# Degradation of Magnesium and Calcium Highpolyphosphate Coacervates[1)]

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The degradation of highpolyphosphates in the coacervates of magnesium and calcium is discussed on the basis of the results of viscosity measurement and paper chromatographic analysis of highpolyphosphates. The initial viscosity and transparency of some magnesium coacervates were maintained with little change at 30 °C for about 2 weeks, while most calcium coacervates changed within 10 days into wet cakes containing $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca_3(HP_2O_7)_2 \cdot 4H_2O$. The formation of pyrophosphates during the course of degradation of both coacervates is remarkable as compared with that on the hydrolysis of alkali highpolyphosphates in aqueous solutions.

In dilute aqueous solutions, highpolyphosphate chain-anion undergoes degradation to produce shorter chain polyphosphates, orthophosphates and ring phosphates. Studies have been carried out on the hydrolyses of alkali highpolyphosphates and their mechanisms.[2-4)] However, only a few reports have appeared on the degradation of non-alkali highpolyphosphates.

In the preceding paper[5)] the thermal change of magnesium highpolyphosphate coacervate(MPC) was discussed on the basis of the results of thermal analysis. For the analysis, the coacervate had to be heated and partially dehydrated at 100 °C in order to avoid swelling and foaming in the sample cell. Consequently, no detail was known about the degradation of MPC below 100°C.

The present paper deals with the viscosity changes of MPC and calcium highpolyphosphate coacervate (CPC) on degradation at temperatures form 25 to 90°C. The changes of the highpolyphosphate chain length were determined by paper chromatography.

## Experimental

*Materials.* Coacervate samples were obtained by adding ethyl alcohol to mixtures of a sodium metaphosphate solution and a solution of magnesium or calcium chloride. The coacervates were also prepared by direct addition of $MgCl_2 \cdot 6H_2O$ or $CaCl_2 \cdot 2H_2O$ powder to a sodium metaphosphate solution. The coacervate was used immediately after coacervation caused by addition of ethyl alcohol or the respective chloride powder. Conditions for the preparation of coacervates were described in detail in a previous paper.[6)]

*Paper Chromatography.* Since MPC and CPC contain $Mg^{2+}$ and $Ca^{2+}$, respectively, ETA (about 1% in a solution) was added to each solution of the coacervates, according to the analytical method proposed by Yamazoe *et al.*[7)] Each individual spot on the filter paper was washed with ammonia water. The phosphate solutions thus obtained were strongly acidified and boiled to give rise to hydrolysis. Phosphorus in the solutions was then analyzed by heteropoly blue colorimetry.

Total absorbance due to all the phosphates was obtained by summation of the individual absorbance values. The phosphorus content of each spot is expressed as a portion of total phosphorus present as follows:

P(%) = (absorbance for each fraction/sum of absorbance) × 100

*Viscosity Measurement.* The viscosities of the coacervates were measured with a rotational viscometer of cone-and-plate type.[6)]

*X-Ray Analysis.* X-Ray powder diffraction patterns of degradation products in coacervates were obtained with a Rigaku Denki Diffractometer Model D-3F.

## Results and Discussion

Linearity of the flow curves for coacervates in the present work was obtained at shearing rates 10—600 $s^{-1}$. Consequently, all the coacervates used were assumed to be Newtonian.

*Viscosity Change with Time at 30 °C.* Figure 1 shows a typical viscosity change with time in one of the MPC samples turned into a coacervate by addition of ethyl alcohol. For the first two weeks viscosity lowering was not remarkable. However, short chain-phosphates such as ortho- and pyrophosphates were detected by paper chromatography. Thus, most highpolyphosphates of long chains probably remained without cleavage, degradation of MPC initially occurring only at terminal parts of the polyphosphates. In spite of the progress of degradation of highpolyphosphates, transparency of most samples was maintained, no precipitate being found in the coacervates at 30 °C for about two months.

Most CPC were less stable than MPC. The viscosity of CPC was lowered and a small amount of white powder began to be suspended in a transparent coacervate within a week. One or two days after the first appearance of the suspension, the coacervate completely turned into a wet cake of white powder, which might consist of calcium phosphates. A calcium pyrophosphate of $Ca_3(HP_2O_7)_2 \cdot 4H_2O$[8)] was identified one or two days after the cake formation, a mixture

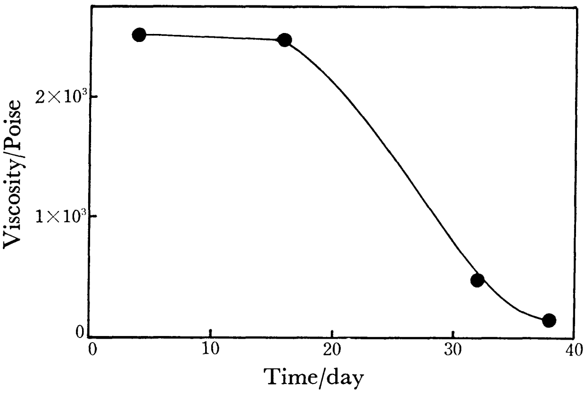

Fig. 1. Viscosity change of MPC with time at 30 °C.

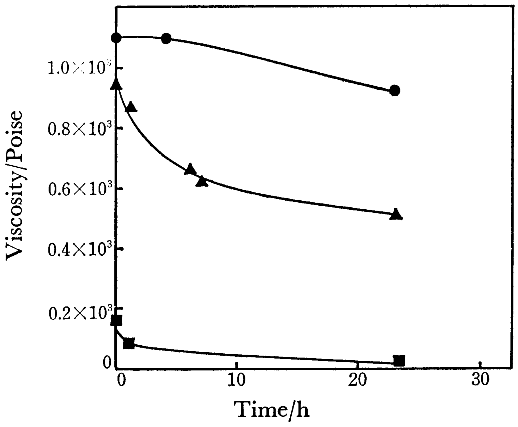

Fig. 2. Viscosity change of various MPC's with time at 50 °C. ●: Sample A, ▲: Sample B, ■: Sample C. (The initial viscosities of A, B, and C were $1.10 \times 10^3$, $0.95 \times 10^3$, and $0.16 \times 10^3$ Poise, respectively.)

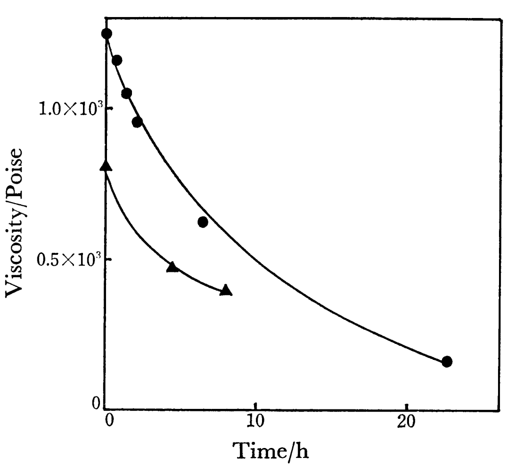

Fig. 3. Viscosity change of various CPC's with time at 50 °C. ●: Sample A, ▲: Sample B. (The initial viscosities of A and B were $1.24 \times 10^3$ and $0.80 \times 10^3$ Poise, respectively.)

of $Ca(H_2PO_4)_2 \cdot H_2O$ and the pyrophosphate being obtained within 3 or 4 weeks after the beginning of degradation experiment.

The difference of stability between MPC and CPC may be interpreted in terms of solubilities of the salts of short chain-phosphates into the coacervates.

*Viscosity Change of Coacervates with Various Initial Viscosities.* The viscosity lowering of some MPC is slightly noticeable only at the first stage of experiments, while CPC became less viscous gradually and continually (Figs. 2 and 3). Concerning MPC, the degree of viscosity lowering decreases with increase in the initial viscosity. Highly viscous MPC is recognized to be considerably stable. From a comparison of viscosity changes in the coacervate samples with various initial viscosities, the mobility of phosphate ions in the coacervates is considered to be closely related to the rates of degradation.

*Viscosity Changes at Various Temperatures.* Viscosity changes with temperature of MPC and CPC are shown in Figs. 4 and 5, respectively. The viscosities of both coacervates lowered rapidly at 80—85 °C.

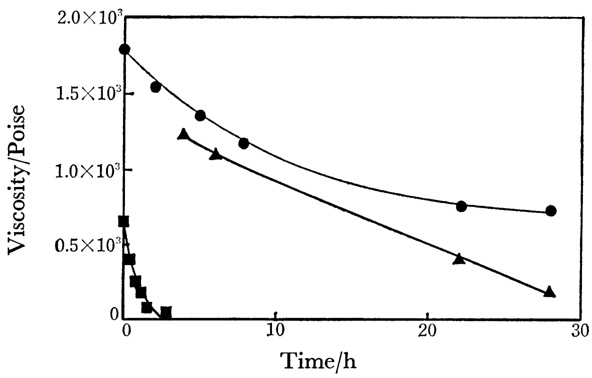

Fig. 4. Viscosity change of MPC with time at various temperatures. ●: 50 °C, ▲: 70 °C, ■: 85 °C.

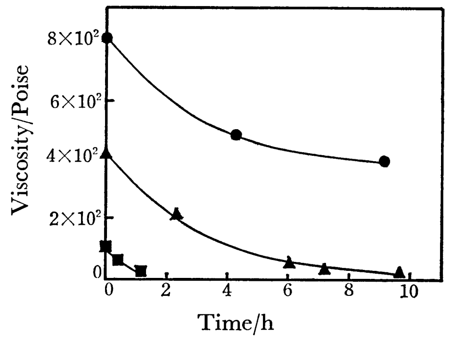

Fig. 5. Viscosity change of CPC with time at various temperatures. ●: 50 °C, ▲: 60 °C, ■: 80 °C.

The magnesium coacervates remained transparent while the calcium coacervates solidified within 10 h above 60 °C. In CPC cakes cooled to room temperature, $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca_3(HP_2O_7)_2 \cdot 4H_2O$ were detected by X-ray diffraction.

Short chain-phosphates formed are given in Table 1. On degradation of MPC, pyro- and tripolyphosphates appeared. On the other hand, only orthophosphates formed during the course of hydrolysis of $NaPO_3$.

As pointed out by van Wazer and his coworkers,[2)] there are three alternative degradation paths of Graham's salts: Splitting of end $PO_4$ groups, random scission along the main chain of highpolyphosphates, and ring formation.

During the degradation of the coacervates, orthophsphates are probably formed by the cleavage of end phosphates, and pyro- and tripolyphosphates by the successive decomposition of highpolyphosphates to shorter chains. It seems difficult to give a quantitative kinetics for degradation on the basis of the results of paper chromatographic analysis since the homogeneity of coacervate samples is somewhat doubtful. However, the portion of pyrophosphates obtained on the degradation of MPC was larger than what might have been expected from the successive cleavage. The polymerization of orthophosphates into pyrophosphates is not likely to occur at low temperatures such as 30—50 °C.

Wieker[9)] and Lowenstein[10)] reported that pyrophosphates are formed by coupling between the terminal $PO_4$ of straight chain polyphosphates and orthophosphate ions in the presence of Mg ions during the

Table 1. Degradation of phosphate anions in magnesium coacervate

| Sample | Temp (°C) | Time (min) | Phosphates formed on degradation (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tripoly | Trimeta | Highpoly |
| MPC | 50 | 0 | —[a] | — | — | — | 100 |
| | | 210 | 14.9 | tr.[b] | — | — | 85.1 |
| | | 4640 | 18.9 | 16.5 | 17.3 | — | 47.3 |
| | | 6060 | 28.5 | 22.0 | 20.7 | — | 28.8 |
| MPC | 90 | 0 | — | — | — | — | 100 |
| | | 20 | 13.3 | tr. | — | — | 86.7 |
| | | 40 | 18.1 | 11.9 | 9.2 | — | 60.8 |
| | | 60 | 18.5 | 13.0 | 10.8 | — | 57.7 |
| $NaPO_3$[c] | 90 | 0 | — | — | — | — | 100 |
| | | 50 | 16.9 | tr. | — | — | 83.1 |
| | | 90 | 22.2 | tr. | — | — | 77.8 |
| | | 120 | 28.2 | tr. | — | — | 71.9 |
| | | 210 | 47.9 | tr. | — | — | 52.1 |

a) Not detected. b) Trace. c) About 15% aqueous solution of $NaPO_3$.

course of hydrolysis of hexakisguanidinium tetraphosphate and adenosintriphosphate, respectively. The above reactions occurred in alkaline solutions. However, the degraded coacervates probably contained a considerable amount of hydrogen ions since calcium acid phosphates were formed during the course of CPC degradation.

In addition to the three degradation processes proposed by van Wazer and his coworkers,[2] and the coupling in alkaline solutions, there may be some other decomposition paths of coacervates and pyrophosphate formation in degraded coacervates.

## Conclusion

From the results of viscosity meausrement and paper chromatography of MPC and CPC, the following conclusions were obtained:

1) Most samples of MPC are more stable than those of CPC. No precipitate in magnesium coacervates was observed at 30 °C for about two months.

2) Most samples of CPC turn into wet cakes of such calcium phosphates as $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca_3(HP_2O_7)_2 \cdot 4H_2O$ at 30 °C in about 10 days.

3) Pyrophosphate may be formed in MPC and CPC probably through a certain path differing from that of degradation of alkali highpolyphosphates in aqueous solutions and also from that of the coupling reaction in alkaline solutions.

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