Aqueous solutions of colloidal nickel: radiation-chemical preparation, absorption spectra, and properties

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Radiation-chemical reduction of Ni^{2+} ions in aqueous solutions of $Ni(ClO_4)_2$ containing sodium formate or isopropyl alcohol was studied. γ-Irradiation of deaerated solutions in the presence of polyethyleneimine, polyacrylate, or polyvinyl sulfate gives stable metal sols containing spherical particles 2—4 nm in diameter. The optical absorption spectra of nickel nanoparticles exhibit a band with a maximum at 215±5 nm ($\varepsilon_{215} = 4.7 \cdot 10^3$ L mol^{-1} cm^{-1}) and a shoulder at 350 nm. A mechanism for the radiation-chemical reduction of Ni^{2+} ions by hydrated electrons and organic radicals ($CO_2^{\cdot -}$ radical anions in the case of HCOONa and $Me_2C^{\cdot}OH$ radicals in the case of Pr^iOH). The redox potentials of the Ni^{2+}/Ni^0 and Ni^+/Ni^0 pairs (Ni^0 is a nickel atom) are approximately −2.2 and −1.7 V, respectively. The nanoparticles are readily oxidized by O_2, H_2O_2, and other oxidants. The reactions of these species with silver ions yield relatively stable nanoaggregates containing both nickel and silver in addition to silver nanoparticles.

Keys words: γ-irradiation, aqueous solutions, reduction, nickel, silver, colloids, sols, optical absorption, redox reactions.

Previously,[1,2] it was reported that γ-irradiation of deaerated aqueous solutions of nickel salts containing Pr^iOH or HCOONa additives results in the formation of colloidal nickel. The addition of polyvinyl alcohol to the solution stabilizes metal sols. In the presence of Pr^iOH, the efficiency of radiation-chemical reduction of nickel ions is very low (the radiation yield is only 0.3 nickel atom per 100 eV of absorbed energy) and the size of the arising metal particles is 10—20 nm.[1] When the alcohol is replaced by HCOONa, the yield increases to about 1.0[2]. It was also found that colloidal nickel in aqueous solutions can be oxidized by oxygen and can reduce some dyes.

Optical spectroscopy is widely used to study the nature and properties of metallic nanosized aggregates in aqueous solutions. The optical absorption of nickel sols in water was calculated in terms of the Mie theory; it was found that spherical metal particles with a diameter of 10 nm should display an absorption band having a maximum at ~220 nm and smoothly declining right up to 900 nm.[3]

In the present study, we obtained stable solutions of nanometer nickel particles using various stabilizing additives (polyethyleneimine, polyacrylate, and polyvinyl sulfate), measured the optical absorption spectra of colloidal solutions, and studied some reactions involving ultrasmall nickel particles.

Experimental

Chemically pure grade $Ni(ClO_4)_2$ and HCOONa and Aldrich polyvinyl sulfate, sodium polyacrylate (molecular weight 2000 to 5000), and polyethyleneimine (molecular weight 5000) were used. The concentrations of polymers in solutions were expressed in moles of monomer units. Solutions were prepared using triply distilled water and deaerated in a high vacuum prior to irradiation. Irradiation was performed using a ^{60}Co source in special glass vessels equipped with a quartz cell for optical measurements. The volume of solutions exposed to radiation was usually 10 mL.

Exposure of aqueous solutions containing sodium formate to γ-radiation affords hydrated electrons (e^-_{aq}) and $CO_2^{\cdot -}$ radical anions with high reduction potentials (−2.9 and −1.9 V, respectively).[4]

$$H_2O \xrightarrow{\gamma} e^-_{aq}\,(2.7) + H^{\cdot}\,(0.5) + {}^{\cdot}OH\,(2.9) + H_2\,(0.5) + H_2O_2\,(0.7) + H^+\,(2.7) \qquad (1)$$

$$HCOO^- + {}^{\cdot}OH\,(H) \longrightarrow CO_2^{\cdot -} + H_2O\,(H_2) \qquad (2)$$

The values in parentheses in the first reaction are the radiation-chemical yields of the corresponding radiolysis products. The yield of electrons was 2.7 and the yield of the $CO_2^{\cdot -}$ radical anions was ~3.4 particles per 100 eV of absorbed energy, while the H and $OH^{\cdot}$ species were completely scavenged by $HCOO^-$ ions. When the Co^{60} γ-radiation dose rate used was 0.5 kGy h^{-1}, ~$2.2 \cdot 10^{-6}$ mol L^{-1} of hydrated electrons and $2.8 \cdot 10^{-6}$ mol L^{-1} of $CO_2^{\cdot -}$ radical anions were generated in aqueous solution upon irradiation for 1 min.

Samples for electron microscopy were prepared by placing a drop of the solution under study onto a copper—carbon grid, which was then dried under argon. A Phillips EM-30 electron microscope was used. The amount of nickel atoms reduced to the metal was determined using the reaction of nickel sols with dimethyl-4,4′-bipyridine (methylviologen MV^{2+}) by a procedure reported previously.[5] For this purpose, a 0.1 *M* solution of

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NaOH (1 mL) and a 10^{-2} *M* solution of MV^{2+} (2 mL) were added successively to a solution to be analyzed (10 mL). The concentration of the $MV^{\cdot +}$ ions formed was determined by spectrophotometry based on the intensity of the absorption band with a maximum at 600 nm (λ_{max} = $1.1 \cdot 10^4$ L mol^{-1} cm^{-1}).[6]

Results and Discussion

Formation of nickel sols. γ-Irradiation of deaerated ($2 \cdot 10^{-4}$—$5 \cdot 10^{-3}$ mol L^{-1}) solutions of $Ni(ClO_4)_2$ containing (10^{-3}—10^{-2}) mol L^{-1} of HCOONa and a stabilizing additive (polyethyleneimine, polyvinyl alcohol, polyacrylate, or polyvinyl sulfate) results in the reduction of Ni^{2+} ions to the metal. The solution remains transparent. In the case of large absorbed doses and concentrated solutions, the solution becomes yellowish. According to the electron microscopy data (Fig. 1), isolated spherical particles of metallic nickel 2—4 nm in diameter with a narrow size distribution are formed under these conditions. In the presence of polyvinyl alcohol, 15—20-nm particles are formed. The solutions of colloidal nickel containing the stabilizing additives are stable over infinitely long periods.

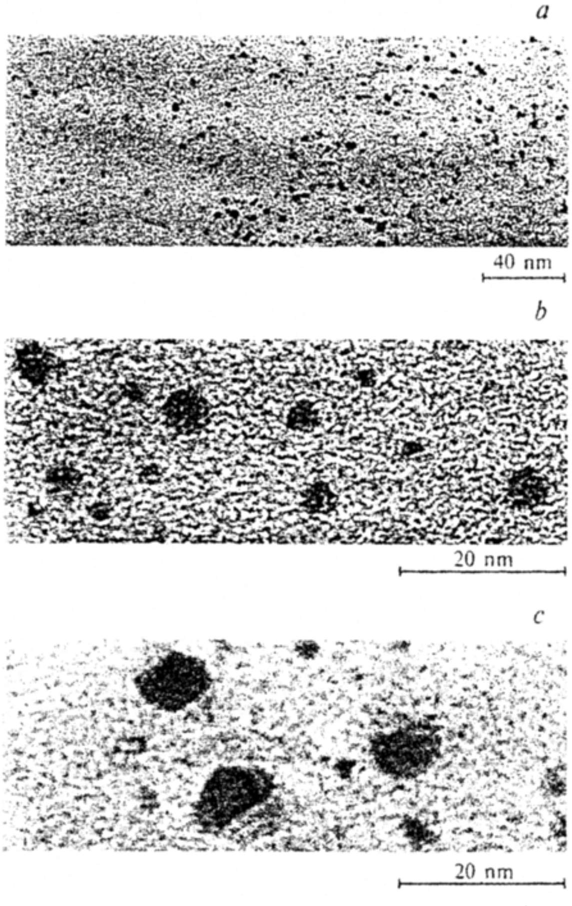

Fig. 1. (*a*) Electron micrographs of the nickel particles formed upon γ-irradiation of a solution containing $1 \cdot 10^{-4}$ mol L^{-1} of $Ni(ClO_4)_2$, $5 \cdot 10^{-3}$ mol L^{-1} of HCOONa, and $2 \cdot 10^{-4}$ mol L^{-1} of polyethyleneimine. (*b*) The same, with higher resolution. (*c*) After the addition of $2 \cdot 10^{-4}$ mol L^{-1} of $AgClO_4$. Absorbed dose rate 0.5 kGy h^{-1}, irradiation time 1 h.

Colloidal nickel is also formed upon γ-irradiation of solutions containing no stabilizing additives. However, in this case, as in the presence of polyvinyl alcohol, particles 10—20 nm in diameter are produced. When the nickel ions have not been completely reduced, the solution of colloidal metal remains stable over a period of 24 h. After several days, the solution becomes turbid and shows the Tyndall effect; later, a metal deposit is formed on the vessel walls and bottom.

Optical absorption spectrum of nickel nanoparticles. The absorption spectrum (Fig. 2) of a solution containing $1 \cdot 10^{-4}$ mol L^{-1} of $Ni(ClO_4)_2$, $5 \cdot 10^{-3}$ mol L^{-1} of HCOONa, and $2 \cdot 10^{-4}$ mol L^{-1} of polyethyleneimine exhibits a weak absorption band at $\lambda < 250$ nm, due to $HCOO^-$ and polyethyleneimine. Upon γ-irradiation of the solution, absorption without clear-cut maxima appears in the optical region of 200—900 nm, declining smoothly toward longer wavelengths (see Fig. 2). As the time of γ-irradiation (absorbed dose) increases, the absorption intensity increases, while the spectral pattern remains the same, and after ~90—120 min, a constant intensity is attained, which is related to the complete reduction of the nickel ions in the solution. Figure 3 shows the absorption spectrum of a nickel sol, which represents the difference between the spectra of irradiated and nonirradiated solutions with allowance made for the concentration of ions present in the irradiated solution ($2 \cdot 10^{-4}$ mol L^{-1} of $NaClO_4$, $2 \cdot 10^{-4}$ mol L^{-1} of polyethyleneimine, and $4.7 \cdot 10^{-3}$ mol L^{-1} of HCOONa) and for the concentration of ions having disappeared during irradiation ($3 \cdot 10^{-4}$ mol L^{-1} of HCOONa). It should be noted that the major contribution to the optical absorption of the initial solution is made by polyethyleneimine, whereas the change in the concentration of the formate ions is not a crucial factor in the "differential" determination of the optical spectrum of colloidal nickel, which is shown in Fig. 3 as the variation of the extinction coefficient (ε) *vs.* wavelength. It can be seen in Fig. 3 that the absorption of nickel sols has a maximum at 215±5 nm and the extinction coefficient at this wavelength is $(4.8 \pm 0.4) \cdot 10^3$ L mol^{-1} cm^{-1} per metal atom. In addition, a feebly defined shoulder at ~350 nm is present. Using the Mie theory,[7] we calculated the absorption spectrum for nickel sols consisting of spherical particles 10 nm in diameter. The experimental data for the dependence of the dielectric losses of the metal on the light wavelength[8] and the refraction index of water (1.33) were used in the calculations. The resulting optical characteristics of nickel sols in water (a maximum at 215 nm, a shoulder at 350 nm, and $\varepsilon = 4.6 \cdot 10^3$ L mol^{-1} cm^{-1}) are in satisfactory agreement with the results of calculations[3] and virtually coincide with experimental data (see Fig. 3). However, the experimental spectrum was found to be broader than the

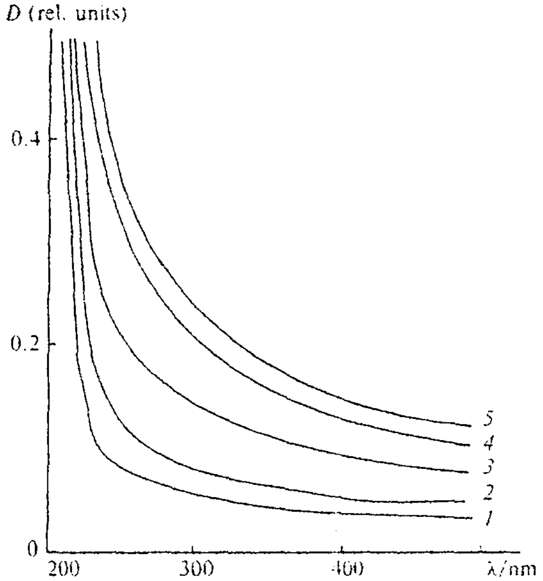

Fig. 2. Absorption spectra of a solution containing $1 \cdot 10^{-4}$ mol L^{-1} of $Ni(ClO_4)_2$, $5 \cdot 10^{-3}$ mol L^{-1} of HCOONa, and $2 \cdot 10^{-4}$ mol L^{-1} of polyethyleneimine for γ-irradiation time of 0 (*1*), 30 (*2*), 60 (*3*), 90 (*4*), and 120 (*5*) min. Absorbed dose rate 0.5 kGy h^{-1}. Irradiation for 1 min gives $2.2 \cdot 10^{-6}$ mol L^{-1} of hydrated electrons (e_{aq}^-) and $2.8 \cdot 10^{-6}$ mol L^{-1} of $CO_2^{\cdot -}$ radical anions.

theoretical one. This can be due to the fact that particles with a broad size distribution are formed in experiments and also to the fact that the theory does not take into account the state of the particle surface and their electromagnetic interactions.

The use of other stabilizing additives (polyvinyl alcohol, polyacrylate or polyvinyl sulfate) instead of polyethyleneimine virtually does not influence the accumulation of nickel sols, their properties, or optical characteristics. The change of the molecular mass of polyacrylate from 2000 to 5000 does not influence the process of formation or the size of nickel nanoparticles either. This is exemplified in Fig. 4, which shows the optical spectra of sols measured by the "differential" method after complete reduction of nickel ions in a $1 \cdot 10^{-4}$ mol L^{-1} solution of $Ni(ClO_4)_2$ containing $5 \cdot 10^{-3}$ mol L^{-1} of HCOONa and various stabilizing additives.

Colloidal nickel is also formed if aliphatic alcohols are used instead of formate ions. This requires longer γ-irradiation and the metal evolution is preceded by an induction period. The best results are attained on the addition of Pr^iOH. However, in this case, too, the degree of reduction of Ni^{2+} ions in a $1 \cdot 10^{-4}$ mol L^{-1} solution does not exceed 25% for irradiation time of 90 min.

The properties of nickel nanoparticles in aqueous solutions. The introduction of air into a solution of colloidal nickel results in its oxidation and in the loss of the sol spectrum. The standard reduction potential $E^0(Ni^{2+}/Ni_{solid}) = -0.25$ V.[9] The potential of the $E^0(Ni^{2+}/Ni^0)$ pair (where Ni^0 is a nickel atom) can be calculated from this value by subtracting the energy of atomization of nickel in the gas phase (3.95 eV[9]). In calculations, we did not take into account the energy of possible solvation of Ni atoms in water, which is expected to be close to zero. This gave $E^0(Ni^{2+}/Ni^0) = -2.2$ V. This means that the reduction potential of Ni atoms is substantially more negative than that of the bulk

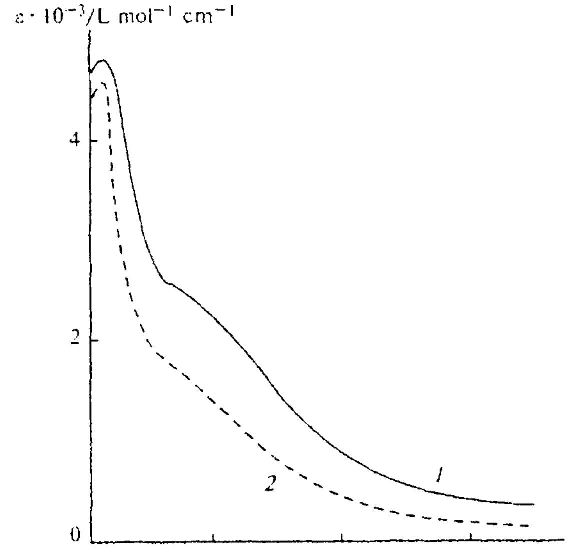

Fig. 3. Optical absorption spectra of nickel nanoparticles in water, experimental (*1*) and calculated by the Mie theory (*2*).

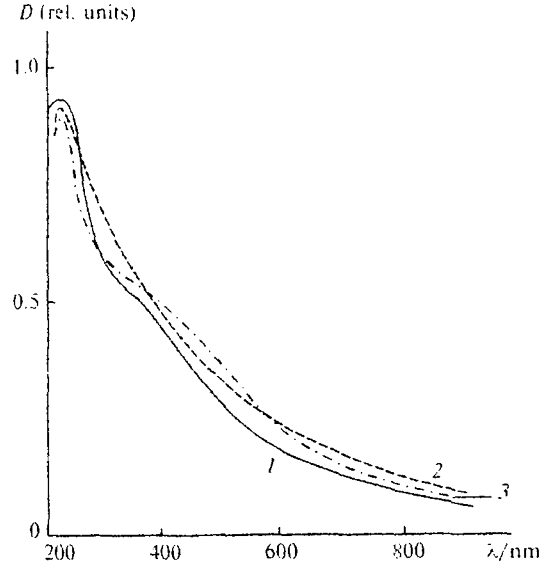

Fig. 4. Optical absorption spectra (*D*) of nickel nanoparticles in an aqueous solution stabilized by polyacrylate (*1*), polyvinyl sulfate (*2*), or polyvinyl alcohol (*3*).

metal. This suggests that the reducing capacity of colloidal nickel would be more pronounced than that of bulk Ni. Indeed, unlike the bulk metal, nickel colloids are rapidly oxidized by oxygen or air and reduce some dyes.[2] We have found that they also react with H_2O_2 and other oxidants.

Nickel sols do not reduce MV^{2+} cations in neutral solutions.[2] However, we found that this process does occur slowly in alkaline media. The overall reaction

$$Ni^0 + 2\,MV^{2+} \longrightarrow Ni^{2+} + 2\,MV^{\cdot +} \qquad (3)$$

yields the $MV^{\cdot +}$ radical cations, responsible for an intense absorption band with λ_{max} = 600 nm (Fig. 5). The known extinction coefficient of $MV^{\cdot +}$ ($1.1 \cdot 10^4$ L mol^{-1} cm^{-1}) and the reaction stoichiometry can be used to determine the concentration of Ni atoms arising upon the radiation-induced chemical reduction of nickel ions. This, in turn, provides the possibility of calculating the extinction coefficient for the optical absorption of the sols by an independent method. It was found that three days after the introduction of MV^{2+} in a solution of colloidal nickel stabilized by polyethyleneimine or by another additive, the concentration of the $MV^{\cdot +}$ ions reached practically a constant value, *i.e.*, colloidal nickel was completely consumed in the reaction with MV^{2+}. The extinction coefficient of nickel sols calculated by the above-described procedure was $\varepsilon_{215} = 4.6 \cdot 10^3$ L mol^{-1} cm^{-1} ($\pm$10%), which is in good agreement with the ε_{215} value that we found previously and with the value calculated in terms of the Mie theory.

Silver ions are reduced by colloidal nickel to give colloidal silver particles. As in the case of MV^{2+}, the reaction occurs slowly. As this takes place, the typical absorption band of silver sols in the optical spectrum (Fig. 6) becomes more intense and narrows down, while the absorption maximum shifts from 420 to 390 nm. Electron microscopy studies showed that the smallest nickel particles are the first to disappear, while larger particles are shown to form mixed aggregates, which are contact pairs containing both silver and nickel (see Fig. 1, *c*). The displacement of the absorption band of colloidal silver at an initial stage of its formation in the reaction of nickel sols with silver ions may be due to the formation of silver—nickel aggregates. In these aggregates free electrons are shifted from silver to nickel to induce displacement of the absorption band to longer wavelengths with respect to that in "pure" silver sols. Similar optical effects are observed upon adsorption of some compounds or metal ions on the surface of silver particles, which also change the electron density and shift the Fermi level.[10,11] The content of silver—nickel aggregates decreases with time and the yielded sols, which consist only of silver, are responsible for the band with a maximum at 390 nm. Methods for the synthesis of bi- and polymetallic particles have been developed previously.[11—13] These particles have an onion-type structure in which a core formed by a single metal is coated by layers of less noble metals. The solution contains only metal ions that constitute the "mantle" of this particle. In this particular case, the particle consists of two metals having a common contact boundary. The standard potentials of the metals forming this electrochemical contact pair are substantially different (recall that $E^0(Ni^{2+}/Ni_{solid})$ = -0.25 V and $E^0(Ag^+/Ag_{solid})$ = 0.799 V) and the solution contains plenty of both metal

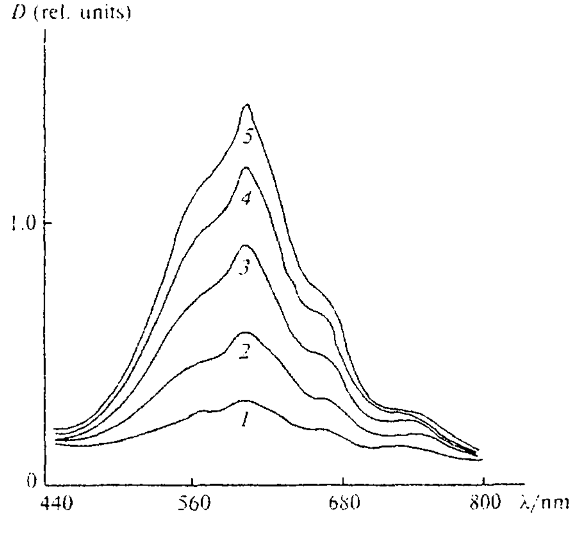

Fig. 5. Appearance of the absorption of the $MV^{\cdot +}$ radical cations after addition of methylviologen MV^{2+} to a solution containing $1 \cdot 10^{-4}$ mol L^{-1} of $Ni(ClO_4)_2$, $5 \cdot 10^{-3}$ mol L^{-1} of HCOONa, and $2 \cdot 10^{-4}$ mol L^{-1} of polyacrylate γ-irradiated for 60 min, after 2 (*1*), 5 (*2*), 20 (*3*), 60 (*4*), and 120 (*5*) min. For irradiation conditions, see Fig. 2.

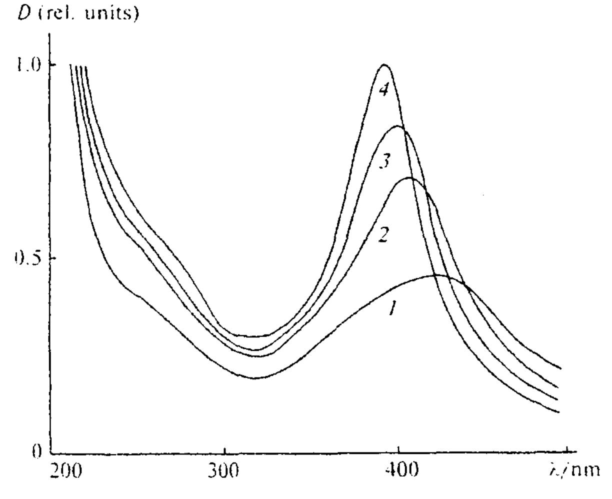

Fig. 6. Appearance of the absorption of silver sols after addition of $5 \cdot 10^{-4}$ mol L^{-1} of $AgClO_4$ to a solution of colloidal nickel after 2 (*1*), 15 (*2*), 30 (*3*), and 120 min (*4*). The colloidal nickel was prepared by γ-irradiation for 60 min of a solution containing $1 \cdot 10^{-4}$ mol L^{-1} of $Ni(ClO_4)_2$, $5 \cdot 10^{-3}$ mol L^{-1} of HCOONa, and $2 \cdot 10^{-4}$ mol L^{-1} of polyacrylate. For irradiation conditions, see Fig. 2.

ions. To the best of our knowledge, this is the first experimental detection of such an ultrasmall mixed metal particle, which is thermodynamically unstable but, nonetheless, has a fairly long lifetime in aqueous solutions.

Mechanism of radiation-induced chemical reduction of Ni^{2+} ions and the formation of metal nanoparticles. Figure 7 shows the variation of the concentration of colloidal nickel formed upon γ-irradiation of aqueous solutions of $Ni(ClO_4)_2$ containing formate ions as a function of the irradiation time (absorbed dose). The concentration was determined by the optical method from the known extinction coefficient of nickel sols and was also measured analytically using the reaction of the sols with MV^{2+}. It was found that in the presence of HCOONa and a stabilizer, the intensity of the optical band of nickel sols increases with an increase in the absorbed dose and the concentrations of the reduced metal found in two independent measurements are virtually equal. The nature of the stabilizer used almost does not influence the sol-formation process. In the initial accumulation section, the plot is linear. The calculated radiation yield is ~2.1±0.2 Ni atoms per 100 eV of absorbed energy, which implies reduction of Ni^{2+} ions with 4.2±0.4 reducing species, either hydrated electrons or $CO_2^{\cdot -}$ radical anions, whose total yield is 6.1. The difference between these yields is apparently due to the fact that some of the Ni atoms formed are oxidized again with H_2O_2, which also arises upon radiolysis of water and aqueous solutions. If Ni^{2+} ions accept all the reduced radicals and nickel re-oxidation involves H_2O_2, it should be expected that $G(Ni^0) = 0.5[G(e_{aq}^-) + G(^{\cdot}OH) + G(H^{\cdot}) - 2G(H_2O_2)] \approx 2.4$ Ni atoms per 100 eV. The yield found in experiments is close to the expected value. An increase in the content of nickel ions in the solution from $1 \cdot 10^{-4}$ mol L^{-1} to $5 \cdot 10^{-3}$ mol L^{-1} has no significant influence on the $G(Ni^0)$ value found from the initial section of the plot for the concentration *vs* irradiation dose. Thus the presence of even $1 \cdot 10^{-4}$ mol L^{-1} of Ni^{2+} ions is sufficient for virtually complete trapping of the hydrated electrons or $CO_2^{\cdot -}$ radical anions resulting from γ-irradiation. The proportion of these radicals participating in the reduction decreases with an increase in the dose, which is due to the decrease in the concentration of Ni^{2+} ions in the solution and to the prevalence of other reactions resulting in the consumption of radicals (*e.g.*, recombination). The steady state, which corresponds to almost complete reduction of $1 \cdot 10^{-4}$ mol L^{-1} of Ni^{2+} in a solution, is attained for an absorbed dose equal to ~$6 \cdot 10^{-4}$ mol L^{-1} (e_{aq}^- + $CO_2^{\cdot -}$), *i.e.*, for a dose ~3 times as great as that required by stoichiometry if e_{aq}^- and $CO_2^{\cdot -}$ are regarded as single-electron reducing agents for the Ni^{2+} ions. Further increase in the absorbed dose by a large factor does not cause a noticeable change in the absorption spectra or in the stability of nickel sols.

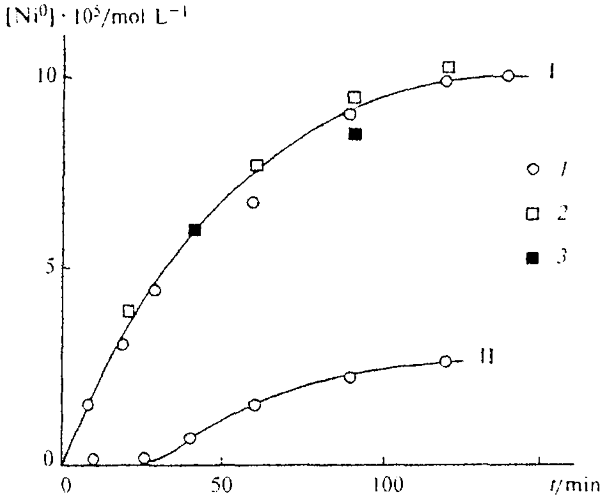

Fig. 7. Variation of the concentration of reduced nickel *vs.* time of γ-irradiation of a $1 \cdot 10^{-4}$ mol · L^{-1} solution of $Ni(ClO_4)_2$ containing $2 \cdot 10^{-4}$ mol · L^{-1} of a stabilizer ((*1*) polyethyleneimine, (*2*) polyacrylate, and (*3*) polyvinyl alcohol) and $5 \cdot 10^{-3}$ mol · L^{-1} of HCOONa (I) or 0.1 mol · L^{-1} of Pr^iOH (II). For irradiation conditions, see Fig. 2.

The reduction of nickel in aqueous solutions containing Pr^iOH instead of formate ions occurs in a different way. As can be seen in Fig. 7, the formation of the metal is preceded by a long induction period and the subsequent accumulation occurs much more slowly. These specific features of the reduction process may point to an autocatalytic mechanism of reduction of the metal ions, which has been established and studied in our previous work for cobalt ions.[14] According to this mechanism, metal particles accelerate those reduction reactions that cannot proceed in the solution bulk for thermodynamic reasons. This mechanism, as applied to the reduction of Ni^{2+} ions in solutions containing Pr^iOH, is discussed in detail below.

A specific feature of the radiation-chemical reduction of Ni^{2+} ions is the stepwise course of the process, whose first step affords unstable, short-lived Ni^+ ions. To understand the mechanism of reduction of Ni^{2+} ions to the metal, it is necessary to know the potentials of the Ni^{2+}/Ni^+ and Ni^+/Ni^0 pairs. The standard potential of the former pair was calculated theoretically to be −2.7 V.[15] This value is confirmed by the fact that Ni^{2+} ions can be reduced only by hydrated electrons ($E^0 = -2.9$ V), not by H atoms ($E^0 = -2.4$ V) or $CO_2^{\cdot -}$ radical anions ($E^0 = -1.9$ V).[16,17] The potential of the Ni^+/Ni^0 pair can be calculated from the equation

$$E^0(Ni^+/Ni^0) = 2E^0(Ni^{2+}/Ni^0) - E^0(Ni^{2+}/Ni^+).$$

It is equal to −1.7 V.

Thus, the Ni^{2+} ions are reduced only *via* the reaction

$$e_{aq}^- + Ni^{2+} \longrightarrow Ni^+, \qquad (4)$$

the rate constant for which is very high ($1.6 \cdot 10^{10}$ L mol^{-1} s^{-1}).[18]

The rate of consumption of Ni^+ ions is known[16] to follow second-order kinetics. The following reactions can be suggested:

$$Ni^+ + Ni^+ \longrightarrow Ni^0 + Ni^{2+}, \qquad (5)$$

$$CO_2^{\cdot -} + Ni^+ \longrightarrow Ni^0 + CO_2. \qquad (6)$$

Indeed, disproportionation of Ni^+ ions and the reaction of Ni^+ ions with the $CO_2^{\cdot -}$ radical anions are thermodynamically favorable. However, the yield of Ni atoms close to the limiting value indicates that virtually all the hydrated electrons and $CO_2^{\cdot -}$ radical anions are consumed to reduce Ni^{2+} ions. This, in turn, implies that the reaction of $CO_2^{\cdot -}$ with Ni^+ is preferred. With a rate constant of $6.6 \cdot 10^9$ L mol^{-1} s^{-1},[16] it provides high efficiency of reduction of nickel ions in aqueous solutions in the presence of formate ions.

The standard potential of the $Me_2C^{\cdot}OH$ radical (-1.4 V)[4] is insufficient for reduction of not only Ni^{2+} but also Ni^+ ions. Unlike the $CO_2^{\cdot -}$ radical anion, the $Me_2C^{\cdot}OH$ radical oxidizes Ni^+ ions *via* the intermediate formation of an organonickel complex[16]:

$$Me_2C^{\cdot}OH + Ni^+ \longrightarrow [Me_2COH \cdot Ni]^{\cdot +}, \qquad (7)$$

$$[Me_2COH \cdot Ni]^{\cdot +} + H_2O \longrightarrow$$
$$\longrightarrow Me_2CHOH + Ni^{2+} + OH^-. \qquad (8)$$

The rate constant for the former reaction, according to the data published previously,[16] is $1.3 \cdot 10^9$ L mol^{-1} s^{-1}, while the subsequent hydrolysis takes place over a period of 1 s. Thus, the presence of Pr^{i}OH does not facilitate the reduction of Ni^{2+} ions; however, prolonged irradiation gives rise to metal particles, which then catalyze the reduction of Ni^{2+} ions by the autocatalytic mechanism. The metal particles may arise in the disproportionation of the Ni^+ ions, resulting from the reduction of Ni^{2+} ions by hydrated electrons. The catalytic action of these metal particles, which act as seeds for the reduction, is due to an electrochemical mechanism involving the transfer of electrons from the reducing radical to the metal sol. As a consequence, the metal sol is charged to a potential required for the reduction to occur. This process can be conventionally represented as follows:

$$(Ni)_n + 2m\,(Me_2C^{\cdot}OH) \longrightarrow$$
$$\longrightarrow (Ni)_n^{2m-} + 2m\,Me_2CO + 2m\,H^+, \qquad (9)$$

$$(Ni)_n^{2m-} + m\,Ni^{2+} \longrightarrow (Ni)_{n+m}. \qquad (10)$$

The nature of the intermediate species preceding the formation of colloidal nickel is unknown. However, the generality of this type of processes for metals[19] suggests the intermediate formation of clusters of different complexity, which coalesce to give ultimately nickel sols. The successive growth of clusters is accompanied by a decrease in their chemical potential, which makes nickel nucleation thermodynamically favorable. The intermediate short-lived nickel clusters are not detected by pulse radiolysis,[16] due either to absorption in the UV region or to a low extinction coefficient.

Radiation stability of nickel nanoparticles in aqueous solutions. In aqueous solutions containing stabilizers, nickel sols exhibit high stability against ionizing radiation. An absorbed dose exceeding that required for the complete reduction of Ni^{2+} ions in solution at least tenfold does not induce coagulation of the sols. However, in the absence of stabilizers, nickel sols are unstable. It was found that in a $1 \cdot 10^{-4}$ mol L^{-1} solution of Ni^{2+} ions (containing HCOONa to trap $^{\cdot}OH$ radicals and H atoms), the initial part of the dose accumulation curve for nickel sols coincides with the corresponding part of the curve for the same solution containing a stabilizer. However, in the region of large absorbed doses corresponding to the formation of approximately $6 \cdot 10^{-4}$ mol L^{-1} of ($e_{aq}^- + CO_2^{\cdot -}$), fast coagulation of metal sols starts. This can also be recognized in a noticeable change in their absorption spectrum, which points to enlargement and coalecence of particles. The spectrum is markedly broadened; its intensity in the UV region decreases, while that in the visible region increases. Determination of nickel concentration using MV^{2+} shows that this dose is sufficient for the complete reduction of Ni^{2+} ions. Previously,[20] we studied the influence of ionizing radiation (accelerated electrons and ^{60}Co γ-rays) on the stability of colloidal solutions of some metals (Ag, Cd, Co, *etc.*). In the absence of stabilizers, the stability is determined by the electrostatic factor, which ensures a decrease in the surface tension due to the formation of the double electric layer on the surface particles. The critical dose for the stability of nickel sols corresponds to the reduction of the Ni^{2+} ions adsorbed thereon, which determine their electric potential. The double electric layer is destroyed and the stability is thus lost. The "radiation" coagulation is similar to the neutralization coagulation known in colloidal chemistry, which is related to the absorption of ions whose charge has the same sign as that of the counterions of the double electric layer. Having entered the adsorption layer, these ions sharply decrease the electric potential, which results in a loss of stability by the colloidal system. A specific feature of "radiation" neutralization is that the decrease in the potential of the nickel sol is caused by the delivery of the electrons generated by ionizing radiation.

In the presence of stabilizers, solvation layers are formed on the surface of colloids. When particles approach one another, these layers overlap, and the osmotic pressure increases; hence, the repulsion pressure also increases, thus decreasing the ability of systems to coagulate. In this case, the double electric layer does not play a crucial role. This accounts for the observed difference between the radiation stabilities of nickel sols with and without stabilizers.

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