

The Effect of pH on Multibubble Sonoluminescence from Aqueous Solutions Containing Simple Organic Weak Acids and Bases

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Abstract: The sonoluminescence (SL) intensity from aqueous solutions containing either alkyl acids or alkylamines is shown to be dependent on both the hydrocarbon chain length of the solute and the pH of the solution. Alkylamines quench the SL only at pH values above about 9 whereas alkyl acids quench only below about pH 7. In the pH ranges where SL quenching occurs, the longer the alkyl chain length the greater the effect. The results have been interpreted in terms of the neutral forms of the solutes adsorbing at the bubble/solution interface and then evaporating into the bubble core during its growth and compression oscillations, leading to the quenching of the SL. Possible processes that may be responsible for the quenching are discussed.

Introduction

Sonoluminescence (SL) stems from the acoustically driven collapse of cavities (bubbles) in a liquid. SL has long been observed in multibubble (MB) systems^{1,2} and more recently in single bubble (SB) experiments.³ The MBSL spectrum extends from the UV to well beyond the red end of the visible wavelength range.⁴ The actual mechanism responsible for the emission remains unclear. However, there is a wide body of evidence adduced from studies on multibubble systems which suggests that a host of vibronically excited-state species are produced during bubble collapse, and under the high temperature and pressure conditions within the bubble these give rise to the broad emission.^{5–11} The possibility that the emission originates from a plasma core,¹² the most likely situation for SBSL, cannot be completely ruled out. Nonetheless, MBSL appears to be significantly different from SBSL and plasma core emission in multibubble systems is likely to be less significant than the other modes of producing light.¹³

The intensity and spectral shape of MBSL, the more widely studied emission, has been shown to be influenced by the type of gas in the liquid, the presence of solutes in the liquid, and the liquid itself.^{5–11,14,15} Recently it was shown that the

quenching of MBSL in water by aliphatic alcohols could be directly related to the surface excess, i.e., the interfacial concentration, of the solutes at the air/water interface and not to the bulk concentration of the alcohol.¹⁵

The present study further examines the role of interfacially adsorbed molecules on MBSL using the solution pH as a means of changing the equilibrium charge and amount of solute adsorbed to the bubble/water interface. The solutes chosen for this study were simple organic weak acids and bases.

Experimental Details

The ultrasound source used in all experiments was an in-house modified Undatim Ultrasonics D-Reactor operating at 515 kHz. The Reactor was placed in a light-shielded housing which also contained an end-on photomultiplier (Hamamatsu) for sensing the sonoluminescence from the solutions insonated. The emission signals were recorded on a LeCroy 7242 digital oscilloscope, then downloaded onto a Macintosh computer for further analysis. All the work reported here was carried out using 4 ms pulses with 12 ms between pulses. The SL intensity from 100 pulses was averaged and these values are given in the figures presented later. The first 20 pulses were not used in the averaging as SL produced in these initial pulses had not yet reached a steady-state intensity.¹⁵

All aliphatic amines and acids used were AR grade and used as received. The "Milli-Q" water used to make all solutions had a conductivity of $<1 \times 10^{-6}$ S cm⁻¹ and a surface tension of 73.8 mN m⁻¹ at 18 °C. The pH of the solutions was adjusted with the appropriate amounts of HCl or NaOH solution. Experiments were conducted at room temperature and any heating of the solutions during sonication was limited to a few degrees. The sonicator was operated at about 15 W. The volume of the solutions sonicated was 25 mL.

Emission spectra were recorded by fitting the reactor into the cell compartment of a Hitachi F-4500 spectrofluorimeter. A quartz cell was used for these experiments with a solution volume of 50 mL. The exit slit width used gave a wavelength resolution of about 20 nm. A full spectral scan was completed in about 2 min. During this time there was only a 1 to 2 deg heating of the solution.

Surface tension measurements were made using a McVan Analite Surface Tension Meter with a glass Wilhelmy plate. The conditions for the experiments are listed with the data presented in the text.

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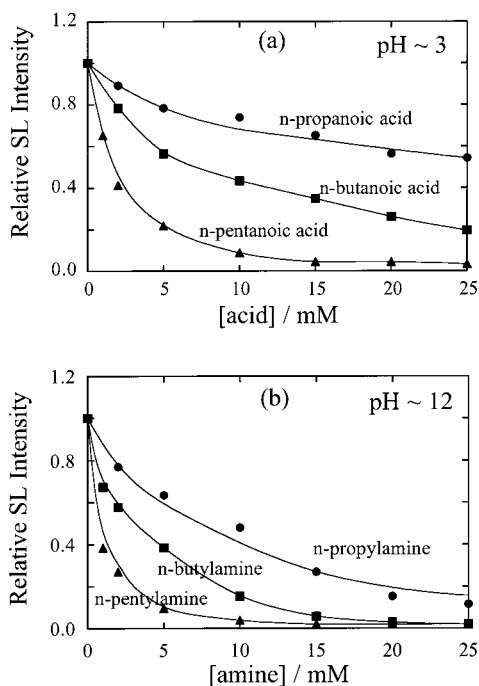


Figure 1. Relative emission intensity as a function of the concentration of *n*-alkyl carboxylic acids and amines at pH 3 and 12, respectively.

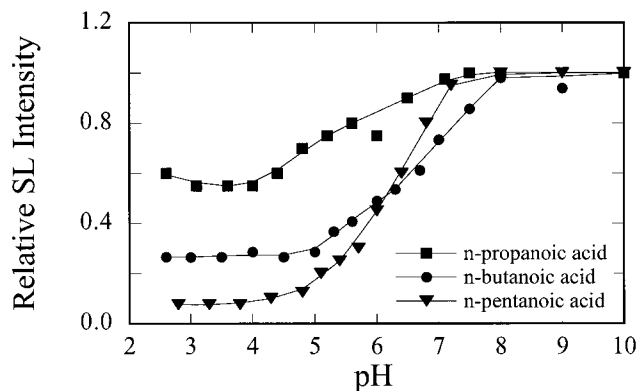


Figure 2. Relative sonoluminescence intensity of 25 mM solutions of *n*-alkyl acids as a function of pH.

Results

The relative emission intensity as a function of the concentration of *n*-alkyl carboxylic acids and amines at pH 3 and 12, respectively, is shown in Figure 1. The pH of the solutions was chosen such that the solutes were in their un-ionized form (see later). Generally, the extent of quenching increased with an increase in the alkyl chain length of the solute, as observed previously for aliphatic alcohols.¹⁵

The effect of changing the pH of the solution was examined at a fixed solute concentration of 25 mM. A background NaCl concentration of 0.1 M was used to maintain a constant solution ionic strength. The results obtained are shown in Figures 2 and 3. It can be seen in both figures that there is a distinct onset pH at which SL quenching occurs. For the alkyl acids this pH is about 7 whereas for the alkylamines it is about 9. Changing the pH of the solution in the range shown in the two figures in the absence of either amine or acid does not affect the SL intensity.

It can also be seen in Figures 2 and 3 that the extent of SL quenching increases with an increase in the alkyl chain length

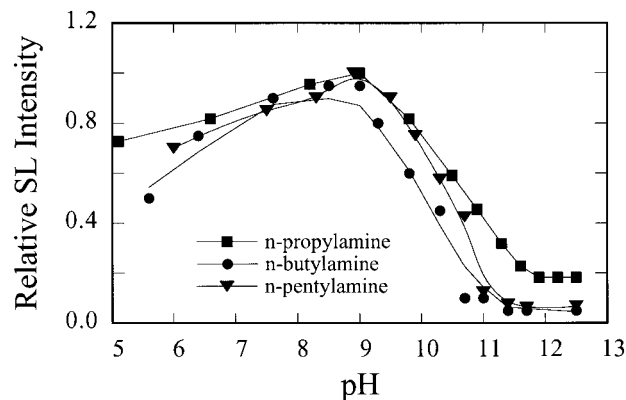


Figure 3. Relative sonoluminescence intensity of 25 mM solutions of *n*-alkylamines as a function of pH.

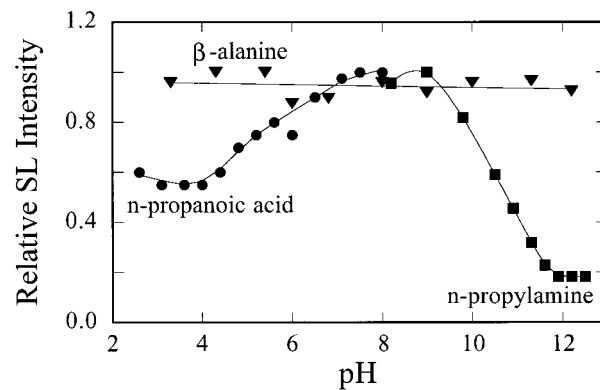


Figure 4. Relative sonoluminescence intensity of 25 mM solutions of *n*-propylamine, *n*-propionic acid, and β -alanine (3-aminopropanoic acid) as a function of pH.

of the solute, and this is in accord with the results shown in Figure 1. In addition it can be noted that maximum quenching for the alkyl acids occurs at low pH whereas for the alkylamines it occurs at high pH. This pH effect is not observed when the solute is an aliphatic alcohol, or in pure water. For any given amount of alcohol the extent of quenching remains constant in the pH range 3–11.

The effect of pH on the SL was also examined using the amino acid, β -alanine (3-aminopropanoic acid). This molecule remains charged at all pH values. The results are shown in Figure 4 in comparison with propanoic acid and propylamine. As can be seen there is no SL quenching at any pH in contrast to the amine and acid solutes.

Measurement of the full spectra, rather than the integrated emission used in the other experiments, of both propanoic acid and propylamine under extreme pH conditions is shown in Figure 5. The profiles of the emission spectra are very similar to what we observe from air-saturated water. It can also be seen that the emission is uniformly reduced when the solutes are in their neutral form. The decrease in the maximum intensity at about 450 nm, with a change in pH, closely matches the integrated emission yields shown for the two solutes in Figures 2 and 3 for equivalent pH values.

Discussion

Before attempting to explain the results obtained it is useful to consider some of the physicochemical properties of the molecules examined. Listed in Tables 1 and 2 are a number of properties relevant to the discussion to follow.

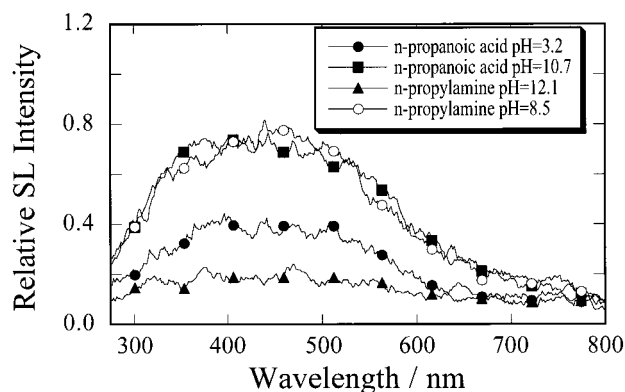


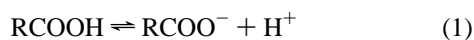
Figure 5. Sonoluminescence spectra from air-saturated solutions (25 mM) of propylamine and propanoic acid under pH conditions at which the solutes exist in either their neutral or ionized forms.

Table 1. Selected Physicochemical Properties of the Solutes Examined

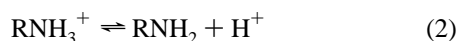
solute	pK_a^a	boiling point ^a (°C)	vapor pressure ^a (kPa; at 25 °C)
<i>n</i> -propanoic acid	4.86 (25 °C)	141	0.553
<i>n</i> -butanoic acid	4.83 (25 °C)	164	0.221
<i>n</i> -pentanoic acid	4.77 (25 °C)	186	0.024
<i>n</i> -propylamine	10.60 (20 °C)	47	42.1
<i>n</i> -butylamine	10.77 (20 °C)	78	12.2
<i>n</i> -pentylamine	10.63 (25 °C)	104	4.0
β -alanine ^b	3.55, 10.24 (25 °C)	solid ^c	
<i>n</i> -propanol		97	2.76
<i>n</i> -butanol		118	0.860
<i>n</i> -pentanol		138	0.259

^a CRC Handbook of Chemistry and Physics, 60th ed.; Weast, R. C., Ed.: CRC Press, Boca Raton, FL, 1981. ^b β -Alanine = 3-aminopropanoic acid. ^c Decomposes above 200 °C.

The acid–base equilibria of the two types of solutes studied can be generically represented by,



and



where R represents the alkyl portion of the weak acid or base.

On the basis of the pK_a values in Table 1 it would seem that the species responsible for the SL quenching are the neutral forms of the solutes used, as SL quenching only begins to occur at pH values where the neutral forms of the solutes start to increase in concentration. This observation is supported by the β -alanine results for which no quenching is observed over the entire pH range examined. As this solute possesses both an amino ($pK_a = 10.24$) and a carboxyl ($pK_a = 3.55$) group it remains charged at both high and low pH.

Considering the boiling point and vapor pressure data in Table 1 it can be seen that the extent of quenching increases as the boiling point increases and the vapor pressure decreases for the acids and bases. That is, the extent of quenching is not primarily associated with the volatility of the solutes. This is an important observation as Suslick et al.¹⁶ have shown that in nonaqueous liquids sonochemical effects decrease with an increase in the vapor pressure of the solvent. The reason for the vapor pressure effect can be attributed to a lowering of the maximum

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Table 2. Surface Tension (measured at 18.2 °C) and Surface Excess Values (calculated using eq 4) for 25 mM Aqueous Solutions of the Solutes Examined, in the Presence of 0.1 M NaCl

pH	surface tension (γ^a) (mN/m)	surface excess (Γ^a) ($/10^{14}$ molecules/cm ²)
	water	
6.3	73.8	
	0.1 M NaCl	
6.4	74.3	
	<i>n</i> -propanoic acid	
3.1	72.2	0.39
10.7	73.8	0.04
	<i>n</i> -butanoic acid	
2.9	69.0	1.04
10.9	73.8	0.04
	<i>n</i> -pentanoic acid	
2.9	56.8	1.85
11.0	69.0	1.04
	<i>n</i> -propylamine	
3.3	73.9	0.04
12.4	69.9	0.92
	<i>n</i> -butylamine	
3.4	73.1	0.14
12.3	68.7	1.07
	<i>n</i> -pentylamine	
3.4	71.9	0.49
12.4	58.6	1.66
	β -alanine	
3.3	73.1	0.14
11.0	73.2	0.14

^a Errors estimated to be ± 0.7 mN/m and $\pm 0.10 \times 10^{14}$ molecules/cm².

temperature generated during the collapse of a vapor filled cavity and is theoretically predicted in the “hot spot” model of acoustic cavitation.¹⁷ The higher the gas pressure within a collapsing bubble the lower the maximum bubble temperature that can be reached (see later).

The acid and amine results do however warrant a comparison with the SL quenching observed with aliphatic alcohols.¹⁵ In the latter case it was found that the SL quenching could be directly correlated with the amount of solute adsorbed at the bubble/water interface.

The amount of solute adsorbed at an interface, in relation to its bulk solution concentration, is thermodynamically described by the Gibbs equation, at constant temperature and pressure conditions, as

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (3)$$

where μ_i is the chemical potential of component *i* in solution, γ the air/water interfacial tension and Γ_i the surface excess of component *i*. For the case of a neutral solute (*s*), its surface excess, Γ_s , relative to the solvent can be calculated from the variation of the air/water surface tension ($d\gamma$) with the natural log of the bulk solute concentration ($d \ln C_s$) using the Gibbs–Duhem equation, at constant temperature and pressure.

$$\Gamma_s = -(1/kT) d\gamma/d \ln C_s \quad (4)$$

For molecules that have a preference for the interface the surface excess is effectively the two-dimensional concentration of the solute at the interface. To obtain the surface excess for the solutes used in our experiments the surface tension at the

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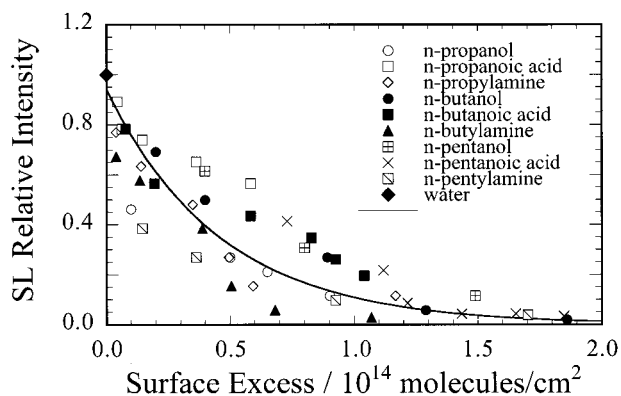


Figure 6. Relative sonoluminescence of *n*-alkyl carboxylic acids (pH 3), amines (pH 12), and alcohols (pH 6) as a function of their air/water surface excess concentration.

air/solution interface was measured as a function of solute concentration. In Figure 6 is shown how the SL intensity changes as a function of the surface excess of the weak acids and amines in their neutral form. Also included in this figure is the data obtained for the SL quenching with aliphatic alcohols, taken from our earlier study.¹⁵ As can be seen there is a good correlation between the degree of quenching and the surface excess of the solute, but not specifically on the alkyl chain length nor on the attached functional group of the solute.

The conclusion that the extent of SL quenching is dependent on the interfacial concentration of the solute does not however provide a direct understanding of the mechanism responsible for the quenching process. A number of possibilities may be considered within the framework of the likely sources of SL mentioned in the Introduction: (i) the presence of the solute decreases the number of bubbles that can undergo collapse; (ii) solute molecules adsorbed at the interface hinder bubble collapse, leading to lower collapse temperatures and hence less SL; (iii) solute molecules evaporate from the interface during bubble expansion and quench, by collisional deactivation or reaction, the excited-state species responsible for SL; and (iv) solute molecules evaporate from the interface into the bubble during its expansion phase and decrease γ' , the heat capacity ratio (C_p/C_v), thereby lowering the bubble core temperature and hence the amount of SL.¹⁷ Quantitatively this effect can be described by the following equation, which stems from a simple hydrodynamic model for cavitation:¹⁷

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

where P_v is pressure within the bubble at the point of collapse, P_a is the pressure exerted on the bubble at the beginning of collapse, T_o is the ambient temperature, and T_{\max} is the peak temperature generated on collapse.

Mechanism i can be discounted because SL quenching, using the same additives as in the present study, has also been observed in single bubble experiments.¹⁸ Furthermore, when the solute adsorbed at the bubble/water interface is charged, no quenching takes place. This can be seen from the results presented in Table 2, which lists the surface excesses of the various solutes at extreme pH values. For example, it can be seen from Table 2 that at pH 11, the ionized form of *n*-pentanoic

acid has a surface excess of 1×10^{14} molecules/cm² and there is essentially no SL quenching. On the other hand, extensive quenching is observed for *n*-butylamine at pH 12.3, where it is in its neutral form and has a similar surface excess to the ionized form of *n*-pentanoic acid. This latter point also tends to rule out mechanism ii, as charged solutes adsorbed at the interface can be expected to provide an even greater resistance to bubble collapse than a neutral species, due to the repulsive electrostatic interaction between the charged molecules adsorbed at the bubble/solution interface.¹⁵

Mechanisms iii and iv both rely on the evaporation of solute into the bubble during collapse. It appears that only volatile solutes lead to SL quenching, as shown to be the case in this study for the alkylamines and acids, and previously for alkyl alcohols.¹⁵ Although a number of theories exist as to the origins of MBSL the one most widely held is that the emission spectrum is composed of a combination of emission bands from a number of excited-state species. Apart from direct formation of the excited states by thermal activation of molecules within the bubble core, the recombination of radical species involving a third body has also been postulated (e.g. refs 5 and 7). Under standard gas phase conditions 3-body collisions are usually far less important than 2-body collisions. However, the conditions within a collapsing bubble, at the point where emission takes place, resemble those of a liquid and 3-body collisions can be expected to be significant. Since water will be the dominant component within the cavity at the levels of the volatile solute used, it will be the main 3-body collision partner and the presence of volatile solute will not change this situation to any significant extent.¹⁹ Therefore, the quenching effect of the volatile solute must be due to either direct deactivation of the excited state species or interaction with thermally produced radicals thereby preventing the radical-radical recombination processes that lead to light emission. As water is also capable of quenching excited-state species the quenching effect would need to be attributed to volatile solute molecules within the bubble reacting with the radicals that are precursors to the emitting species. However, if specific excited-state species were prevented from forming it could also be expected that there would be a change in the SL spectrum. From the spectra recorded at different degrees of quenching, as noted earlier (see Figure 5), there does not appear to be a change in the profile of the emission envelope when quenching occurs. On the basis of the above argument mechanism iii does not explain the quenching process.

According to mechanism iv the solute molecules that have evaporated into the bubble core decrease the core temperature of the bubble in the same way any polyatomic molecule does. The importance of the evaporated solute on γ' is difficult to calculate absolutely but its relative effect can be estimated. It can be seen in Figure 6 that most of the SL is quenched when a surface excess of about 1×10^{14} molecules/cm² is reached. This value corresponds to an area per solute molecule of 1 nm². Since alkyl acids, amines, or alcohol molecules at an air/water interface all occupy an area²⁰ of about 0.2 nm², over 80% of the bubble surface is still water. If we accept that the neutral molecules adsorbed at the bubble/liquid interface evaporate into the bubble during the expansion phase of the bubble then so too will surface water molecules. On this basis water molecules will always dominate and their presence in the bubble will be the main influence on γ' during bubble collapse and not the

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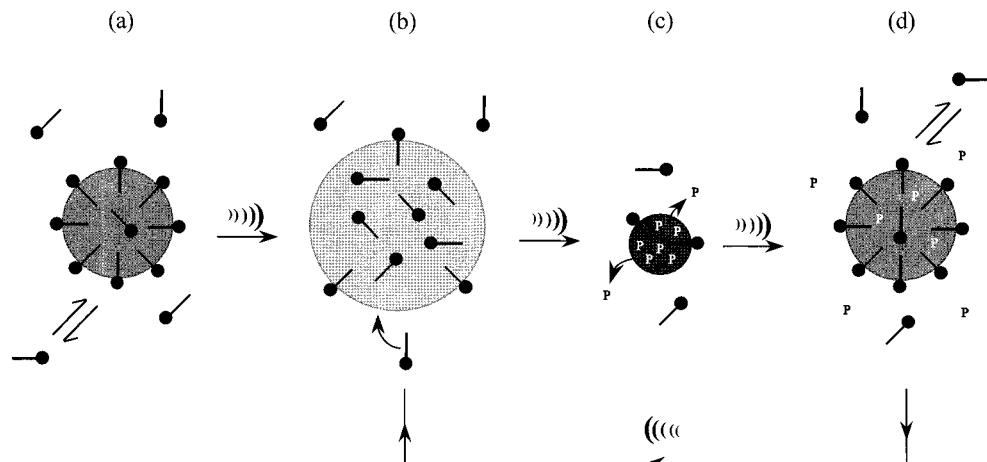


Figure 7. Diagrammatic representation of (a) solute adsorption at the bubble/solution interface, (b) evaporation into the bubble, (c) decomposition, and (d) solute re-adsorption at the bubble/solution interface. This cycle is repeated and more decomposition products (P) progressively accumulated in the bubble core.

neutral solutes. Therefore it can also be concluded that this mechanism is not responsible for the decrease in MBSL.

There is, however, one further aspect to mechanism iv that should be considered. In the above discussion it has been assumed that just one surface layer of solute is taken into the bubble. This may not be so. It is highly likely that the solute molecules that have entered the bubble will decompose during the high temperatures of the collapse phase.^{21–23} Solute molecules from bulk solution will then re-adsorb at the bubble interface and the cycle will continue. Some of the decomposed material in the bubble will of course diffuse into bulk solution but the hydrocarbon decomposition products will favor the gas phase and can be expected to build up in concentration within the bubble²¹ over many cycles of bubble expansion and compression. It can be expected that a steady state is established between the amount of decomposition products produced and that which remains within a bubble. This will depend on the amount of solute that can adsorb at the bubble/solution interface (i.e., the surface excess) and the physical lifetime of an oscillating bubble under the conditions of the experiment. This scenario is depicted in Figure 7. Therefore, with the increase in decomposition products within the bubble, γ' may indeed decrease and so too then the SL intensity.²⁴ In addition, the core temperature will also be reduced because the accumulated molecules within the bubble will consume energy through thermal dissociation processes. Our work^{18b} with single bubble

sonoluminescence, using the same solutes, lends itself to a similar interpretation and is consistent with the conclusions arrived at by Henglein²¹ in his work on the sonochemical decomposition of similar organic solutes used in the present study. Further support for the above mechanism can be found in the recent study by Tauber et al.²⁵ on the sonolysis of *tert*-butyl alcohol. They found that numerous volatile products were produced during sonication of argon saturated aqueous solutions of *tert*-butyl alcohol and that as the concentration of *tert*-butyl alcohol was increased, the bubble core temperature decreased.

In conclusion, the results obtained clearly show that MBSL quenching is directly related to the concentration of neutral solute at the bubble/solution interface. The arguments presented support the idea that volatile solutes adsorbed at the bubble/solution interface evaporate into the core of the bubble during bubble growth. It is proposed that the solutes decompose under the high-temperature conditions within the bubble and that there is an accumulation of solute decomposition products, over many bubble oscillation cycles. Overall, the presence of accumulated products within the bubble results in a decrease in the bubble's core temperature, leading to fewer excited-state species and hence less SL.

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(24) It is also possible that the gas pressure within the bubble rises as the decomposition products accumulate. This will also decrease the core temperature, as predicted by eq 5.