A Study of the Partitioning of Colloidal Particles Based on Their Size during Electrostatic Immobilization at the Air−Water Interface Using Fatty Amine Monolayers

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We have recently demonstrated that carboxylic acid derivatized silver and gold colloidal particles can be immobilized through electrostatic interaction with fatty amine Langmuir monolayers at the air−water interface and that good quality multilayer films of the clusters can be deposited by the Langmuir−Blodgett (LB) technique. In this paper, we extend our study on the electrostically controlled immobilization process through an investigation of the partitioning of carboxylic acid derivatized clusters based on their size. Simultaneous immobilization of gold and silver clusters (130 ± 30 and 70 ± 12 Å diameter, respectively) from the same colloidal subphase at the air−water interface using octadecylamine Langmuir monolayers has been followed by π−A isotherm measurements as well as optical absorption, quartz crystal microgravimetry (QCM), and X-ray fluorescence (XRF) analysis of the built-up LB films. Even for small concentrations of gold relative to silver clusters in the subphase, the density of the larger gold clusters in the LB films was found to be surprisingly high in relation to the smaller silver clusters. While the π−A isotherms stabilized within 3 h of spreading the fatty amine monolayer, the cluster density at the air−water interface continued to increase, taking up to 12 h to reach equilibrium. The larger gold clusters reached an equilibrium density at the interface much faster than the smaller silver clusters. The "reverse" fractionation of clusters observed is discussed in terms of an electrostatic model.

Introduction

Among the many different approaches being currently investigated for organization of nanoscale structures, the air−water interface as an organizational medium has received considerable attention.[1−5] In this laboratory, research effort has been focused on studying the electrostatic immobilization of suitably derivatized colloidal metal particles at the air−water interface using Langmuir monolayers[6,7] as well as by diffusion into thermally evaporated organic films.[8] It has been shown that the cluster density at the air−water interface and consequently in the built-up Langmuir−Blodgett (LB) films as well as in the thermally evaporated films can be effectively controlled through variation of the subphase pH.[7,8] In this paper, we advance our investigation of cluster immobilization at the air−water interface further through a study of *simultaneous complexation* of carboxylic acid derivatized gold and silver colloidal particles (130 ± 30 and 70 ± 12 Å diameter, respectively) differing vastly in size with octadecylamine Langmuir monolayers. It is observed that even though expansion of the Langmuir monolayer is complete within 3 h of spreading the monolayer, the cluster density at the air−water interface takes up to 12 h to stabilize. Stabilization of the density of larger gold clusters at the air−water interface occurs much more rapidly than for smaller silver clusters. Mixed cluster LB films show a higher than expected gold cluster density in the films. These observations are discussed in terms of an electrostatic model and considering the effects of cluster size-dependent distortion of the fatty amine Langmuir monolayer.

Experimental Details

Preparation of the colloidal solutions of gold and silver and their capping with the bifunctional molecule 4-carboxythiophe-

nol (4-CTP) has been described in detail elsewhere.[6,7] Thiolate linkage of 4-CTP with the gold and silver particle surface leads to carboxylic acid derivatization of the colloidal particles. Transmission electron microscopy (TEM) of the gold and silver sols yielded 130 ± 30 and 70 ± 12 Å diameter, respectively.[6,7] Hydrosols containing both silver and gold clusters were prepared by mixing the individual sols in different volume ratios to obtain varying silver:gold cluster concentrations in solution. In this study, solutions of silver:gold ratios of 2:1, 1:1, and 1:2 were prepared for use as the subphase. Unless otherwise mentioned, a ratio of *x:y* should be taken to imply a mixture of *x* parts (by volume) of the silver sol with *y* parts of the gold sol. The mixed hydrosol pH was adjusted to 9 using HCl since the cluster incorporation in the amine films was found to be maximum close to this pH.[6,7] We would like to caution here that the volume ratio of the individual sols used throughout this study is not to be confused with the actual cluster concentration ratios. In fact, for the cluster sizes reported earlier and assuming complete reduction of the salt solution, a 1:1 solution would contain ca. 4 times as many silver clusters per unit volume as gold clusters. Optical absorption spectra of the mixed sols indicated that the clusters were stable over weeks with no evidence for flocculation or cross-linking of the clusters.

Pressure−area (π−A) isotherms of octadecylamine Langmuir monolayers on the different colloidal subphases were recorded at a temperature of 25 °C on a Nima 611 Langmuir trough equipped with a Wilhelmy plate for surface pressure sensing. The π−A isotherms were recorded as a function of time at a compression rate of 25 cm^2/min. Multilayer films of the octadecylamine monolayer complexed to the colloidal particles were grown by the Langmuir−Blodgett technique on lead arachidate-coated quartz substrates[9] as well as gold-coated AT-cut quartz crystals for quartz crystal microgravimetry (QCM) and optical absorption spectroscopy measurements, respectively. The film transfer was done at different times after spreading the octadecylamine monolayer on the colloidal subphase. Ex

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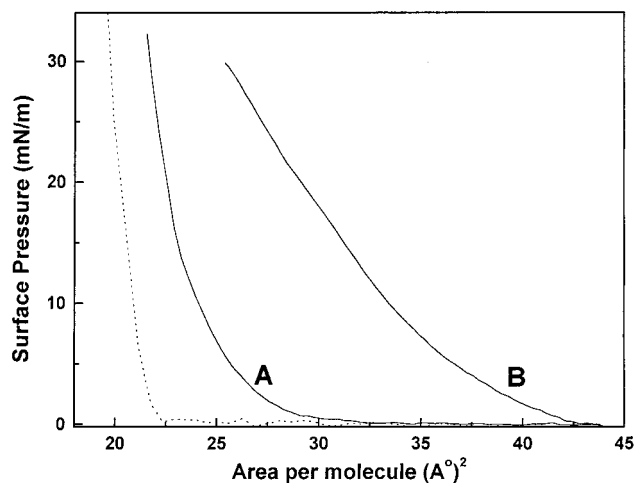*J. Phys. Chem. B, Vol. 101, No. 47, 1997* **9791**

Figure 1. $\pi-A$ isotherms of an octadecylamine Langmuir monolayer spread on the 1:1 colloidal subphase at pH = 9 measured at different times after spreading the monolayer: curve a, after 30 min of monolayer spreading; curve b, after 180 min of monolayer spreading on the 1:1 subphase; dashed line, isotherm for octadecylamine on pure water at pH = 9.

situ QCM measurements were carried out on the 6 MHz quartz crystals using an Edwards FTM5 frequency counter which had a frequency stability and resolution of ±1 Hz (~12 ng/cm^2 mass resolution). The change in the crystal resonance frequency on transfer of the films was converted to a mass loading using the Sauerbrey formula.[10] Optical absorption measurements of the LB films transferred to hydrophobized quartz substrates were performed on a Hewlett-Packard 8542 diode array spectrophotometer operated at a resolution of 2 nm. X-ray fluorescence (XRF) measurements were carried out on a Rigaku 3070 instrument.

Results and Discussion

Measurement of $\pi-A$ isotherms can provide important information on the process of complexation occurring at the air—water interface in the presence of Langmuir monolayers. Figure 1 shows the $\pi-A$ isotherms recorded as a function of time for the octadecylamine monolayer on a 1:1 colloidal subphase (solid lines; (A) 30 min and (B) 180 min after monolayer spreading) along with the isotherm for amine on pure water at pH = 9 for comparison (dashed line). This isotherm is representative of the isotherms measured on the 2:1 and 1:2 colloidal subphases and is quite similar to the time dependence of the isotherms observed for the pure gold[6] and silver subphase[7] reported earlier. The important point of similarity is that an expansion of the monolayer occurs up to ca. 3 h of spreading the amine monolayer, after which negligible changes were observed.

The kinetics of cluster immobilization at the air—water interface was also studied by QCM and optical absorption spectroscopy in the following manner. Bilayers of the octadecylamine monolayer complexed to the colloidal particles were transferred to the gold-coated quartz crystals at a surface pressure of 25 mN/m at different times after spreading the amine monolayer on pure silver, 1:1, and pure gold subphases. For the optical absorption measurements, 4 monolayers (ML) of the colloidal particle complex was transferred to hydrophobized quartz substrates in a similar manner. Figure 2 shows the QCM mass uptake per bilayer measured for the films transferred from the different subphases (a, 1:1; b, pure silver; c, pure gold subphase). The solid curves have been drawn to aid the eye and have no physical significance. It is seen that while the mass uptake per bilayer increases steadily with time up to ca. 12 h
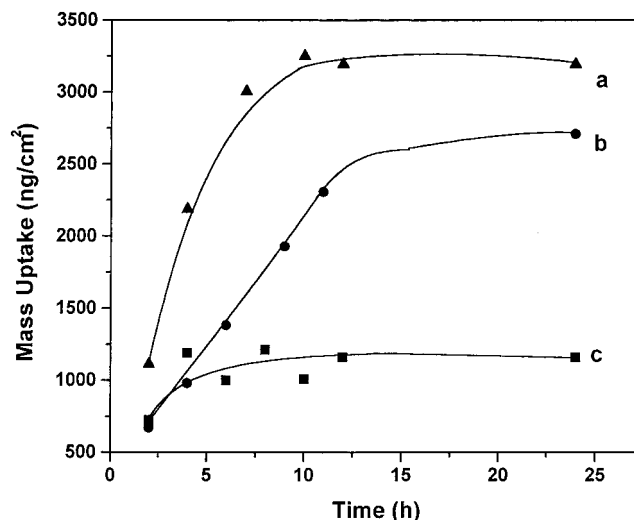

Figure 2. QCM mass uptake per bilayer versus time after spreading octadecylamine monolayers on the different colloidal subphases: curve a, 1:1 subphase; curve b, pure silver subphase; curve c, pure gold subphase.

for films transferred from the pure silver and 1:1 subphases, the mass per bilayer is fairly constant for bilayers transferred from the pure gold colloidal subphase. This clearly shows that even though the $\pi-A$ isotherms stabilize after 3 h of spreading of the monolayer, the cluster density at the air—water interface increases steadily with time and stabilizes only after 12 h for the subphases containing silver particles. This, in our opinion, is an important observation and indicates that $\pi-A$ isotherms are insensitive to changes occurring at the air—water interface, especially when the monolayer is in an expanded state, and also that the kinetics of cluster incorporation at the air—water interface is extremely slow. This is an aspect we had not anticipated in our earlier studies where the monolayer was compressed to 25 mN/m and allowed to remain under isobaric conditions until the change in the area/molecule was negligible, and then the monolayers were transferred for additional measurements.[6,7] However, since the observed time scale for equilibration of the cluster density at the air—water interface is much larger than the time required for preparation of multilayer LB films, the conclusions of the earlier investigations are not expected to be significantly different. The equilibrium mass uptake per bilayer for films deposited from the pure silver, 1:1, and gold subphases are 2700, 3200, and 1160 ng/cm^2, respectively (Figure 2).

While QCM measurements can detect overall mass changes in the film during the cluster diffusion process, it cannot differentiate between the presence of gold and silver clusters simultaneously in the film. Optical absorption spectroscopy is an excellent tool for the study of partitioning of the clusters in amine films since gold and silver colloidal particles exhibit strong (and well separated) surface plasmon resonances.[11] The optical absorption spectra of 4 ML octadecylamine films complexed with the colloidal particles deposited at different times on hydrophobized quartz substrates are shown in Figures 3a−5a for monolayers transferred from pure silver, 1:1, and pure gold subphases, respectively. The times indicated next to the curves refer to the time interval (in hours) after spreading the octadecylamine monolayer, and as mentioned earlier, the transfers were carried out at a surface pressure of 25 mN/m. The surface plasmon resonance of silver and gold clusters in the octadecylamine LB films occur at ca. 475 and 600 nm, respectively (indicated by arrows, Figure 4a). It is seen from the figures that, except for the films transferred from the gold colloid subphase whose absorption spectrum stabilizes close to 5 h after spreading the octadecylamine monolayer, the intensity
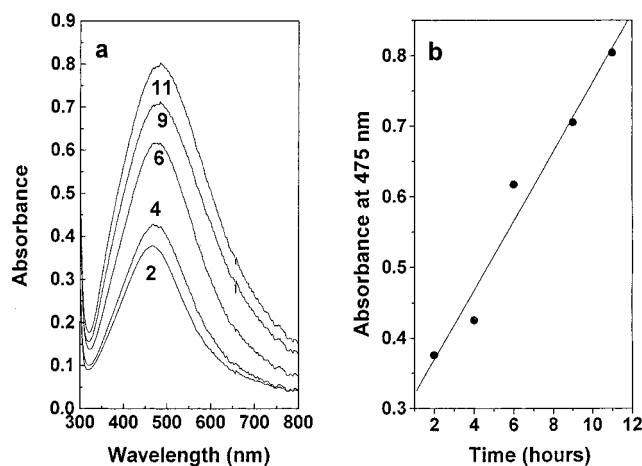
Figure 3. (a) Optical absorption spectra of 4 ML octadecylamine films transferred from the pure silver subphase after different times of spreading the fatty amine monolayer. The times are indicated next to the curves. (b) Intensity of the plasmon resonance at 475 nm plotted as a function of time for the spectra shown in (a).
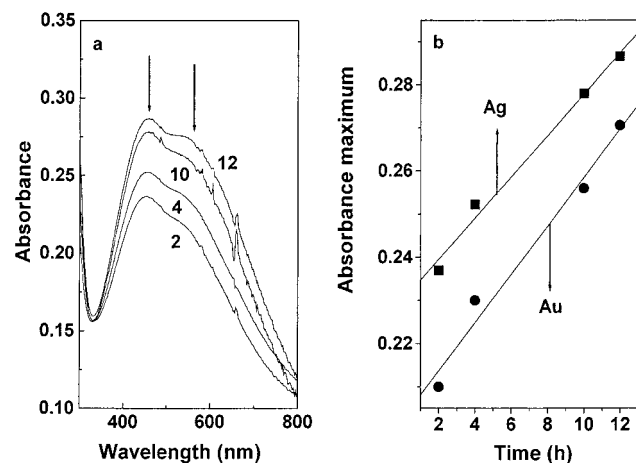

Figure 5. (a) Optical absorption spectra of 4 ML octadecylamine films transferred from the pure gold subphase after different times of spreading the fatty amine monolayer. The times are indicated next to the curves. (b) Intensity of the plasmon resonance at 600 nm plotted as a function of time for the spectra shown in (a).

Figure 4. (a) Optical absorption spectra of 4 ML octadecylamine films transferred from the 1:1 composite subphase after different times of spreading the fatty amine monolayer. The times are indicated next to the curves. The arrows indicate the position of the silver and gold plasmon resonances. (b) Intensity of the gold (600 nm) and silver (475 nm) plasmon resonance plotted as a function of time for the spectra shown in (a).

of the absorption maximum increases steadily with time for the pure silver and 1:1 subphases. This is indicated clearly in Figures 3b−5b where the intensity of the absorption maximum has been plotted as a function of time for the corresponding optical absorption spectra. The resonance intensity increases until ca. 12 h after spreading the fatty amine monolayer and is in agreement with the QCM results shown in Figure 2. While the optical absorption spectra of films transferred from the pure gold subphase showed changes until 5 h of monolayer spreading, the QCM data (Figure 2, filled squares) indicated very small change in the cluster density in the bilayers after 2 h of monolayer spreading. The reason for this discrepancy is not understood at present since identical film preparation conditions were used in both cases. From Figure 4a,b, it is seen that the resonance corresponding to gold (ca. 600 nm) increases slightly relative to the silver resonance at 475 nm with increasing time. This is interesting given that the cluster density in the pure gold films stabilize within 5 h of spreading of the fatty amine monolayer.

As demonstrated above, the cluster density at the air−water interface stabilizes within ca. 12 h of spreading the fatty amine monolayer on the different subphases. Optical absorption spectra of 4 ML LB films of octadecylamine transferred onto
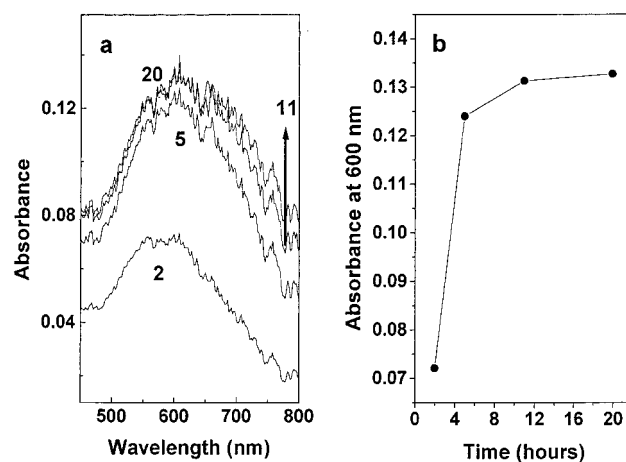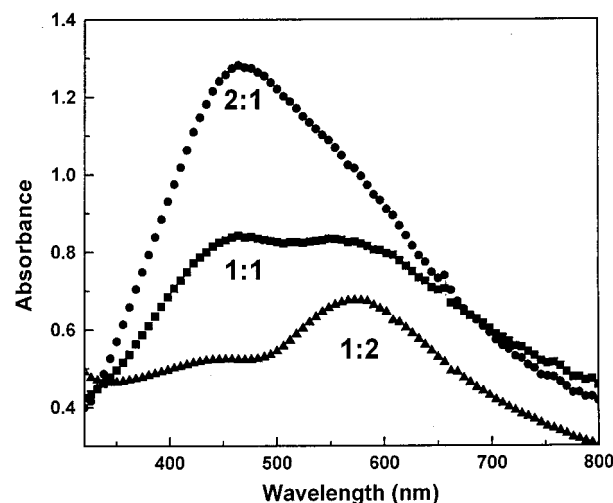

Figure 6. Optical absorption spectra of 4 ML octadecylamine LB films transferred after 15 h of spreading the fatty amine monolayer on the different subphases. The subphase concentration ratios are indicated next to the curves.

hydrophobized quartz substrates after 15 h of monolayer spreading were recorded and are shown in Figure 6 for the 2:1 (filled circles), 1:1 (filled squares), and 1:2 subphases (filled triangles). As expected, the intensity of the gold plasmon resonance relative to the silver resonance (indicated by arrows in the figure) increases as the concentration of the gold clusters in the subphase increases. However, determination of the gold: silver cluster density ratio in the films would be illuminating. It is difficult to make an estimate of the molar concentration of Au and Ag in the mixed cluster films from the optical absorption spectra shown in Figure 6 due to damping and shifts of the surface plasmon resonance of the clusters on capping with the 4-CTP molecule, which currently cannot be quantified.[11b] Multilayer films of different thicknesses transferred from the different subphases onto hydrophobized quartz substrates were studied by optical interferometry. A linear increase in thickness was observed with number of monolayers transferred, indicating good layer-by-layer growth of the built-up films, and is in agreement with our earlier studies on LB films of gold[6] and silver[7] colloidal particles. Attempts to image the LB films transferred onto electron microscope grids were not successful due to electron beam heating of the films which led to melting and a fair degree of aggregation of the colloidal particles.

An estimate of the gold:silver cluster density ratio for the 4

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ML 1:1 film shown in Figure 6 may be made from XRF measurements of the film together the QCM data presented in Figure 2 (curve a) as shown below. The gold:silver molar ratio determined from XRF measurements for the 1:1 film was 4.5. For the cluster sizes of this study, this molar ratio implies 0.7 clusters of gold for every silver cluster[12] in the 1:1 film. The main point to note from the above calculation is that while the gold:silver cluster density in the 1:1 subphase is 0.25, the corresponding cluster density in the LB film is 0.7, indicating that there is an enhancement of the gold cluster density in the film by a factor of 2.8. The mass balance constraint determined from QCM measurements can be written as

$$n(Ag)\, m(Ag) + 0.7n(Ag)\, m(Au) = 3200 \text{ ng} \qquad (1)$$

where $n(Ag)$ is the number of silver clusters/cm^2 and $m(Ag)$ and $m(Au)$ are the mass per silver (2×10^{-9} ng) and gold clusters (24×10^{-9} ng), respectively. From eq 1, the volume fraction of gold in the bilayers for the 1:1 film is determined to be 18.3% while the corresponding value for silver clusters is 6.2%. Comparison of these volume fractions with the volume fraction values of gold (13%) and silver clusters (26%) in the films transferred from the pure gold and silver subphases (Figure 2, curves c and b, respectively) indicates that, during simultaneous immobilization of the clusters at the air–water interface, the cluster density of gold is enhanced relative to the pure gold film, and concomitantly, the silver cluster density is reduced. It appears, therefore, that the competitive process of electrostatic immobilization promotes the incorporation of large gold clusters in preference to the smaller silver clusters.

The main observations of the studies presented above may be summarized as follows:

(1) π–A isotherm measurements show negligible expansion of the octadecylamine monolayer after 2 h of spreading of the monolayer whereas considerable change in the cluster density at the air–water interface is observed using QCM and optical absorption spectroscopy.

(2) The cluster density of larger gold clusters at the air–water interface stabilizes faster than for the smaller silver clusters.

(3) The cluster density ratios of gold and silver in the mixed cluster films is quite different from the cluster density ratios in the colloidal subphase. The gold:silver cluster density ratio in the 1:1 film is 0.7 whereas the concentration ratio in the 1:1 subphase is 0.25.

Observation 1 indicates that π–A isotherms are rather insensitive to changes in the cluster density occurring at the air–water interface when the monolayer is in an expanded state. Conclusion 2 appears contradictory at first since the diffusivity of the smaller silver clusters in the aqueous medium would be expected to be higher than for the bigger gold clusters. However, it must be kept in mind that the charge on the cluster for gold is nearly 3.5 times that for silver, assuming complete ionization of the exposed carboxylic acid groups from 4-CTP. From a purely electrostatics point of view, the attractive interaction between the negatively charged colloidal particles and the positively charged amine monolayer would be much larger for the gold clusters and could account for the smaller diffusivity expected based on the cluster size.

Another factor contributing to the smaller stabilization times for gold colloidal particles at the air–water interface could be the following. During immobilization of the clusters at the fatty amine Langmuir monolayer, the amine molecules are expected to coordinate to the carboxylic acid terminal groups on the clusters through a Coulombic attractive interaction. This leads to a disruption of ordering in regions of the amine monolayer in immediate contact with the clusters. Such a disruption in

the packing of bilayers has been observed in LB films with clusters chemically inserted[13] as well as in stearate LB films with Fe$_2$O$_3$ nanoparticles attached at the air–water interface.[5] The area per terminal methyl group of the amine molecules on silver and gold clusters can be calculated to be 92 and 56 Å^2, respectively.[14] The larger surface curvature of the silver clusters leads to larger volumes available to the terminal groups of the amine molecules and, consequently, weaker van der Waals interaction between the chains. In other words, the immobilization of large colloidal particles would distort the packing of the hydrocarbon chains in the amine monolayers less than smaller clusters and would be energetically more favorable. The above two factors would satisfactorily explain the smaller cluster equilibration times observed for the gold clusters and would also explain observation 3 wherein the density of gold clusters in the films is larger than that in the composite subphase. We would like to mention here that a similar enhanced incorporation of larger gold clusters at the expense of smaller silver clusters has been observed during the simultaneous diffusion of the particles in thermally evaporated octadecylamine films.[15] This indicates that the energetics of the cluster immobilization process is the same in both cases and further strengthens the results obtained in this investigation on the reverse fractionation at the air–water interface.

Future work will be directed toward understanding the kinetics of cluster immobilization (for a range of different cluster sizes) at the air–water interface in the presence of a charged Langmuir monolayer in terms of a Poisson–Boltzmann–Stern formalism.

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(9) It was observed that hydrophobic substrates gave better monolayer transfer ratios, and therefore, quartz substrates were rendered hydrophobic by transfer of 1 ML of lead arachidate. The gold-coated quartz crystals for QCM were hydrophobic and used without further treatment.

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(12) Assuming a volume of 16 Å^3 per silver atom in the cluster, the number of atoms in a 70 Å diameter cluster is $= [(4\pi/3)(35)^3]/16 \approx 11225$. From a similar calculation, the number of gold atoms in a 130 Å size cluster is ca. 71897. Therefore, the gold:silver molar ratio in a film containing equal numbers of silver and gold clusters is $71897/11225 \approx 6.5$. Since the Au:Ag molar ratio from XRF measurements for the 1:1 film is 4.5, this implies a Au:Ag cluster density ratio of $4.5/6.5 \approx 0.7$.

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(14) For a 70 Å diameter Ag cluster ($R = 35$ Å), the number of 4-CTP molecules on the surface (25 Å^2 area/4-CTP molecule) $= (4\pi R^2)/ 25 = 616$. Assuming coordination of 1 amine molecule of length 25 Å to each 4-CTP molecule (of 7 Å dimension) leads to a modified cluster radius of $35 + 7 + 25 = 67$ Å. Area per terminal methyl group of the amine molecules on Ag clusters is therefore approximately $(4\pi67^2)/616 = 92$ Å^2. By a similar calculation, this value can be shown to be ca. 56 Å^2 for gold clusters of 65 Å radius.

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