0.1%, 0.5% and 2%, all cuboid crystals changed into a pyramidal shape in which four of the side surfaces formed an equilateral triangle. When one side of each equilateral triangle face was rotated so the square face of the crystal was soaked in the NaCl sol, all crystals grew into octahedrons of high transparency. Sodium polyacrylate, even under a low concentration, caused morphological change in the NaCl crystals. Many carboxylate anions in the sodium polyacrylate attracted sodium ions and the repulsive force between the carboxylate anions became weak, excluding the water in the internal space of the polymer. We considered that the stabilizing {111} faces of gathered sodium ions attached to carboxylate anions. Chloride and sodium ions coordinated continuously to minimize the NaCl surface area, growing into an octahedral and lowering the surface energy of the NaCl crystal. [3]

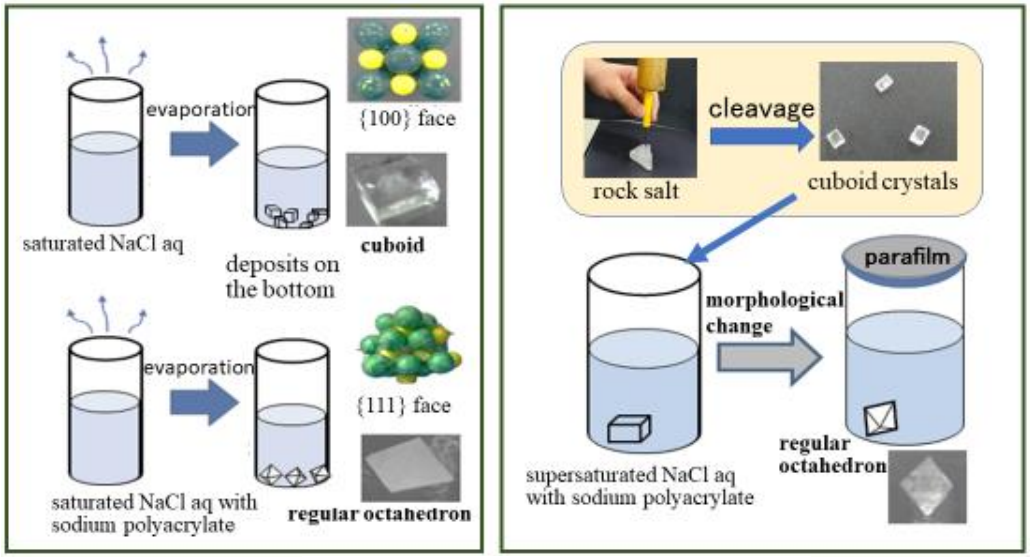

Fig.1 Graphical abstract of this research

Introduction

We noticed that a floating growth of NaCl crystals in a test tube of saturated NaCl solution gradually evaporated at room temperature.[1] The shape of the crystal surface in contact with air was an equilateral triangle. The crystal figure was a cube cut in a regular triangular pyramidal shape in an oblique direction (Fig2). This equilateral triangle surface of the crystal was found to be a Miller indices {111} face (Fig3) by X-ray diffraction.[2] Because generated surface tension on the floating crystal surface becomes larger when a {111} face comes into contact with air than when a {100} face comes into contact with air [5], the floating crystal could grow stably, but it cannot become a large-sized crystal. After sinking to the bottom, the crystal changed to a cuboid shape with a {100} face.

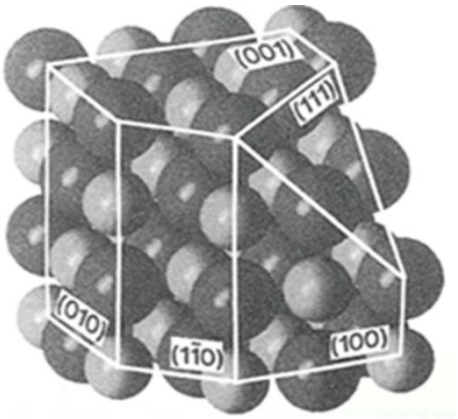

Fig.2 taken from Hitoshi Shindo: "Big world seen from nanoscale and microscale" (Chuo University Press) 2013【4】

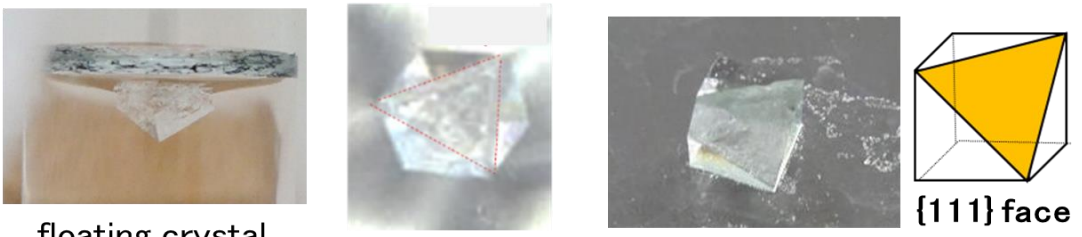

Fig.3 floating growth of NaCl crystals in a test tube of saturated NaCl solution

In order to gain the crystals with {111} faces in the NaCl saturated solution, 2% or 4% sodium polyacrylate were added to the supersaturated NaCl solution as habit modifier. Generated crystals at the surface of sol were sinking over several days, and standard milky-white octahedral NaCl crystals grew gradually on the bottom of the container [1] [2] (Fig4). Eight faces of Octahedron are equilateral triangles, we considered all the faces of octahedral NaCl crystal were {111} faces.

Purposes of this study are as follows. First, find out whether or not rock salt crystals in this sol change from cuboids to octahedrons by adding sodium polyacrylate to saturated NaCl solution. Secondary, find out of this change possible or not by adding small amount of polyacrylate into saturated NaCl solution.

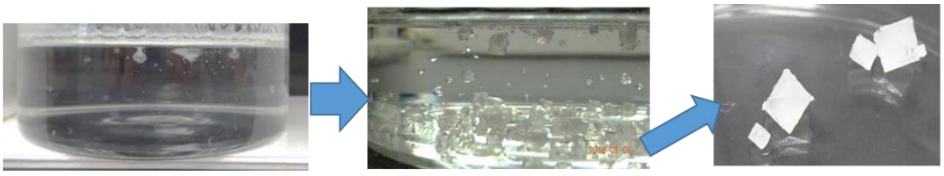

Fig.4 generated crystals in the supersaturated NaCl aqueous solution with 4% sodium polyacrylate

Experiments (experiments and results)

Experiment I

Changing forms of cleaved rock salt crystals in supersaturated NaCl aqueous solutions with sodium polyacrylate

- 2% sodium polyacrylate; high concentration and viscosity
- 0.01%～0.5% sodium polyacrylate; low concentration and viscosity

Experiment II

Growing NaCl crystal deposits in saturated NaCl aqueous solutions with 0.01%～0.5% sodium polyacrylate by natural evaporation

Experiment III

Forming NaCl crystals on the boundary surface between saturated NaCl solution (upper side) and NaCl sol with 6% sodium polyacrylate (lower side)

Experiment IV

KCl crystal deposits grown in KCl saturated solution with 0.025% sodium polyacrylate

All crystals grew at room temperature (20～30℃) in our senior high school's chemical laboratory.

【Reagent】

NaCl; guaranteed reagent (FUJIFILM Wako Pure Chemical Co.)

KCl ; first grade (FUJIFILM Wako Pure Chemical Co.)

sodium polyacrylate ;degree of polymerization 22,000～70,000) (Wako Pure Chemical Co.)

Rock salt; Mongorian; (Na 38.35%, Ca 0.43%, Mg 0.01%, Cl 59.17%) Mongolian salt (Niwakyu Ltd.)

Crystals were growing at room temperature (20～30℃) in our senior high school's chemical laboratory.

【Experiment I-1】Changing forms of cleaved rock salt crystals in supersaturated NaCl aqueous solution with 2% sodium polyacrylate

<Method>

1) A flat-head screwdriver stood on a rock salt was knocked by a hammer, and rock salt was cleaved to the cuboid crystals (Fig5), which weight and three lengths of the cuboid side were measured.

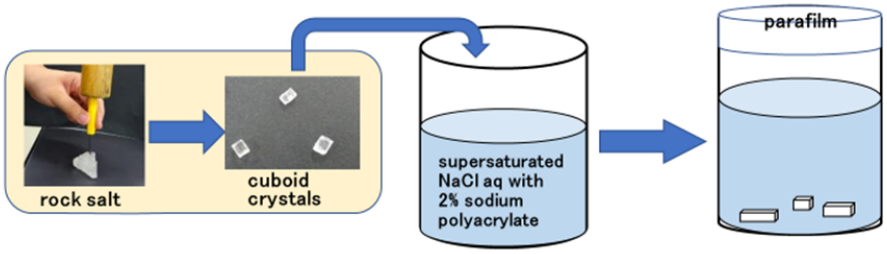

Fig. 5 Experiment Ⅰ-1 procedure

2) Sodium polyacrylate was added into the saturated NaCl aqueous solution and mixed uniformly. The top of the beakers was covered with gauze so as to allow the sol to evaporate gradually. The sol became supersaturated state when NaCl crystal deposits formed on the bottom.

3) Only the supersaturated state sol taken up using a pipette was poured into another beaker, and three cuboid rock salt crystals about 0.01g were put into it. The top of the beaker was sealed with parafilm and changing the form of these crystals in the sol had been recorded.

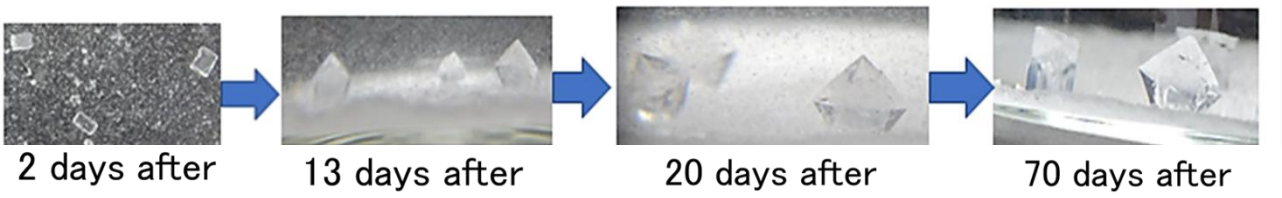

Fig. 6 Experiment Ⅰ-1 results

Table 1. Changing the volume of the rock salt crystals in the sol included 2% sodium polyacrylate

Cuboid rock salt crystals (2019.3.10)					Octahedral NaCl crystals (2019.9.2)	
sample	length (mm)	width (mm)	height (mm)	volume (mm^3)	Length of a side (mm)	volume (mm^3)
1	1.40	2.30	1.10	3.54	3.2	15.5
2	2.00	1.90	1.10	4.18	3.7	23.9
3	2.20	1.80	2.00	7.92	4.0	30.2

<Results>

All the cuboid crystals changed gradually to their regular octahedral forms on the bottom of the beaker (Fig6). These octahedral crystals were high transparency and crystal volume increased about 4 times (Table1).

【Experiment I-2】-part1-

Changing forms of cleaved rock salt crystals in saturated NaCl aqueous solution with 0.01%～0.5% sodium polyacrylate of low concentration

<Method> step1

0.01%, 0.02%, 0.05%, 0.1% and 0.5% sodium polyacrylate were mixed uniformly in to the saturated NaCl aqueous solution. Four cleaved rock salts were put into each sol and saturated NaCl aqueous solution. The tops of the beakers were sealed with parafilm (Fig7). In this experiment, the operations of natural evaporation for supersaturated NaCl state like Experiment I-1 were not done.

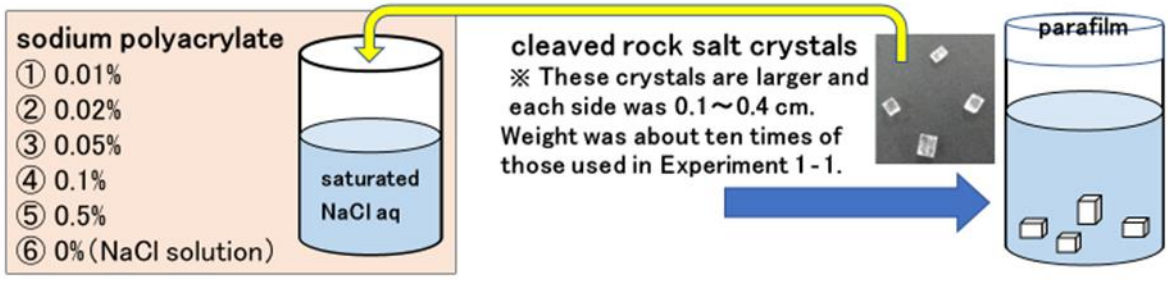

Fig. 7 Experiment Ⅰ-2 part1 step1 procedure

<Results of step1>

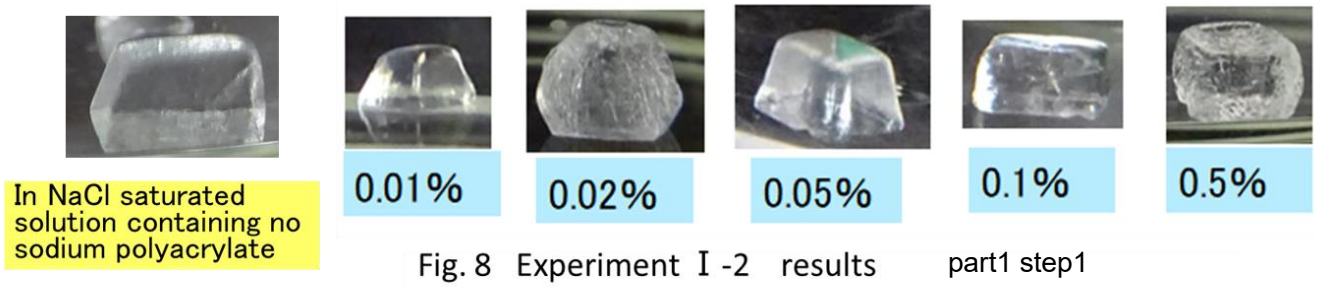

Fig. 8 Experiment Ⅰ-2 results part1 step1
value: mass percentage concentration of sodium polyacrylate

All crystals gradually became smaller with gentle slope sides which shapes like “flat-topped burial mounds” (Fig8).

※ Flat-topped burial mounds are one of the kofun in ancient times, which were constructed as graves for powerful people in the East.

<Hypothesis>

It is considered that such a changing form of crystals were caused from slowly dissolution because the NaCl solutions were not supersaturated. The reason for the consideration is from the facts that the same change was seen in NaCl saturated solution containing no sodium polyacrylate, all crystals gradually became smaller and four upper peaks of each crystal changed to round. So, It is considered also that such a changing form of crystals were different process from the changing process into octahedral NaCl crystals.

【Verification of the hypothesis of experiment I-2】

Changing forms of cleaved rock salt crystal in 5% NaCl aqueous solution were photographed at 30 second intervals.

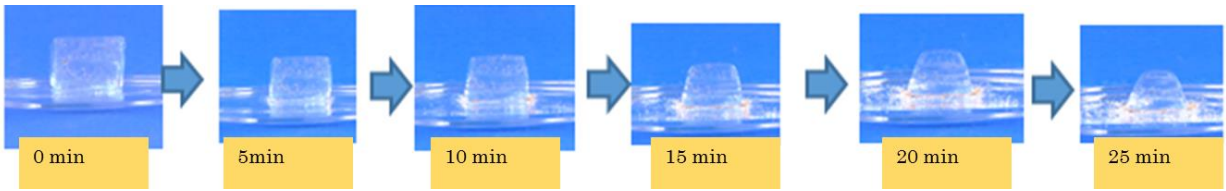

Fig. 9 changing forms of cleaved rock salt crystal in 5% NaCl aqueous solution
photographs at 5 minute intervals

This cuboid shaped crystal dissolved, gradually changing form to the expected shape like “flat-topped burial mounds” (Fig9). This result means that only the four upper peaks of the NaCl crystal dissolved rapidly in the unsaturated NaCl solution.

<Method> step2

It became clear that cleaved rock salt crystals in Experiment I-2 were dissolved slowly. It is necessary that supersaturated states of NaCl solution in order to change for the octahedral NaCl crystals. Therefore, the parafilm of each beaker was replaced with gauze so as to allow the sol to evaporate gradually and reach a supersaturated state (Fig10).

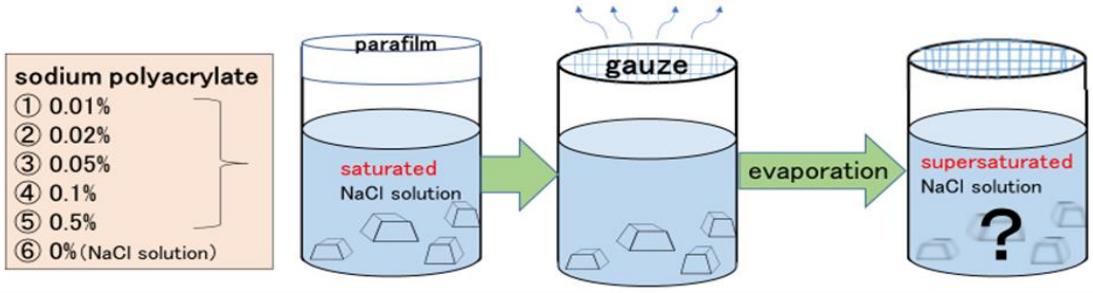

Fig. 10 Experiment Ⅰ-2 part1 step2 procedure

<Results of step2>

All the crystals in sodium polyacrylate sol changed to a "pyramid" shape (Fig11). Four sides of square pyramid are equilateral triangle which considered {111} faces. In contrast, no octahedral crystal was observed in the NaCl aqueous solution (Fig12).

<Method> step3

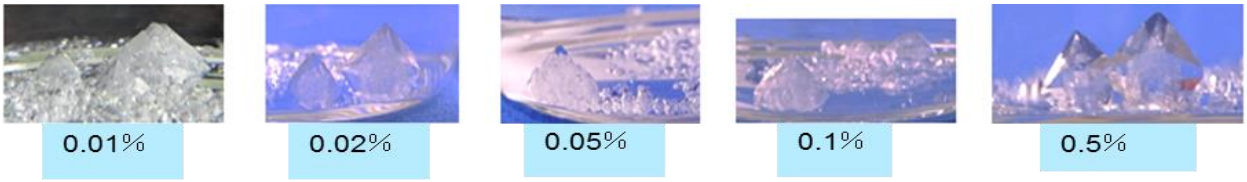

Fig. 11 Experiment Ⅰ-2 results part1 step2

value: mass percentage concentration of sodium polyacrylate

One side of each equilateral triangle face considered {111} face was rotated so the square face of the crystal considered {100} face of rock salt was soaked in the NaCl sol.

<Results of step3>

all crystals grew into big octahedrons of high transparency (Fig13).

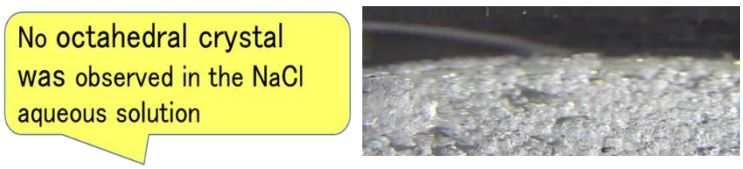

Fig. 12 Experiment Ⅰ-2 results part1 step2
in the NaCl aqueous solution

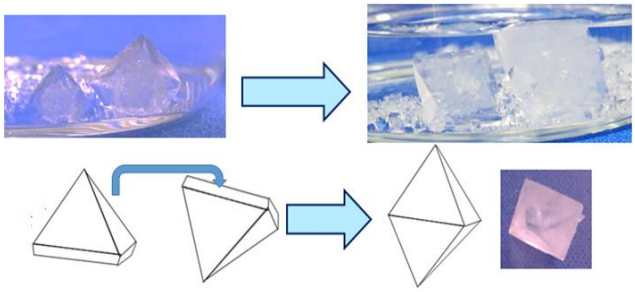

Fig. 13 Experiment Ⅰ-2 part1 step3 procedure and results

【Experiment I-2】-part2-

Changing forms of cleaved rock salt crystals in supersaturated NaCl aqueous solution with 0.01%～0.5% sodium polyacrylate of low concentration

<Method>

0.01%, 0.02%, 0.05%, 0.1% and 0.5% sodium polyacrylate were mixed uniformly in to the saturated NaCl aqueous solution. After the operations of natural evaporation for supersaturated NaCl state like Experiment I-1 were done, three cleaved rock salts were put into each sol and saturated NaCl aqueous solution. The tops of the beakers were sealed with parafilm

<Results >

Fig14 is shown the crystals in process of changing into square pyramid form. In the center of all crystals white parts could be seen which considered the rock salts put into each sol. The NaCl crystal growing around the rock salts was understood clearly to see down from the upper side of container (Fig15).

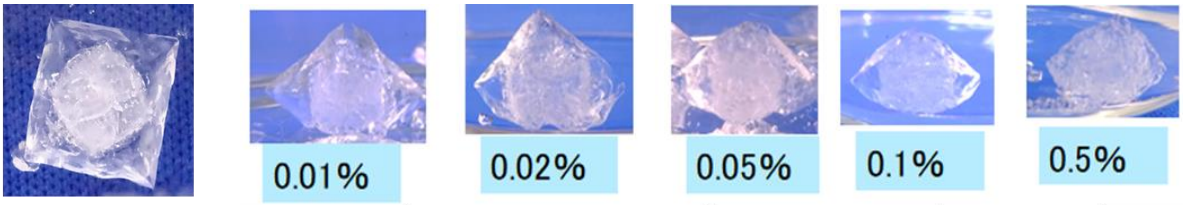

Fig. 15 Experiment Ⅰ-2 part2 results
0.01% sodium polyacrylate
(picture from the upper side of container)

Fig. 14 Experiment Ⅰ-2 part2 results
value: mass percentage concentration of sodium polyacrylate

【Experiment I-3】Changing forms of big cleaved rock salt crystals in supersaturated NaCl aqueous solution

with 2% sodium polyacrylate

<Method>

From observation of changing the shape of a big NaCl crystal is useful to understand the changing coordination on the surface of the NaCl crystal. That is to say, what occurs in micro scale parts could be seen through the macro size observation.

A big cube of cleaved rock salt (three side length14.5mm, 19.0mm, 15.5mm) was sunk in saturated NaCl solution with 2% of sodium polyacrylate (Fig16).

<Results >

It is difficult to recognize the changing of the crystal during about the initial 10 days, but surface of the crystal was become rough over time, and has changed into the complicated shape. From this result of the big crystal changing, it is considered that cubic NaCl crystal with {100} faces can hardly grow on the surface of the rock salt in the NaCl solution included sodium polyacrylate (Fig17).

Fig.16 Experiment Ⅰ-3
first day

Fig.17 Experiment Ⅰ-3 results

【Experiment II】NaCl crystals grown from saturated NaCl aqueous solution with sodium polyacrylate at relatively low concentration

From the results of experiment I, it is confirmed that the shape of cuboid NaCl crystals in the supersaturated NaCl solution change using sodium polyacrylate as habit modifier at relatively low concentration. Next, shape of the microscopic crystals formed at the primary stage of crystallization was

observed with an optical microscope.

<Method>

1) Sodium polyacrylate at five different concentrations was added to the saturated NaCl aqueous solutions in five 100mL beakers.
2) The tops of the beakers were covered with gauze so as to allow the sol to evaporate gradually.
3) After a week, deposits on the bottom were observed with an optical microscope (magnification was 40-100).

<Results >

Many small or microscopic crystals whose shapes were nearly octahedrons and had {111} faces were observed in all NaCl solutions with sodium polyacrylate (Fig18). These fact means that sodium polyacrylate stabilized {111} faces of the NaCl crystal at an early stage of crystallization even under the low concentration. On the other hand, many complicated figures of polyhedrons were observed, {110} and {100} faces were also formed at an early stage of crystallization.

Fig.18 Experiment Ⅱ results

【Experiment III】 NaCl crystals formed on the upper part of boundary saturated NaCl sol with 6% sodium polyacrylate

<Method>

1) Add 6% sodium polyacrylate to NaCl saturated solution. This sol was cloudy.
2) Gently pour NaCl saturated solution into the upper part of the sol. Then, seal the top of the beaker with parafilm and observe crystals which appear from the boundary of the two solutions with an optical microscope.

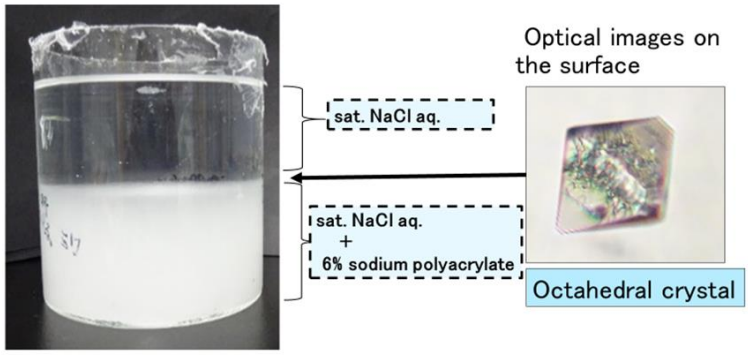

Fig.19 Experiment Ⅲ results

<Results >

In the boundary between high concentration sol of 6% sodium polyacrylate and aqueous solution, regular octahedral crystals were observed (Fig19).

Crystals could grow to every direction because they were suspended in the boundary of the polymer sol and the aqueous solution. While suspended condition, crystal growing in every direction is possible.

【Experiment IV】 KCl crystal deposits grown in KCl supersaturated solution with 0.025% sodium polyacrylate

<Hypothesis>

Because crystal structure of KCl is NaCl type structure. KCl crystal figure also change using sodium polyacrylate as a habit modifier like a NaCl crystal.

<Method>

1) Saturated KCl aqueous solution was put into a beaker.
2) 0.025% of sodium polyacrylates was added to the saturated KCl aqueous solutions, and the sol was put into other beaker.
3) The tops of the beakers prepared of 1) and 2) operations were covered with gauze so as to evaporate gradually.
4) Crystal deposits growing on the bottom were observed for a long time, and KCl crystal deposits were picked up from each beaker.

<Results >

KCl is a NaCl type crystal, but KCl crystals grown in the sol with 0.025% sodium polyacrylate were formed differently than the ones in the aqueous solution with no sodium polyacrylate. To use sodium polyacrylate as a habit modifier, KCl crystal forms were not cuboid, but have several diagonal cutting faces different from {100} faces, and the KCl crystal were larger and massive (Fig20), but not octahedron.

In contrast, tiny thin cuboid crystals were grown overlapping and were not massive in the supersaturated KCl aqueous solution with no sodium polyacrylate.

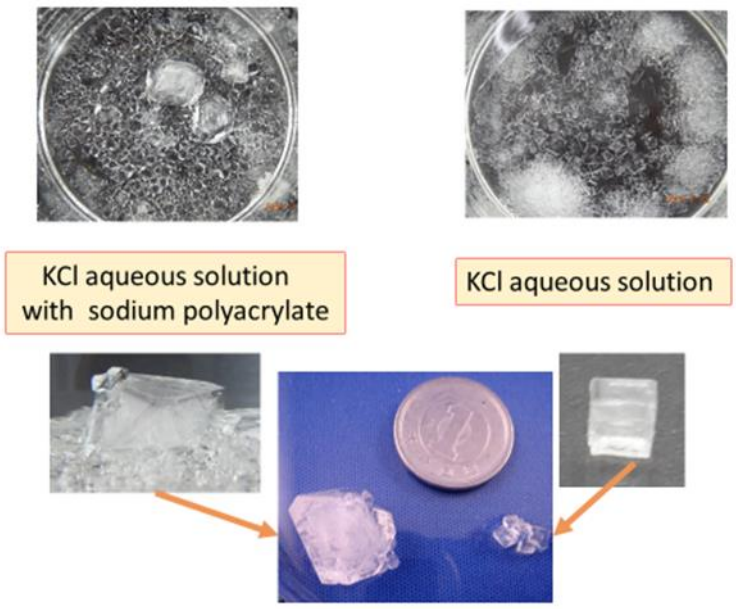

Fig.20 Experiment Ⅳ results

Discussion

It is cleared from the results of experiment I～III , low concentration sodium polyacrylate as 0.01% causes the NaCl crystals' shape change from cubic to octahedron considered all faces surrounding {111}faces.

Why unstable {111} faces by the repulsive force generated

Fig.21 {111} faces

between same charge ions (Fig21) became stable in addition of sodium polyacrylate? Ordinary, cuboid crystals grow in the supersaturated NaCl aqueous solution because {100} faces are stable. More attractive force generated between Na^+ and Cl^- than repulsive force between same charge ions.

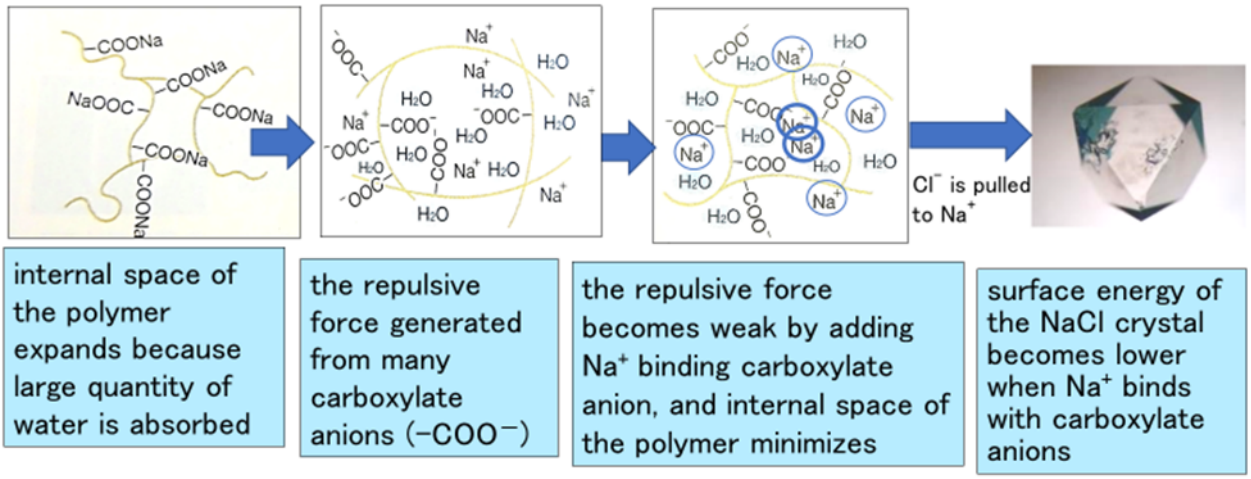

Fig. 22 Discussion of Experiment 1 and 2
figures taken from【7】The textbook "Kaitei Kagaku" (Tokyo Shoseki) 2018

When sodium polyacrylate [-CH_2-CH(COONa)-]*n* is added into the water, large quantity of water is absorbed because repulsive force generated from many carboxylate anions (-COO^-) electrolytically dissociated (Fig22). By addition NaCl into the sol, the repulsive force becomes weak because Na^+ supplied from NaCl bind carboxylate anion, and internal space of the polymer minimizes. Coordinate Na^+ surface energy of the growing NaCl crystal in the sol also becomes lower binding with carboxylate anions, so {111} faces are become stable.

Surface energy stability of the crystal is related to the phenomena not grow {100} faces but {111} faces on the NaCl crystal surfaces with sodium polyacrylate. When an ionic crystal is growing slowly for a longtime, ions coordinate to minimize the surface area smaller so that surface energy of the crystal becomes lower. [3] In the case of NaCl crystal, decrease of {111} surface energy of the crystal generated repulsive force between same charge ions by additional carboxylate anions -CH(COO^-) occurs, {111} surfaces grow to octahedral crystal because surface area of octahedoron is smaller than that of cubic. Sodium polyacrylate is effective habit modifier using in low concentration to change NaCl crystal to octahedral crystal.

A variety of morphological studies for NaCl crystal have been conducted [8] [9] and many studies have reported to obtain {111} surfaces on NaCl crystals using urea, formamide, and metal ions as habit modifiers. [10] - [12] Sodium polyacrylate is effective in changing NaCl crystal figures in comparison with these habit modifiers. In the supersaturated aqueous NaCl solution, using a small amount of sodium polyacrylate, ions coordinate on the surface of the NaCl crystal to form an octahedral crystal. Additionally, sodium polyacrylate is a safe substance that can be used easily.

Using sodium polyacrylate as a habit modifier, KCl crystals did not change into cuboid or octahedral shapes, but instead had several diagonal cutting faces different from {100} faces. Both NaCl and KCl crystals are NaCl-type crystals but have different forms. This difference may be caused by the difference in ionic radius between K^+ and Na^+.

Conclusion

By adding sodium polyacrylate to NaCl saturated solution, cubic crystals with{100} faces changed to octahedral crystals with {111} faces.

Low concentration sodium polyacrylate causes the NaCl crystals' shape change, because many carboxylate anions within sodium polyacrylate stabilizes {111} faces in the aqueous solution. The sodium ions and chloride ions coordinate to minimize the surface area smaller so that surface energy of the NaCl crystal becomes lower. Finally, the shape of the crystals changes into an octahedral shape.

Future tasks

Investigation of reaction rate for changing form of the NaCl crystal is necessary to clarify the mechanisms of ion coordination when crystallization occurs in NaCl aqueous solutions with various concentration of sodium polyacrylate. We will research about the influence of sodium polyacrylate on the various crystallizations of NaCl type crystal like the KCl crystal. We also need to research changing the cuboid shape of NaCl crystal using other habit modifiers included many carboxylate anions.
Today, new experimental technique is developed for a single-crystalline metal film on NaCl(001) substrate.[13] There is a possibility to apply the NaCl(111) of the regular octahedral crystal as a substrate for heteroepitaxial growth. Establishment of the method of growing regular octahedral NaCl crystal of high purity is necessary.

Acknowledgements

We are deeply grateful to Prof. Kiyoshi Tsuge (Univ. of Toyama) for his assistance in crystal analyzing by X-ray diffractometer and for valuable advice.
We would also like to thank Prof. Hitoshi Miura (Nagoya City University) for his useful advice.

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【評語】030036

Very interesting research. It is possible to extend the research to confirm the conclusion. If -COO- is important, simple acids with short and long aliphatic group, such as acetic acid and oleic acid, would be good comparisons. A polymer without -COO- should be compared too.

Polymers like allylamine (PAA) with amino groups will extremely interesting to compare the outcomes.