

Electrochemistry of Colloidal Silver Particles in Aqueous Solution: Deposition of Lead and Indium and Accompanying Optical Effects

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Colloidal silver particles (ca. 8 nm in diameter) act as microelectrodes in aqueous solution. They are charged via electron transfer from free radicals which are generated radiolytically. The stored electrons reduce adsorbed Pb^{2+} and In^{3+} ions. — The first monolayer of lead atoms deposited on the silver particles does not absorb at 215 nm where metallic lead has an absorption band. The Pb atoms cause the 380 nm surface plasmon band of the silver particles to be shifted to shorter wavelengths. This is explained in terms of electron donation from chemisorbed Pb atoms to the silver carrier. The Pb atoms of a submonolayer (which are formed by “under-potential” deposition) do not react with methyl viologen, MV^{2+} , whereas the lead atoms deposited in subsequent layers (“Nernst potential” deposition) are readily oxidized by MV^{2+} . The absorption spectrum of colloidal lead in water is also discussed ($\epsilon_{\text{max}} = 3.2 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 215 nm). — Reduction of In^{3+} on the silver particles also leads to a blue-shift of the plasmon band. It is attributed to electron transfer from deposited In atoms. However, as In metal deposition proceeds, In^+ is produced by the disproportionation of the indium metal with In^{3+} . When almost all the In^{3+} ions have been reduced, indium metal is further deposited by In^+ reduction. Silver particles carrying a tight indium shell absorb at 225 nm with $\epsilon = 3.8 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. This ϵ -value is somewhat lower than the calculated one, and attributed to a reduction in mean free path for conduction electrons in small In colloids.

Introduction

Colloidal silver particles in aqueous solution can be used as “microelectrodes” in electrochemical experiments [1,2]. These microelectrodes cannot be connected by a wire to an outer potential source to establish a desired interfacial potential. However, the Fermi level in these particles can be changed in a controlled manner by deposition of excess electrons or injection of positive holes into the particles via reducing or oxidizing free radicals. The radicals are generated radiolytically or photolytically in silver solutions containing an additive in low concentration, the radiation chemistry or photochemistry of which is known. For example, when 1-hydroxy ethylmethyl radicals, $(\text{CH}_3)_2\text{C}(\text{OH})$, are generated in solutions containing propanol-2, electrons are transferred to the silver particles, and each particle can store up to several hundred electrons. The stored electrons can initiate multielectron reduction of solutes or of the aqueous solvent; for example, hydrogen is produced from water by 1-hydroxy alkyl radicals in the presence of silver particles [2a].

In our more recent studies, the changes in the electronic properties and the accompanying optical properties following the chemisorption of anions were investigated [3]. It was shown that adsorption of nucleophilic solutes is accompanied by a shift of the Fermi level to a more negative potential, the result being an increased reactivity of the metal particles towards electron acceptors. The adsorption-desorption equilibrium can be shifted by storing excess electrons on the particles. It has also been shown that modifi-

cation of the surface by chemisorbed molecules can lead to photoactive silver particles [4].

A large branch of electrochemistry is concerned with the deposition of metals on electrodes. Certain metals can be deposited onto silver particles that carry excess electrons. We have recently reported on the deposition of cadmium and found that the chemical reactivity and optical properties of the first layer of Cd atoms are different from those of subsequent layers [5]. In the present paper, similar experiments on the deposition of lead and indium are reported.

In these studies, one takes advantages of the fact that silver possesses an absorption band at 380 nm (in water) which is very sensitive to changes to the surface of the particles. This band is caused by a longitudinal surface oscillation of the electron gas. Such collective oscillations occur in metals at the wavelength where the negative value of the real part of the dielectric constant of the metal is equal to twice the dielectric constant of the surrounding aqueous medium. (A second prerequisite is that the imaginary part of the dielectric constant of the metal is not too large). Silver is the only noble metal where the plasmon absorption band appears at a longer wavelength than interband transitions, which is the reason for the sensible response of this band to surface changes. An increase in the concentration of free electrons in the metal, for example by electron donation from free radicals, leads to a blue-shift and a narrowing of the plasmon absorption band. On the other hand, upon the chemisorption of a molecule, a dipolar layer is produced on the surface of the colloidal particles which causes damping

of the collective surface oscillation, the result being a broadening of the absorption band.

In order to discuss the optical effects which are caused by metal deposition one has to know the absorption spectrum of the pure metal in aqueous solution. Experiments were therefore carried out to prepare solutions of colloidal lead. That metallic lead is the final product of the radiolytic of Pb^{2+} ions has already been found previously [6]. Mie calculations were also carried out to compare the experimental spectrum of lead in water with the calculated one. In the case of indium, it was not possible to obtain the pure colloidal metal by the radiolytic reduction of In^{3+} with a quality that would allow a meaningful comparison of the experimental and theoretical spectra.

2. Experimental

The silver sol was prepared by exposing an evacuated solution of $1 \cdot 10^{-4}$ M AgClO_4 containing propanol-2 and acetone to the γ -rays of a ^{60}Co -source. The solution also contained poly(ethyleneimine) as stabilizer. After one hour at a dose rate of $8.7 \cdot 10^4$ rad/h, all the silver ions were reduced and the solution had a slightly yellow colour. The plasmon band close to 380 nm became a little weaker upon ageing of the solution for 30 min; this effect is due to the fact that the silver particles carry excess electrons immediately after the γ -irradiation, which slowly disappear upon ageing (forming H_2).

Lead or indium perchlorate was then added under the exclusion of air. The solution was then reexposed to γ -radiation to reduce the lead or indium ions. The absorption spectrum was recorded at various times. In the case of lead, a small amount of an aqueous solution of NaOH and methyl viologen (dimethylbispyridinium dichloride, MV^{2+}) was finally added to oxidize the reduced metal: $\text{Pb} + 2\text{MV}^{2+} \rightarrow \text{Pb}^{2+} + 2\text{MV}^+$ (The colloidal silver is not oxidized during this step because the redox potential is far more positive than that of MV^{2+}). As the absorption coefficient of MV^+ is known ($1.2 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 600 nm), the amount of reduced lead could be calculated. Indium metal was only oxidized very slowly by MV^{2+} ; its concentration could therefore not be determined by this method.

Samples for electron microscopy were prepared in a glove box filled with pure argon. A drop of the solution was put on a thin carbon film mounted on a copper mesh and the solvent evaporated. The sample came into contact with air for less than 20 seconds during the transfer into the electron microscope.

Results

Lead Reduction

Fig. 1 shows the absorption spectrum of the silver sol before and after the addition of lead perchlorate. Before the addition, the surface plasmon absorption band is located at $\lambda_0 = 385$ nm. The band shifts to $\lambda_1 = 393$ nm and decreases in intensity upon Pb^{2+} addition. The narrow absorption band of Pb^{2+} at 208 nm is also seen in the spectrum.

The figure also shows the absorption spectrum after various doses of γ -radiation, i.e. when various amounts of lead metal have been produced. The reduction of the lead ions is brought about by the 1-hydroxy ethylmethyl radicals, $(\text{CH}_3)_2\text{COH}$, which are radiolytically generated in solutions containing both acetone and propanol-2. Colloidal lead has an absorption band at 215 nm (see below). This band does not appear in the first stages of Pb^{2+} reduction (2 and 5 min). Instead, the silver plasmon band experiences a blue-shift. Fig. 2 shows the peak wavelength of this band as a function of irradiation time. It can be seen that the band shifts more and more slowly with increasing time. On the other hand, the build up of the absorption band of colloidal lead becomes faster as the irradiation proceeds. This can be seen from Fig. 2 where the 220 nm

absorption of the solution is also plotted as a function of the time of irradiation.

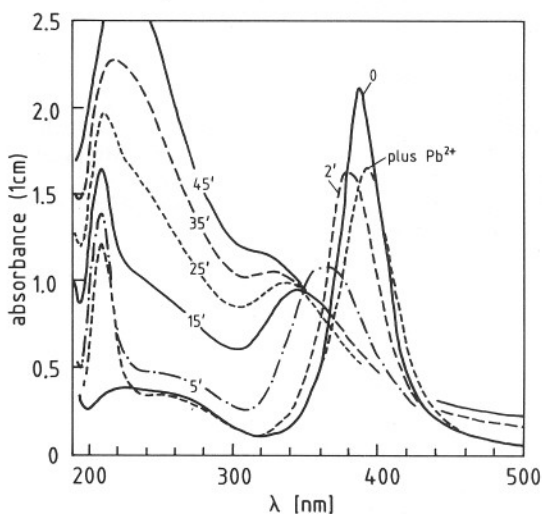


Fig. 1 Absorption spectrum of an evacuated $9.5 \cdot 10^{-5}$ M silver sol before and after addition of $9.5 \cdot 10^{-5}$ M $\text{Pb}(\text{ClO}_4)_2$, and at various times of γ -irradiation. Dose rate: $8.7 \cdot 10^4$ rad/h. pH of solution: 4.5. The solution also contained $3 \cdot 10^{-3}$ M acetone and 0.1 M propanol-2, and $1 \cdot 10^{-4}$ M poly(ethyleneimine). γ -radiation produces hydrated electrons and OH radicals. The electrons react with acetone, and the OH radicals with propanol-2 to yield 1-hydroxy ethylmethyl radicals. These organic radicals react too slowly with Pb^{2+} at the lead ion concentration used to produce lead atoms free in solution [6]; rather they react via electron transfer with the silver particles [2a], and the stored electrons then reduce Pb^{2+} ions on the surface of the colloidal particles

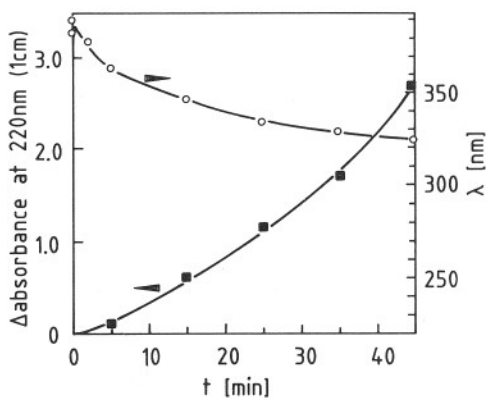


Fig. 2 Wavelength of the peak of the silver plasmon absorption band and 260 nm absorption as functions of the irradiation time. Data from Fig. 1

Electron microscopy of the particles which were present after complete reduction of the lead ions in Fig. 1 revealed that different kinds of particles were present: Most of the particles had roughly the size of the original silver particles (about 8 nm), but a smaller number of strongly agglomerated particles could also be seen. Energy dispersive X-ray analysis of the latter showed that they consisted of lead. It thus seems that the reduced lead is not evenly distributed on the surface of the silver particles; instead, individual lead particles are formed as well as lead layers on the silver particles.

Fig. 3 shows the concentration of reduced lead as determined by the MV^{2+} method as a function of the irradiation time. At the beginning, i.e. at times ($t < 4$ min) where the absorption band of

silver is most strongly influenced, no lead was detected by this method. One concludes that the initially deposited lead is not reactive towards methyl viologen. It should be mentioned, however, that exposure of such an irradiated solution to air led practically immediately to the restoration of the original silver band; this is attributed to the reoxidation of deposited lead by oxygen. At longer times, the concentration of deposited lead increases linearly over a wide range until it more slowly approaches the final value which corresponds to the reduction of all the lead ions. The extrapolated curve in Fig. 3 (dashed line) crosses the ordinate axis at $-1.5 \cdot 10^{-5}$ M. This is interpreted as the concentration of deposited lead which is unable to react with MV^{2+} .

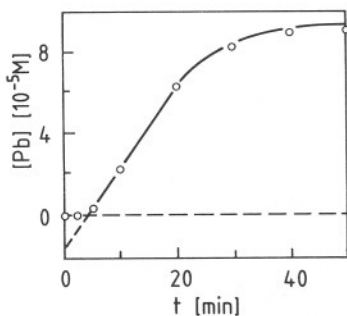


Fig. 3 Concentration of deposited lead as a function of irradiation time. Dashed line: extrapolation of the experimental values to $t = 0$. The ordinate axis is crossed at $-1.5 \cdot 10^{-5}$ M

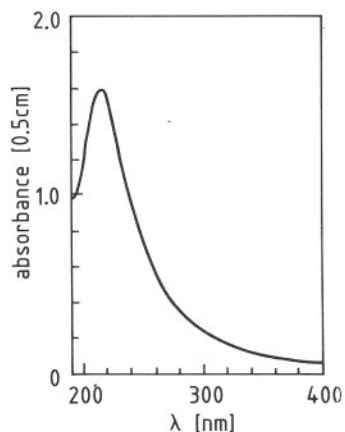


Fig. 4 Absorption spectrum of colloidal lead in water. An evacuated $1 \cdot 10^{-4}$ M $Pb(ClO_4)_2$ solution containing $1 \cdot 10^{-4}$ M poly(ethyleneimine) and 0.1 M propanol-2 was γ -irradiated at a dose rate of $8 \cdot 10^4$ rad/h for 1 h

As far as we know, the absorption spectrum of small Pb particles in aqueous solution has not yet been reported. Creighton and Eadon [7] have recently calculated the spectrum from the optical data of lead metal using Mie theory. They found an increasing absorption with decreasing wavelength down to 220 nm. Colloidal lead is formed during the radiolytic reduction only in the presence of a stabilizer. Poly(ethyleneimine) in very low concentrations turned out to be an efficient stabilizer. Fig. 4 shows the absorption spectrum of a γ -irradiated solution. It can be seen that the colloid formed has a rather narrow absorption band peaking at 215 nm. The colloid rapidly dissolves upon exposure of the solution to air. It also reacts with methyl viologen. From the intensity of the blue colour of the produced MV^+ it was determined that the reduction was complete. The absorption coefficient at 215 nm is $3.2 \cdot 10^4$ M $^{-1}$ cm $^{-1}$.

Indium Reduction

When an In^{3+} solution containing 0.1 M propanol-2 and 0.01 M acetone is irradiated, no absorption changes are observed. In this solution, the hydrated electrons are scavenged by acetone before they can attack In^{3+} ions and only organic radicals are available as reducing agents. Obviously, the organic radicals are not able to reduce indium-III. However, when the solution contains $1 \cdot 10^{-4}$ M colloidal Ag, the reduction of In^{3+} by organic radicals is observed. Fig. 5 shows the absorption spectrum of the sol before and after the addition of In^{3+} and at different times after the subsequent radical production by γ -irradiation.

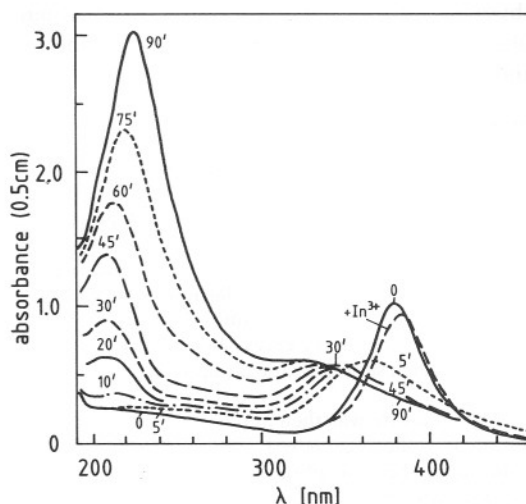


Fig. 5 Absorption spectrum of an evacuated silver sol before and after addition of $2 \cdot 10^{-4}$ M $In(ClO_4)_3$ and after different times of subsequent γ -irradiation at a dose rate of $8.7 \cdot 10^4$ rad/h. Silver concentration: $1.0 \cdot 10^{-4}$ M. The solution contained 0.1 M propanol-2, 0.01 M acetone, and $1 \cdot 10^{-4}$ M poly(ethyleneimine), pH = 5.7

The spectral shifts observed initially are similar to those observed during lead reduction: the plasmon band of silver is slightly red-shifted upon In^{3+} addition, but is then blue-shifted during the subsequent γ -irradiation. During the first ten minutes, no significant absorption is built-up at 208 nm where In^+ absorbs. However, at longer times an absorption band develops at this wavelength. At still longer times (i.e. $t > 45$ min), this band changes continuously into a new band at 225 nm. After 90 min irradiation, the 225 nm band no longer changed. At this point, all the indium had been reduced. A weak shoulder at about 340 nm is still present after the complete reduction of indium, i.e. in the range where silver particles carrying about one or two monolayers of indium absorb. The 225 nm band disappeared rapidly upon the exposure of the solution to air and the original silver band at 380 nm re-appeared. This is attributed to the oxidation of the deposited indium by oxygen.

Electron microscopy showed that the mean size of the silver particles prepared with polyethyleneimine as stabilizer was about 8.0 nm. After the complete reduction of indium, the mean particle size was about 12 nm. The energy dispersive X-ray analysis of the colloids showed the presence of both silver and indium. No metal could be detected in the free space between the particles.

Experiments were also carried out to prepare colloidal indium without the silver carrier. γ -irradiation of an In-III solution containing poly(ethyleneimine) led only to the formation of In^+ (the reducing species being the hydrated electron). However, when the In^+ solution was then made weakly alkaline, a band at 260 nm appeared and the 208 nm band of In^+ disappeared. This is explained by the disproportionation of In^+ :



The 260 nm band is attributed to $\text{In}(\text{OH})_3$ coated In particles. If this solution was made slightly acid again, the $\text{In}(\text{OH})_3$ absorption disappeared immediately and the In band appeared at 230 nm. It was also found that the 260 nm band could be produced by reduction of In-III with NaBH_4 ; the 230 nm band was again formed when the solution was acidified. In both types of reduction, the reduction of In-III was incomplete and the peak of the In band was at a slightly longer wavelength than that of the indium shell around a silver nucleus. Under these circumstances, the indium spectrum obtained in the latter case is regarded as the more reliable candidate for comparison with the calculated spectrum (see below).

Discussion

Lead Reduction

The optical changes during the deposition of very small amounts of lead strongly resemble the ones which have recently been observed during the reduction of Cd^{2+} ions on silver particles [5]. When Pb^{2+} ions are added to the silver sol, the plasmon band of silver is slightly red-shifted and decreases in intensity. We attribute the shift to a decreased electron density in the silver particles in the presence of adsorbed Pb^{2+} ions. However, when the reduction of adsorbed lead ions takes place, the band shifts to shorter wavelengths (Figs. 1 and 2).

The blue-shift of the surface plasmon band has two distinct origins. During the initial stages of reduction Pb (and In) atoms are generated on the surface by underpotential deposition. The polarity of the surface bond formed between the adatoms and the substrate depends on the difference in electronegativity of the two metals [8]. Both Pb and In are less electronegative than Ag. Thus at low surface coverages (<1 monolayer) the surface atoms of the silver colloid will gain electron density at the expense of the Pb atoms due to the ionic character of the adatom-substrate bond. During the initial stages of electrodeposition, the major effect is an increase in the surface free electron concentration of the silver, and the observed shifts can be attributed to changes in the dielectric properties of the substrate, rather than to the optical properties of the chemisorbed metal atoms.

However, once the coverage of the surface layer exceeds one monolayer, the bulk properties of the coating metal will begin to assert themselves. The increasing thickness of the surface layer will lead to a gradual shift of the dielectric constant of the surrounding medium. The condition for surface plasmon resonance absorption is that $\epsilon_1(\text{Ag}) = -2\epsilon_m$ where ϵ_m is the dielectric constant of the medium. Around 380 nm, ϵ_1 for both Pb and In are large and negative [9], which will cause the effective dielectric constant of the medium to decrease. This will shift the plasmon band to shorter wavelengths, and since the metal coat is absorbing, will also lead to damping of the absorption band.

Thus a continuous blue-shift is likely throughout the reduction process, regardless of whether the surface layer is assumed to consist of chemisorbed metal atoms or of a metallic surface layer.

Since lead deposition starts at redox potentials positive of the reversible (Nernst) potential, the electrode potential becomes more negative as the coverage increases. Once bulk metal deposition occurs, the Fermi level of the colloid par-

ticle is located at the Nernst potential. To cathodically polarize the electrode, some of the electrons transferred by the radicals are not neutralized by metal ions but serve to shift the redox potential to more negative values. This process occurs concomitantly with the deposition of metal ions, and may also contribute to the observed blue-shift, by increasing the electron concentration in the surface layers.

When larger amounts of lead are deposited (Figs. 1 and 2), differences between the cases of cadmium [5] and lead deposition emerge. First of all, the silver band shifts more and more slowly (Fig. 2) at longer irradiation times, and even after the complete deposition of Pb^{2+} the silver band can still be seen as a shoulder at 320 nm. In the case of cadmium, there was an almost linear shift with the time of reduction, i.e. a single plasmon band was always present that finally reached the wavelength (280 nm) at which pure colloidal Cd adsorbs [5]. This difference can be understood in terms of lead not being able to form an even layer around the silver particles at greater degrees of deposition; individual lead particles are formed (which may stick to the silver particles). Colloidal lead absorbs at 215 nm (Fig. 4). This band does not show up during the first stages of lead deposition on silver. However, at greater degrees of deposition, it grows rapidly (Fig. 2) which is also understood in terms of formation of separate lead particles.

Another common feature of Cd and Pb deposition is the existence of an "induction" period before the detection of reduced metal at the beginning of the deposition, although the shift in the position of the silver band indicates that metal is deposited during this period. As in the case of cadmium, we explain the effect by postulating that the first monolayer of adsorbed lead atoms is not reactive towards methyl viologen. The reaction does not consist of a direct electron transfer from an adsorbed Pb atom to a MV^{2+} molecule, but a reaction of the colloid particle as a whole. Electrons are transferred to MV^{2+} from the Fermi level in the particle. This can occur only when the Fermi level is at a sufficiently negative potential; this situation is not reached unless a sufficiently large number of Pb atoms are adsorbed. This occurs after 5 minutes (see. Fig. 3) when the concentration of reduced Pb is $1.5 \cdot 10^{-5}$ M. This corresponds to about one monolayer (as calculated from the simple geometric considerations described in Ref. [5]). The deposition of the first Pb atoms occurs at a relatively positive potential of the silver particles; in the language of electrochemistry, these adsorbed atoms are formed under "underpotential" conditions. As more and more Pb is deposited and outer layers are formed, the Fermi level shifts to a more negative potential, which means that the subsequent Pb deposition occurs under "Nernst potential" conditions.

For less than one monolayer of deposited lead, one may treat the plasmon absorption band as a silver resonance band shifted by increased electron density to shorter wavelengths. As pointed out previously [5], one would expect the following relationship to hold between the wavelengths λ_1 and λ before and after Pb deposition, respectively:

$$(\lambda_1/\lambda)^2 = 1 + f([\text{Pb}]/[\text{Ag}]) \quad (2)$$

Using the values $\lambda_1 = 393$ nm, $\lambda = 364$ nm (at 5 min in Figs. 1 and 2), $[\text{Pb}] = 1.5 \cdot 10^{-5}$ M and $[\text{Ag}] = 9.5 \cdot 10^{-5}$ M, one obtains $f = 1.1$. f is the number of excess electrons donated per adsorbed Pb atom into the metal lattice (or, more correctly, is the difference in elementary charge of a silver and a lead atom in the lattice). This shows that a Pb atom adsorbed under "underpotential" conditions is not in a zero valence state.

The reported absorption spectrum of small Pb particles in aqueous solution is incomplete as wavelengths below 220 nm were not considered in the calculations made by Creighton and Eadon [7]. To determine whether the optical spectrum of the poly(ethyleneimine)-stabilized lead in Fig. 4 is that of the pure colloidal metal, we have calculated the Mie spectrum [10] using the data of Lemonnier et al. [11] which extend farther into the UV. The predicted maximum is at 201 nm (observed value in Fig. 4: 215 nm) and the absorption coefficient is $3.2 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in excellent agreement with the observed value. The full width at half maximum of the absorption band is predicted to be 54 nm, and the experimental value of 60 nm is close to this value.

It is useful to compare the observed position of the plasmon absorption band in media with different refractive indices. As long as ϵ_2 remains small, the position of the band is given by

$$\lambda^2 = \lambda_p^2(\epsilon_0 + 2n_0^2) \quad (3)$$

where ϵ_0 is the high frequency dielectric constant, n_0 the refractive index of the medium and λ_p the bulk plasma wavelength. Fig. 6 shows a plot of λ^2 vs. $2n_0^2$ for lead particles in alkali halide glasses [12] and our aqueous sol. The slope of the straight line obtained corresponds to a volume plasma energy of 12.2 eV, and from the intercept one finds $\epsilon_1 = 1.1$, in very good agreement with the data of Ashton and Green [13]. The predicted value from the optical constants of Lemonnier et al. (201 nm), which is also shown in the figure, is too low; this is possible due to the values of ϵ_1 in Lemonnier's work being too low. The optical spectrum of lead and its pale yellow colour in aqueous solution are purely due to the surface plasmon absorption. The high frequency dielectric constant is only slightly above that expected according to the Drude model, and this shows that bound electrons contribute only very weakly to the dielectric properties at optical frequencies.

Indium Reduction

Indium is reduced by organic radicals only in the presence of the silver sol. A similar phenomenon has been observed for the radiolytic reduction of Cd^{2+} [5]. It is therefore postulated that the radicals transfer electrons to the silver particles. The reduction of indium then takes place electrochemically as on a compact silver electrode which is cathodically polarized.

The optical changes to the silver sol upon addition of In^{3+} and subsequent formation of reducing radicals by γ -irradiation resemble the changes observed for Cd and Pb deposition. Again, electron donation from deposited indium into the silver particles is postulated. However, a new phe-

nomenon occurs: After small amounts of indium have been deposited ("underpotential" deposition), the formation of In^+ accompanies the following indium metal deposition ("Nernst potential" conditions). A possible explanation invokes the conproportionation of indium and indium-III ions [14]:



The free energy of this reaction is -0.08 eV. As the first monolayer does not undergo this reaction, one concludes that In atoms are bound to the silver particles with an energy exceeding that for the binding of In to indium metal by at least 0.08 eV. Only the indium atoms which are deposited in outer layers are able to react according to Eq. (4). When the concentration of In^{3+} has been sufficiently depleted during the reduction, the remaining In^+ ions are electrochemically reduced. We ascribe the 225 nm band at longer times in Fig. 5 to silver particles which are covered with a few layers of indium metal. They have practically the absorption spectrum of indium metal. $\epsilon = 3.0 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ is obtained for the maximum absorption coefficient from the spectrum at 90 min in Fig. 5. In this experiment, the spectrum was measured repeatedly during the irradiation. If one irradiated the solution for 90 minutes without interruption, the 225 nm band was a little narrower and higher, and $\epsilon = 3.8 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was found. The different shapes of the 225 nm band are possibly due to differences in the evenness of the deposited indium layer.

The silver particles carrying an indium deposit of about one or two monolayers absorb at 330 to 340 nm (Fig. 5). Even after the complete reduction of indium, the spectrum of the solution contains a shoulder in this wavelength range. This may indicate that not all the silver particles received the same amount of deposited indium. Reproducible electrochemical reduction of In^{3+} is not readily attained since reaction 4 leads to competitive redissolution of the colloidal metal formed by the radiolysis.

The spectrum of indium particles in water has recently been calculated by Creighton and Eadon [7]. These authors found an increasing absorption with decreasing wavelength. Unfortunately, these calculations did not extend to wavelengths below 250 nm as little data is available for indium metal. Using the data of Lemonnier et al. [15], the predicted Mie spectrum, which is shown in Fig. 7, is seen to have an absorption maximum at 205 nm (observed at 225 nm, Fig. 5) and an absorption coefficient as high as $1.2 \cdot 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. The predicted full width at half maximum of the absorption band is 16 nm, which is narrower than the observed width of 40 nm for In deposited on Ag.

These differences can possibly be explained by the effect of surface scattering of conduction electrons in small In colloids. For this metal, $\epsilon_2(\text{bulk})$ is very small (0.36) at the wavelength of maximum absorption [15]. Kreibitz [16] has shown that for particles with a radius R smaller than the bulk mean free path, ϵ_2 is approximated by

$$\epsilon_2(\omega, R) = \epsilon_2(\text{bulk}) + \omega_p^2 \cdot v_l / \omega^3 \cdot R \quad (5)$$

Thus, the second term in Eq. (5) mainly determines ε_2 for the approximately 2 nm indium shell around the silver particles, the increased value of ε_2 leading to the changes in height and width of the plasmon absorption band as compared to the theoretical spectrum of the bulk material. The fact that the observed peak lies at a longer wavelength than the calculated one cannot, however, be explained by Eq. (5), since the wavelength is primarily determined by the value of ε_1 . We must assume that the deviation is due to small errors in the measurement of ε_1 (bulk). One can also use Eq. (3) to calculate the position of the plasmon band, taking the bulk plasma photon energy to be 11.42 eV [15] and assuming the high frequency dielectric constant to be 1.0. This leads to a value of 230 nm, very close to the value observed experimentally.

Granular indium films show a resonance at 258 nm [17], which is also in agreement with Eq. (3) using $n_0 = 1.5$. Thus we conclude again that the observed absorption band in Fig. 5 truly represents that of the colloidal metal and that indium behaves as a perfect free electron metal without any contribution to the dielectric constant from bound electrons ($\varepsilon_0 = 1.0$).

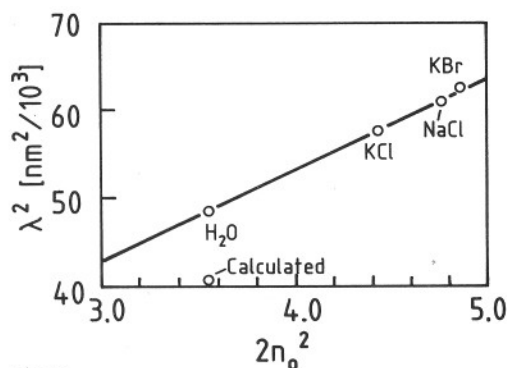


Fig. 6 Plot of λ^2 versus twice the square of the refractive index of the medium in which the lead particles are imbedded

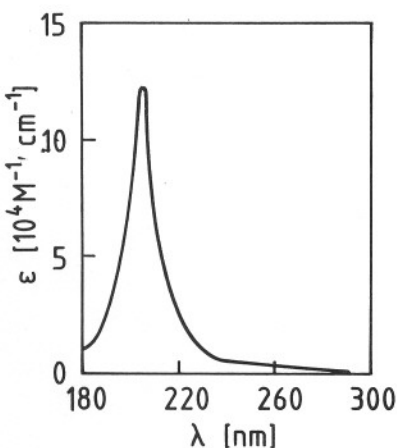


Fig. 7 Calculated absorption spectrum of colloidal indium in water

Final Remarks

The colloidal metal particles have a large interface of a few m^2 per liter, which makes them attractive for studies in

surface chemistry. Electrochemical processes, which are initiated by chemical charging of these tiny particles can readily be detected using simple spectrophotometric techniques. At the small particle sizes used, the solutions are transparent and the optical measurements are not disturbed by light scattering. In the case of silver particles, the surface reactions can be followed optically with particular sensitivity, as the surface plasmon band of silver is not superimposed by absorptions due to interband transitions (which are less influenced by surface modification). Studies on the interaction of deposited metals with the silver carrier are of special interest: It is shown here and in a preceding paper [5] that the optical and chemical properties of the first monolayer of deposited metal atoms (deposited at underpotential) are different from those of atoms in subsequent layers (deposited at the Nernst potential). The experiments on the electronics of colloidal particles thus complement adsorption studies on compact electrodes in conventional electrochemistry, where optical measurements are difficult to perform and most of the information is gained from electrical current measurements.

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