

Sonoluminescence Quenching in Aqueous Solutions Containing Weak Organic Acids and Bases and Its Relevance to Sonochemistry

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Multibubble sonoluminescence from water was found to be quenched by the addition of low levels of unsubstituted or 2-chloro-substituted aliphatic carboxylic acids and the aromatic solutes, phenol and aniline. In all cases, the sonoluminescence intensity could be restored to the level obtained in pure water by adjusting the solution pH to a point where the solutes were completely in their ionized form. A comparison of the sonochemical decomposition of phenol at pH levels above and below its pK_a revealed that only when the solute was in its neutral form was there significant decomposition. It is shown that both the sonochemical decomposition of phenol and the sonoluminescence quenching by all solutes studied can be directly correlated with the amount of solute adsorbed at the bubble/solution interface. The relationship between sonochemical activity and sonoluminescence quenching by water-soluble organic solutes is discussed.

Introduction

The passage of ultrasound through a liquid in many cases gives rise to a broad wavelength emission of light, referred to as sonoluminescence (SL).^{1,2} Although it has long been known that the emission is a consequence of the sound-driven collapse of microbubbles in the liquid, the actual details of the processes responsible for the emission have been the subject of considerable speculation. The relatively recent discovery³ of single bubble sonoluminescence (SBSL) has allowed the development of quantitative models on the origins of the emission which satisfactorily account for most of the experimental observations reported.^{4,5} These recent calculations assume that the implosion of a microbubble briefly produces a thermally conducting, partially ionized plasma core which relaxes on a tens of picosecond time scale⁶ to emit light.

SL from multibubble (MBSL) systems, although still a broad wavelength emission signal, shows some structure.^{7–9} This has set it apart from SBSL.¹⁰ It has been suggested that the core temperature in MB systems is lower than that produced in the more symmetrical collapse of single bubbles. This lower temperature situation is more conducive to the formation of radicals and electronically excited atoms and molecules, and consequently MBSL spectra most likely consist of an overlap of pressure- and temperature-broadened emission bands from a number of vibrationally activated excited-state species.^{7,8}

SL, both SBSL and MBSL, is also known to be affected by the presence of solutes in the liquid.^{11–14} Small amounts of water-soluble organic solutes, such as aliphatic alcohols, amines, and carboxylic acids, induce quite strong SL quenching. The effect has been shown to be linked to the amount of solute adsorbed to the bubble/solution interface, and with the additional requirement that the solute be volatile.¹³ We have suggested that solutes that are adsorbed to the bubble surface evaporate into the core where they then thermally decompose. The

accumulation of decomposition products over many bubble oscillation cycles leads to lower core temperatures of the collapsing bubbles and hence less direct SL, and in the case of MBSL, less excited-state species to produce the SL.

SL provides a means of monitoring at least part of the cavitation process and therefore determining the effect solutes have on SL can be expected to provide some insight into the primary mechanistic steps involved in sonochemical reactions. In the present study the connection between sonochemistry and SL is examined for the specific case of the organic solute, phenol. The sonochemical decomposition of phenol has been measured under conditions similar to those used in studying the effect of this solute on the SL emanating from water exposed to 4 ms pulses of ultrasound.

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 detecting the sonoluminescence from the solutions. In all experiments, the solution volume used was 30 mL. Emission signals were recorded on a Tektronics TDS 360 oscilloscope. All sonoluminescence experiments were carried out with 4 ms pulses and 12 ms between pulses. The area of the transducer was 9.63 cm² and the measured power input in 30 mL was 5.1 W, determined by calorimetry. Solutions were presonicated for approximately 30 s then left to stand for about 2–3 min before emission measurements were recorded. The latter procedure eliminates the often large variability in the SL signal obtained when fresh solutions are first pulsed after being poured into the reaction cell.

The organic solutes used were 1-propanoic acid (Mallinckrodt), 2-chloropropanoic acid (Aldrich (99%)), 1-butanoic acid (BDH), 2-chlorobutanoic acid (Fluka), phenol (AP Chemicals), and aniline (BDH). The chemicals were all of the highest purity available and used as received. All concentrations of the acids,

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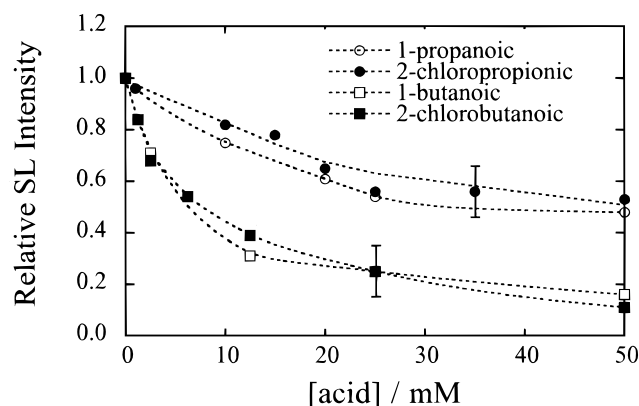


Figure 1. Relative SL intensity (relative to the pure water signal) as a function of the concentration of the carboxylic acids in 0.1 M NaCl at pH ≈ 2 . The representative error bars shown are applicable to all data points.

aniline, and phenol were made in 0.1 M NaCl or 0.1 M NaClO₄. Electrolyte was added to the solution to ensure an approximately constant ionic strength when the pH of the solutions was changed. Some experiments were conducted in the absence of added electrolyte and similar results were obtained. The pH levels of the solutions were adjusted by adding appropriate amounts of HCl or HClO₄ and NaOH solutions.

The sonication in the sonochemistry experiments was performed under the same conditions of pulse width, duty cycle, and input power setting as in the sonoluminescence experiments. During the examination of phenol decomposition, the phenol concentration was monitored by HPLC (Shimadzu LC-10Ai). The column used was a 25 cm long, 4.6 mm i.d. C18 column with a mobile phase composition of MeOH/H₂O in a ratio of 60/40 with 1% acetic acid. The wavelength of detection was 268 nm.

Surface tension measurements were made using a Wilhelmy glass plate and a McVan Analite Surface Tension meter. All measurements were made under ambient pressure and temperature conditions.

Results

The effect of propanoic acid and butanoic acid and their chlorinated analogues on the SL signal obtained from air-saturated aqueous solutions at pH ≈ 2 is shown in Figure 1. In all cases the signal is quenched with increasing concentration of the solute. The effect is more pronounced for the butanoic acids than that for the propanoic acids, but between the two analogue couples there is little, if any, difference.

The influence of the solution pH, at a fixed solute concentration of 25 mM, on the SL signal is shown in Figures 2 and 3. At the extremes of the pH range the solute couples show the same behavior, namely, SL quenching at low pH and essentially no SL quenching at high pH. At pH values between the two extremes, however, there is a clear difference between the carboxylic acids and their corresponding chlorinated analogues. It can be seen that the transition between quenching and no quenching occurs at a much lower pH for the chlorinated solutes.

The effect on the SL signal when aromatic solutes are added to air-saturated water is shown in Figure 4 for phenol and aniline. The pH of the solution was chosen to ensure that the solutes were in their neutral forms (see Discussion section). The consequence of changing the pH is illustrated in Figure 5 at a fixed solute concentration of 50 mM. The apparent opposite trend in the quenching behavior with changing pH of the phenol

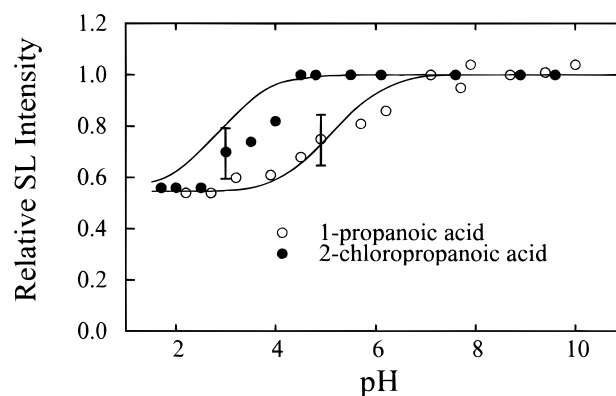


Figure 2. Relative SL intensity (relative to the pure water signal) of 25 mM solutions of 1-propanoic and 2-chloropropanoic acids in 0.1 M NaCl as a function of pH. Lines represent theoretical curves calculated by determining the concentrations of the free acids at a given pH using literature pK_a values and then using these concentrations of free acids to determine the relative SL intensities from Figure 1. The representative error bars shown are applicable to all data points.

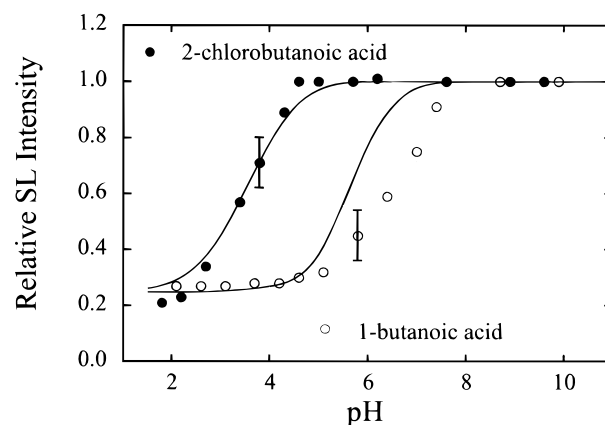


Figure 3. Relative SL intensity (relative to the pure water signal) of 25 mM solutions of 1-butanoic and 2-chlorobutanoic acids in 0.1 M NaCl as a function of pH. Lines represent theoretical curves calculated by determining the concentrations of the free acids at a given pH using literature pK_a values and then using these concentrations of free acids to determine the relative SL intensities from Figure 1. The representative error bars shown are applicable to all data points.

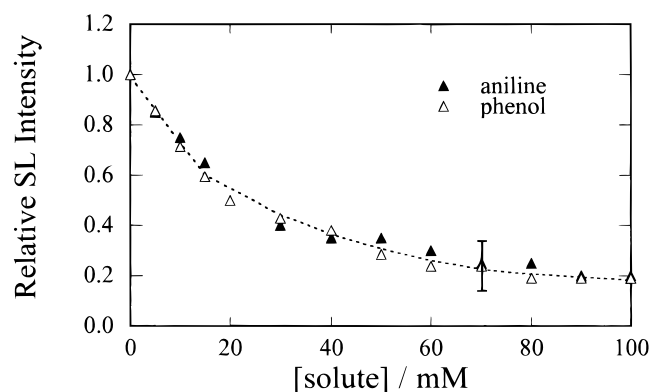


Figure 4. Relative SL intensity (relative to the pure water signal) as a function of the concentrations of the phenol and aniline in 0.1 M NaClO₄ at pH ≈ 3 and ≈ 11 , respectively. The representative error bar shown is applicable to all data points.

and aniline systems is quite similar to the results previously reported with alkyl acids and amines as solutes.¹³

The sonochemical decomposition of phenol was also examined under the same experimental conditions. The extent of decomposition as a function of sonication time at pH ≈ 3 and

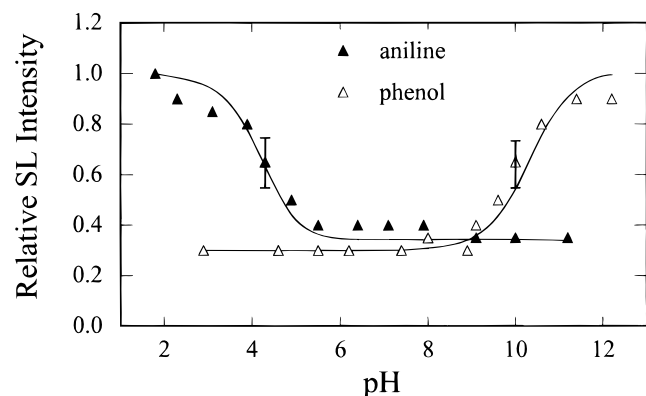


Figure 5. Relative SL intensity (relative to the pure water signal) of 50 mM solutions of aniline and phenol in 0.1 M NaClO₄ as a function of pH. Lines represent theoretical curves calculated by determining the concentrations of the free acids at a given pH using literature pK_a values and then using these concentrations of free acids to determine the relative SL intensities from Figure 4. The representative error bars shown are applicable to all data points.

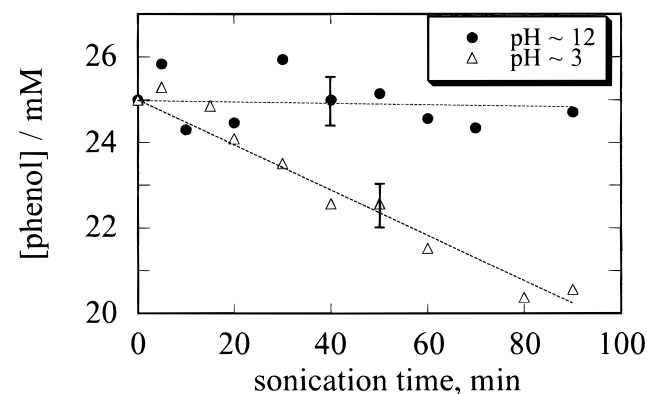
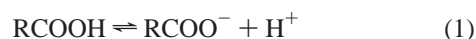


Figure 6. Decay kinetics following the sonication of 50 mL of a 25 mM solution of phenol at pH ≈ 3 and ≈ 12. The sonication was performed under the same conditions of pulse width, duty cycle, and input power setting as in the SL experiments. The representative error bars shown are applicable to all data points.

≈ 12 is displayed in Figure 6. The pH values of these experiments were chosen in order to compare the sonochemical behavior with the quenching and nonquenching conditions observed with phenol as per Figure 5. The observation that phenol is depleted only at low pH is qualitatively in agreement with results reported by Currell et al.¹⁵

Discussion

Considering the acid–base nature of the solutes examined, it would appear that the species responsible for the SL quenching are the neutral forms of the solutes. This can best be appreciated by considering the following equilibria,



where R represents the alkyl or chlorinated alkyl group, and ϕ represents the phenyl moiety. The generic equilibrium constant for reactions 1–3 is given by

$$K_a = \frac{[\text{B}][\text{H}^+]}{[\text{HB}]} \quad (4)$$

TABLE 1: pK_a Values of the Organic Solutes Used in the Study

solute	pK _a ^a
1-propanoic acid	4.86 (25 °C)
2-chloropropanoic acid	2.83 (25 °C)
1-butanoic acid	4.83 (25 °C)
2-chlorobutanoic acid	2.86 (20–22 °C)
phenol	9.89 (20 °C)
aniline	4.63 (25 °C)

^a CRC Handbook of Chemistry and Physics, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 60th Edition, 1981.

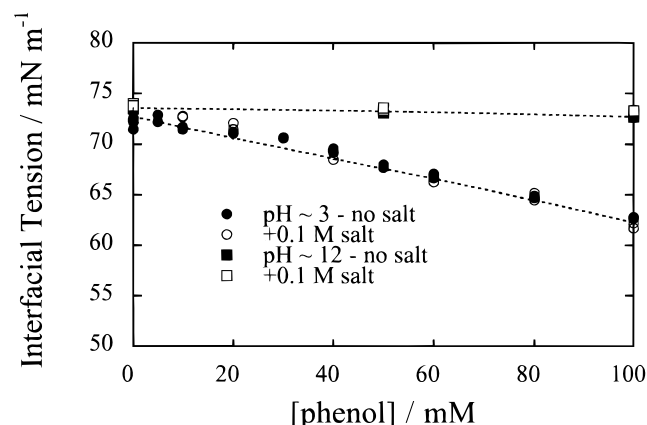


Figure 7. Interfacial tension of the air/solution interface as a function of phenol concentration at pH ≈ 3 and ≈ 12 in the presence and absence of 0.1 M NaClO₄.

where HB represents the acid form of the solute, and B represents its conjugate base. The pK_a values for the solutes represented by eqs 1–3 are given in Table 1. Assuming that only the neutral forms of the solutes quench the sonoluminescence, SL–pH quenching profiles can be calculated using the data of Figures 1 and 4 and eq 4. For example, on choosing a particular pH, eq 4 can be used to calculate the concentration of B ([B] + [HB] = total solute concentration), and the corresponding relative SL signal from the appropriate curve in Figures 1 and 4. Repeating this process for different pH generates the solid lines in Figures 2, 3, and 5. Note that the representative error bars for the data points shown in the figures are equally applicable to the solid lines because the calculations are based on the SL quenching data. The relatively good correspondence between the solid lines (which as stated above assumes that only the neutral forms of the solutes are involved in the SL quenching) and the experimental results indicates that the charged forms of the solutes play no role at all in SL quenching.

When the extent of quenching of the solutes at a particular concentration is compared, the order of effectiveness is propanoic acid ≈ 2-chloropropanoic acid < aniline ≈ phenol < butanoic acid ≈ 2-chlorobutanoic acid. However, we have shown that the bulk solution concentration of a solute does not directly relate to the extent of SL quenching; a more direct correlation is the surface excess of the solute at the air/water interface.^{12–14} The surface excess of a surface-active solute is effectively its two-dimensional concentration at an interface. The more hydrophobic a solute, the greater its surface excess for a particular bulk solution concentration. Figure 7 illustrates the effect of phenol on the air/water surface tension under various conditions and Table 2 lists the surface tensions measured for all of the solutes examined in neutral and ionized forms at the highest concentrations used. The mean surface excess concentrations calculated at these concentrations are also listed.

TABLE 2: Surface Tension and Surface Excess Values for the Aqueous Solutions of the Solutes (25 mM) Used in Study ($T = 22.3\text{ }^{\circ}\text{C} - 22.8\text{ }^{\circ}\text{C}$)

pH	surface tension ^a (γ) (mN/m)	surface excess (Γ) ^a (/10 ¹⁴ molecules/cm ²)
	water/0.1 M NaCl/0.1 M NaClO ₄	
3.1	72.6/73.3/73.6	
12.2	72.9/73.6/73.9	
	1-propanoic acid/0.1 M NaCl	
1.5	72.4	<0.4
10.6	72.9	<0.4
	2-chloropropanoic acid/0.1 M NaCl	
1.5	72.1	<0.4
10.6	72.9	<0.4
	1-butanoic acid/0.1 M NaCl	
2.0	68.2	1.4
10.6	73.4	<0.1
	2-chlorobutanoic acid/0.1 M NaCl	
1.8	68.0	1.7
10.6	73.3	<0.1
	phenol/0.1 M NaClO ₄	
3.1	70.5	0.9
12.2	73.4	<0.1
3.1	67.8 (50 mM)	2.1
12.2	73.2 (50 mM)	<0.1
	aniline/0.1 M NaClO ₄	
1.2	73.0	<0.1
11.0	70.8	0.8
1.2	72.3 (50 mM)	<0.4
11.0	66.9 (50 mM)	2.3

^a Errors estimated to be ± 0.7 mN/m and $\pm 0.1 \times 10^{14}$ molecules/cm².

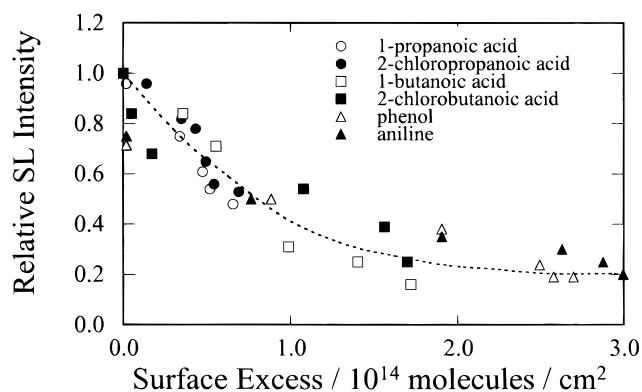


Figure 8. Relative SL intensities (relative to the pure water signal) of carboxylic acids (pH \approx 2) and their 2-chloro derivatives (pH \approx 2), aniline (pH \approx 11) and phenol (pH \approx 3), as a function of their air/water surface excess concentrations (all solutes in their neutral forms).

These data clearly show that the surface excess concentrations of the neutral solutes increase in the same order as their effectiveness in the SL quenching.

Using surface tension measurements over the full range of the solute concentrations examined provides the corresponding surface excess concentrations, which along with the data from Figures 1 and 4 allow for the construction of Figure 8. Figure 8 relates the extent of quenching to the surface excess of the neutral form of the solute. It shows that the extent of quenching is not solute-dependent but is only related to the amount of solute that can adsorb to the air/water, and therefore the bubble, interface.

The conclusions reached in this study are in essence the same as those arrived at in our previous work on SL quenching in aqueous solutions containing aliphatic alcohols, acids, and

amines.^{12,13} The present study adds to our earlier work in that it shows that more chemically complex solutes affect SL quenching in the same way as the simpler solutes previously examined. Specifically it emphasizes that it is the concentration of the solute at the bubble/solution interface that is relevant, not the solute per se.

The actual mechanism responsible for the SL quenching is somewhat more difficult to elucidate. On the basis of our work with alkylamines and acids, we have proposed that volatile solutes that are adsorbed to the bubble/solution interface evaporate into the bubble core during bubble growth and are decomposed during the heating phase of bubble collapse. This process is repeated over many bubble oscillation cycles and although some products are expelled from the bubbles, overall there is an accumulation of volatile decomposition products within the bubble.¹³ These retained products have the effect of decreasing the bubble's core temperature, thereby producing fewer excited state species and consequently less SL. The results from the present study fit this explanation just as well as our earlier results, even though the solutes themselves have quite different chemical compositions and acid-base properties.

The events described above must also take place as part of the sonochemical processes that occur in solution. On the basis of the discussion on the mechanism of SL quenching by volatile organic solutes, the temptation is to simply ascribe the lower rate of phenol decomposition at a pH of 12, relative to pH 3, to the nonvolatile phenoxide anion at pH 12 (Figure 6). Indeed, the insonation of phenol in an alkaline medium yielded only trace amounts of acetylene as a pyrolysis product, while under acidic conditions a significant amount of acetylene was detected.¹⁵ However, several other studies have also shown that among the initially formed products of sonication of phenol in aqueous solution are catechol and hydroquinone.^{16–19} The evidence is quite strong that OH radicals formed within the cavitation bubble are scavenged by phenol molecules at the bubble surface. Furthermore, because quantitative yields of catechol and hydroquinone are produced, the implication is that OH radical addition reactions are much more significant than pyrolysis reactions. That is, the initial pathway in the degradation of phenol is primarily associated with radical attack and not via thermal decomposition. The general conclusions on the mode of degradation of phenol is applicable to other phenol derivatives because they show much the same type of initial decomposition products as phenol and exhibit reaction extent variation with pH.^{20–22}

The lack of OH attack on the phenoxide ion can be understood in terms of its lower interfacial concentration, compared to phenol—a point previously raised by Colarusso and Serpone.¹⁶ Quantitatively this can be seen for 50 mM of phenol, for example, which has a surface excess of 2.1×10^{14} molecules/cm², whereas that for the phenoxide anion is $<0.1 \times 10^{14}$ molecules/cm². In the absence of OH scavengers adsorbed at the bubble–solution interface, most OH radicals must recombine within the bubble. If this were not the case, OH reaction with the solute in bulk solution should still occur because the rate constant for OH addition to phenoxide is almost the same as that for phenol.²³

Considering the results of the present and related studies, several conclusions can be drawn. Primary sonochemical reactions involving simple organic solutes in water need not involve solute evaporation into the bubble core; however, it is a requirement for SL quenching.^{12,13} The presence of solute at the bubble interface is important for both processes. Although this is a common factor that affects both types of ultrasound-

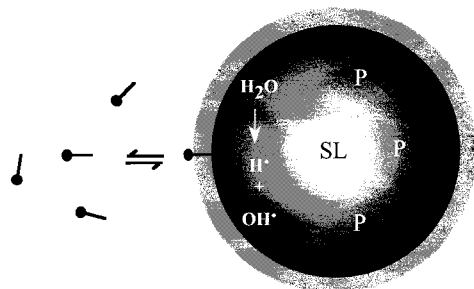


Figure 9. Schematic representation of the regions within a collapsing bubble where SL and sonochemical reactions occur. Surface-active solutes scavenge the primary radicals produced within the bubble and volatile products (P) stemming from the decomposition of solute affect the SL yield.

induced phenomena, the primary sonochemical reaction steps are not directly coupled to the processes responsible for SL quenching. This latter conclusion is supported by the observation that sonochemical reactions continue to occur, with increased yield, as the added solute concentration is increased, even though SL is almost completely quenched. This occurs in both MB¹⁴ and SB²⁴ systems.

A diagrammatic way of rationalizing the effect of organic solutes on sonochemical reaction and SL yield is depicted in Figure 9. Solute molecules adsorbed at the bubble solution interface scavenge the primary radicals^{25–27} produced in the core of the collapsing bubble initiating sonochemical reactions. The volatile solutes adsorbed at the interface that are drawn into the bubble during its expansion phase are decomposed, producing volatile products which accumulate over several bubble oscillation cycles, lowering the core temperature and reducing the SL intensity.^{13,28} The presence of two quite distinct regions in which the primary sonochemical reactions take place and SL quenching occurs, the interface and core, respectively, is the reason that the two acoustically generated processes are not directly linked.

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