Radiation-chemical reduction of Co^{2+} ions in aqueous solution. Metal sols and their properties

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The radiation-chemical reduction of Co^{2+} ions in an aqueous solution of $Co(ClO_4)_2$ containing sodium formate was studied. Stable metal sols containing spherical particles with a diameter of 2—4 nm are formed under γ-irradiation in the presence of polyacrylate as the stabilizing additive. An aqueous solution of colloidal cobalt has an optical absorption that increases smoothly in the UV region without a maximum to 200 nm ($\varepsilon_{200} = 1.3 \cdot 10^4$ mol^{-1} L cm^{-1}). It is established that the radiation-chemical reduction of the Co^{2+} ions occurs *via* an autocatalytic mechanism. The metal sols catalyze the reduction of the Co^{2+} ions by $CO_2^{\cdot -}$ radical ions formed under irradiation. The properties of the sols were studied, and it is shown that they are readily oxidized by hydrogen peroxide and other oxidants. The mechanism of chemical reactions involving the sols is discussed.

Key words: γ-irradiation, aqueous solution, reduction, cobalt, colloids, sols, optical absorption, autocatalysis.

It is known (see, *e.g.*, Refs. 1—4) that ionizing irradiation of deaerated aqueous solutions of salts of noble and some other metals (cadmium, lead, nickel, *etc.*) with addition of organic compounds (alcohols, salt of organic acids) results in the reduction of the metal ions. In the presence of stabilizers (polyelectrolytes are commonly used), stable metal hydrosols, including those of cadmium,[5] thallium,[6] lead,[7] and others, can be obtained. The sols have intense optical absorption bands in the UV or visible spectral region, and their characteristics are determined to a considerable extent by their size and shape[8—10] and the state of the particle surface.[11] Therefore, optical spectroscopy is widely used as an efficient method for the study of the nature and properties of metallic nanoaggregates in aqueous solutions.

This work is aimed at obtaining stable aqueous solutions of colloidal cobalt and studying its properties. The theoretically calculated absorption spectrum[9] of the sol of spherical cobalt particles with a diameter of 10 nm is a band with $\lambda_{max} < 200$ nm, which increases smoothly from the visible to UV region. It is known[12] that γ-irradiation of deaerated aqueous solutions of Co^{2+} ions containing $HCOO^-$ ions as scavengers of hydroxyl radicals (the reaction of $OH^{\cdot}$ with $HCOO^-$ affords the $CO_2^{\cdot -}$ radical ion) results in the formation of carbon dioxide. This suggested that $CO_2^{\cdot -}$ can reduce Co^{2+} ions. The formation of a metal precipitate was not reported. It has been shown[13] by pulse radiolysis technique that hydrated electrons reduce the Co^{2+} ion (the rate constant of the reaction is controlled by diffusion and is equal to $1.2 \cdot 10^{10}$ mol^{-1} L s^{-1}) to form a short-lived Co^+ ion (absorption with λ_{max} at 310 and 370 nm). Reaction of the $CO_2^{\cdot -}$ radical ion with the Co^{2+} ion under pulse irradiation conditions was not observed. The authors of the known work[13] believe that this indicates that the rate constant of this reaction is very low and ranges within 10^2—10^5 mol^{-1} L s^{-1}. These data suggest a possibility to obtain stable aqueous solutions of colloidal cobalt if a stabilizing additive is successfully chosen. Our studies showed that sodium polyacrylate is an efficient stabilizer of colloidal cobalt particles.

Experimental

Cobalt(II) perchlorate, sodium formate (specially pure), and sodium polyacrylate (Aldrich) were used. The average molecular weight of the latter was 2100. Its concentration in a solution was expressed in moles of monomeric units. Solutions were prepared with triply distilled water and deaerated by deep evacuation prior to irradiation. Irradiation was carried out by a ^{60}C source in a glass vessel with a quartz cell for optical measurements. The volume of the irradiated solution was 10 mL. Samples for electron microscopic studies were prepared by supporting a droplet of the solution analyzed onto a copper-carbon support followed by drying in an argon atmosphere. A Philips CM12 electron microscope equipped with an EDAX 9800 analyzer was used. The amount of cobalt ions reduced to a metal state was determined using the procedure suggested previously[5,14] by the addition of a 0.1 *M* solution of NaOH (1 mL) and then a 10^{-2} *M* solution of methylviologen (2 mL) to the solution under study (10 mL). The concentration of the methylviologen reduced (MeV^{2+}) was determined spectrophotometrically by the absorption of the MeV^+ radical cation with a maximum at 600 nm ($\varepsilon_{max} = 1.2 \cdot 10^4$ mol^{-1} L cm^{-1}).[14]

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Results and Discussion

The γ-irradiation of aqueous solutions containing sodium formate results in the formation of hydrated electrons (standard reduction potential −2.7 V) and CO_2^- radical ions (−1.9 V).[1]

$$H_2O \rightarrow e^-_{aq}\ (2.7),\ H\ (0.5),\ OH\ (2.9),\ H_2\ (0.5),\ H_2O_2\ (0.7),\ H^+\ (2.7)$$

$$HCOO^- + OH\ (H) \rightarrow CO_2^{\cdot -} + H_2O\ (H_2)$$

In the first reaction, the values of radiation-chemical yields of the radiolysis products are presented in parentheses. The yield of the $CO_2^{\cdot -}$ radical ions when hydrogen atoms and $OH^{\cdot}$ radicals are completely consumed by $HCOO^-$ ions should be ~3.4 particles per 100 eV of the absorbed energy. When the power of the absorbed dose of Co^{60} γ-radiation of 1 kGy h^{-1} is used in experiments, ~$4.4 \cdot 10^{-6}$ mol L^{-1} of hydrated electrons and ~$5.6 \cdot 10^{-6}$ mol L^{-1} $CO_2^{\cdot -}$ radical ions are generated in an aqueous solution during 1-min irradiation.

The addition of sodium polyacrylate to a neutral aqueous solution containing $Co(ClO_4)_2$ virtually does not change the optical absorption of the Co^{2+} ions, which is characterized by a band with $\lambda_{max} < 200$ nm and a low-intensity band with $\lambda_{max} = 500$ nm. Therefore, for the 1 : (1—3) ratio of Co^{2+} and polyacrylate concentrations used in the experiment, no complexes between these compounds are formed.

Formation of metal sols. γ-Irradiation of deaerated $2 \cdot 10^{-4}$—$5 \cdot 10^{-2}$ *M* solutions of $Co(ClO_4)_2$ containing (10^{-3}—10^{-1}) mol L^{-1} HCOONa results in the reduction of the metal. The solution becomes yellow-brown, and the intensity of the color increases as the irradiation time increases. The optical spectrum of the solution irradiated exhibits an absorption in the whole region from 200 to 900 nm, and its intensity increases monotonically toward shorter waves in the absence of a pronounced maximum (Fig. 1). The electron microscopic study shows the existence of metallic cobalt particles with a broad size distribution. The average diameter of the particles ranges within 10—30 nm. However, there are particles with a diameter of 4—6 nm, substantially larger particles, and their aggregates. At low concentrations of $Co(ClO_4)_2$ ($<10^{-3}$ mol L^{-1}) and low irradiation doses, the solution of colloidal cobalt that formed is stable at least for 1 day. As the absorbed dose and the concentration of the dissolved salt increase, a relative increase in the intensity in the long-wave region is observed. The Tyndall cone is observed in transmitted light, which indicates the presence of sufficiently large metal particles. A metal film is precipitated with time on the bottom and walls of the vessel from these solutions.

When polyacrylate (10^{-4}—10^{-3} mol L^{-1}) is added, the solutions irradiated retain their transparency and remain almost colorless during irradiation. A very weak yellow color due to the metal sols that formed appears at very high absorbed doses. The electron microscopic data show that in the presence of a stabilizer, the metallic particles formed have almost a spherical shape, a narrow size distribution, and an average diameter of 2—4 nm and are spatially separated from each other. These solutions are stable within a very long time.

Optical absorption spectrum of sols. The irradiation results in the appearance of an optical absorption without a maximum propagating in the whole optical region and increasing from the visible to UV spectral region (Fig. 2). The optical density of the solution increases

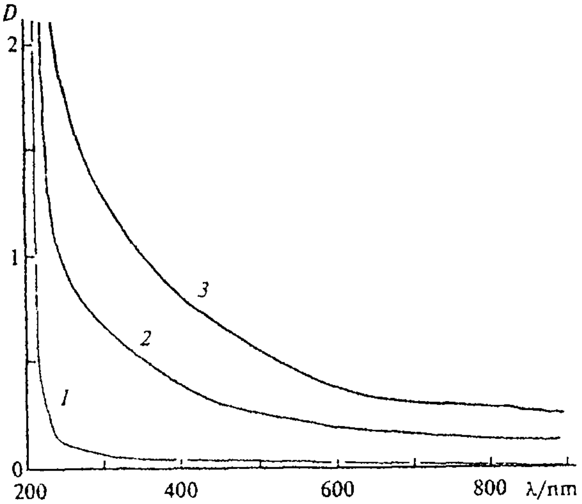

Fig. 1. Absorption spectra of a $2 \cdot 10^{-3}$ *M* solution of $Co(ClO_4)_2$ containing $5 \cdot 10^{-3}$ mol L^{-1} HCOONa at γ-irradiation time 0 (*1*), 60 (*2*), and 120 (*3*) min. The absorbed dose was 1 kGy h^{-1}. Irradiation within 1 min produces $4.4 \cdot 10^{-6}$ mol L^{-1} e_{aq}^- and $5.6 \cdot 10^{-6}$ mol L^{-1} $CO_2^{\cdot -}$.

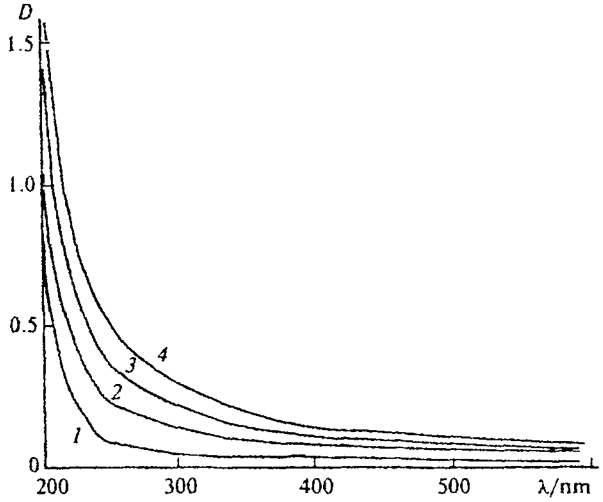

Fig. 2. Absorption spectra of a $2 \cdot 10^{-4}$ *M* solution of $Co(ClO_4)_2$ containing $2 \cdot 10^{-3}$ mol L^{-1} HCOONa and $2 \cdot 10^{-4}$ mol L^{-1} sodium polyacrylate at γ-irradiation time 0 (*1*), 60 (*2*), 90 (*3*), and 120 (*4*) min. For irradiation conditions, see Fig. 1.

when the absorption dose increases. The shape of the optical absorption band remains almost unchanged. Admission of air into the solution leads to the disappearance of the optical absorption due to the oxidation of the metal sols with dioxygen. The optical absorption of the solution returns to the initial one. In an alkaline medium, the cobalt sols reduce the MeV^{2+} cation

$$Co^0 + 2\ MeV^{2+} \rightarrow Co^{2+} + MeV^{+}.$$

It is noteworthy that the interaction of cadmium,[5] thallium,[6] and lead[7] sols with methylviologen occurs almost instantly. In the case of cobalt, this process is completed in several hours. This reaction gives the MeV^{+} radical cations with an intense absorption band with λ_{max} = 600 nm (Fig. 3). Taking into account the known extinction coefficient of MeV^{+} ($1.2 \cdot 10^4$ mol^{-1} L cm^{-1}) and stoichiometry of the reaction, we can determine the overall concentration of cobalt atoms in the solution and thus calculate the extinction coefficient of the optical absorption of the sols (calculated per metal atom). We used this fact for the calculation of the optical absorption spectrum of the cobalt sols in the aqueous solution as the difference between the spectra of the irradiated and initial solutions (minus the absorption of the cobalt and formate ions disappeared in the radiation-chemical transformations). The absorption of polyacrylate makes the main contribution to the spectrum of the initial solution; therefore, the change in the concentrations of the cobalt and formate ions during irradiation is not a determining factor in the calculation procedure. The spectrum obtained (Fig. 4) is in good agreement with that calculated theoretically[9] and represents an absorption with $\varepsilon = 1.3 \cdot 10^4$ mol^{-1} L cm^{-1} (±20%) at 200 nm, decreasing monotonically to the long-wave region. This has been reported previously[15] on the preparation of cobalt nanoparticles during the chemical reduction of the metal ions by $NaBH_4$ in so-called inverse micelles (water microdroplet dispersed in isooctane and stabilized by sodium diethylhexylsulfonyl succinate). Optical measurements were carried out only in the region from 250 to 650 nm. The metal particles with an oxide admixture showed an increasing absorption from longer to shorter waves. An increase in the water content was accompanied by a decrease in the particle size and an increase in the content of cobalt oxide (an additional band with a maximum at 350 nm). For this method of preparation of colloidal cobalt particles, the presence of admixtures of various boron compounds with the metal along with the metal oxide cannot be ruled out.

Properties of colloidal cobalt. The standard redox potential is the following: $E^0(Co^{2+}/Co(s)) = -0.22$ V.[16] The cobalt sols react rapidly with air and methylviologen in an alkaline medium, as well as with other oxidants (hydrogen peroxide, permanganate, *etc.*). The addition of silver ions to a solution of colloidal cobalt results in their reduction to form colloidal silver particles, which can be determined by the appearance of the characteristic absorption with a maximum at approximately 400 nm in the optical spectrum.

Radiation-chemical reduction of Co^{2+} in aqueous solution. The accumulation of metallic nanoaggregates during γ-irradiation of a solution of $Co(ClO_4)_2$ has an unusual character (Fig. 5). As the absorbed dose (irradiation time) increases, the rates of reduction of Co^{2+} ions increase noticeably (see Fig. 5) rather than decrease or remain unchanged, which is typical of a standard radiation-chemical process. This is valid for all the solutions in the range of concentrations studied (($2 \cdot 10^{-4}$—$5 \cdot 10^{-2}$) mol L^{-1} $Co(ClO_4)_2$). The reduction of the Co^{2+} ions in the presence of polyacrylate

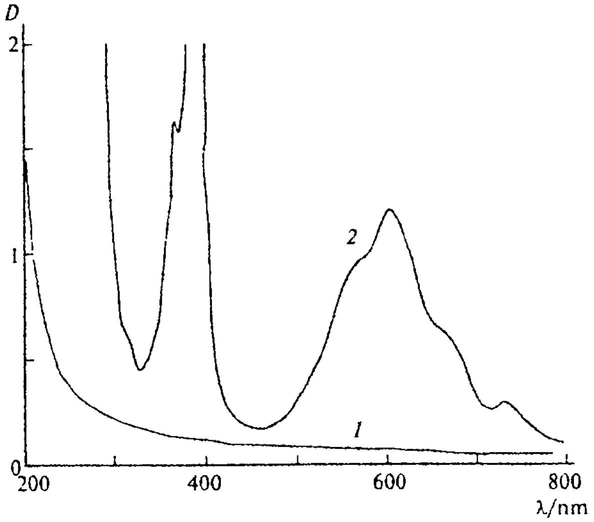

Fig. 3. Absorption spectra of a $2 \cdot 10^{-4}$ *M* solution of $Co(ClO_4)_2$ containing $2 \cdot 10^{-3}$ mol L^{-1} HCOONa and $2 \cdot 10^{-4}$ mol L^{-1} sodium polyacrylate after 90-min γ-irradiation (*1*) and after addition of a solution of methylviologen (*2*). For irradiation conditions, see Fig. 1.

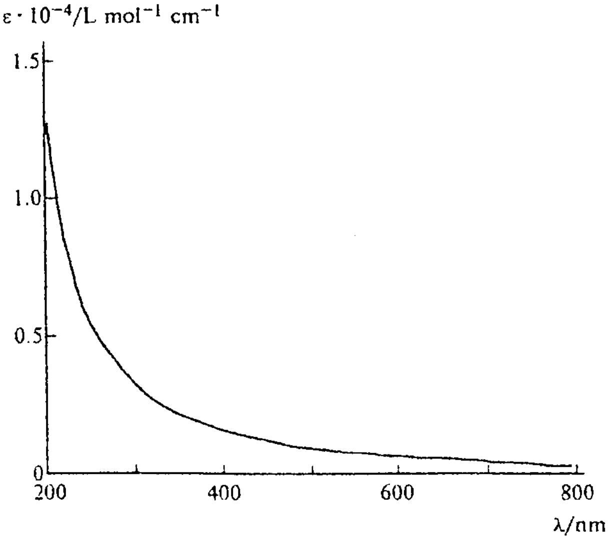

Fig. 4. Optical absorption spectrum of cobalt sols.

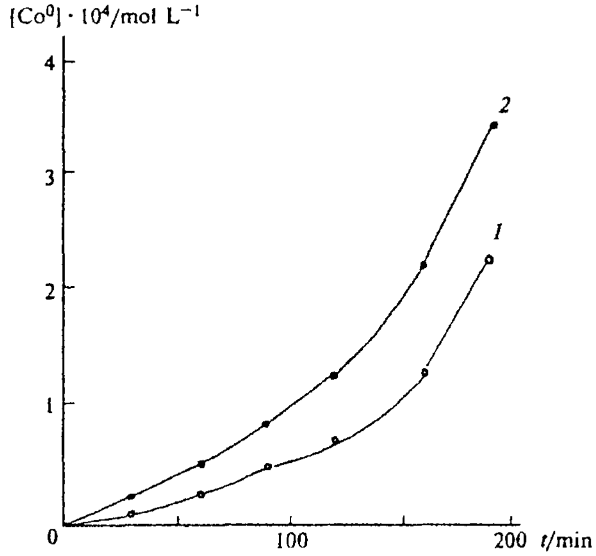

Fig. 5. Change in the concentration of colloidal cobalt on the time of γ-irradiation of solutions of $1\cdot 10^{-3}$ (*1*) and $5\cdot 10^{-3}$ mol L^{-1} (*2*) $Co(ClO_4)_2$ containing $1\cdot 10^{-2}$ mol L^{-1} HCOONa and $1\cdot 10^{-3}$ mol L^{-1} sodium polyacrylate. For irradiation conditions, see Fig. 1.

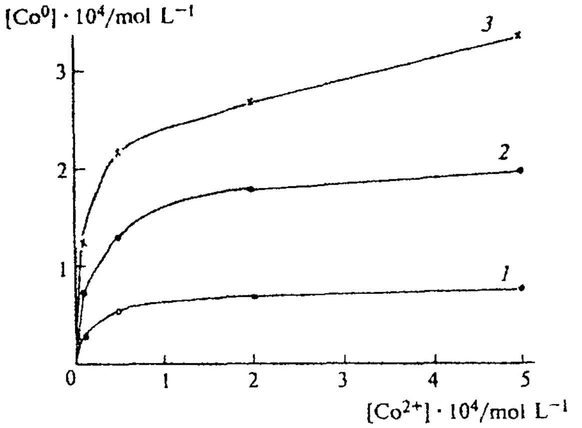

Fig. 6. Dependences of the concentration of the colloidal cobalt formed on the concentration of $Co(ClO_4)_2$ in a solution containing $1\cdot 10^{-2}$ mol L^{-1} HCOONa and $1\cdot 10^{-3}$ mol L^{-1} sodium polyacrylate at γ-irradiation times of 60 (*1*), 120 (*2*), and 160 (*3*) min. For irradiation conditions, see Fig. 1.

occurs in the autocatalytic regime: the appearance of the metal sols and an increase in their concentration accelerate the process. An increase in the concentration of $Co(ClO_4)_2$ results in an increase in the concentration of colloidal Co which, however, remains lower than that expected for the complete acceptance of hydrated electrons and $CO_2^{\cdot -}$ radicals by the Co^{2+} ions even in sufficiently concentrated solutions of $Co(ClO_4)_2$ (Fig. 6).

Redox potentials of intermediate valence forms should be known for understanding the mechanism of reduction of the Co^{2+} ions. It has been established recently[17] that the Co^+ ions in aqueous solutions can form mixed short-lived $(AgCo)^{2+}$ clusters with Ag^+ ions. It follows from this that the standard potentials of the Co^{2+}/Co^+ and Ag^+/Ag^0 pairs coincide or are rather close, *i.e.*, $E^\circ(Co^{2+}/Co^+) \cong E^\circ(Ag^+/Ag^0) = -1.8$ V. The reduction potential of the $CO_2^{\cdot -}$ radical ion is equal to -1.9 V. It can be assumed that at close values the direction of the reaction

$$CO_2^{\cdot -} + Co^{2+} \rightleftharpoons CO_2 + Co^+$$

is determined by the ratio of concentrations of the reagents involved in the reaction and the contribution of the competing recombination reaction of the $CO_2^{\cdot -}$ radicals ($2k = 1.6\cdot 10^9$ mol^{-1} L s^{-1}).[18] Under pulse irradiation conditions, no reaction of $CO_2^{\cdot -}$ with the Co^{2+} ion has been observed.[13] However, the formation of carbon dioxide upon γ-irradiation of a 10^{-2} *M* aqueous solution of the cobalt(II) salt and formate ions allowed the authors of Ref. 13 to assert that the $CO_2^{\cdot -}$ radical ion can reduce the Co^{2+} ion. According to the estimation performed, the rate constant of this reaction can range within 10^2—10^5 mol^{-1} L s^{-1}. The results of our studies agree with the lower limit of this value. The contribution of this reaction to the reduction of the Co^{2+} ions can be pronounced in sufficiently concentrated solutions of $Co(ClO_4)_2$ only, as this has been observed previously.[13] The aforementioned autocatalytic character of the reduction of the cobalt ions indicates unambiguously the participation of the metal sols. In our opinion, the $CO_2^{\cdot -}$ radical ions cannot reduce efficiently the Co^{2+} ions, especially in dilute solutions. However, the metal sol can catalyze reduction reactions on the surface that do not occur in the bulk or are too slow. This is due to the difference in values of potentials of the redox pairs on the surface or in the bulk solution. The standard potential of $Co^{2+}/Co(s)$ is equal to -0.22 V. The potential of the Co^{2+}/Co^0 pair calculated by the subtraction of the heat of sublimation of the metal atoms from $E^\circ(Co^{2+}/Co(s))$ is equal to -2.33 V. Thus, the reduction of the Co^{2+} ions by the $CO_2^{\cdot -}$ radicals on the metal sol (microelectrode) is energetically more favorable than their reduction in the bulk solution to the atomic state.

Let us consider a possible mechanism for the reduction of the Co^{2+} ions. The formation of the cobalt sols at the initial stage of the radiation-chemical reduction is related to the one-electron reduction of the Co^{2+} ion by hydrated electrons

$$\bar{e}_{aq} + Co^{2+} \to Co^+.$$

By analogy with other transition metals,[1] one could expect that the disproportionation of the Co^+ ions

$$2\,Co^+ \to Co^0 + Co^{2+}.$$

is the next stage. Based on the values $E^\circ(Co^{2+}/Co^+) = -1.8$ V and $E^\circ(Co^{2+}/Co^0) = -2.33$ V, we found $E^\circ(Co^+/Co^0) = -2.8$ V. It follows from this that the disproportionation of the Co^+ ions is thermodynamically unfavorable, since the exothermicity of the $Co^+ \rightarrow Co^{2+}$ transition is lower than that of the $Co^+ \rightarrow Co^0$ transition. This conclusion is confirmed by the pulse radiolysis data[13] on the kinetics of the disapperance of Co^+, which appear in the reaction of Co^{2+} with hydrated electrons. This process is described by an equation of first order rather than of second order, as can be expected for the disproportionation or the reaction of Co^+ with the CO_2^- radical ions. Therefore, it can be assumed that the Co^+ ions disappear in a reaction of the type

$$Co^+ + Co^{2+} \longrightarrow Co_2^{3+}.$$

It is known[19] that the formation of positively charged clusters is a sufficiently general process for transformation of metal ions with one electron on external s- (silver, copper, cadmium, and others) or p-orbitals (thallium, indium, lead, and others). The successive enlargement of the clusters is accompanied by a decrease in the reduction potential and thus makes the disproportionation process thermodynamically favorable at a certain stage of agglomeration. This process can be presented as the following reaction:

$$2n\, Co_2^{3+} \longrightarrow 2\,(Co_2^{3+})_n \longrightarrow (Co)_n + 3n\, Co^{2+},$$

where the intermediate stage reflects conventionally the possibility of formation of different cobalt clusters.

The participation of the $CO_2^{\cdot -}$ radical ions in the reduction of the Co^{2+} ions in an aqueous solution is restricted by the reaction catalyzed by the metal sols. These processes have an electrochemical nature and occur *via* the following scheme:

$$(Co)_n + 2m\, CO_2^{\cdot -} \longrightarrow (Co)_n^{2m-} + 2m\, CO_2,$$

$$(Co)_n^{2m-} + m\, Co^{2+} \longrightarrow (CO)_{n+m}.$$

Reactions of this type are well studied (see, *e.g.*, review[11]). It is known, in particular, that when microelectrodes (silver or gold sols) are charged by the discharge of organic radicals obtained by the radiation-chemical method upon irradiation of aqueous solutions, a potential is achieved at which water is reduced to form molecular hydrogen.[20–23]

The mechanism of radiation-chemical reduction of Co^{2+} ions with account of the catalytic effect of the metal sols explains the acceleration observed with an increase in the concentration of the sols.

The radiation-chemical method of preparation of solutions of colloidal metals developed in this work was successfully used for nickel. In the presence of formate ions, Ni^{2+} ions are reduced to form stable sols. Sodium dodecyl sulfate, polyethylenimine, or polyacrylate were used for the stabilization of the colloidal particles. In all cases, colloidal nickel is characterized by the optical absorption band with a maximum at 220 nm, decreasing smoothly toward longer waves. The extinction coefficient in the absorption maximum was approximately $8 \cdot 10^3$ mol^{-1} L cm^{-1}.

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