

Preparation of Colloidal Silver Using Various Reductants in the Presence of Copolymers of Vinyl Alcohol-*N*-Vinyl Pyrrolidone

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SYNOPSIS

Colloidal silver was prepared using various reductants such as hydrazine, ascorbic acid, ribose, and hydrogen in aqueous solution in the presence of copolymers of vinyl alcohol-*N*-vinyl pyrrolidone. The average particle size of colloidal silver decreased with increasing amount of copolymers added. The reduction by hydrogen provided smaller silver particles compared with the other reductants. The stability of colloidal silver against AlCl_3 increased with increasing amount of copolymers added.

INTRODUCTION

There are many methods¹⁻¹² to prepare precious metal particles, and, as one of the methods, precious metal ions have often been reduced in mixtures of protective colloids and reducing agents. As protective colloids, water-soluble polymers such as poly(vinyl alcohol), poly(*N*-vinyl pyrrolidone), and poly(methyl vinyl ether)^{8,13-16} have been used. However, since such homopolymers are not effectively adsorbed on precious metal particles, mono-dispersed fine particles are hard to obtain.

Hirai et al.⁸ have reported that the methanol reduction of some precious metal ions in the presence of poly(vinyl alcohol) provides colloidal rhodium, palladium, platinum, iridium, and osmium but not silver and gold. Further, Hirai¹⁵ has found that colloidal silver and gold are obtained by the reduction with methanol and sodium hydroxide in the presence of poly(*N*-vinyl pyrrolidone).

On the other hand, we have performed a preparation of colloidal silver by reduction with methanol using copolymers of vinyl alcohol and *N*-vinyl pyrrolidone, which are expected to adsorb on colloidal

particle effectively. As a result, a very stable colloidal silver has been obtained.¹⁷

In this work we extended this study for preparation of colloidal silver in the presence of copolymers of vinyl alcohol and *N*-vinyl pyrrolidone using various reductants such as hydrazine, ascorbic acid, hydrogen, and ribose. A relationship between particle size and amount of protective copolymers was studied. A stability of colloidal silver was also examined.

EXPERIMENTAL

Materials

Silver nitrate was obtained from Tokyo Kasei Co. Ltd. Poly(vinyl alcohol) (PVA) and poly(*N*-vinyl pyrrolidone) (PVP) were obtained from Kishida Chemicals Co. Ltd. and Tokyo Kasei, Co. Ltd., respectively. Vinyl acetate (VAc) and *N*-vinyl pyrrolidone (VP) were obtained from Wako Chemical Industries. They were distilled under reduced pressure before use.

Hydrazine and ascorbic acid were obtained from Wako Chemical Industries and ribose from Tokyo Kasei Co., Ltd. The other chemicals were of extra pure grades.

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Preparation of Copolymers

Mixtures of VAc and VP in various ratios were added to acetone, and the polymerization was carried out under a nitrogen gas atmosphere at 70°C, using α, α' -azobisisobutyronitrile as the initiator. Then, the products, as purified with petroleum ether, were dissolved into methanol and saponified upon the addition of sodium methoxide at 40°C under a nitrogen gas atmosphere. The samples thus obtained were purified with diethyl ether and acetone.

The determinations of molecular weight and content ratio of the copolymers have been described elsewhere.¹⁷

Preparation of Colloidal Silver

An aqueous solution containing the copolymer and an aqueous solution containing silver nitrate were mixed, resulting in a total solution of 0.05 dm³. This resulting solution was stirred for 30 min and then reduced at 70°C upon addition of aqueous solution of hydrazine. In the case of ascorbic acid and ribose, an aqueous solution containing silver nitrate and the polymer was also reduced upon addition of aqueous solution of ascorbic acid and ribose at room temperature. The reduction with hydrogen gas was carried out by bubbling it through the aqueous solution at room temperature. The concentration of silver nitrate used in all experiments was 0.33 mmol/dm³.

Stability of Colloidal Silver

To evaluate a stability of colloidal silver, 0.001 dm³ of 0.2 mol/dm³ AlCl₃ was added to 0.02 dm³ of prepared colloidal silver, and the solution was centrifuged at 5000 rpm for 7 min. The absorbance of the colloidal silver before and after the centrifugation was measured at 410 nm by means of a UV spectrophotometer. The stability of the colloidal silver was evaluated by the ratio of absorbance before and after the centrifugation: A high ratio indicates a high stability of the colloidal silver.

Measurements

The viscosity of aqueous solution containing polymers was measured by means of an E-type viscometer.

The particle size of the colloidal silver obtained was determined by means of transmission electron microscopy with a Hitachi H 800 microscope. The electron diffraction pattern was also taken to determine a crystal structure of silver.

For fluorescence experiments, an ammonium salt of 8-anilino-1-naphthalene sulfonic acid (ANS) was used as a probe. The concentration of ANS was 1×10^{-5} mol/dm³. The steady-state emission spectra were obtained using a Hitachi 650-10S fluorescence spectrophotometer. The ANS aqueous solutions containing polymers were excited at 377 nm.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between average particle size of colloidal silver and amount of added

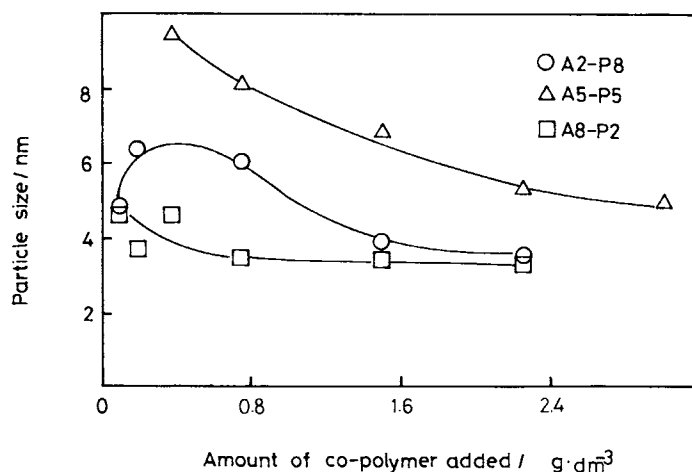


Figure 1 Relationship between average particle size of colloidal silver and amount of copolymer added using hydrazine.

Table I Molecular Weight of Polymers Used

Polymer	Molar Ratio in Copolymer		Molecular Weight
	VA	VP	
A2-P8	1.47	8.53	4.4×10^4
A5-P5	3.53	6.47	6.4×10^4
A8-P2	7.44	2.56	3.1×10^4
PVA			4.0×10^4
PVP			4.0×10^4

copolymers using hydrazine. Here, the concentration of hydrazine was 1.32 mmol/dm^3 . Table I also shows the pertinent properties of these copolymers. The average particle size of the colloidal silver decreased gradually with increasing amount of the copolymers and became constant for three copolymers, where in the case of A2-P8 the constant value was about 6 nm and in the case of A5-P6 and A8-P2 about 4 nm. The particle size distribution of the colloidal silver was quite broad below 0.4 g/dm^3 of the copolymers but became narrow above 0.75 g/dm^3 of the copolymers. This result indicates that in a lower amount of the copolymers, the copolymers are not fully covered on most of the particles, and the protective action by the copolymers is not enough to stabilize the colloidal silver particles. The color of the colloidal silver was yellow for three copolymers. When PVA and PVP were used, a stable colloidal silver was not obtained because the colloidal silver

Table II Intrinsic Viscosity of Polymers with Different Concentrations

Polymer	Concentration (g/dm^{-3})				
	0.50	1.00	1.50	2.00	4.00
A2-P8	0.62	0.63	—	—	0.69
A5-P5	0.73	0.62	0.65	0.69	0.67
A8-P2	0.60	0.61	0.63	0.63	0.66
PVA	1.26	1.19	1.19	1.24	1.24
PVP	0.90	0.86	1.02	—	1.00

sedimented after 2 days. Also, even using a mixture of PVA and PVP (1 : 1), no stable colloidal silver was obtained. Thus, these copolymers are also found to be useful to prepare a stable colloidal silver using hydrazine.

Figure 2 shows the change in average particle size of the colloidal silver as a function of amount of added copolymers using ascorbic acid. Here, the concentration of ascorbic acid used was 57 mmol/dm^3 . The color of the colloidal silver changed from green to yellow with increasing amount of copolymers. Additionally, the particle distribution of the colloidal silver prepared using ascorbic acid was similar to that using hydrazine; its distribution decreases with increasing amount of the copolymers. Although the average particle sizes did not change monotonously, unlike the case of hydrazine, they were much smaller than in the case of hydrazine. In the case of PVA and PVP, colloidal silver was im-

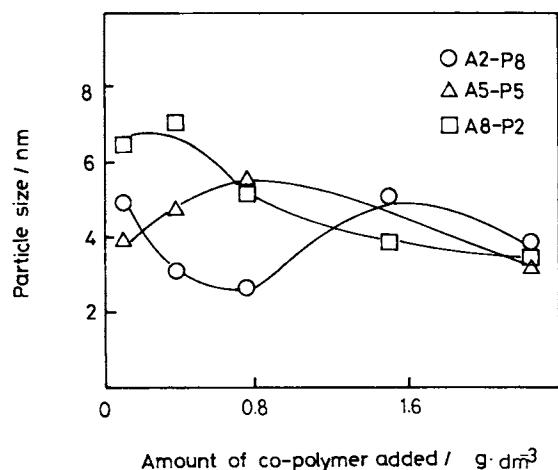


Figure 2 Relationship between average particle size of colloidal silver and amount of copolymer added using ascorbic acid.

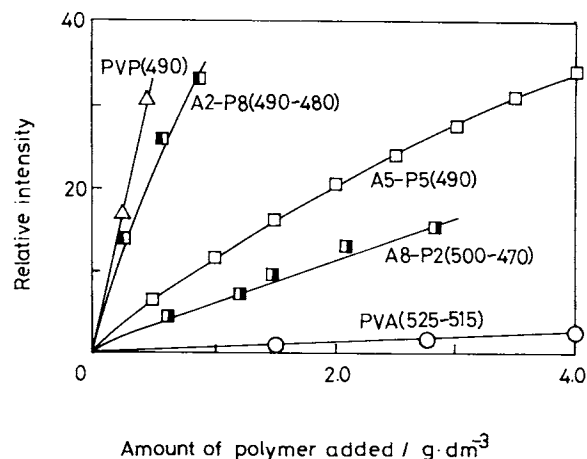


Figure 3 Intensity of fluorescence of ANS in aqueous solution of polymer. Maximum wavelength (nm) is given in bracket.

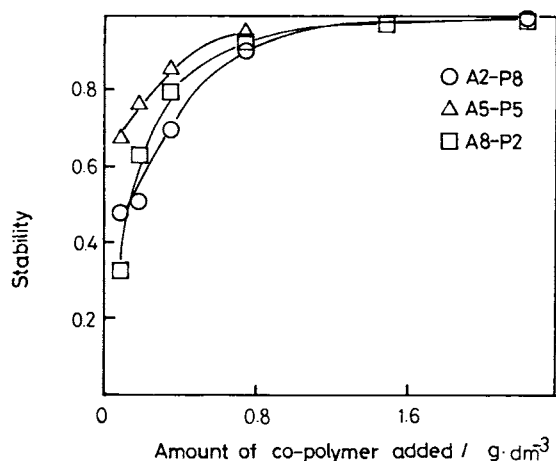


Figure 4 Effect of amount of copolymer added on stability of colloidal silver prepared using hydrazine.

mediately flocculated and sedimented after the reduction.

A stable colloidal silver in the presence of the copolymers was also obtained using hydrogen gas and ribose. In particular, in the reduction with hydrogen gas, a red colloidal silver having an average diameter of 2 nm was obtained. Reproducibility of particle formation, however, was poor due to difficulty of controlling the flow rate and reduction time.

Comparing the present data with the average particle size obtained by the reduction with methanol,¹⁷ it was found that the reduction with hydrazine, ascorbic acid, ribose, and hydrogen gas provided much smaller sizes.

In order to elucidate a role of the copolymers as a protective colloid, the viscosity and fluorescence for aqueous solutions of the copolymers were measured. Table II shows that the intrinsic viscosities of the copolymers (A2-P8, A5-P5, and A8-P2) are rather smaller than that of PVA and PVP. Figure 3 shows the intensity of fluorescence of ANS in the aqueous solution of the copolymers. When excited at 377 nm, the single broad band, which has an emission peak at 520 nm in water, can shift to a wavelength as low as 462 nm when ANS is in a hydrophobic region. It is said¹⁸ that a blue shift in the wavelength maximum of the fluorescence as the microenvironment changes from hydrophilic to hydrophobic. In the aqueous solution of PVA, the intensity of a single band having an emission peak at 520 nm was very low, whereas in the aqueous solution of PVP and the copolymers an emission band was observed at 490 nm, and its intensity increased with

the concentration. These data indicate that the hydrophobicity of copolymers is intermediate between PVA and PVP. Accordingly, these viscosity and fluorescence data may support a view that the protective action of the copolymers is caused by the configuration and an appreciable hydrophobicity of the copolymers.

The destabilization of the colloidal silver by an electrolyte, AlCl_3 is shown in Figure 4. The stability of the colloidal silver against AlCl_3 increased with increasing amount of the added copolymers, and more than 0.75 g/dm^3 the stability was very high and little affected against AlCl_3 . Here, the stability behaviors of the colloidal silver against AlCl_3 were almost the same for three copolymers. A similar result for the stability was obtained in the case of ascorbic acid. These results suggest that since the colloidal particles obtained more than 0.75 g/dm^3 of the amount of the added copolymers are rather monodispersed and covered fully with the copolymer, the stability of silver particles becomes insensitive against AlCl_3 . This stability is attributed to the steric stabilization¹⁹ by the copolymers.

This study shows that the colloidal silver is obtained in the presence of the copolymers of VA-PVP using hydrazine, ascorbic acid, ribose, and hydrogen. The distribution of the silver particle size becomes narrow at some amount of the copolymers where the particles seem to be fully covered. Further, the average particle size of the colloidal silver obtained by these reductants is much smaller than by methanol, and they show high dispersion stability against AlCl_3 .

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