

Multibubble Sonoluminescence from Aqueous Solutions Containing Mixtures of Surface Active Solutes[†]

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The effect of mixing surfactants (anionic, zwitterionic, and nonionic) and alcohols on the sonoluminescence (SL) generated by 3.5 ms pulses of 515 kHz ultrasound in air-saturated aqueous solutions has been examined. Each surfactant/alcohol system influenced the SL in significantly different ways. It was concluded that the surface active solutes competitively adsorbed to the cavitation bubble/solution interface and affected the sonoluminescence through both inter- and intrabubble processes. Modeling of the competitive adsorption of the solutes based on Langmuir type adsorption isotherms, however, could not completely account for the trends observed in the SL data. The poor quantitative correlation between the experimental results and model calculations was attributed to the cavitation bubbles not being sufficiently long-lived to allow the solution species to equilibrate with the surface of the cavitation bubbles. It was estimated that the persistence time of the sonoluminescing bubbles in the sound field, under the experimental conditions used, was less than 10 ms.

Introduction

When a fluid is exposed to high intensity ultrasound it is possible, under certain conditions, to observe the emission of light from the fluid, commonly referred to as multibubble sonoluminescence (MBSL).^{1,2} The emission is as a result of the inertial collapse of microbubbles that are generated by the passage of the acoustic field in the liquid. The microbubbles that produce SL collapse almost adiabatically, creating high temperatures and high pressures within the core of the bubbles. These conditions produce a variety of transient species, in vibrationally excited states, from the gas/vapor that is present within the bubbles, which subsequently emit light ranging from the UV into the IR.^{1,2}

There have been several studies dealing with MBSL in aqueous solutions that have shown that the presence of trace amounts of surface active solutes, e.g., surfactants, aliphatic, and aromatic alcohols, can significantly affect the intensity of the sonoluminescence (SL) produced.^{3–8} The underlying causes of the effects brought on by the solutes have been identified with both inter- and intrabubble events, stemming from the adsorption of the solutes at the cavitation bubble/solution interface.^{3,4,9} The highly sensitive nature of the sonoluminescence signal to the presence of solutes makes SL a useful probe with which to examine how different solutes influence cavitation bubbles in the dynamic environment of an acoustic field.

In this paper we report on the effects of mixtures of aliphatic alcohols and surfactants on the SL intensity generated in aqueous solution by pulsed 515 kHz ultrasound. The mixed systems were chosen because they allow an examination of the competitive adsorption between surface active solutes at the cavitation bubble/solution interface. This is the type of situation that can be expected to exist in sonochemical reactions where reactants are consumed and/or products produced.

Experimental Details

Materials. All chemicals were used as received, unless noted otherwise: NaCl (99.9%, Ajax Chemicals, Univar label),

propan-1-ol (99.5%, BDH), pentan-1-ol (AR grade, Mallinckrodt), sodium dodecyl sulfate (SDS) (99%, BDH specially pure grade), octaethylene glycol monodecyl ether (C₁₂E₈) (98%, Fluka), *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (DDSA) (99%, Calbiochem). The water used to prepare all solutions was obtained from a three-stage Milli-Q purification system and had a conductivity of less than 10^{−6} S cm^{−1} and a surface tension of 72.0 mN m^{−1}, at 20 °C.

Procedures. SL measurements were carried out using 25 mL of solution that was poured into an open Pyrex vessel constructed to fit over the 35 mm flat plate of a 515 kHz transducer. The 515 kHz generator was an Undatim Ultrasonics D-reactor (model no. UL03/1). The power absorbed (with the generator operated in pulse mode), as measured by calorimetry,¹⁰ was in the range 0.04–0.4 W/cm².

The generator was modified in-house to allow it to function in either pulsed or continuous mode. Unless otherwise stated experiments were performed in pulsed mode, using 3.5 ms pulses and a duty cycle (on:off) of 1:5. The sonoluminescence intensity was recorded with a Hamamatsu end-on-photomultiplier (model no. E849-34) that is responsive to light over a wavelength range of 300–650 nm. Signals were displayed on a digital oscilloscope (Tektronix, model no. TDS 360) and then stored on a personal computer.

In a typical experiment, the transducer, reaction vessel, and photomultiplier were placed in a light-proof enclosure to minimize the detection of ambient light. The SL intensity was obtained by first sonicating the solution for about 30 s to reach stable SL conditions and then using the averaging function of the oscilloscope to record and average at least 100 of the subsequent pulses. During experiments the temperature was monitored using a Jenway electronic thermometer (model 2003, with a precision of 0.1 °C). Generally the solution temperature did not change by more than 4 °C during the course of an experimental run.

Results

The effects of adding the anionic surfactant, SDS, on the average SL intensity observed from aqueous solutions containing

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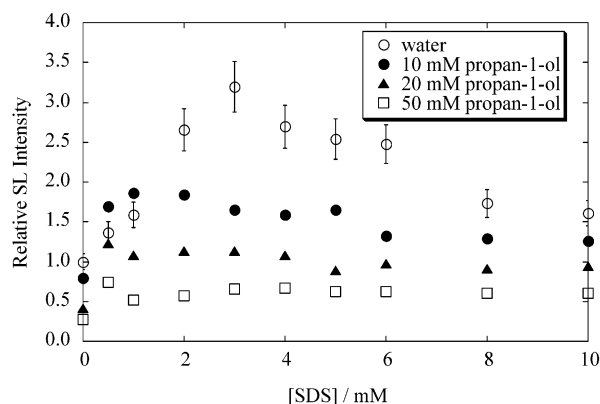


Figure 1. Averaged relative sonoluminescence intensity as a function of SDS concentration with three concentrations of propan-1-ol for 3.5 ms pulses at 515 kHz ultrasound. The error in SL data is 10%, as shown for water, which is typical for all SL data given in this figure.

different concentrations of propanol at 515 kHz ultrasound are presented in Figure 1. The data have been normalized with respect to the SL intensity obtained in pure water. The salient features to note in this figure are that the emission intensities initially increase and then decrease with the addition of SDS, and the emission intensity maxima decrease with increasing levels of added propanol.

The maxima in the emission intensities have been observed previously in alcohol-free aqueous surfactant solutions. The cause of the maximum has been attributed to changes in the spatial distribution of bubbles, as a function of surfactant concentration, within multibubble clouds that are produced by the acoustic field in the solution.^{3,5,8} The spatial changes induced in the bubble clouds are a direct consequence of repulsive interbubble electrostatic interactions brought about by the negatively charged SDS molecules adsorbing to the bubble/solution interface.⁵ It has been argued that the repulsive interactions between bubbles led to the formation of more open bubble clouds and an increase the number of *active* cavitation bubbles, i.e., those microbubbles that are of the right size that on collapse they generate the conditions needed for SL. The decline in the SL intensity at higher SDS concentrations (>2 mM) occurs because the increase in total ionic strength of the solution, due to SDS being a strong electrolyte, reduces the repulsion between bubbles, thereby forming more compact bubble clouds and less *active* bubbles.

The electrostatic effect brought on by SDS adsorbing to the cavitation bubbles can be largely negated by adding an electrolyte that screens the electrostatic field between bubbles.³ The consequences of adding 0.1 M NaCl to the systems used in Figure 1 are shown in Figure 2.

To gauge the effect of alcohols, in general, on the maximum in the SL intensity in the presence of SDS, some experiments were conducted with the more hydrophobic alcohol pentan-1-ol. The results are shown in Figure 3. On comparing these results with those seen in Figures 1 and 2, it is clear that pentanol induces similar trends to those of propanol. However, it is significant to note that comparable effects to those of the propanol system are achieved at much lower concentrations of pentanol.

In Figures 1 and 3 it can also be noticed that the initial rise in the SL intensity at low levels of added SDS is more pronounced when 10 mM propanol or 2 mM pentanol is present compared with just SDS being added to water. This is a real effect and outside the range of experimental error. Since the effect is eliminated when NaCl is added to the solutions, its

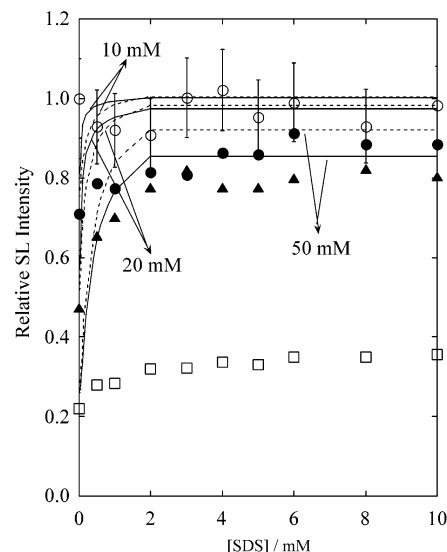


Figure 2. Averaged relative sonoluminescence intensity as a function of SDS concentration with 0.1 M NaCl and three concentrations of propan-1-ol [(○) water, (●) 10 mM propan-1-ol, (▲) 20 mM propan-1-ol, and (□) 50 mM propan-1-ol] for 3.5 ms pulses at 515 kHz ultrasound. The lines represent calculated SL intensity for SDS with 0.1 M NaCl and 10, 20, and 50 mM propanol (from top to bottom, respectively). The solid and dashed lines are obtained using eqs 1 and 3, respectively. The error in SL data is 10%, as shown for water, which is typical for all SL data given in this figure.

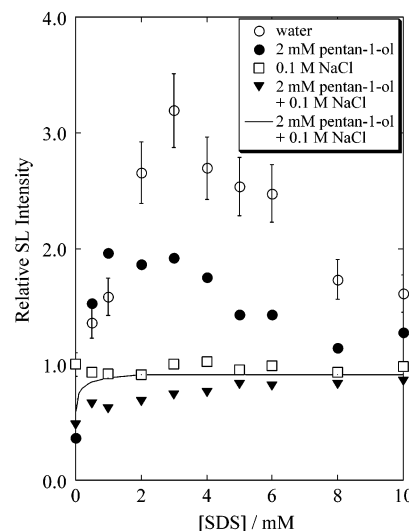


Figure 3. Averaged relative sonoluminescence intensity as a function of SDS concentration with 2 mM pentan-1-ol in the absence and presence of 0.1 M NaCl for 3.5 ms ultrasound pulses at 515 kHz. The solid line represents the calculated (using eq 1) SL intensity for SDS with 0.1 M NaCl and 2 mM pentanol. The error in SL data is 10%, as shown for water, which is typical for all SL data given in this figure.

origins are probably electrostatic in nature. It is known that SDS binds counterions when assembled at interfaces, e.g., micelles, and that when alcohol molecules are adsorbed in the interface the bound counterions are released.¹¹ This would have the effect of increasing the local charge density and hence increase the electrostatic field near the surface. It is possible then that the conditions exist in the combined alcohol/surfactant system that produce more open bubble cloud than in the SDS system alone.

It was of interest to compare the influence of other surfactants on the SL signal, in part, to better understand the electrostatic effects of SDS on the SL signal. Two systems were investigated, a zwitterionic surfactant and a nonionic surfactant. These two surfactants were selected because their headgroups are electro-

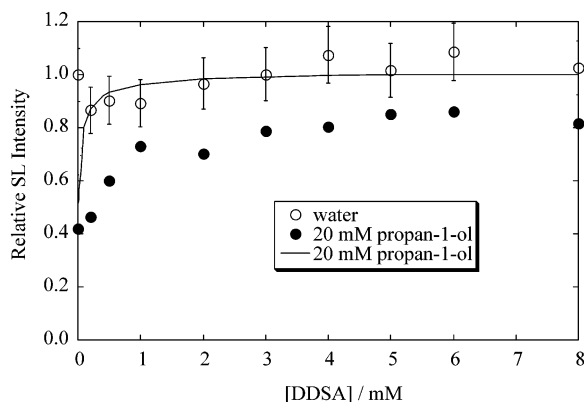


Figure 4. Averaged relative sonoluminescence intensity as a function of DDSA concentration with 20 mM propanol for 3.5 ms ultrasound pulses at 515 kHz. The solid line represents the calculated (using eq 1) SL intensity for DDSA with 20 mM propanol. The error in SL data is 10%, as shown for water, which is typical for all SL data given in this figure.

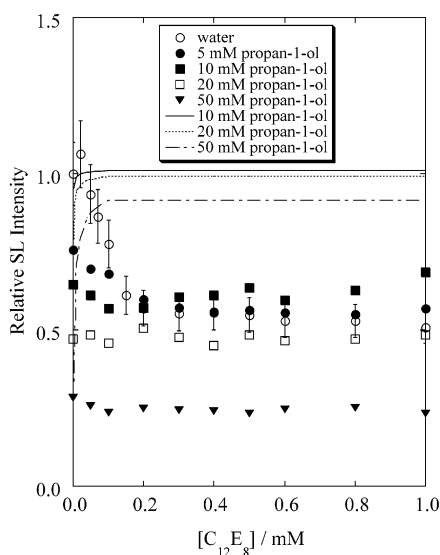


Figure 5. Averaged relative sonoluminescence intensity as a function of $C_{12}E_8$ with four concentrations of propanol for 3.5 ms ultrasound pulses at 515 kHz. Solid lines represent calculated (using eq 1) SL intensity for $C_{12}E_8$ with 10, 20, and 50 mM propanol (top to bottom, respectively). The error in SL data is 10%, as shown for water, which is typical for all SL data given in this figure.

statically neutral yet both surfactants still possess the intrinsic surfactant properties of SDS, i.e., the ability to adsorb at the bubble/solution interface and the capacity to lower the surface tension to a similar level to that achieved by SDS.¹² The results obtained with these two surfactants in the presence of propanol are shown in Figures 4 and 5. The results from the zwitterionic system are very similar to those observed for 20 mM propanol/SDS/0.1 M NaCl. These results provide added support that electrostatic effects are primarily responsible for the enhanced SL signal in the SDS/alcohol systems.

For the nonionic system the trends observed are considerably different than those of the SDS/alcohol/NaCl and zwitterionic/alcohol systems. The surfactant $C_{12}E_8$ in the absence of alcohol reduces the SL intensity by as much as 50% relative to that of pure water (Figure 5), in marked contrast to the other two surfactant systems. However, in the presence of propan-1-ol concentrations between 10 and 50 mM, the addition of $C_{12}E_8$ appears to have little effect on SL intensity. If $C_{12}E_8$ were acting simply as a nonionic surfactant, then the results with this system

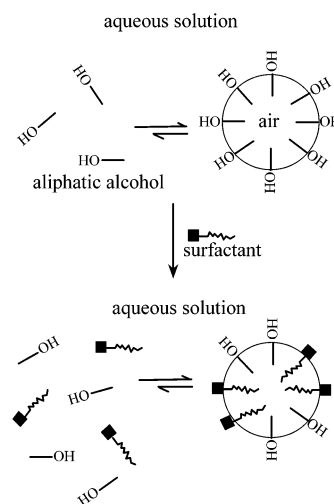


Figure 6. Diagrammatic representation of solutes adsorbing to the cavitation bubble interface. The top part of diagram shows alcohol adsorption to the bubble/solution interface and the bottom part of diagram displays competitive adsorption in solutions containing both alcohol and surfactant.

could be expected to be comparable to the two surfactant systems indicated above. Clearly, there is a process that comes into play when $C_{12}E_8$ is in solution that does not occur in solutions containing the other two surfactants.

Discussion

As indicated earlier, the effects of SDS on the SL intensity in aqueous solutions have been demonstrated to be linked to electrostatic interbubble interactions,^{3,5} with SDS primarily affecting the number of *active* bubbles emitting light. On the other hand, it has been determined that aliphatic alcohols, such as propan-1-ol, quench SL at high frequencies, such as at 515 kHz, via a complex process.⁴ The mechanism proposed for the quenching is associated with the build up and continuous decomposition, over many bubble oscillations, of gaseous hydrocarbon products originating from the thermally decomposed alcohol molecules that have evaporated into the cavitation bubbles from the bubble surface during expansion. The presence of the products within an active bubble leads to a lowering of the bubble core temperature and hence a reduction in the SL intensity. This interpretation is supported by both single bubble¹³ and multibubble³⁻⁷ experimental and theoretical studies,^{14,15} although it is relevant to point out that the theoretical studies attribute a drop in the core temperature principally to the energy consumed in the decomposition of the alcohol molecules that have entered the bubble; i.e., the further decomposition of the initial products is not taken into account in the calculations.^{14,15}

An examination of data for the three systems shown in Figures 2–4, i.e., propanol/SDS/0.1 M NaCl, pentanol/SDS/0.1 M NaCl, and propanol/DDSA, reveals that they have very similar characteristics. Namely, that as the level of surfactant in solution increases, the emission intensity increases as well. The increase in the SL intensity cannot be due to electrostatic effects as NaCl is present in two of the systems and in the zwitterionic system the headgroup is neutral.

A reasonable model that can be put forward to explain the observations, consistent with the surface active nature of the two solutes, is shown in Figure 6. On the basis of this model, it can be seen that as the surfactant increases in concentration it competes with the alcohol for adsorption at the bubble/solution interface. This in effect would lower the amount of alcohol at

TABLE 1: Maximum Surface Excess, Maximum Molecular Area, Langmuir Constant (*K*), and Representative Surface Excess Values for Surface Active Solutes Used in This Study

solute	Γ_{\max}^a (molecules/cm ²)	unit area (Å ² / molecule)	K^b (M ⁻¹)	n_i^c	sample Γ (molecules/cm ²)
SDS	1.93×10^{14}	51.9	1200	5	1.36×10^{14} at 2 mM
SDS + 0.1 M NaCl	2.20×10^{14}	45.2	7700	4	2.07×10^{14} at 2 mM
DDSA	2.39×10^{14}	41.8	8200	4	2.13×10^{14} at 1 mM
C ₁₂ E ₈	1.50×10^{14}	66.4	1.29×10^6	6	1.49×10^{14} at 0.1 mM
propan-1-ol	5.30×10^{14}	18.9	20	2	1.51×10^{14} at 20 mM
pentan-1-ol	5.30×10^{14}	18.9	60	2	0.57×10^{14} at 2 mM

^a Γ_{\max} refers to the maximum surface excess of the solutes at a saturated air/water interface. ^b K has been calculated from the equilibrium surface tension data (experimentally determined) assuming the solutes adsorb to the air/water interface following the Langmuir isotherm. ^c n_i have been calculated using the area of the solvent (water) as 11 Å²/molecule.

the bubble interface for a given bulk concentration of alcohol and hence increase the SL intensity for the reasons briefly described above.

A quantitative test of the model can be made if it is assumed that the solutes reach equilibrium with the bubble/solution interface during the lifetime of the bubbles that are exposed to the acoustic field. In such a case the expected surface concentration [approximately equal to the surface excess (Γ) of a surface active solute] of each solute can be calculated by using an adsorption isotherm described by the following equation¹⁶

$$B_i c_i = \frac{\theta_i}{(1 - \theta_1 - \theta_2)^{n_i}} \quad (1)$$

where θ_i is the fraction of the surface occupied by species i (1 or 2). $B_i = K_i \exp(n_i - 1)$, and K_i is the Langmuir adsorption constant of component i , c_i is the bulk concentration of species i , n_i is the ratio of molar surface areas of species i to that of the solvent, and the subscripts 1 and 2 refer to the two surface active solutes in the system. Equation 1 applies to solutes and solvent of different size and ideal enthalpy of mixing. The fraction of the surface covered by a solute can be calculated using eq 2

$$\theta_i = \Gamma_i / \Gamma_{\max} \quad (2)$$

If solvent and solutes are taken to be all of the same molecular size, eq 1 takes the form of the Langmuir isotherm

$$K_i c_i = \frac{\theta_i}{(1 - \theta_1 - \theta_2)} \quad (3)$$

To determine the relative SL signal in a mixed alcohol/surfactant system, the following procedure was undertaken. Equation 1 (or eq 3) was used to calculate the amount of alcohol that would be expected to adsorb to the bubble/solution interface under equilibrium conditions in a mixed alcohol/surfactant system. The data assembled in Table 1 was required to make these calculations. Having calculated the amount of alcohol at the bubble/solution interface, the concentration of alcohol in the bulk solution that was required to achieve this amount in the absence of surfactant could then be determined. This was accomplished by again using the Langmuir constants in Table 1 for the specific alcohol being considered. At this point, the extent of SL quenching for a particular bulk alcohol concentration was obtained from published data (ref 3 for pentanol and ref 6 for propanol). The calculated curves shown in Figures 2–5 represent the relative SL intensity as a function of the amount of alcohol at the bubble/solution interface in mixed alcohol/surfactant systems. It should be noted that it is implicit in eqs 1 and 3 that the alcohols and surfactants do not specifically interact in the system.

Although the general trends of the calculated SL intensities profile the experimental data of Figures 2–4, the fits are clearly quite poor. Also, there is not a great deal of difference between the two forms of the adsorption isotherm (see Figure 2). This indicates that the molecular size of the solutes or, expressed in another way, the entropy of mixing of the solutes does not play a major role in the adsorption process.

The most likely reason for the poor quantitative match is that the assumption that the solutes equilibrate with the bubble/solution interface during the active life of the bubbles is not valid. This conclusion is also supported by the recent work of Sostaric and Riesz¹⁷ dealing with surfactant adsorption at the cavitation bubble/solution interface.

It should be added that in a previous study it was concluded that bubbles exposed to 515 kHz undergo a large number of oscillations during their active life span.⁶ However, the actual number of oscillations an acoustic bubble in a multibubble field undergoes could not be established. On the basis of the above conclusion that surface active solutes do not come to interfacial equilibrium during the lifetime of sonoluminescing bubbles irradiated with 515 kHz, and using dynamic surface tension results on alcohols and surfactants,^{18–20} an upper limit on the number of oscillations can be estimated. It has been found that aliphatic alcohols and surfactants, including SDS and C₁₂E₈, reach near equilibrium interfacial adsorption levels in about 3–10 ms at solute concentrations similar to those used in the present study—this equates to an upper value of about 5000 oscillations.

In consideration of the above it is unexpected, therefore, that the model calculations completely fail to predict the trends of the experimental data of Figure 5. In the first instance the neutral surfactant C₁₂E₈ could be expected to behave in a similar way to the zwitterionic surfactant. There is, however, some evidence available from another study²¹ that indicates that surface adsorbed nonionic surfactants decompose following radical attack from OH radicals produced in the bubble core. In the light of this observation, it can be concluded that competitive interfacial adsorption probably still operates in the C₁₂E₈/alcohol systems but is complicated by the sonochemical instability of the nonionic surfactant.

Summary

In aqueous mixtures of alcohols and surfactants the solutes competitively adsorb to the cavitation bubble/solution interface for bubbles exposed to 515 kHz ultrasound and in doing so affect the SL generated in the system. The solutes, however, do not fully equilibrate with bubble/solution interface during the lifetime of the bubbles. The acoustic bubbles are estimated to have an upper limit of about 5000 oscillations during their life span.

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