

Effect of Solutes on Single-Bubble Sonoluminescence in Water

Muthupandian Ashokkumar,[†] Lawrence A. Crum,[‡] C. Allen Frensley,[‡] Franz Grieser,^{*,†}
Thomas J. Matula,^{*,‡} William B. McNamara III,[§] and Kenneth S. Suslick^{*,§}

Particulate Fluids Processing Center, School of Chemistry, University of Melbourne, Parkville, VIC 3010, Australia, Applied Physics Laboratory, University of Washington, 1013 NE 40th Street, Seattle, Washington 98105, and School of Chemical Sciences, University of Illinois at Urbana–Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

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Low concentrations of short chain aliphatic alcohols and organic acids and bases suppress single-bubble sonoluminescence (SBSL) in water. The degree of SL quenching increases with the length of the aliphatic end of the alcohol, and is related to the concentration of the alcohol at the bubble/water interface. The light is preferentially quenched in the shorter wavelength region of the spectrum. Radius–time measurements of the bubble are not dramatically affected by the low levels of alcohol used. Butyric acid and propylamine behave in the same manner, but only in their neutral forms, indicating that the SBSL suppression is due to processes occurring within the bubble.

Introduction

It has long been known that liquids irradiated with high intensity ultrasound generate extremely active cavitation bubbles. The violent collapse of these bubbles generates extreme temperatures and pressures in the interior of the bubbles, and light is emitted: multi-bubble sonoluminescence (MBSL).^{1–3} It has more recently been discovered that a single bubble levitated in a standing wave may also emit light,^{4,5} and there is much interest in deciphering the link, if any, between this single-bubble sonoluminescence (SBSL) and MBSL. In both cases the diffuse energy of the sound wave is concentrated in a nonlinear fashion by a collapsing bubble, and both occur on the same time scale.⁶ There are, however, many differences between the two. MBSL can be generated using widely different acoustic powers in almost any liquid saturated with almost any gas, while SBSL can be generated only within a comparatively tiny parameter space.⁷ Furthermore, MBSL spectra contain bands and lines that are characteristic of the solvent and gas used, and are very similar to flame spectra.^{8,9} SBSL spectra, on the other hand, are essentially featureless continua.^{10,11}

The effects of different gases on MBSL can be well explained by the physics of adiabatic compression. Those observed in SBSL,¹² on the other hand, can be best explained by viewing the bubble as a chemical microreactor that consumes polyatomic species and, in essence, rectifies noble gases.^{13,14} These observations all point to the conclusion that SBSL is, in actuality, MBSL taken to an extreme; the collapse of the spherical SBSL bubble is more violent than that of the less spherical MBSL bubble, leading to greater temperatures and pressures inside the bubble.

To probe this hypothesis, and to gain insight into the relationship of SBSL to MBSL, we have studied SBSL from systems whose MBSL behavior is well documented. In particular we have examined the effects of small concentrations of short chain alcohols and organic acids and bases on SBSL from water

containing dissolved air. Previous work has conclusively shown that small amounts of these solutes substantially suppress MBSL from water^{15,16} and similar behavior for short chain alcohols has been briefly noted in SBSL.^{17,18} It is unclear, however, if this quenching is due to a change in bubble dynamics, a change in inter-bubble forces (for MBSL), or a change in the properties of the bubble contents. An SBSL bubble by definition is not subject to inter-bubble forces, and the dynamic behavior of the bubble can be studied using well-established techniques; it is an ideal laboratory for separating and understanding the effects observed in MBSL. To that end we have studied the SBSL intensity and spectral distribution, as well as the dynamical behavior of bubbles in water containing small amounts of organic solutes.

Experimental Details

Two designs were used for the SBSL apparatus. For collection of spectra, a spherical quartz 100 mL cell that had a hollow cylindrical piezoceramic transducer cemented to the bottom of the flask was used. The transducer was driven by a function generator and amplifier at a resonance frequency of about 31 kHz. A calibrated needle hydrophone (DAPCO) was used to measure approximate pressure amplitude in the place where the bubble is located. SBSL spectra were collected at 295 K under 0.17 bar of air, using an Acton Research Monochromator 505 F (and a variety of gratings and order sorting filters) with an intensified, UV-enhanced, diode array detector (Princeton Instruments, IRY 512N). Spectra were corrected for both the light absorbance by the solutions and the response of the optical system against NIST-traceable standard lamps. Light intensity measurements and radius–time curves were collected using a rectangular cell operating at 22 kHz. The experimental system used was similar to the one described by Matula.¹⁹

High purity nonaqueous liquids (>99% purity) were used as purchased. Water was purified by ion exchange (to 18 Mohm cm resistance) and micron filtration and was degassed to 0.17 bar. The required amount of pure solute was added to the SBSL cell, using a microsyringe, while the bubble was glowing. A

* Authors to whom correspondence should be addressed.

[†] University of Melbourne.

[‡] University of Washington.

[§] University of Illinois at Urbana–Champaign.

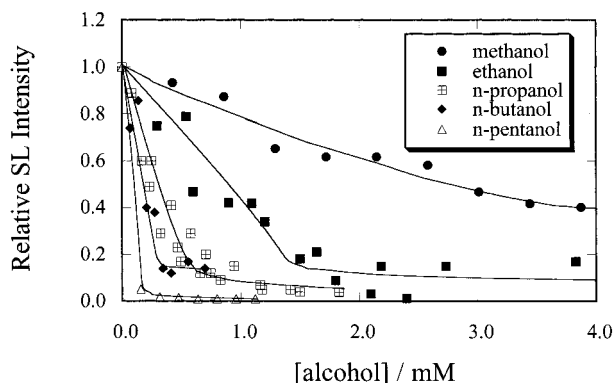


Figure 1. SBSL intensity as a function of alcohol concentration. Single-bubble cavitation was induced in water degassed to 0.17 bar in a rectangular cell operating at 22 kHz.

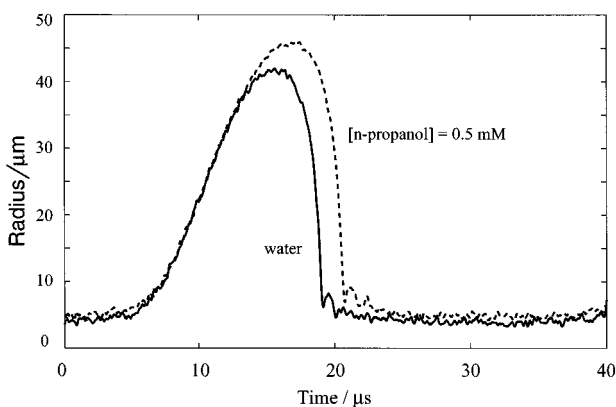


Figure 2. Radius versus time profile of a single bubble in the presence and absence of 0.5 mM *n*-propanol. This concentration of alcohol quenches 60% of the SBSL intensity.

drop in the SBSL intensity occurred within about a second following the addition of the solute. The convective transport of the added solute from the surface of the water in the cell toward the acoustically “trapped” bubble could be readily observed.²⁰ The intensity and spectra of SBSL from pure water were unchanged when a similar volume of water was added to the cell.

Results and Discussion

Figure 1 shows the decrease in SBSL intensity from water upon the addition of low levels of alcohols. It can be seen that the intensity of the emitted light decreases with increasing concentrations of alcohols, and that the extent of quenching increases as the length of the alkyl chain increases. This behavior is very similar to what has been reported in MBSL.^{15,16} The concentrations of alcohol required to achieve a given degree of quenching, however, are an order of magnitude greater for MBSL than for SBSL; SBSL is much more sensitive to the presence of these solutes.

To determine if this quenching is due to a change in the general dynamics of cavitation, bubble radius vs time profiles, i.e., $R(t)$ curves, were collected for these systems. Figure 2 shows the $R(t)$ curves for an SBSL bubble in the presence (0.5 mM) and absence of *n*-propanol. The general dynamical motion of the bubble does not appear to be greatly affected by the low concentrations of alcohols used. Direct imaging of the bubble does show, however, that the equilibrium and maximum bubble sizes do change by a small amount. The equilibrium bubble radius changed from approximately 3.2 to 4.1 μm , while the

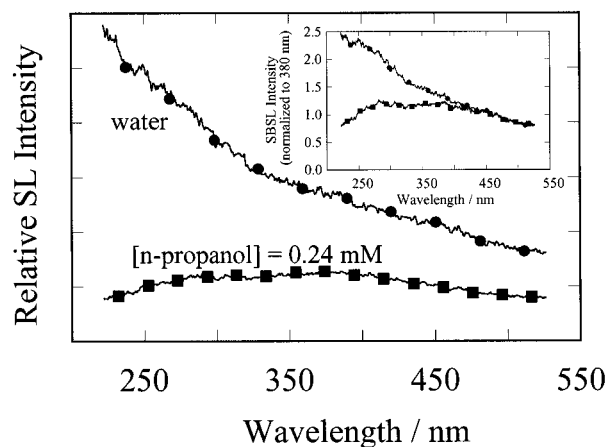


Figure 3. SBSL emission spectra in the presence and absence of 0.24 mM *n*-propanol. The inset shows the spectra normalized to 500 nm. Single-bubble cavitation was induced in water degassed to 0.17 bar in a spherical cell driven at 31 kHz.

maximum radius changed from approximately 42.5 to 46.5 μm , under a particular set of conditions in the experiment.

The change in the maximum bubble radius is consistent with the bubble expanding from the two different equilibrium bubble sizes, under the same forcing pressure. The Rayleigh-Plesset calculations we have undertaken to describe the bubble dynamics show that the change in surface tension, due to the added alcohol, is too small to account for the observed changes in the equilibrium bubble size. The change in the equilibrium radius is most probably due to changes in gas (or vapor) diffusion. As described further below, we believe that at least some of the alcohol is drawn into and retained in the bubble. Indeed, our simulation results show that a small increase in the internal gas content of a bubble results in an increase in the equilibrium bubble radius. Note that to obtain a similar change in intensity through changes in driving pressure alone, the $R(t)$ curves would look dramatically different than shown here.²¹

The SBSL spectra of water and 0.24 mM *n*-propanol in water are shown in Figure 3. An SBSL bubble was first generated in pure water and the spectra from this bubble were collected. The appropriate amount of alcohol was then injected into the cell. The intensity drops as soon as the alcohol is observed to reach the bubble, and continues to do so over a few minutes as the alcohol diffuses throughout the water. The net intensity decreases in accord with that shown in Figure 1. The inset shows the spectra normalized to 500 nm. It can be seen that the emission is preferentially quenched at lower wavelengths: 50% quenching at 500 nm vs 85% at 220 nm. Similar but less pronounced preferential quenching was observed at lower concentrations of *n*-propanol, and from slightly higher concentrations of ethanol in water.

It has been shown that in MBSL the extent of quenching is directly linked to the equilibrium amount of alcohol at the air/water interface, as defined by the surface excess (Γ_s) concentration of the alcohol.¹⁵ The Γ_s can be calculated from the Gibbs–Duhem equation which has the form shown in eq 1 at constant pressure and temperature:

$$\Gamma_s = - (1/kT)(d\gamma/d \ln C_s) \quad (1)$$

where γ is the air/water surface tension (N/m) at a bulk alcohol concentration of C_s .²² Figure 4 shows the SBSL intensity as a function of the alcohol Γ_s , which were calculated from extrapolated surface tension data reported in the literature for the alcohol and water mixtures used in these experiments.²³ As

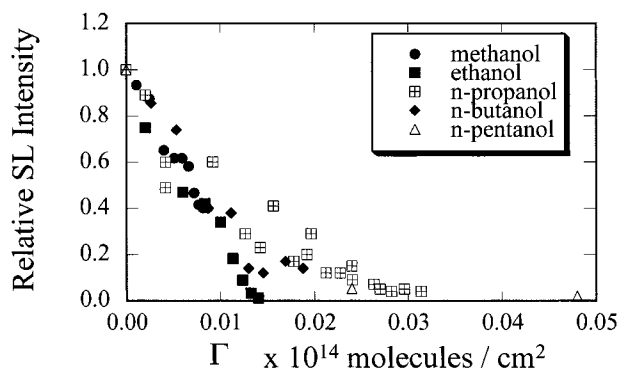
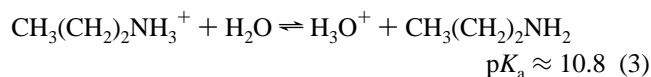
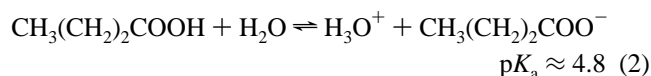


Figure 4. SBSL intensity as a function of the Gibbs surface excess of alcohols.

can be seen, within the experimental error range of both the γ and the intensity measurements, there is a good correlation between the SBSL intensity and the equilibrium two-dimensional concentration of the alcohols at the air/water interface.

Given that the bubble dynamics cannot account for the observed quenching, and that the quenching correlates with the concentration of dopant at the interface, it is reasonable to propose that the changes in SBSL intensity are associated with the evaporation of the solute from the bubble/solution interface. To determine if this is the factor responsible for quenching, similar experiments were conducted using water doped with small concentrations of organic acids and amines. These solutes are particularly well suited to such studies as their properties vary strongly as a function of pH. In particular, their volatility dramatically changes as the solution pH changes. At all pH values, the hydrophobicity inherent in the aliphatic ends of these molecules causes them to selectively adsorb at the air/liquid interface of the bubble. In their neutral forms these solutes will behave much like water and enter the gas phase of the bubble as the bubble is expanding. Changing the solution pH, and thus converting these acids and bases into their ionic forms, eliminates this volatility. The solutes will still adsorb at the bubble/solution interface, leaving the bubble dynamics relatively unchanged, but they will not enter the gas phase of the bubble. This is quantitatively expressed in the acid/base equilibria shown below for *n*-butanoic acid (eq 2) and *n*-propylamine (eq 3):



At low pH *n*-butanoic acid will be in its neutral form and *n*-propylamine will exist as the protonated propylammonium cation; *n*-butanoic acid will evaporate into the bubble while propylammonium will remain at the bubble interface. As the pH is raised, the situation will be reversed; *n*-butanoic acid will exist in its deprotonated and nonvolatile state while *n*-propylamine will be neutral and able to evaporate into the bubble.

Figure 5 shows the effect of pH on the SL intensity from aqueous solutions of *n*-butanoic acid and *n*-propylamine. It can be clearly seen that the neutral forms of both species significantly suppress SBSL, but no quenching is observed when these compounds are in their ionic forms. This result is consistent with our recently reported MBSL work^{15b} and supports our proposal that the quenching is due to processes occurring within the bubble. As with the alcohols, the extent of quenching is

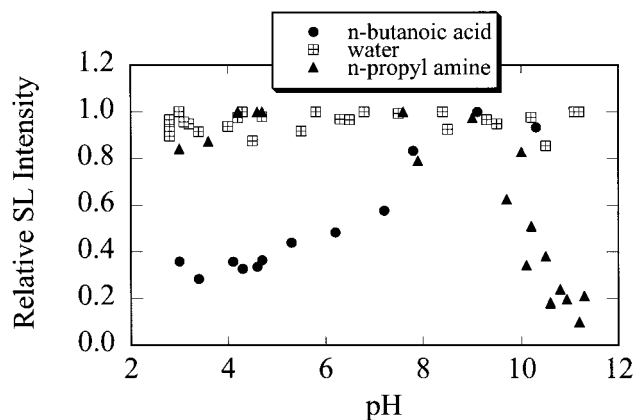


Figure 5. The effect of pH on the SBSL intensity of 0.65 mM *n*-butanoic acid and 0.71 mM *n*-propylamine. Control experiments showed that pH changes (using HCl or NaOH) have no significant effect on the SBSL intensity from water in the absence of these solutes.

also strongly dependent on the concentration of the amine and acid, but only when the solutes are at a pH where they exist in their neutral form. The pH of undoped water was changed by the addition of NaOH and HCl. Neither substance affects the SBSL intensity or bubble dynamics.

It is unclear exactly how these volatile solutes suppress SBSL. The model of SBSL most consistent with experimental data^{13,14} proposes that a stable and non-SBSL bubble contains an equilibrium mixture of air and water vapor, when levitated by an acoustic pressure below the SL threshold. As the driving acoustic pressure is increased, the radial oscillations of the bubble become more violent, and the interior of the bubble is successively heated to higher and higher temperatures. At sufficiently large pressure amplitudes, the bubble is heated to a temperature sufficient to consume both water vapor and the polyatomic components of air: i.e., N_2 and O_2 . The sonolysis products, such as NO and NO_2 , are soluble in water and would be removed from the bubble. This reduces the heat capacity of the bubble interior and allows successive compressions to further heat the bubble contents. The rate of air pyrolysis is faster than the rate at which air can diffuse into the bubble, and after several thousand acoustic cycles of this extreme heating the bubble would no longer contain an appreciable amount of air.^{14,24} Rather, at the point of SBSL emission, the bubble would contain mostly water vapor and argon, argon being the primary nonreactive component of air: this rectification of argon is believed to be the key to SBSL. It has been predicted that the interior of the collapsed bubble consists of a partially ionized plasma,²⁵ reaching temperatures that can exceed 20 000 K. Simplified calculations for the light mechanism (assuming thermal bremsstrahlung and radiative recombination) agree qualitatively with these estimates.²⁶

The changes in spectra and intensity observed here can best be explained in light of the expected chemistry within the collapsing bubble. As described below, the spectral and intensity changes are not well explained by arguments based on standard adiabatic compression alone. As the bubble expands, solvent evaporates from the liquid/gas interface and populates the interior of the bubble. Given a surface excess of, say 0.05×10^{14} molecules/cm², there will be one alcohol molecule per every 20 nm² at the air–water surface. Given that the cross-sectional area of an alcohol molecule is about 0.19 nm²,²² water occupies approximately 99% of the liquid/gas interface, and will similarly be the dominant vapor species within the bubble.²⁷ This low concentration of alcohol is insufficient to significantly lower the final temperature during bubble compression if the heating

is due to adiabatic compression. The polytropic ratio (C_p/C_v) of water at 3000 K and above differs by less than 1% from the polytropic ratio of 1% *n*-propanol in water at the same temperature. If a single cavitating bubble reaches temperatures^{25,26} on the order of 20 000 K, then the changes also cannot be due to collisional quenching of excited-state species by the alcohol. The chemical bonds within an alcohol molecule are weaker than those in N₂, O₂, and H₂O, and there should be no alcohol present within the bubble at the temperatures predicted for SBSL.

It is possible, however, that the rectification of argon within the bubble is accompanied by the rectification of small organic gases. The reaction of water vapor with alcohols at high temperatures will produce small hydrocarbons in addition to CO and CO₂. In contrast to NO and NO₂, these hydrocarbons do not readily dissociate in or react with water. As such they will remain in the gas phase of the bubble, and could accrue over many cycles. The result would be an SBSL bubble that contains a significant amount of polyatomic gas when at its maximum radius, much like an air bubble below the onset of SL. Air bubbles glow very dimly at first, due to the large amounts of N₂ and O₂ in the bubble. As these diatomic molecules are consumed and the products are expelled over the period of a few seconds the intensity increases to a constant and maximum level.^{7,24} In contrast to these air/water bubbles, in which the rate of gas diffusion is too slow to maintain a sizable amount of air within the bubble, the bubbles in the systems studied here are readily replenished with alcohol via evaporation from the interface. They could thus reach a "steady-state" concentration of polyatomic gases that would dampen the increase in temperature during bubble collapse. The bubble would be trapped in a state similar to that of the dimly glowing air bubbles described above, and this would be reflected in the spectra as a decrease in high energy emission relative to lower energy emission; i.e., the SBSL would be preferentially quenched at lower wavelengths. This is in accord with the experimentally observed spectra.

The interiors of MBSL bubbles, on the other hand, are not heated to the degree predicted for SBSL bubbles. It has been conclusively shown that the interior of cavitating bubbles driven by high acoustic pressures (≈ 8 atm) at 20 kHz are heated to 5000 K via adiabatic compression,^{2,3} and that the pulse width of the emitted light is much less than 1.1 ns.⁶ These relatively mild conditions and short times would imply that only a fraction of the molecular constituents within the bubble are consumed during the collapse of an MBSL bubble. Recent work at the University of Illinois indicates that the continuum in MBSL spectra arises from emission by small molecules formed by radical mechanisms during bubble collapse. As such, the diminution in MBSL intensity upon the addition of these solutes is likely due to scavenging of these radicals within the bubble¹⁶ and collisional quenching,²⁸ as have been previously proposed.

Conclusions

We have found that very low concentrations of volatile organic molecules substantially quench SBSL from water. The dynamics of these bubbles are not significantly perturbed by the low concentration of solutes used in this study, indicating

that the decrease in intensity is not principally due to changes in bubble dynamics. The degree of quenching, however, is correlated to the amount of solute present at the bubble interface. Furthermore, the quenching occurs only when the solute is able to evaporate into the interior of the bubble, indicating that processes within the interior of the bubble are responsible for this quenching.

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References and Notes

- (1) Suslick, K. S.; Crum, L. A. *Sonochemistry and Sonoluminescence*. In *Handbook of Acoustics*; Crocker, M. J., Ed.; Wiley-Interscience: New York, 1998; pp 243–253.
- (2) McNamara, W. B., III; Didenko, Y. T.; Suslick, K. S. *Nature* **1999**, *401*, 772.
- (3) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1325.
- (4) Gaitan, D. F.; Crum, L. A.; Church, C. C.; Roy, R. A. *J. Acoust. Soc. Am.* **1992**, *91*, 3166.
- (5) Barber, B. P.; Putterman, S. J. *Nature* **1991**, *352*, 318.
- (6) Matula, T. J.; Roy, R. A.; Mourad, P. D. *J. Acoust. Soc. Am.* **1994**, *101*, 1994.
- (7) Barber, B. P.; Wu, C. C.; Lofstedt, R.; Roberts, P. H.; Putterman, S. J. *Phys. Rev. Lett.* **1994**, *72*, 1380–1383.
- (8) Flint, E. B.; Suslick, K. S. *J. Phys. Chem.* **1991**, *95*, 1484.
- (9) Flint, E. B.; Suslick, K. S. *J. Am. Chem. Soc.* **1989**, *111*, 6987.
- (10) Hiller, R.; Putterman, S. J.; Barber, B. P. *Phys. Rev. Lett.* **1992**, *69*, 1182.
- (11) Matula, T. J.; Roy, R. A.; Mourad, P. D.; McNamara, W. B., III; Suslick, K. S. *Phys. Rev. Lett.* **1995**, *75*, 2602.
- (12) Hiller, R.; Wenginger, K.; Putterman, S. J.; Barber, B. P. *Science* **1994**, *266*, 248.
- (13) Hilgenfeldt, S.; Lohse, D.; Brenner, M. P. *Phys. Fluids* **1996**, *8*, 2808.
- (14) Lohse, D.; Brenner, M. P.; Dupont, T. F.; Hilgenfeldt, S.; Johnston, B. *Phys. Rev. Lett.* **1997**, *78*, 1359.
- (15) (a) Ashokkumar, M.; Hall, R.; Mulvaney, P.; Grieser, F. *J. Phys. Chem. B* **1997**, *101*, 10845. (b) Ashokkumar, M.; Mulvaney, P.; Grieser, F. *J. Am. Chem. Soc.* **1999**, *121*, 7355.
- (16) Sehgal, C.; Steer, R. P.; Sutherland, R. G.; Verrall, R. E. *J. Phys. Chem.* **1977**, *81*, 2618.
- (17) Hiller, R. A.; Putterman, S. J. *Phys. Rev. Lett.* **1996**, *77*, 2345.
- (18) Wenginger, K.; Hiller, R.; Barber, B. P.; Lacoste, D.; Putterman, S. J. *J. Phys. Chem.* **1995**, *99*, 14195.
- (19) Matula, T. J. *Philos. Trans. R. Soc. London A* **1999**, *357*, 225.
- (20) The difference in the refractive indices between the solute and water was sufficiently great to allow this transport to be observed before the solute dissolved.
- (21) Barber, B. P.; Putterman, S. J. *Phys. Rev. Lett.* **1992**, *69*, 3839.
- (22) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley-Interscience: New York, 1990; pp 71–86.
- (23) Sostaric, J.; Mulvaney, P.; Grieser, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2483.
- (24) Matula, T. J.; Crum, L. A. *Phys. Rev. Lett.* **1998**, *80*, 865.
- (25) Moss, W. C.; Young, D. A.; Harte, J. A.; Levatin, B. F.; Rozsnyai, G. B.; Zimmerman, G. B.; Zimmerman, I. *Phys. Rev. E* **1999**, *59*, 2986.
- (26) Hilgenfeldt, S.; Grossmann, S.; Lohse, D. *Nature* **1999**, *398*, 402.
- (27) An alternative proposal has recently been put forward by Lohse and co-workers (Tögel, R.; Hilgenfeldt, S.; Lohse, D. *Phys. Rev. Lett.* **2000**, *84*, 2509), in which surface-adsorbed alcohol molecules are "squeezed" into the bubble during the final stages of the collapse. In this model, multiple oscillations of the bubble are not required to build up a significant amount of material within the bubble to lower the core temperature and hence reduce SL. Further work is required to distinguish between this model and the one being proposed in the present report.
- (28) Didenko, Y. T.; Pugach, S. P. *Ultrason. Sonochem.* **1994**, *1*, s10.