

## Sonoluminescence from Aqueous Alcohol and Surfactant Solutions

Muthupandian Ashokkumar, Robert Hall, Paul Mulvaney, and Franz Grieser\*

Advanced Mineral Products Research Centre, School of Chemistry, University of Melbourne, Parkville 3052, Australia

Received: July 29, 1997; In Final Form: October 6, 1997<sup>®</sup>

The sonoluminescence generated in water with pulsed 515 kHz ultrasound has been studied in the presence of different chain length ( $C_1$ – $C_5$ ) aliphatic alcohols and the surfactants sodium dodecyl sulfate (SDS), dodecyltrimethylammonium chloride (DTAC), and *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (DAPS). The ultrasound pulse widths used ranged from 1 to 10 ms, with duty cycles (on/off ratios) of 1:3 to 1:9. It was found that the sonoluminescence from the initial pulses was very low but increased in intensity and reached a maximum after 20–50 pulses, for all systems studied, depending on the pulse width and duty cycle. In the presence of alcohol the maximum signal decreased with increasing alcohol concentration, and the signal decline was more pronounced with increasing chain length of the alcohol. A good correlation was found to exist between the decline in the sonoluminescence signal and the Gibbs surface excess of the alcohol at the air/water interface. In the presence of SDS (an anionic surfactant) and DTAC (a cationic surfactant), quite different behavior was observed. At low concentrations of these two surfactants the maximum signal was significantly enhanced over that obtained in pure water, reaching a maximum at about 1 mM of surfactant. At higher concentrations the signal decreased again reaching a limiting value similar to that obtained in pure water. The sonoluminescence signal in DAPS (a zwitterionic surfactant) solutions remained much the same as in pure water. On the addition of 0.1 M NaCl to the three different types of surfactant solutions, the intensities of the emission signals obtained were essentially the same as in pure water. Possible mechanisms responsible for the different behavior in the sonoluminescence signal in the presence of the alcohols and surfactants are discussed.

### Introduction

Although the phenomenon of sonoluminescence has been known for a considerable time and observed from a range of fluids, its origin is still under debate. It is generally accepted that sonoluminescence is associated with the rapid, sound-driven, collapse of a bubble in a fluid. It is also known that the broad wavelength emission of light associated with sonoluminescence occurs at the final stages of compression<sup>1</sup> of the bubble and that it is extremely short-lived. In the case of a single bubble the pulse width has been recently measured to be in the range of 60–270 ps, depending on the gas concentration and acoustic driving pressure.<sup>2</sup> In a multibubble field such precise values have not yet been measured, but a sonoluminescence pulse width of less than 1.1 ns has been inferred from the response time of the detection system used.<sup>3</sup>

Sonoluminescence has been suggested to be due to blackbody radiation, emission from excited-state species (electronic and pressure-broadened vibration–rotation lines), bremsstrahlung from a relaxing plasma within the collapsed bubble, and other more exotic processes.<sup>3–5</sup> A good review of most of the explanations offered for sonoluminescence is given by Leighton.<sup>4</sup>

We have recently studied the effects of surface active agents, aliphatic alcohols, and surfactants on the sonochemical formation and dissolution of various aqueous sols as a means of understanding the primary processes taking place at the bubble/water interface during bubble collapse.<sup>6,7</sup> To complement this work we have begun to examine the effect of a range of surface active agents on the sonoluminescence in aqueous solution. This

aspect has not been considered to any significant extent in the past. Our results show quite dramatic variation in the intensity of sonoluminescence depending on the type of surface active solute present in solution.

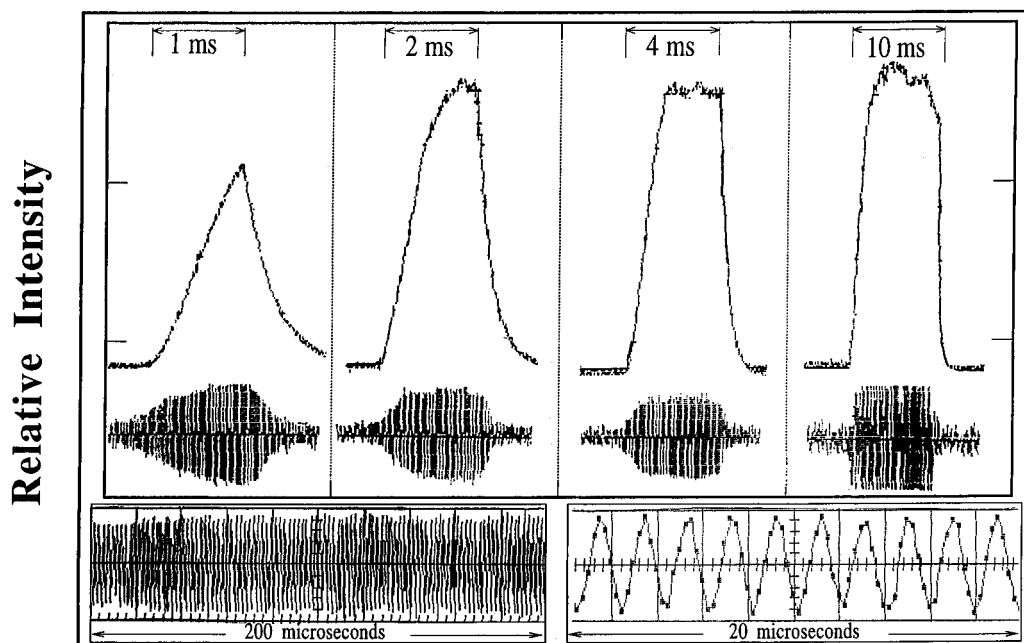
### Experimental Details

The ultrasound source used in all experiments was an in-house modified Undatim Ultrasonics D-Reactor operating at 515 kHz. The modifications made to the instrument allowed us to deliver pulsed ultrasound with variable pulse widths in the range of 0.1–25 ms and separations in the pulses from 0.8 ms to 6 s. The Reactor was placed in a light-shielded housing, which also contained an end-on photomultiplier (Hamamatsu) for recording the sonoluminescence from the solutions insonated. The emission signals were recorded on a LeCroy 7242 digital oscilloscope. A homemade hydrophone with an active sensor of  $1 \times 2 \text{ mm}^2$  was also used to examine the pulses delivered by the reactor during sonication of the aqueous solutions.

All aliphatic alcohols used were AR grade. The “Milli-Q” water used to make all solutions had a conductivity of  $<1 \times 10^{-6} \text{ S cm}^{-1}$  and a surface tension of  $72 \text{ mN m}^{-1}$  at  $22^\circ\text{C}$ . The pH of the water after equilibration with air was  $5.8 \pm 0.1$ . Sodium dodecyl sulfate (SDS) was BDH special purity grade, dodecyltrimethylammonium chloride (DTAC) was obtained from Kodak Chemicals and *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (DAPS) was a Calbiochem product. The latter surfactant is a pH-insensitive zwitterionic; that is, at no pH does it act like an anionic or cationic surfactant. All were used as supplied. Experiments were conducted at room temperature and any heating of the solutions during sonication was limited to a few degrees. The mean power deposited in solution by the sonicator was  $0.2 \text{ W/cm}^2$ , as determined by calorimetry. The volume of the solutions sonicated was 25 mL.

\* Author for correspondence. FAX: +61-3-93446233. Email: f.grieser@chemistry.unimelb.edu.au.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1997.

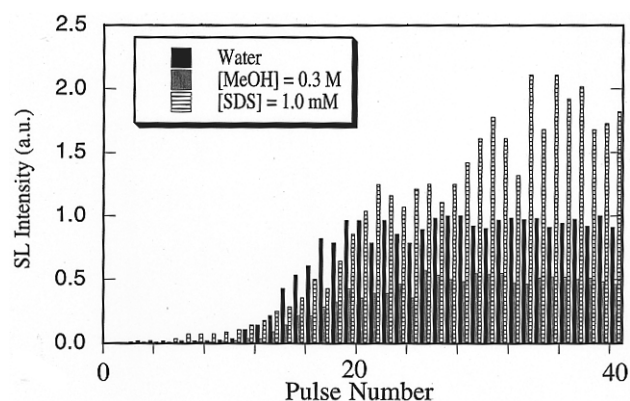


**Figure 1.** Comparative sonoluminescence signals generated in water with different ultrasound pulse widths. Also shown is the corresponding ultrasound pulse shape as measured by a hydrophone. The hydrophone signal on expanded time scales shows the uniformity of the individual cycles making up the pulse.

## Results

Typical air-saturated water sonoluminescence pulse shapes and relative pulse intensities for several pulse widths along with their corresponding hydrophone signals are shown in Figure 1. These signals were obtained after several seconds of insonation of the water and were relatively constant both in height and shape. Also shown in the figure are different time expansions of the hydrophone signal to illustrate the uniformity of the pressure oscillations within a pulse generated by the sonifier. It can be seen that for pulse widths of less than 2 ms the full sonoluminescence intensity is not attained. At pulse widths greater than about 2 ms the maximum emission intensity is reached, indicating some sort of saturation of the number of bubbles able to produce sonoluminescence. Based on these results most of the experiments reported in this paper were carried out using 4 ms pulses at a duty cycle (on/off ratio) of 1:3, unless noted otherwise.

In a series of experiments examining the sonoluminescence intensity as a function of the number of pulses, and duration between pulses, it was found that for a fresh sample of water<sup>8</sup> no sonoluminescence was obtained for the first few pulses. After that, the signal gradually grew in, reaching a maximum after about 20 pulses in the case of a 1:3 duty cycle. It was found that the longer the separation between pulses, the more pulses were required to achieve the maximum intensity. This was observed up to the highest duty cycle examined of 1:9. If the sonifier was switched off after reaching a maximum emission signal and quickly (<2 s) switched on again, the maximum signal was immediately regained. However, if the sonifier was left off for increasing periods of time, the number of pulses required to achieve the maximum signal also increased. Under our conditions, the number of pulses required to reach a full signal, as well as the intensity of the maximum signal, were highly reproducible if the sonicator was left off for periods longer than 3 min. This reproducibility was remarkably consistent even from day to day. Qualitatively all these observations are very similar to results reported on the emission from luminol solutions and from aqueous solutions saturated with argon/oxygen gas mixtures, using 1 MHz pulsed ultra-

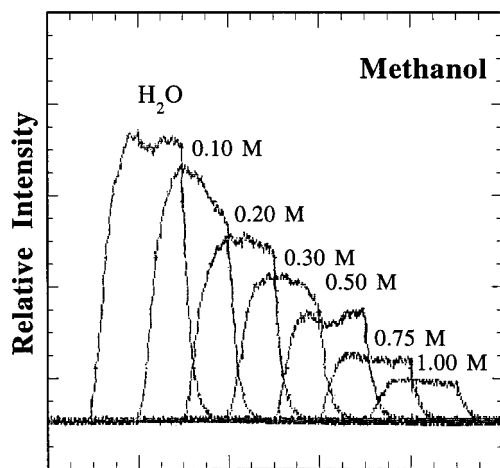


**Figure 2.** Growth of the emission signals following a series of 4 ms pulses separated by 12 ms (1:3 duty cycle) for water, 1 mM SDS, and 0.3 M methanol.

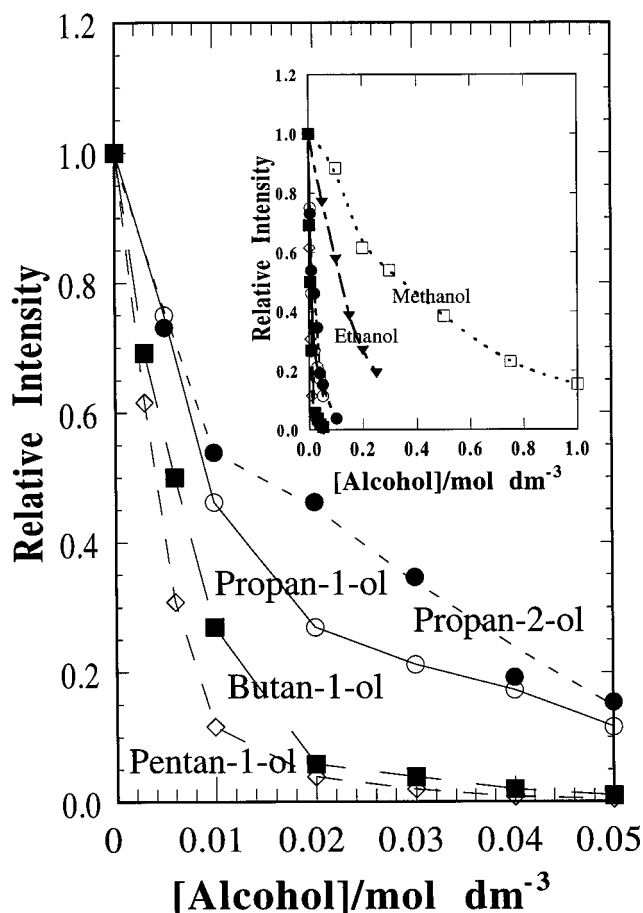
sound.<sup>9,10</sup> Collectively, our results along with the other data on pulsed systems strongly indicate that the effects seen are due to the physical characteristics of the sonoluminescing bubbles rather than some chemical or frequency based phenomenon.

In the case of aqueous solutions containing aliphatic alcohols or surfactants similar trends as reported above were seen, but the intensity of the maximum signal reached was different to that seen in the case of pure water, and in some cases the number of pulses required to reach the maximum signal was also different. In Figure 2 is shown the increase in intensity with pulse number for air-saturated water, an aqueous solution containing 0.3 M methanol, and one with 1 mM SDS. It can be seen that the final signal intensity for the three different systems is different in each case, and although about the same number of pulses are required to reach the maximum for the water and alcohol solutions (about 20 pulses), considerably more are needed in case of the SDS system (about 50 pulses). This variation in final emission intensity was examined over a range of additive concentrations and type.

In Figure 3 is shown the change in the final emission intensity of a 4 ms pulse, relative to pure water, as a function of methanol



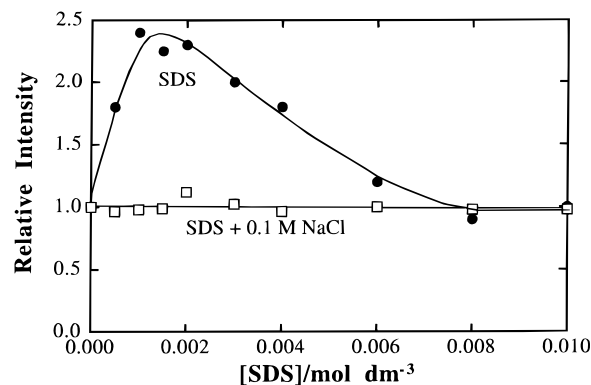
**Figure 3.** Relative limiting emission signals of a 4 ms pulse (1:3 duty cycle) at different concentrations of methanol.



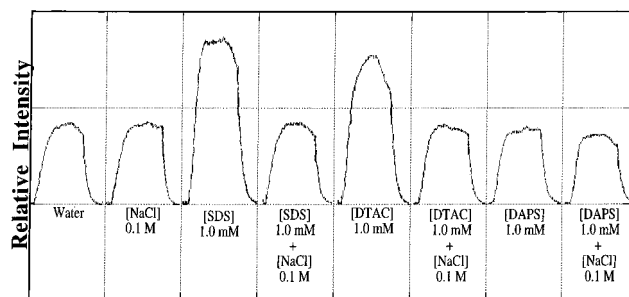
**Figure 4.** Relative limiting emission signals of 4 ms pulses (1:3 duty cycle) in the presence of a range of aliphatic alcohols as a function of concentration.

concentration, whereas in Figure 4 is plotted the final signal behavior as a function of concentration for a series of *n*-alcohols. It can be clearly seen that the extent of signal diminution, relative to water, increases with an increase in the chain length of the alcohol in solution. This result is similar to that obtained in earlier studies of sonoluminescence from aqueous solutions containing small amounts of alcohol.<sup>11</sup>

In Figure 5 is shown the variation in the final emission signal as a function of concentration of the anionic surfactant SDS. Unlike the effect of alcohol, the signal increases up to concentrations of about 1 mM after which it decreases again, but never reaches a value lower than that seen in pure water. In



**Figure 5.** Relative limiting emission signals of 4 ms pulses (1:3 duty cycle) as a function of SDS concentration. The top curve is SDS alone, and the bottom line is for SDS in the presence of 0.1 M NaCl. The cmc measured for the SDS was 7.9 mM and 1.5 mM in the absence and presence of 0.1 M NaCl, respectively.



**Figure 6.** Relative limiting emission signals of 4 ms pulses (1:3 duty cycle) under various solution conditions.

the presence of 0.1 M NaCl this effect is eliminated, as can be seen in Figure 5. Almost identical behavior was observed for the cationic surfactant DTAC. In contrast, addition of the zwitterionic surfactant DAPS over the same concentration range as that for DTAC and SDS resulted in no change in the emission intensity.

The possibility that the sonoluminescence signal behavior is somehow dictated by the formation or the presence of surfactant micelles can be completely dismissed. The cmc for SDS was measured as 7.9 mM, that for DTAC, 20 mM, and for DAPS, 2 mM. As seen in Figure 5, the growth in the sonoluminescence signal and its subsequent decay is essentially completed by the point at which the SDS concentration reaches its cmc. For DTAC the concentrations examined were always below the cmc. In the case of the DAPS system the concentration range examined was predominantly above the cmc. However, we also examined the decyl derivative of the zwitterionic surfactant, which has a cmc about 10 times greater than DAPS, and still obtained the same sonoluminescence behavior as for DAPS.

The difference in behavior between the charged surfactants and net neutral DAPS suggests the influence of electrostatics on the way the signal is generated. This possibility was tested in the standard way by adding electrolyte to the surfactant solutions in order to screen any electrostatic interactions between bubbles. The consequence of adding NaCl to the three different surfactant solutions is summarized in Figure 6. It shows that the sonoluminescence of the two charged surfactant solutions is clearly affected by the presence of the added electrolyte but neither water nor the zwitterionic DAPS solution is much influenced by its presence. It was also observed that the number of pulses required to reach the maximum signal for the SDS/0.1 M NaCl solution was comparable to that found for pure water, i.e., about 20 pulses.

## Discussion

The growth in the sonoluminescence signal with the number of pulses has been previously interpreted as a growth in the number of bubbles that are capable of producing sonoluminescence, until a saturation level is achieved. It has been suggested that the mechanism for attaining a saturation level is controlled by the competing processes of bubble growth to the critical size and bubble growth beyond the critical size<sup>10,12</sup> and/or bubble shrinkage.<sup>9</sup> This proposal is supported by two observations. First, as the duty cycle is increased from 1:3 to 1:9 it takes more pulses to reach the maximum sonoluminescence signal in a pulse train. Second, there is the effect that the initial sonoluminescence intensity obtained when the pulses are switched off, then on again, decreases with an increase in the delay time. Both types of behavior are consistent with the interpretation that microbubbles in water are inherently unstable and shrink away during periods when sonication is halted. We also note that it takes about 2–3 min for the unstable bubbles that are ultrasonically generated to “dissolve”. It is however less straightforward to understand why there is such a marked difference in the eventual maximum signal of the three systems shown in Figure 2. To explain this behavior it is best to consider the ionic surfactant systems first.

For both the anionic and cationic surfactant solutions almost identical sonoluminescence dependence on surfactant and electrolyte concentration is observed. It is well-known that surfactants adsorb at the air/water interface,<sup>13</sup> and as Riesz and co-workers have shown<sup>14</sup> this also occurs at the bubble/water interface during sonication. When charged surfactants adsorb at the air/water interface the bubbles will become negatively or positively charged<sup>13</sup> depending on the headgroup charge of the surfactant. The consequence of this interfacial adsorption is that neighboring bubbles will repel each other. This electrostatic repulsion will of course be decreased by the addition of electrolyte, which acts to screen the electric field between the bubbles. A schematic drawing of this description is shown in Figure 7. The top of the diagram shows electrostatically dispersed bubbles, as a result of a layer of adsorbed charged surfactant at the bubble/water interface. In the lower part of the diagram is shown a bubble cluster brought about by attractive van der Waals forces between bubbles<sup>15</sup> as a consequence of the electrolyte decreasing the electrostatic repulsion between the bubbles.

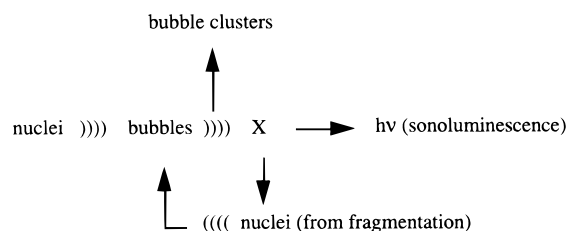
A model that can qualitatively tie together the physical characteristics of the bubbles and their solution interaction, with the sonoluminescence variation, is referred to as “impedance shielding”.<sup>4</sup> This model simply argues that if there is a cluster of bubbles, only those bubbles on the outside of the cluster will sonoluminesce, as the inside bubbles are shielded from the sound waves and therefore will not experience a local acoustic pressure sufficient to cause collapse.

Applying this idea to the charged surfactant systems means that the behavior seen in Figure 5 can be rationalized. Initially, as the bubbles become charged with increasing surfactant, less bubble clustering will occur in solution, and hence an increase in the sonoluminescence signal above that of pure water will be observed. At SDS concentrations of about 2–3 mM the surface concentration of surfactant reaches saturation.<sup>13</sup> Beyond this concentration the addition of the ionic surfactant (a strong electrolyte) will act to reduce the repulsion between the bubbles, thereby increasing bubble clustering again. Similarly, by adding the electrolyte NaCl, electrostatic screening between bubbles will also come into effect, and bubble clustering is again returned to the level attained in pure water.

The zwitterionic surfactant DAPS has a similar affinity for the air/water interface as SDS and DTAC. For all three surfactants a saturation level of between  $2$  and  $3 \times 10^{14}$  molecules/cm<sup>2</sup> is reached at a solution concentration of about 2 mM.<sup>13</sup> However, in DAPS solutions there is no long-range electrostatic interaction between bubbles and bubble clustering remains at much the same level as in pure water, and hence a similar emission intensity as seen in water is observed.

The model above has an additional prediction that is relevant in understanding the saturation level of the sonoluminescence signal within a given ultrasound pulse as shown in Figure 1 for the 2 and 10 ms pulses. It has been shown that the adsorption of surfactants at the bubble/water interface severely decreases the rate of bubble coalescence.<sup>16</sup> This means that the bubbles in pure water, SDS/0.1 M NaCl, DTAC/0.1 M NaCl, and DAPS solutions will have different coalescence/fusion efficiencies. Since there is not much difference in the emission signals from these four systems (Figure 6), it can be inferred that the growth of bubbles via coalescence as suggested by others<sup>9,10,12</sup> cannot be an important factor determining the limiting emission signal attained.

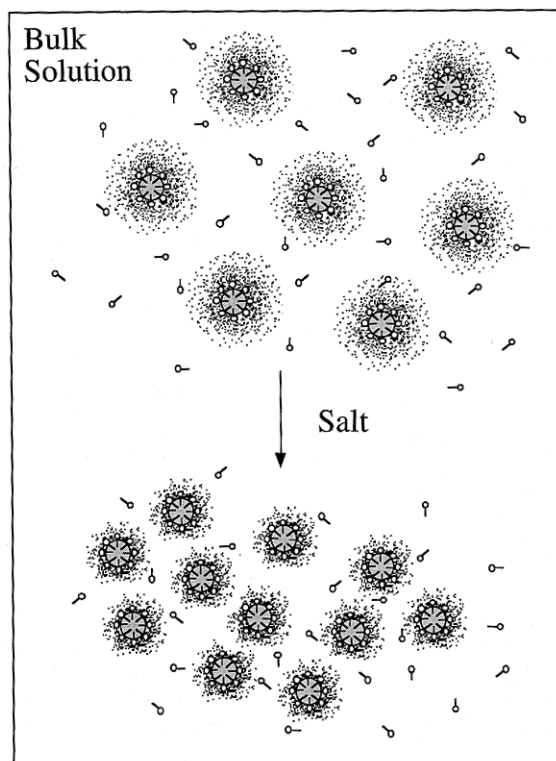
A simple scheme to account for the observations discussed above is presented below.



Initially, adventitious bubble nuclei in solution are acoustically grown, by rectified diffusion of gas in solution into the bubbles, to a size (X) that on collapse generates sonoluminescence. Some of the bubbles that collapse, fragment, and also generate nuclei, presumably over a range of sizes. These newly created bubble nuclei subsequently grow to their critical resonance size. In the scheme above the limiting sonoluminescence intensity is controlled by the rate of bubble clustering and not by bubble coalescence as has been suggested previously.<sup>9,10,12</sup> Bubbles inside a cluster that are acoustically shielded<sup>4</sup> can be expected to shrink away, providing another pathway that limits the number of bubbles of the appropriate size that are able to sonoluminesce. When the bubbles carry adsorbed charged surfactant, repulsive electrostatic interaction between the bubbles hinders bubble clustering and hence a comparatively greater emission signal results.

Other evidence to suggest that bubble clusters are responsible for the limiting emission intensity is seen in the moderate fluctuations of the emission intensity at higher pulse numbers (see Figure 2); these are particularly noticeable for the SDS system. All systems we have examined showed these signal fluctuations at high pulse numbers, and we note this behavior has been seen previously.<sup>10</sup> As the number and size of bubble clusters build up, the uniformity of the generated ultrasound field will be lost due to ultrasound scatter from the bubble clusters. This effect would result in changes in the local pressure intensity in solution and consequently the intensity of the sonoluminescence.

This account of the sonoluminescence variation with surfactant concentration on the spacial distribution of bubbles qualitatively rationalizes the behavior of all the surfactant systems, but it cannot account for the trends seen in the alcohol solutions. In all cases the addition of alcohol to water lowers

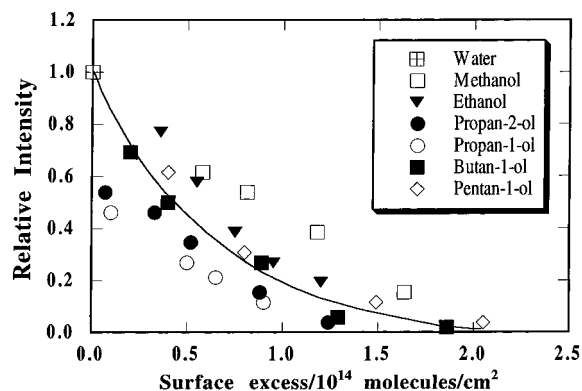


**Figure 7.** Schematic diagram showing a number of bubbles with adsorbed ionic surfactant molecules and their associated diffuse countercharge regions. The bubbles are kept apart because of the electrostatic repulsion between the charged surfaces. The bottom part of the diagram represents bubble clustering brought about by the van der Waals attraction between the bubbles, which outweighs the reduced electrostatic repulsion due to the presence of added salt. In these bubble clusters the inner bubbles are "screened" from the full acoustic pressure by the outer bubbles and do not contribute to the sonoluminescence.

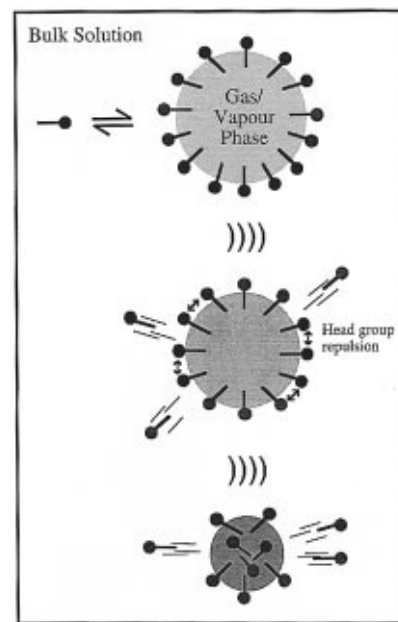
the sonoluminescence intensity. The possibility that the alcohol increases the coalescence rate in bubble clusters can be discarded because alcohols, like surfactants, retard the rate of bubble coalescence.<sup>16</sup> The decrease in sonoluminescence is not then some property of the spacial makeup of a group of bubbles in solution. To reinforce this it should be noted that the addition of butan-1-ol resulted in a marked decrease in the sonoluminescence signal observed from a single bubble.<sup>17</sup>

We have previously shown that certain sonochemical reactions are influenced by the amount of alcohol adsorbed at the bubble–water interface and not directly by the type or bulk concentration of the alcohol in solution.<sup>6,7</sup> To see if the same correlation holds for the effect of alcohol on the sonoluminescence intensity we have plotted in Figure 8 the relative sonoluminescence signal against the air/water Gibbs surface excess (the equilibrium interfacial concentration of the solute) of the different alcohols.<sup>18</sup> It can be seen that although this figure does not show perfect agreement between the relative sonoluminescence intensity and the equilibrium surface concentration there is a much better correlation with the surface excess than with the bulk alcohol concentration (Figure 3). The correlation in Figure 8 is perhaps more impressive when taking into consideration the fact that the scatter seen is predominantly due to the experimental difficulty in determining accurate surface excess values at low alcohol concentrations.<sup>19</sup>

The other important point to note from the results obtained with the alcohols is that almost complete sonoluminescence quenching is achieved at the higher alcohol concentrations for each system. Considering that the surface excess of the alcohols under these conditions is comparable to that of the surfactants



**Figure 8.** Relative limiting emission signal of 4 ms pulses as a function of the surface excess of the alcohols shown in Figure 4.

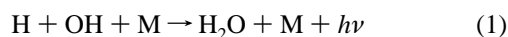


**Figure 9.** Idealized diagram of a collapsing microbubble with alcohol adsorbed at the gas/water interface. As collapse occurs lateral interaction between the interfacial alcohol molecules will force some into bulk solution, and at greater degrees of compression evaporation into the core of the bubble occurs.

used, it must be concluded that a different mechanism operates for the two types of surface active molecules.

The quenching effect of the alcohols can be explained if it is assumed that the interfacially adsorbed molecules are able to evaporate into the bubble core during bubble collapse and quench the precursors of the sonoluminescence. An idealization of this event is shown in Figure 9. The diagram illustrates the interaction occurring between adsorbed alcohol molecules as the bubble size is reduced during collapse. Due to this interaction, some interfacial alcohol molecules can be expected to be expelled into bulk solution, and we hypothesize that some of the interfacial alcohol is also evaporated into the core of the bubble. The ionic and zwitterionic surfactants on the other hand, are nonvolatile solutes, and while they can be expected to be forced into the surrounding water during bubble collapse they will not volatilize into the bubble core. It is also relevant to point out that it cannot be the alcohol vapor already present in the bubble before collapse that is responsible for the quenching effect. If this were the case then the quenching trend in Figure 3 would follow the order of increasing alcohol volatility, that is, the reverse of what is seen. This point has been discussed previously when examining the sonochemical dissolution of  $\text{MnO}_2$  colloids in the presence of aliphatic alcohols.<sup>7</sup>

The question remains as to the origin of the sonoluminescence. The quenching experiments so far conducted do not provide an unequivocal answer. It has been suggested that emission from excited-state species<sup>20–22</sup> and the reaction<sup>21</sup>



where M represents a third body collision partner, are responsible for the broad sonoluminescence continuum in water. Alcohols, known H and OH scavengers,<sup>23</sup> would certainly interfere with reaction 1 and probably quench, via an internal energy deactivation process, the other postulated excited-state species.<sup>20–22</sup> Our results certainly do not exclude the above proposal. We can also conclude from our results with the surfactants, themselves good H and OH scavengers<sup>14,24</sup> and capable of excited-state deactivation, that emission cannot be occurring at the bubble/water interface, otherwise there would be some quenching of the signal when surfactants were present in solution.

Our work clearly shows the significance of interfacial phenomena in the expression of the sonoluminescence intensity, and any theory that is to account for sonoluminescence yields in aqueous solutions must incorporate this aspect into the model.

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