Effect of ionizing radiaton on the stability of colloidal silver and other metals in aqueous solutions

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The effect of ionizing radiation (accelerated electrons and γ-rays of ^{60}Co) on the stability of aqueous solutions of colloidal silver was studied. The threshold of absorbed dose, at which the stability dramatically decreases and coagulation of the metal occurs, was found. This critical dose corresponds to the reduction of silver ions that determine the electrical potential of the sols. "Radiation" neutralization was also found for cadmium sols and was not observed in the case of thallium, copper, or platinum. A mechanism of the effect of radiation, taking into account the electrostatic factor in the stability of metal sols, was considered.

Key words: radiation stability; accelerated electrons; γ-rays; lyophobic colloids; metal sols, silver.

Hydrophobic disperse systems (colloidal solutions of metals are typical examples of these systems) possess aggregative stability without stabilizing additives, since electrostatic repulsion forces predominate in them.[1] They coagulate when electrolytes are added to the solutions. The formation and coagulation of colloidal silver are greatly affected by the ionic strength of the solution and by the presence of anions that are adsorbed specifically on metal sols.[2—4] This is due to the compression of the double electric layer following an increase in the ionic strength, and to its destruction or variation of its structure upon adsorption of anions. In the latter case, the charge of the sol is neutralized and its stability is thus lost.

Optical absorption of metal sols is due to intraatomic transitions or to the interaction of light with surface plasmons.[5] The degree of this interaction depends substantially on the sizes and shapes of particles[6,7] and also on the state of the surface.[8,9] Therefore, in this case, electronic spectroscopy is a very efficient method for investigation of structural states of nano-sized aggregates, in addition to direct observation of these aggregates by electron microscopy.

In this work we studied the effect of ionizing radiation on the stability of colloidal silver and some other metals in aqueous solutions.

Experimental

Metal perchlorates with high degrees of purity were used as initial compounds. Solutions in bidistilled water were saturated with argon prior to irradiation. Irradiation was carried out using an electron accelerator with an energy of 4 MeV and a pulse duration of 0.5 μs or an U-12 accelerator with an energy of 5 MeV and a pulse duration of 2 μs. In a series of pulses, the interval between them was approximately 10 μs. γ-Irradiation was carried out using a ^{60}Co source. Samples for electron microscopy were prepared under argon by applying a drop of the solution to be analyzed on a copper-carbon plate and subsequent drying.

Optical absorption spectra were measured on a Specord UV-VIS or Shimadzu UV-3100 spectrophotometer. The microscopic examination was carried out using a Philips EM-301 transmission electron microscope.

Results and Discussion

When aqueous solutions containing metal ions and isopropyl alcohol are exposed to ionizing radiation, the following reactions occur:

$$H_2O \longrightarrow \bar{e}_{aq}, OH, H, H^+, H_2, H_2O_2,$$

$$Me_2CHOH + OH(H) \longrightarrow Me_2\dot{C}OH + H_2O(H_2).$$

As a result, species with high reducing potentials, *viz.*, hydrated electrons ($\bar{e}_{aq}$) (−2.9 V) and $Me_2\dot{C}OH$ radicals (−1.5 V) are generated in the solution.[10] The radiation dose per electron pulse was ~35 Gy, which ensured the formation of approximately equal amounts ($2.5 \cdot 10^{-6}$ mol L^{-1}) of both of these species. Their interaction with metal ions results finally in the formation of colloidal metal particles.

Optical absorption of colloidal silver. Colloidal silver is produced *via* consecutive transformations of the Ag_2^+, Ag_3^{2+}, Ag_4^{2+}, and Ag_4^+ clusters.[11,12] The formation of the metal is immediately preceded by the "magic" cluster Ag_8^{2+},[12] whose lifetime amounts to tens of minutes

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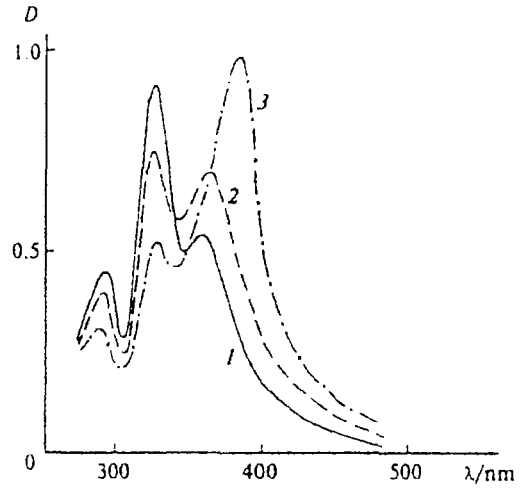

Fig. 1. Optical absorption spectra of a solution ($1 \cdot 10^{-4}$ mol L^{-1}) of $AgClO_4$ containing 0.1 mol L^{-1} of isopropyl alcohol, after irradiation with 100 electron pulses: immediately after irradiation (*1*); after 0.3 s (*2*) and 5 s (*3*) (absorbed dose in a pulse ~35 Gy, duration 0.5 μs, interval 10 ms).

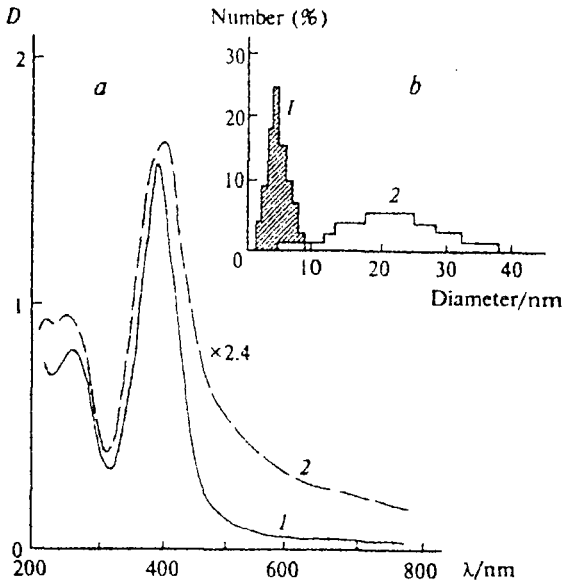

Fig. 2. *a*. Optical absorption spectra of colloidal silver. *b*. Size distribution of metal particles: in the presence of polyethylene imine ($2 \cdot 10^{-4}$ mol L^{-1}) (*1*) in the absence of this compound (*2*). Irradiation with 30 electron pulses (the solution used and irradiation conditions are described below Fig. 1). The spectra were recorded 5 min after irradiation.

after irradiation with single electron pulses or with short series of pulses with large absorbed doses.[11] Figure 1 shows the last stage of the formation of the metal phase after irradiation of a solution ($1 \cdot 10^{-4}$ mol L^{-1}) of $AgClO_4$ containing 0.1 mol L^{-1} of isopropyl alcohol with a series of electron pulses, which includes the decay of the Ag_8^{2+} clusters on the second time scale (optical bands with maxima at 295 and 325 nm) and appearance of colloidal silver (a typical band with a maximum at 390 nm). Under the conditions chosen (long series of pulses with small doses absorbed in each pulse), the formation of the colloid is completed several minutes after irradiation. Subsequently, we used mostly this method of irradiation, which made it possible to generate colloidal metal in solution over a short period and to measure its optical absorption spectrum using a stationary spectrophotometer.

Figure 2, *a* presents the absorption spectra of colloidal silver particles obtained in the presence and in the absence of a stabilizing compound added. In both cases, the absorption maxima are exhibited at ~390 nm, but they differ markedly in the shape and intensity. In the absence of a stabilizing compound, the intensity of the absorption maximum is ~2.5 times lower, and the band is broader and stretches far to the long-wavelength region. Figure 2, *b* shows the size distribution of the ultrasmall metal particles formed. Sols arising in the presence of a stabilizing reagent contain spherical particles with relatively narrow size distribution and an average diameter of 4—6 nm. Without a stabilizing compound, the size distribution is broad, and the shapes of particles are diverse; both large particles and conglomerates of small particles can be found. The diameter of the greater part of the particles lies in the 10—30 nm range. Silver colloids are relatively stable even in the absence of stabilizing compounds added. The smaller the absorbed dose and, correspondingly, the smaller the fraction of the silver ions reduced, the more stable these colloids. Thus, silver ions exert a stabilizing effect on them.

The effect of the absorbed dose. Figure 3 presents the variation of the absorption spectra of the silver colloids formed as a function of the number of electron particles (Fig. 3, *a*) as well as the variation of the intensity of the absorption maximum at 600 nm and its half-height width $W_{1/2}$ (Fig. 3, *b*). It can be seen that up to ~50 pulses, the form of the spectrum virtually does not change. Simultaneously, the intensity of the absorption band and, consequently, the concentration of colloidal metal increases in direct proportion to the absorbed dose. The situation changes after irradiation with 60—70 electron pulses: the intensity of the band decreases somewhat, structureless absorption appears over the whole visible region, and, as a result, the width of the band increases jumpwise. The narrow range of absorbed doses, in which the above changes occur, corresponds to the formation of $\sim 2 \cdot 10^4$ mol L^{-1} of reducing species, which is twice as high as the concentration of silver ions. It can be suggested that under these conditions, the latter are reduced almost completely. In fact, exposure of the solutions to a larger number of electron pulses does not have a noticeable effect on the reduction of Ag^+. When the critical dose is attained, colloidal silver becomes unstable. Tens of minutes later, the solution develops a grey color and then finely dispersed

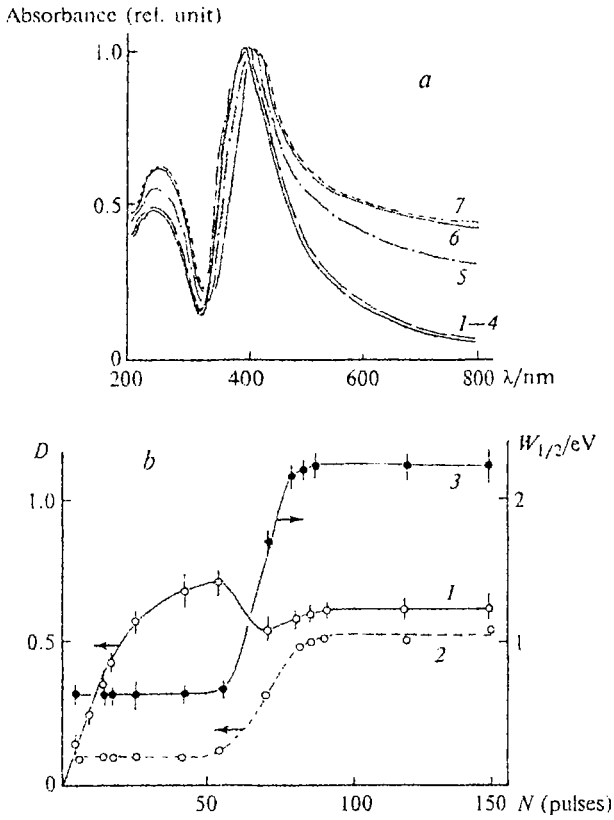

Fig. 3. *a*. Variation of the optical absorption spectra of colloidal silver depending on the number of electron pulses: 10 (*1*), 25 (*2*), 32 (*3*), 45 (*4*), 70 (*5*), 90 (*6*), and 125 (*7*). *b*. Variation of the optical density of the absorption at 390 nm (*1*) and 600 nm (*2*) and of the half-height width of the absorption band (*3*) as functions of the number of electron pulses (the solution used and irradiation conditions are described below Fig. 1). The spectra were recorded 5 min after irradiation.

metal precipitates. Photographs of silver particles obtained at small and large absorbed doses are shown in Fig. 4; it can be seen that in the former case, separate particles with an average size of 20 nm are formed, while in the latter case, large dendrite-like conglomerates of particles are observed.

When the above-mentioned critical dose of irradiation has been attained, a sharp increase in the intensity of scattered light (scattering of unfiltered light was measured) is observed during pulse radiolysis; this is accompanied by some decrease in the intensity of the absorption at λ_{max} and by a substantial enhancement of the absorption at $\lambda = 600$ nm (Fig. 5). The kinetics of the increase in the intensity of light scattering and of the absorption in the visible region are described quite adequately by exponential equations characterized by virtually identical $\tau_{1/2}$. This indicates that the enhancement of the "absorption" in the visible region following

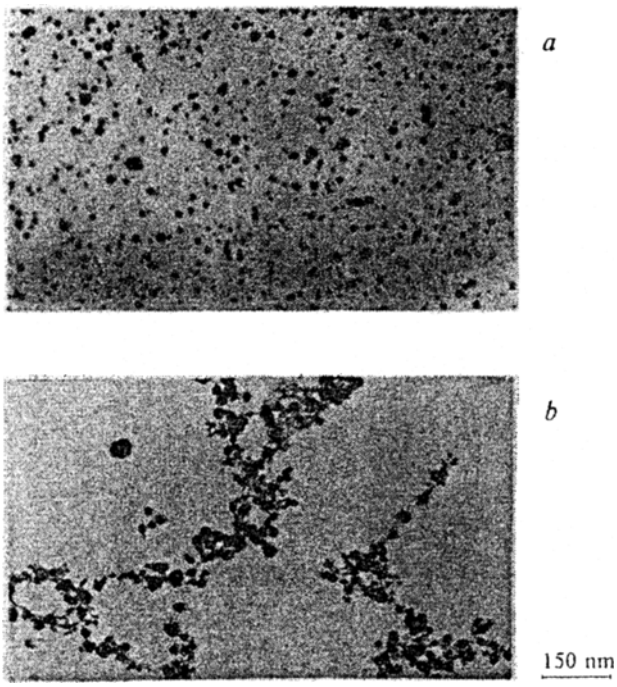

Fig. 4. Silver particles obtained after irradiation with 30 (*a*) and 80 (*b*) electron pulses (the solution used and irradiation conditions are described below Fig. 1).

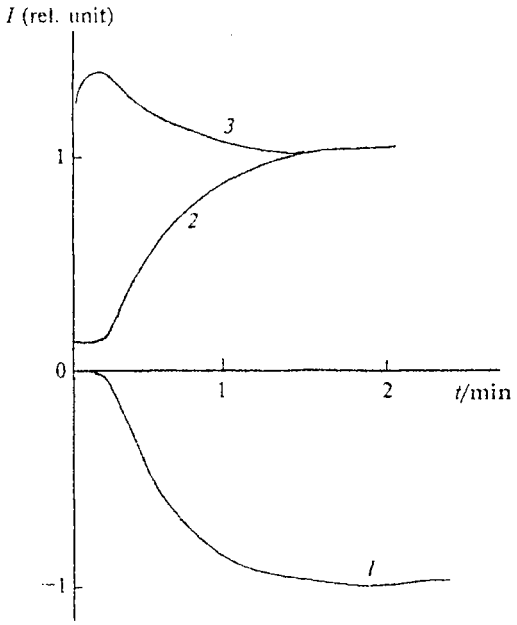

Fig. 5. Kinetics of the variation of the intensity of scattered light (*1*) and of absorption of colloidal silver at 390 nm (*2*) and 600 nm (*3*) after irradiation with 80 pulses (the solution used and irradiation conditions are described below Fig. 1).

exposure to the critical radiation dose is largely caused by scattering or reflection of light by agglomerates of metal particles formed under these conditions.

In the case where γ-irradiation of ^{60}Co was used, a critical absorbed dose was also found; this was equal to (1.4 to 1.6) · 10^{-4} mol L^{-1} ($\bar{e}_{aq}$ + $Me_2\dot{C}OH$) for a solution (1 · 10^{-4} mol L^{-1}) of $AgClO_4$. After attainment of this dose, the form of absorption of colloidal silver markedly changes (Fig. 6). The spectral pattern differs from that observed in the case of irradiation with accelerated electrons in that a shoulder appears in the optical spectrum at 550 nm. The specific features mentioned above are due to the fact that the slow reduction (over a period of tens of minutes) caused by γ-rays results in aggregates of particular shapes and sizes being formed predominantly. In fact, examination by electron microscopy shows that the number of large particles is greater than that formed upon irradiation with electrons, the absorbed doses being the same.

Theoretical calculations show that the optical absorption band of silver sols with a maximum at ~390 nm virtually does not change as the size of particles increases from 1 to 10 nm.[6] When the particle size increases further, the absorption band is broadened, its intensity decreases, and the maximum shifts to longer wavelengths. Our calculations of absorption spectra for very large particles indicate that when the radius of particles becomes 40 nm, an additional broad band appears in the long-wavelength region. For particles of 50 nm radius, the absorption maximum is located at ~500 nm, and for 60 nm particles, it is at 550 nm. Under the conditions of our experiments with γ-irradiation, sols of various sizes and shapes arise; nevertheless, up to the critical dose, relatively large spherical particles predominate. An electron-microscopy examination indicates that particles 20—30 nm and 50—60 nm in radius are present in approximately equal amounts. These results are in good agreement with the absorption spectrum, recorded for these doses, which exhibits a maximum at 420 nm and an additional shoulder at 550 nm (see Fig. 6). When this solution is kept for some period, larger particles and particle aggregates are formed. The blurred absorption spectrum observed in this case over the whole optical region with maxima at 400 nm and 700—800 nm indicates that the effects of light scattering and reflection are likely to predominate.

Solutions of other metals. Similar processes occur, when solutions (1 · 10^{-4} mol L^{-1}) of $Cd(ClO_4)_2$ containing isopropyl alcohol and no stabilizing additives are exposed to pulse radiation. In the case of low radiation doses that correspond to the formation of $<2 \cdot 10^{-4}$ mol L^{-1} of reducing species, an absorption band with λ_{max} = 270 nm appears; this band smoothly decays toward longer wavelengths (Fig. 7). The absorption is due to colloidal cadmium.[13] The critical irradiation dose, at which the absorption band is broadened, its maximum shifts to 310 nm, and an additional shoulder at 600 nm appears, corresponds to the formation of (4—5) · 10^{-4} mol L^{-1} of reducing species. This concentration is approximately twice as high as that required for the reduction of 1 · 10^{-4} mol L^{-1} of Cd^{2+} ions.

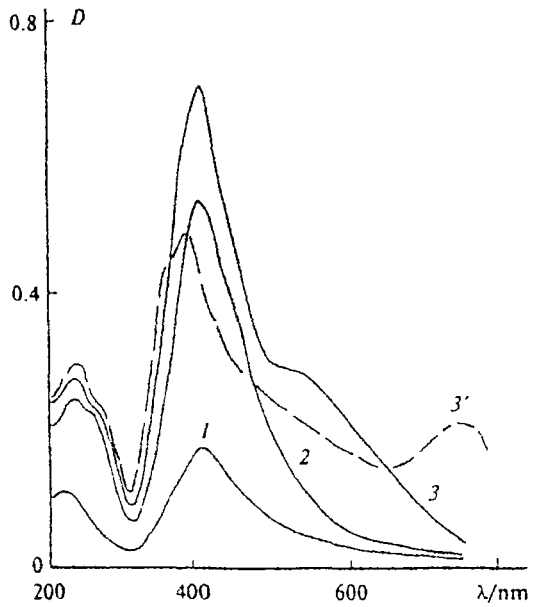

Fig. 6. Optical absorption spectra of colloidal silver under γ-irradiation. Irradiation time (min): 8 (*1*), 20 (*2*), 80 (*3*); after keeping for 2 h (*3'*) (solution: 1 · 10^{-4} mol L^{-1} of $AgClO_4$ and 0.1 mol L^{-1} of isopropyl alcohol, absorbed dose rate 0.2 kGy h^{-1}).

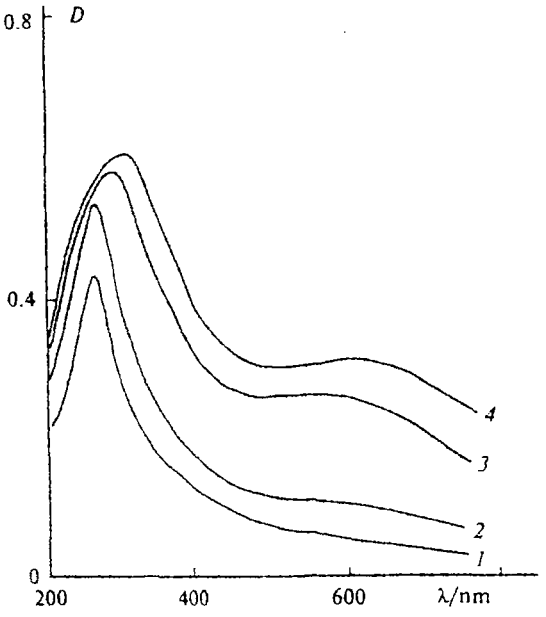

Fig. 7. Variation of the optical absorption spectra of colloidal cadmium depending on the number of electron pulses: 50 (*1*), 100 (*2*), 150 (*3*), 250 (*4*) (solution: 1 · 10^{-4} mol L^{-1} of $Cd(ClO_4)_2$ and 0.1 mol L^{-1} of isopropyl alcohol; for irradiation conditions, see Fig. 1).

The reduction of thallium, copper, and palladium salts at any absorbed dose did not lead to the appearance of characteristic absorption bands peculiar to small colloidal particles of these metals.[14–16] The metal particles resulting from the reduction were responsible mostly for structureless absorption observed over the whole optical region, and a short period after irradiation, they separated as a grey precipitate.

Stability of solutions of colloidal metals. In the presence of stabilizing compounds (surfactants or high-molecular-weight compounds), adsorption layers are formed on the surface of colloids. This decreases the ability of systems to coagulate when particles approach one another. In this case, the double electric layer is not among the factors that determine the stability of the colloid. Stabilized silver sols are known[17] to be stable up to large absorbed doses, which is also confirmed by the results obtained in the present study. Moreover, sols are able to accumulate substantial negative charges, and, when the critical potential is achieved, they can decompose water with evolution of H_2.

In the absence of stabilizing additives, as was the case in our experiments, the stability of colloidal systems is determined by the electrostatic factor. According to the Deryagin—Landau—Verwey—Overbeek[1] theory, it ensures a decrease in the surface tension, due to the formation of double electric layers on the surface of particles. In terms of chemical symbols, the structure of a silver sol and its double electric layer can be expressed by the formula $\{[[Ag_m]nAg^+](n - x)ClO_4^-\}xClO_4^-$. Chemically sorbed silver ions (potential-forming ions) are located on the surface of the metallic nucleus. Their positive charge is neutralized by opposing ClO_4^- anions. They all form the dense part of the double electric layer of a granule, which is surrounded by counterions forming a diffusion layer. The fact that silver ions are sorbed efficiently on the surface of the sols is confirmed by the following data. Previously[18] it has been found that when these ions are added into a solution of colloidal silver ($1 \cdot 10^{-4}$ mol L^{-1}) stabilized with polyphosphate, the absorption band is broadened and displaced to the red region, and its intensity decreases. The absorption maximum shifts by 10—15 nm even when only $8 \cdot 10^{-6}$ mol L^{-1} of Ag^+ ions is introduced into the solution. The results obtained indicate that the ions are tightly bound to the surface silver atoms and that the density of the electron gas in the metal decreases. This leads to a displacement of the Fermi level, which is manifested as the change in the optical characteristics. We carried out similar experiments with cadmium, thallium, copper, and platinum. Only in the case of cadmium, did we observe the effect of added ions (in this particular case, Cd^{2+} ions), similar to the effect of silver ions, on the optical absorption of colloidal particles, which confirms the fact that they are sorbed efficiently on the surface. Since both metals are characterized by high surface charge densities, this accounts for the enhanced stability of colloidal particles in aqueous solutions.

In general, the stability of colloidal systems is determined by the relationship between electrostatic repulsion forces (the first term) and molecular attraction forces (the second term), according to the following equation:[1]

$$U_{(p)} = A^* \exp(\sigma/r) - B^*(1/r^2),$$

where r is the distance between colloidal particles, σ is the thickness of the diffusion layer, and A and B are coefficients whose numerical values are determined by the size and shape of particles, their potentials, and other factors.

The stability of colloids is a consequence of the appearance of a potential barrier caused by electrostatic repulsion forces. The higher the charge density on the surface of the nucleus, the stronger these forces. A similar phenomenon occurs in the case of cadmium, where sorption of Cd^{2+} ions also ensures predominance of the repulsion forces. However, for thallium, copper, and platinum, this factor is insignificant, and when no other stabilizing compounds have been added, coagulation is the predominant process. Neutralization of the surface charge by addition of counterions capable of being adsorbed specifically on the surface decreases the stability of colloids. In the case of colloidal silver, this effect is exerted by OH^-, SO_4^{2-}, $MeCOO^-$, and some other anions.[2–4]

In our experiments, the loss of stability of colloidal silver was also associated with neutralization of the positive charge of the nuclei of sol particles. The critical dose corresponds to the reduction of the adsorbed silver ions, which determine the electric potential of sols. The double electric layer is destroyed, and, as a consequence, stability dramatically decreases. Colloidal particles rapidly coagulate to give large aggregates, which is manifested as a change in the optical properties and intense light scattering. This process corresponds to neutralization coagulation known in colloid chemistry and can be expressed by the following reaction:

$$\{[[Ag_m]nAg^+](n - x)ClO_4^-\}xClO_4^- + 1/2\, n(\bar{e}_{aq} + Me_2\dot{C}OH) = [Ag_{m+n}] + nClO_4^- + 1/2\, n[Me_2CO] + 1/2\, nH^+.$$

Coagulation is due to specific adsorption of added ions of the same sign as the counterions in the double electric layer. When these ions occur in the adsorption layer, they sharply decrease the electric potential, which results in lost stability of the colloidal system. A specific feature of the "radiation" neutralization is the fact that the decrease in the potential of a silver sol is accomplished by electrons generated by ionizing radiation.

The stability of colloidal systems is known[19,20] to change due to radiation. Depending on the nature of the sol, its stability can both increase and decrease; in some cases, a decrease in the stability ends in coagulation. The results obtained in this study indicate that these changes should be attributed to the fact that the prod-

ucts of radiolysis are involved in the physicochemical transformations in disperse systems, thus changing the structure of the double electric layer of colloidal particles.

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