Effect of surfactants, polymers, and alcohol on single bubble dynamics and sonoluminescence

Muthupandian Ashokkumar,[1,*] Jingfeng Guan,[2] Rohan Tronson,[1] Thomas J. Matula,[2] John W. Nuske,[1] and Franz Grieser[1]

[1]*Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Victoria 3010, Australia*

[2]*Centre for Industrial and Medical Ultrasound, Applied Physics Laboratory, University of Washington, 1013 NE 40th Street, Seattle, Washington 98105*

The radial dynamics of an acoustically driven single bubble, levitated in water, along with the sonoluminescence (SL) signal, were recorded in the absence and in the presence of micromolar quantities of different surfactants and polymers. It was observed that these nonvolatile solutes, in the low concentration range used, did not significantly affect the radial dynamics nor the SL intensity of a single bubble in water. In contrast, the addition of micromolar quantities of a volatile solute, pentanol, quenched ∼90% of the SL without affecting the radial dynamics of the bubble.

INTRODUCTION

The effect of surface active solutes on single bubble (SB) and multibubble (MB) sonoluminescence (SL) has been investigated by several groups in recent years [1–5]. Experiments conducted using a SB are particularly useful because of the highly repetitive and reproducible nature of the system. The effect of several experimental parameters on SB systems have been investigated [6–9]. For example, Holt and Gaitan [7] studied the region of parameter space (acoustic driving pressure, maximum and equilibrium bubble radii, etc.) in which stable single bubble sonoluminescence occurs. Theoretical investigations on the effect of surfactants on SB SL have also been reported [10–13].

In MB systems, the SL intensity is affected by solutes in a number of ways depending upon the solute being considered [1]. A decrease in the SL intensity (relative to the SL intensity observed in water) has been observed when low concentrations of volatile solutes, such as alcohols, amines, and carboxylic acids, were present in the water [1]. The presence of surfactants in water was found to affect the SL intensity in both SB [3] and MB [1] systems. Stottlemyer and Apfel [3] reported that the surfactant, Triton X-100 (a nonionic surfactant) reduced the maximum size of the SB from 65 μm in water to 62 μm in 0.1 CMC Triton X-100 (CMC of Triton X-100=0.21 mM [14]; 0.1 CMC=21 μM) solution. Nevertheless, the magnitudes of the SL intensity as well as the acoustic emission intensity were reduced by a factor of about 2.

In the present investigation, we have studied the SB dynamics and SL in the absence and in the presence of four different surfactants and two different polymers. The experimental data from the surfactant and polymer solutions have been compared with those observed from an aqueous solution containing a simple aliphatic alcohol.

EXPERIMENTAL DETAILS

Research grade surfactants, British Drug House special purity grade sodium dodecyl sulfate (SDS), Kodak Chemi-

cals' dodecyltrimethylammonium chloride (DTAC), Calbiochem's *N*-dodecyl(*N,N*-dimethyl-3-ammonio-1-propane sulfonate) (DAPS), and Nikko Chemical Company's octaethylene glycol monodecyl ether (C$_{10}$E$_8$), were used as received. Poly(vinyl alcohol) (PVA; M$_w$ of 14 000), polyvinylpyrrolidone (PVP; M$_w$ of 10 000) were purchased from Aldrich. Milli-*Q* water was used in all the experiments. AR grade pentanol was used as received. Surface tension measurements were made using a McVan Analite Surface Tension Meter with a glass Wilhelmy plate.

The wave generator, amplifier, and other instruments used in the SB experiments were similar to the ones described by Matula [15], and Ashokkumar and Grieser [16]. A rectangular cell driven at a resonance frequency of ∼22.5 kHz or a cylindrical cell driven at ∼23 kHz was used as the SB cell. In a typical experiment, a single bubble was levitated in degassed water and the SB parameters ($R_{\max}$, R_0, $P_{\max}$, $P_{\min}$, and SL) measured. $R_{\max}$ and R_0 (maximum and equilibrium radii of the bubble, respectively) measurements were recorded at a driving pressure of ∼1.3 atm. $P_{\max}$ and $P_{\min}$ represent the maximum and minimum driving pressures, respectively, at which a stable single bubble could be levitated, i.e., the bubble became unstable if the driving pressure was greater than $P_{\max}$ or less than $P_{\min}$. A known volume (normally about 50–100 μl) of an aqueous solution containing the desired concentration of the surface active solute was then added to the water in the SB cell and gently mixed. An equal volume (to that added) of the (mixed) solution was removed from the cell in order to maintain the same total volume. A single bubble was generated without changing the driving conditions. The SB parameters were again measured in the presence of the added solute. For the purpose of solute addition, an open cell was used where the solutions were exposed to the open atmosphere during the measurements.

In order to correct for any time dependent changes to the SB parameters, "control" experiments were performed. In the control experiments, a single bubble was levitated in water and the SB parameters were recorded as a function of time. It was observed that there was a continuous increase in the $R_{\max}$ R_0, and SL intensity with increasing time. For example, the initial values of maximum ($R_{\max}$) and equilibrium (R_0) radii of the bubble increased by ∼4 μm and 1 μm,

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*Corresponding author. Email address: m.ashokkumar@chemistry.unimelb.edu.au
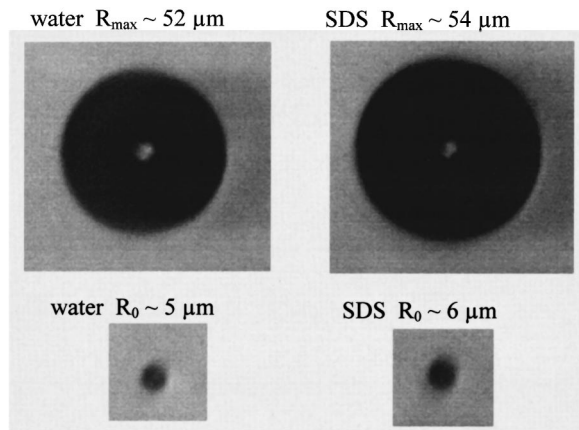
FIG. 1. Strobe images of a single bubble levitated in water at its maximum and equilibrium stages before and after the addition of 30 μM SDS. Driving $P \sim 1.3$ atm; frequency ~ 22.5 kHz.

respectively, over a period of 10 min. Similarly, the SL intensity observed from the same bubble increased by about 15–20% (under the measurement settings used) in 10 min. These values are an average of three independent control experiments. The data presented in this study have been corrected for the time dependent changes in the SB parameters.

A needle hydrophone (DAPCO or Precision Acoustics) was used to measure the acoustic driving pressure at the position of the bubble. Bubble size measurements were performed by a strobe technique [17]. The SL and scattered light intensities were detected by an end-on photomultiplier

(Hamamatsu) and recorded on an oscilloscope. The data were transferred to a PC for further analysis.

RESULTS

In Fig. 1 are shown typical strobe images of a SB, levitated in water, at its maximum and equilibrium dimensions during an acoustic cycle. The changes to the bubble size by the addition of 30 μM SDS are also shown in Fig. 1. As can be observed in this figure, there is little change in the maximum and equilibrium radii of the bubble due to the addition of SDS. In Table I, the changes in the R_{max}, R_0, P_{max}, P_{min}, and SL intensity observed in water in the absence and presence of low concentrations of the surfactants, SDS, DTAC, DAPS, and $C_{10}E_8$ and the polymers, PVA and PVP have been summarized. The values presented in this table have been corrected based on a ''control'' experiment with water (see experimental section). Considering the data in Table I, it can be stated that the addition of micromolar quantities of surfactants and polymers to water does not significantly affect the bubble dynamics, R_{max}, R_0, acoustic pressure, and SL intensity (relative to those parameters observed in pure water).

Figure 2(a) shows that the addition of 100 μM pentanol does not significantly affect the maximum and minimum bubble sizes, observed from a bubble levitated in pure water. The slight changes in the maximum and minimum radii of the water bubble, by the addition of 100 μM pentanol are similar to those observed in the surfactant/polymer solutions.

TABLE I. The effect of surfactants and polymers on SB parameters. R_{max} and R_0 values were measured at a driving pressure of ~ 1.3 atm R_{max}, R_0, and SL data have been corrected based on a ''control'' experiment with water (see experimental section).

| SDS					
[SDS] (μM)	R_{max} (μm)	R_0 (μm)	P_{max} (atm)	P_{min} (atm)	SL intensity (mV)
0	52 ± 3	5 ± 1	1.31 ± 0.01	1.18 ± 0.01	5 ± 2
30	54 ± 3	6 ± 1	1.31 ± 0.01	1.19 ± 0.01	7 ± 2
DTAC					
[DTAC] (μM)	R_{max} (μm)	R_0 (μm)	P_{max} (atm)	P_{min} (atm)	SL intensity (mV)
0	58 ± 3	5 ± 1	1.33 ± 0.01	1.23 ± 0.01	3 ± 2
30	56 ± 3	6 ± 1	1.27 ± 0.01	1.22 ± 0.01	4 ± 2
DAPS					
[DPAS] (μM)	R_{max} (μm)	R_0 (μm)	P_{max} (atm)	P_{min} (atm)	SL intensity (mV)
0	51 ± 3	5 ± 1	1.33 ± 0.01	1.18 ± 0.01	4 ± 2
30	52 ± 3	5 ± 1			6 ± 2
$C_{10}E_8$					
[$C_{10}E_8$] (μM)	R_{max} (μm)	R_0 (μm)	P_{max} (atm)	P_{min} (atm)	SL intensity (mV)
0	61 ± 3	6 ± 1	1.31 ± 0.01	1.17 ± 0.01	5 ± 2
30	57 ± 3	6 ± 1	1.23 ± 0.01	1.16 ± 0.01	8 ± 2
PVA ($M_w = 14\,000$)					
[PVA] (μg/ml)(μM)	R_{max} (μm)	R_0 (μm)	P_{max} (atm)	P_{min} (atm)	SL intensity (mV)
0	53 ± 3	5 ± 1	1.33 ± 0.01	1.18 ± 0.01	6 ± 2
5.4 (0.42)	52 ± 3	4 ± 1	1.31 ± 0.01	1.19 ± 0.01	7 ± 2
PVP ($M_w = 10\,000$)					
[PVP] (μg/ml)(μM)	R_{max} (μm)	R_0 (μm)	P_{max} (atm)	P_{min} (atm)	SL intensity (mV)
0	58 ± 3	5 ± 1	1.30 ± 0.01	1.17 ± 0.01	8 ± 2
5.4 (0.6)	57 ± 3	6 ± 1	1.30 ± 0.01	1.15 ± 0.01	7 ± 2
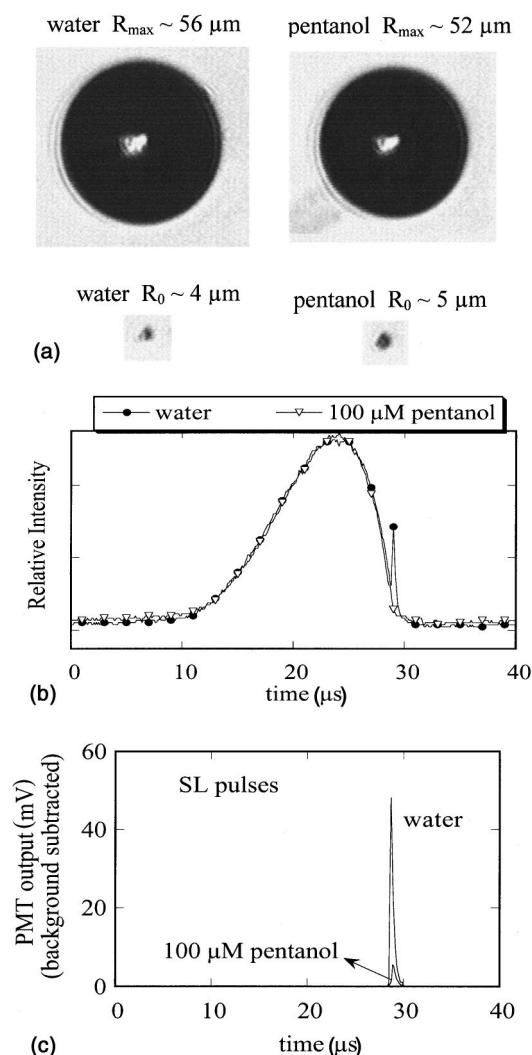
FIG. 2. (a) Strobe images of a single-bubble levitated in water at its maximum and equilibrium stages before and after the addition of 100 μM pentanol. Driving $P \sim 1.24$ atm; frequency ~ 22.5 kHz. (b) Relative scattered light (laser) intensity as a function of time from a SB levitated in water before and after the addition of 100 μM pentanol. Driving $P \sim 1.24$ atm; frequency ~ 22.5 kHz. (c) Relative intensity of the SL pulses (in the absence of a laser beam) as a function of time from a SB levitated in water, before and after the addition of 100 μM pentanol. Driving $P \sim 1.24$ atm; frequency ~ 22.5 kHz.

Figure 2(b) shows the scattered (laser) light intensity from the oscillating bubble as a function of time within an acoustic cycle. Under suitably chosen experimental conditions, the SL emission pulse can be made comparable to the scattered light intensity. As shown in Fig. 2(b), along with the light scattering curve observed from a water bubble, the SL emission pulse is clearly visible. However, it can be noticed that the SL emission pulse is barely visible in the light scattering curve observed from the bubble after the addition of 100 μM pentanol. As shown in Fig. 2(c), a SL measurement in the absence of a laser beam produced photomultiplier tube (PMT) outputs of ~ 50 mV for the water bubble and ~ 5 mV (under the measurement settings used) after the addition of 100 μM pentanol.

DISCUSSION

The key observations that can be noted from the results shown in Figs. 1 and 2, and in Table I are (i) low concentrations of the solutes, surfactants, polymers, and alcohol, do not significantly affect the radial dynamics of the SB; (ii) the nonvolatile solutes, surfactants, and polymers, do not quench the SBSL, whereas the volatile solute (pentanol) does.

The observation that the SB parameters are not significantly affected by the presence of the low levels of surface active solutes (surfactants and polymers) suggests that these solutes, in the concentration range used, do not interfere with the kinetics of bubble growth, bubble collapse, and the oscillation frequency of the bubble. In contrast, Stottlemyer and Apfel [3] have shown that the presence of ~ 21 μM Triton X-100 decreased the R_{max} of a water bubble by 3 μm. They [3] also reported a 50% decrease in SL (relative to the SL intensity observed from a water bubble) in the presence of ~ 21 μM Triton X-100. Referring to the work of Asaki, Thiessen, and Marston [18] on the effect of surfactants on mass diffusion into and out of the bubble, Stottlemyer and Apfel suggested that the effect of the addition of Triton X-100 was related to the changes in the mass diffusion of gas across the bubble/solution interface, caused by the surfactant adsorbed at the bubble/solution interface. In support of the interpretation of the data reported by Stottlemyer and Apfel [3], Yasui [10], in his theoretical work on the effect of 21 μM Triton X-100 on SBSL, suggested that the decrease in SL was due to an enhancement in the amount of water vapor that undergoes endothermic chemical reactions within the collapsing bubble. This increase in the core content of water vapor was suggested to be due to the inhibition of condensation of water vapor at the bubble wall by the adsorbed surfactants during the compression phase of the SB oscillation.

The observation that pentanol is the only surface active solute that quenches the SL argues against the previously proposed mechanisms discussed above for SL quenching. In order to gain some insight into the possible effects on SL that can be attributed to surface active solutes, it is relevant to consider the surface excess (two dimensional concentration of the solutes at the bubble/solution interface [1]) of the solutes. It is possible to estimate the number of molecules at the bubble/solution interface for both surfactants and alcohols using the experimentally measured (at higher concentrations of these solutes) surface tension data. The estimated surface excess values [19] for the surfactants and pentanol have been summarized in Table II.

It can be noticed from the values in Table II that the total number of molecules at the bubble/solution interface are comparable or significantly greater for the 30 μM surfactants than that for 100 μM pentanol. If gas diffusion in and out of the bubble and water vapor condensation at the bubble wall were affected by the presence of solutes at the bubble/solution interface, then 30 μM SDS and $C_{10}E_8$ should show greater SL quenching compared to that of 100 μM pentanol. The fact that the surfactants do not quench the SL and pentanol significantly quenches the SL indicates that neither gas transport across the bubble/solution interface nor water vapor

TABLE II. Maximum surface excess, air/water adsorption constant, and the surface excess values of the surface active solutes at the concentrations used in this study.

[Solute][a]	Γ_{max}[b] (molecules/cm^2)	K[c]	$\Gamma_{[solute]}$ (molecules/cm^2)
100 μM pentanol	5.3×10^{14}	60	3.2×10^{12}
30 μM SDS	1.9×10^{14}	1 200	6.6×10^{12}
30 μM DTAC	2.4×10^{14}	300	2.2×10^{12}
30 μM DAPS	1.8×10^{14}	8 200	3.6×10^{13}
30 μM C$_{10}$E$_8$	1.4×10^{14}	14 300	4.2×10^{13}

[a]At these concentrations these solutes have a minimal effect on the surface tension of the air/water interface ($\gamma_{a/w} \sim 72$ mN at 20 °C).
[b]Γ_{max} refers to the maximum surface excess of the solutes at a saturated air/water interface [20].
[c]K values have been calculated using equilibrium surface tension data (experimentally obtained) assuming that the solutes adsorb to the air/water interface following a Langmuir isotherm [20].

condensation at the bubble wall is responsible for SL quenching.

The observation that the SL is quenched by the addition of a neutral and volatile aliphatic alcohol, pentanol, can be understood by considering the explanation provided for the SL quenching by the volatile solutes in both MB [1] and SB [2] experiments. A volatile solute can evaporate into an oscillating bubble. Under the extreme conditions reached within the bubble during the collapse, these solutes may be thermally decomposed resulting in the formation of volatile products, such as methane, ethane, etc. The accumulation of these volatile polyatomic molecules within the bubble over a number of acoustic cycles will then lead to a decrease in the maximum temperature reached by the bubbles and hence a decrease in the SL [1,2].

The surfactants SDS, DTAC, DAPS, and C$_{10}$E$_8$ and the polymers, PVA and PVP are all surface active solutes. However, unlike pentanol, they are not volatile and their inability to quench the SL from the single bubble can be directly attributable to their lack of volatility. Hence, we conclude that the adsorption of surface active solutes at the bubble/solution interface does not hinder gas diffusion or water vapor condensation processes at the interface, and consequently, will not interfere with the generation of SL.

ACKNOWLEDGMENTS

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