

Sonoluminescence Quenching of Organic Compounds in Aqueous Solution: Frequency Effects and Implications for Sonochemistry

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Abstract: Solute-induced quenching of sonoluminescence (SL) is reported for aqueous solutions of two homologous series of methyl esters and ketones using low (20 kHz) and high (515 kHz) ultrasound frequencies. SL data at 20 kHz from aqueous solutions containing alcohols and carboxylic acids are also presented to compare with previously published results at 515 kHz. In addition to supporting the previous findings on the existence of stable and transient bubbles at 515 and 20 kHz, respectively, the results suggest that the hydrogen-bonding characteristics of the solutes also play a major role in the extent of SL quenching. An increase in the SL intensity at low concentrations for most of the solutes suggests that these solutes increase the number of "active" bubbles by hindering the coalescence of bubbles. It is concluded that the effect of the solutes on the SL signal from aqueous solutions at both frequencies is primarily due to the balance of two factors, namely, the incorporation of solute within the bubble, leading to SL quenching, and the prevention of coalescence of the bubbles, leading to SL enhancement. At the higher frequency, SL quenching by the solutes is the main influence on the emission yield. However, at the lower frequency, hindrance to coalescence by the solutes dominates at lower concentrations and leads to SL enhancement. The implications of these results for optimizing conditions for aqueous sonochemical reactions are discussed.

Introduction

There is increasing interest in the use of high-intensity ultrasound (US) to promote chemical processes. The effects produced by US largely result from cavitation,¹ that is, the growth and violent collapse of microscopic bubbles in a liquid as the alternate compressions and rarefactions of the sound wave propagate through the liquid. Applications range from organic and organometallic synthesis,^{2,3} electrochemistry and electroanalysis,^{4–6} the production of metal and other inorganic particles^{7–10} through to the synthesis and modification of polymers^{11–13} and colloids, and the destruction of pollutants in water.^{14–16} However, despite this widespread interest, some doubts remain as to the precise mechanisms of many of these reactions.

In aqueous solutions, the primary reaction is the sonolysis of water to give H[•] and OH[•] radicals.¹⁷ The former species mainly recombine to form H₂ gas while the latter form H₂O₂. If solutes are present, they may react with the radicals inside the bubble if they are volatile or in the bulk solution and at the bubble–solution interface if the radicals escape the bubble. Volatile solutes that enter a cavitation bubble may also undergo pyrolysis due to the high temperatures generated inside the bubble during collapse.

Cavitation collapse in a multibubble system also results in the emission of a brief flash of light, sonoluminescence (SL), from vibrationally excited states of molecules produced during the high temperatures and pressures that are generated within the bubble.^{18,19} Several recent reports have demonstrated that SL quenching may under certain circumstances act as a sensitive probe of the sonochemistry that occurs under particular conditions. For example, at an US frequency of 515 kHz, the presence of small amounts of alcohols, amines, or carboxylic acids in solution results in the quenching of the SL. This is caused by

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the evaporation of solutes into the bubbles and the possible subsequent reaction with excited-state intermediates and/or by lowering the effective temperature at the bubble core.^{20,21} Ashokkumar et al. showed that SL quenching by carboxylic acids depended on the pH and occurred only at pH's where unionized acid, a volatile species, was present in solution,^{21,22} whereas ionized, nonvolatile species caused no quenching. Conversely, it has recently been shown that the SL emission can be enhanced by the addition of small amounts of surfactants, attributed to electrostatic repulsion between bubbles hindering bubble clustering.²⁰ The major conclusion from the work of Ashokkumar et al. was that, under the conditions used, the SL quenching correlated with the surface excess concentration of the solute. Thus, the determining factor was the amount of solute adsorbed at the bubble–solution interface rather than the concentration in bulk solution.

Among the experimental parameters that affect sonochemistry and SL, the least understood is the effect of the ultrasound frequency. Up to now, most sonochemical effects have been reported using a frequency of 20–25 kHz, largely for reasons of equipment availability. However, the limited number of publications dealing with frequency effects has shown significant variation of products and rates of reaction. For example, some sonochemical reactions, such as the production of hydroxyl radicals, are more efficient at high frequencies.²³

Tronson et al. recently reported²⁴ that SL quenching by short-chain alcohol solutes in water showed a marked frequency dependence. At 20 kHz, no change in the emission intensity was noted for solutions up to 200 mM concentrations, whereas at 515 kHz, the SL was completely quenched in solutions of 50 mM butanol or 200 mM propanol. Similar differences in SL behavior as a result of changing frequency were recently reported using acrylic and methacrylic acids.²⁵ More recent measurements on a number of vinyl monomers in water showed that the SL quenching behavior at 20 kHz was more complex than at 515 kHz.²⁶ At the higher frequency, all solutes quenched efficiently, and the extent of quenching depended on the solute concentration at the bubble–solution interface. However, at 20 kHz some solutes caused a small degree of quenching while others enhanced the SL by up to 50%. It was clear that the observed effects depended on a wider range of solute properties than simply the tendency for the solute to accumulate at the bubble–solution interface.

To clarify these effects on SL and to increase our understanding of the frequency dependence of sonochemical effects, we have extended the previous studies of SL quenching. Cavitation is known to be influenced by a range of physical properties of dissolved solutes such as vapor pressure, surface tension, and hydrophobicity.^{1,27,28} Measurements of SL emission at two frequencies have therefore been carried out for two homologous

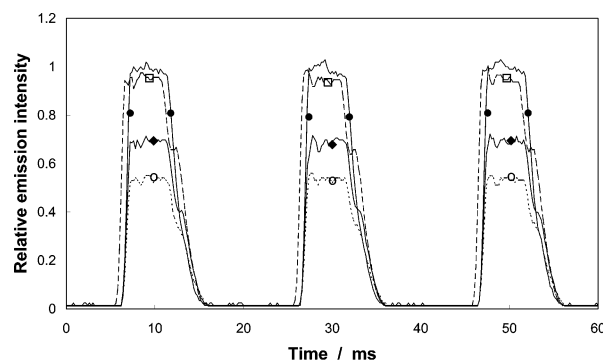


Figure 1. Sonoluminescence emission due to pulsed ultrasound at a frequency of 20 kHz. Each pulse is averaged over ~ 100 individual pulses. Key: ●, water; □, 0.50 M ethanol; ◆, 0.025 M 2-pentanone; ○, 0.05 M 2-pentanone.

series of ketones and esters covering a range of these physico-chemical properties. In addition, the 20 kHz SL of a number of alcohols and carboxylic acids previously shown to quench at 515 kHz has also been measured for further comparison.

Experimental Details

For the measurements using 20 kHz ultrasound, the light emission was recorded from 100 cm³ of solution placed in a 50-mm diameter cell fitted over a 40-mm cup-horn with a Branson B-30 sonicator. Experiments conducted using 515 kHz ultrasound involved 25 cm³ of solution in a vessel fitted over the 35-mm flat plate transducer powered by an Undatim Ultrasonics UL03/1 D-reactor. Sonoluminescence spectra were recorded by placing the sonication cell in the cell compartment of a Hitachi F-4500 fluorescence spectrometer.

All measurements were performed in air using a cylindrical Pyrex cell placed over the transducer-horn assembly. The emission intensities were measured on a Hamamatsu end-on photomultiplier responsive between 300 and 650 nm. Signals were displayed and averaged on a digital oscilloscope and stored on a personal computer for further data processing. Each reported value was averaged over at least 500 pulses. For both frequencies, calorimetric intensities in the range 0.1–0.4 W cm⁻² were used with pulse widths of 5- and 15-ms “off-periods” between pulses. The solution temperatures were within the range 20–25 °C. The reaction vessels were contained in lightproof enclosures to minimize the detection of external light. Typically, sonication of fresh solutions at 515 kHz gave unsteady SL measurements. Sonication for 30–45 s followed by a 2-min “off” period allowed consistent SL measurements to be made thereafter. This phenomenon was not observed at 20 kHz.

The solutes were of high purity (99+%) grade (Aldrich), and solutions were prepared in Milli-Q water with a resistance > 10 M Ω . For experiments involving carboxylic acids, the pH was varied by adding small volumes of NaOH or HClO₄, and a background electrolyte of 0.1 M NaClO₄ was maintained to prevent any possible effects due to varying ionic strength.

The surface tensions of aqueous solutions of the compounds were measured at room temperature using a McVan Analite surface tension meter with a glass Wilhemy plate.

Results

Previous work at 20 kHz using short-chain alcohols ($< C_4$) showed that concentrations of up to 200 mM caused no change in the SL emission compared with that in air-saturated pure water. That this is not a universal phenomenon for all solutes is illustrated in Figure 1, which shows the emission signal from consecutive SL pulses obtained from water and dilute ethanol and 2-pentanone solutions. The addition of ethanol caused little

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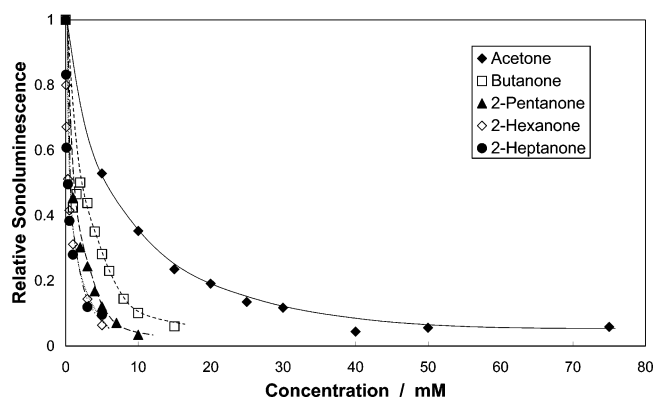
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Table 1. Physical Properties of Solutes⁵⁰

| solute | vapor pressure at 25 °C/Torr | bp (°C) | log ₁₀ (<i>P</i>) ^a | water solubility at 20 °C/mM |
|--------------------------|---------------------------------|------------|---|---------------------------------|
| methanol | 127.0 | 64.6 | -0.77 | > 10 M |
| ethanol | 59.3 | 78.2 | -0.31 | > 10 M |
| <i>n</i> -propanol | 21.0 | 97.2 | 0.25 | > 10 M |
| <i>n</i> -butanol | 6.7 | 117.1 | 0.88 | 853 |
| <i>n</i> -pentanol | 2.2 | 137.9 | 1.51 | 250 |
| <i>n</i> -hexanol | 0.93 | 157.6 | 2.03 | 57.7 |
| <i>n</i> -propanoic acid | 3.5 | 141.1 | 0.33 | > 10 M |
| <i>n</i> -pentanoic acid | 0.2 | 186.1 | 1.39 | 196 |
| acetone | 231.5 | 56.0 | -0.24 | > 10 M |
| 2-butanone | 90.6 | 79.5 | 0.29 | 3050 |
| 2-pentanone | 35.4 | 102.2 | 0.91 | 499 |
| 2-hexanone | 11.6 | 127.6 | 1.38 | 175 |
| 2-heptanone | 3.9 | 151.0 | 1.98 | 37.7 |
| methyl acetate | 216.2 | 56.8 | 0.18 | 3280 |
| ethyl acetate | 93.2 | 77.1 | 0.73 | 908 |
| propyl acetate | 35.9 | 101.5 | 1.24 | 185 |
| butyl acetate | 11.5 | 126.1 | 1.78 | 72.3 |
| pentyl acetate | 3.5 | 149.2 | 2.30 | 13.1 |

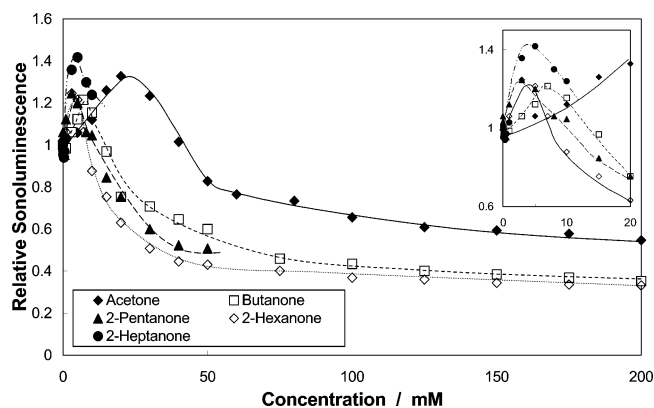
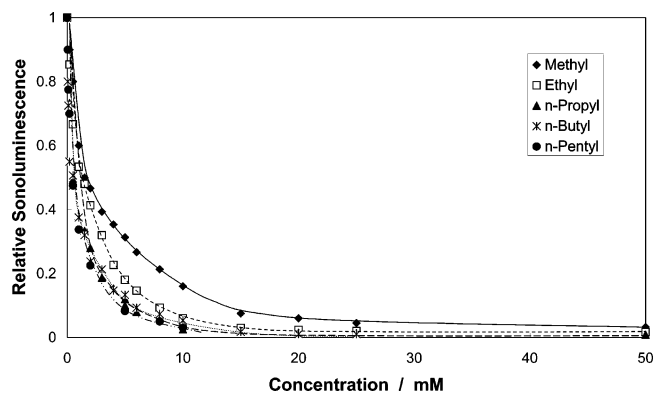
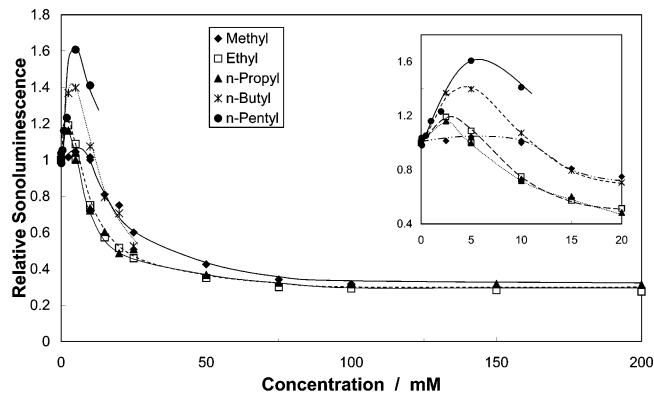
^a *P* = octanol:water partition coefficient at 25 °C.

**Figure 2.** Sonoluminescence emission relative to pure water as a function of concentration for ketones in water sonicated at 515 kHz.

change in the output intensity even up to concentrations of 500 mM. In contrast, the addition of 2-pentanone caused significant quenching of the SL emission, which increased as the solute concentration was raised. For example, a concentration of 50 mM reduced the SL intensity by about half. It should be noted that the vapor pressure of ethanol (Table 1) is higher than that of 2-pentanone, and thus, the effect is not due to the volatility of the solute.

Figures 2 and 3 show the SL emission relative to that in pure water for a homologous sequence of methyl ketones using ultrasound of 515 kHz (Figure 2) and 20 kHz (Figure 3). There are considerable differences in behavior at the two frequencies. At the higher frequency, each compound quenches efficiently, with the order of quenching efficiency increasing up the homologous series. At 20 kHz, the SL behavior is more complex. All of the solutes showed enhancement of the SL at very low concentrations (<10 mM) before quenching occurred as the concentration increased. However, the minimum emission observed was around 40% of that from water even at a concentration >100 mM, whereas at 515 kHz, 95% of the SL signal was removed at 40 mM. This was so even for acetone, which displayed the lowest quenching efficiency.

The effect of the ketones on the SL signal was different from that previously reported with alcohol solutes, where no quenching was observed at 20 kHz. Therefore, a further homologous

**Figure 3.** Sonoluminescence emission relative to pure water as a function of concentration for ketones in water sonicated at 20 kHz. The inset shows an enlargement of results at low concentrations.**Figure 4.** Sonoluminescence emission relative to pure water as a function of concentration for *n*-alkyl acetates in water sonicated at 515 kHz.**Figure 5.** Sonoluminescence emission relative to pure water as a function of concentration for *n*-alkyl acetates in water sonicated at 20 kHz. The inset shows an enlargement of results at low concentrations.

series was investigated. The results for *n*-alkyl acetate solutes at the two frequencies are shown in Figures 4 and 5. Here, the behavior parallels that of the ketones with efficient quenching being observed at 515 kHz ultrasound. Also, the higher molecular weight members of the series generally were better quenchers, although the progression in quenching efficiency is not smooth along the series. As with the ketones, at 20 kHz, the observed results are again a combination of SL enhancement and quenching. However, it is noteworthy that the extent of quenching is greater here than with the ketones, with up to 80% of the SL being quenched. At the higher concentrations, all the acetates showed the same degree of quenching although the lower water solubility of *n*-pentyl acetate meant that only the

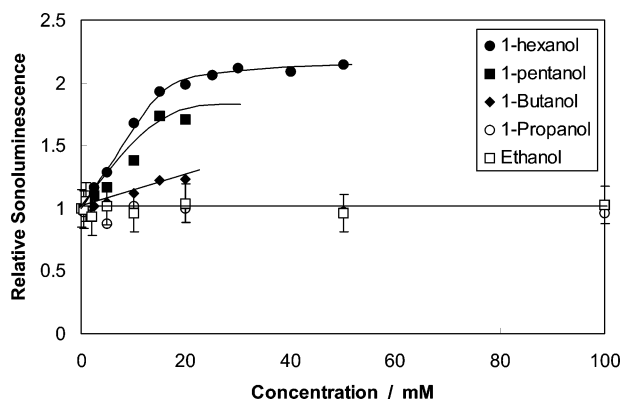


Figure 6. Sonoluminescence emission relative to pure water as a function of concentration for alcohols in water sonicated at 20 kHz.

“enhancement region” could be explored. At low concentrations, the SL enhancement increased with the size of the alkyl substituent.

Since the degree of enhancement is clearly dependent on the chain length of the solute molecule, a wider range of alcohol solutes was investigated. The SL emission from solutions of longer-chain alcohols at 20 kHz is shown in Figure 6; also included for comparison are the previously published data on shorter-chain alcohols. It is clear that no quenching of the SL occurs for any of the compounds but that an enhancement of up to 2-fold in the emission is seen with the longer-chain (>C₄) alcohols. Neither of these two phenomena was observed at 515 kHz.

As a further comparison with previously published high-frequency results, the SL of solutions containing propanoic and pentanoic acids as a function of solution pH when exposed to 20 kHz ultrasound was measured (the results can be seen in the Supporting Information). With propanoic acid, there was no quenching of the SL across the whole pH range. This is in contrast to the results²¹ using 515 kHz ultrasound when at low pH the volatile, unionized acid was able to enter the bubble and quench the SL (e.g., ~50% of the SL was quenched by 25 mM propanoic acid at pH 3). The frequency difference was even more pronounced with pentanoic acid. At low pH, the SL was increased by ~25% when sonicated at 20 kHz, whereas at 515 kHz a 10 mM solution quenched 90% of the SL. In the previous work,²¹ it was also found that 515 kHz SL was quenched by organic bases such as *n*-pentylamine in their unionized form, i.e., at high pH. Following the pattern of the organic acids and alcohols, no quenching was detected for solutions of *n*-pentylamine sonicated at 20 kHz.

Discussion

The results reported here confirm the main conclusion arrived at in previous studies,²⁴ namely, that the effect of organic solutes on the SL emission intensity from aqueous solutions irradiated with ultrasound of 20 kHz is significantly different from that at higher frequencies. To account for this difference, there are several key observations that need to be explained: the lower efficiency of all solutes in quenching the SL at 20 kHz compared with 515 kHz, including the lack of effect of the lower alcohols; the enhancement of 20 kHz SL by the higher molecular weight members of the homologous series of solutes; and the lack of enhancement by the lower molecular weight alcohols and acids.

Table 2. Surface Excess (Γ) Concentrations of the Solutes at 10 mM Bulk Solution Concentration

| solute | Γ , molecules/nm ² ([solute] _{bulk} = 10 mM) | solute | Γ , molecules/nm ² ([solute] _{bulk} = 10 mM) |
|-------------|--|----------------|--|
| acetone | 0.26 | methyl acetate | 0.06 |
| 2-butanone | 0.18 | ethyl acetate | 0.36 |
| 2-pentanone | 0.45 | propyl acetate | 0.66 |
| 2-hexanone | 0.89 | butyl acetate | 1.12 |
| 2-heptanone | 1.34 | pentyl acetate | 1.26 |

The mechanism by which SL is quenched by volatile solutes is not fully understood. The solutes that enter the bubble may scavenge or quench the various excited state species that emit light. However, this proposition is not supported by the observation that the emission spectrum hardly changes as the SL is quenched²⁹ and that when some volatile hydrocarbons enter a bubble their decomposition leads to light emission from excited C₂* species.³⁰ A more likely explanation for the SL quenching is that the evaporation of volatile solutes into a bubble leads to a lowering of the mean bubble temperature so that fewer excited-state species are produced, leading to a lower SL emission intensity. The lowering of the core temperature is due to some extent to the change of polytropic ratio of the gaseous contents of the bubble,¹ as well as the thermal energy of collapse being expended in endothermic bond rupture of the solutes and their decomposition products within the bubble.^{31,32}

If material entered the bubble simply by evaporation from the bulk solution, it would be expected that for any given concentration the solute with the highest vapor pressure would quench more effectively. However, the observed effects are in the opposite order with both the ketone and ester solutes (cf. trends observed in Table 1 and with Figures 2–5). Previous studies at 515 kHz have shown a good correlation of quenching with the concentration of the solute at the gas–solution interface. This indicates that the volatile solutes entering the bubble come primarily from the evaporation of solutes adsorbed at the bubble–solution interface, presumably during the expansion phase of the bubble.

A thermodynamic measure of the affinity of a solute for the air–water interface is given by the Gibbs surface excess concentration.³³ Table 2 lists the surface excess of 10 solutes at the same bulk solution concentration. The values were obtained from the measurement of surface tension as a function of solute concentration and processed as described elsewhere.³⁴ The table shows that for a given bulk concentration, the more hydrophobic the solute the greater is its surface concentration.

The SL quenching as a function of the surface excess concentration for the 515 kHz data for all 10 solutes is shown in Figure 7. On this basis, all solutes have a similar effect. Also shown is the best-fit line to all the alcohol, acid, and amine (11 compounds in all) previously reported,^{20,21} and it can be seen that there is somewhat more efficient quenching by the ketones and acetates compared with the alcohols. The results obtained

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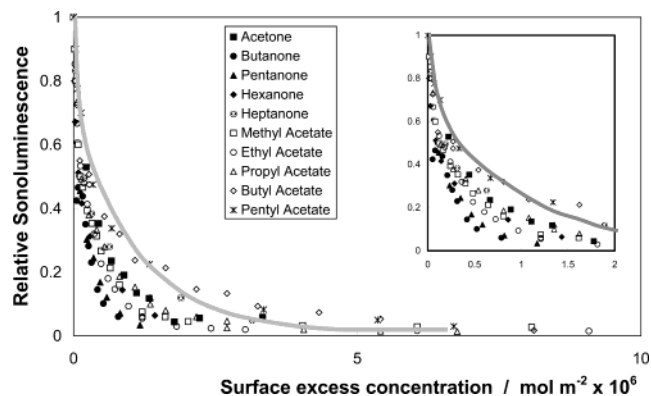


Figure 7. Relative sonoluminescence intensity as a function of surface excess of the solutes at 515 kHz. The solid line indicates the best-fit line to all the alcohol, acid, and amine (11 compounds in all) SL vs surface excess data previously reported.^{20,21}

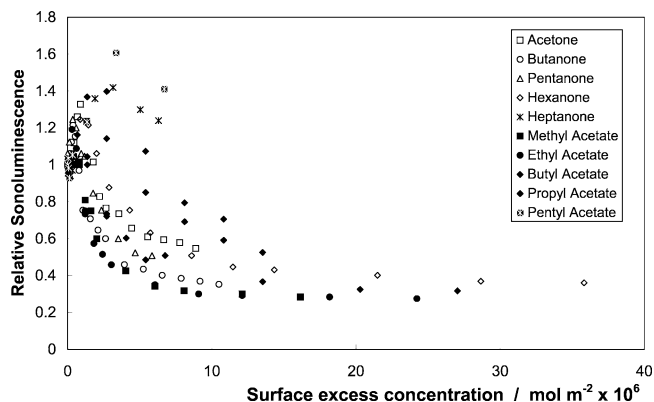


Figure 8. Relative sonoluminescence intensity as a function of surface excess of the solutes at 20 kHz.

at 20 kHz are plotted in this form in Figure 8, where it is readily apparent that there is little correlation between the SL signal and the surface excess of the solute.

The reasons for the difference in behavior between the two frequencies can be attributed to the different types of cavitation that can take place.^{1,27} Although each type involves the growth and collapse of micrometer-sized bubbles, different types of inertial cavitation can be identified depending on a number of factors. At low frequencies such as 20 kHz, the predominant form of cavitation would be *transient* cavitation where each bubble will undergo only a few oscillations before the collapse results in fragmentation and loss of the bubble. Conversely, at higher frequencies, *stable* cavitation would be the major form. Here, a bubble will undergo many hundreds or thousands of oscillations. Hence, at low frequencies the bubble contents will be limited to the amount of volatile material that can enter the bubble over a few cycles, whereas at 515 kHz, there is time for the buildup of both solute and its decomposition products within the bubble. This interpretation is supported by the observation that pyrolysis products can be detected when aqueous organics are sonicated at 515 kHz but not at 20 kHz.²⁶

Another aspect of the results to note is that the extent and efficiency of quenching is greater at the higher frequency. Aliphatic alcohols reach near equilibrium adsorption levels at the air–aqueous solution interface in about 3–10 ms³⁵ at solute concentrations comparable to those used in this study. It can

be expected that solutes used in the present study will behave similarly. On this basis, true equilibrium adsorption of the solute at the bubble–solution interface will not be established during the “active” life of a cavitation bubble. This is the case for bubbles exposed to both 20 and 515 kHz ultrasound, although more solute adsorption should occur at 515 kHz because of the longer lifetime and hence larger total number of oscillations at the higher frequency. This latter conclusion is supported by the recent work of Sostaric and Riesz.³⁶ Also, the good correlation between the relative SL quenching and the surface excess of the solutes (an equilibrium measurement) at 515 kHz demonstrated by Figure 7 supports the argument that solute adsorption to the bubble–solution interface has reached near-equilibrium levels at 515 kHz.

A major difference between the 20 kHz results for the alcohols and acids compared with the esters and ketones is that some degree of quenching is seen with the latter classes of compounds, albeit to a lower degree than at a high frequency. With the acids and alcohols, the SL is either constant or reaches a consistent value after an initial rise, but no quenching was observed, suggesting that no significant amount of volatile material enters the bubble on the time scale of the growth and collapse. The reasons for this are not totally clear. However, we speculate that the intermolecular interactions will be stronger in the acids and alcohols due to hydrogen bonding with the solvent. Thus, the rate of evaporation for these solutes would be lower, and hence, no significant amount of solute vapor will enter the bubble. At high frequency, the large number of growth–collapse cycles means that the rate of evaporation is no longer such a dominating factor, as the accumulation of hydrocarbon products within the bubbles over many cycles controls the final SL intensity.

The effect of hydrogen bonding on evaporation rates has been seen clearly for the liquids, glycerol, diethylene glycol, and triethylene glycol. McFeely and Somorjai³⁷ concluded that the breaking of hydrogen bonds at the liquid surface was the rate-limiting step in the mechanism of vaporization. Also, in our work³⁸ with water–ethylene glycol mixtures at 515 kHz, it was found that no SL quenching occurred even at ethylene glycol concentrations of 3.5 M. It is noteworthy that at 25 °C ethylene glycol has a vapor pressure similar to *n*-pentanoic acid, but 20 mM of *n*-pentanoic acid completely quenches the SL signal at 515 kHz.²¹ This observation suggests that if there is strong hydrogen bonding between the organic solute and water, the solute will not evaporate into the bubble during the time of the expansion phase of the bubble oscillation.

The final series of observations that needs to be explained is the enhancement of SL at 20 kHz seen with the higher molecular weight members of the homologous series used. One possible explanation for the SL enhancement might be that the compounds that exhibit enhanced SL form some additional emitting species inside the bubble. However, this would be expected to change the appearance of the SL spectrum. The low-resolution spectra of water and ~50 mM butyl acetate solution show no significant difference in the wavelength dependence of the emission (see Supporting Information). Enhancement of SL has previously been noted with solutions of charged surfactants.^{20,24}

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It has been argued that the adsorption of charged surfactant molecules at the bubble–solution interface leads to an increase in the number of “active” bubbles due to the electrostatic repulsion between bubbles preventing clustering of the “charged” bubbles. The SL enhancement observed in this study at 20 kHz cannot be due to electrostatic interaction between bubbles because the solutes are not charged. We attribute the SL enhancement noted at 20 kHz in this work to the effects, other than electrostatics, that the smaller solutes have on bubble–bubble interactions.

In pure water, small bubbles in the size range that are sonochemically and SL active can collide and coalesce forming larger bubbles. Some of these would be either sufficiently buoyant that they would be expelled from the liquid or too large to be SL active. However, dissolved solutes can interfere with the coalescence process by adsorbing to the bubble surface. Oolman and Blanch³⁹ showed that the addition of alcohol solutes could prevent such bubble coalescence. The concentration needed to prevent coalescence depended on the surface activity or hydrophobicity of the solute as reflected by the concentration dependence of the surface tension ($\partial\gamma/\partial c$) and was reduced with increasing alkyl chain length of a series of alcohols. For example, a bulk ethanol concentration in solution of 0.18 M was needed to keep the bubbles separated, but the corresponding value was 1.8 mM for butanol and 0.2 mM for pentanol. Similar concentration effects have been observed⁴⁰ for methanoic (formic), ethanoic (acetic), and propionic acids.

Thus, we should expect that sonochemically generated bubbles in the presence of methanol, ethanol, propanol, and compounds of comparable hydrophobicity at the concentrations used here would interact in a manner similar to those in water. This accounts for the lack of any SL enhancement with the lower alcohols. However, in the presence of more hydrophobic solutes, bubble coalescence would be prevented even at the low (<5 mM) concentrations at which enhancement was observed. Therefore, more relatively small, sonochemically active bubbles, would remain in the system compared with pure water, so that the SL intensity would rise. Although there is no comparable coalescence data for the ketones and esters, it is reasonable to assume that the more hydrophobic members of the series would act in a manner similar to the higher alcohols. Acetone is the least surface active solute (Table 2), and at lower concentrations, there may not be sufficient acetone evaporated into the bubble to cause significant quenching. However, at this concentration range, there may be enough at the bubble–solution interface to prevent the coalescence. The increase in the SL intensity at lower acetone concentrations may then be due to the effect of coalescence being the dominant factor.

To understand that the SL is not enhanced at the higher frequency, a general view of the different processes affecting the SL has to be considered. On the basis of the previous discussion, it can be stated that SL intensity is affected by two major factors: quenching and bubble coalescence. The former influences the intensity emitted by an individual bubble while the latter influences the total number of emitting bubbles. Neutral solutes that do not have strong hydrogen-bonding characteristics can evaporate into the bubble leading to SL quenching. However, the same solute may lead to an enhancement in the

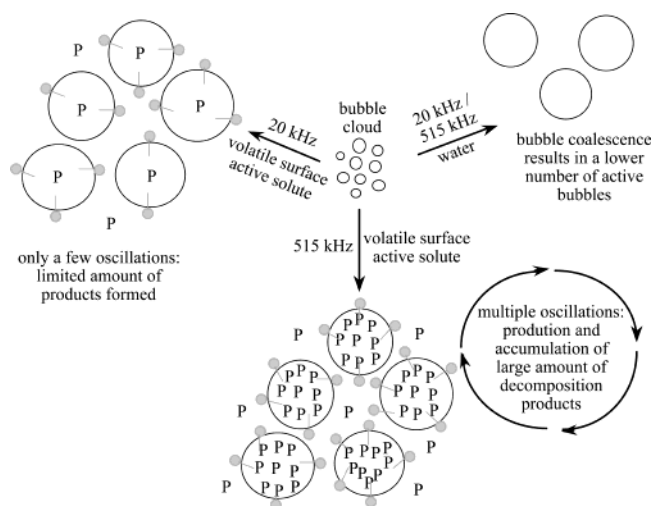


Figure 9. Diagrammatic representation of the effects of bubble coalescence and SL quenching in the presence and absence of surface active solutes.

SL by preventing bubble coalescence. These events can be expected to occur at both 20 and 515 kHz frequencies, but the overall effect on the relative SL intensity will depend on the balance between them. Because of the relatively *stable* bubble situation at 515 kHz, the quenching factor always dominates. At 20 kHz, since the bubbles are *transient*, SL quenching can be considered to be appreciably lower than at 515 kHz, and the solute hindrance to coalescence becomes significant in enhancing the number of bubbles contributing to the SL signal. At higher concentrations of the solutes, accompanied by an increase in the amount of solute evaporation, the coalescence factor diminishes in relative importance, and SL quenching dominates. A diagrammatic representation of the above situations is shown in Figure 9.

The frequency dependence of SL quenching demonstrated here has not previously been reported other than with alcohol solutes.²⁴ This mechanistic difference in cavitation between the two frequencies has implications for the sonochemistry of compounds in aqueous solution. A number of workers have reported faster reaction rates when using higher ultrasound frequencies but assumed that the mechanism remains unchanged. However, the work reported here suggests that mechanistic differences might be expected. For example, under the conditions used here, operation at the higher frequency would favor the consumption of hydrophobic compounds by pyrolysis when solutes can evaporate into the bubbles. Conversely, 20 kHz ultrasound would favor processes such as polymer chain cleavage or heterogeneous reactions, which rely mainly on mechanical effects due to solvent motion around the bubbles. The situation involving reactions with OH• radicals is more complex. These will be formed in both types of cavitation due to water sonolysis. A larger concentration of radicals will be formed on each individual bubble collapse at 20 kHz since the bubbles will collapse from a large radius and hence contain relatively more water vapor than at 500 kHz. However, at the high frequency, there are more collapse events per unit time, and thus, the overall rate of radical production may be higher.

The results presented here help to interpret some sonochemical effects that have been reported. For example, Henglein⁴¹

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found that for a range of solutes in water, solvolysis (i.e., pyrolysis) was the main reaction pathway at 1 MHz, but that radical production and mechanical effects dominated at 20 kHz. Theron and co-workers⁴² reported a similar difference in mechanism for the degradation of phenyltrifluoromethyl ketone in water at 30 and 500 kHz. Weavers et al. looked¹⁶ at the degradation of pentachlorophenol (PCP) in aqueous solution and found it to be faster at 500 kHz, although the results suggested the presence of parallel pyrolysis and OH[•] reaction pathways that were altered by a change in both frequency and PCP concentration.

Additional examples of a frequency dependence can be found in the work of Petrier and co-workers. They measured^{43,44} the production of hydrogen peroxide and the degradation rate of both phenol and carbon tetrachloride at 20, 200, 500, and 800 kHz. It was shown that the rates of reactions involving hydroxyl radicals (H₂O₂ formation and phenol degradation) had a maximum at 200 kHz, while the degradation rate for CCl₄, which decomposes inside the bubble, increased with frequency. Significantly, a calculation of the reaction rate for one bubble collapse showed that the efficiency of each cycle decreased with increasing frequency. The degradation of hydrophobic chlorobenzene was compared⁴⁵ with that of the hydrophilic 4-chlorophenol; that of the former was faster at 500 kHz and yielded products characteristic of pyrolysis. For 4-chlorophenol, degradation was slower, and hydroxylated products resulting from OH[•] attack were seen. Drijvers et al.⁴⁶ investigated the degradation of trichloroethylene (TCE) in aqueous solution and showed that it was energetically more efficient at 520 kHz where the products were typical for pyrolysis of TCE.

In work involving other sonochemical effects, the ultrasound-assisted electrooxidation at a platinum electrode of dissolved organics was investigated⁴⁷ at 20 and 500 kHz. At high frequency, hydroxyl radicals were generated, whereas at low frequency, the major effect was the acceleration of mass transfer rates of the electroactive species to the electrode and of adsorption–desorption processes. Hua and Thompson⁴⁸ found that the sonochemical inactivation of *Escherichia coli* showed a marked frequency dependence. The inactivation was due to a combination of disruption of the bacterial cell walls due to shearing forces around the bubbles and oxidation by OH[•] and H₂O₂. Four frequencies from 205 to 1017 kHz were studied, and the most efficient inactivation was at the lowest frequency, although the rate of generation of H₂O₂ passed through a maximum at 358 kHz. Another process relying on the physical effects of cavitation is mass transport to surfaces in heterogeneous systems. Ligier et al. investigated⁴⁹ the corrosion of zinc coatings on steels at 20 and 500 kHz. They showed that H₂O₂ production was faster at 514 kHz, although the mass transfer coefficient of ions in solution to the surface was greater at

20 kHz, attributable to the more violent collapse and jetting at the lower frequency. Thus, it is clear that when attempting to optimize a particular sonochemical process or reaction the mechanistic differences at the various ultrasound frequencies must be considered.

In interpreting these results, care must be taken since additional factors such as the sound intensity and the gas atmosphere under which the reactions were carried out can be expected to play a significant part in product distributions, etc. However, the mechanistic difference in cavitation suggested by the SL measurements at the two frequencies of this study does provide an understanding for these previously reported chemical effects. The possibility of the ultrasound intensity influencing the results obtained here should also be considered. For example, it is possible that the use of much higher intensities at 515 kHz might produce transient cavitation. However, variation across the range of intensity available with the current apparatus showed no significant change in the relative SL quenching properties of the solutes.

Conclusions

The observations from the results described here along with those from previous work can be summarized as follows. At 515 kHz, all the volatile solutes studied quench the SL efficiently, the extent of quenching depending on the concentration of the solute at the bubble–solution interface. At 20 kHz, the more hydrophobic compounds studied enhance the SL at low concentrations, while at higher concentrations a degree of quenching occurs. The extent of SL quenching at 20 kHz is significantly less than at 515 kHz.

The results also indicate that the SL signal is influenced by two major factors at both 20 and 515 kHz. At the lower frequency, an increase in the SL intensity at lower concentrations of the solutes has been attributed to a decrease in the coalescence between the acoustically driven bubbles. Such a coalescence effect has less importance at higher solute concentrations where solute-induced quenching plays a more significant role in the overall SL signal generated. At the higher frequency, SL quenching is found to dominate at all (solute) concentrations.

It might be expected that the longer lifetime of a single bubble growth–collapse cycle at low frequency would allow a closer approach to thermodynamic equilibrium conditions to be reached. Since the 20 kHz bubbles undergo transient cavitation, the approach to equilibrium could be kinetically limited as it takes about 3–10 ms for the solutes to reach adsorption equilibrium at the bubble–solution interface. Because of the *stable* cavitation occurring at 515 kHz, experimental data shown suggest that the solutes do approach near-equilibrium adsorption conditions. This difference in the cavitation properties can account for observed differences in the rates and product distributions in a range of published sonochemical reactions.

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Supporting Information Available: Sonoluminescence emission at 20 kHz relative to water as a function of pH for 25 mM solutions of propanoic and pentanoic acids and pentylamine and normalized sonoluminescence spectra observed from water and

50 mM butyl acetate solution at 20 kHz (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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