A Solubility Study of Coacervates of Magnesium, Calcium and Aluminum Highpolyphosphates in Acid Solutions

Takafumi KANAZAWA, Takao UMEGAKI, Yōzō KITAJIMA, and Takeshi OGAWA

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University,
Fukazawa, Setagaya-ku, Tokyo, 158

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Dissolution of the highpolyphosphate coacervates of magnesium, calcium and aluminum was studied in order to understand the conformational feature of polyphosphate chains in the coacervates. Electrical conductivity and viscosity of the coacervate solutions were measured. Paper chromatographic technique was employed for the analysis of the solutions. It was concluded that the polyphosphates dissolve into acid solvents without cleavage of phosphate chains, the degree in the extension of the chains being considerably small. Dissolution processes of the three coacervates were compared. Optimum conditions on the syntheses of the threadforming coacervates are given.

Magesium highpolyphosphate coacervate (MPC), calcium highpolyphosphate coacervate (CPC) and aluminum highpolyphosphate coacervate (APC) with high viscosity (10—10^3 poise) and transparency were prepared from mixed solutions of sodium highpolyphosphate and metal chlorides.

The main purpose of this study was to clarify the dissolution processes of the three coacervates from the results of electrical conductivity and viscosity. Paper chromatography was utilized to examine whether cleavage of the chain phosphate anions occurred during the course or after the completion of the dissolution process.

The degradation of some highpolyphosphates has been investigated by Thilo and Wieker[1,2] and Gill and Riaz.[3] However, a detailed study of the dissolution process of polyphosphates into acid solvents does not seem to have been dealt with.

The synthetic conditions of CPC and APC are briefly described in the present report. The preparation of MPC and its thermal change were discussed in previous papers.[4-6]

Experimental

Materials. The synthetic conditions for CPC and APC were partly the same as those for MPC.[4] CPC was obtained from a mixture of 15% sodium highpolyphosphate solution (400 parts) and 20% calcium chloride solution (166 parts) by the addition of ethyl alcohol. In the synthesis of APC, the threadforming property of the coacervates changes with the molar ratio of P to aluminum ion. Acids such as HCl (0.05%, 0.1%) and citric acid (H_3Cit) (2%, 10%) were used as solvents.

Measurements. Viscosities of the coacervate solutions were measured with an Ostwald capillary viscometer with efflux time of ca. 120 s for distilled water. The conductivities of the coacervate solutions of various concentrations were measured with an apparatus consisting of an alternating current bridge and a conductivity cell. All the measurements of viscosities and conductivities were carried out in a bath maintained at 30±0.02 °C.

Paper chromatography. Each strip of filter paper (Toyo Roshi No. 51A) on which 25 μl of sample solution was spotted was immersed in Kolloff solvent No. 92-D5.[7] The filter paper was left at about 5 °C for 7—10 hr during which time the solvent rose 10—15 cm.

TABLE 1. SPINNABILITY AND RATIO OF METAL ION(M) TO P IN THE MIXED SOLUTIONS

Coacervate	M : P(mole ratio)	Note
MPC	1 : 2	spinnability
CPC	1 : 2	spinnability
APC	1 : 3	no spinnability
APC	1 : 6	
APC	1 : 12	spinnability

Results and Discussion

A comparison of spinnability among the three coacervates is given in Table 1. Threadforming MPC and CPC were obtained when the metal chloride solution and the sodium highpolyphosphate solution were mixed in the molar ratio P : metal=2 : 1. Threadforming APC formed from the mixture with a lower ratio of aluminum chloride to sodium polyphosphate. The optimum conditions for the synthesis of threadforming coacervate seem to be related to the acidity of the mixtures and the content of sodium ion in the coacervates.

No cleavage of highpolyphosphates occurred in the course of dissolution since such short chain phosphates as orthophosphates, pyrophosphates and tripolyphosphates were not detected by the paper chromatography. In a few hours after the complete dissolution of APC, orthophosphate ions were formed in the APC solution by the hydrolysis of polyphosphates, which was accelerated by the hydrogen ion and aluminum ion[1,2] in the coacervate solution. Consequently, all the

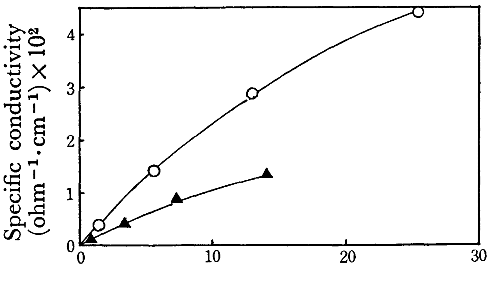

Fig. 1. Conductivity of aqueous solutions of polyphosphates.
○: sodium metaphosphate, ▲: MPC

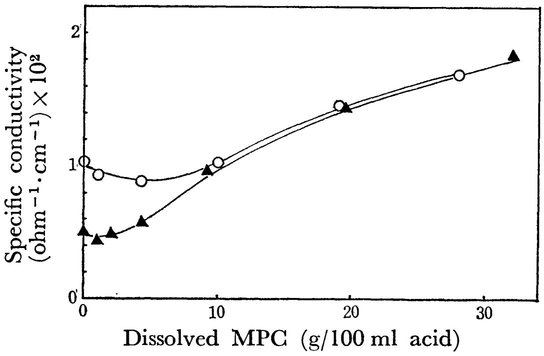

Fig. 2. Conductivity of MPC-HCl systems.
○: 0.1% HCl, ▲: 0.05% HCl

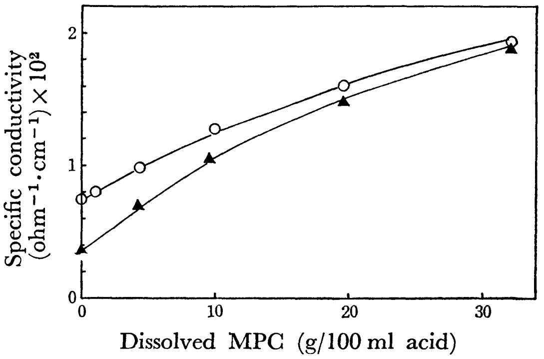

Fig. 3. Conductivity of MPC-H_3Cit systems.
○: 10% H_3Cit, ▲: 2% H_3Cit

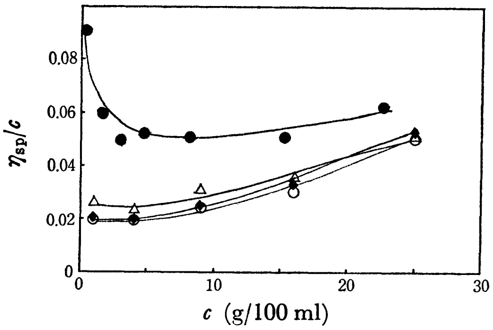

Fig. 4. Viscosity of MPC solutions.
●: sodium metaphosphate-H_2O, △: MPC-H_2O, ○: MPC-0.1% HCl, ◆: MPC-10% H_3Cit,

highpolyphosphates of magnesium, calcium and aluminum dissolved without degradation.

Figure 1 shows the electrical conductivity-concentration curves of the aqueous solutions of MPC and sodium highpolyphosphate used as a starting material of the coacervates. The coordination of magnesium ions to polyphosphate chains seems to depress the ionic dissociation of MPC. The conductivities of MPC solution were lower than those of the sodium highpolyphosphate solution. Figures 2 and 3 show the electrical conductivity *versus* concentration curves of the acid solutions of MPC. The conductivities of the citric acid solutions of MPC increased monotonically and the conductivity-concentration curves nearly coincide in the same manner as in the case of the HCl solution of MPC.

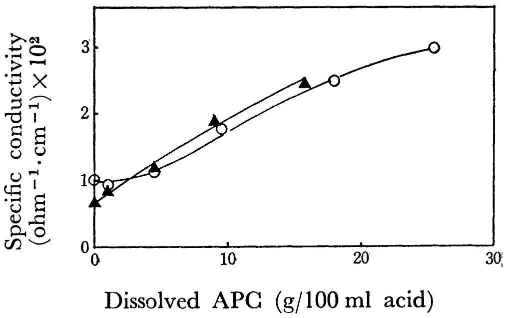

Fig. 5. Conductivity of APC solutions.
○: 0.1% HCl, ▲: 10% H_3Cit

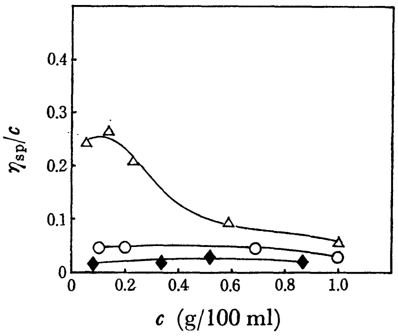

Fig. 6. Viscosity of APC solutions.
△: H_2O, ○: 0.1% HCl, ◆: 10% H_3Cit.

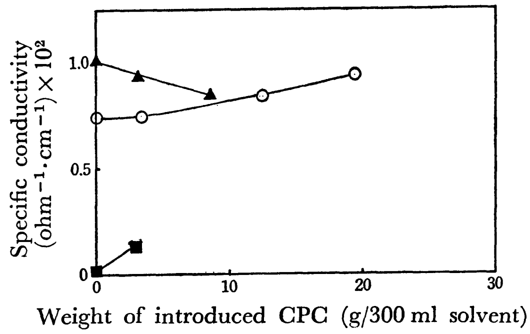

Fig. 7. Conductivity change of CPC solutions with amount of introduced CPC.
■: H_2O, ▲: 0.1% HCl, ○: 10% H_3Cit

The electrical conduction by hydrogen ion was predominant in the dilute HCl solutions of MPC. The bonding between the hydrogen ions in the HCl solution and the polyphosphate ions from the dissolved MPC caused a decrease of the hydrogen ions in the MPC solution, the conductivities decreasing with the concentration of MPC. The citrate ions in the citric acid solutions of MPC acted as a buffer and enhanced the concentration of hydrogen ion when the polyphosphate ion linked with the hydrogen ions in the acid solvent. Thus no conductivity decrease was observed at low concentrations of MPC in the case of citric acid. On both acid solvents the contribution of the dissolved ions to the conductivity increased with concentration of the MPC, the convergence of the conductivities to one curve occurring when the effect of the hydrogen ions in the acid solvents almost disappeared.

With the decrease in the concentration of polyelectrolyte the net charge on a polymer ion increases due to the increase of the ionic dissociation of the polyelectrolyte, and polymer chains extend owing to the intermolecular repulsive force among the charges with equal sign. Then the reduced viscosity of the polyelectrolyte solutions at low concentration often exhibits a curve considerably concave upward.[8]

Figure 4 gives a plot of the reduced viscosity of the MPC solution against concentration c. We see that the reduced viscosity of the MPC solution at low concentration does not increase with dilution although some curves indicate a slight extention of polymer coils of polyphosphates. Most of the polyphosphate chains of the MPC solutions were to some extent tightly coiled since the intermolecular repulsion was restricted owing to the neutralization of the charges on the chains by such cations as Mg^{2+}, H^+ and Na^+. The results of the viscosity measurement confirmed the conclusion from the conductivity measurement that the initial conductivity lowering of the HCl solution of MPC (Fig. 2) was caused not by the extention of the polymer chains but by the depression in the ionic dissociation of hydrogen. The changes in the conductivity and the viscosity of the acid solutions of threadforming APC were similar to those of the MPC solution (Figs. 5 and 6). The electrical conductivity change of the CPC solutions (Fig. 7) was also similar to that of the MPC solutions indicating that the more CPC was introduced into a solvent, the more electrolytes dissolved. However, a very small amount of viscous substance remains undissolved in the solution at a concentration of about 0.5 g/100 ml. CPC might contain some undissolved species, none of which was identified in the present study.

From the results obtained so far it was concluded that MPC, APC and soluble part of CPC dissolved without degradation of polyphosphate chains, which do not extend so much in the solutions. The polyphosphate ions in the coacervates seem to be more tightly coiled than those in the solutions of the coacervates since polyphosphates and some other electrolytes were much more concentrated as compared with those in the coacervate solutions.

Hydration of such cations as Mg^{2+}, Al^{3+}, Ca^{2+} and Na^+ and the coordination of these ions to polyphosphate ions should be clarified for more detailed discussion on the dissolution of the coacervates.

Some of the data in this report was cited from Ref. 4.

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