Linear silver clusters in aqueous solution (clusterites): radiation-induced chemical synthesis and properties

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The formation and properties of the products of the radiation-induced chemical reduction of silver ions in aqueous solutions containing sodium polyacrylate were investigated. The absorption spectra of these species exhibit a band at 290 nm and a band in the visible region. The latter shifts from 470 nm to ~800 nm with time or after the addition of silver ions. The species obtained (clusterites) are linear silver clusters bound to the carboxyl groups of the ion exchanger. The red shift of the visible band is due to the increase in their size. The mechanism of the formation and the structure of the clusterites are discussed.

Key words: silver salt; polyacrylate; reduction; γ-irradiation; clusters.

Studies of the early stages of the reduction of Ag^+ ions in aqueous solutions by pulse radiolysis made it possible to establish that the formation of the colloidal metal is preceded by the formation of positively charged clusters of various degrees of complexity.[1—3] Quick optical detection of short-lived products and electrical conductivity measurements have shown that the silver atoms (λ_{max} = 360 nm), resulting from the reduction of Ag^+ ions by hydrated electrons, react then with Ag^+. These reactions afford Ag_2^+ (λ_{max} = 310 nm) and Ag_3^{2+} (λ_{max} = 310 and 265 nm) species. Subsequently, in consecutive enlargement reactions, Ag_4^{2+} (λ_{max} = 270 nm) and a species having absorption bands with λ_{max} at 295 and 325 nm arise. Quantum-chemical calculations[4] give grounds to believe that the latter species is the Ag_8^{2+} cluster having a cubic structure. The relatively high kinetic stability of this cluster made it possible to classify it as a "magic" cluster.[1] It is a precursor of the colloidal metal. As the Ag_8^{2+} clusters coalesce, subcolloidal particles arise, which occupy an intermediate position between clusters, which exhibit molecular properties, and colloidal metal, in which valence electrons exist as an electron gas. Apparently, these clusters exhibit broad and overlapping absorption bands in the 360—380 nm region. Coagulation of the subcolloidal particles leads to the formation of silver sols, whose intense optical absorption band with λ_{max} = 390 nm is due to interaction of the electron gas with light (absorption of plasmons).

It has been found[5,6] that polyphosphates stabilize silver clusters. In their presence, these clusters exist for periods of several hours and slowly coagulate to give the metal. However, in the presence of another polyelectrolyte, sodium polyacrylate, the reduction of silver yields species whose optical characteristics differ from those of the clusters considered above. In fact, immediately after γ-irradiation, bands at 290 and 470 nm have been detected.[7—10] Previously[9,10] these bands have been attributed to the Ag_4^{2+} cluster, although the optical characteristics observed were in no way consistent with this species. The additional band at 470 nm has been attributed to charge transfer between the carboxyl group of the polyacrylic acid and the cluster. In essence, a similar approach to the interpretation has also been followed by other authors,[8] who found that the band in the visible region, unlike that at 290 nm, is unstable and smoothly shifts to longer wavelengths over a period of dozens of days, and reaches approximately 700 nm. It has been suggested that the observed absorption bands at 290 nm and in the visible region are associated with the same cluster, arising *via* recombination of Ag_4^{2+}. The bathochromic shift of the band in the visible region was explained by different degrees of bonding of the carboxyl groups to the cluster surface.

A different interpretation of the nature of the products of silver reduction in aqueous solutions containing polyacrylate was suggested in our previous study.[11] We proceeded from the known ability of the added compound to bind silver ions and to hold them tightly in a polymeric chain.[12] Consequently, the reduction affords linear clusters in which the metal atoms and ions are bound to one another either directly or through carboxyl groups. In this case, the optical absorption in the visible region is due to the cooperative excitation in the cluster chain. The successive growth of the cluster with time accounts for the observed red shift of the absorption band. This assumption was confirmed by the study of the transformations of the clusters during radiation-induced chemical reduction. It was shown[11] that "blue" silver, which absorbs at 700—800 nm, cannot be related

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to the usual three-dimensional clusters. Conversely, when "blue" silver is exposed to large radiation doses, it decomposes to give Ag_4^{2+} and Ag_8^{2+} clusters, which then coagulate to form colloidal silver.

The present work is devoted to the study of the mechanism of the formation and the properties of linearly structurized silver clusters. In view of the unusual nature of these new species it is expedient to classify them as a separate group and to call them "clusterites", which would best reflect their relation to the notions "cluster" and "polyelectrolyte", "polyanionite", and "ionite".

Experimental

$AgClO_4$ and sodium polyacrylate (molecular weight 2000) from Aldrich were used. The concentration of polyacrylate was expressed in moles of monomeric units. Solutions were prepared using tridistilled water with the addition of NaOH to pH ~10. The prepared solutions (usually 5—10 mL) were evacuated in special vessels having a bend with a 1—10 mm-thick optical cell. γ-Irradiation (~20 Gy min^{-1}.) was carried out at room temperature using a ^{60}Co source. In some of the experiments, pulse radiation with accelerated electrons was carried out using a U-12 unit (energy of the electrons 5 MeV, τ_{pulse}= 2.3 μs, dose per pulse up to 50 Gy). Optical spectra were recorded on Specord-M40 and Shimodzu UV-3100 spectrophotometers.

Results and Discussion

Formation of silver complexes with polyacrylate. Silver ions are efficiently captured by the carboxyl groups of polyacrylate. It can be seen from Fig. 1 that Ag^+ ions in water absorb in the deep ultraviolet region exhibiting two bands at 210 and 225 nm. Polyacrylate has increasing structureless absorption in the same region. The optical absorption of a mixture of these compounds (see Fig. 1) is not merely the sum of the absorptions of the components, which indicates that they interact to give a new compound. As the content of polyacrylate increases, the intensities of the absorption bands characteristic of silver ions decrease, and in the presence of a 2—3-fold excess of the polyacrylate the inherent absorption of the Ag^+ ions can no longer be detected. The observed changes are due to the reaction, which yields a complex of silver with polyacrylate.

$$PA_n^{n-} + nAg^+ \rightleftharpoons Ag_nPA_n, \qquad (1)$$

here PA_n^{n-} is polyacrylate in which some of the carboxyl groups are bound to silver ions.

Computer analysis of the dependence of the optical absorption of the Ag^+ ions on the concentration of polyacrylate made it possible to distinguish the individual absorption of the product of reaction (1), which has a weakly pronounced shoulder at 230 nm ($\varepsilon \cong (2.0\pm0.4)\cdot 10^3$ mol^{-1} L cm^{-1}). The equilibrium constant of the process is $2\cdot 10^3$ mol^{-1} L (±20 %).

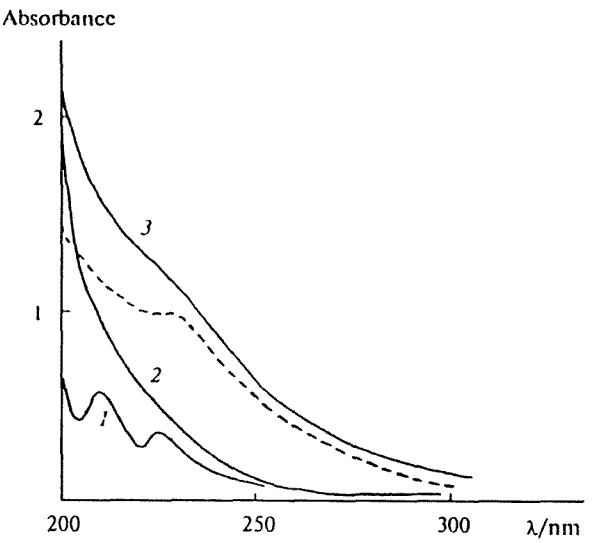


Fig. 1. Absorption spectra of solutions: $1\cdot 10^{-3}$ mol L^{-1} of $AgClO_4$ (*1*); $8\cdot 10^{-3}$ mol L^{-1} of sodium polyacrylate (*2*); $1\cdot 10^{-3}$ mol L^{-1} of $AgClO_4$ and $2\cdot 10^{-3}$ mol L^{-1} of sodium polyacrylate (*3*). The dashed line corresponds to the absorption spectrum of a $1\cdot 10^{-3}$ mol L^{-1} solution of silver polyacrylate (calculation). From here on, a 10 mm-thick cell was used.

Radiation-induced chemical reduction. The exposure of water and aqueous solutions to ionizing radiation leads to the formation of radical-ion products, capable of reacting with dissolved substances. In the presence of organic compounds, this process, in general the case, can be expressed by the following reactions:

$$H_2O \longrightarrow e_{aq}^-(2.7),\ H(0.5),\ OH(2.9) \qquad (2)$$

$$RH + OH(H) \longrightarrow R^{\cdot} + H_2O(H_2). \qquad (3)$$

The values of the radation-chemical yields of the species per 100 eV of absorbed energy are given in parentheses. Thus, in reaction (3), hydroxyl radicals possessing a high oxidative potential are converted into organic radicals $R^{\cdot}$, which are efficient reducing reagents. For example, in the present study in which isopropanol was used as the acceptor for the OH radicals, the Me_2COH radical is formed (E^0 = −1.5 V).[13] The reducing potential of the hydrated electron is 2.7 V.[13] Polyacrylate can participate in reaction (3) to give polymeric radicals. Our studies showed that when the relative content of polyacrylate with respect to that of the silver ions is great, the latter are reduced in the same way as in solutions containing isopropyl alcohol. Thus, when an aqueous solution is irradiated with γ-quanta or with accelerated electrons, species that reduce silver ions are generated uniformly throughout the solution. At the absorbed dose rate of 20 Gy min^{-1} mostly used by us, ~$1.2\cdot 10^{-5}$ mol L^{-1} of reducing species arise.

Reduction of silver. Figure 2 shows the optical spectrum of a $1 \cdot 10^{-3}$ *M* solution of $AgClO_4$ in the presence of 0.1 mol L^{-1} of polyacrylate, recorded immediately after γ-irradiation or some time later. During recording of the spectrum, the absorption spectra of the solutions of polyacrylate and isopropanol were subtracted from it. Preliminary experiments showed that irradiation of the latter has virtually no effect on their absorption. The contribution of the absorption of silver ions in the optical region studied can also be neglected without substantial error. Thus, the spectra presented in the figures are the absorption spectra of the products of the reduction of silver ions. It can be seen from Fig. 2, *a* that, along with the bands at 290 and 470 nm, the spectrum contains a new band with a maximum at 350 nm. Its decay over a period of several hours leads to a proportional increase in the intensities of the band at 290 nm and of the absorption band in the visible region of the spectrum, which simultaneously shifts to longer wavelengths. The disappearance of the band at 350 nm accelerates as the absorbed dose increases, *i.e.*, as the concentration of reduced silver increases. Therefore, one may assume that the products of the reduction of silver (the band at 350 nm) undergo recombination, affording a new species characterized by two absorption bands in the UV and in the visible regions; we attribute the latter to linear silver clusters stabilized in an ionite chain (clusterite).

Figure 2, *b* shows the development of the absorption of a solution having the same composition as the solution used in the previous experiment (see Fig. 2, *a*) over a long period of time. In this case, the absorbed dose is 4 times greater. It can be seen that the band in the visible region shifts from 470 nm to ~750 nm over a period of 35 days. However, as this takes place, the position and the intensity of the band in the UV region (290 nm) undergoes no substantial changes. The transformation of the "pink" products of silver reduction into "blue" products is accelerated with an increase in the relative content of silver ions with respect to that of polyacrylate (Fig. 3). A solution of $AgClO_4$ of concentration $2 \cdot 10^{-3}$ mol L^{-1}, containing $5 \cdot 10^{-3}$ mol L^{-1} of polyacrylate, exhibits no band at 350 nm immediately after γ-irradiation, unlike a solution containing 0.1 mol L^{-1} of polyacrylate (see Fig. 2, *a*). The band at 290 nm and the visible band at 580 nm are recorded. The latter shifts to the red region, to 660 nm, over a period of less than 24 h. Apparently, this should be attributed to the facts that the length of continuous sections of the salt groups in the polyacrylate chain increases as the relative content of Ag^+ ions in the solution increases and that ion exchange by reaction (1) is facilitated. Consequently, reactions in which clusters are formed and transformed are accelerated. The role of the Ag^+ ions in the transformation of the products of silver reduction is most clearly demonstrated in the following experiment. Additional portions of Ag^+ ions were introduced into a solution in which, after γ-irradiation, clusterites absorbing at 290 and 470 nm were formed. The greater the concentration of the introduced Ag^+ ions, the greater the subsequent shift of the visible band to longer wavelengths (Fig. 4). However, the band at 290 nm remained practically unchanged (after subtraction of the absorption of additional Ag^+ ions). It may be concluded with sufficient justification that the addition of silver ions is favorable to an increase in the size of clusterites.

The results of the experiments also indicate that recombination of the clusterites plays an important role in their transformations. To confirm this, we selected conditions that would be favorable for this process. For

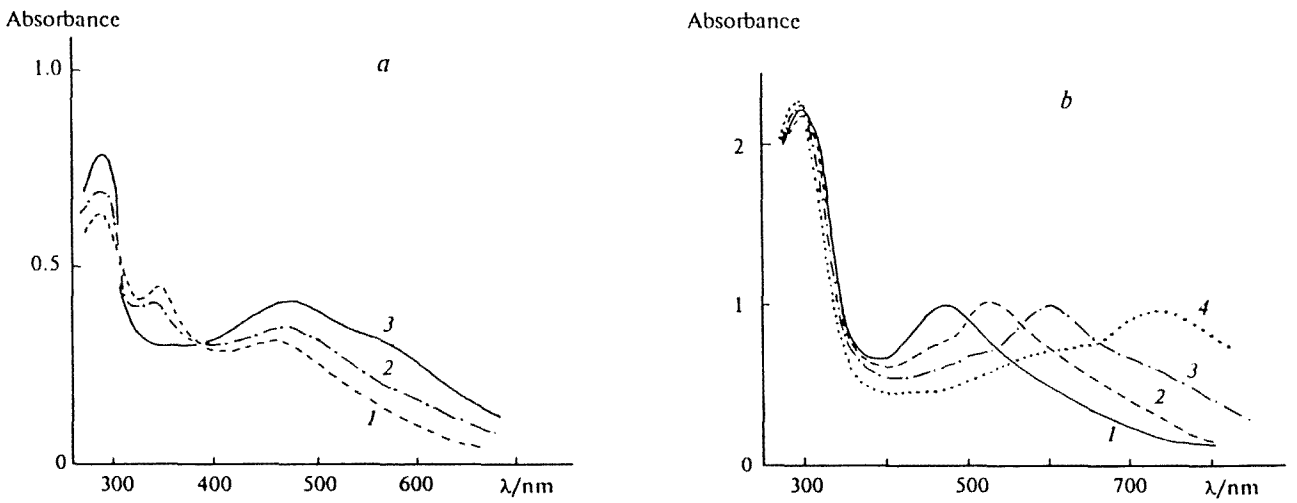


Fig. 2. Variation of the absorption spectrum with time after γ-irradiation. Solution: $2 \cdot 10^{-3}$ mol L^{-1} of $AgClO_4$, 0.1 mol L^{-1} sodium polyacrylate, and 0.2 mol L^{-1} of isopropanol. *a* — after 5 min (*1*); 2 h (*2*); 16 h (*3*). An absorbed dose of ~100 Gy corresponds to the formation of $5 \cdot 10^{-5}$ mol L^{-1} of reducing species; *b* — after 2 h (*1*); 2 days (*2*); 8 days (*3*); 35 days (*4*). The absorbed dose corresponds to $2 \cdot 10^{-4}$ mol L^{-1} of reducing species.

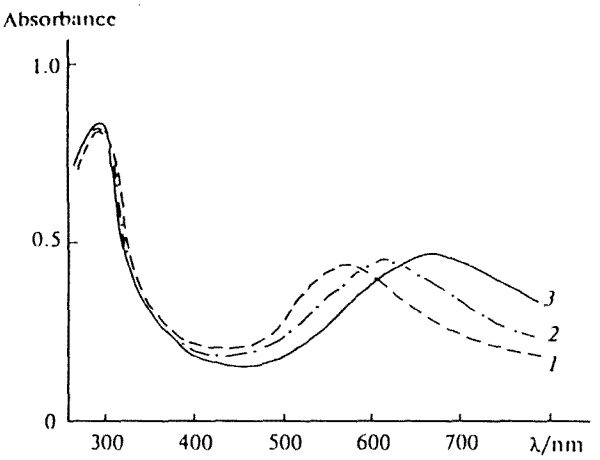


Fig. 3. Variation of the absorption spectrum with time after γ-irradiation: after 5 min (*1*); 2 h (*2*); 16 h (*3*). Solution: $2 \cdot 10^{-3}$ mol L^{-1} of $AgClO_4$, $5 \cdot 10^{-3}$ mol L^{-1} of sodium polyacrylate, and 0.2 mol L^{-1} of isopropanol. The absorbed dose corresponds to $5 \cdot 10^{-5}$ mol L^{-1} of reducing species.

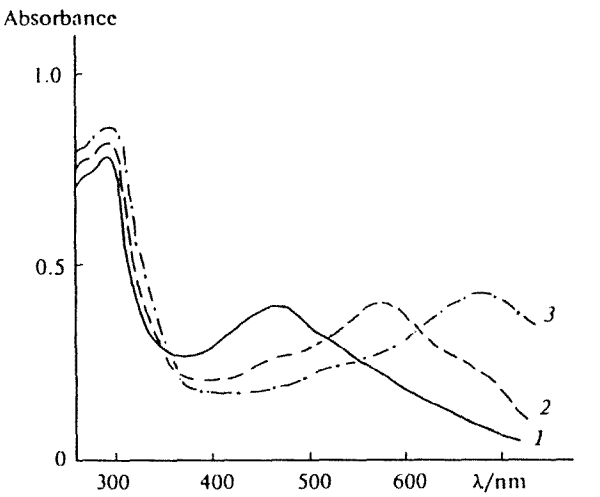


Fig. 4. Absorption spectra of a $1 \cdot 10^{-3}$ mol L^{-1} solution of $AgClO_4$ containing 0.1 mol L^{-1} of sodium polyacrylate and 0.2 mol L^{-1} of isopropanol; 24 h after γ-irradiation (*1*), after the increase in the concentration of $AgClO_4$ to $3 \cdot 10^{-3}$ mol L^{-1} (*2*), and to $2 \cdot 10^{-2}$ mol L^{-1} (*3*). The absorbed dose corresponds to $5 \cdot 10^{-5}$ mol L^{-1} of reducing species.

this purpose, a $2 \cdot 10^{-3}$ *M* solution of $AgClO_4$ containing 0.1 mol L^{-1} of polyacrylate was irradiated with accelerated electrons up to a relatively high absorbed dose (~0.75 kGy) over a short period of time. It can be seen from Fig. 5 that the band at 470 nm is slowly transformed into a new band with λ_{max} at 580 nm. An isobestic point at 520 nm appears. The kinetics of this transformation are not described by simple equations for first-order or second-order reactions. This may be due not only to the difficulty of distinguishing the overlapping individual bands, but also to complications associated with the consecutive reactions of transformation of the clusterites. However, the results of the experiments

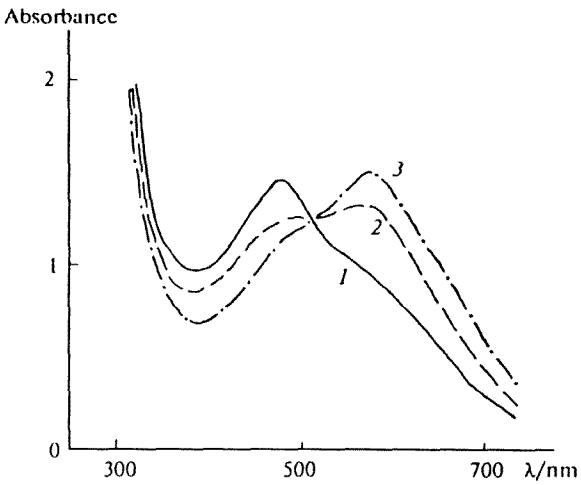


Fig. 5. Variation of the absorption spectrum with time after irradiation with accelerated electrons: after 5 min (*1*); 2 h (*2*); 10 h (*3*). Solution: $2 \cdot 10^{-3}$ mol L^{-1} of $AgClO_4$, 0.1 mol L^{-1} of sodium polyacrylate, and 0.2 mol L^{-1} of isopropanol. The absorbed dose corresponds to the formation of approximately $4 \cdot 10^{-4}$ mol L^{-1} of reducing species.

indicate quite convincingly that the rate of the transformation of the clusterites determined from the transition of the band at 470 nm to the band at 580 nm increases proportionally with the increase in the absorbed dose. Hence, the increase in the length of clusterites occurs not only with the addition of silver ions to them but also with the coalescence of clusterites. Of course, these reactions are complex and apparently proceed *via* both the transfer of silver ions and atoms along the polymeric chain by a relay-race mechanism and exchange between the clusters in the solution bulk. Note that the position and the intensity of the band at 290 nm remains virtually unchanged.

Clusterites and the mechanism of their formation. The formation of clusterites can be most generally represented by two steps. The first of them is the reduction of silver ions bound by the carboxyl groups of the ionite:

$$Ag_nPA_n + me \longrightarrow Ag_nPA_n^{m-} . \qquad (4)$$

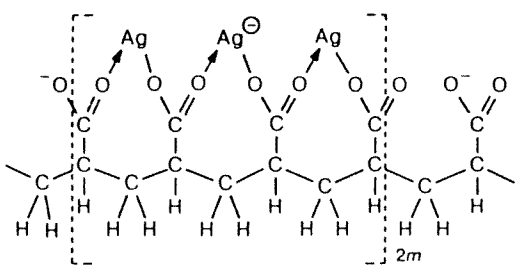
The process is complex and involves not only the single-electron reduction of silver ions by hydrated electrons and organic radicals, but also subsequent recombination of the products and their transformations. The second step consists of the growth of the clusterite formed by the addition of silver ions to it or by coalescence of the clusterites:

$$Ag_nPA_n^{m-} + xAg^+ \longrightarrow Ag_{n+x}PA_{n+x}^{(m-x)-} \qquad (5)$$

$$2Ag_nPA_n^{m-} \longrightarrow Ag_{2n}PA_n^{2m-} + PA_n . \qquad (6)$$

The concentration of free Ag^+ ions in the solution, *i.e.*, the position of the equilibrium of reaction (1), exerts a crucial effect on this process.

The following structure for the clusterite can be suggested:



The silver ions are bound to the oxygen atoms of two neighboring carboxyl groups by covalent and coordination bonds. The repetition of these units in the chain results in the C—O and C=O bonds in them becoming equivalent. Following the reduction of silver ions the additional electrons become delocalized along the chain incorporating alternating silver ions and carboxyl groups. An increase in the length of the clusterite and in the degree of polyconjugation in it is apparently manifested as a displacement of the absorption band to longer wavelengths. The band at 290 nm, which undergoes no substantial changes (±10 nm) while the band in the visible region of the spectrum "floats", can probably be assigned to a transition that practically does not depend on the length of the clusterite. In our opinion, this may be an intraatomic S→P transition in silver. The long-wavelength absorption can be attributed to the cooperative excitation of the additional electrons, which move freely in the clusterite, thus giving rise to electrical currents.

There is a certain qualitative analogy between the optical properties exhibited by clusterites and those exhibited by ultrasmall metal particles. The state of the electrons in a metal is described qualitatively by the model of a potential well with infinitely high walls. The valence electrons are free to move in the metal bulk, reflecting from its surface. The absorption of light by particles is described quantitatively by the Mie theory and its modifications.[14,15] A spherical particle of a metal, for example, silver, 5—10 nm in diameter, exhibits an absorption band with λ_{max} = 390 nm, which smoothly decays toward longer wavelengths.[15] When the particles change from spherical to ellipsoid in shape, the main band shifts only slightly to the UV region of the spectrum; a new band appears in the long-wavelength region, which smoothly shifts to the red region. For example, when the ratio of the length of the ellipsoid to its radius is 2 or 3, the position of the main band remains practically unchanged, and a new band of approximately the same intensity is located at 480 or 580 nm, respectively.[15,16] Calculations[16] show that infinite stretching causes the main band to tend to 368 nm, and the additional band to pass to the red region of the spectrum.

Unlike a colloidal metal particle in which the electron gas is distributed throughout the bulk, a clusterite is a linear conductor with a single degree of freedom for the propagation of electromagnetic vibrations.

For a linear polyene, the absorption band associated with the excitation of delocalized π-electrons also shifts to the red region as the length of the conjugated chain increases, and the quantitative correlation between the magnitude of the shift observed and the number of double bonds is explained by the quantum-chemical theory.[17] The development of an adequate theory for the clusterite, which is an organometallic compound, is a more complicated task.

Preliminary studies of the early steps of the reduction of silver in aqueous solutions containing polyacrylate, carried out by pulse radiolysis 1 μs after the pulse of accelerated electrons, have shown that the Ag_2^+ species is formed. This species is apparently localized at the polyacrylate chain and is converted, in a first-order reaction, into a new species accounting for a band with λ_{max} = 350 nm. This process can be explained by the formation of the elementary unit of future clusterites; it involves structural rearrangement of neighboring COOAg groups. The next stage consists of the transformation of the species absorbing at 350 nm into species absorbing at 290 nm and, possibly, at 470 nm. This process is described by a second-order equation and affords the simplest clusterites. Note that solutions of the clusterites exhibit no ESR signals, *i.e.*, they incorporate no radical sites. It can be assumed that a clusterite, according to its structure, can contain along with two silver atoms, up to 4—6 silver ions and carboxyl groups, whose number is equal to the overall number of silver atoms and ions. Further elongation of the clusterite leads to a shift of the absorption band in the visible region to longer wavelengths.

Destruction of clusterites. Clusterites are the products of the incomplete reduction of silver polyacrylate. Their stability is determined by the optimal ratio of the silver atoms and ions. When the number of atoms exceeds the optimal one, the clusterite is destroyed, due to weakening of the bonds with the carboxyl groups. Figure 6 illustrates the destruction of clusterites occurring during γ-irradiation, when successive and extensive reduction of silver ions occurs. When the absorbed dose corresponds to the reduction of ~30 % of the silver ions present, the formation of clusterites absorbing at 600—650 nm is achieved. On further irradiation, this absorption begins to disappear, and a band at ~480 nm appears initially, and then two bands at 295 and 325 nm appear. The latter, as was noted above, are due to the Ag_8^{2+} cluster. The process ends in the formation of the absorption band corresponding to the colloidal metal. When this takes place, examination by electron microscopy detects the appearance of small metal particles with diameters of 1—2 nm.

Figure 7 shows that the addition of ammonia to a solution of clusterites having an absorption band at 660 nm leads to their destruction. As this takes place, Ag_8^{2+} clusters and, later, the colloidal metal appear. Processes of this type have also been observed previously,[9,10] when KCN, NaSH, and ammonia were added, which led to the disappearance of the band at 470 nm. It was suggested that the above-mentioned compounds,

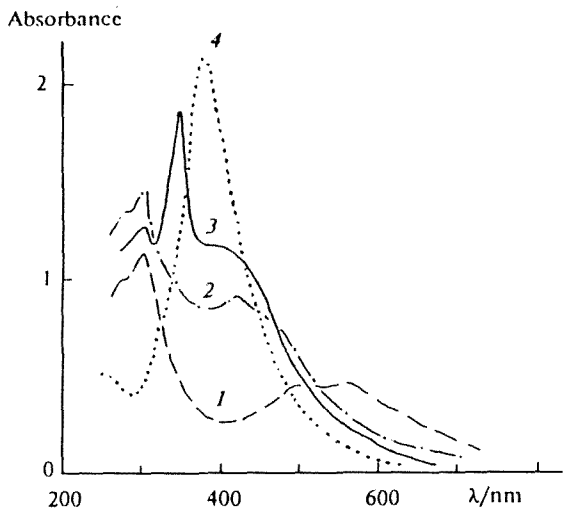


Fig. 6. Variation of the absorption spectrum with time after additional γ-irradiation. The absorbed doses correspond to the formation of reducing species, mol L^{-1}: $3 \cdot 10^{-4}$ (*1*); $9 \cdot 10^{-4}$ (*2*); $2.5 \cdot 10^{-3}$ (*3*); and $4 \cdot 10^{-3}$ (*4*) (24 h later). The composition of the solution is given in the caption to Fig. 5. A 2 mm-thick cell was used.

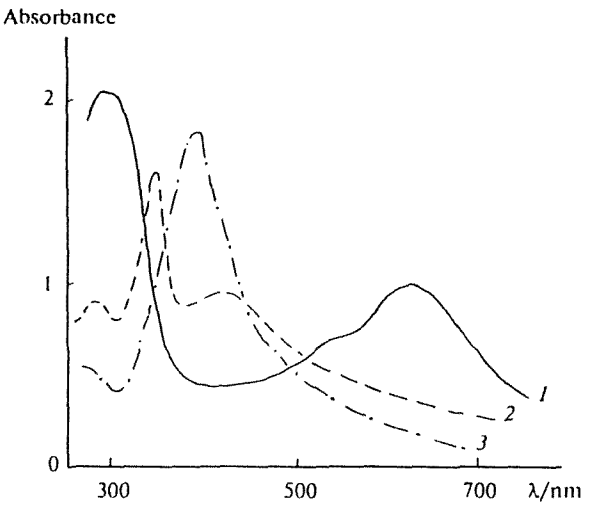


Fig. 7. Variation of the absorption spectrum after the addition of a 0.1 *M* solution of ammonia: after 2 min (*1*); 1 h (*2*), and 12 h (*3*). The composition of the solution and the conditions are given below Fig. 3.

which are strong nucleophiles, form complexes with silver clusters, stabilized by polyacrylate, and thus promote coagulation. However, we found that this process occurs in the same way irrespective of the position of the visible band (from 470 nm up to 850 nm). Within the framework of the concept of the nature of clusterites developed in the present paper, these transformations can be explained by the fact that the compounds used are efficient complex-forming agents; they bind silver ions and carry them from the ion exchanger into the bulk of the solution. A decrease in the number of silver ions within clusterites decreases their stability and leads to their destruction. Apparently, after extensive reduction or when efficient ligands are used, fragmentation of clusterites occurs, accompanied by the emergence of the Ag_2^+ or Ag_4^{2+} species in the solution bulk, by their enlargement to Ag_8^{2+}, and then by the formation of colloidal metal. Thus, the process under consideration includes the main steps of the nucleation of silver, which have been established for solutions containing no added stabilizing compounds.[2,4]

Radiation-induced chemical reduction is a quite convenient and easily controllable method for the preparation of clusterites. However, the results of our recent studies indicate that clusterites can also be obtained by using normal chemical reducing agents, in particular, molecular hydrogen, hydrazine, and other compounds.

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