Absorption spectra of large colloidal silver particles in aqueous solution

N. L. Sukhov,* N. B. Ershov, V. K. Mikhalko, and A. V. Gordeev

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: 007 (095) 952 7414. E-mail: ershov@redline.ru

Calculations of the optical absorption spectra of spherical particles of silver with a radius (r) of 10 to 80 nm in water were performed. The single intense absorption band for small particles (r = 10 nm) with a maximum at about 395 nm is gradually broadened and shifted to the long-wave region with an increase in the particle size (to 435 nm at r = 40 nm). In the case of large particles, the band splits into several components absorbing light in the visible spectral region. The results are in good agreement with the optical characteristics of colloidal solutions of silver obtained upon radiochemical reduction of Ag^+ ions in aqueous solution.

Key words: light, absorption; silver, colloids, size of particles, theoretical calculations; Ag^+ ions, reduction, aqueous solution.

Light absorption by metallic particles is described by the Mie theory.[1] The optical spectra are calculated using the dependence of the complex dielectric constant of the metal and the medium on the wavelength. In the case of a sphere of arbitrary size, the theory gives the following expression for the extinction coefficient (C)[2]:

$$C = \lambda^2/(2\pi)\sum_{n=1}^{\infty}(2n + 1)Re\{a_n + b_n\}, \qquad (1)$$

where λ is the wavelength, Re is the real part of the complex values a_n and b_n which are the coefficients obtained on solution of the scalar wave equation and are expressed *via* Bessel functions. The arguments of the Bessel functions are $x = 2\pi r/\lambda$ (r is the radius of the sphere) and m (the complex refractive index of the metal).

In most works on calculations of the absorption spectra of colloidal particles of various metals (see, for instance, Ref. 3) only the simplest case is considered: the particles are spherical, their radii are appreciably smaller than the light wavelength ($2\pi r \ll \lambda$), and the distance between the particles is large. The latter condition implies single light scattering on the particle. With these requirements in mind, it is sufficient to use merely the first term of the expansion in Eq. (1) (n = 1). Such calculations are only valid for particles with r < 10 nm. However, good agreement with the experiment is only observed if the effect of the particle size on the dielectric constant of the metal is taken into account. This is associated with the fact that if the particle size is smaller than the mean free path of the electron (for instance, 52 nm for Ag), the absorption band is significantly broadened. Therefore, in accordance with the published data[4] one should use corrected values of the dielectric constant. The absorption spectra of numerous metals both *in vacuo* and in water were calculated previously.[3] In particular, an intense absorption band with a maximum at about 390 nm, due to the interaction between light and surface plasmons of the metal, is observed for silver particles. The calculation for the spectra of ellipsoids of revolution[3,5] shows that this absorption band is split. For prolate particles in aqueous medium with $r_a/(r_b = r_c)$ equal to 1.5, 2.0, and 3.0, the maximum of the band in the long-wave region is shifted to 430, 480, and 590 nm, respectively.[3] On the contrary, the main band in the UV region is only insignificantly (by 10—20 nm) shifted to the short-wave region. Analogous calculations, previously performed for silver sols in gelatin,[5] appear to be in good agreement with the experimental data.

In this work, the absorption spectra of large spherical silver particles in water were calculated and compared with the spectra of nanoaggregates generated in the course of radiochemical reduction of Ag^+ ions in aqueous solutions. The values of the complex dielectric constant for silver were taken from Ref. 5. The complexity of analogous calculations is determined by the necessity of taking into account a larger number of expansion terms in Eq. (1) with an increase in the particle size and calculations of the Bessel functions of the complex argument. Therefore, a special program for numerical calculations on a personal computer was developed.

Experimental

Silver perchlorates of "high purity" grade were used. The solutions were prepared in distilled water and saturated with argon before irradiation. Reduction of the metal ions in aqueous solution was carried out by a radiolytic procedure.[6] γ-Irradiation was performed with a ^{60}Co source. The optical

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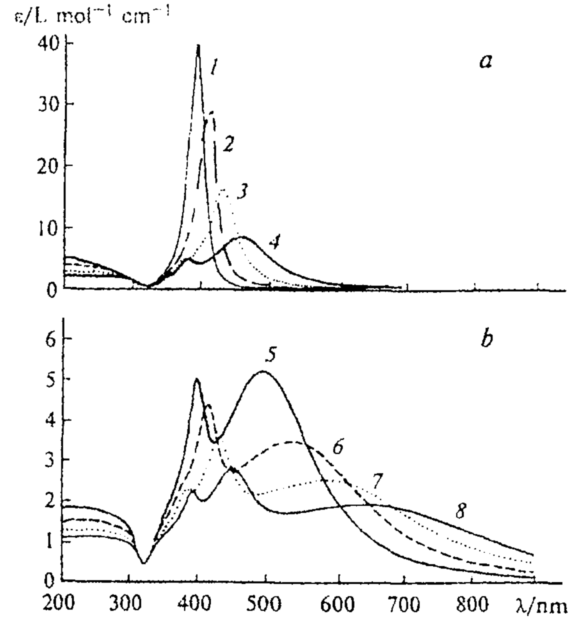

Fig. 1. Calculated optical absorption spectra of spherical silver particles of various size (*r*) in water: *r*/nm = 10 (*1*), 20 (*2*), 30 (*3*), 40 (*4*), 50 (*5*), 60 (*6*), 70 (*7*), and 80 (*8*).

absorption spectra were recorded 5 min after irradiation. The specimens for the electron microscopic studies were prepared by placing a drop of the analyzed solution on a copper-carbon plate under argon atmosphere. The measurements were carried out on a Phillips CM12 electron microscope equipped with an EDAX 9800 analyzer.

Results and Discussion

We used the number of expansion terms in Eq. (1) used in calculating the optical absorption spectra of spherical silver particles with a radius of 10 to 80 nm in water so that an accuracy of 0.5% was obtained (Fig. 1). In the case of a sphere with r = 20 nm, it took place when the number of terms in the expansion was equal to three, whereas for r = 80 nm the number of terms was equal to six. For particles of small size (10—30 nm), a single intense absorption band with the maximum gradually shifted from ~395 to ~435 nm is observed. The extinction coefficient ($\varepsilon = 4 \cdot 10^4$ L mol^{-1} cm^{-1}) obtained in calculations of particles with r = 10 nm is in good agreement with the value $3 \cdot 10^4$ L mol^{-1} cm^{-1} measured in experiments[7] on nearly monodisperse spherical silver sols (r = 7 nm). The absorption band splits with a further increase in the particle size, while its components are shifted to the long-wave region. Overall broadening of the spectrum and a decrease in the extinction coefficient at the maximum of the absorption bands also occur. The presence of several absorption bands for large spherical particles is caused by periodic minimization of Eq. (1).

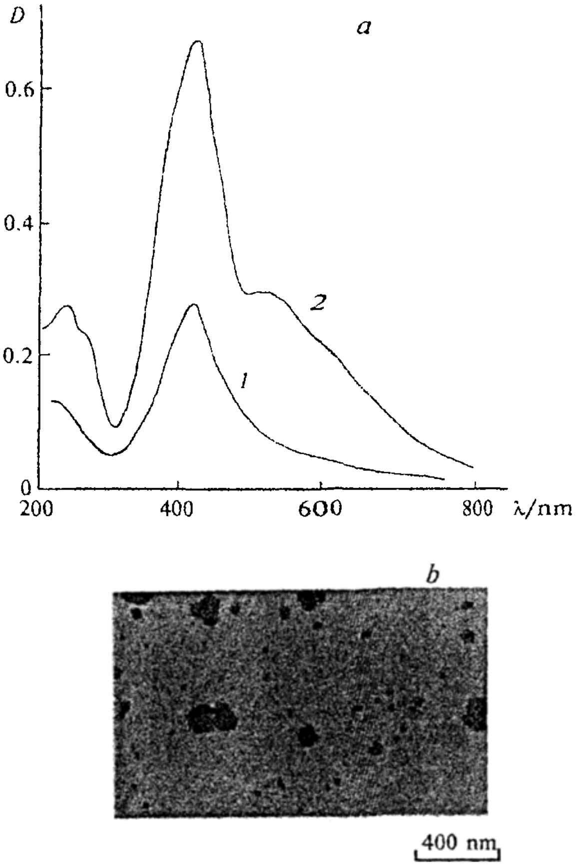

Fig. 2. *a*. Optical absorption spectra of silver particles in solution ($1 \cdot 10^{-4}$ mol L^{-1} AgClO$_4$, 0.1 mol L^{-1} Pr^{i}OH, saturated by argon) after γ-irradiation: absorbed dose is 0.04 (*1*) and 0.2 (*2*) kGy.
b. Photomicrograph of silver particles (the solution and the absorbed dose are the same as in Fig. 2, *a*, spectrum *2*).

The optical absorption spectra of the colloidal silver obtained by γ-irradiation of an aqueous solution of AgClO$_4$ ($1 \cdot 10^{-4}$ mol L^{-1}) containing 0.1 mol L^{-1} of isopropyl alcohol are shown in Fig. 2, *a*. In the initial stage of radiochemical reduction (~20% reduced Ag$^+$ ions), one smooth optical absorption band with a maximum at 420 nm is observed (spectrum *1*). As shown by electron microscopic studies, spherical particles with a radius of 20—30 nm are predominant. For a deeper reduction (~90% reduced Ag$^+$ ions) an additional shoulder appears at ~550 nm (spectrum *2*). The data from electron microscopic analysis of arising particles are evidence of their increasing size and an essential increase in the fraction of approximately spherical particles with r = 40—60 nm (Fig. 2, *b*). Unfortunately, we failed to obtain particles having a narrow size distribution. A comparison of the experimental spectrum with the theoretical one for silver particles of different size allows one to consider it as a spectrum consisting of two absorption spectra for particles with a radius of

20—30 nm (~40 wt.%) and 40—60 nm (~60 wt.%), respectively. Such a conclusion is in good agreement with the data from microscopic studies.

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Ring expansion of 4,4-diethyl-1,2-dithiolane in the reaction with butylacetylene. Involvement of anion and radical intermediates

D. V. Demchuk and G. I. Nikishin*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: 007 (095) 135 5328. E-mail: demchuk@ioc.ac.ru

The action of lithium butyl acetylenide in THF causes 4,4-diethyl-1,2-dithiolane to undergo ring-opening to form 2,2-diethyl-4-thia-5-decyne-1-thiol, which cyclizes to give 2-butyl-6,6-diethyl-5,6-dihydro-1,4-dithiepin by either a homolytic or a nucleophilic mechanism.

Key words: 4,4-diethyl-1,2-dithiolane, ring opening; 2,2-diethyl-4-thia-5-decyne-1-thiol, homolytic or nucleophilic cyclization; 2-butyl-6,6-diethyl-5,6-dihydro-1,4-dithiepin.

The high reactivity of the disulfide bond both in open and cyclic systems in reactions with nucleophilic, electrophilic, and radical reagents is widely used for the synthesis of functionally substituted sulfides.[1] It is well known that 1,2-dithiolanes undergo ring opening to form 3-alkylthio-substituted propanethiols when they are reacted with nucleophilic agents such as either Grignard reagents[2] or organolithium compounds.[3] When acetylenide anions generated from terminal acetylenes react with 1,2-dithiolanes in *tert*-butyl alcohol in the presence of catalytic amounts of $\mathrm{Bu^tOK}$, 2-substituted 5,6-dihydro-1,4-dithiepins are formed directly.[4]

In a continuation of studies concerning the application of homolytic methods to the synthesis of sulfur-containing rings and thiacrown-ethers[5] and, in order to develop novel approaches to the construction of sulfur-containing rings, we studied the reaction of a five-membered cyclic disulfide, 4,4-diethyl-1,2-dithiolane (**1**), with butylacetylene. This reaction involves cleavage of the S—S bond and the intermediate formation of 2,2-diethyl-4-thia-5-decyne-1-thiol (**2**) followed by its cyclization with the C≡C moiety included in the ring.

Dithiolane **1** readily interacts with lithium butyl acetylenide obtained by the reaction of BuLi with butylacetylene in a THF—hexane mixture (Scheme 1). Ring opening with acetylenide anion rapidly occurs at temperatures below 0 °C to give a solution of 3-alkynylthiopropanethiol lithium salt **4**. Decolorization of the reaction mixture, which was yellow initially, indicates that the reaction is completed.

Acidification of the reaction mixture at this instant makes it possible to obtain thiol **2**, which has not been reported earlier. This fact is confirmed by the ^{1}H NMR spectra recorded just after the treatment of the mixture. In the spectrum of a solution of thiol **2** in $CDCl_3$ there are signals of two nonequivalent CH_2S groups at 2.57 and 2.81 ppm, and one of these signals is a doublet as a result of coupling with the adjacent SH group. We also observed a triplet at 1.25 ppm assigned to the proton bound to sulfur. The attempts to isolate pure thiol **2** failed: in all cases the thiol contained 2-butyl-6,6-diethyl-5,6-dihydro-1,4-dithiepin (**3**) (5—20%), which is the product of intramolecular cyclization (see Scheme 1). When this solution was kept for

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