

Sonochemistry and Sonoluminescence in Aqueous AuCl_4^- Solutions in the Presence of Surface-Active Solutes

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The 515 kHz ultrasound-initiated reduction of AuCl_4^- to $\text{Au}(0)$ was examined as a function of the concentration of various surface-active solutes. The amount of AuCl_4^- reduced in the presence of ethanol, propan-1-ol, and butan-1-ol was found to be dependent on the surface excess of the alcohol at the gas/solution interface, i.e., the relative concentration of the alcohol at the gas/solution interface compared to the bulk solution concentration. The efficiency of reduction of AuCl_4^- in the presence of the surfactants sodium dodecyl sulfate or octaethylene glycol monodecyl ether was found to be related to the monomer concentration of the surfactant in solution. The light emitted (sonoluminescence) during ultrasonic irradiation of the aqueous solutions was also monitored and compared with the trends observed in the sonochemical experiments. The sonoluminescence was observed to be significantly reduced in the presence of alcohol, and the effect was correlated with the surface excess of the alcohols at the gas/solution interface. In contrast, the effect of the surfactants on the sonoluminescence was highly dependent on concentration and headgroup type of the surfactant.

1. Introduction

It is only within the last couple of decades that there has been a growing interest in the application of ultrasound to influence or initiate chemical processes, even though its effects have been known since the 1940s.¹ Similarly, there has been a renewed interest in sonoluminescence, the emission of light when ultrasound passes through a liquid, especially since the development of single-bubble sonoluminescence.²

The underlying cause for both sonochemistry and sonoluminescence is cavitation.³ Cavitation is the term given to the acoustically driven formation, growth, and subsequent collapse of bubbles in a liquid. In the final stages of the process the more diffuse energy of the sound wave is concentrated into the almost adiabatic heating of the gas and vapor within the bubble. It is the collapse of the bubble that leads to localized increases in temperature, commonly referred to as “hot spots”, of the order of several thousand degrees, and pressures of several hundred atmospheres.^{3–5} These conditions, as may be expected, produce radicals^{6,7} and excited-state species^{8–10} within the bubbles and, consequently, chemical activity.

In our previous work on sonochemistry^{11,12} and sonoluminescence^{13,14} processes in aqueous solutions, we have been concerned with the effects that surface-active solutes have on the two ultrasound-generated phenomena. It was found that the additives can dramatically affect the extent of certain sonochemical reactions as well as enhance or quench the sonoluminescence. These studies, however, were not conducted under the same conditions and the trends observed between the two processes could not be directly compared. This paper is concerned with an examination of the influences of surface-active solutes, aliphatic alcohols and surfactants, on both the sonochemistry and sonoluminescence in aqueous solution. The

reduction of AuCl_4^- to colloidal gold has been used to monitor the effects of the surface-active reagents on the sonochemistry that occurs in solution. The effects of the same solutes on the sonoluminescence was followed by measuring the changes in the emission intensity and the emission spectra produced from the various solutions examined. The solution and insonation conditions for sonochemical and sonoluminescence measurements were chosen to be identical, thereby allowing a direct comparison of the effects of the surface-active agents on the two, quite different, acoustically produced phenomena.

2. Experimental Section

2.1. Materials. All alcohols used were AR grade. Ethanol was supplied by Merck Chemicals, propan-1-ol by BDH, and butan-1-ol by Tokyo Kasei. The anionic surfactant sodium dodecyl sulfate (SDS) was BDH special purity grade and the nonionic surfactant, octaethylene glycol monodecyl ether (C_{10}E_8) was from the Nikko Chemical Company. Hydrogen tetrachloroauric(III) acid (HAuCl_4 , ACS Reagent) was obtained from Sigma Chemicals, and NaClO_4 (>99%) was purchased from BDH Chemicals. The argon used to saturate the solutions prior to sonication was BOC ultrahigh purity grade. All chemicals were used as received. Water was taken from a three-stage “Milli-Q” purification system and had a conductivity of less than $10^{-6} \text{ S cm}^{-1}$ and a surface tension of 72.0 mN m^{-1} at 25°C .

2.2. Methods. In the present study 25 mL of solutions of $2 \times 10^{-4} \text{ M AuCl}_4^-$ at a pH of 3.2 ± 0.2 containing alcohol or surfactant were used. The solutions were saturated with argon and sonicated using pulsed 515 kHz ultrasound from a modified Undatim reactor.¹³ The pulses were 4 ms long with 12 ms between pulses. The intensity of the sonoluminescence signal resulting from the individual ultrasound pulses was detected with a Hamamatsu photomultiplier and recorded on a LeCroy 7242 digital oscilloscope. A steady-state emission intensity was usually achieved after about 50 pulses,¹³ and the intensities reported are from the average of the next 100–150 individual

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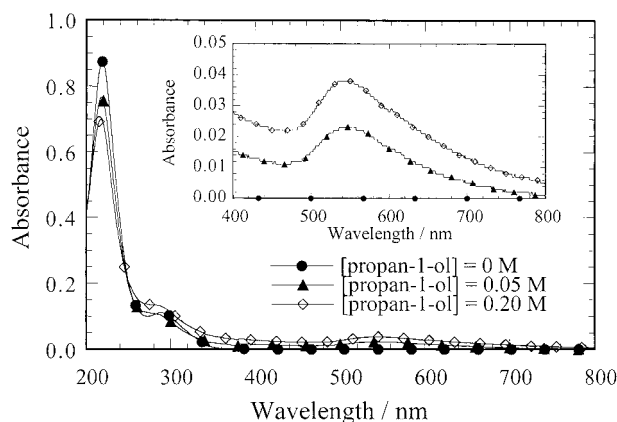


Figure 1. Absorbance spectra (using a 0.2 cm path length cell) of argon-saturated aqueous AuCl_4^- solutions (0.2 mM) following 2.5 min of pulsed sonication at 515 kHz in the presence of varying amounts of propan-1-ol. Insert shows an expansion of the region where the colloidal gold band absorbs.

pulses. Emission spectra were recorded on a Hitachi F-4500 spectrofluorimeter. The solutions used to obtain spectra were run in the absence of AuCl_4^- to avoid the buildup of colloidal $\text{Au}(0)$ which increasingly absorbs the sonoluminescence as sonication proceeds.

For the sonochemical experiments, the pulsed sonication was conducted for 2.5 min for the alcohol systems and 7.5 min for the surfactant solutions. This equates to a total sonication time of 37.5 and 112.5 s, respectively, for the two systems. The power absorbed by the solutions, measured by calorimetry, was 0.3 W cm^{-2} and delivered by a 3.5 cm diameter transducer plate.

The quantitative reduction of the AuCl_4^- was measured by optical absorption using the band centered around 220 nm. Before these measurements were made the solutions were centrifuged at 20 000 rpm for 20 min to remove any colloidal gold from solution, which absorbs to some extent over most of the 200–800 nm range.

3. Results

3.1. Sonochemistry in AuCl_4^- (aq)/Alcohol Solutions. Examples of absorption spectra obtained from argon-saturated AuCl_4^- solutions sonicated for 2.5 min in the presence of different concentrations of propan-1-ol are shown in Figure 1. It can be seen that following sonication the absorption band at 220 nm decreased to a greater extent with increasing concentrations of propan-1-ol, and the $\text{Au}(0)$ band at 530 nm increased. These results indicate that AuCl_4^- is being reduced to form colloidal gold and that the amount of reduction, for a given time of sonication, is dependent on the concentration of alcohol in solution. Similar results were obtained when AuCl_4^- solutions were sonicated with 20 kHz ultrasound; however, the efficiency of reduction was considerably lower at this lower frequency.¹¹

The effect of changing the concentration of the alcohols examined on the amount of AuCl_4^- reduced, for a fixed time of sonication, is shown in Figure 2. For all three alcohols examined a common plateau in amount of AuCl_4^- reduced, within experimental error, is reached at around 0.04–0.05 mM (about 25% of the initial concentration of AuCl_4^-). However, the alcohol concentration at which this plateau is reached decreases as the hydrocarbon chain length of the alcohol increases. For ethanol the plateau is reached at $\sim 0.06 \text{ M}$, for propan-1-ol it is at $\sim 0.04 \text{ M}$, and for butan-1-ol it is at $\sim 0.01 \text{ M}$. These trends are similar to what has been observed using other alcohols and at other ultrasound frequencies.¹⁵

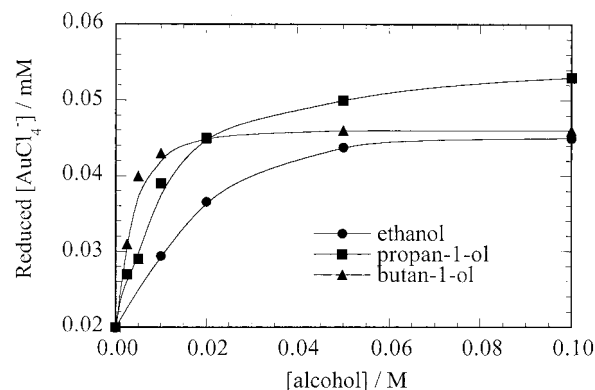


Figure 2. Reduction of aqueous AuCl_4^- (0.2 mM) as a function of bulk alcohol concentration following 2.5 min of pulsed sonication at 515 kHz in argon-saturated solutions.

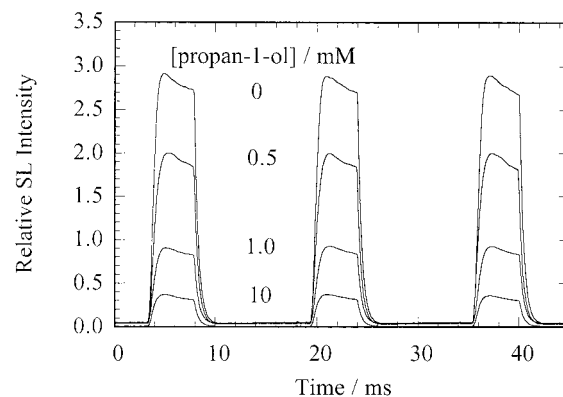


Figure 3. Typical 4 ms sonoluminescence pulse "trains" obtained in the presence of increasing amounts of propan-1-ol.

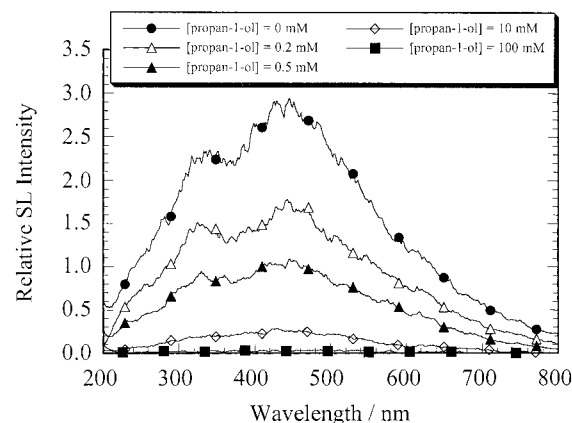


Figure 4. Sonoluminescence spectra of argon-saturated aqueous solutions containing propan-1-ol. The alcohol concentrations overlap those shown in Figure 3. Spectra are uncorrected for detection sensitivity changes across the wavelength range shown.

3.2. Sonoluminescence from AuCl_4^- (aq)/Alcohol Solutions. The relative sonoluminescence intensities (wavelength integrated) and sonoluminescence spectra under pulsed ultrasound conditions at a few selected concentrations of propan-1-ol are shown in Figures 3 and 4, respectively.

It can be seen in Figure 3 that the emission pulse shape remains constant as the intensity decreases with increasing concentration of propan-1-ol. This was observed with all three alcohols studied. Similarly, the emission spectrum is uniformly quenched with increasing alcohol concentration. The degree of quenching of the sonoluminescence spectrum, at a specific alcohol concentration, is in good agreement with the decrease

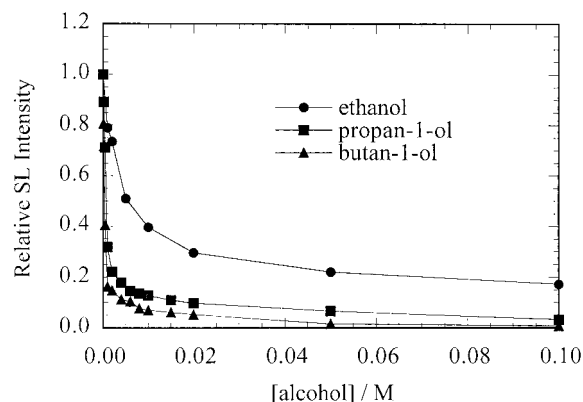


Figure 5. Relative sonoluminescence intensities from argon-saturated aqueous solutions as a function of bulk alcohol concentration.

in the emission pulse intensity observed at the same alcohol concentration.

The features of the spectrum are similar to those reported in the literature for argon-saturated water undergoing multibubble sonoluminescence.¹⁶ Although it is still not completely clear what is responsible for the broad wavelength sonoluminescence, a number of researchers have suggested it is due to the overlap of the emission bands from a range of electronically excited-state species, e.g., OH^* , H_2O^* , Ar-OH^* , etc.^{8,9}

However, due to the high temperature and pressure conditions within the bubble, band broadening occurs and therefore it is extremely difficult to unequivocally identify the various postulated transitions. The one exception being the OH^* emission band at about 310 nm.

The normalized (relative to pure water) sonoluminescence intensities obtained from solutions containing a range of concentrations of ethanol, propan-1-ol, and butan-1-ol are shown in Figure 5. The same intensities were obtained whether or not AuCl_4^- was present in the solution.

It can be seen in Figure 5 that the sonoluminescence is quenched, by all three alcohols, in two distinct concentration regimes. There is an initial sharp decline in sonoluminescence with added alcohol until the normalized intensity is less than about 0.2 for propan-1-ol and butan-1-ol and about 0.4 for ethanol, followed by a much more gradual reduction in intensity with increasing alcohol concentration. Also, an increase in the alkyl chain length of the alcohol results in a more pronounced effect on the reduction in the sonoluminescence signal. These trends have also been observed in single-bubble sonoluminescence experiments indicating they are not specific to multibubble systems.¹⁴

3.3. Sonochemistry in AuCl_4^- (aq)/Surfactant Solutions.

The amount of AuCl_4^- reduced after 7.5 min of sonication, as a function of the concentration of C_{10}E_8 , SDS, and SDS in the presence of 0.1 M NaClO_4 is presented in Figure 6. This figure shows that the amount of AuCl_4^- reduced increases as the surfactant concentration increases until a plateau in the amount reduced occurs. The surfactant concentrations at the point of reaching the plateaus are 7.5 mM for SDS, 1.5 mM for SDS with 0.1 M NaClO_4 added, and 1 mM for C_{10}E_8 . These concentrations correspond to the critical micelle concentrations (cmc) of the surfactants under the conditions indicated.¹⁷ Another point to note is that the plateau value of AuCl_4^- reduced is different for each surfactant system.

3.4. Sonoluminescence from AuCl_4^- (aq)/Surfactant Solutions. The normalized (relative to water) sonoluminescence intensity as a function of SDS concentration is shown in Figure 7. At low SDS concentrations the sonoluminescence exceeds

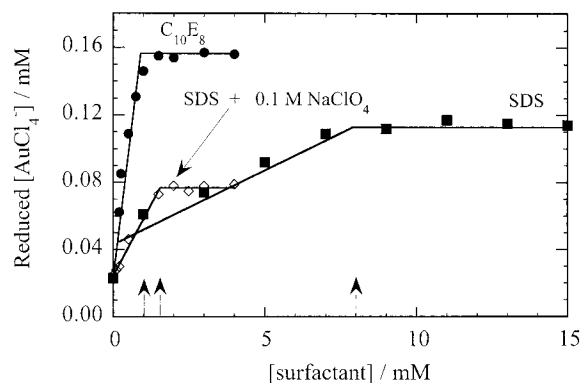


Figure 6. Reduction of aqueous AuCl_4^- (0.2 mM) as a function of surfactant concentration following 7.5 min of pulsed sonication at 515 kHz in argon-saturated solutions. The arrows indicate the experimentally determined cmc's of the three surfactant systems shown.

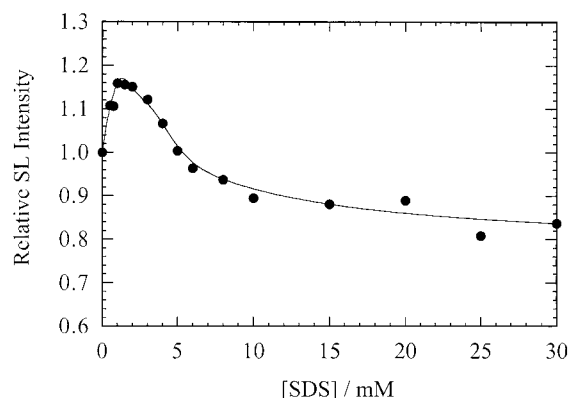


Figure 7. Relative sonoluminescence intensities from argon-saturated aqueous solutions as a function of SDS concentration.

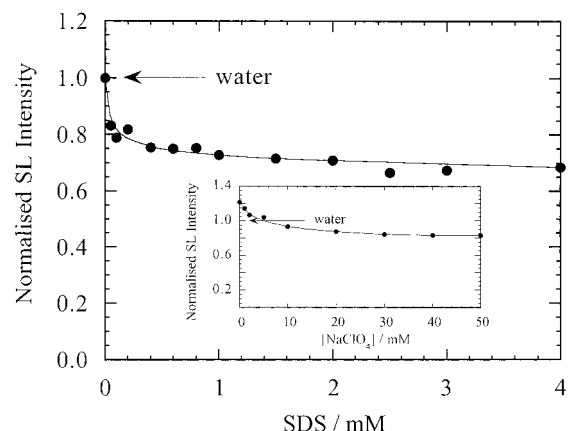


Figure 8. Sonoluminescence intensities (relative to argon-saturated water) from argon-saturated water as function of SDS concentration in the presence of 0.1 M NaClO_4 . Insert: Sonoluminescence intensities in the presence of SDS (1.5 mM) and varying NaClO_4 concentrations.

that obtained in pure water, reaching a maximum at a SDS concentration of about 1.5 mM. The intensity then decreases at higher concentrations with little change at concentrations above about 8 mM.

The effect of adding an electrolyte was also examined, and these results are shown in Figure 8. It can be seen that increasing the concentration of either SDS or NaClO_4 , while keeping the other constant, decreases the sonoluminescence to a level that is lower than that obtained in water at the higher end of the concentration ranges examined.

The effect of increasing concentration of the nonionic surfactant, C_{10}E_8 , on the sonoluminescence is shown in Figure

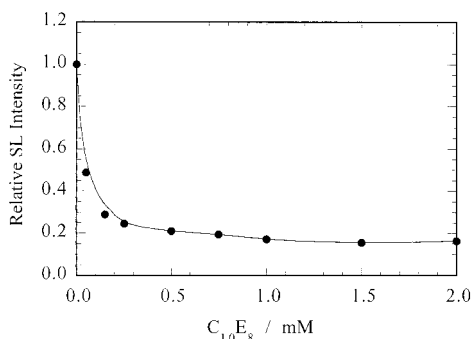


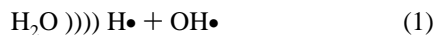
Figure 9. Relative sonoluminescence intensities from argon-saturated aqueous solutions as a function of $C_{10}E_8$ concentration.

9. $C_{10}E_8$ reduces the emission intensity over the whole concentration range studied. The effect is considerably more pronounced than that obtained from SDS in the presence of $NaClO_4$, but comparable to the quenching levels obtained from the alcohol systems. Addition of $NaClO_4$ (up to 0.1 M) to $C_{10}E_8$ solutions had essentially no effect.

4. Discussion

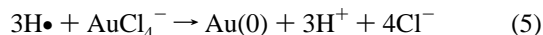
In the discussion to follow, the alcohol systems are considered separately from the surfactant results. The trends observed from the two types of surface-active agents are, in general, quite different and as will become clear in the discussion the two types of solutes influence the cavitation process in quite different ways.

4.1. Sonochemistry and Sonoluminescence in $AuCl_4^-$ (aq)/Alcohol Solutions. The primary reactions occurring during the sonication ()))) of water are^{3,18}



Henglein¹⁸ has estimated that about 80% of the primary radicals recombine within the bubble. The fraction that escape from the bubble may also recombine or react with solutes in the bulk solution.

In Figure 2 it can be seen that about 10% of the initial amount of $Au(III)$ is reduced when no alcohol is present in solution. It is likely that this occurs by H atoms that have escaped the cavitation region, reducing the gold chloride in solution,^{11,19} possibly by the overall reaction



although it is also likely that the reduction process is more complex²⁰ than indicated by eq 5. It is also possible that some $AuCl_4^-$ decomposes thermally in the "hot shell" around a collapsing bubble to form $Au(0)$.

An enhancement in the amount of oxidant reduced when alcohols are added has been previously observed in the reduction of $AuCl_4^-$, and also colloidal MnO_2 , using 20 kHz ultrasound.^{11,12} The effect was explained by assuming that alcohol molecules adsorb at the bubble/solution interface and scavenge some of the primary radicals produced within the bubble, thereby producing alcohol radicals. These secondary radicals then diffuse away from the interface and react with the solute in solution.

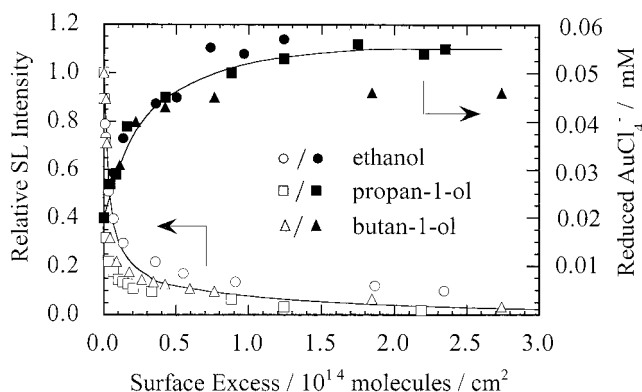
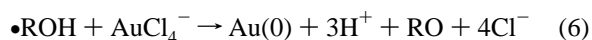


Figure 10. Amount of $AuCl_4^-$ reduced and sonoluminescence intensity as a function of the surface excess concentration of alcohol. Data taken from Figures 2 and 5, and additional data not shown.

This last process can be described by the generic overall stoichiometric reaction



where $\bullet ROH$ represents an alkyl alcohol radical and RO the corresponding aldehyde or ketone that is formed in the reaction.²¹ Reactions 2–4, which lead to unreactive products, become less important as the concentration of alcohol is increased. The plateau in the amount of $AuCl_4^-$ reduced then relates to the maximum number of primary radicals that can be scavenged by interfacial alcohol.

This model is supported by the observations that added alcohols and other surface-active solutes decrease the amount of H_2O_2 produced^{6,18} and that there is a good correlation between the extent of reduction and the Gibbs surface excess concentration (Γ_s , molecules/cm²) at the air/solution interface of the alcohols.^{11,12} To illustrate the latter correlation, the data in Figure 2 and other data at higher concentrations (not shown) have been converted to concentration of $AuCl_4^-$ reduced as a function of Γ_s and are presented in Figure 10. The trend displayed in Figure 10 clearly shows that the amount of $AuCl_4^-$ reduced is not dependent on the particular alcohol in solution, but only on the amount that is present at the bubble/solution interface. These results agree quite well with our previous work¹¹ conducted at 20 kHz, and this shows that the correlation is not frequency dependent.

The effect of the alcohols on the sonoluminescence from $AuCl_4^-$ /alcohol solutions can also be considered in the same way as the sonochemistry results, and the result of doing so is shown along with the sonochemical data in Figure 10. It can be seen here that the degree of quenching is also directly related to the surface excess concentration of the alcohol. This trend is similar to that reported in air-saturated solutions;¹³ however, the concentration range of the quenching is about 10 times lower in the argon-saturated systems of the present study.

The comparison of the sonoluminescence and sonochemistry in identical solutions (Figure 10) shows that while both phenomena scale to the surface excess of the alcohols, the range over which the effect occurs is not the same. Almost 80% of the sonoluminescence signal is quenched before any significant enhancement in $AuCl_4^-$ reduction takes place. That is, surface-active solutes have a comparatively greater influence on sonoluminescence than on sonochemical activity.

A possible explanation for this result may rest with the effect the alcohols have on the temperature within the bubble. If it is assumed that some alcohol molecules, or more likely their decomposition products, accumulated within a bubble over many

oscillations, it can be expected that the bubble core temperature will be decreased. Quantitatively this effect can be partly described by the following equation, which stems from a simple hydrodynamic model for cavitation:³

$$T_{\max} \approx T_o P_a (\gamma - 1) / P_v \quad (5)$$

where P_v is pressure within the bubble at the point of collapse, P_a is the pressure exerted on the bubble at the beginning of collapse, T_o is the ambient temperature and T_{\max} the peak temperature generated on collapse. The presence of complex molecules within the bubble will act to decrease the heat capacity ratio, $\gamma = C_p/C_v$, and hence the core temperature. In addition, the core temperature will be reduced because the molecules within the bubble will consume energy through thermal dissociation processes.²² With lower core temperatures the high-energy electronic excited states are less likely to form and consequently there will be less sonoluminescence.

The lower core temperatures would also be expected to decrease radical formation within the bubble. However, because less energy is required to form these than excited-state species, the effect should be comparatively less significant. In addition, the increased competition to scavenge primary radicals by alcohol molecules adsorbed at the bubble surface may off-set a small decrease in the total number of radicals produced at higher solute concentrations.

4.2. Sonochemistry and Sonoluminescence in AuCl_4^- (aq)/Surfactant Solutions. The increase in the amount of AuCl_4^- reduced with increasing surfactant concentration can be explained in a way similar to that given for the alcohol systems. Surfactant molecules that adsorb at the bubble/solution interface scavenge²³ the primary radicals created within the bubble and the secondary radicals produced diffuse away from the interface and react with AuCl_4^- in bulk solution. The observation that the plateaus in the amount of AuCl_4^- reduced occur at the cmc of the different surfactant solutions suggests that only surfactant in monomer form is involved in the scavenging reaction. At surfactant concentrations above the cmc the excess surfactant forms micelles in solution and therefore the surfactant concentration at the bubble/solution interface remains essentially constant. The differences in the plateau values for the three systems shown in Figure 6 are difficult to explain. A possible explanation may rest with the effect that the interfacially adsorbed surfactants have on bubble–bubble interactions. This is developed a little more below when discussing the sonoluminescence results.

The sonoluminescence behavior observed with SDS is similar, but not identical, to what we have seen previously in air-saturated solutions.¹³ The behavior is best explained with reference to Figure 11. In pure water, little electrostatic repulsion between bubbles exists and subject to a sound field bubbles will aggregate.^{3a} The bubbles at the center of an aggregate are somewhat shielded from the applied sound field, referred to as impedance shielding,^{3a} and are less likely to undergo collapse. The adsorption of SDS at the bubble water interface will make the cavitation bubbles electrostatically charged, and the more surfactant adsorbed the larger the surface charge and also the greater the electrostatic repulsion between bubbles. On the basis of this model the increase in sonoluminescence at low concentrations of added SDS is associated with the dispersion of bubbles. Therefore, a greater number of bubbles may be expected to undergo collapse under these conditions compared to the situation in pure water.

The decrease in the sonoluminescence at concentrations above about 1.5 mM, at which point the equilibrium concentration of

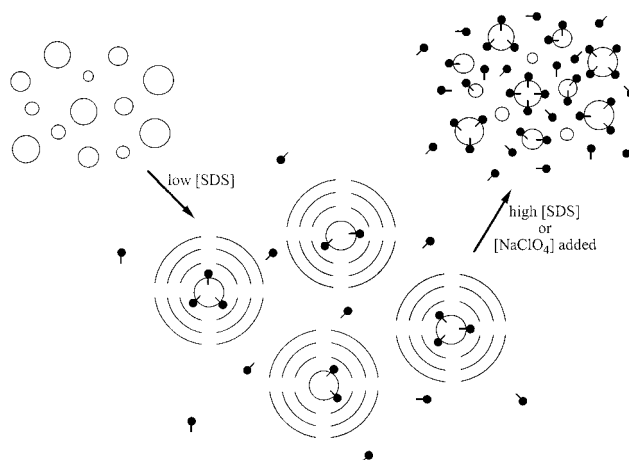


Figure 11. Diagrammatic representation of cavitation bubbles in an acoustic field. In the absence of the anionic surfactant, SDS, bubbles aggregate. In the presence of SDS at low concentrations, the bubbles adsorb surfactant and become negatively charged and electrostatically interact leading to dispersion of the bubbles. At higher concentrations of SDS, or added electrolyte, the increase in ionic strength leads to electrostatic screening between bubbles and clustering again occurs.

surfactant at the air/solution interface is about 90% saturated,²⁴ can be ascribed to the increasing ionic strength of the solution which will act to screen the electrostatic repulsion between bubbles and lead once again to greater levels of bubble clustering. This explanation is supported by the results shown in Figure 8. The presence of an inert electrolyte eliminates the maximum in the sonoluminescence intensity with added SDS, and adding electrolyte to the SDS solution giving the maximum sonoluminescence, causes the emission intensity to decrease.

The decrease in the sonoluminescence intensity following the addition of the nonionic surfactant (Figure 9), C_{10}E_8 , is very similar to the behavior observed with the alcohols. C_{10}E_8 , like SDS, is not volatile and would not be drawn into a bubble during its expansion phase as is likely to occur with the alcohols. It is possible, however, that due to the higher collapse temperatures of argon bubbles some surface-adsorbed molecules decompose in the “hot shell” around the bubble surface and the decomposition products enter the bubble and decrease the sonoluminescence in the same way as has been discussed for the alcohol results. To a lesser extent this must also happen in the SDS system as the intensity of the sonoluminescence at high concentrations reaches lower levels than that obtained in air-saturated solutions.^{13,25}

One final point to note in the comparison of sonoluminescence and sonochemistry in the surfactant systems is that, like the situation observed for the alcohol-containing solutions, the sonoluminescence is affected at lower solute concentrations than the sonochemistry (cf. Figures 6, 8, and 9). The sonoluminescence behavior in SDS solutions is complicated by interbubble electrostatic effects, but there does not seem to be any corresponding effects in the sonochemical activity. This too suggests that sonoluminescence is far more sensitive to changes in the conditions of the bubble core than is sonochemical activity.

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