Colloidal copper in aqueous solutions: radiation-chemical reduction, mechanism of formation, and properties

B. G. Ershov

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 7514

Colloidal copper has been obtained by γ-irradiation of aqueous solutions of copper (II) perchlorate in the presence of alcohol and polyethyleneimine (PEI). The sols are spherical particles about 4 nm in diameter, which are quickly oxidized by oxygen or other oxidants. When Cu^{II} is not entirely incorporated into the complex with PEI, disproportionation of Cu^{I} aqua complexes formed affords the metal, along with Cu_2O. Reduction of the PEI complex of Cu^{I} by hydrated electrons gives only colloidal copper. The copper ions can be reduced on the surface of silver sols. Optical parameters of the resulting bimetallic particles have been studied. The presence of copper ions leads to broadening of the absorption band associated with the silver sols and shifts it to the UV region, which is due to the transfer of electrons from copper to silver. Three copper monolayers are enough to cause plasmon absorption of colloidal copper.

Key words: colloids; reduction; copper salts; γ-irradiation.

The radiation-chemical reduction of many metal ions in aqueous solutions involves the intermediate formation of short-lived clusters and results in the precipitation of the metal as a separate phase.[1] It has been shown[2–4] by pulse radiolysis that at intermediate steps of the reduction of mono- and bivalent copper in solutions containing alcohols or formate ions as scavengers of hydroxyl radicals, short-lived Cu_2^+ and Cu_4^{2+} clusters arise. They participate in the subsequent reactions to form bigger clusters of a nonmetallic nature, whose coalescence results in the formation of colloidal copper (Cu_{coll}). The latter is manifested in the UV spectrum as a band with a weakly expressed maximum at 570 nm,[3,4] which is due to the absorption of the surface plasmons in the metal. Without stabilizing additives, Cu_{coll} is unstable and coagulates to form large aggregates, which then precipitate.

In this work we present the data on the preparation of solutions of copper sols and bimetallic silver-and-copper sols in the presence of polyethyleneimine (PEI), which are stable in the absence of oxidants, and discuss the mechanism of the formation of the metal phase.

Experimental

Reactants of «chemically pure» grade were used. Thrice distilled water was used for preparing solutions. The solutions were deaerated prior to γ-irradiation by holding them in a high vacuum. Polyethyleneimine had a molecular weight of 50000. Its concentration in solutions was expressed in moles of monomeric units. Normally its concentration amounted to $1 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ *M*.

^{60}Co was used as the source of γ-radiation. The dose rate was 1.8 kGy h^{-1}.

The amount of Cu^{2+} reduced to the metal was determined by adding 1 mL of 0.1 *M* NaOH and then 2 mL of a 10^{-2} *M* solution of methylviologen (MV^{2+}) to 20 mL of an irradiated solution. The concentration of the reduced methylviologen (MV^+) was measured by spectrophotometry (λ_{max} = 600 nm, $\varepsilon = 1.2 \cdot 10^4$ L mol^{-1} cm^{-1}).[5]

The optical absorption spectra were recorded on a Specord UV-VIS spectrophotometer. The samples for electron-microscopic investigations were prepared by applying a drop of an irradiated solution onto a copper-carbon plate which was dried under argon.

Results and Discussion

We studied aqueous solutions of $Cu(ClO_4)_2$ containing 0.1 *M* of isopropyl alcohol as an scavenger of $^{\cdot}OH$ radicals. Elementary reactions occurring through the action of ionizing γ-irradiation on water include the formation of hydrated electrons (e_{aq}^-), H^+ and OH^- ions, and $H^{\cdot}$ and $OH^{\cdot}$ radicals. The $H^{\cdot}$ and $OH^{\cdot}$ radicals react with the alcohol to give organic radicals.

$$(CH_3)_2CHOH + {}^{\cdot}OH(H^{\cdot}) \longrightarrow (CH_3)_2\dot{C}OH + H_2O(H_2) \qquad (1)$$

Thus, the radiation produces approximately equal numbers of particles which have extremely high reducing abilities and are uniformly distributed throughout

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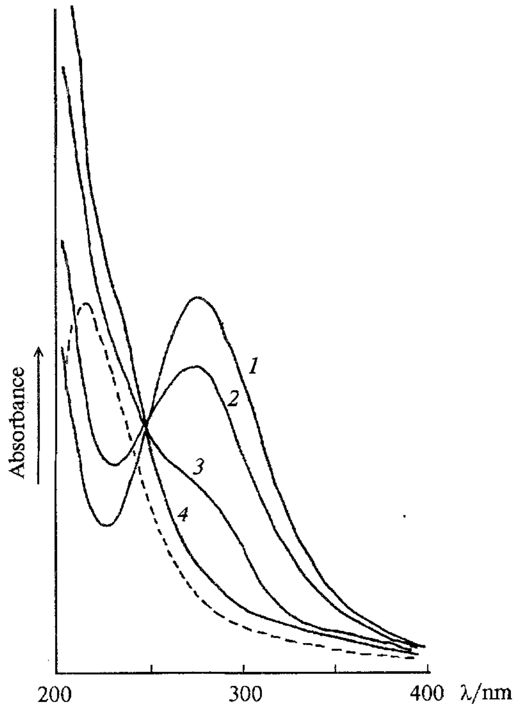

Fig. 1. The absorption spectra at a γ-irradiation time of, min: 0 (*1*), 3 (*2*), 10 (*3*), 30 (*4*). The solution contained: $2 \cdot 10^{-4}$ *M* of $Cu(ClO_4)_2$, 0.1 *M* of $(CH_3)_2CHOH$, and $2 \cdot 10^{-3}$ *M* of PEI (pH 9.8). The dose rate was 30 Gy min^{-1} (the dashed line corresponds to the absorbance of $[Cu \cdot PEI]^+$).

the bulk of the solution: hydrated electrons (reduction potential is −2.9 V) and $(CH_3)_2\dot{C}OH$ (−1.5 V).[1] The radiation yield of e_{aq}^-, $^{\cdot}H$, and $^{\cdot}OH$ is 6.2 particles per 100 eV of energy absorbed,[1] therefore the absorbed dose rate (1.8 kGy h^{-1}) used in this work corresponds to the formation of $\sim 1.8 \cdot 10^{-5}$ *M* of reducing radicals during 1 min of irradiation.

Complexes of Cu^{2+} and Cu^+ with polyethyleneimine. Introduction of PEI into neutral aqueous solutions containing Cu^{2+} results in the appearance of an intense absorption band (AB) with a maximum at 272 nm and a weak band at 640 nm caused by the formation of the $[Cu \cdot PEI]^{2+}$ complex. As the concentration of PEI increases, the intensity of these AB increases and attains a constant value at a $[Cu^{2+}]$:[PEI] ratio of approximately 1:5. The Cu^{2+} ions predominantly exist as complexes with PEI. The nature of these complexes is apparently based on the donor-acceptor character of the chemical bond between the nitrogen atom of PEI and a Cu^{2+} ion, which is characteristic of other Cu^{2+} complexes with nitrogen-containing compounds. Fig. 1 shows the short-wave region of the absorption spectrum of the $[Cu \cdot PEI]^{2+}$ complex. Its extinction coefficients are $4.2 \cdot 10^3$ and $2.6 \cdot 10^2$ L mol^{-1} cm^{-1} (±10 %) for the AB at 272 nm and 640 nm, respectively.

When solutions of Cu^{2+} containing PEI are γ-irradiated, the intensity of the absorption of $[Cu \cdot PEI]^{2+}$ decreases. Finally, a new AB with a maximum at 214 nm appears (see Fig. 1). This AB was obtained by subtracting the absorbance of a solution containing no Cu^{2+} from that of a solution containing Cu^{2+} after γ-irradiation. This band corresponds to the complex of monovalent copper with PEI, $[Cu \cdot PEI]^+$ ($\varepsilon = 3.7 \pm 0.5 \cdot 10^3$ L mol^{-1} cm^{-1}), formed upon one-electron reduction of $[Cu \cdot PEI]^{2+}$. This compound is stable in an aqueous solution. Introduction of oxygen or other oxidants leads to its rapid decomposition. As this takes place, the initial spectrum caused by the absorption of $[Cu \cdot PEI]^{2+}$ is restored.

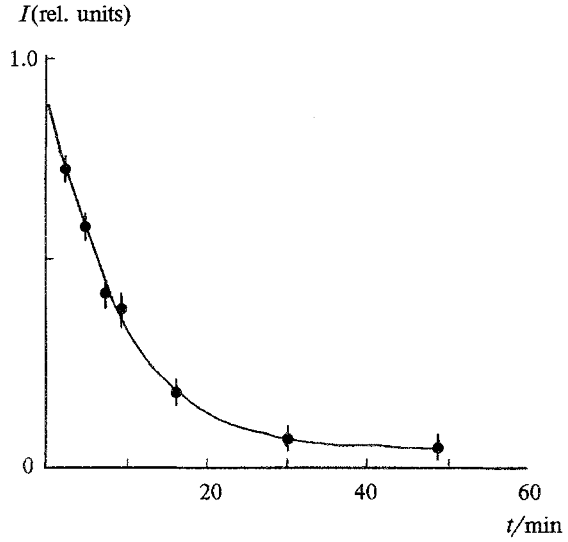

Fig. 2. The dependence of the intensity of the absorption of $[Cu \cdot PEI]^{2+}$ on the duration of γ-irradiation. For conditions, see Fig. 1.

Fig. 2 shows the loss of $[Cu \cdot PEI]^{2+}$ occurring in the course of irradiation. The radiation yield of the reduction of Cu^{II} in a $2 \cdot 10^{-4}$ *M* solution of $Cu(ClO_4)_2$ is 4.2±0.4 ions per 100 eV of ionizing radiation energy absorbed. When isopropyl alcohol is replaced by methyl or ethyl alcohol the yield remains practically the same. As the concentration of $Cu(ClO_4)_2$ is increased, the yield increases and at a concentration of 10^{-3} *M* it reaches an approximately constant value of 6.0 ions/100 eV, which implies that practically all of the reducing radicals are scavenged (≈6.2 radicals/100 eV). Reduction of $[Cu \cdot PEI]^{2+}$ to $[Cu \cdot PEI]^+$ occurs as well in solutions containing acetone. Under these conditions all of the e_{aq}^-, $H^{\cdot}$ atoms, and $OH^{\cdot}$ radicals formed during the radiolysis of water are converted to alcohol radicals according to reactions (1) and (2).

$$(CH_3)_2CO + e_{aq}^- \xrightarrow{H^+} (CH_3)_2\dot{C}OH \qquad (2)$$

The potential of the latter is sufficient to reduce Cu^{II} to Cu^I ($E_0(Cu^{2+}/Cu^+) = -0.15$ V).[5]

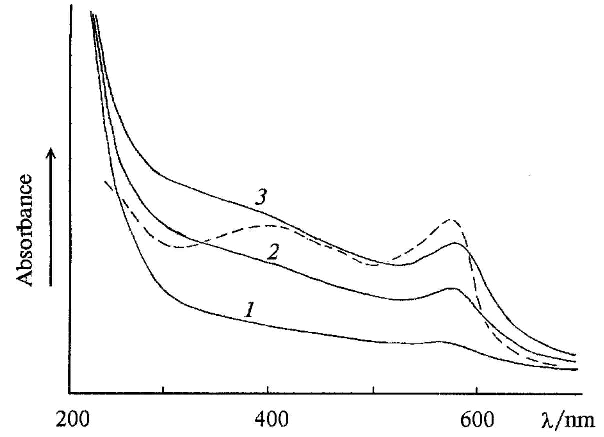

Fig. 3. The absorption spectra at a γ-irradiation time of, min: 60 (*1*), 120 (*2*), 200 (*3*). For conditions, see Fig. 1. The theoretical spectrum of the copper sol (*d* = 5 nm) is shown by the dashed line.

Formation of metal sols. The solution of $[Cu \cdot PEI]^+$ obtained after the complete reduction of Cu^{2+} ions turns out to be stable with respect to the formation of colloidal copper. The latter does not form after the solution is stored for several days, *i.e.*, the monovalent copper bound in a complex with PEI does not participate in disproportionation. Copper sols are only formed after very prolonged subsequent γ-irradiation, when the concentration of the reducing particles formed throughout the whole irradiation time is *ca.* 10-fold higher than the concentration of $[Cu \cdot PEI]^+$. This process is illustrated in Fig. 3. The copper sols formed have an absorption at 565 nm typical of surface plasmons in the metal. Unlike copper sols obtained by the pulse irradiation of neutral or weakly acidic aqueous solutions of $Cu(ClO_4)_2$ containing HCOONa or alcohols,[3,4] these sols are stable due to the presence of PEI. Fig. 3 also shows the absorption of copper sols of a spherical shape, 5 nm in diameter, calculated by the Mi theory.[6] Dielectric constants of the metal were used in the calculation.[7] Previously, a similar calculation was carried out for spherical sols (d = 10 nm) of many metals including copper.[8] The theoretical predictions of the position of λ_{max} and the form of the absorption of the colloidal copper in water are in good agreement with the experimental results. In solutions containing acetone the metal is not formed at all owing to the very high reduction potential of the Cu^0 atom ($E^0 = -2.7$ V).[1] The alcohol radicals cannot reduce Cu^I. Thus, the exclusion of hydrated electrons from the reduction of $[Cu \cdot PEI]^+$ prevents the formation of the metal phase.

The results of an electron-microscopic examination indicate that in solutions containing excess PEI, nearly spherical copper sols of average diameter *ca.* 4 nm are formed.

In order to determine the extinction coefficient for sols, we studied their reaction with methylviologen (MV^{2+}). It was preliminarily found that MV^{2+} is not reduced by the $[Cu \cdot PEI]^+$ ions. However, it is reduced in the reaction with the metal.

$$Cu^0 + MV^{2+} \longrightarrow Cu^+ + MV^+ \qquad (3)$$

Based on the known extinction coefficient of the latter ($1.2 \cdot 10^4$ L mol^{-1} cm^{-1}) and the stoichiometry of reaction (3) we calculated the extinction coefficient for copper sols at λ_{max} = 565 nm with reference to one copper atom. It turned out to be equal to $2.5 \cdot 10^3$ L mol^{-1} cm^{-1} (± 10). We also found that by prolonged irradiation of $(1-5) \cdot 10^{-4}$ *M* solutions of $Cu(ClO_4)_2$ containing excess PEI, practically all of the copper ions can be reduced to the metal. In the presence of oxygen, hydrogen peroxide, or another oxidizing agent, colloidal copper is quickly oxidized to give Cu^{II}. When metal ions, whose potential is more positive than that of copper, are added to the solution, they are reduced to form a sol of the corresponding metal. This method was used, in particular, to prepare colloidal silver. Both colloidal copper and Cu^+ ions participated in the reduction of Ag^+.

When PEI is present in the solution at a concentration less than or equal to that of $Cu(ClO_4)_2$, *i.e.*, only part of Cu^{2+} ions can form complexes, the spectrum exhibits a weak absorption maximum in the region corresponding to the absorption of colloidal copper. In this case, the process has some special features. Fig. 4 presents the change in the absorption of a $2 \cdot 10^{-4}$ *M* solution of $Cu(ClO_4)_2$ in the presence of 10^{-4} *M* of PEI. One can see that the absorption at 565 nm peculiar to copper ions arises already at the initial step of γ-irradiation, even when the reduction of $[Cu \cdot PEI]^{2+}$ (λ_{max} = 272 nm) is not complete. A similar picture is observed in solutions containing acetone in which the only reducing agents are alcohol radicals. On the other hand, the absorption spectrum recorded for a dilute solution of

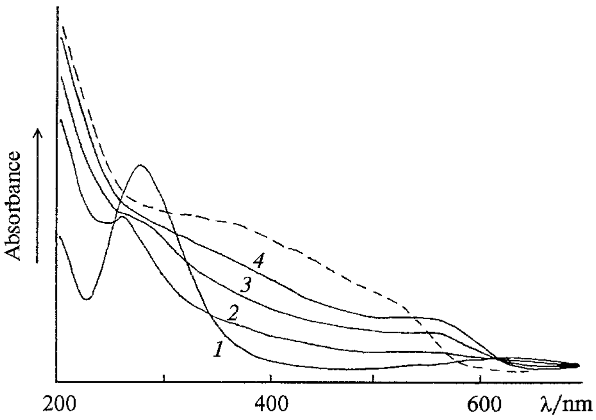

Fig. 4. The absorption spectra at a γ-irradiation time of, min. 0 (*1*), 10 (*2*), 20 (*3*), 40 (*4*). The solution contained: $2 \cdot 10^{-4}$ *M* $Cu(ClO_4)_2$, 0.1 *M* $(CH_3)_2CHOH$, $1 \cdot 10^{-4}$ *M* PEI (pH 7.6). The dashed line signifies the spectrum of a buffered solution with pH 7.8, t = 40 min.

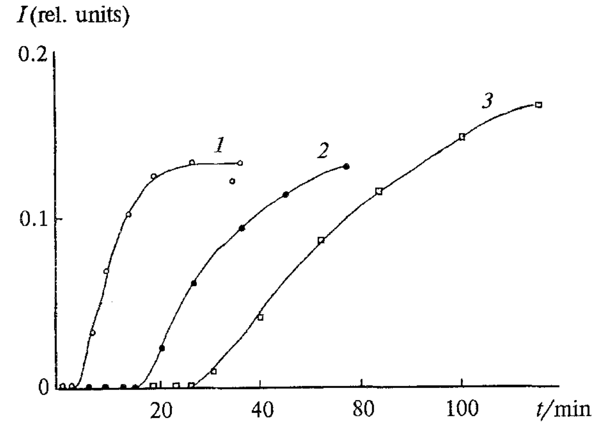

Fig. 5. The dependence of the absorption intensity at 565 nm on the duration of γ-irradiation. The solution contained: $2 \cdot 10^{-4}$ *M* $Cu(ClO_4)_2$, 0.1 *M* $(CH_3)_2CHOH$, [PEI]/10^4 *M*: *1* — 1, *2* — 2, *3* — 20.

PEI (see Fig. 4) is somewhat different from those for copper sols (see Fig. 3): it is more diffuse and exhibits an additional broad AB in the range 300—400 nm. Thus, when Cu^{2+} is not entirely bonded in the complex with PEI, an additional product of radiation-chemical reduction of copper ions is formed, along with the metal. After reduction of the Cu^{2+} ions was over, which could be detected by the constant optical absorbance observed, we determined the amount of the resulting metal. In a 10^{-4} *M* solution of $Cu(ClO_4)_2$ containing 10^{-4} *M* PEI, ~20—30 % of the Cu^{2+} was reduced to give the metal. As the concentration of PEI increases, the proportion of metal increases and amounts to 100 % at a 10-fold excess of PEI.

The mechanism of the formation of the metal. Fig. 5 shows the dependence of the intensity of the absorption at λ_{max} = 565 nm on the irradiation time for solutions with various concentrations of PEI. Notice that only in the case of a $2 \cdot 10^{-3}$ *M* solution of PEI (curve *3*) does the dependence reflect the process of the formation of metal sols. All of the dependences are S-shaped; the induction period increases as the content of PEI is increased. Two mechanisms of the formation of the new phase are possible, depending on the state of Cu^{II} in the solution.

Aqua complexes of Cu^+ are known[5] to be unstable, and the equilibrium constant for disproportionation (4)

$$Cu^+ + Cu^+ \rightleftharpoons Cu^0 + Cu^{2+} \qquad (4)$$

amounts to ≈ 10^6. In addition, in water the Cu^+ ions participate in another reaction (reaction (5))

$$Cu^+ + OH^- \rightleftharpoons 1/2\, Cu_2O + 1/2\, H_2O \qquad (5)$$

whose equilibrium constant[5] is ≈ $7 \cdot 10^{14}$. It should be noted that these equilibrium constants correspond to the conditions for the existence of the solid phase. For a 10^{-4} *M* solution of $Cu(ClO_4)_2$, the equilibrium concentrations of Cu^+ in reactions (4) and (5) at pH ≈ 7 are ≈ 10^{-5} *M* and 10^{-7} *M*, respectively. The actual concentrations of Cu^+ formed may be substantially higher, since the precipitation of the new metal or oxide phase would be preceded by supersaturation of the solution. The induction period corresponds to the duration of the radiation-chemical reduction of Cu^{II}, until the critical concentration of Cu^+ necessary for these reactions is achieved. The foregoing is confirmed by the following fact. Alkalizing the solution in which Cu^{2+} is not entirely bonded in the complex would be favorable for reaction (5). In fact, in the presence of the H_3BO_3 buffer (10^{-3} *M*) a solution with a pH of 7.8 turns yellowish-pink upon irradiation, and the optical spectrum exhibits a broad maximum in the region between 300 nm and 400 nm and a diffuse absorbance at 550 nm. The maintenance of a constant pH is necessary to keep the solution from becoming acidic due to the reduction of the copper ions. We assign the absorbance observed to the formation of colloidal particles of Cu_2O (or CuOH). Pure Cu_2O is known to have a yellow-red color, very similar to that of metallic copper. Thus, when copper is not entirely bound in the complex with PEI molecules, radiation chemical reduction in neutral or weakly alkaline aqueous solutions may afford both the metal phase and Cu_2O. An increase in the content of PEI is beneficial for the formation of the metal and an increase in pH favors the formation of the oxide. Notice as well that the presence of PEI in the solution stabilizes the colloidal form of the metal. In the absence of PEI the Cu^{2+} ions, as has been noted previously,[4] are reduced in an acidic medium (pH < 5) to yield the metal.

At a high content of PEI the $[Cu \cdot PEI]^{2+}$ ions are reduced to give the stable complex, $[Cu \cdot PEI]^+$. Disproportionation of the latter proves to be thermodynamically unfavorable. Therefore the metal can only be obtained by the subsequent reduction of $[Cu \cdot PEI]^+$. Due to the extremely high reduction potential of the copper atoms (−2.7 V) only hydrated electrons (E^0 = −2.9 V) can act as the reducing agent. However, the efficiency of this reduction (Eq. 6) is low, due to the reverse oxidation of the resulting copper atoms by the $(CH_3)_2\dot{C}OH$ radicals (Eq. 7).

$$Cu^I + e^-_{aq} \longrightarrow Cu^0 \qquad (6)$$

$$Cu^0 + (CH_3)_2\dot{C}OH \longrightarrow Cu^I + \text{products} \qquad (7)$$

Nevertheless, centers for the nucleation of the metal are formed in the solution in a low energy yield.

$$Cu^I \xrightarrow{e^-_{aq}} Cu^0 \xrightarrow{Cu^I} Cu_2{}^I \xrightarrow{Cu_2{}^I} Cu_n{}^{m+} \longrightarrow Cu_{coll}$$

The mechanism of the consecutive reactions for the enlargement of the clusters was considered in Refs. 2—4. The prolonged induction period is due to the occurrence of this process. The resulting nucleation centers (the metal nuclei) favor the reduction of Cu^I on their surface, since $E^0(Cu^+/Cu_{solid}) = -0.34$ V (see Ref. 5). Consequently, participation of not only e_{aq}^- but also the $(CH_3)_2\dot{C}OH$ radicals in the reduction is thermodynamically favorable:

$$Cu_nCu^+ + (CH_3)_2\dot{C}OH \longrightarrow Cu_{n+1} + (CH_3)CO + H^+ \qquad (8)$$

Thus, the formation of the metal phase catalyzes the subsequent reduction of the copper ions on the surface. In order to verify this assumption, we added small amounts of Ag^+ ions. The silver sols formed act in this case as nucleation centers for the metal. In fact, in a $\approx 10^{-6}$—10^{-5} *M* solution of $AgClO_4$ in the presence of excess PEI the reduction of copper substantially accelerates, and the induction period is very short and is associated with the formation of silver sols which catalyze the reduction of the copper ions.

Deposition of copper onto silver sols. The silver sols were preliminarily prepared by irradiation of a deaerated aqueous solution containing $7 \cdot 10^{-5}$ *M* of $AgClO_4$, 0.1 *M* of $(CH_3)_2CHOH$, and $2 \cdot 10^{-4}$ *M* of PEI for 20 min. The conditions of the irradiation ensured practically complete reduction of Ag^+. Silver sols (the average diameter of the particles is ≈ 4 nm) exhibit an intense narrow AB of the surface plasmons with $\lambda_{max} = 380$ nm (Fig. 6). $2 \cdot 10^{-4}$ *M* of $Cu(ClO_4)_2$ and $5 \cdot 10^{-3}$ *M* of acetone were added to the solution, and the concentration of PEI was increased to $2 \cdot 10^{-3}$ *M*. The addition of Cu^{2+} resulted in displacement of the AB to the visible region and in a decrease in its intensity. This is due to both oxidation of a part of the silver and sorption of the copper ions at the surface of the sols. The ions sorbed withdraw the electrons of the metal which causes the bathochromic shift of the AB of the sol.[9,10] After that, the solution was irradiated; the changes in its optical properties are shown in Fig. 6. As was noted above, owing to the presence of acetone, the Cu^{2+} ions could not be reduced in the bulk of the solution to produce the metal. The $(CH_3)_2\dot{C}OH$ radicals only reduced Cu^{2+} to Cu^+. This process was monitored by the decrease in the intensity of the AB of $[Cu \cdot PEI]^{2+}$ at 272 nm, superimposed on which is the weaker acetone absorption. Fig. 6 indicates that at the initial step of the irradiation the intensity of the absorption of the silver sols increased and the AB shifted slightly to the UV region. This is due to the reduction of those Ag^+ ions on the surface produced upon contact of the sols with the solution containing Cu^{2+}. The change in the absorption during the subsequent irradiation was caused by the deposition of copper on the silver sols. The reduction only occurred on the sol surface owing to the supply of electrons from the discharge of $(CH_3)_2\dot{C}OH$ on the sol. After the necessary negative potential was achieved, the Cu^+ ions were reduced at silver microelectrodes. We determined the amount of metal deposited from its reaction with MV^{2+}. Silver does not react with MV^{2+}. The examination of the dependence of the formation of MV^+ on the irradiation time made it possible to determine the degree with which the silver sols were filled with copper layers.[11,12] It was assumed that the deposition itself, as in the case of cadmium,[11] lead, and indium,[12] occurs uniformly over the surface. It was found that spectra *3*, *4*, and *5* in Fig. 6 correspond to one, two, and approximately four copper monolayers on the surface of the silver sol. The diameter of the copper atom was taken to be equal to that in the metal (~0.26 nm). It can be seen that the first monolayer results in substantial broadening of the AB from the silver sols and a decrease in its intensity. It was also found that the copper atoms of the first monolayer (adatoms) do not reduce MV^{2+}, as had been the case with cadmium, lead, and indium.[11,12] Thus, the copper adatoms, upon the contact with silver, took on its properties. As the second monolayer arises, the AB in the region of silver absorption is broadened, and a diffuse absorption in the region of copper sols appears. Well-defined absorption of the latter is only detected after the third and, especially, the fourth layers are formed (see Fig. 6). The displacement of the AB for the silver sols to the UV region during the deposition of copper can also be observed. In accordance with the theory of the absorption of light by free electrons in ultrafine spherical particles of a metal, this is caused by an increase in the electron density in them.[9,10] The electrons of the copper adatoms are withdrawn to the bulk, and the electron density in silver increases. A similar effect has been observed during the deposition of other metals onto silver sols.[11,12]

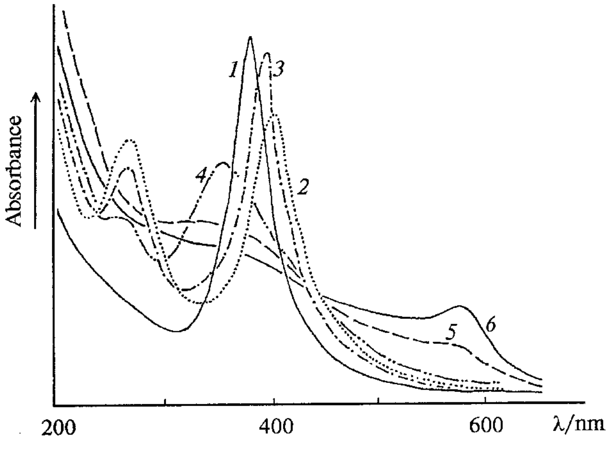

Fig. 6. The absorption spectra of a $7 \cdot 10^{-5}$ *M* silver sol (*1*), after adding $2 \cdot 10^{-4}$ *M* of $Cu(ClO_4)_2$, $5 \cdot 10^{-3}$ *M* of acetone, and $2 \cdot 10^{-3}$ *M* of PEI (*2*), after γ-irradiation for, min: 5 (*3*), 15 (*4*), 30 (*5*), 60 (*6*).

In recent years stable solutions of sols of chemically active metals, such as lead and indium,[12] cadmium[13] and thallium[14] have been prepared. This became possible due to the use of the radiation-chemical method for reducing metal ions providing the formation of powerful radical reducing agents uniformly over the solution bulk, and to the use of new efficient stabilizing agents. The present work illustrates this, using the preparation of colloidal copper and bimetallic silver—copper particles as examples. Due to a great interphase boundary, ultrafine metal particles possess a series of unusual physicochemical properties. This stimulates the search for the fields of their possible application, specifically, in the development of efficient catalysts and novel materials.

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