"Blue silver": transformation of clusters and metal coagulation

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The formation and transformations of "blue silver" ($\lambda_{max} \gtrsim 700$ nm) during γ-irradiation of a weakly alkaline (pH 9) aqueous solution containing $AgClO_4$, polyacrylic acid (PAA), and isopropanol were studied. We believe that "blue silver" is a linear silver cluster stabilized on a polymeric molecule. During radiation-chemical reduction the cluster is transformed into new clusters (λ_{max} = 365 and 460 nm). When all of the Ag^+ ions present in the solution have been reduced, clusters coalesce and a new phase, *i.e.*, colloidal silver particles, forms. The mechanism of the radiation-chemical transformations is discussed.

Key words: "blue silver", clusters; sols, coagulation; γ-irradiation, radiation-chemical transformations; reduction, mechanism.

Colloidal silver (particles 1—20 nm in diameter) is yellow-colored in aqueous solutions. Its electronic absorption spectrum exhibits an intense band in the 380—400 nm[1] region caused by the collective oscillation of the electron gas in the metal and by the periodic variation of the electron density at the surface (absorption of plasmons). The optical band shifts to longer wavelengths as the sizes of the particles increase and, especially, when they change from a spherical shape to an ellipsoid shape.[2] It has been found previously[3] that when polyacrylic acid (PAA) is used as a stabilizing agent, the radiation-chemical reduction of Ag^+ ions in weakly alkaline (pH 8—10) aqueous solutions is accompanied by a change in their color to bright blue. As this takes place, absorption bands with maxima at 290 and 700 nm appear in the electronic spectrum. The "blue silver" thus prepared possesses remarkable stability even in the presence of oxygen and can be isolated in the pure state by the evaporation of water. It has been suggested that this phenomenon is caused by stabilization of silver on an uncoiled chain of the PAA polyanion.

In this work we present new data on "blue silver" that concern, most of all, its conversions when the degree of reduction of the Ag^+ ions is high, as occurs in aqueous solutions.

Experimental

"Chemically pure" reagents were used. The molecular weight of the polyacrylic acid used as a stabilizing agent was 70 000.

NaOH was added to aqueous solutions containing $AgClO_4$, PAA, and isopropyl alcohol up to pH 9, then the solutions were evacuated in special vessels having optical cells (l = 0.1 to 10 mm). The solutions were irradiated at ambient temperature using a ^{60}Co source at a dose rate of 11 kGy h^{-1}. Optical spectra were recorded on Specord UV-Vis and Specord M40 spectrophotometers.

Microscopic investigations were carried out on a Philips EM-301 transmission electron microscope. To prepare a sample, a drop of a solution under study was applied to a copper grid coated with sprayed graphite and then dried in a vacuum.

Results and Discussion

The radiation-chemical reduction of Ag^+ ions in aqueous solutions containing additives of organic compounds can be represented[4] in general as the set of reactions (1)—(3):

$$H_2O \xrightarrow{\gamma} e^-_{aq},\ H,\ OH, \quad (1)$$

$$RH + OH(H) \rightarrow R + H_2O(H_2), \quad (2)$$

$$Ag^+ + e^-_{aq}(\text{or } R) \rightarrow Ag^0(+ R^+), \quad (3)$$

where RH and R are the organic compound and the radical, respectively; e^-_{aq} is a hydrated electron.

Isopropanol was used as the acceptor of OH radicals and H atoms. Reaction (2) afforded the Me_2COH radical. Owing to the high concentration of PAA in the solution, it could also participate in reaction (2) to give polymeric radicals.

Thus, when aqueous solutions of $AgClO_4$ are subjected to γ-irradiation in the presence of organic compounds, e^-_{aq} and R species possessing high reducing abilities (φ = −2.7 V for e^-_{aq} and −1.5 V for Me_2COH)[4] appear uniformly throughout the solution. By varying the absorbed dose rate and the duration of irradiation it is possible to control the process of the reduction of Ag^+. At the dose rate used by us, the concentration of

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e^-_{aq} and R produced over a period of 1 min was $1.1 \cdot 10^{-4}$ mol L^{-1}.

Figure 1 shows the variation of the optical absorption spectra of a $2 \cdot 10^{-1}$ *M* solution of $AgClO_4$ (pH 9.2) containing PAA (0.2 mol L^{-1}) and isopropanol (0.5 mol L^{-1}). During the initial stage of γ-irradiation (see Fig. 1, *a*), an absorption band with λ_{max} = 290 nm and a weak band at 510 nm arise. As the absorbed dose increases the band in the visible region gradually shifts to longer waves up to 700—750 nm. As this takes place, the solution turns blue. An examination of the ESR spectra of "blue silver" showed the absence of radical species; thus, the silver atoms are united into molecular clusters.

When the solution is irradiated for ~60 min, the optical density of the band at 700 nm reaches its maximum value, and after that it decreases (see Fig. 1, *b*). Simultaneously a broad absorption band in the 300—500 nm region with slightly defined maxima at 365 and 460 nm appears. The absorption at 290 nm practically does not change. The isobestic point at 550 nm corresponds to the transformation of silver clusters with λ_{max} = 700 nm into clusters having a spectral maximum at 460 nm. The maximum intensity of the band at 460 nm is attained after ~120 min of irradiation; further γ-irradiation results in the disappearance of this band and the appearance of a band at 385 nm. As has already been mentioned, this is caused by the absorption of the surface plasmons in the ultra small silver particles. The appearance of the absorption band at 385 nm and the increase in its intensity are accompanied by a decrease in the absorption at 290 nm. It is noteworthy that these transformations of the silver solution in the presence of PAA during γ-irradiation are accompanied by surprising changes in its color: it turns from blue to green, then to red and to brown and in the final stage it changes to an intense yellow color.

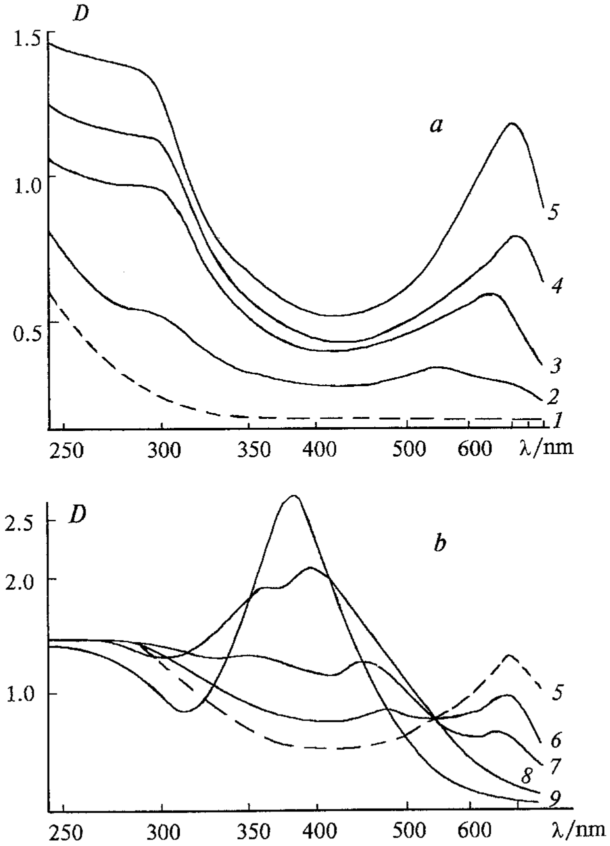

Fig. 1. Variation of the electronic absorption spectra during γ-irradiation of a $2 \cdot 10^{-2}$ *M* solution of $AgClO_4$ (pH 9.2) containing PAA (0.2 mol L^{-1}) and isopropanol (0.5 mol L^{-1}). Duration of irradiation/min: *a*, the original unirradiated solution (*1*); 6 (*2*); 20 (*3*); 40 (*4*); 60 (*5*); and *b*, 60 (*5*); 80 (*6*); 110 (*7*); 180 (*8*); 260 (*9*).

Electron-microscopic studies made it possible to see that at those stages when the absorption at 700 nm appears and declines, virtually no metal particles are produced. An avalanche-like formation of colloidal particles of silver occurs as the optical band with λ_{max} = 385 nm is formed. At this final stage of irradiation of the solution, the whole field of the plate being examined under the electron microscope is covered with silver particles, mostly spherical, of diameter 1—2 nm. Thus, the above-described variations in the optical spectra of PAA-containing solutions of $AgClO_4$ during γ-irradiation are associated with the formation of silver clusters and their subsequent transformation resulting in their coalescence to produce colloidal particles. It should be noted that "blue silver" is not formed in acidic or neutral solutions. Radiation-chemical reduction of Ag^+ ions results in the formation of colloidal metal particles even at the initial stage of γ-irradiation.

In our opinion, the mechanism of the formation and transformation of "blue silver" may be represented in general as follows. In an aqueous alkaline solution, polymeric PAA molecules exist as polyanions and are uncoiled due to the repulsion between the COO^- groups.[5] The Ag^+ ions are efficiently bound by the COO^- anions to give a sequence of —COOAg salt groups. Reduction of silver affords linearly structurized clusters in which atoms and ions of silver are linked to each other. The collective excitation of these linear silver clusters is probably responsible for the absorption in visible region. The successive growth of the cluster chain and the increase in the content of silver atoms in it, which occur with the increase in the dose absorbed is the reason for the observed shift of the absorption band from 500 nm to 700 nm. The stability of these clusters is ensured by the presence of Ag^+ ions and of a strong bond with PAA.

Reduction of silver in aqueous solutions is also known[7] to be accompanied by the formation of positively charged clusters, some of which ("magic" clusters) possess high stabilities (Ag_4^{2+}, Ag_8^{2+}). However, neutral clusters are kinetically unstable. Quantitative analysis of the results implies that at the concentrations of $AgClO_4$ used (10^{-2} to $5 \cdot 10^{-2}$ mol L^{-1}), the maximum absorption for the 700 nm band is attained when no more than 30 % of the Ag^+ ions have been reduced. Assuming that all of the e^-_{aq} and R species formed are consumed by the reduction, we can evaluate the extinction coefficient of the linear cluster of silver in relation to the concentration of Ag atoms. It amounts to $\sim 2 \cdot 10^4$ L mol^{-1}. Notice that this value is close to the extinction coefficients measured previously[6] for Ag_2^+, Ag_4^{2+}, and Ag_8^{2+} clusters.

The consecutive reduction of the PAA-stabilized silver clusters results in their transformation into new clusters in which the proportion of reduced Ag^+ ions is higher. These clusters exhibit broad absorption bands with weakly pronounced maxima at 365 and 460 nm. Finally, after complete reduction, neutral clusters (or their fragments) are formed whose bonds with PAA are weakened, and they coagulate to liberate the metal phase.

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