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SHORT COMMUNICATION

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Formation of colloidal silver in the presence of a nonionic surfactant, Surfynol 465

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Abstract The formation of colloidal silver in the presence of a nonionic surfactant, Surfynol 465, was studied at various temperatures. By simply mixing equal volumes of $AgClO_4$ aq. (1–10 mmol kg^{-1}) and Surfynol 465 aq., the colloidal silver was formed. The colloidal solution had well over ten times the amount of fine silver particles in the solution formed by the ordinary methods. The first factor to form the colloidal silver without aggregation was the molar ratio of Surfynol 465 to $AgClO_4$, and the optimum ratio increased with increasing the concentration of $AgClO_4$ or the temperature. In the fraction of colloidal silver collected through the gel filtration, Surfynol 465 was also found in the micellar state. From these results, it was suggested that Surfynol 465 was a protecting agent of colloidal silver as well as a reducing agent of $AgClO_4$ in the similar manner to the case of colloidal gold.

Key words Colloidal silver – nonionic surfactant – Surfynol 465 – UV-VIS spectrum – TEM

Introduction

Surfynols, which are nonionic surfactants with one acetylenic group and two polyoxyethylene chains in molecule, are sufficiently promising for forming colloidal metals [1–3]. When chloroauric acid aqueous solution ($HAuCl_4$) was simply mixed with Surfynol aqueous solution in a test tube, a colloidal gold was formed at room temperature [4, 5]. From the results of UV-VIS spectra, Surfynols were considered to function as protecting agents of colloidal gold formed as well as reducing agents of $HAuCl_4$. In this work, we studied the formation of colloidal silver in the same manner as in the case of colloidal gold by using Surfynol 465, which was selected out from among Surfynols.

Experimental

Materials

Silver perchlorate hydrate ($AgClO_4 \cdot H_2O$) was obtained from Aldrich Chem. Surfynol 465 (number average molar mass: 600 g mol^{-1}) was a gift from Air product and Chemicals, U.S.A. Sephadex G-50 (medium) was from Pharmacia Biotech. Deionized and distilled water was used.

Methods

A colloidal silver was prepared from two aqueous solutions of $AgClO_4$ and Surfynol 465 in a test tube at various

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temperatures. The gel filtration of solution was performed by using a glass tube packed with Sephadex G-50. As the eluent the water was used. The UV-VIS absorption spectrum of solution was measured by a spectrophotometer (type U-3000, Hitachi, Japan) with quartz cell (optical path: 1 or 2 mm). The transmission electron micrograph (TEM) of solution was obtained by using an electron microscope (type H-500, Hitachi, Japan).

Results and discussion

Formation of colloidal silver

The UV-VIS spectrum of mixture of $AgClO_4$ aq. and Surfynol 465 aq. showed plainly the absorption peak around 405 nm, which differed from the wave length for the peak characteristic of $AgClO_4$ or Surfynol 465, i.e., 210 or 235 nm, respectively (Fig. 1). From the TEM in Fig. 2, the mixture was found to be the dispersion of fine particles of metal. Thus, it was suggested that a colloidal silver could be formed from $AgClO_4$ in the presence of Surfynol 465.

When Surfynol 465 aqueous solution (0.1 mol kg^{-1}, 5 cm^3, colorless) was added to $AgClO_4$ aqueous solution (4 mmol kg^{-1}, 5 cm^3, colorless) at 35 °C, the mixture gradually changed color to yellow, brown and dark reddish brown with time. In the UV-VIS spectrum in Fig. 3, the absorption peak newly appeared around 415 nm by mixing, showing the formation of colloidal silver. At 1 week after mixing, the peak began to be much broader together with another absorption around 545 nm, which was considered to be due to the aggregation of colloidal silver. From the relation of the absorbance at 415 nm or 545 nm and the mixing time, it was clearly found that the formation of colloidal silver was very slow compared with that of colloidal gold and the colloidal silver formed tended to aggregate with each other at 7 days or more after mixing, although the formation of colloidal silver was not fully completed. However, if the mixture was transferred from 35° to 4 °C at 5 days after mixing, we could keep the mixture in good colloidal solution without aggregation over 1 year.

Influence of concentration and temperature

We have reported that the first factor to form the colloidal gold from $HAuCl_4$ in the presence of Surfynols was the molar ratio of Surfynol to $HAuCl_4$, and Surfynols functioned as protecting agents of colloidal gold formed as well as reducing agents of $HAuCl_4$ [4, 5]. If Surfynol 465 in the formation of colloidal silver played a similar role to the case of formation of colloidal gold, the molar ratio of Surfynol 465 to $AgClO_4$, R, would be significant for the formation of colloidal silver.

Then, we examined the formation of colloidal silver by mixing two equal volumes of $AgClO_4$ aq. and Surfynol 465 aq. The concentration of $AgClO_4$ before mixing, c_{Ag}, was fixed at 4 mmol kg^{-1}, and the concentration of Surfynol 465 before mixing, c_s, was varied from 0.05 to 0.6 mol kg^{-1}.

The UV-VIS spectra of mixture of $AgClO_4$ aq. and Surfynol 465 aq. were measured after a mixing of 4 days' duration at 35 °C (Fig. 4). The height and the shape of absorption peak around 415 nm depended on c_s. It was noted that there was the optimum c_s or R for the formation of colloidal silver. Consequently, we could evaluate 0.1 mol kg^{-1} and 25 as the optimum c_s and R at 35 °C, respectively.

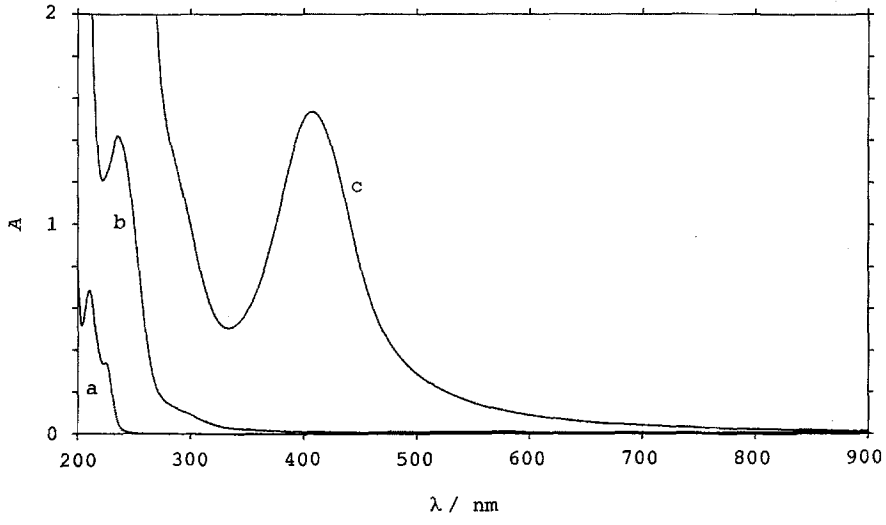

Fig. 1 UV-VIS absorption spectra. a: $AgClO_4$ aq. (4 mmol kg^{-1}), b: Surfynol 465 aq. (0.05 mol kg^{-1}), c: mixture of equal volumes of $AgClO_4$ aq. (4 mmol kg^{-1}) and Surfynol 465 aq. (0.4 mol kg^{-1}). The mixing time was 5 min at 95 °C. The optical path was 2 mm

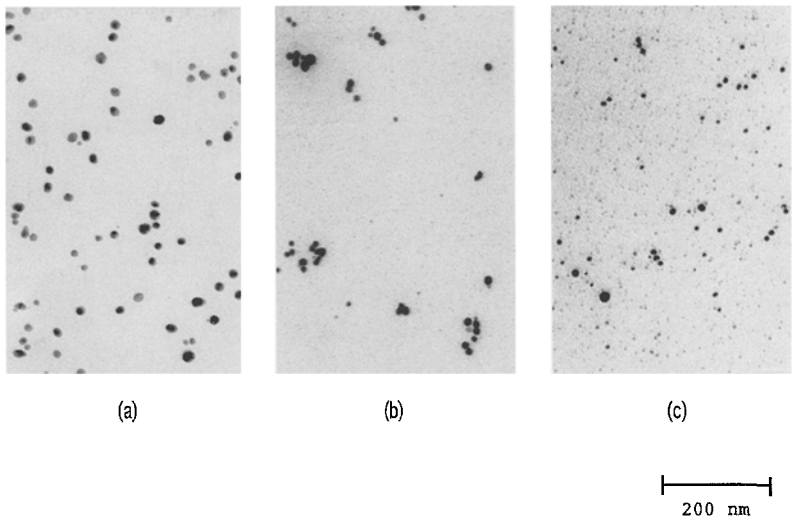

Fig. 2 Transmission electron micrograph of mixture of equal volumes of $AgClO_4$ aq. (4 mmol kg^{-1}) and Surfynol 465 aq. at various temperatures. The concentration of Surfynol 465 and the temperature were a: 0.1 mol kg^{-1} at 35 °C, b: 0.2 mol kg^{-1} at 45 °C and c: 0.4 mol kg^{-1} at 95 °C. These concentrations were optimum for the formation of colloidal silver

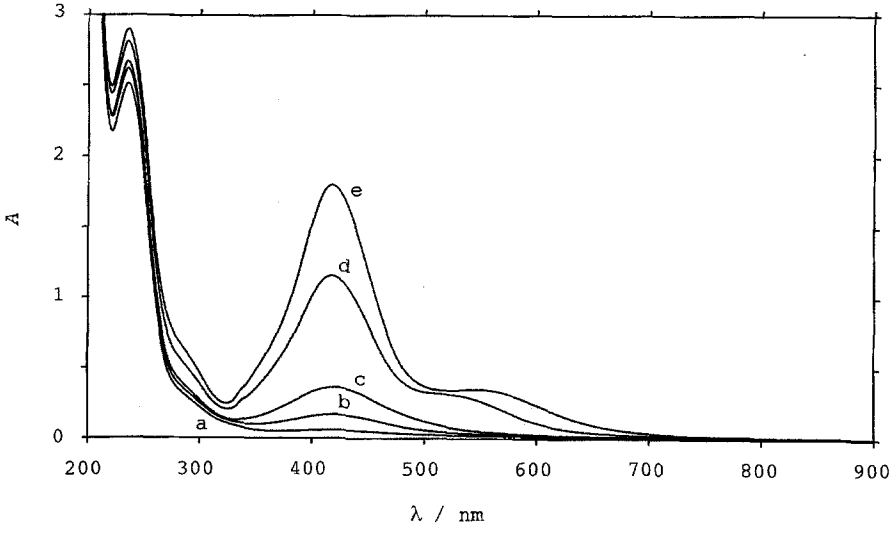

Fig. 3 UV-VIS absorption spectra of colloidal silver prepared by mixing equal volumes of $AgClO_4$ aq. (4 mmol kg^{-1}) and Surfynol 465 aq. (0.1 mol kg^{-1}) at 35 °C. The mixing time was a: 3, b: 4, c: 5, d: 7 and e: 8 days. The optical path was 1 mm

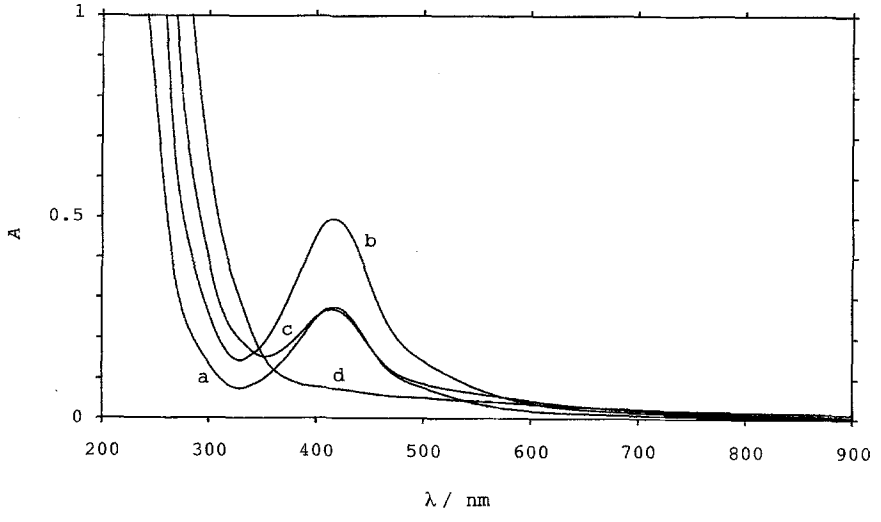

Fig. 4 UV-VIS absorption spectra of colloidal silver prepared by mixing equal volumes of $AgClO_4$ aq. and Surfynol 465 aq. at 35 °C. The concentration of $AgClO_4$ was 4 mmol kg^{-1}. The concentration of Surfynol 465 was a: 0.05, b: 0.1, c: 0.2 and d: 0.4 mol kg^{-1}. The mixing time was 4 days. The optical path was 2 mm

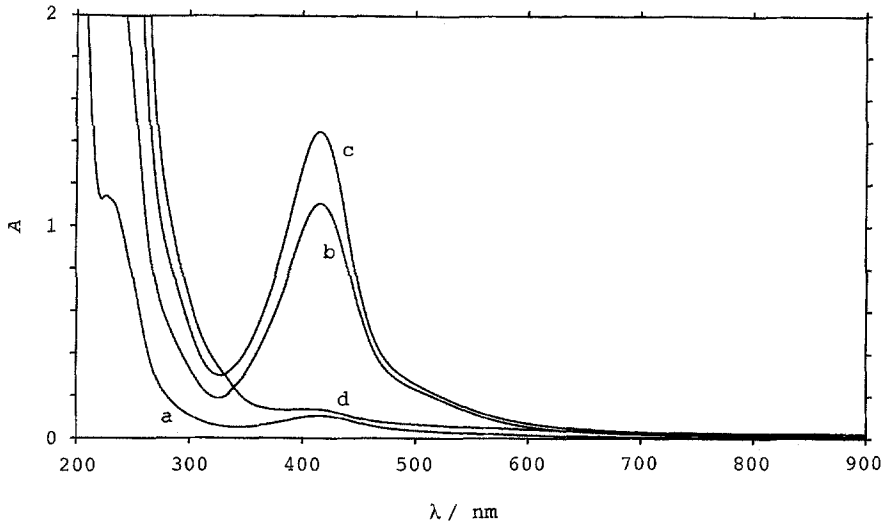

Fig. 5 UV-VIS absorption spectra of colloidal silver prepared by mixing equal volumes of $AgClO_4$ aq. and Surfynol 465 aq. at 45 °C. The concentration of $AgClO_4$ was 4 mmol kg^{-1}. The concentration of Surfynol 465 was a: 0.05, b: 0.1, c: 0.2 and d: 0.4 mol kg^{-1}. The mixing time was 1 day. The optical path was 2 mm

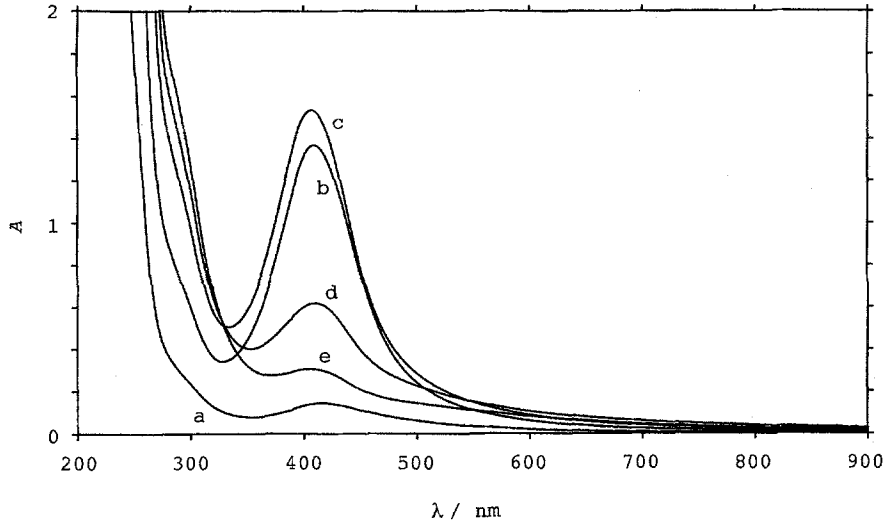

Fig. 6 UV-VIS absorption spectra of colloidal silver prepared by mixing equal volumes of $AgClO_4$ aq. and Surfynol 465 aq. at 95 °C. The concentration of $AgClO_4$ was 4 mmol kg^{-1}. The concentration of Surfynol 465 was a: 0.1, b: 0.2, c: 0.4, d: 0.6, and e: 0.8 mol kg^{-1}. The mixing time was 5 min. The optical path was 2 mm

At various c_{Ag}, we could form the colloidal silver by mixing $AgClO_4$ aq. with Surfynol 465 aq., if c_s and R was optimum at any c_{Ag}. Thus, it was found that the amount of silver particles in colloidal solution was very high compared with the amount in colloidal silver formed by other methods [6–10].

The colloidal silver could be formed up to 100 °C. The higher the mixing temperature, the faster the rate of formation of colloidal silver. The quite adequate times to form the colloidal silver at 35°, 45° and 95 °C were 4 days, 1 day and 5 min, respectively. However, the colloidal silver preferred aggregating with each other at higher temperature. If the colloidal silver formed at any temperature was immediately transferred to 4 °C, we could keep the colloidal silver in dispersion state without aggregation for a long time. Meanwhile, the optimum c_s at 35°, 45° and 95 °C for 4 mmol kg^{-1} $AgClO_4$ were 0.1, 0.2 and 0.4 mol kg^{-1}, respectively (Figs. 4–6). Since the optimum c_s was very large compared with c_{Ag}, we could expect another function than the reducing agent from Surfynol 465.

Next, we observed the UV-VIS spectra of colloidal silver formed from 4 mmol kg^{-1} $AgClO_4$ in the presence of Surfynol 465 with the optimum c_s. At higher temperature the wave length of peak shifted toward the lower value and the absorbance at peak increased (Figs. 4–6). If Mie's theory on the red or blue shift of colloidal gold in the UV-VIS spectrum could be also applied to the case of colloidal silver [12], the silver particle formed at higher temperature would be smaller than the particle at lower temperature, supported by the TEM in Fig. 2.

The optimum c_s as well as the absorbance at peak increased with increasing temperature. It was suggested that the formation of colloidal silver from $AgClO_4$ significantly depended on the temperature, i.e., the reduction of

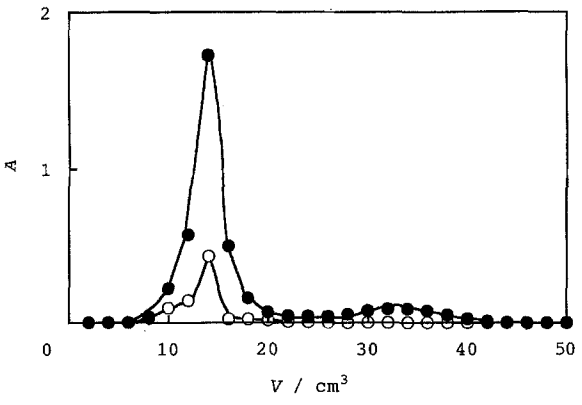

Fig. 7 Elution pattern of gel filtration of colloidal silver prepared by mixing equal volumes of $AgClO_4$ aq. (4 mmol kg^{-1}) and Surfynol 465 aq. (0.2 mol kg^{-1}) at 95 °C. ●: the absorbance at 235 nm, ○: the absorbance at 415 nm. The mixing time was 5 min. The optical path was 2 mm

$AgClO_4$ to atomic silver to form the colloidal silver was almost completed at 95 °C, but it was incomplete at 35 °C. Thus, for the colloidal silver formed at 95 °C in the condition that the range of c_{Ag} was from 2 to 9 mmol kg^{-1} and R was 100, we estimated the molar absorption coefficient of colloidal silver at 1320 m^2 mol^{-1}, which was slightly smaller than that of colloidal silver formed from $AgClO_4$ (below 0.1 mM) by Mulvaney [10].

Figure 7 showed the result of gel filtration of colloidal silver. The elution pattern of the absorbance at 235 nm, which was due to an acetylenic group of Surfynol 465, had two elution peaks at 14 and 34 cm^3 of elution volume. On the basis of the elution pattern of Surfynol 465 aqueous solution, the two peaks were assigned to micelle and monomer of Surfynol 465, respectively. The elution peak of colloidal silver coincided in elution volume with the peak of Surfynol 465 micelle. It was suggested that silver particle was surrounded by Surfynol 465 micelles to be prevented from aggregating.

In conclusion, we could form the colloidal silver by simply mixing two aqueous solutions of $AgClO_4$ and Surfynol 465, if R was optimum. The optimum R increased with increasing c_{Ag} or temperature. From the results of the UV-VIS spectra and the gell filtration of colloidal silver, it was considered that Surfynol 465 played a key role in the reduction of silver ion to atomic silver and the prevention of aggregation of silver particles in a manner similar to the case of colloidal gold.

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