

Sonochemical Formation of Gold Sols

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Received March 20, 2002. In Final Form: July 17, 2002

The reduction of AuCl_4^- to colloidal gold in the presence of aliphatic alcohols and sodium dodecyl sulfate in aqueous solutions using 20 kHz ultrasound is described. The extent of reduction of AuCl_4^- was found to be directly dependent on the gas–solution interfacial activity of the solutes used. The diameters of the gold colloids produced were in the size range of 9–25 nm. The particle size was dependent on the alcohol concentration in solution and on the hydrophobicity of the alcohol. For a particular alcohol concentration, smaller particles were obtained the greater the hydrophobicity of the alcohol. A detailed mechanism is presented that describes the overall sonochemically initiated reduction of AuCl_4^- leading to the formation of colloidal gold.

Introduction

The passage of high-intensity ultrasound through water can lead to acoustic cavitation, which is the formation, growth, and violent collapse of small gas bubbles in the sonicated solution. The near-adiabatic compression of the gas molecules inside the microbubbles in the liquid leads to a dramatic rise in the temperature and pressure within the bubbles.^{1–3} In an aqueous solution, water vapor within the imploding bubble dissociates, producing hydrogen and hydroxyl radicals.⁴ Solute adsorbed at the bubble–solution interface may act as radical scavengers, preventing the total recombination of these primary radicals.^{5,6} The longer-lived secondary radicals so produced can diffuse into the bulk solution, allowing further reaction to occur.^{5,6}

In recent years there has been a growing interest in the chemistry occurring when ultrasound is applied to colloidal systems.⁷ Colloids in the nanometer size range have been readily produced through the ultrasonically initiated reduction of solutions containing metal salts or metal complexes. Included among the nanoparticles produced are Au, Tl, Pt, Pd, Fe, MnO_2 , and CdS colloids.^{7–14} Also,

ultrasound has been used for the dissolution of MnO_2 ,¹³ Ag,¹⁵ and CdS¹⁶ colloids. These colloids have all been formed or dissolved by sonochemical reactions, and not by the fragmentation and dispersion of bulk material that can also be accomplished using ultrasound.¹⁷

This study deals with the sonochemically initiated reduction of AuCl_4^- in the presence of several different radical scavenging solutes and the subsequent formation of gold sols. Information is provided on the scavenging mechanism of the primary radicals in sonicated solutions, and the role that radical scavengers play in affecting the size of the gold particles produced is considered.

Experimental Section

All solutions were prepared using Milli-Q water (surface tension 72.0 mN m^{-1} , conductivity $<10^{-6} \text{ S/cm}$ at 25°C). Tetrachloroauric(III) acid (ACS reagent) was obtained from Sigma Chemical Company. All alcohols used were analytical reagents. Sodium perchlorate (AnalaR >99.0%) and specially pure sodium dodecyl sulfate (>99%) were obtained from BDH.

The solutions used in all sonication experiments were prepared from higher concentration stock solutions and were purged for 15 min with argon (high purity, CIG) that was first bubbled through an aqueous solution containing an equivalent concentration of alcohol. During sonication an argon atmosphere was kept above the solution in a custom-made reaction vessel. A 20 kHz, 450 Branson Probe Sonifier with a stepped horn (19 mm diameter tip) was used to deliver the ultrasound to 40 mL of solution. The power was 9 W/cm^2 , as determined by calorimetry. Pulsed sonication (0.5 s on; 0.5 s off) was used in conjunction with an ice–water bath in which the reaction vessel was contained during sonication in order to maintain a relatively narrow temperature range for the solutions at $20 \pm 5^\circ\text{C}$.

Absorption spectra of the solutions were measured on a U2000 Hitachi UV–vis spectrophotometer. Samples for electron microscopy were prepared by placing a drop of the completely reduced AuCl_4^- solution onto a copper grid covered with a thin carbon film. The grid was placed on filter paper to dry and was transferred to a Philips CM10 transmission electron microscope (TEM), and the Au particles were imaged.

Results

Changes in the AuCl_4^- Absorption Spectra and the Calculation of AuCl_4^- Concentration. The reduc-

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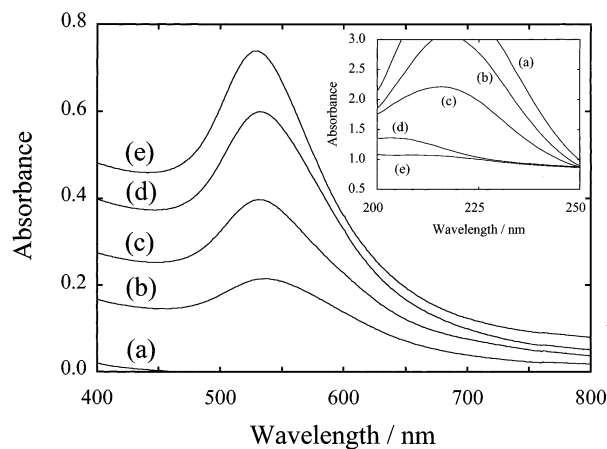


Figure 1. Absorption spectra of solutions of 2×10^{-4} M AuCl_4^- and 0.6 M 1-propanol (a) before sonication and after (b) 1.5, (c) 3.5, (d) 5, and (e) 20 min sonication. The pH of the solutions before and after sonication was between 3.1 and 3.4. The bulk solution temperatures were maintained at 21 ± 2 °C. The insert shows a decrease in the absorbance spectra at lower wavelengths for the same sonication times.

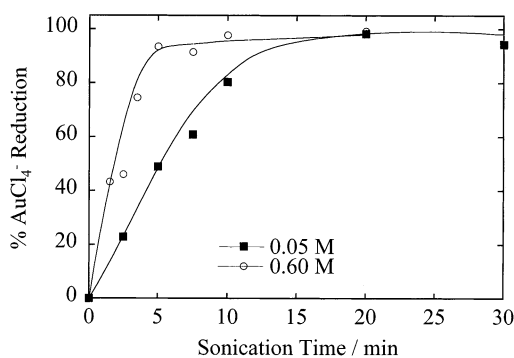


Figure 2. Amount of AuCl_4^- reduced (shown as % reduced) as a function of the time of sonication for 2×10^{-4} M AuCl_4^- and either 0.05 or 0.60 M 1-propanol. The pH of the solutions before and after sonication were between 3.0 and 3.4. The bulk solution temperatures were maintained at 20 ± 2 °C.

tion of AuCl_4^- was monitored by observing changes in the absorption spectra of the gold(III) chloride solutions. Figure 1 shows the effect of different sonication times on the absorption spectra of a 2×10^{-4} M AuCl_4^- solution containing 0.6 M 1-propanol. As the sonication time is extended, the absorption band (due to colloidal gold centered at about 540 nm) increases. This increase coincides with a decrease in the AuCl_4^- absorption band centered at 220 nm because of the chemical reduction of AuCl_4^- (see Figure 1 insert). The amount of AuCl_4^- reduced during sonication was obtained by monitoring the absorption changes of the AuCl_4^- band following sonication using an extinction coefficient of $9823 \text{ M}^{-1} \text{ cm}^{-1}$ at a wavelength of 240 nm (note: this not at the band maximum). As the gold colloids also absorb in this wavelength region, the sonicated solutions were first centrifuged (at 20 000 rpm for 15 min), and the absorbance of the supernatants was measured so that a final AuCl_4^- concentration could be obtained.

Sonochemical Reduction of AuCl_4^- : Identification of Optimal Experimental Conditions. A series of experiments were conducted in which the sonication time, alcohol concentration, and alkyl chain length were all varied to identify the optimal conditions for studying the reduction of AuCl_4^- . Figure 2 shows the amount of AuCl_4^- reduced as a function of sonication time for 0.05 M 1-propanol/ 2×10^{-4} M AuCl_4^- and 0.6 M 1-propanol/ $2 \times$

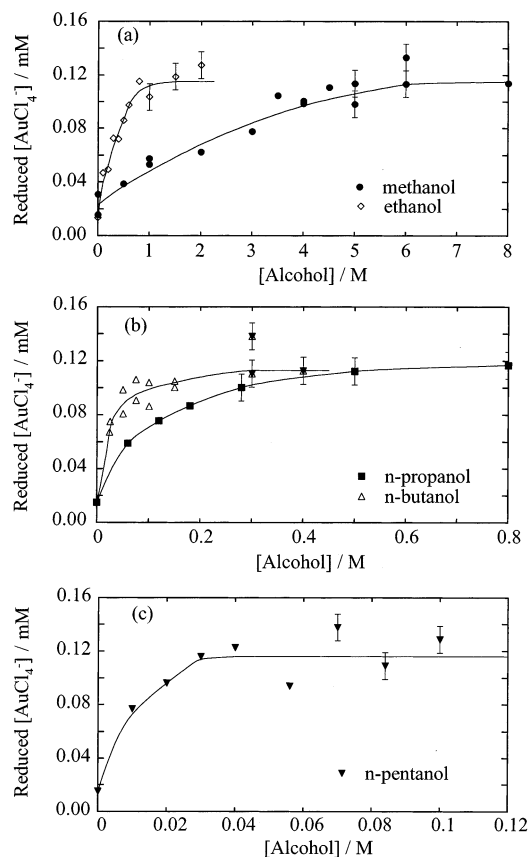


Figure 3. Amount of AuCl_4^- reduced as a function of the alcohol concentration for (a) methanol and ethanol, (b) 1-propanol and 1-butanol, and (c) 1-pentanol. All solutions initially contained 2×10^{-4} M AuCl_4^- and were sonicated for 2.5 min. The pH of the solutions before and after sonication were between 3.1 and 3.5. The bulk solution temperatures were maintained at 21 ± 3 °C.

10^{-4} M AuCl_4^- . The data show an increase in the amount of AuCl_4^- reduced with longer sonication times until all of the AuCl_4^- is reduced. It can be seen that initially the rate at which AuCl_4^- is reduced is greater for the higher concentration of 1-propanol. Similar experiments using other alkyl alcohols show that all of the AuCl_4^- is eventually reduced by sonication, with the longer alkyl chain alcohols (1-butanol and 1-pentanol) showing a faster rate of reduction of the AuCl_4^- as compared with the short chain length alcohols. As there was clearly a difference in the rate of reduction with time of sonication, not only in the concentration of the alcohol but also in the type of alcohol used, a fixed sonication time of 2.5 min was chosen for the next set of experiments undertaken.

Effect of Alcohol Type on the Sonochemical Reduction of AuCl_4^- . Figure 3 shows the effect of different straight-chain alcohols at varying concentrations on the amount of AuCl_4^- reduced after sonicating 0.2 mM AuCl_4^- solutions for 2.5 min. The amount of AuCl_4^- reduced increases with increasing alcohol concentration until a limiting level is reached. The initial rate of reduction of the AuCl_4^- is most pronounced for 1-pentanol (as seen in Figure 3c) and becomes relatively less significant as the alcohol chain length becomes progressively shorter. This trend is continued in Figure 3a,b for higher concentrations of the short chain length alcohols. Also, the limiting amount of AuCl_4^- reduced is much the same for all the alcohols (1-pentanol to methanol) at around 60% of the initial concentration.

Effect of Surfactant and Electrolyte on the Sonochemical Reduction of AuCl_4^- . The reduction of

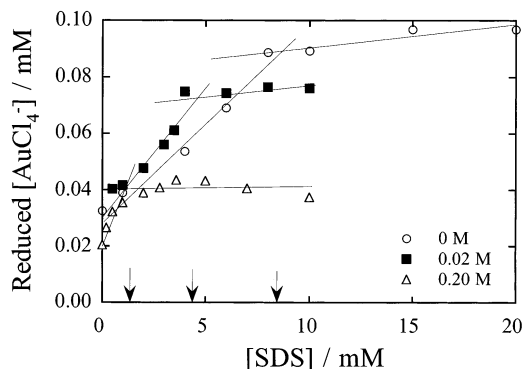


Figure 4. Effect of varying SDS concentration on the amount of AuCl_4^- reduced after sonicating 2×10^{-4} M AuCl_4^- solutions for 7.5 min is shown by the circles. The addition of 0.02 and 0.2 M NaClO_4 to 2×10^{-4} M AuCl_4^- solutions with varying SDS concentration are shown by the squares and triangles, respectively. The arrows along the concentration axis show the cmc values of SDS for the three systems. The pH of the solutions before and after sonication were between 3.2 and 3.7. The bulk solution temperatures were maintained at 21 ± 3 °C.

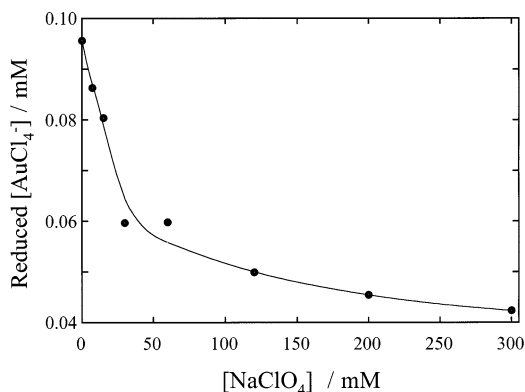


Figure 5. Effect of varying NaClO_4 concentration on the amount of AuCl_4^- reduced after sonicating 2×10^{-4} M AuCl_4^- with 10 mM SDS solutions for 7.5 min. The pH of the solutions before and after sonication were between 3.3 and 3.6. The bulk solution temperatures were maintained at 21 ± 3 °C.

AuCl_4^- , in the presence of SDS and SDS with 0.02 and 0.2 M NaClO_4 added, is shown in Figure 4. It can be seen that as the SDS concentration is increased, the amount of AuCl_4^- reduced increases. However, once the critical micelle concentration¹⁸ (cmc) of SDS is reached there is little change in the amount of AuCl_4^- reduced with increasing levels of SDS. A further point to note is that the limiting amount of AuCl_4^- reduced for the different systems decreases with increasing salt concentration.

Using a set concentration of SDS above the cmc, the amount of AuCl_4^- reduced was measured for varying NaClO_4 concentrations, and the results are shown in Figure 5. It can be seen that as the electrolyte concentration increases, the amount of AuCl_4^- reduced decreases. Similar results were obtained when NaCl was used as the electrolyte. However, a problem was encountered when using the latter salt in that it induced a change in the 220 nm band, and at concentrations of NaCl higher than 50 mM the solutions became cloudy. For solutions containing NaClO_4 , no cloudiness was seen even up to 300 mM of added electrolyte.

Particle Size Determinations. The average particle diameter of the gold colloids was estimated by measuring over 600 particles per system on enlarged TEM prints. As

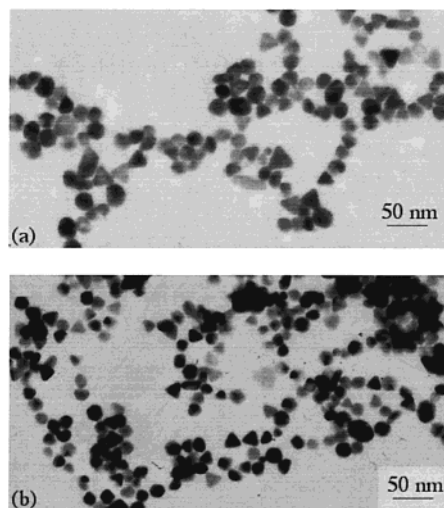


Figure 6. Electron micrograph prints showing the gold particles obtained following the sonication of (a) 2×10^{-4} M AuCl_4^- and 0.2 M ethanol and (b) 2×10^{-4} M AuCl_4^- and 1.0 M ethanol for 10 min.

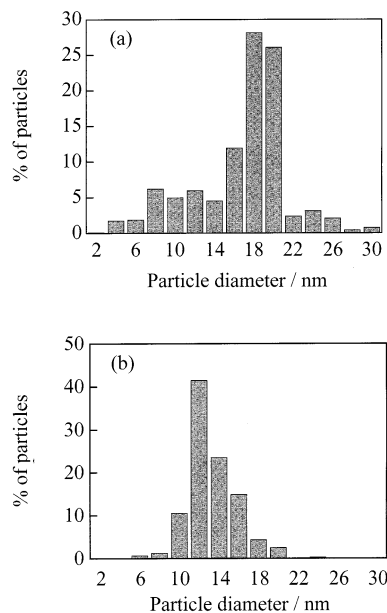


Figure 7. Typical particle diameter histograms for gold colloids produced at two different alcohol concentrations and alcohol type: (a) 1.0 M ethanol and (b) 0.15 M 1-pentanol.

seen from the electron micrograph prints in Figure 6, the gold particles produced (following 10 min sonication) are quite polydisperse in size and shape. Typical histograms of the particle diameters (taken as spheres) are shown in Figure 7. The average particle diameter and standard deviations for all the systems examined are listed in Table 1. It can be seen that the general trend with the higher alcohol concentrations is that the average particle diameter decreases as the chain length of the alcohol increases and that the particle size generally decreases with increasing alcohol concentration. Particle diameters obtained when 12 mM SDS was used instead of an alcohol were 12 ± 2 nm. (It should be noted that the AuCl_4^- solutions used for electron microscopy were totally reduced as it was found that if this was not done the AuCl_4^- remaining in solution would crystallize out onto the grids, making it difficult to clearly view the Au particles.)

γ -Irradiation of AuCl_4^- Solutions. Radiolytic reduction of AuCl_4^- solutions was conducted using a Co^{60} source (dose rate of 30 krad/h) to gain an understanding of the

(18) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978.

Table 1. Average Diameters of Gold Particles Produced on Sonication of 2×10^{-4} M AuCl_4^- Solutions in the Presence of Various Alcohols

alcohol	concentration (M)	average diameter (nm)
methanol	5	16 ± 4
ethanol	0.2	23 ± 7
ethanol	1	16 ± 5
1-propanol	0.1	15 ± 7
1-propanol	1	14 ± 4
1-butanol	0.04	13 ± 6
1-butanol	0.4	15 ± 3
1-pentanol	0.01	18 ± 5
1-pentanol	0.07	13 ± 4
1-pentanol	0.15	12 ± 2

Table 2. Calculated G Values and Number of One-Electron Reducing Species for the Reduction of $\text{Au(III)} \rightarrow \text{Au(0)}$ after 30 Min γ -Irradiation

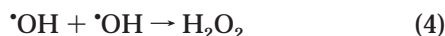
experiment no. ^a	G	no. of e^- per $\text{Au(III)} \rightarrow \text{Au(0)}$
1	3.4	1.8
2	3.0	2.0
3	3.2	1.7
4	3.5	1.7
average	3.3	1.9
With Au(0) Present		
1	3.4	1.8
2	3.3	1.8
3	3.2	1.9
average	3.3	1.8

^a Argon-saturated solutions of 0.2 mM $\text{AuCl}_4^-/0.1$ M 2-propanol.

$\text{Au(III)} \rightarrow \text{Au(0)}$ reduction process. Under the conditions of the radiolysis experiments, the yield (G value) of reducing species produced was taken to be 6.2/100 eV of adsorbed radiation energy.¹⁹ Table 2 shows the G values and the number of electrons from radiolytically produced one-electron reducing species that would be used for conversion of $\text{Au(III)} \rightarrow \text{Au(0)}$ obtained for 30 min irradiation of a 0.2 mM AuCl_4^- solution containing 0.1 M 2-propanol and the same solution containing some Au(0) before irradiation. The results obtained are in very good agreement with those reported elsewhere^{20,21} but more significantly indicate that the reduction process of $\text{Au(III)} \rightarrow \text{Au(0)}$ is partly catalytic, as significantly less than three electrons from reducing radicals radiolytically produced are required to achieve the reduction.

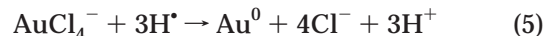
Discussion

The major reactions occurring when water is sonicated [] can be summarized by the following steps:²⁻⁴



For solutions containing only AuCl_4^- (i.e., no added alcohol or sodium dodecyl sulfate), some colloidal gold is produced

on sonication, although not as much as when the added surface active solute is present (see Figure 3). The reduction process can be expected to involve the primary reducing species H^\bullet (considering that all of the gold(III), gold(II), and gold(I) chloride species have positive reduction potentials),²¹ and an overall stoichiometric equation, comprising three separate near diffusion-controlled one-electron transfer steps may be written as

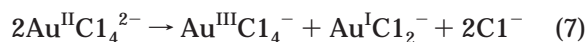


Particle growth can be described by reaction 6:



where n may range from a few atoms to many thousands, as would be the case for particles of diameters around 20 nm. The growth of a particle may be the result of single atoms adding onto a small particle, as implied by reaction 6, or through the coalescence of two smaller particles.²¹

The reduction of AuCl_4^- and the subsequent particle formation and growth, however, is known to be much more complex than indicated by the reactions described by reactions 5 and 6. Apart from the disproportionation reaction (reaction 7) (rate constant²¹ for this reaction is $0.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),



colloids of the type $(\text{Au}^{\text{I}}, \text{Au}_n) \cdot \text{Cl}^-$ (consisting of an Au^0 core with adsorbed Au(I) atoms and associated chloride ions) have been implicated in the overall process yielding colloidal gold.²¹

It has also been suggested that a slow disproportionation reaction of Au(I) occurs after its adsorption onto gold colloids, that is,



which is then followed by Au(II) disproportionation (reaction 7) also on the surface of the colloidal gold.

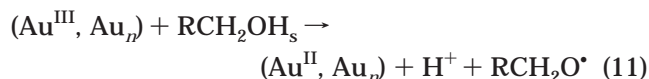
For example, in the presence of a primary alcohol (RCH_2OH ; R = H or alkyl group) that can act as a radical scavenger,²² the following additional reactions can take place:^{6,13}



followed by a more complex sequence of three separate one-electron transfer reactions that (similar to reaction 5) can be naively summarized by:



In addition to these reactions, it has been proposed that alcohol adsorbs (RCH_2OH_s ; s \rightarrow surface adsorbed) onto Au colloids and reduces adsorbed Au(III)²³ in a reaction of the type²¹



(21) Gachard, E.; Remita, H.; Khatouri, J.; Keita, B.; Nadjio, L.; Belloni, J. *New J. Chem.* **1998**, *22*, 1257–1265.

(22) The formation of radicals within the collapsing bubbles because of the evaporation and subsequent fragmentation of the alcohols is considered insignificant. Headspace analysis of aqueous solutions containing alcohols after about 15 min sonication at 20 kHz showed no detectable pyrolysis products (i.e., methane, ethane, etc.).

(19) Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*, 3rd ed; Wiley and Sons: New York, 1990.

(20) Baxendale, J. H.; Koulkes-Pujo, A. M. *J. Chim. Phys.* **1970**, *67*, 1602–1602.

followed by the disproportionation reactions 7 and 8 and further reactions of $\text{RCH}_2\text{O}^\bullet$.²⁴

The relative importance of the above reactions will of course change during the overall reduction process, depending on the concentrations of the various intermediates (Au(III) and alcohol) in solution at any particular time. It may also be expected that the alcohol type will influence the reduction rate, as the amount adsorbed onto the gold surface favors the more hydrophobic alcohol.²⁵ Apart from its influence on reaction 11, the amount of adsorbed alcohol will most likely affect the amount of adsorbed gold(III), gold(II), and gold(I) chloride species on colloidal gold and, therefore, the rates of reaction involving these species. The complex interrelationship between the different gold species and their reactions has been used to explain the γ -irradiation results (Table 2) that suggest that only two electrons from radiolytically produced reducing species are required to convert Au(III) \rightarrow Au(0).²¹ It has also been found that the G -value involved in the overall reduction changes during the course of the conversion to colloidal gold, and this result is consistent with a change in the relative importance of the various intermediate reduction steps involved.

The possibility that the reduction of Au(III) \rightarrow Au(0) occurs through some thermal reaction of AuCl_4^- with alcohol within the high-temperature volume around a collapsing bubble²⁶ was also considered. However, the trends observed for the alcohols shown in Figure 3 do not suggest that a thermal process is responsible for the reaction. The different alcohols, at the same concentration, would be expected to react at a similar rate with AuCl_4^- considering the high positive redox potential (E°) for the reduction of Au(III) to Au(II),²¹ yet this is not what is observed. In addition, the observation that a limiting rate is reached at relatively low alcohol concentrations also argues against a thermal reaction reducing AuCl_4^- , as the alcohol concentrations in solution immediately surrounding the cavitation bubbles are considerably below the saturation conditions.

The reactions listed above, while describing the complex sequence of steps leading to the production of colloidal gold, cannot account for the alcohol trends shown in Figure 3. However, it is noteworthy that the results are very similar to those obtained in the sonochemical dissolution of colloidal MnO_2 in the presence of alcohols.¹³ It was found in this latter study that irrespective of which alcohol was used in the experiment it was the concentration of the alcohol at the bubble-water interface that determined the extent of reaction of the colloid during sonication. It was proposed that, on bubble collapse, surface-adsorbed alcohol molecules scavenged the primary radicals produced within the bubble and in doing so prevented the recombination reactions 2–4. The secondary radicals produced at the bubble interface could then diffuse into bulk solution and react with other solution species. The observation that a maximum amount of AuCl_4^- is reduced at higher alcohol concentrations can be simply ascribed to there being sufficient alcohol adsorbed at the bubble interface to scavenge the maximum number of the primary radicals produced from bubble collapse. This proposal is supported

(23) Wall, J.; Grieser, F.; Zukoski, C. F. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4017–4020.

(24) The reduction potential of the $\text{RCH}_2\text{O}^\bullet$, $\text{H}^+/\text{RCH}_2\text{OH}$ couple is about 1.3 V at pH 6, based on related compounds given in Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(25) (a) Holze, R.; Beltowska-Brzezinska, M. *Electrochim. Acta* **1985**, *30*, 937–939. (b) Vukusic, P. S.; Bradberry, G. W.; Sambles, J. R. *Surf. Sci. Lett.* **1992**, *277*, L34–L38.

(26) Suslick, K. S.; Hammerton, D. A.; Cline, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5641–5642.

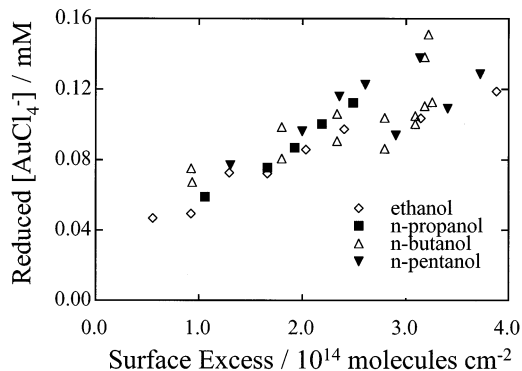


Figure 8. Amount of AuCl_4^- reduced as a function of the surface excess of the alcohols for 2×10^{-4} M AuCl_4^- solutions sonicated for 2.5 min with varying alcohol type and concentration.

by the observation that increasing the concentration of alcohols in solution decreases the yield of H_2O_2 through their ability to scavenge OH radicals.⁵

The above model can be applied to the results of Figure 3 by converting the bulk alcohol concentrations to the amount of alcohol adsorbed at a gas–solution interface (the surface excess, Γ). Γ can be calculated from surface tension data for the alcohols using the Gibbs adsorption equation.¹³ In Figure 8 is shown how the amount of AuCl_4^- reduced varies as a function of the surface excess of the various alcohols. The result that the extent of AuCl_4^- reduced correlates well with the surface excess of the alcohol and not directly with its bulk solution concentration lends strong support for the mechanism proposed.

The results obtained with SDS also lend themselves to the same explanation as that given for the alcohols. SDS molecules will adsorb to the bubble–water interface and scavenge²⁷ the primary radicals produced within the cavitating bubble in much the same way as that of interfacially adsorbed alcohol. The more surfactant that adsorbs to the bubble–water interface, the greater the number of primary radicals that will be scavenged, and consequently the more Au^0 that will be produced. The plateau obtained, which occurs at the cmc for all three salt/SDS systems, is significant because it indicates that only the monomer of the surfactant is involved in the reaction scheme. Surfactant molecules in excess of the cmc form micelles, and therefore, the amount of SDS at the bubble–water interface remains constant at SDS concentrations above the cmc.¹⁸ The plateaus obtained at SDS concentrations above the cmc reflect a limit in the amount of primary radicals that can be scavenged by the surfactant.

The other noticeable difference of the SDS results, as compared to the alcohol systems,²⁸ is that the addition of electrolyte causes the plateau in the amount of AuCl_4^- that is reduced to decrease the higher the electrolyte level. This result is difficult to explain but it is unlikely that the electrolyte, at the levels used, affects the bubble population or the bubble dynamics at 20 kHz.²⁹ Also, adding elec-

(27) Surfactant molecules such as SDS are able to efficiently scavenge both H and OH radicals, and the secondary radicals produced are able to reduce ferricyanide ions under similar conditions to those used in the AuCl_4^- solution experiments. See Almgren, M.; Grieser, F.; Thomas, J. K. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1674–1687. As AuCl_4^- is a stronger oxidant than ferricyanide, the surfactant radicals can be expected to react at least as well with AuCl_4^- as with ferricyanide.

(28) In experiments conducted with 2×10^{-4} M AuCl_4^- /alcohol (with up to 100 mM NaClO_4 in solution) the same amount of AuCl_4^- was reduced after 2.5 min sonication as in solutions in the absence of the electrolyte. See ref 31 for experimental results.

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trolyte does not decrease the amount of surfactant that can adsorb at the solution–gas interface—in fact, the presence of electrolyte slightly enhances the interfacial adsorption of surfactant.¹⁸ It is possible that the added salt affects the levels of adsorption of the surfactant and other solution species onto the gold colloids produced and that this decreases the amount of AuCl_4^- reduced for a given period of sonication. It has been suggested that the rate of Au^I disproportionation (reaction 8) is particularly sensitive to the type of Au^I complex that is on the surface of the gold colloid.²¹

A final aspect of the results to consider is the influence of the alcohols on the particle size of the gold colloids produced. The particle size is seen to decrease with increasing alcohol concentration and alkyl chain length (Table 1). It is well-known that the adsorption of solutes on the surface of a growing particle limits the particle growth (e.g., ref 30). As alcohols can adsorb onto gold in aqueous solutions,³¹ it is mostly likely that the adsorbed molecules stabilize the particles at a smaller size and

prevent further growth of the colloid. The amount of alcohol adsorbed will depend on the alcohol used and its concentration, with the more hydrophobic alcohols being adsorbed more readily³¹ and higher solution concentrations enhancing the amount adsorbed. The stabilization to particle growth is likely to affect both small particle–small particle coalescence processes as well as single atom addition to a small particle, as commented on earlier. Irrespective of which is the more dominant process, the role of adsorbed alcohol will be the same, and as more alcohol covers the surface of a gold particle, the effect will be to reduce the final particle size.

Acknowledgment. R.A.C. acknowledges the receipt of an Australian Postgraduate Research Award. This work was supported by a grant from the Australian Research Council. Support from the EC (COST Chemistry D10 program) is also gratefully acknowledged.

LA020276F

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