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ICPS' 94: The Physics and Chemistry of Imaging Systems

IS&T's 47th Annual Conference

Volume I

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May 15-20, 1994
The Radisson Hotel at Rochester Plaza
Rochester, New York

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Reduction and Aggregation of Silver in Aqueous Gelatin and Silica Suspensions*

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Introduction

The investigation of silver reduction and aggregation processes are of specific interest to the photographic industry, which relies heavily on photochemical equivalents of these reactions. Mechanistic insights into the formation of small silver clusters in aqueous solution have been obtained from both pulse and γ -radiolytic studies.¹⁻³ This paper examines the reduction of silver ions and the subsequent formation of silver clusters in aqueous gelatin solutions and on colloidal silica particles using the pulse radiolysis technique. The aggregation processes are compared with the parallel reactions in aqueous solutions.

Pulse Radiolysis

Irradiation of argon saturated aqueous solutions with high-energy electrons generates radicals as shown by equation 1:

In basic solution the yield of the latter three species is small and may be neglected. In the presence of *tert*-butanol the hydroxyl radicals will be scavenged to generate the relatively unreactive β -hydroxyl radicals as shown in equation 2:

Thus the only radical which will remain in significant yields in solution is the solvated electron which reacts with silver ions to initiate aggregation processes as described below.

Mechanism of Silver Cluster Formation in Aqueous Solution:

Pulse radiolytic studies of the reduction and aggregation of silver in aqueous solution has established that the primary steps in the growth of colloidal silver may be described by equations 3 and 4:¹

In solution, Ag_2^+ dimerizes to form Ag_4^{2+} (reaction 5)¹.

This sequence may be modified by the presence of colloidal silica and gelatin stabilizers.

Silver Cluster Formation on Colloidal Silica

The adsorption of Ag^+ to the surface of SiO_2 may be described by equation 6:

Using ultra-filtration and analyzing the filtrates for silver we determined an average value for the adsorption/desorption equilibrium constant, $K = 3.4 \times 10^5 \text{ M}^{-1}$. This value is consistent with the silver ions predominantly being adsorbed on the silica surface.

The lifetime of the solvated electron was independent of the silica concentration, thus SiO_2 does not react with e_{aq}^- . Figure 1 shows the evolution of the absorption spectra of a solution containing $2.5 \times 10^{-5} \text{ M Ag}^+$ with an average ratio of Ag^+/SiO_2 of 1:2 following a 4 ns electron pulse. Initially a band centered at 360 nm is formed. This band is assigned to Ag^0 .⁴ Significantly, concomitant with the species growing in at 360 nm, a shoulder at approximately 315 nm develops. Based on a comparison to parallel reactions in aqueous solution, this band is attributed to Ag_2^+ .⁴ It should be noted that at this Ag^+/SiO_2 ratio the formation of an Ag_2^+ species requires migration of a silver ion or atom from one SiO_2 particle to another. Increasing the average number of silver ions per silica particle from one to four does not lead to the appearance of any new spectral feature indicating that within the time window of 100 μs species such as Ag_4^{2+} ($\lambda_{\text{max}} = 275 \text{ nm}$)⁴

are not formed. However, as the concentration of silver is increased, the rate of formation of the absorption bands at 360 and 315 nm increase. We therefore conclude that the desorption of Ag_2^+ from the surface of the particles is very slow. In contrast, in the absence of the silica particles the formation of Ag_4^{2+} during this time window is clearly noticeable. As can be seen from figure 1, the absorption band at 360 nm (Ag^0) decreases without any noticeable increase in absorption across the range of 300–600 nm. These atoms must be converted to species larger than Ag_4^{2+} which have smaller extinction coefficients in the spectral range shown in figure 1.

Figure 1. Absorption spectra of transients formed after a 4 ns electron pulse in a solution containing $5 \times 10^{-5} \text{ M}$ SiO_2 , $2.5 \times 10^{-5} \text{ M}$ Ag^+ , 10^{-3} M sodium borate buffer (pH 9) and 0.1 M *t*-butanol.

The observed rate constant (in sec^{-1}) for the decay of e_{aq}^- can be described as the sum of two processes; the rate of free Ag^+ ions and the rate of those adsorbed on the silica surface with e_{aq}^- (equation 7):

$$k_{\text{obs}} = k_f[\text{Ag}^+]_f + k_{\text{ads}}[\text{Ag}^+]_{\text{ads}} \quad (7)$$

where k_f is the rate constant for the reaction of free Ag^+ with e_{aq}^- , taken as $3.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and k_{ads} is the rate constant for the reaction of adsorbed silver ions with e_{aq}^- . Figure 2 shows the dependence of k_{corr} ($k_{\text{corr}} = k_{\text{ads}}[\text{Ag}^+]_{\text{ads}}$) on the number of adsorbed Ag^+ ions per SiO_2 particles. At Ag^+/SiO_2 ratios of approximately 12:1 the rate becomes independent of silver concentration at the silica surface. As can be seen from figure 2, the important parameter is the ratio Ag^+/SiO_2 and not the absolute concentration of either of them, as long as the concentration of silica particles, $[\text{SiO}_2]_p \geq 5 \times 10^{-5} \text{ M}$. Two distinct regions can be observed in figure 2: a region where in-

creasing Ag^+/SiO_2 ratio results in a linear increase in k_{corr} followed by a region where k_{corr} is independent of the amount of silver ions at the surface of SiO_2 . These observations are rationalized by considering the mechanism illustrated in scheme 1. The reduction process in this scheme is viewed as a two step mechanism: diffusion of e_{aq}^- to the particle and its lateral diffusion along the surface to an adsorbed Ag^+ ion. The probability that e_{aq}^- will encounter an Ag^+ ion, and thus form Ag^0 , will increase with increasing silver concentration [scheme 1]. In the linear region of the curve in figure 2 the rate determining step is the reaction of the electron with silver ions adsorbed to the silica surface. At some point the rate determining step will be the rate at which the electron encounters a silica particle. This is the region where the rate plateaus in figure 2. For the 40 Å SiO_2 particles used in this study at $5 \times 10^{-5} \text{ M}$ of particles this plateau is reached at a Ag^+/SiO_2 ratio of approximately 12:1. The bimolecular rate constant obtained from the plateau of figure 2 is $8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; i.e the reaction is diffusion controlled.

Figure 2. Corrected rate constant at 600 nm as a function of silver concentration at the SiO_2 particle surface; (*) The concentration of SiO_2 was $5 \times 10^{-5} \text{ M}$ and concentration of Ag^+ varied, (*) concentration of Ag^+ was $5 \times 10^{-5} \text{ M}$ and concentration of SiO_2 varied. In all cases the solutions also contained 10^{-3} M sodium borate buffer (pH 9) and 0.1 M *t*-butanol.

Scheme 1. (a) reaction of the electron with a silica particle containing only 1 Ag^+ atom (b) reaction of the electron with a silica particle containing 5 Ag^+ atoms. The probability, and hence rate of reaction, of the electron reacting with the Ag^+ is greater in (b). In both cases the diffusion of e_{aq}^- to the particle is not rate determining.

Silver Cluster Formation in Gelatin

Reactions of gelatin with e_{aq}^- have not been observed in the concentration range of gelatin used in our experiments. Figure 3 illustrates the transients obtained when a solution containing $1 \times 10^{-4} M Ag^+$ and 0.1% gelatin (w/v) was irradiated with a 4 ns electron pulse. At 1 μs after the pulse the formation of Ag^0 is complete (figure 3). However, a comparison of the spectra obtained under identical conditions but in the absence of gelatin indicates that the absorption due to Ag^0 was dramatically decreased in the gelatin containing solutions. This observation implies that the Ag^0 -gelatin complex has a smaller extinction coefficient relative to free silver atoms in solution. The silver atoms reacted with Ag^+ within 5 μsec to form Ag_2^+ ($\lambda_{max}=325$ nm, figure 3). The decrease of this species resulted in the formation of new bands at 275, 308 and 325 nm. These spectral features do not appear upon reduction of identical silver solutions in the absence of gelatin. They are assigned to larger than Ag_4^{2+} species.

Figure 3. Transient absorption spectra obtained using 4 ns electron pulses from a solution containing $1 \times 10^{-4} M AgClO_4$, 0.1 M *t*-butanol, 0.01 M $NaClO_4$ and 0.1 % gelatin (w/v) at pH 9.5. Spectra taken at 5 nm intervals.

Increasing the gelatin concentration decreases the rate of reaction of e_{aq}^- with Ag^+ . The decrease in the observed reaction rate is rationalized by assuming that complexation of Ag^+ by the amino acid moieties of the gelatin reduces the reactivity of silver ions towards e_{aq}^- . However, the rate of formation of Ag_2^+ is independent of gelatin concentration. This result is understandable assuming the reaction between Ag^0 and Ag^+ occurs within a gelatin chain. Increasing the concentration of gelatin does not affect the concentration of either Ag^+ or Ag^0 within the chain. When the concentration of e_{aq}^- was greater than the concentration of Ag^+ ions (i.e. at near complete reduction of silver) the bands at 305 and 325 nm decay rapidly. The results suggest that Ag^+ ions stabilize smaller silver aggregates ($Ag_n < 10$).

Formation of Long Lived Silver Clusters

Three long lived aggregates of different sizes were stabilized by either the gelatin or the silica particles upon complete reduction of the silver ions using trains of 40 ns electron pulses. Figures 4 and 5 illustrate the absorption spectra obtained in the SiO_2 and gelatin systems respectively.

Figure 4. Changes in the absorption spectra with time for silver species formed in an argon purged solution containing $5 \times 10^{-5} M$ SiO_2 , $5 \times 10^{-5} M$ Ag^+ , $10^{-3} M$ sodium borate buffer (pH 9) and $0.1 M$ t -butanol irradiated with eight 40 ns electron pulse trains within 4 seconds. The path length of the cell was 1 cm.

Figure 5. Changes in the absorption spectra with time for silver species formed in an argon purged solution containing $1 \times 10^{-3} M$ Ag^+ , 1 % gelatin (w/v) and $1 M$ t -butanol at pH 9.5. The path length of the cell was 1 cm.

In the case of the Ag^+/SiO_2 system distinct long lived spectral bands at 290, 330 and 400 nm developed. The different temporal behavior of the various bands in the Ag^+/SiO_2 indicates that these are particles of different sizes rather than different bands of a single size particle. In the absence of SiO_2 , the spectral bands at 290 and 330 nm were not observed. Addition of $10^{-2} M$ $NaClO_4$ to the

solution prior to irradiation did not hinder the formation of the spectral bands observed in figure 4. Based on our observations that sodium displaces silver ions from the silica surface, this indicates that the silver clusters are re-adsorbed on the SiO_2 surface. Addition of methyl viologen or Cu^{+2} ions to the solutions containing the clusters affected only the 290 nm absorption band. Earlier studies⁵ showed that the largest cluster capable of reducing the viologen moiety contain 4 atoms. The 330 nm and 400 nm spectral bands were also unaffected by the addition of $Ru(NH_3)_6Cl_3$ indicating that the redox potential of these clusters was greater than 0.2 V.⁶ From this potential, it can be estimated that the size of these clusters was greater than 10 silver atoms.⁷

In the case of nearly complete reduction of silver ions in gelatin solutions, three distinct spectral bands were also observed (figure 5). However, the spectral bands attributable to smaller silver clusters in the vicinity of 300 nm were not present. Instead, bands at 380, 450 and 510 nm corresponding to larger clusters of silver were apparent. Addition of methyl viologen (as a coagulating agent) affected the three spectral bands to different degrees verifying that the three bands originated from three different clusters.

Acknowledgments

The gift of gelatin from Dr. S. Ehrich is much appreciated. Support by the Natural Sciences and Engineering research Council of Canada (NS) and by the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE, under contract W-31-109-ENG-38 to ANL is gratefully acknowledged.

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