

## **Influence of negative charge on the optical properties of a silver sol**

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The effects of negative charge on the optical properties of a silver sol prepared using sodium borohydride as a reductant were studied. The oscillations in the position of the maximum and the intensity of the surface plasmon absorption band were observed. The observed effects were explained as a consequence of the fluctuation of the density of free electrons due to the alternate charging and discharging of the silver particles. The charging process involves electron injection from borohydride ions and intermediate species formed during the course of the metal-catalyzed hydrolysis of borohydride ions ( $\text{BH}_3\text{OH}^-$ ,  $\text{BH}_2(\text{OH})_2^-$  and  $\text{BH}(\text{OH})_3^-$ ) into the silver particles, while discharge of the silver sol, by reduction of water to hydrogen, limits the attainable negative charge on the particles.

**Keywords:** silver sol, sodium borohydride, surface plasmon, electron transfer.

### INTRODUCTION

Recently, the investigation of nanometer-scale metal particles in solution has attracted the attention of many researchers.<sup>1,2</sup> Although many of the optical effects associated with nanosized metal particles are now reasonably well understood, there are large discrepancies between the optical properties of metal sols prepared in water, particularly those of silver, and sols in other matrices.<sup>3-10</sup> The experimentally measured positions of the surface plasmon absorption band of silver sols vary enormously (ranging from 375 to 405 nm) and the absorption coefficient vary by factor of 3 or 4.<sup>3-14</sup> Recently, Mulvaney<sup>2</sup> estimated that an uncharged silver colloid should have a maximum at  $382 \pm 1$  nm; wavelengths shorter than this are due to cathodic polarization, and longer wavelength are due to incomplete reduction of silver ions. Blue shifted spectra were found when the preparation utilized a strong reductant (borohydride), or when strong reducing conditions were achieved with  $\gamma$ -irradiation, and, also, in spectroelectrochemical experiments.<sup>15</sup> The first attempts to quantify the effects of change in the electron density in the particles on the optical properties of colloidal metals were those of Blatchford and coworkers.<sup>11,12</sup> They pointed out that the spectrum of colloidal silver prepared with citrate could be drastically altered by addition of borohydride ions. The band was blue shifted and increased in intensity by a factor of 50 %.

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In the present study, the oscillatory behavior of the absorption spectrum of a silver sol prepared without stabilizer and using sodium borohydride as the reductant is described. The position of the absorption maximum oscillated in the range from 375 to 385 nm as a function of the aging time, while changes of the extinction coefficient were up to 20 %.

#### EXPERIMENTAL

All reagents were commercial products of the highest purity available. Solutions were prepared with triply distilled water. Oxygen was removed by bubbling with argon.

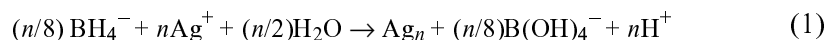
Spectrophotometric measurements of the colloidal solutions were carried out on a Perkin-Elmer Lambda 5 UV-vis spectrophotometer.

##### *Preparation of silver sols by using NaBH<sub>4</sub> as the reducing agent*

Silver sols were prepared by the reduction of silver ions using NaBH<sub>4</sub>, as described elsewhere.<sup>16,17</sup> Briefly, a 10 mg sample of NaBH<sub>4</sub> was added to 100 mL of a vigorously mixed Ar-saturated solution of  $5 \times 10^{-5}$  M Ag<sub>2</sub>SO<sub>4</sub>. A clear yellow sol resulted. The pH increased due to the hydrolysis of excess NaBH<sub>4</sub> and after several tens of minutes reached 9.8

#### RESULTS AND DISCUSSION

The addition of sodium borohydride (NaBH<sub>4</sub>) to a deaerated solution of silver sulfate containing no stabilizers led to the complete reduction of the silver ions, and the yellow color of colloidal silver appeared, Eq. (1):



The initial pH of the solution increased to 9.8 upon addition of NaBH<sub>4</sub> due to the hydrolysis of excess NaBH<sub>4</sub>. The homogeneous hydrolysis of BH<sub>4</sub><sup>-</sup> can be described by Eq. (2).

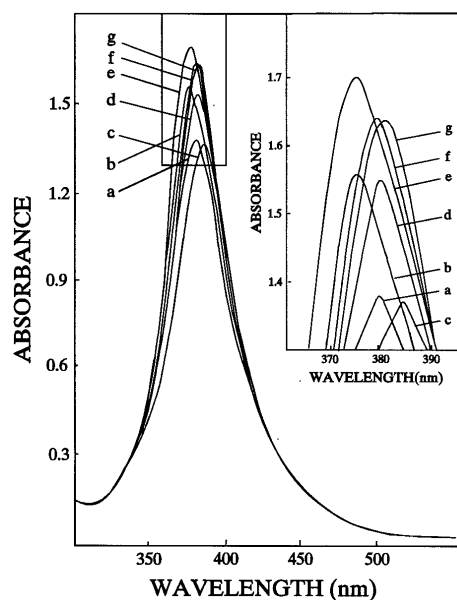
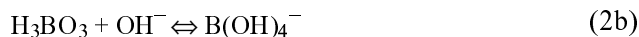
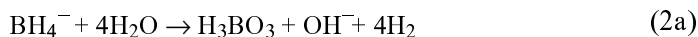
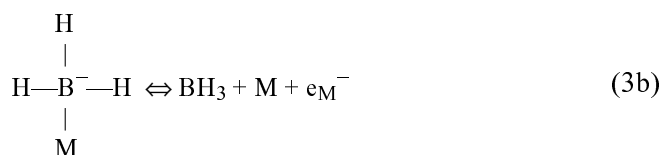
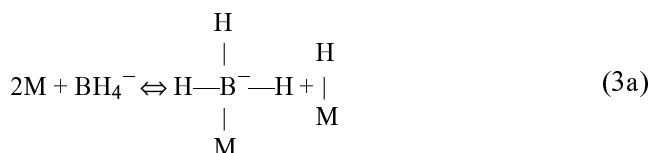


Fig. 1. Absorption spectrum of a  $1 \times 10^{-4}$  M silver sol obtained after addition of NaBH<sub>4</sub> (10 mg/100 mL) into  $5 \times 10^{-5}$  M Ag<sub>2</sub>SO<sub>4</sub> as a function of aging time: a) 5 min; b) 10 min; c) 15 min; d) 30 min; e) 60 min; f) 90 min; g) 120 min.



Typical changes of the absorption spectrum of the silver sol as a function of aging time are shown in Fig. 1. Although repeated experiments did not give exactly the same spectra with time, the characteristic oscillations in the position of the absorption maximum and its intensity were always present. In order to avoid any possibility for reversible formation and dissolution of silver particles,<sup>18</sup> special care was taken to perform the experiments in the complete absence of oxygen.

We believe that the observed optical effects during the aging of the silver sol are a consequence of metal-catalyzed hydrolysis of the borohydride ions, which proceeds concurrently with homogeneous hydrolysis. The kinetics of the metal-catalyzed hydrolysis of borohydride ions were studied by Holbrook and Twist<sup>19</sup> and recently by Kaufman and Sen.<sup>20</sup> The mechanism proposed by Holbrook and Twist is given by Eq (3):



Step (3a) represents the reversible dissociative chemisorption of the borohydride ion. Step (3b) expresses the tendency of the charge associated with the species  $\text{MBH}_3^-$  to be associated with the metal. Step (3c) is the rapid reaction of a borine molecule with a hydroxyl ion to give the relatively stable intermediate  $\text{BH}_3\text{OH}^-$ . If this species is of a similar reactivity to the borohydride ion, then it can undergo reaction steps (3a), (3b), and (3c) to produce  $\text{BH}_2(\text{OH})_2^-$  which can further react to give  $\text{BH}(\text{OH})_3^-$  and finally  $\text{B}(\text{OH})_4^-$ . It is important to notice that during the course of the metal-catalyzed hydrolysis of borohydride ions association of negative charges with the metallic silver particles takes place (step 3b). It is well-known that colloidal silver particles can store several hundreds of electrons,<sup>7</sup> and step (3b) represents negative charging of silver particles or cathodic polarization. On the other hand, discharge of the sol, by reduction of water to hydrogen, limits the attainable negative charge on the particles, Eq. (4):



It is clear that the upper limit of the cathodic polarization of the silver particles lies around  $-0.4$  V NHE where hydrogen evolution begins.

The transfer of electrons between the silver particles and the solution, and *vice versa*, alters the density of free electrons. The wavelength of the maximum absorption can be described by Eq. (5):<sup>21</sup>

$$\lambda_{\max}^2 = (2\pi c)^2 m_e (\epsilon_0 + 2n_0^2) / 4\pi N_e e^2 \quad (5)$$

where  $m_e$  is the effective electron mass,  $\epsilon_0$  is the wavelength independent high-frequency dielectric constant of the metal,  $n_0$  is the refractive index of the solvent and  $N_e$  is the density of free electrons. It is clear that fluctuation of the density of free electrons due to alternate charging and discharging of the silver particles is responsible for the oscillation of the position of the absorption maximum. Our results are in agreement with results obtained by Henglein and coworkers.<sup>22</sup> These authors presented direct evidence that exposure of a silver sol to a microsecond pulse of electrons from a Van de Graaff generator that produces  $(\text{CH}_3)_2\text{COH}$  radicals and consequent electron injection into the silver particles is followed with a blue shift of the surface plasmon absorption band.

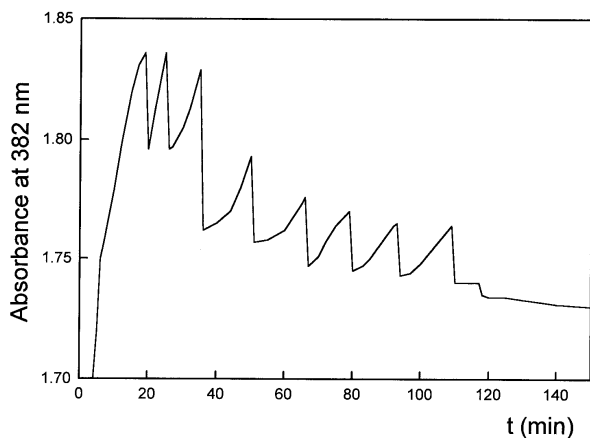


Fig. 2. Dependence of the 382 nm absorbance on aging time for a  $1 \times 10^{-4}$  M silver sol.

The oscillatory behavior of the extinction coefficient as a function of aging time is demonstrated in Fig. 2. Since the dependence of the extinction coefficient on the density of free electrons is rather complicated, it is more useful to analyze the relationship between the bandwidth at half-maximum absorption ( $w$ ) and the density of free electrons ( $N_e$ ), Eq. (6):<sup>21</sup>

$$w = (\epsilon_0 + 2n_0^2) c m_e v_F / 2N_e e^2 R \quad (6)$$

where  $v_F$  is the electron velocity at the Fermi level and  $R$  is the mean free path of the electron in the colloid. An increase in the density of free electrons leads to a decrease in the bandwidth, and, consequently, to an increase in the extinction maximum. As a result of this, the increase of the extinction coefficient can be attributed to the negative charging of the silver particles and the increase of the density of free electrons, while a sudden decrease of the extinction coefficient occurs

when a sufficient accumulation of electrons has take place to initiate the reduction of solvent, and the consequential decrease of the density of free electrons. Also, the damping of the oscillations can be observed in Fig. 2, as well as the complete disappearance of the oscillatory behavior after a sufficiently long time when the  $\text{BH}_4^-$  ions have been completely consumed in the hydrolysis reaction.

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## ИЗВОД

### УТИЦАЈ НЕГАТИВНОГ НАЕЛЕКТРИСАЊА НА ОПТИЧКЕ ОСОБИНЕ СОЛА СРЕБРА

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Изучавани су ефекти негативног наелектрисања на оптичке особине сола сребра припремљеног коришћењем натријум-борхидрида као редукционог средства. Примењене су осцилације положаја максимума и интензитета апсорпционе траке површинског плазмона. Ови ефекти су објашњени флукуацијом густине слободног електронског гаса услед наизменичног наелектрисавања и разелектрисавања честица сребра. Процес наелектрисавања се одвија преносом електрона са борхидридних јона и интермедијера насталих током металом катализоване хидролизе борхидридних јона ( $\text{BH}_3\text{OH}^-$ ,  $\text{BH}_2(\text{OH})_2^-$ ,  $\text{BH}(\text{OH})_3^-$ ) на честице сребра, док разелектрисавање сола сребра редукцијом воде до водоника ограничава присуство негативног наелектрисања на честицама.

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