From the van't Hoff-Laboratorium, Rijksuniversiteit Utrecht, Utrecht (Netherlands)

Carey Lea's colloidal silver

By G. Frens and J. Th. G. Overbeek

With 4 figures and 3 tables

Introduction

The reddish-brown hydrosol of silver that was first prepared by *Carey Lea* (1) in 1889 was studied rather extensively around the turn of the century. One of the properties of this colloid which attracted attention was the easy repeptization of the sol particles after they had been coagulated with electrolytes. It is often sufficient to wash away the flocculating salt from the coagula in order to redisperse the original particles.

This is not common for a colloidal dispersion of a noble metal. Therefore, the idea has arisen that *Carey Leas* preparation, although it resembles the lyophobic colloids in many respects, must not be classified among the "electrocratic" systems which owe their stability to the electrical double layer at the particle-solution interface. Instead, it would be a protected colloid (2). The surface of the particles might be covered with some, as yet unidentified, macromolecular substance.

As a part of a general study on the repeptization of electrocratic (lyophobic) sols (3), we reinvestigated *Carey Leas* sol. To characterize the silver-electrolyte interface in this colloid we could use some methods that were not available half a century ago. We did not find proof of the hypothetical "macromolecular substance" that was assumed to adhere to the particles. Somewhat surprisingly, we had to conclude that *Carey Leas* sol is a rather normal electrocratic colloid.

Experimental

Chemicals were of "Analytical Reagent" quality. Radioactive citric acid was purchased from The Radiochemical Centre, Amersham, England. Water was redistilled twice, the last time from a tinned still with a silver cooler. Glassware was cleaned with hot, concentrated nitric acid, rinsed with distilled water, and thoroughly steamed before use.

a) Preparation of a silver sol according to Carey Lea

The following solutions are used to prepare the sol:

a – Na$_3$citrate $\cdot$ 2 H$_2$O	400 g/l	
b – FeSO$_4$ $\cdot$ 7 H$_2$O	300 g/l	
c – AgNO$_3$	100 g/l	
d – NaNO$_3$	1 M	or
d' – KNO$_3$	1 M	

By mixing 3.5 ml of solution a with 2.5 ml of the freshly prepared solution b, a strongly reducing agent is obtained ($E_{red} = -0.2$ V vs. n.h.e.). This mixture is added under vigorous stirring to 2.5 ml of solution c, and the blue-black precipitate of flocculated silver is isolated by centrifugation. The sediment is redispersed in 5 ml water, and then reflocculated with 5 ml of either solution a, d, or d'. Redispersion and reflocculation are repeated three times. Finally the precipitate is redispersed in water and a dark brown concentrated sol is obtained.

If we wanted a radioactive label on the citrate in the sol, we added 1 mg citric acid – 1,5 C^{14}, containing 0.05 mc to 1 l of solution a prior to the preparation and washing procedures.

b) Fractionated coagulation

Odén (4) has described how fractions of different stabilty and colour can be isolated from a *Carey Lea* sol by "fractionated coagulation" with 1-1 electrolytes. As we wanted our sols free from the large concentrations of intermicellar salt which result from *Odéns* procedure, we followed a related technique, which gives the same type of fractions from a sol.

To the original sol KNO$_3$ or NaNO$_3$ was added up to a concentration C_1. The flocculated material – the least stable fraction – can be centrifuged off. Then the salt concentration is raised to C_2. The now flocculating material is isolated by centrifugation and redispersed in water. The resulting sol behaves like a complete *Carey Lea* sol, but it will flocculate between concentrations C_1 and C_2. Such a fraction of the sol will be indicated as F C_1–C_2 throughout this paper.

c) Analytical procedures

The Ag content of sols was determined after dissolution of the metallic silver in some H$_2$SO$_4$ and H$_2$O$_2$. The Ag$^+$ concentration was obtained from a potentiometric titration with NaCl. Alternatively Ag could be determined directly in the sol by the use of a Unicam SP 900 flame photometer. Measurements were made at $\lambda = 328$ nm with AgNO$_3$ solutions as standards. The accuracy and the agreement of both methods was about 1%.

The Na$^+$ concentrations were also determined with the Unicam SP 900 ($\lambda = 592$ nm) with NaNO$_3$ solutions as standards. For Na$^+$ determinations the sols were diluted 100 X. The accuracy of the Na$^+$ determinations was better than 1%.

Fe was determined colorimetrically as Fe^{2+} with the thiocyanate method. 5 ml sol, diluted to contain approximately 100 mg Ag were heated on a water bath with 0.08 ml 65% HNO$_3$ (Fe – free, Merck) and 2 ml 5% H$_2$O$_2$ until the metallic Ag was dissolved. 115 mg KCl, dissolved in 2 ml H$_2$O were added and the AgCl precipitate was coarsened by prolonged heating. The precipitate was removed by centrifugation. The supernatant solution and 5 ml 20% KCNS were mixed and made up to 50 ml. A standard solution was prepared, containing 100 mg Ag, 0.1 mg Fe and 15 mg Na citrate

in 5 ml, and a blank which contained 100 mg Ag and 15 mg Na citrate. Standard sol and blank underwent identical treatment (described above) at the same time. The resulting color was measured at 470 nm and at 500 nm.

Citrate was either determined colorimetrically or by a radiochemical determination of labeled citrate. In the colorimetric method, which was developed and described by *Huizinga* (5), the citrate is degraded and brominated to penta-bromoacetone. This compound is isolated through extraction with petroleum ether. The petroleum ether fraction is shaken with an aqueous solution of thiourea and $Na_2B_4O_7$, and a yellow complex forms. Its concentration was determined at 450 nm in a Unicam SP 500 spectrophotometer. The optical density of the samples was compared to that obtained from standard citrate solutions by the same procedure at the same time. The accuracy of the method is better than 10%.

For the radioactive determination, 0.05 ml of a labeled sol or solution were absorbed in filter paper and dried at 60 °C. The radioactivity of such samples was measured in a "Nuclear Chicago System 725" liquid scintillation counter. A series of internal standards, where known amounts of radioactive citrate had been added to the sol was run with each determination.

Although the results of the radioactive determinations looked more precise than those of the colorimetric method, they were systematically lower. In good experiments the results of the two methods agreed within 10%.

d) Electrophoresis

The electrophoretic mobility of the sol particles was measured in moving boundary-type experiments. The boundary was formed between a sol and a portion of the supernatant liquid from the same sol when it had been centrifuged 1 hour at 80,000 g. The conductivity of the two solutions was equal, which indicates that the transport of electricity by the particles is negligible compared to that of the intermicellar electrolyte. The Pt-electrodes of the cell were located in open electrode compartments at 25 cm from the boundaries. Measurements were made during 10 minutes in two directions of the current, and at 24 °C ± 0.3°. The current density at the boundary did not exceed 5 mA/cm². Double layer charges and ζ-potentials were calculated as indicated by *Wiersema* (6).

e) Electron microscopy

A sol, diluted to contain an appropriate number concentration of particles was sprayed over collodion-covered Cu grids from an all-glass vaporizer. Only small droplets, a few μ in diameter, reach the grid in this device. They will rapidly evaporate and leave the particles behind on the collodion.

This evaporation process tends to concentrate many particles on a small area. Therefore, sometimes the collodion membranes were rendered hydrophilic through treatment with a surfactant solution (Cetyl-pyridinium nitrate) before the sol was sprayed upon them. Then, the droplets would spread over the collodion and leave individual particles all over the grid.

The electron microscopical work was done in the Centre for Electron Microscopy of the Utrecht University. Electron micrographs were made in the Philips EM 200, or in the Siemens Elmiskop I microscopes. Particle sizes were obtained from micrographs with a 282,000 × magnification. Averages were taken over at least 1000 measured particles for each sol. Obvious aggregates were not taken into account.

Particles were counted on at least four different micrographs, obtained from three or more different preparations of each of the sols. The size of an individual particle could be determined within 10%. The uncertainty in the magnification of each micrograph was less than 5%. Therefore, the reliability of the obtained average particle radii is about 2%.

f) Absorption spectra

Absorption spectra, both of the sols and of the fractions of various colours, as mentioned under *b*, were determined in a Beckman DK-2 spectrophotometer. Distilled water was used as a reference liquid.

Results

a) Particle size, surface area

Electron micrographs of the *Carey Lea* sol (fig. 1) show crystalline particles of a fairly uniform size. The average particle radius varies from $\bar{a} = 37 \pm 1$ Å to $\bar{a} = 45 \pm 1$ Å for different sols. Casting a Pt-shadow over the particles reveals that they are spherical.

In the course of our electron microscopic work on the *Carey Lea* sol we observed in our preparations many of the phenomena that are known (7–10) to occur in the electron-microscopic observation of vacuum-deposited "thin" discontinuous metal films:

Fig. 1. Electron micrograph of a *Carey Lea* silver sol

e. g. the liquid-like coalescence of particles, and the empty traces that are left behind when coalescing particles move over the substrate to recrystallize in larger units.

The vacuum-deposited films consist of "islands". These are small particles, formed through nucleation and growth when individual metal atoms are deposited on the substrate (10, 11). In our sol, however, the particles were formed in an aqueous suspension. They went through cycles of flocculation and repeptization. Eventually they were left behind on the substrate when the water evaporated from between them. It is obvious that there is no analogy in the preparation of "thin films" according to these two procedures. However, the particle size in the "films" is the same as in the dried colloidal silver. The analogy in behaviour of these preparations is so striking that we suppose that such observations are a common property among very small metal particles on solid substrates. The presence of surfactant on the collodion immobilizes the particles at larger interparticle distances and effectively prevents their coalescence. In the absence of the surfactant a weak electron beam was used to reduce the chances of coalescence.

A distribution diagram of the particle sizes in one typical sol is shown in fig. 2. From this type of diagram the ratio between the volume and the surface area of the silver in each sol may be obtained through summation of these quantities over the particle fractions with different sizes.
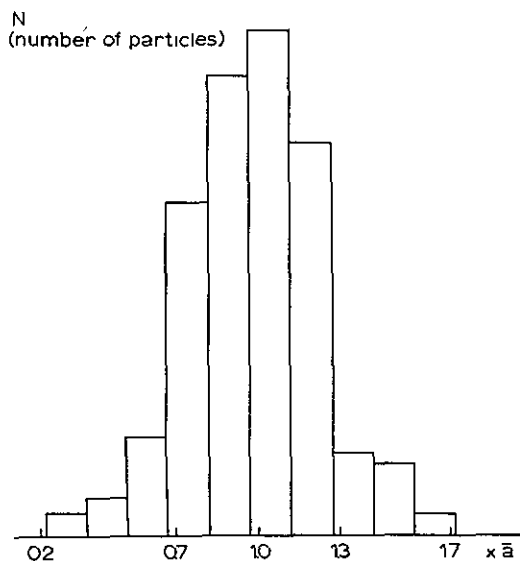
N
(number of particles)

Fig. 2. Distribution of particle sizes in a *Carey Lea* sol.
$\bar{a} = 37$ Å

An X-ray diffraction pattern of the coagulated, but still repeptizable, *Carey Lea* sol was obtained. It shows the powder diagram of the normal Ag-lattice and, of course, a considerable broadening of the lines. Thus, assuming that the density of the particulate material equals that of normal bulk silver ($d = 10.5$), we can calculate the surface area per g Ag in the sol. This quantity can be related to the analytically determined Ag concentrations. It turns out that 1 g Ag has an area of about 70 m^2 in a normally prepared sol.

This result changes to a considerable extent the picture of a *Carey Lea* sol as it was obtained from the early investigations. *Odén* had counted particles in an ultramicroscope. He determined the Ag content of the sol and calculated that $\bar{a} = 385$ Å (12)[1]. *Schneider* (13) had determined that 97% of the solid material in the sol is Ag. The remaining 3% could not be analysed at that time since there was no suitable determination method for citrate available.

Such results left room for the theory that the unidentified 3% was macromolecular material which covers the particles and protects the colloid. However, if the surface area is ten times larger than *Odéns* estimate – as our data indicate – 3% of the material would hardly be enough to cover the particles with a single layer of citrate ions.

b) Analytical data, surface coverage

The protecting agent that allegedly covers the particles of a *Carey Lea* sol must be built from the materials that were used to prepare the sol. It must be formed under the conditions of the sol preparation. It must be stable under the conditions that prevail in the sol. It must be present in the flocs from the sol after their coagulation.

Such ions as Na$^+$, Ag$^+$, SO$_4^{2-}$ or NO$_3^-$ are not likely to form protecting polymers. An insoluble iron oxide layer could possibly cover the particles. Citrate might have undergone polymerization and protect the sol, or there might be an adsorbed polymer, consisting of both iron and citrate (2, 28). Therefore, the amount of Fe, of citrate and of Ag in 1 ml of the sol was determined.

[1] One year earlier, however, *Zsigmondy* (2) described how he could only see a few particles in a *Carey Lea* sol when he used an ordinary electric arc as the light source for the ultramicroscope, but that he saw a few large and very many small particles when he illuminated his sol by focusing sunlight on it. *Odén* must have missed the smaller particles.

The same analysis was made on 1 ml of the supernatant solution after coagulation of the same sol and centrifugation. Subtraction of the quantities so determined gives the amounts of material which are carried from 1 ml sol by the coagulated, but still repeptizable Ag particles. The amount of Ag in that ml, and its surface area as obtained from electron microscopy give the surface that is covered by this adherent material.

The tables 1 and 2 present some typical results of this determination method for the amount of adsorbed citrate in sols of different age, history and treatment during their eventual coagulation.

Table 1. Surface coverages in some types of
Carey Lea sol

A is the area (in $Å^2$) that is available for every adsorbed citrate molecule. N indicates a freshly prepared sol, 0 a sol that is 1 week old. F 100–140 means a fraction that flocculates between 100 and 140 mmol/l 1–1 electrolyte. γ is the concentration of inert salt used to separate the particles from the solution by flocculation. $\bar{a}$ is the mean particle radius, + means that the flocs would and – that they would not repeptize in water.

Sol	γ (mmol/l, KNO_3)	$\bar{a}$ (Å)	A (Å²)	
N, complete	500	45	35	+
N, F 100–140	200	51	62	+
N, F 250–300	350	47	48	+
0, complete	500	42	40	+
0, F 75–100	120	60	57	+
0, F 175–200	250	45	47	+

Table 2. Influence of flocculating electrolyte on surface coverages (symbols as in table 1)

Sol	γ (mmol/l)	Salt	A (Å²)	
0, F 75–100	250	KNO_3	57	+
0, F 75–100	500	KNO_3	200	–
0, F 175–200	250	KNO_3	50	+
0, F 175–200	500	KNO_3	200	–
0, complete	500	KNO_3	40	+
0, complete	2	$La(NO_3)_3$	35	–

Indeed there is a considerable adsorption of citrate. In its flattest conformation one citrate ion could cover about 50 $Å^2$. If we compare the area per molecule A to the dimensions of a citrate ion, we see that in the – still repeptizable – flocs there is about one monolayer of adsorbed citrate. Therefore, there is no building material for a bulky citrate polymer structure which covers the particles, extends into the solution, swells upon dilution in order to cause repeptization, and so protects the *Carey Lea* sol.

The results of the iron determinations depend very much on the previous treatment of the sol and bear no relation to its colloid chemical properties. In the preparation process of a *Carey Lea* sol the coagulated silver particles were always washed with solutions of inert salts. If KNO_3 or $NaNO_3$ solutions were used, the sol might, in accordance with earlier observations (1, 15), contain as much as 4 mg Fe for each g Ag. If, however, the washings with KNO_3 or $NaNO_3$ were preceded by a single washing with a Na-citrate solution, the eventual amount of Fe in the complete sol (particles + intermicellar solution) was reduced to 0.3 mg Fe per g Ag. In such sols, which were as repeptizable as the previous type, there is only one atom of Fe for every 40 of these citrate ions that are adsorbed at the surface of the particles. This result makes the presence of a macromolecular compound of Fe and citrate very unlikely and rules out the possibility that the particles are covered with iron oxide. It appears that the polyvalent Fe ions are indeed strongly adsorbed in the double layers around the particles, but that they are not of special importance in respect to the repeptization of the flocculated sol.

c) Charge on the silver particles, the electrical double layer

Around the particles of a *Carey Lea* sol there is an electrical double layer, and the adsorbed citrate ions are a part of that system of charges. We tried to estimate the charge that is located in the particles by determining the concentrations of all charged species in some sols. Electroneutrality demands that the sol as a whole is uncharged. So, if we succeed in a quantitative determination of all the ions in the sol, and find a difference in the summed charges of cations and anions, the remaining charge must reside in the particle material.

We used sols that had been washed 3 times with Na-citrate solutions after their preparation, and that were not treated with KNO_3 or $NaNO_3$ afterwards. From such sols, Fe^{2+}, Fe^{3+}, SO_4^{2-}, and NO_3^- are absent beyond the limits set by the accuracy of the citrate determination. Of the remaining species, Ag^+ and H^+ (or OH^-) are not significant in this respect either. We have determined these ions because they may have a potential-determining role in the silver-electrolyte interface. The major part of the ionic charge in the solution is carried by the Na^+ and the citrate ions. We measured

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the concentrations C_{H^+}, C_{Ag^+}, C_{Na^+}, and $C_{citrate}^{3-}$ (eq/1), and present these in table 3 together with the silver content of the sol m_{Ag} (mol/l). From these data the missing charge, $q_0 = -\dfrac{C_{Na^+} - C_{citr}^{3-}}{m_{Ag}}$ (eq/mol Ag) is found.

Electron microscopy has already given us the area S (cm²/mol Ag) of these silver sols. We calculate the surface charge density $\sigma_0 = \dfrac{q_0 \times F \times 10^6}{S}$ (μC/cm²) from these data.

The surface charge density, σ_0, of the particles, the charge of the adsorbed ions, and the charge in the diffuse part of the double layer at the particle surface compensate each other. From measurements on the electrophoresis of these citrate-washed sols, we calculate ζ-potentials of -80 mV with a variation of 5 mV around this value for the different preparations. Such a value, together with the data on the salt concentration, shows that the charge in the diffuse part of the double layer in these sols does not exceed 10 μC/cm². Thus, the adsorbed negative ions find a small part of their charge compensated by the positive charge of the diffuse layer, but most of their charge is compensated by positive core of the particle.

d) Discussion of the analytical data

The results, obtained from the analytical determinations, are of limited accuracy due to some 10% uncertainty inherent in the determination of citrate. In the experiments on surface coverage the sols were washed with NaNO₃ and the particles carry over 50% of the total citrate. Therefore, the surface coverages in the tables 1 and 2 are accurate within some 15%. The situation is worse in the determination of the particle charge σ_0 (table 3). This is obtained from a relatively small difference between the Na⁺ and the citrate concentrations. Both these concentrations are large in citrate-washed sols; they represent the bulk of the intermicellar salt. A 10% accuracy in the citrate determination makes the values of the

surface charge density uncertain within 50%. We can only draw conclusions about the positive sign and about the order of magnitude (70 ± 35 μC/cm²) of the charge density. If, however, we dare conclude from data in table 3 that all the described sols are alike, we might consider averaging the individual results. In that case a value near 70 μC/cm² for σ_0 would seem somewhat more trustworthy.

The data of table 3 allow two essentially different interpretations of the missing charge (q_0). We have interpreted it as a positive charge on the silver core of the particles. A positive q_0 would also be obtained if we had overestimated the charge of the citrate ions because of incomplete ionization. At the pH of our sols, complete dissociation is a good approximation for the free citrate ions in solution, which constitute up to 80% of the available citrate. The electrophoresis data show that only about 3% of the Na⁺ ions, or 10 μC/cm², act as counterions of the sol particles. The rest is present in solution and compensated by an equivalent amount of citrate. Citrate adsorption, expressed in equivalents, is about 10 times larger than Na⁺ adsorption (tables 1 and 2, 1 ion/50 Å² = 95 μC/cm²). Only if the dissociation of the citrate were limited to about 10% would the silver core have no positive charge. However, this is extremely unlikely since free citric acid has $pK_1 = 3.0$; $pK_2 = 4.7$; $pK_3 = 5.4$. The mutual interaction of neighboring COO⁻ groups raises the pK's at the surface just like there is a difference between pK_1, pK_2, and pK_3. It is improbable, though, that at the surface the pK's have risen as high as $pK_1 = 7$. Such a rise would be necessary to explain the low degree of dissociation.

Our data agree with *Schneider*'s early analytical results. He found that the sol contained 97% Ag. We would find that 96% of the material in our sols is Ag if we could dry them and wash all the extra salts away – as *Schneider* did – without changing the adsorbed amount of citrate.

Table 3. Surface charge of the silver particles

pH	C_{Ag^+} eq/l.10⁵	C_{Na^+} eq/l.10²	$C_{citrate}^{-3}$ eq/l.10²	m_{Ag} mol/l.10²	q_0 eq/mol. 10³	σ_0 μC/cm²
6.4	1.4	1.20	1.76	6.1	90	+ 110
6.5	1.8	2.00	2.46	5.3	87	+ 106
7.6	1.5	1.38	1.68	6.1	48	+ 59
6.5	1.1	1.42	1.76	5.8	60	+ 73
6.4	0.7	1.32	1.67	5.9	60	+ 73

Electrochemistry of noble metal sols

In a *Carey Lea* sol positive silver particles are covered with citrate ions in a "super-equivalent" specific adsorption. Such a reversal of charge is the rule with sols of noble metals. On electrodes the zero charge potentials (vs. n.h.e.) have been determined (15) as $E_{zcp} = -0.7$ V for Ag, $E_{zcp} = -0.4$V for Pt, $E_{zcp} = -0.2$ V for Hg and $E_{zcp} = +0.1$ V for Au.

In a sol the (redox) potential will normally be on the positive side of these values and on the negative side of the potentials where noble metals have surface oxides. The metal of the particles will come to equilibrium with the solutions after the formation of the particles. Typically in the systems of table 3 the pAg $= 5$ would make the potential of a piece of silver immersed in these solutions $E_{Ag} = +0.5$ V. Therefore, the silver particles in these sols must carry positive charges.

In electrokinetic experiments, however, all these positive Au, Pt, and Ag particles in sols show negative ζ-potentials: the charge in the diffuse layer is positive too. Specific adsorption of such anions as Cl$^-$, Br$^-$ or citrate^{3-} at the metal/solution interface overcompensates the particle charge. It is the experience (16, 17, 18) of colloid chemistry that such ions must be present in a stable metal suspension. Our results with the *Carey Lea* sol are in line with this general idea about the electrochemistry of noble metal sols.

Colloid chemistry of the *Carey Lea* sol

a) Stability and repeptization

Sven Odén (4) studied the coagulation of the *Carey Lea* sol with electrolytes. It obeys the *Schulze-Hardy* rule, which indicates that it is an electrocratic colloid. Salts with monovalent cations give flocs that can be repeptized by washing. Ions of higher valency give irreversible precipitates. *Odén* discovered the fractionation of the sol in portions of different colour and stability. He followed a suggestion by *Ostwald* and *Lüppo Cramer* and related the colour differences to differences in particle size. And, indeed in the ultramicroscope he could only observe individual particles in the least stable ("coarser") fractions.

In 1922 *Freundlich* and *Loening* (19) re-established *Odén*s observations. They determined flocculation concentrations for 18 electrolytes which obey the *Schulze-Hardy*

rule again. They reported a decrease of the sol stability with age, and established that the sol follows the *Burton-Bishop* rule for the relation between stability and sol concentration.

Freundlich and *Loening* used *Carey Leas* sol as a lyophobic colloid in their study of the sensitizing and the protective action of such lyophilic colloids as gelatin and gum arabic on lyophobic sols. Instead of determining the more common "gold numbers" on the formol gold sol they obtained "silver numbers" with the *Carey Lea* sol. The analogy (20) of the gold and the silver numbers indicates once more that the *Carey Lea* sol is not already covered with polymers before the lyophilic colloids are added.

We confirmed these earlier observations and added a few other colloid chemical experiments to improve our understanding of some of these phenomena.

In table 2 we see that flocs which were coagulated with 2 mmol/l La(NO$_3$)$_3$ would not re-dissolve in water. To such precipitates 0.5 M KNO$_3$ was added and decanted. The flocs remained intact, of course, but after this washing their repeptization was as easy as if the sol had been coagulated with KNO$_3$ from the beginning.

Analogous observations on other colloids have been described (3, 21). It is a general phenomenon that polyvalent ions in a floc make it irreversible, but that these ions can be exchanged against monovalent ions. Such a change alters the properties of the coagulum with respect to repeptization.

In table 2 it is seen that repeptization is impossible when the citrate ions have been expelled from the particle surfaces by large concentrations of monovalent ions. This suggests that the citrate ions are in an adsorption-desorption equilibrium with the solution. The data of table 2 reflect their influence on stability and repeptization.

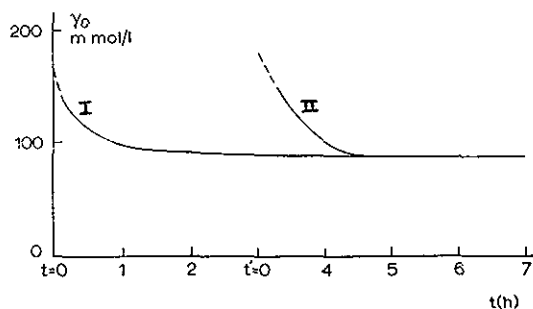Fig. 3. Changes of the flocculation limit (γ_0) with time. I: Fresh sol. II: After flocculation with citrate solution at $t' = 0$

We observed the decrease in stability that was mentioned by *Freundlich*, and determined the lowest concentration (γ_0) that will cause observable flocculation by 1-1 electrolytes, as a function of the age of the sol (fig. 3).

Next, at time $t' = 0$ ($t > 3$ h) we coagulated the sol with 0.5 M freshly prepared Na-citrate, and repeptized with water after 5 min. A considerable restabilization was observed. The new stability decreases with time like that of fresh sols. This indicates that slow desorption of normal citrate ions is responsible for the diminishing stability of the sol.

b) Fractionation

Odén's idea that the least stable fractions of the *Carey Lea* sol are the coarser ones is not supported by our electron microscopic data. Although the fractions contain somewhat coarser particles, there is a considerable overlap of the particle size distribution curves among the fractions. Only the most stable fractions do indeed show small particles of a narrow size distribution. But these fractions also carry the closest coverage with citrate.
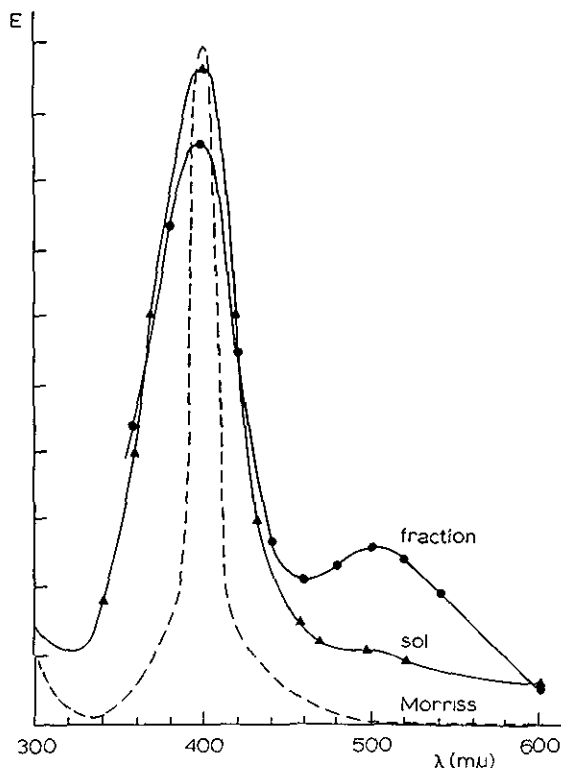

Fig. 4. Optical extinction (E). Spectra of a *Carey Lea* sol and of one of its fractions compared with the theoretical spectrum of 100 Å silver spheres *(Morriss)*

The fractionation seems to depend on citrate adsorption (surface charge density) rather than on size. This observation, however, does not yet explain the different colours of the fractions.

In a Beckman DK-2 spectrophotometer we recorded the absorption spectra of the sol and of its fractions (fig. 4). The sol, and also its stablest fractions, show a single absorption maximum at 400 nm. Calculations by *Doremus* and by *Morriss* (22–25) show that such a spectrum must be expected from a dispersion of silver spheres with the properties of the bulk material and a diameter of 100 Å. The peak in the measured spectrum is broadened due to the size distribution of the particles.

In less stable fractions this same maximum is accompanied by a broad, lower peak at larger wavelength. The wavelength of this secondary peak decreases when the stability of the fraction increases. It is 570 nm in the violet fractions of low stability, 510 nm in the more stable red fractions, and it disappears towards the orange fractions and the original sol. If salt is added to these last very stable dispersions, they, too, develop a second peak, whereas the original maximum at 400 nm is lowered. This behaviour is completely analogous to that of gold sols under conditions of slow flocculation. The presence of secondary peaks shows that some particles are clustered together in rather small aggregates (26). Therefore, it seems that the difference in colour between the fractions must be attributed to differences in the amount and the size of aggregates present.

The green colour of *Odén*s least stable fraction is entirely due to "limited flocculation" (27) of primary particles. If obtained in concentrated form, the least stable fraction has a violet colour. This fraction turns green upon dilution but not because the particle concentration is changed. There is a time lag between the act of dilution and the colour change, and if a citrate solution is used instead of water for the dilution, there is no colour change at all (3). It seems that in this fraction the dilution causes desorption of the stabilizing citrate ions below some critical level, and thereby brings about flocculation.

The presence of aggregates in the fractions of the *Carey Lea* sol explains the much too large particle sizes obtained from ultramicroscopy. *Odén* describes that he was not able to see individual particles in the stable

fractions, but he saw, and counted what he saw, in fractions of low stability. If there are only few visible aggregates in these fractions, such a procedure results in an overestimation of the average particle size because the material of the unseen primary particles is reckoned to belong to the aggregates. Reversing the argument we can also say that the discrepancy between the particle sizes that are obtained in the electron microscope and the ultramicroscope respectively are a clear indication for the presence of (a few) aggregates in the fractions of a *Carey Lea* sol. For it is obvious that in the electron microscopic observation, particles ten times larger than the average cannot simply be overlooked.

Conclusion

*Carey Lea*s silver sol has been described in some detail and in different respects. Our conclusion is the same as *Freundlichs*: "it is an exemplary, negatively charged hydrophobic sol" (19). This conclusion contradicts earlier ideas that *Carey Lea*s colloidal silver is a protected colloid. The particle size of the sol is much smaller than was previously expected. The colloidal stability of the *Carey Lea* sol is due to the superequivalent reversible adsorption of citrate ions, and its peculiar properties like fractionation and repeptization must be explained from this point of view.

Summary

*Carey Lea*s silver sol is investigated with electron microscopy and analytical methods. Its colloidal behaviour is studied. Coagulation, repeptization and fractionation are described. The *Carey Lea* sol is not a protected colloid. It consists of small (80 Å diameter) spherical, rather monodisperse, positively charged silver particles. Citrate ions are adsorbed at the particle surface in superequivalent adsorption.

Zusammenfassung

Das *Carey Lea*sche Silbersol wurde untersucht mit den Methoden der Elektronenmikroskopie und der chemischen Analyse sowie nach seinen kolloidchemischen Eigenschaften. Flockung, Repeptisation und fraktionierte Koagulation werden beschrieben. Es stellt sich heraus, daß das Sol aus feinkörnigen (80 Å Durchmesser), kugelförmigen, ziemlich monodispersen, positiv geladenen Silberteilchen besteht, an denen Zitrationen, in superäquivalenter Adsorption, angelagert sind.

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Authors' addresses:

Dr. *G. Frens*
R. J. Reynolds Tobacco Co., Research Department, Winston-Salem, N. C. 27102 (U.S.A.)

Dr. *J. Th. G. Overbeck*
van't Hoff-Laboratorium, Rijksuniversiteit Utrecht Utrecht (Netherlands)