

# Formation and Reduction of Semiconductor-Like Aggregates of Silver-Carboxy-Alkane-Thiolates in Aqueous Solution

Anton Fojtik

Heyrovsky Institute of Physical Chemistry and Electrochemistry, Academy of Sciences, Prague, CSFR

Paul Mulvaney, Thomas Linnert, Michael Giersig, and Arnim Henglein

Hahn-Meitner-Institut Berlin GmbH, Bereich S, 1000 Berlin 39, Federal Republic of Germany

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In slightly acidic solutions of  $\text{Ag}^+$  and carboxy-methane-thiol (CMT) or carboxy-ethane-thiol (CET), aggregates are formed whose absorption spectrum is significantly different from that of the monomeric silver-carboxy-alkane-thiols. The build-up of the aggregates occurs slowly. They develop a band at 335 nm ( $\text{Ag}-\text{CMT}$ ) or 355 nm ( $\text{Ag}-\text{CET}$ ), and simultaneously, acquire fluorescence. Silver is produced upon the photolysis of the aggregates. A very small amount of silver atoms deposited on the aggregates is sufficient to quench the fluorescence substantially. Both the absorption and fluorescence bands are blue-shifted as the aggregates become smaller during photolysis or dissolution in alkaline solution. The aggregates are proposed to have semiconductor-like ionic planes separated from each other by the organic groups. Electron microscopy shows that the aggregates are partly crystalline and have a size of about 25 Å when they are freshly prepared. The crystallinity increases and the structure changes upon aging for several days. — When  $\text{Ag}^+$  is reduced by  $\text{NaBH}_4$  in the presence of carboxy-alkane-thiols, stable silver aggregates of different sizes are formed. The absorption bands and chemical behaviour of some of the aggregates resemble those of oligomeric silver clusters investigated previously. The stability of the clusters is explained in terms of "pre-complexation" of silver surface atoms by the carboxy-thiols.

## Introduction

During the past ten years, the investigation of the neglected nanometer dimension in colloid chemistry, i.e. the investigation of extremely small particles of semiconductors [1] and metals [2] in solution, has attracted the attention of many laboratories. These investigations started because it was hoped that such particles would be useful as sensitizers of photochemical reactions and catalysts of free radical processes [3]. A further development, during the past few years, has been the preparation of surface modified particles. For example, a number of reports on the properties of CdS particles carrying organic thiol groups on their surface have appeared; such particles are soluble in organic solvents [4]. Similarly, in the case of metals, the preparation of metallic silver particles and non-metallic oligomeric silver clusters in solution was reported, where surface atoms of the agglomerates were "pre-complexed" or "pre-oxidized" by nucleophilic reagents such as  $\text{CN}^-$  or  $\text{SH}^-$  [5a].

In the present paper, a new method for making inorganic particles (both semiconductors and metals) carrying organic groups is described. The starting materials are silver salts and carboxy-alkane-thiols in aqueous solutions. Under certain conditions they form aggregates which have optical properties like small inorganic semiconductor particles. The two organic components used were carboxy-methane-thiol, CMT,  $\text{HS}-\text{CH}_2-\text{COOH}$ , and carboxy-ethane-thiol, CET,  $\text{HS}-\text{CH}_2\text{CH}_2\text{COOH}$ .

It is also shown that reduction of these materials in aqueous solution by sodium borohydride leads to silver agglomerates with properties different from those of the colloidal

silver particles usually generated by the reduction of silver ions. The differences are due to two facts: 1) some of the silver particles are extremely small and exhibit properties of oligomeric silver, and 2) the silver particles carry thiolate derivatives on their surface.

## Experimental

The two carboxy-alkane-thiols were commercial products (Fluka:  $\text{HS}-\text{CH}_2\text{COONa}$  and  $\text{HS}-(\text{CH}_2)_2-\text{COOH}$ ), and were used as received. In the reduction experiments with  $\text{NaBH}_4$ , mg amounts of the solid reductant were added to a solution under an atmosphere of argon. The glass vessel was equipped with an optical 1 cm cuvette to allow recording of the spectrum at various times without exposing the solution to air.

Photolysis was carried out with a 450 watt xenon lamp (10 cm water filter; 280 nm cut-off filter).

To prepare the samples for electron microscopy (Phillips EM CM 12, 120 kV) a drop of the colloidal solution was applied for 30 s to a copper mesh covered with a thin carbon film and then most of it removed with a paper tip. The water of the sample evaporated before the sample was put into the microscope. It was found that under these conditions aggregation of the primary colloidal particles took place during water evaporation. To prevent this, a freeze-drying technique was used: the copper mesh with the sample was put on a metal holder cooled by liquid nitrogen and the solvent slowly evaporated overnight under vacuum.

## Results

### Agglomerates of Silver-Carboxy-Methane-Thiolate

Fig. 1 shows the absorption spectrum of a  $4 \cdot 10^{-4}\text{M}$  CMT solution at various times after the addition of  $4 \cdot 10^{-4}\text{M}$   $\text{AgClO}_4$ . The initial pH of the solution was 5.0 It decreased immediately to 3.5 upon the addition and then changed little with time. During aging

of the solution for 50 minutes, a band at 335 nm developed; a close inspection of Fig. 1 reveals that the maximum of this band shifted to slightly longer wavelengths during this development. When the CMT concentration was doubled after 50 minutes, the intensity of the band did not increase further. A lower rate of development was observed when the starting CMT solution was more acidic (pH = 4). When an aged equimolar solution was brought to pH = 10 by the addition of NaOH, the 335 nm absorption band almost completely disappeared. When the pH was brought back down to 3.5 with HClO<sub>4</sub>, the band developed again. It is thus concluded that the solution contains a species which exists in two interconvertible forms, depending on the pH of the solution.

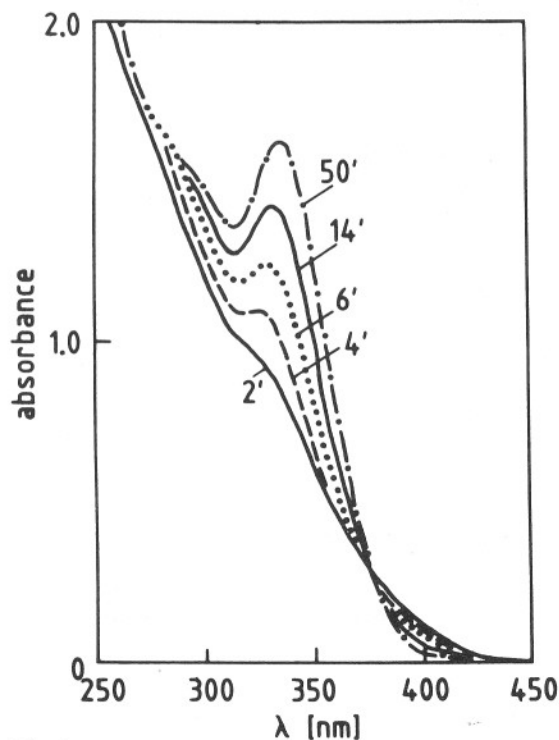


Fig. 1  
Temporal development of the absorption spectrum of aggregates in a solution containing  $4 \cdot 10^{-4}$  M AgClO<sub>4</sub> and  $4 \cdot 10^{-4}$  M CMT

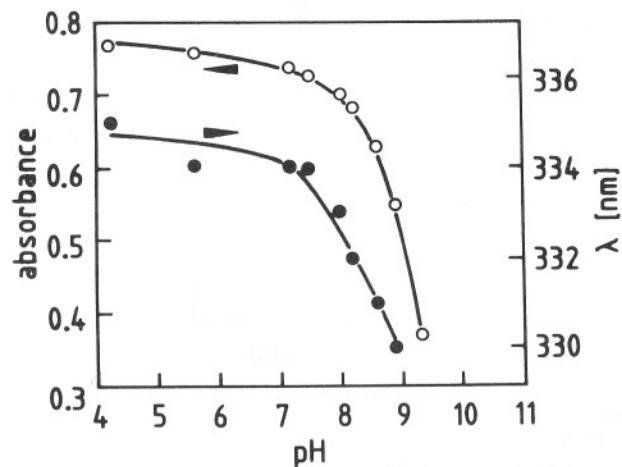


Fig. 2  
Absorption spectrum of a solution of aggregated Ag-CMT ( $2 \cdot 10^{-4}$  M; initial pH = 4.2) upon addition of NaOH: absorbance and wavelength of the absorption band as functions of pH

The slow development of the 335 nm band in slightly acidic solution is regarded as an indication for an agglomeration process. This process is essentially finished after 50 minutes when the 335 nm band is fully developed. However, further changes in the agglomerate seem to take place during aging for days: in solutions several days old, the 335 nm band disappeared more slowly when the solution was made alkaline.

The species mainly present in alkaline solution is thought to be the monomer or dimer of Ag-CMT. In the experiments of Fig. 2, tiny amounts of NaOH were added to an Ag-CMT solution of pH = 4.2. After each NaOH addition, the solution was equilibrated for 20 minutes before the absorption spectrum was recorded. Fig. 2 shows how the intensity of the 335 nm band decreased with increasing pH. It is also seen that the maximum of the band shifted to slightly shorter wavelengths.

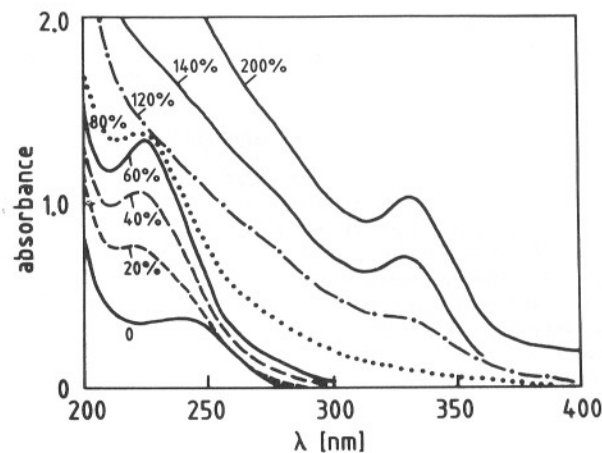


Fig. 3  
Spectrum of a  $2 \cdot 10^{-4}$  M CMT solution at pH = 10 after addition of various amounts of AgClO<sub>4</sub>. The Ag<sup>+</sup> concentration is given as a percentage of the CMT concentration

The agglomerate absorbing at 335 nm can be made in alkaline solution when excess silver ions are present. In Fig. 3, the spectrum of a solution is shown which originally contained  $2 \cdot 10^{-4}$  M CMT at pH = 10. Various amounts of silver ions were now added. At the beginning, a peak at 275 nm develops, which is attributed to monomeric or dimeric Ag-CMT. It reaches its maximum value after about  $1.6 \cdot 10^{-4}$  M AgClO<sub>4</sub> (i.e. 80% of the CMT concentration) are added; at the same time, the solution acquires absorption at longer wavelengths, which possibly indicates the formation of larger aggregates. The 275 nm peak disappears upon further addition and the 335 nm band builds up simultaneously. The final height of the 335 nm band is reached after the addition of  $4 \cdot 10^{-4}$  M Ag<sup>+</sup> ions, i.e. twice the molar concentration of CMT. It should also be noted that the 335 nm band develops practically instantaneously in alkaline solution containing excess Ag<sup>+</sup>, contrary to the slow development in slightly acidic solution.

Fluorescence observations were also made which corroborate the postulate of a monomer → aggregate conversion with pH. The slightly acidic solution develops a fluorescence band at 380 nm at the same rate as the 335 nm absorption band in Fig. 1 develops. During aging for several days, the fluorescence band still gains in intensity, although the 335 nm absorption band has long since reached its maximum value. Again, one concludes that slow rearrangements take place in the aggregate upon aging for longer times. A 1:1 solution of Ag<sup>+</sup> and CMT in the alkaline range does not fluoresce. However, the 380 nm fluorescence band is produced upon the addition of excess Ag<sup>+</sup> ions. When a slightly acidic solution is stepwise made alkaline (Fig. 2), the fluorescence band decreases and shifts to shorter wavelengths. In short, the fluorescence is always observed when the species absorbing at 335 nm is present, i.e. the

fluorescence is caused by the aggregate, the monomer not being able to fluoresce.

It should also be mentioned that the aggregate is not stable in solutions of  $\text{pH} < 2.5$ . These solutions become opalescent and after several minutes flocculation occurs. It thus seems that the aggregates of Ag-CMT are stable only in a limited range of pH. In alkaline solution they tend to dissociate to a certain extent to form the monomer, in strongly acidic solution they coagulate to yield insoluble Ag-CMT.

Experiments were also performed to find out whether the aggregates are stable in very dilute solutions. A  $2 \cdot 10^{-4} \text{ M}$  Ag-CMT solution at  $\text{pH} = 4$  was diluted with an aqueous  $\text{HClO}_4$  solution of the same pH and the intensity of the 335 nm band measured at various degrees of dilution. It turned out that the absorbance was proportional to the Ag-CMT concentration over the whole concentration range (down to  $1 \cdot 10^{-6} \text{ M}$ ) investigated.

A CMT-solution was also titrated with NaOH solution and the changes in pH recorded. From the two turning points in the titration curve one calculated a  $\text{p}K$  of 3.6 for the dissociation of the carboxyl group and  $\text{p}K = 10.2$  for that of the thiol group.

### Agglomerates of Silver-Carboxy-Ethane-Thiolate

A new absorption peak at 355 nm is formed when equimolar quantities of  $\text{AgClO}_4$  and CET are dissolved. As in the case of CMT, the new absorption band grows with time. The rate of growth is rather fast; after 5 minutes at  $\text{pH} = 4.5$  (Fig. 4), the band at 355 nm has already reached its maximum value. Upon aging for longer times, a second peak develops at 295 nm and the 355 nm peak becomes smaller. In the experiment of Fig. 4, the initial pH of the CET solution was 7.5; it dropped to 5.3 after the addition of  $\text{AgClO}_4$ . When solutions were prepared, where the final pH after addition of silver was below 4.2, a long-wavelength tail was present and the solutions became opalescent. At still lower initial pH's, a white precipitate was formed. It is concluded that hydrophilic agglomerates are present in slightly acidic solutions which become unstable and coagulate in more acidic solution. The process of flocculation is more pronounced than in the case of Ag-CMT at the same pH-value.

The fluorescence spectrum at various times after mixing the components is shown in Fig. 5. It has two bands at 370 nm and 325 nm. It can be seen that the 370 nm band is stronger in the beginning.

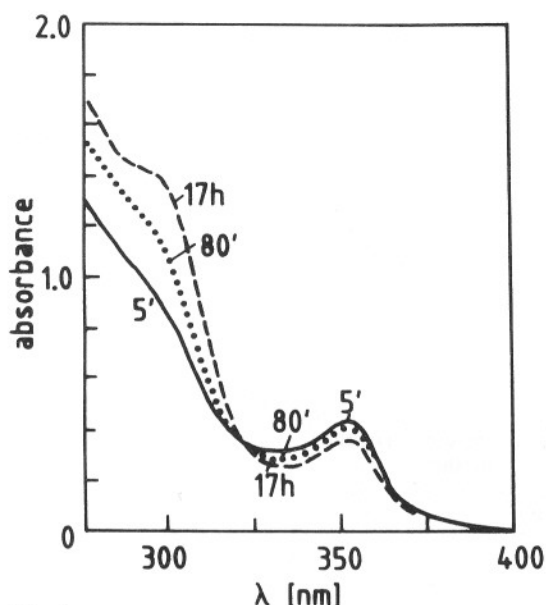


Fig. 4  
Temporal development of the absorption spectrum of aggregates in a solution containing  $2 \cdot 10^{-4} \text{ M}$   $\text{AgClO}_4$  and  $2 \cdot 10^{-4} \text{ M}$  CET

However, as the intensity of the fluorescence strongly increases upon aging, the 325 nm band becomes more prominent. This shows that the two fluorescence bands are not caused by the same species. After aging for 8 days the 335 nm absorption has almost disappeared and the fluorescence band at 370 nm is also very weak. We therefore attribute the 325 nm fluorescence to the species absorbing at 295 nm and the 370 nm fluorescence to the species absorbing at 355 nm. The two species must be agglomerates of different structure.

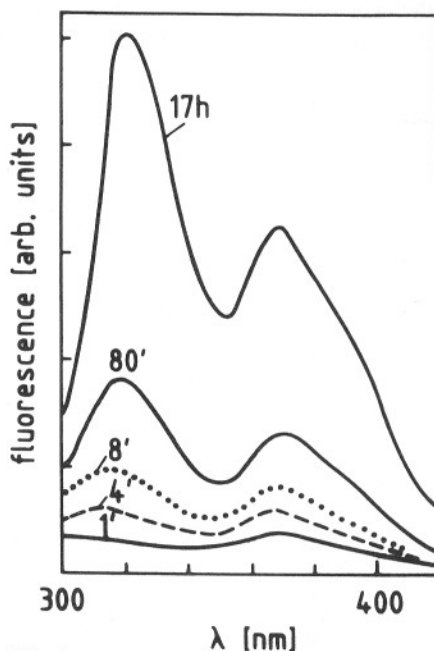


Fig. 5  
Fluorescence spectrum of an Ag-CET solution during aging. After 5 days, the fluorescence intensity was further increased by a factor of 5. Excitation at 280 nm

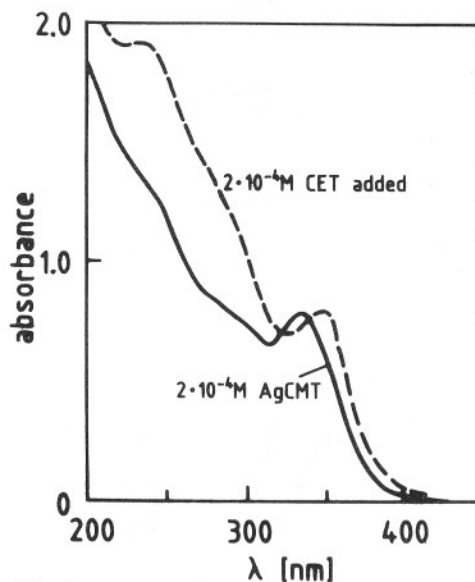


Fig. 6  
Absorption spectrum of an agglomerated Ag-CMT solution before and after addition of CET

When the slightly acidic solution of agglomerated Ag-CET was brought to  $\text{pH} = 10$ , both the 355 nm and the 295 nm absorptions

and the fluorescence disappeared. Contrary to Ag-CMT it was not possible to obtain agglomerates in alkaline solution containing excess  $\text{Ag}^+$  ions.

Titration of a CET-solution with NaOH yielded the pK-values of 10.2 and 4.2 for the dissociation of the SH and COOH groups, respectively. The carboxyl group of CET is much weaker than the carboxyl group of CMT.

### Relative Stability of the Aggregates

The Ag-CMT aggregate is less stable than the Ag-CET aggregate. This can be concluded from the experiments of Fig. 6, where  $2 \cdot 10^{-4}$  M CET was added to a slightly acidic solution of agglomerated Ag-CMT (1 hour old). It can be seen that the addition of CET caused the spectrum to switch to that of agglomerated Ag-CET with its maximum at 355 nm.

The greater stability of the Ag-CET aggregate was also encountered in experiments, in which the thiol group was to be exchanged by iodide or other halide anions. When  $2 \cdot 10^{-4}$  M KI was added to aggregated Ag-CMT, the spectrum switched to that of colloidal AgI (exciton peak at 425 nm) and the fluorescence of AgI was produced (narrow band at 430 nm). With added bromide, the reaction occurred more slowly, whereas added chloride did not have any effect. On the other hand, addition of  $2 \cdot 10^{-4}$  M iodide to a solution of agglomerated Ag-CET led to the formation of only a tiny amount of AgI. However, when CET was added to a colloidal AgI solution, the spectrum of AgI remained almost unchanged; it thus seems that agglomerated AgI and Ag-CET have about the same stability. (It may also be noted that the fluorescence of AgI was quenched upon CET addition, which indicates that molecules of the thiol are somehow bound to the AgI particles; similar quenching has previously been observed for adsorbed sulfide [6].)

Stable solutions of both Ag-CMT and Ag-CET aggregates coagulated when  $\text{NaClO}_4$  was added at concentrations greater than 10 mM. The precipitates were not peptized when the ionic strength was lowered again by washing with water. This shows that the aggregates are only metastable and electrostatically stabilized in solution.

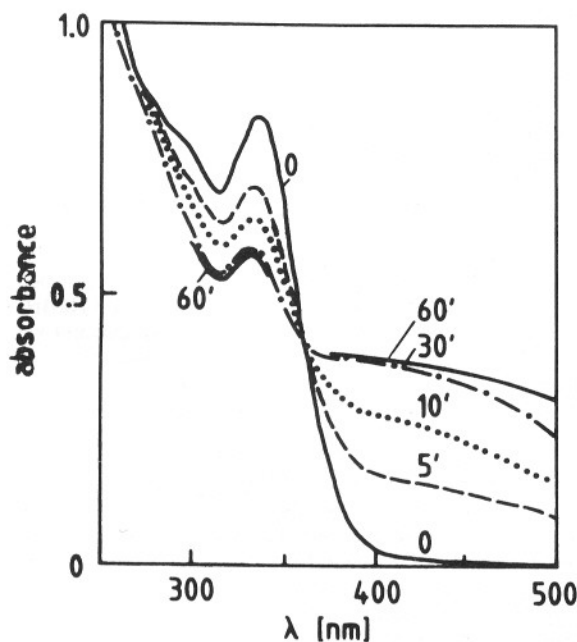


Fig. 7  
Illumination with 306 nm light of a  $2 \cdot 10^{-4}$  M Ag-CMT solution at pH = 3.7. Spectrum after various times of illumination under air

### Electron Microscopy

The electron microscopic pictures obtained corroborate the conclusion that small aggregates of Ag-CMT and Ag-CET are formed which grow upon aging and become more crystalline during the growth. In detail, the following observations were made:

The electron micrograph of a 1 h Ag-CET sample prepared by the freeze-drying technique contained particles of 25 Å with a rather narrow size distribution. The particles were electron beam amorphous. However, some particles were clustered, and in these structures lattice planes with a characteristic distance of 2.65 Å could be seen. An Ag-CET sample which had been aged for 1 week (no longer containing the 355 nm absorption band but a well developed 300 nm band, see Fig. 4) contained larger particles of about 100 Å with well developed lattice planes, the distance being 2.65 Å again.

When the room-temperature evaporation method for the preparation of an Ag-CET sample was used, the micrograph showed many plates several 100 nm large. Some plates overlapped; the lattice planes of the underlying plate could still be recognized which indicates that the plates were rather thin (<100 Å). The lattice spacing was 4.3 Å in these structures.

In the case of agglomerated Ag-CMT samples (1 hour old), small amorphous particles ranging in size between 20 and 60 Å were seen.

To sum up the observations: the well defined crystallinity and large lattice spacing of the aged samples indicates that the hydrocarbon chains may be fully extended in the lattice, which perhaps consists of tiers of hydrophobic monolayers with Ag-S planes sandwiched in between. The younger samples are less ordered.

### Photolysis

Fig. 7 shows the absorption spectrum of an Ag-CMT solution before and after illumination for various time periods. It can be seen that the 335 nm absorption decreases and a broad band develops in the 400 to 500 nm range. The latter absorption is attributed to large colloidal silver particles. A closer look at the 335 nm peak reveals that it moves towards slightly shorter wavelengths with increasing illumination time, i.e. as the particles become smaller. The rate of photolysis decreases with time. This can also be seen in Fig. 8 where the 500 nm absorbance of the photolysis product is plotted as a function of time. Practically no differences exist between illumination in the presence and absence of air. Likewise the fluorescence of the unphotolysed solutions was the same in the presence and absence of air. Fig. 8 also contains a curve for the photolysis of Ag-CET. One can see that this compound photolyzes at an appreciably lower rate.

Photolysis leads to a dramatic decrease in the intensity of the fluorescence band of Ag-CMT as can be seen from Fig. 9. Note

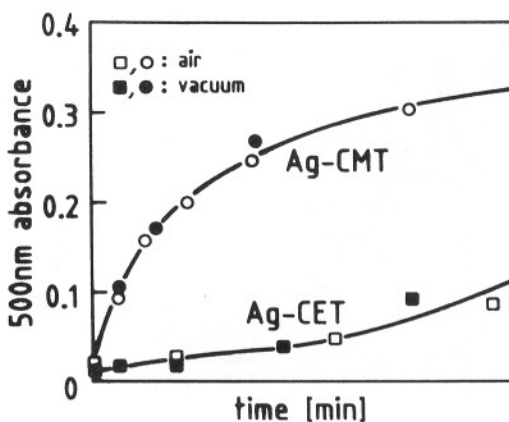


Fig. 8  
500 nm absorbance as a function of time for  $2 \cdot 10^{-4}$  M Ag-CMT (upper curve) and Ag-CET solutions (lower curve) illuminated in the presence (□, ○) and absence (■, ●) of air



the strong shift of this band to shorter wavelengths as the photolysis proceeds, i.e. as the particles become smaller. After just 0.5 minutes in Fig. 9, the fluorescence intensity is already significantly decreased while practically no decrease in the 335 nm absorption is observed after this short time. It is concluded that the decrease in fluorescence intensity is not due to the consumption of Ag-CMT but to a quenching action of the silver formed.

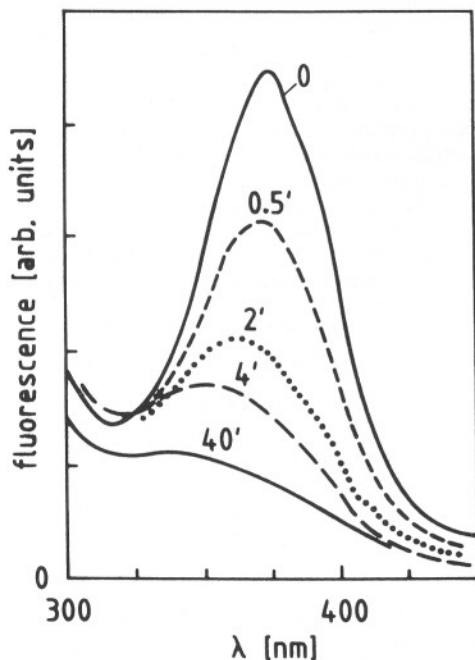


Fig. 9  
Fluorescence band of Ag-CMT after various times of illumination (compare with Fig. 7)

### Reduction of Silver-Carboxy-Alkane-Thiolates

When small amounts of sodium borohydride,  $\text{NaBH}_4$ , are added to a deaerated solution of silver perchlorate, the yellow color of colloidal silver appears [5a]. The absorption spectrum contains the strong surface plasmon absorption band at 380 nm, which is caused

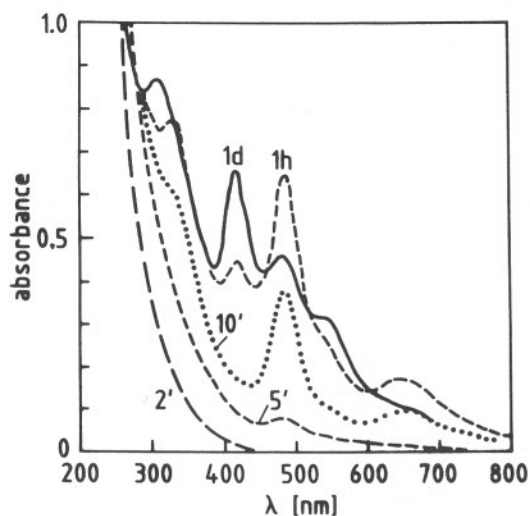


Fig. 10  
Reduction of a Ag-CET solution ( $2 \cdot 10^{-4}$  M  $\text{AgClO}_4$  plus  $3 \cdot 10^{-4}$  M CET at pH = 9.8) by  $\text{NaBH}_4$ . Absorption spectrum at different times after the addition of the reducing reagent

by the excitation of the electron gas in the metallic silver particles. The particles formed have a size of about 4 nm.

Quite different phenomena are observed when this reduction of silver ions is carried out in the presence of a carboxy-alkane-thiol. Fig. 10 shows the absorption spectrum of a solution at different times after the addition of  $\text{NaBH}_4$  (10mg/100ml). Several absorption bands are produced, the relative intensities of which change with time. After 10 minutes, a rather narrow band at 485 nm and a broader one at 645 nm are present. After 1 hour, these two bands are more intense and a new band at 415 nm starts to be formed. After 1 day, the 485 and 645 nm bands are still present but with decreased intensity and the 415 nm band dominates the spectrum. Note also that a band at 350 nm develops at the beginning which finally produces a maximum at 340 nm. It is quite clear from these observations that the silver particles formed in the presence of CET are different from the usual silver colloids generated in the absence of carboxy-alkane-thiol.

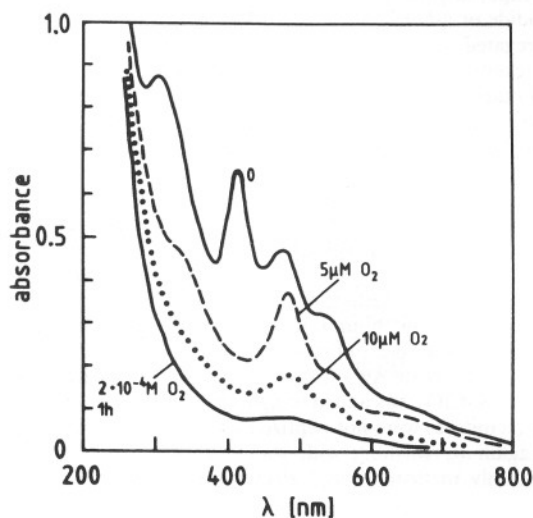


Fig. 11  
Absorption spectrum (0) of a Ag-CET solution (see Fig. 10;1d) and spectra after the addition of various concentrations of oxygen

Interesting changes also occur when a reduced Ag-CET solution is exposed to oxygen. As can be seen from Fig. 11, a concentration of  $5 \mu\text{M O}_2$  makes the 415 nm band disappear practically instantaneously. At  $10 \mu\text{M O}_2$ , the 485 and 645 nm bands also decrease. Finally, when the oxygen concentration was increased to  $2 \cdot 10^{-4}$  M and the solution aged for 1 hour, these two latter bands disappeared almost completely. The solution was now brought to pH = 3.5 by adding  $\text{HClO}_4$ ; it was then observed that the 355 nm absorption of the Ag-CET agglomerate developed as described above (Fig. 4). To sum up the observations: reduction by  $\text{NaBH}_4$  in the presence of a thiol compound leads to silver species not yet described in the literature. They have different reactivities towards oxygen. They are oxidized by  $\text{O}_2$ , and the  $\text{Ag}^+$  ions thus released can reform aggregated Ag-CET in acidic solution.

The question arises whether the silver particles formed in solutions containing CET are different because CET is already present during their formation or because CET changes the properties of the silver particles after their formation. To answer this question the experiment of Fig. 12 was carried out. A deaerated solution of colloidal silver (particle size about 40 Å) was prepared by UV illumination of a solution containing  $1 \cdot 10^{-4}$  M  $\text{AgClO}_4$ ,  $1 \cdot 10^{-4}$  M sodium polyacrylate (as stabilizer), 0.5 M propanol-2 and 0.01 M acetone. After complete reduction of the silver ions, the spectrum contained the 380 nm surface plasmon absorption band (curve 0 in Fig. 12). Various amounts of CET were now added under the exclusion of air. It can be seen that the plasmon absorption band decreased and shifted towards longer wavelengths. CET concentra-

tions exceeding  $3 \cdot 10^{-4}$  M did not cause further changes. This experiment shows that the spectrum of silver particles is indeed changed by CET. However, the spectrum obtained is not structured as the one in Fig. 10 is. One concludes therefore that the silver particles formed in the presence of CET are not the same as the ones which are formed in its absence.

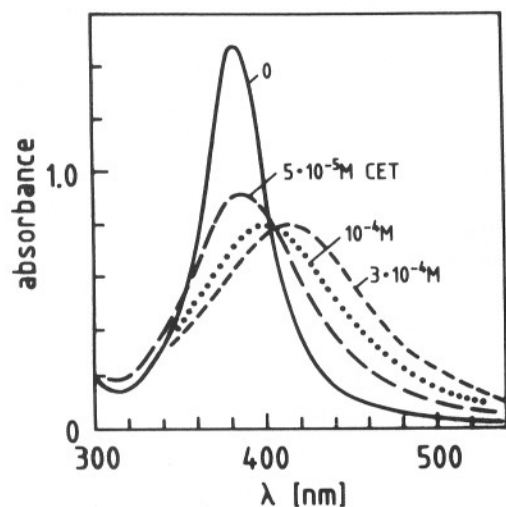


Fig. 12 Spectral changes upon addition of various amounts of CET to a colloidal solution of metallic silver particles

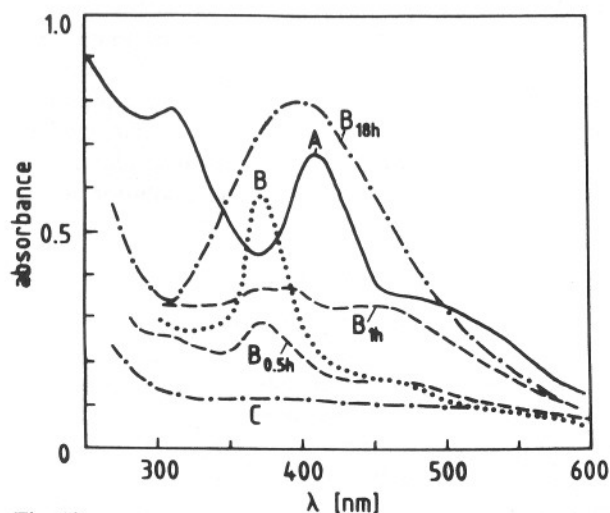


Fig. 13 A: Spectrum of a reduced Ag-CET solution at pH = 9.8. B: spectrum shortly after addition of  $1 \cdot 10^{-3}$  M KCN.  $B_{0.5 \text{ to } 18 \text{ h}}$ : spectrum after various times of aging. C: spectrum after final addition of air

We now turn our attention to the extreme sensitivity of the silver particles producing the 415 nm absorption band towards oxygen (Fig. 11). The only silver species which are known to be oxidized so rapidly are clusters consisting of a small number of atoms [5]. One may thus suspect that the silver agglomerates formed in the reduction of silver ions in the presence of CET are, at least in part, oligomeric clusters.

It is further known that silver particles react with nucleophilic reagents such as  $\text{CN}^-$  and  $\text{SH}^-$  via "pre-complexation" of surface atoms [5a]. Thiolates are expected to have some nucleophilic properties, although possibly not as strong as  $\text{CN}^-$ . In the experiment of Fig. 13, an Ag-CET solution was completely reduced. Curve A

is the spectrum after reduction which contains the strong band of the 415 nm cluster. Upon addition of  $1 \cdot 10^{-3}$  M KCN, the spectrum changed practically instantaneously; it now contained a rather narrow band at 370 nm (spectrum B). This is explained by exchange of the thiolate surface groups for  $\text{CN}^-$  ions, and this exchange is accompanied by a shift in absorption from 415 to 370 nm. Note that a cluster absorbing at 370 nm has been observed previously in the reaction of a naked 345 nm cluster with  $\text{CN}^-$  [5a]. It is possible that the 415 nm cluster observed in the present work is identical to the 345 nm cluster in the previous work, but absorbing at longer wavelengths simply because of its complexation by a thiol.

The 370 nm band in Fig. 13 faded away within about 1 hour to produce an absorption around 460 nm. Similar behaviour has been observed previously for the  $\text{CN}^-$ -complexed 345 nm cluster mentioned above [5a]. After longer times, the plasmon absorption band of larger silver particles finally developed in the experiment of Fig. 13. These effects are explained by the fact that  $\text{CN}^-$  groups on a cluster do not stabilize it (as do CET molecules); the clusters therefore react with each other to yield larger metallic particles [5a]. When air was finally admitted to the aged solution, the plasmon absorption band disappeared rapidly to yield spectrum C in Fig. 1. In fact, it has already been shown that silver particles carrying  $\text{CN}^-$  groups on their surface are very rapidly dissolved by oxygen [5a]. To sum up the experiments of Fig. 13: Evidence is obtained that during the reduction of  $\text{Ag}^+$  in the presence of CET reactive small silver particles are generated which are chemically similar to the very small silver clusters previously investigated [5].

Distinct absorption bands were also observed during the reduction of Ag-CMT by sodium borohydride, which showed similar behavior towards oxygen as the bands described for reduced Ag-CET. It is concluded that CMT has a similar effect in the reduction of  $\text{Ag}^+$  as CET: various silver aggregates including oligomeric clusters are formed.

## Discussion

### Micelle Formation

As pointed out above, the experimental findings are best understood in terms of Ag-CMT and Ag-CET forming agglomerates in slightly acidic solution. The size of the agglomerates must be rather limited as these solutions are transparent. Only more acidic solutions are opalescent. The aggregates are less stable in alkaline solution.

The question arises whether the agglomerates are dimers or consist of a larger number of molecules, comparable to the size of organic micelles. Generally, when monomer molecules agglomerate to form an organic micelle, no significant changes in the absorption spectrum occur. However, in our present cases, the agglomeration is accompanied by important changes in the optical properties: In the case of Ag-CMT, a new absorption band is produced, and in the case of Ag-CET, even two bands appear. Furthermore, the agglomerates fluoresce while the monomers do not.

Two observations on the fluorescence indicate that the agglomerates consist of a larger number of molecules. It was observed in the photolysis experiments that even a very small amount of reduced silver significantly quenched the fluorescence, although the amount of Ag-CET material decomposed was practically negligible (Figs. 7 and 9). Per silver atom formed, many molecules of Ag-CMT must have been deactivated with respect to their ability to fluoresce. This effect cannot be explained by the postulate of dimeric agglomerates. It must be the property of a large agglomerate, where fluorescence is produced by a cooper-

ative action of all participating molecules. The second observation is the blue-shift of the fluorescence band (accompanied by a weak blue-shift of the absorption band) with increasing illumination time in the photolysis. The size of the agglomerates possibly becomes smaller as more and more molecules are decomposed. One then has to postulate that the absorption and fluorescence are dependent on the size of the agglomerates. Such a conclusion can also be drawn from the observed red-shift of the absorption maximum as the agglomerates slowly develop (Fig. 1), and from the blue-shift upon dissolution of the aggregates in alkaline solution (Fig. 2). Again, these phenomena would not be expected for dimeric agglomerates.

At this point we would like to draw attention to numerous observations made on the absorption and fluorescence behaviour of extremely small inorganic semiconductor particles in colloidal solution [1]. Their absorption and fluorescence bands shift with decreasing particle size to shorter wavelengths. The electrons and positive holes generated by light absorption feel the restriction in space; their electronic energy levels become less and less dense. Particles which show this behavior are often called "quantized" or "Q-particles". The absorption peak in the spectrum of such particles is due to the optical transition to the first excitonic state. The fluorescence, which often shows a Stoke's shift with respect to the position of the exciton absorption band, is due to the recombination of charge carriers.

The agglomerates of Ag-CMT and Ag-CET show exactly the same behavior as the inorganic semiconductor particles. This striking parallelism makes us propose a structure for the agglomerates with an "inorganic" part consisting of planes of  $\text{Ag}^+$  cations and  $\text{S}^-$ -anions, which is semiconductor-like. The planes are separated from each other by the  $-\text{CH}_2-\text{COOH}$  (CMT) or  $-\text{CH}_2-\text{CH}_2-\text{COOH}$  (CET) groups on the  $\text{S}^-$ -anions. The whole structure is a "micelle" with semiconductor-like ionic planes in the interior and organic head groups that stabilize it in aqueous solution. Maximum stability exists in slightly acidic solutions, where the carboxyl groups on the surface are only slightly dissociated. When the solutions are too acidic, the COOH groups are fully protonated and this leads to a coagulation of the micelles to yield a precipitate. In alkaline solution, the electrostatic repulsion between the completely ionized carboxyl headgroups forces the monomeric units out of the micelles which would explain why aggregates are less stable under these conditions. That micelles of Ag-CMT can be stable in alkaline solution in the presence of excess  $\text{Ag}^+$  ions is possibly due to the electrical neutralization of the carboxylate groups by bound  $\text{Ag}^+$  ions, the above electrostatic repulsion thus being decreased. The absorption bands at 335 nm (Ag-CMT) and 355 nm (Ag-CET) are attributed to the optical transition to the first excitonic state. The rather short wavelengths of the excitonic absorption bands indicate that the excitons are rather small. This may be the reason why these bands can already be seen in very small agglomerates which have a rather disordered structure.

The micelles of Ag-CMT develop rather slowly in slightly acidic solution. The immediate pH-drop upon mixing the components is attributed to the partial substitution

of the protons of the carboxy groups by  $\text{Ag}^+$  ions. The molecules of  $\text{HS}-\text{CH}_2-\text{COOAg}$  thus formed are then transformed into  $\text{Ag}-\text{S}-\text{CH}_2-\text{COOH}$ , which subsequently agglomerates. The transformation requires the dissociation of the thiol group, which is a rather slow process in acidic solution. On the other hand, Ag-CMT agglomerate formation is fast in alkaline solutions containing excess silver ions because of the faster dissociation of the thiol group.

Ag-CET also forms agglomerates in acidic solution. The rate of formation is greater than for CMT and it seems that two kinds of agglomerates with different absorption and fluorescence bands are formed. Furthermore, Ag-CET does not form agglomerates in alkaline solutions in the presence of excess silver ions.

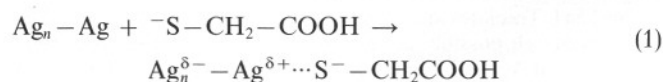
The critical concentration of conventional organic micelles with ionized head groups is generally of the order  $10^{-3}$  M. In these structures, the adhesive forces keeping the micelle together are the weak Van der Waal interactions between the hydrocarbon chains. The great stability of semiconductor-like silver carboxy-alkane-thiol aggregates at low concentrations is understood in terms of the strong ionic interactions in the "inorganic"  $\text{Ag}^+ - \text{S}^-$  planes, and the weak ionization of the head groups.

According to the above proposal for the structure of the agglomerates, the interaction between  $\text{Ag}^+$  ions and the thiol group is the decisive factor, whereas the carboxyl group on the organic chain serves only as a hydrophilic head group. This is corroborated by first experiments with the compound  $\text{HS}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  in alkaline solution. It was found that the aggregate formed had its band at 355 nm, just like aggregated Ag-CET. (We may also add that in this case the monomer is present in acidic solution where the amino group is protonated).

### Silver Clusters as Reduction Products

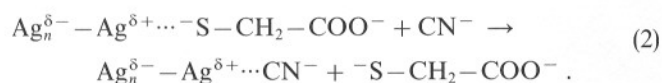
It has been found previously that silver ions can be reduced by sodium borohydride in solutions containing a polyanion (such as sodium polyphosphate or polyacrylate) to yield long-lived clusters of non-metallic silver [5]. These clusters are stabilized by the nucleophilic anion groups of the polymer. In the present work on the reduction of silver ions in the presence of a carboxy-alkane-thiols similar effects are observed: some of the reduced silver species have absorption bands and chemical reactivities which resemble the ones observed previously by radiolytic reduction of silver ions in the presence of a polyanion. It thus seems that the carboxy-alkane-thiols have a stabilizing effect similar to the effect of the polyanions. However, the thiols have a much stronger influence on the position of the absorption bands of the silver clusters than the phosphate or carboxyl groups of the polyanions used previously.

This interaction with nucleophilic reagents has already been described in terms of the "pre-complexation" or "pre-oxidation" of surface atoms [5a].



As the thiolate interacts with a surface atom (designated by italic letters), this atom receives a small positive charge, the rest of the silver particle acquiring an excess negative charge. Such aggregates are especially sensitive to oxygen, which picks up the excess negative charges, thus facilitating the complete complexation (or oxidation) of the silver atoms. The great reactivity of small silver particles towards nucleophilic reagents is attributed to the coordinative unsaturation of the surface atoms. In the case of metallic silver particles (consisting of about a thousand atoms) the interaction with thiolates leads to a decrease and broadening of the surface plasmon absorption band (Fig. 12).

The silver clusters formed in the presence of thiolate do not have the same absorption bands as the non-complexed clusters. When another reagent with stronger nucleophilic properties is added, the surface atoms of the cluster may undergo an exchange of nucleophiles. In the present experiments, this was shown to occur upon the addition of  $\text{CN}^-$  ions:



Contrary to the  $\text{S} - \text{CH}_2 - \text{COO}^-$  surface group, the  $\text{CN}^-$  group on the surface of the particle has a destabilizing effect since it provides little steric hindrance to particle collisions, the result being reactions among such pre-complexed clusters to yield larger silver particles.

### Final Remarks

It is known in analytical chemistry that thiols can be determined using  $\text{Ag}^+$ , coloured complexes being formed by their interaction [7]. Andersson obtained the first evidence for the formation of "polymers" when he carried out amperometric and spectrophotometric (280 nm) titrations of various organic thiols with  $\text{Ag}^+$  ions [8]. He even proposed chains of the type  $-\text{Ag} - \text{S}(\text{R}) - \text{Ag} - \text{S}(\text{R}) - \text{Ag} - \text{S}(\text{R}) -$  in these polymers.

Our present conclusions about the formation of agglomerates of silver-carboxy-alkane-thiolates which are comparable in size to conventional organic micelles in aqueous solutions, are based mainly on optical absorption and fluorescence measurements. In the interpretation of the data, use is made of the comprehensive knowledge about the optical properties of extremely small inorganic semiconductor particles, which has been accumulated during the past few years. On the basis of this knowledge, structures with a

semiconductor-like ionic planes are formulated for the  $\text{Ag} - \text{CMT}$  and  $\text{Ag} - \text{CET}$  aggregates, which show the typical properties of quantized materials. The layered structure of crystalline compounds  $\text{AgSR}$  has also been derived recently from powder X-ray diffraction studies [9]. The absorption changes of the silver particles in the presence of a thiol are also of interest with respect to the "toning" of photographic plates [10].

The results of the electron microscope studies corroborate the idea of the existence of such structures. However, the details of the structures are not yet clear and their complete elucidation requires further investigations. Naturally, one intends to change the structure of the thiols and even to substitute other cations for the silver ions to find out whether this class of semiconductor-like materials is only restricted to the examples described in this paper or encompasses many more materials. It seems possible that various metal-thiol complexes previously described may indeed form aggregates with the optical properties of ionic semiconductors.

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