1452 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1452—1454 (1975) [Vol. 48, No. 5

Viscosity Behavior of Coacervates of Magnesium and Calcium Highpolyphosphates[1]

Takao UMEGAKI and Takafumi KANAZAWA

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

(Received December 6, 1974)

The viscosities of magnesium and calcium highpolyphosphate coacervates were measured in the temperature range of 20 to 90 °C. The Andrade's Equation was an approximate representation for the temperature dependence of viscosities of the coacervates. The activation energies of flow for the highpolyphosphate coacervates of magnesium and calcium were calculated to be about 7 kcal/mol and about 15 kcal/mol, respectively. The extension of the phosphate chains in coacervates was considered to be restricted, and the spinnability of the coacervates was probably originated, not by an elastic network structure, but by high viscosity of the coacervates. The viscosities of the magnesium coacervates decreased with an increase in water content and no remarkable effect of ethyl alcohol on the preparation of the coacervates was found.

Viscometric studies of dilute solutions of alkaline highpolyphosphates were carried out by Strauss, Smith, and Wineman[2] for the determination of the molecular dimensions. In the previous paper[3] viscosities of magnesium, calcium and aluminum highpolyphosphate coacervate solutions were measured in order to examine their conformational features during the dissolution into acid solvents. The viscoelasticity of the composite specimen of the magnesium highpolyphosphate coacervate and glass cloth was also determined by torsional braid analysis.[4] However, there has been no quantitative study on the viscosity behavior of the coacervates themselves.

The present paper deals with temperature dependence of viscosity at temperatures, from 20 to 90 °C, for magnesium highpolyphosphate coacervate (MPC). Moreover, the viscosities for MPC and CPC prepared according to the new methods without addition of ethyl alcohol were compared with those of the coacervates obtained by the procedures already reported,[4,5] and the viscosity change of MPC with water content was studied.

On the basis of the results on the viscometric experiments, the extension of phosphate anion chains and the complex formation in the coacervates were discussed, and viscosity behaviors of MPC and CPC were compared.

Experimental

Materials. According to the methods for synthesizing MPC and CPC[4,5] both coacervates were obtained by adding ethyl alcohol to the mixture of a 15% sodium metaphosphate solution and a 20% solution of magnesium or calcium chloride. MPC and CPC were also prepared by direct addition of $MgCl_2 \cdot 6H_2O$ (167 g) and $CaCl_2 \cdot 2H_2O$ (73.5 g), respectively, to a 20% sodium metaphosphate solution (500 g). Then all the coacervates separated became transparent in a week at room temperature.

Analysis. The coacervates were analyzed for calcium by ETA titration and for phosphorous by the vanadomolybdate colorimetry.[6] Sodium was determined by titrating a standardized HCl, which was partially neutralized by the liberated sodium ion in advance adsorbed on Amberlite IR-120 from a coacervate solution.[7] Paper chromatography of the polyphosphate ions in MPC and CPC was carried out according to the method by Kolloff.[8]

Viscosity Measurement. Shearing stresses of MPC and CPC at shear rates, from 10 to 600 s^{-1} and temperatures, from 20 to 90 °C, were measured with a rotational viscometer of cone-and-plate type (Shibayama Kagaku Co., Ltd.). The viscometer was calibrated at 20 °C by using JS 200 (1.78 P), JS 1000 (8.918 P), JS 2000 (18.14 P), 60H (497.3 P) and 200H (1683 P) as standard liquids for viscosity manufactured by Showa Oil Co., Ltd. All the above oils were assumed to be Newtonian fluid whose shearing stress is proportional to shear rate. A strain gauge was used for the measurement of torque of the cone evolved by the rotation of viscous fluid on the plate. The viscometer was so designed that the electromotive force of the strain gauge was proportional to shearing stress in the fluid. Consequently, the shearing stress was calculated from the electromotive force of the strain gauge.

Results and Discussion

From the linearity of flow curves for MPC and CPC (Figs. 1 and 2), most coacervates were recognized to be Newtonian, although the curve for MPC at 20 °C was concave upward very slightly. The non-Newtonian flow of MPC at 20 °C might be attributed to the heterogeneity of vicosity in the coacervate, which formed on coacervation and remained on viscosity measurement

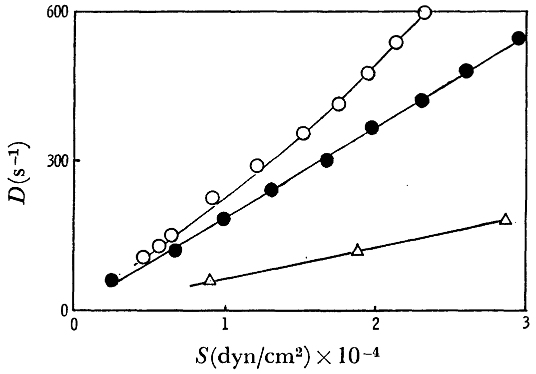

Fig. 1. Flow curves of MPC samples.
○: coacervated by $MgCl_2 \cdot 6H_2O$ powder, settled for 240 hr at 20 °C (P_2O_5 20%), ●: coacervated by $MgCl_2 \cdot 6H_2O$ powder, settled for 240 hr at 30 °C (P_2O_5 25%), △: coacervated by ethyl alcohol, settled for 912 hr at 30 °C (P_2O_5 45%)

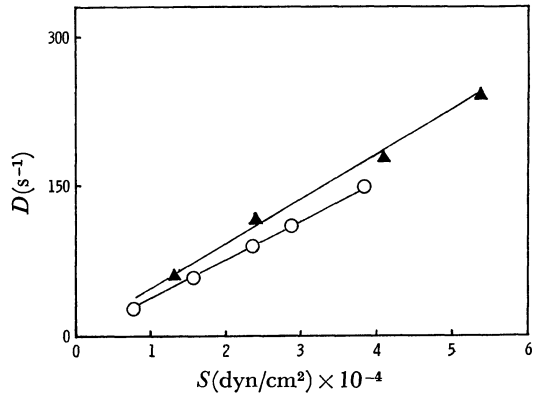

Fig. 2. Flow curves of CPC samples at 30 °C.
▲: coacervated by $MgCl_2 \cdot 6H_2O$ powder, ○: coacervated by ethyl alcohol

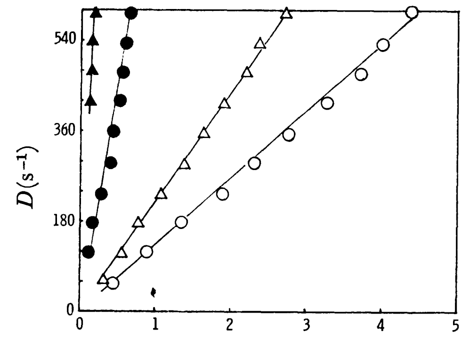

Fig. 3. Effect of the addition of distilled water to MPC on flow curve of MPC.
The ratios of MPC to water by weight are as follows: 85: 15 (○), 80: 20 (△), 75: 25 (●), and 70: 30 (▲).

at 20 °C. The viscous part remaining locally in the coacervate might act like the so-called scaffolding structure formed suspended particles in solutions.[9]

Figure 3 shows the viscosity change with water content. These samples in Fig. 3 were prepared by the mere addition of water to MPC (P_2O_5 31.8%), being settled in a week. The viscosity of MPC decreased remarkably with decrease in P_2O_5 content. For example, the addition of distilled water to MPC (P_2O_5 31.8%), in a ratio of 1 : 1 in weight changed the viscosity of the coacervate from 10^2 to about 2 P. Then, no degradation of highpolyphosphates upon the water addition was recognized by the paper chromatography. This viscosity change was attributed to the easily weakened interaction of various electrolytes with each other in the coacervates.

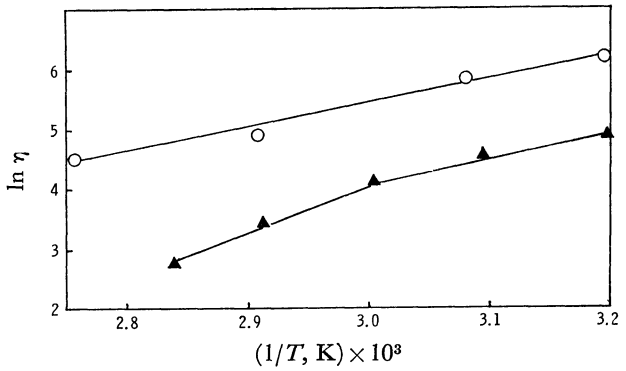

Fig. 4. Temperature dependence of viscosity of MPC.
○: coacervated by ethyl alcohol, ▲: coacervated by $MgCl \cdot 6H_2O$

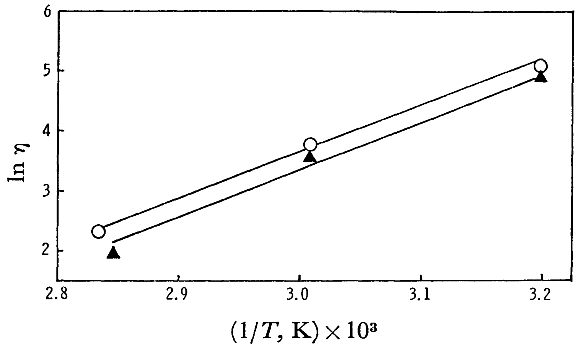

Fig. 5. Temperature dependence of viscosity of CPC.
▲: coacervated by ethyl alcohol, ○: coacervated by $MgCl_2 \cdot 6H_2O$

Figures 4 and 5 show the temperature dependence of viscosity for MPC and CPC, respectively. Although some flow curves of coacervates showed non-Newtonian behavior, the apparent viscosity (η) was calculated by assuming a linear relationship between shearing stress and shear rate concerning the coacervates used here. According to the Andrade's Equation ($\eta = Ae^{B/T}$, where A and B are quantities independent of temperature), a plot of the logarithmic viscosity against the reciprocal of absolute temperature should be a straight line. The apparent activation energy of flow (E) was obtained from the slope of the line (B) and gas constant (R) as follows: $E = B \times R = 1.986B$ (cal/mol).

The values of E for MPC and CPC calculated from the slopes in Figs. 4 and 5 are given in Table 1. The values of E for MPC were found to be 6—8 kcal/mol. This value is probably interpreted in terms of the presence of the cross-linking due to the weak bonding like a hydrogen bond in MPC, both values for MPC and water having the same order of magnitude.[10] However, the values of E for two MPC were somewhat larger than those for water. From the comparison of E for MPC with that for water, it is concluded that hydrogen bond in coacervates has a considerable effect on the viscosity of the coacervates and that the difference of the potential barriers on flow process between MPC and water is brought about by the difference in both dimension and mutual interaction of solute molecules.

TABLE 1. ACTIVATION ENERGIES OF FLOW (E) OF COACERVATES

Sample	P_2O_5 content (%)	Temperature range (°C)	E (kcal/mol)
MPC	60.1[a]	40— 90	6.4
	36.0	40— 60	8.1
CPC	63.9[a]	40— 79	16.4
	51.8	40— 80	13.9
H_2O	—	0— 20	4.61[b]
	—	50—100	3.10[b]

a) Coacervated by the addition of ethyl alcohol. b) Cited from Ref. 9.

Although MPC prepared by the addition of ethyl alcohol might contain the alcohol, the slope of $\ln\eta$ plot against $1/T$ was recognized to be almost the same as that of MPC obtained by the direct addition of $MgCl_2 \cdot 6H_2O$. Then, probably, no essential change in the configuration of highpolyphosphate ion in MPC was induced by the addition of alcohol, but in the course of the synthesis of MPC ethyl alcohol was effective only for the depression in the ionic dissociation in the mixture of sodium highpolyphosphate and magnesium chloride solutions, the dielectric constant of the mixture being reduced by the addition of alcohol.

The linearity of flow curves for most MPC indicates no remarkable conformational change of highpolyphosphate chains with an increase in shear rate. Since the values of E for MPC and water are comparable, the extension of the highpolyphosphate chains is considered to be small and the chains might be coiled spherically and somewhat tightly.

The values of E for CPC are larger than those for MPC, although the apparent viscosities for CPC are smaller or the same compared with those for MPC. Therefore, the interaction among highpolyphosphate chains in CPC is considered to be stronger than that in MPC, and the phosphate coils are extended more widely in CPC than in MPC.

The complex formation between highpolyphosphate and metal ion is well-known and sodium highpolyphosphate has been industrially utilized as a masking agent for Ca^{2+}, Mg^{2+} and other metal ions.[11] Moreover, the stability constants of some complexes were calculated from the pH lowering during the titration of highpolyphosphate ion with hydrogen ion.[11,12] It was reported that the treatment of some calcium highpolyphosphate coacervates with ammonium fluoride solution yielded no calcium fluoride, indicating that the calcium ions were strongly masked by the highpolyphosphate.[13] Then, there is no doubt about the presence of a certain stable complex between calcium and polyphosphate, even in CPC. The activation energies of flow for CPC (14—16 kcal/mol) may indicate the slight extension of the highpolyphosphate chains, and some part of the calcium-polyphosphate complex may be expected to form a network structure with the cross-linkage of the chains by calcium ions.

Erbring[14] and Nakagawa[15] found that some liquids having an elastic network structure are spinnable and some highly viscous substances (40—50 poise or more) with no anomalous structure also possess a thread-forming property. The origin of the spinnability for MPC and CPC reported in the previous paper[3] might be explained on the basis of the results on the viscosity measurement described above. The viscosity measurement of dilute solutions of the coacervates suggested the presence of the tightly coiled highpolyphosphate chains in the acid solvents.[3] On the other hand, in the coacervates themselves the extension of the highpolyphosphate chains is also supposed to be restricted from a consideration of the low activation energies of flow for coacervates compared with those for ordinary linear high molecular organic polymers. The linearity of flow curves for the coacervates used here indicates no anomalous structure, while the electron micrographs by Danno[16] and the observation with an optical microscope by Yamaguchi and Kashiwase[17] showed the network structure in such thread-forming liquids as mercury sulfosalicylate solution and potassium highpolyphosphate solution, respectively. It is concluded that the spinnability of the coacervates in this work was originated, not by an elastic network structure, but by high viscosity of the coacervates as well as that of sodium silicate solution or sugar solution with high concentration.

Conclusion

From the results of the viscometric studies on MPC and CPC, the following facts were obtained.

(1) The coacervates used here were mostly Newtonian.

(2) The Andrade's Equation was an approximate representation for the temperature dependence of the viscosities of MPC and CPC, from which the activation energies for flow process of MPC and CPC were calculated to be about 7 kcal/mol and about 15 kcal/mol, respectively.

(3) The addition of water to MPC caused the viscocity lowering, but no degradation of polyphosphate chains occurred.

(4) No essential change in the configuration of highpolyphosphate ion in MPC was induced by the addition of ethyl alcohol.

(5) The extension of the phosphate chains was restricted and the spinnability of MPC and CPC were originated, not by an elastic network structure, but by high viscosity of the coacervates.

References

1) This paper was read at the Autumn Meeting of the Union of Chubu Branches of the Chemical Societies and Associations, Nagoya, October, 1973.

2) U. P. Strauss, E. W. Smith, and P. Wineman, *J. Amer. Chem. Soc.*, **75**, 3935 (1953).

3) T. Kanazawa, T. Umegaki, Y. Kitajima, and T. Ogawa, This Bulletin, **47**, 1419 (1974).

4) T. Umegaki and T. Kanazawa, *ibid.*, **46**, 3587 (1973).

5) T. Kanazawa, T. Umegaki, and H. Kawazoe, *Asahi Garasu Kogyo Gijutsu Shorei-Kai Kenkyu Hokoku*, **21**, 81 (1972).

6) "Official Methods of Analysis of Fertilizers," ed. by the National Institute of Agricultural Sciences, Tokyo, (1972), p. 24.

7) H. Kakihana, *Nippon Kagaku Zasshi*, **72**, 203 (1951).

8) R. H. Kolloff, *Anal. Chem.*, **33**, 373 (1961).

9) T. Nakagawa, "Rheology," Iwanami Publishing Co., Tokyo, (1968), p. 142.

10) T. Nakagawa, *ibid.*, (1968), p. 112.

11) E. Kobayashi, "Chemistry of Phosphates and their Utilization," ed. by S. Hori, Kagakukogyo-sya Co., Ltd., Tokyo, (1971), p. 185.

12) T. Sugano and K. Kubo, *Nippon Kagaku Kaishi*, **1974**, 1068.

13) E. H. Brown and J. R. Lehr, *J. Agr. Food. Chem*, **12**, 201 (1964).

14) H. Erbring, *Kolloid. Z.*, **98**, 164 (1942).

15) T. Nakagawa, This Bulletin, **25**, 88, 93 (1952).

16) T. Danno, *ibid.*, **32**, 1033 (1959).

17) T. Yamaguchi and H. Kashiwase, *Kogyo Kagaku Zasshi*, **66**, 576 (1963).