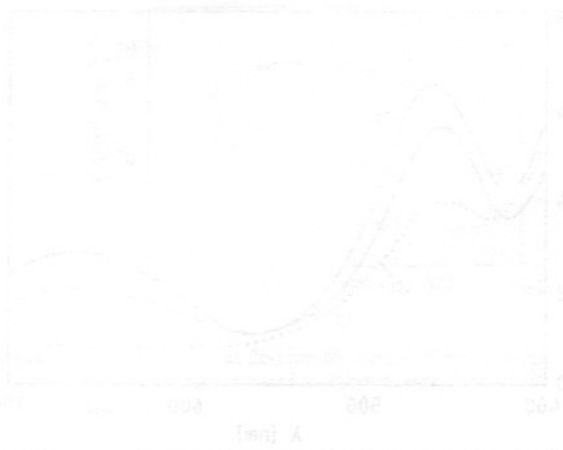


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## Electrochemistry of Mixed Metal Clusters in Aqueous Solution: Reduction of $\text{Ag}^+$ by the Lead Atom

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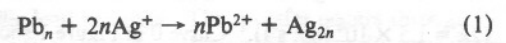
The electron transfer between lead and silver particles in the micro size range, where conventional electrode-potential considerations are not applicable, is studied by pulse radiolysis. In deaerated solutions containing  $1 \times 10^{-2}$  M  $\text{Pb}(\text{ClO}_4)_2$ ,  $2.5 \times 10^{-5}$ – $2.0 \times 10^{-4}$  M  $\text{AgClO}_4$ , and  $1 \times 10^{-2}$  M  $\text{NaCO}_2\text{H}$ ,  $\text{Pb}^0$  is the first and metallic silver the final product of reduction, and no metallic Pb particles are formed as intermediates. A mechanism is proposed in which the crossover from reduced lead to reduced silver occurs via the mixed lead–silver cluster  $(\text{PbAg})^+$ , which absorbs weakly at 460 nm. In the reaction of this cluster with  $\text{Ag}^+$ , the Pb component is oxidized and dimeric silver is formed that starts an agglomeration chain leading to larger metallic Ag particles. During these agglomeration steps, intermediate oligomeric silver species, which absorb at 330 and 365 nm, are detected. The results are discussed in the framework of our limited knowledge about the redox potentials of small nonmetallic lead particles.

### Introduction

Whereas the electrochemistry of metals has been well established since the beginning of this century, the electrochemical behavior of small clusters of metals in the atom-to-metal transition range (with increasing particle size) has not yet been fully explored. Pulse radiolysis is a method for generating metal atoms in aqueous solution, which form clusters and then finally colloidal particles of metallic character. During the growth, the optical and electrochemical properties of the particles change.<sup>1,2</sup> An important question, for example, is at which particle size does the typical metal absorption spectrum first appear? Typical studies have been made with silver<sup>3</sup> and lead<sup>4</sup> solutions.

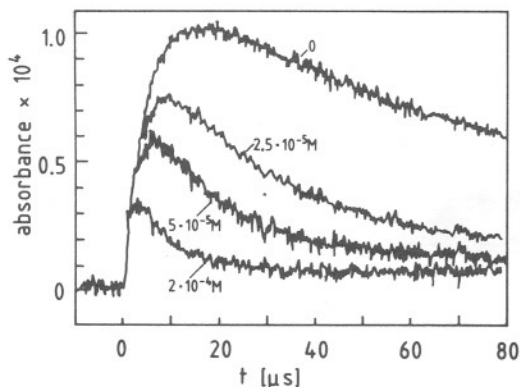
In the present studies, a mixed system, i.e., a system containing both lead and silver, is investigated. To describe the problem, let us first consider a *conventional* electrochemical experiment: silver ions in the form of  $\text{AgClO}_4$  are added to the solution of colloidal lead particles. The lead particles, which have a diameter of about 6 nm and have metallic properties, possess a narrow

absorption band at 215 nm.<sup>4</sup> This band disappears immediately upon the addition of the  $\text{Ag}^+$  ions, and the typical 380-nm absorption band of colloidal silver is produced. The reaction



takes place, as the  $\text{Ag}^+/\text{Ag}$  redox potential is much greater than that of the  $\text{Pb}^{2+}/\text{Pb}$  system. The question now arises whether reaction 1 occurs when  $n$  is very small, for example, equal to one. Will the Pb atom or a small Pb cluster be able to undergo reaction 1, or will they grow by association until they have metallic character, enabling the trivial reaction of macroscopic electrochemistry to take place?

The pulse radiolysis experiment is performed in the following manner: a deaerated solution containing both  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  ions as well as sodium formate is exposed to a 0.5- $\mu\text{s}$  pulse of high-energy radiation. The reducing species which are generated during the pulse are hydrated electrons and carboxyl radical anions. Both  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  react rapidly with these reductants. However,



**Figure 1.** Kinetic traces at 660 nm for solutions containing various concentrations of  $\text{Ag}^+$ .  $[\text{Pb}(\text{ClO}_4)_2]$ :  $1 \times 10^{-4}$  M;  $[\text{NaCO}_2\text{H}]$ :  $1 \times 10^{-2}$  M, pH = 4.  $1.2 \times 10^{-5}$  M reducing radicals ( $e_{\text{aq}}^-$  plus  $\text{CO}_2^-$ ) were produced in the pulse.

because a large  $\text{Pb}^{2+}/\text{Ag}^+$  concentration ratio is used, practically only  $\text{Pb}^{2+}$  ions are reduced:



These reduction reactions also occur during the pulse under the concentration conditions chosen. Thus, a well-known concentration of  $\text{Pb}^+$  is instantaneously generated at zero time. It is known that the  $\text{Pb}^+$  ions—in the absence of  $\text{Ag}^+$ —react after the pulse with each other to form  $\text{Pb}^0$  atoms which then agglomerate until metallic colloidal particles are formed.<sup>4</sup> In the presence of  $\text{Ag}^+$  ions, the final product is certainly colloidal silver. When does the transfer of the electrons, which were first deposited on lead ions, to the silver ions occur? The question is not trivial, if one remembers that the standard reduction potential  $E^\circ$  of the redox couple  $\text{Ag}^+/\text{Ag}^0$  in aqueous solution is as negative as  $-1.8$  V<sup>1,2,5,6</sup> and that  $\text{Pb}^0$  is "more noble" with  $E^\circ = -0.93$  V.<sup>2</sup> These potentials for the free atoms were calculated from the known standard reduction potentials of the compact electrodes and the free enthalpies of sublimation of the metals; the free enthalpies of hydration of the atoms were assumed to be negligible in these calculations. In the case of the silver atom, it was found experimentally that it is a strong electron donor in aqueous solution.<sup>5</sup>

The pulse radiolysis equipment has been described previously<sup>7</sup> (0.5- $\mu\text{s}$  pulses; 3.8 MeV).

## Results

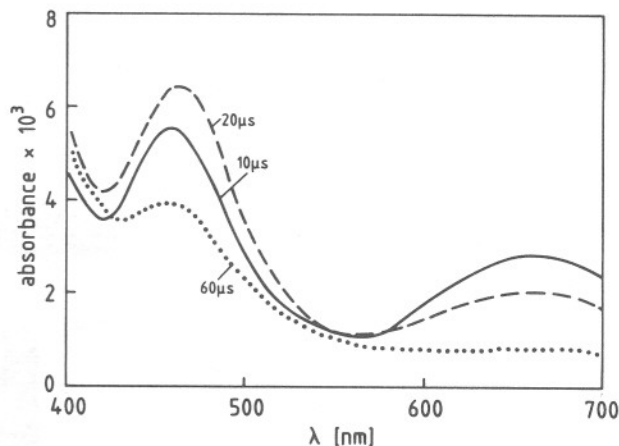
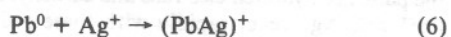
The  $\text{Pb}^+$  ions which are formed during the pulse react rapidly with each other to yield  $\text{Pb}^0$  atoms:



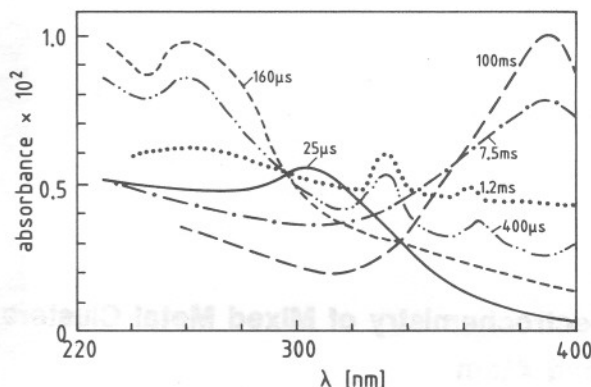
( $2k = 8.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>4</sup> As  $\text{Pb}^0$  has an absorption band at 660 nm, the bimolecular reaction of the  $\text{Pb}^+$  ions can be monitored at this wavelength. After reaching a maximum, the 660-nm absorption decreases, as the  $\text{Pb}^0$  atoms disappear via



( $2k = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>4</sup> Curve 0 in Figure 1 shows the 660-nm absorption as a function of time for a solution in which silver ions were not present. The other curves were obtained with solutions containing  $\text{Ag}^+$  at different concentrations. The buildup of the 660-nm absorption also occurs in the presence of  $\text{Ag}^+$ , although the maximum is lower and is reached at a shorter time than in the absence of  $\text{Ag}^+$ . Whereas the decay of the 660-nm absorption occurs via second-order kinetics in the absence of  $\text{Ag}^+$ , it follows pseudo-first-order kinetics at higher  $\text{Ag}^+$  concentrations, the half-life being reciprocally proportional to the concentration of  $\text{Ag}^+$ . It is concluded that  $\text{Pb}^0$  is able to react with  $\text{Ag}^+$ . Reasons are given below for the cluster  $(\text{PbAg}^+)$  being the product of this reaction. The rate constant for the reaction



**Figure 2.** Long-wavelength spectrum of a solution containing  $5 \times 10^{-5}$  M  $\text{Ag}^+$  ions at various times after the pulse. Other concentrations as in Figure 1.



**Figure 3.** Absorption spectrum of a solution at various times after the pulse.  $1 \times 10^{-4}$  M  $\text{Pb}(\text{ClO}_4)_2$ ;  $5 \times 10^{-5}$  M  $\text{AgClO}_4$ ;  $1 \times 10^{-2}$  M  $\text{NaHCO}_2$ . Radical concentration as in Figure 1.

is  $8.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  as obtained from a computer fit to the curves in Figure 1.

The long-wavelength spectrum at different times after the pulse is shown in Figure 2 for a solution containing  $5 \times 10^{-5}$  M  $\text{Ag}^+$  ions. It can be seen how the 660-nm absorption of  $\text{Pb}^0$  disappears. A new absorption at 460 nm is also built up. This absorption is not produced in the absence of  $\text{Ag}^+$  ions; it is therefore attributed to the  $(\text{PbAg}^+)$  cluster formed in reaction 1. As can be seen, the 460-nm absorption is not long-lived, which indicates that the cluster undergoes further reaction in the  $10^{-5}$ -s range.

The spectrum of the solution at shorter wavelengths is shown in Figure 3. Note that the absorptions in the UV range are much stronger than those in the visible wavelength range in Figures 1 and 2. At 25  $\mu\text{s}$  after the pulse, the spectrum contains a maximum at 305 nm. At this time, reactions 5 and 6 are not yet complete; thus, some  $\text{Pb}^+$  (maximum at 320 nm<sup>4</sup>) and some  $\text{Pb}^0$  (maximum at 290 nm<sup>4</sup>) are still present. Under the concentration and pulse dose conditions in Figure 3, reaction 5 can practically be neglected. Within 160  $\mu\text{s}$  after the pulse, a strong absorption at 260 nm is built up. At 400  $\mu\text{s}$ , the 260-nm absorption has decreased a little and the absorption in the 300–400-nm range has increased. Most noteworthy are the absorption bands at 330 and 365 nm, which are superimposed on the 300–400-nm absorption underground. These bands have previously been observed in the pulse radiolysis<sup>8</sup> and in the  $\gamma$ -radiolysis<sup>9,10</sup> of silver salt solutions; they were attributed to intermediate oligomeric clusters of silver. It can thus be said that the transfer of the electrons from lead to silver has occurred rather rapidly in the experiment of Figure 3, i.e., at a time shorter than 400  $\mu\text{s}$ . At longer times, the bands of the oligomeric species disappear and the plasmon absorption band in the 380–400-nm range of larger metallic silver particles is built up.

The build up of the absorption at 260 nm at times shorter than 400  $\mu\text{s}$  is rather complex as can be seen from Figure 4 where

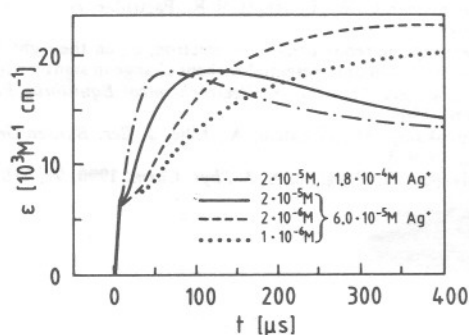


Figure 4. Kinetic traces at 260 nm for various doses and  $\text{Ag}^+$  concentrations. The doses are expressed as the concentrations of the reducing radicals generated.

kinetic traces are shown for two silver concentrations and various doses in the pulse. To compare the shape of the curves at different doses, the entity  $\epsilon$  is plotted on the ordinate scale.  $\epsilon$  is obtained by dividing the observed absorbance signal by the concentration of radicals ( $e_{\text{aq}}^-$  plus  $\text{CO}_2^-$ ) produced in the pulse and by the thickness of the optical cell (1.5 cm).

Immediately after the pulse, the absorption is increased as  $\text{Pb}^+$  is formed during the pulse. We first regard the traces for  $[\text{Ag}^+] = 6.0 \times 10^{-5} \text{ M}$ . At the highest dose applied, i.e., the production of  $2 \times 10^{-5} \text{ M}$  radicals in the pulse, reaction 4 has a first half life of only 6.3  $\mu\text{s}$ . Reaction 6 occurs with a half life of 14  $\mu\text{s}$ . Thus, after roughly 30  $\mu\text{s}$ ,  $(\text{PbAg})^+$  formation is 75% complete. During this time, the 260-nm absorption increases which is attributed to  $(\text{PbAg})^+$  absorbing more strongly than  $\text{Pb}^+$  at 260 nm. However, the absorption continues to increase substantially until a maximum is reached at 100  $\mu\text{s}$ . This additional increase follows another rate law as can be seen from the initially convex shape of the 260-nm traces. The additional increase becomes faster with increasing  $\text{Ag}^+$  concentration. This indicates that the first product,  $(\text{PbAg})^+$ , which is essentially formed during 30  $\mu\text{s}$ , undergoes reaction with  $\text{Ag}^+$  ions. The following process is postulated:

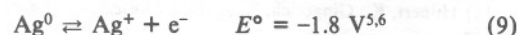
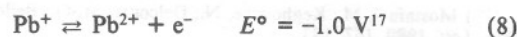


Reaction 7 is the process in which the transfer of the reduction equivalents from lead to silver occurs.  $\text{Ag}_2$  is the particle that possesses the strong 260-nm absorption (see 160- $\mu\text{s}$  curve in Figure 3). Upon its agglomeration to yield oligomeric silver clusters and finally metallic particles, the 260-nm absorption decreases. At the lower pulse doses in Figure 4, reaction 4 is slowed down substantially: the first half-life of reaction 4 amounts to 63 and 126  $\mu\text{s}$  at the respective doses of  $2 \times 10^{-6}$  and  $1 \times 10^{-6} \text{ M}$  radicals, which is now much longer than those of the pseudo-first-order processes 6 and 7. Thus, the rate of reaction 4 determines the rate of the increase in absorption due to  $\text{Ag}_2$  formation and a change in  $\text{Ag}^+$  concentration has little influence on the rate of the  $\text{Ag}_2$  buildup.

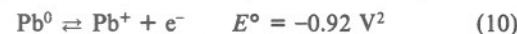
## Discussion

The detailed discussion of redox reactions of metal clusters requires knowledge of their thermodynamic properties. These data are known to only a limited extent as pointed out in a recent consideration of the redox potentials of silver clusters.<sup>6</sup> Most of the information stems from gas-phase studies, such as mass spectrometry of metal vapors,<sup>11,12</sup> electron exchange as studied by cytotron resonance,<sup>13</sup> molecular beam experiments,<sup>14</sup> and theoretical calculations.<sup>15</sup> When using gas-phase data to describe clusters in solution, one also needs the hydration free enthalpies. No data are available here. However, as pointed out previously, as long as neutral clusters are considered, the hydration energies may be neglected, as they are expected to be small.<sup>5,6</sup> In some cases, known dissociation energies are used instead of free enthalpies of dissociation; again, the neglect of the accompanying entropy effects seems admissible.

$\text{Pb}^+$ , the first reduction product, cannot reduce a silver ion as is seen from the standard potentials of the redox systems involved:<sup>16</sup>



The transfer of an electron from  $\text{Pb}^+$  to  $\text{Ag}^+$  would be endoergic by 0.8 eV. In fact, the  $\text{Pb}^+$  ion reacts with  $\text{Pb}^+$  to yield  $\text{Pb}^0$  within some  $10^{-5} \text{ s}$  after the pulse as in the absence of silver ions. However, the 660-nm absorption of  $\text{Pb}^0$  disappears much more rapidly in the presence of  $\text{Ag}^+$ , the rate being proportional to the  $\text{Ag}^+$  concentration (Figure 1). It is therefore concluded that  $\text{Pb}^0$  reacts with  $\text{Ag}^+$ . However, the transfer of an electron to form  $\text{Ag}^0$  is not possible as the standard potential of the system



is not negative enough. It must be concluded that  $\text{Pb}^0$  forms an adduct with  $\text{Ag}^+$  (eq 6).

This product reacts further with  $\text{Ag}^+$  to build up the absorption of  $\text{Ag}_2$  within about 100–200  $\mu\text{s}$  after the pulse, depending on dose rate and silver ion concentration. The overall reaction taking place is the sum of reactions 6 and 7:



To examine the energetics of this overall reaction, the following cycle of reactions is considered:



Thus, reaction 11 is practically thermoneutral. However, as it is rather fast, it must have a negative value of  $\Delta G$ . One must conclude that the redox potentials used in the above calculation are not known well enough to predict the energetics of a reaction with a small  $\Delta G$  value. The free hydration enthalpies of the free atoms have to be taken into consideration, which is not possible at the present time. For example, if the free silver atom had a slightly negative value of  $\Delta G_{\text{hydr}}$ , say  $-0.1 \text{ eV}$ , or if the free enthalpy of hydration of  $\text{Ag}_2$  were more negative by 0.03 eV than that of  $\text{Pb}^0$ , reaction 11 would already be exoergic. Another source of error could lie in the values for the free energies of sublimation, which were used to calculate the standard potentials of the redox systems of eqs 12 and 13. One also has to conclude that the binding energy of the  $(\text{PbAg})^+$  cluster must be very low, as otherwise reaction 7 would become too endoergic to occur rapidly.

The thermodynamics of the overall reaction 11 would also become more favorable, if the dimeric silver molecule formed would be complexed by  $\text{Ag}^+$ . In fact, in the previous studies on silver agglomeration processes, the formation of complexed particles such as  $\text{Ag}_3^+$  and  $\text{Ag}_4^{2+}$  in solutions containing excess silver ions have been discussed.<sup>18</sup>

To summarize the results of the experiments and of the potential considerations, it can be said that the transfer of the electrons from the lead to the silver component of the solution occurs neither in the very first step, i.e., via interaction of  $\text{Pb}^+$  with  $\text{Ag}^+$ , nor via the normal electrochemical reaction through the formation of larger metallic lead particles. The transfer occurs through  $\text{Pb}^0$ , i.e., still at a very early stage, although the thermodynamic driving force is certainly very small.

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