

## Comparison of the Effects of Water-Soluble Solutes on Multibubble Sonoluminescence Generated in Aqueous Solutions by 20- and 515-kHz Pulsed Ultrasound

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The influence of aliphatic alcohols, sodium dodecyl sulfate and sodium chloride on the intensity of sonoluminescence (SL) generated by 3.5-ms pulses of 20-kHz and 515-kHz ultrasound in air-saturated aqueous solutions has been examined. The water-soluble solutes were found to affect the SL quite differently at the two frequencies when applied at approximately the same range of power. At 20 kHz, the solutes had only a small effect on the SL signal generated, whereas at 515 kHz, the effect observed depended strongly on the specific solute present in solution. The contrasting results obtained at the two ultrasound frequencies have been interpreted in terms of transient bubbles giving rise to the SL at 20 kHz and repetitive transient bubbles producing the SL at 515 kHz.

### Introduction

Sonoluminescence (SL) is the term used to describe the broad-spectrum light emitted when a liquid is induced to cavitate under certain conditions.<sup>1,2</sup> The cavitation event that leads to light emission can be produced by a number of quite diverse means (e.g., the passage of high-intensity ultrasound through certain liquids, by a focused laser beam pulse into a fluid, by imposing high shear forces on a fluid, such as in a Venturi tube, and other more exotic processes<sup>1,3</sup>).

Since SL was first detected, there have been numerous suggestions of the origin of this phenomenon.<sup>1,2,4,5</sup> However, it is only in relatively recent years that experimental and theoretical studies have provided a convincing account of the physical and chemical events that produce SL.<sup>6–9</sup>

Strong experimental evidence exists that indicates that the SL in multibubble systems is from vibronically excited-state species.<sup>8,9</sup> These species are produced from the recombination of free radicals created within the high temperature and pressure environment of bubbles undergoing near-adiabatic compression.<sup>8</sup> In addition, there may exist some component to the emission from thermal bremsstrahlung, as appears to be the case in single-bubble sonoluminescence,<sup>5,7</sup> but this is yet to be firmly established.<sup>10</sup>

It is well documented that MBSL spectra and intensity are strongly influenced by the type of liquid undergoing cavitation, the type of gas dissolved in the liquid, and the acoustic frequency used to generate the emission.<sup>1,9,11</sup> Of the various factors that affect SL, frequency effects are perhaps the least understood. It has been postulated that repetitive transient bubbles (sometimes also called “stable” bubbles<sup>2</sup>) are responsible for SL at high frequencies and that transient bubbles (referring to cavitation bubbles that undergo one or only a few oscillations<sup>2</sup>) are responsible at low frequencies.<sup>9,11</sup> This speculation is not, however, supported by the results of Crum and Reynolds,<sup>12</sup> who observed SL from both stable and transient bubbles at the low ultrasound frequency of 20 kHz.

Recently it has been found that the SL intensity generated in an aqueous medium can be quenched by adding low-level

amounts of aliphatic and aromatic alcohols, amines, and carboxylic acids.<sup>13–17</sup> In contrast, the SL intensity can be enhanced relative to that of pure water by the presence of anionic and cationic surfactants<sup>14,15</sup> as well as salts<sup>18</sup> (e.g., NaCl, MgSO<sub>4</sub>, etc). The effect that various solutes have on the SL intensity generated in aqueous solutions has allowed for the development of a qualitative understanding of how solutes interact with, and affect, the physical behavior of bubbles in an acoustic field.<sup>14–18</sup>

In this communication, we compare the effect that several water-soluble solutes have on the SL intensity generated by low (20 kHz) and high (515 kHz) ultrasound frequencies in aqueous solutions. As will be discussed, the selected solutes in conjunction with the SL generated can be used to examine the behavior of bubbles exposed to different acoustic frequencies.

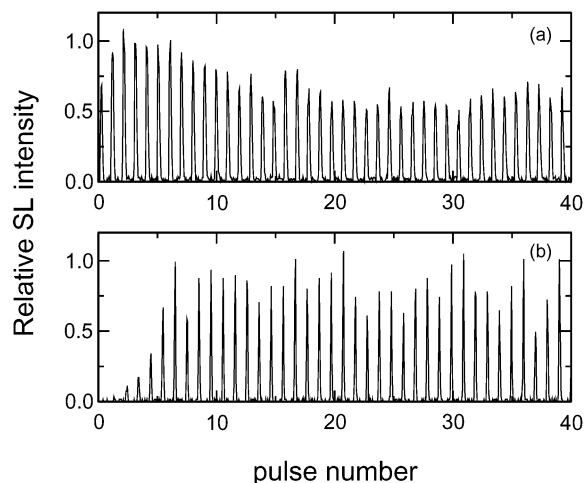
### Experimental Details

**Materials.** Methanol (99.8%), ethanol (99.5%), butan-1-ol (99.4%), and NaCl (99.9%) were purchased from Ajax Chemicals (Univar label). Propan-1-ol (99.5%) was purchased from BDH. Sodium dodecyl sulfate (SDS) was BDH specially pure grade and was used as received. The water used to prepare all solutions was obtained from a three-stage Milli-Q purification system and had a conductivity of less than  $10^{-6}$  S cm<sup>-1</sup> at 20 °C and a surface tension of 72.0 mN m<sup>-1</sup> at 20 °C.

**Procedures.** For SL measurements carried out using 20-kHz ultrasound, 100 mL of solution was placed in a cylindrical Pyrex cell of diameter 50 mm that was fitted over a 40-mm cup-horn transducer (Branson). One hundred milliliters of solution was sufficient to cover the horn completely to a depth of 35 mm. Because the wavelength of 20-kHz ultrasound is about 75 mm in water, no standing would exist in this experimental setup. The 20-kHz generator used was a (Branson B-30 Cell Disruptor). The power absorbed by the insonated solutions (with the generator operated in pulse mode), as measured by calorimetry, was in the range 0.09–0.2 W/cm<sup>2</sup>.

Experiments conducted at 515-kHz ultrasound used 25 mL of solution that was placed in an open Pyrex vessel constructed to fit over the 35-mm flat plate, 515-kHz transducer. The 515-

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**Figure 1.** Sonoluminescence emissions from the initial pulse train in water at (a) 20 kHz and (b) 515 kHz. The average power was 0.19 W/cm<sup>2</sup> and 0.35 W/cm<sup>2</sup> for 20 and 515 kHz, respectively. These solutions were presonicated for 30 s using 3.5-ms pulses and were then left to stand for about 3 min before recommencing the pulsing.

kHz generator was an Undatim Ultrasonics D-reactor (model no. UL03/1). The power absorbed (with the generator operated in pulse mode), as measured by calorimetry, was in the range 0.04–0.4 W/cm<sup>2</sup>.

Both generators were modified in-house to allow them to function in a pulsed or continuous mode. Unless otherwise stated, experiments were performed in pulsed mode, using 3.5-ms pulses and a duty cycle (on/off) of 1:5.

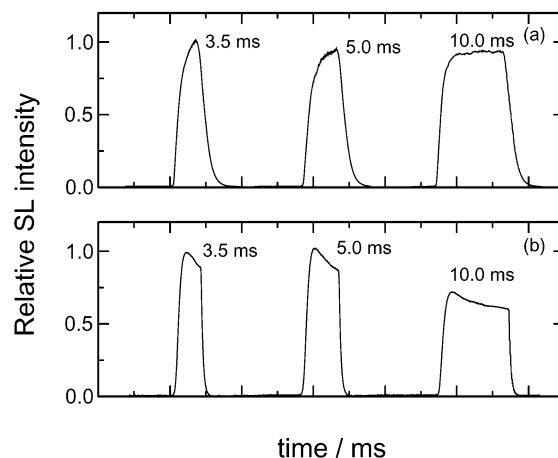
The sonoluminescence intensity was recorded with a Hamamatsu end-on photomultiplier (model no. E849–34) that is responsive over a wavelength range of 300–650 nm. Signals were displayed on a digital oscilloscope (Tektronix, model no. TDS 360) and stored on a personal computer.

In a typical experiment, the transducer, reaction vessel, and photomultiplier were placed in a dark enclosure to minimize the background light level. The SL intensity was obtained by first presonating the air-saturated solution (~30 s) and then allowing it to stand quietly for about 3 min. This preconditioning procedure gave reproducible SL results. Ultrasound pulsing was then commenced again, and when the SL intensity had reached a steady level, the averaging function of the oscilloscope was used to record and average at least 100 pulses.

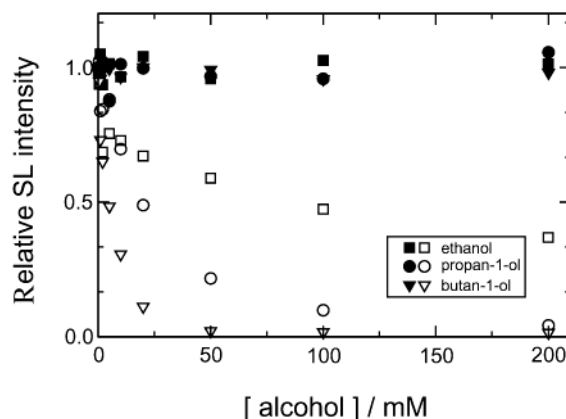
During experiments, the temperature was monitored using a Jenway electronic thermometer (model 2003, with a precision of 0.1 °C). Generally, the solution temperature did not change by more than 2 °C during the course of an experimental run.

## Results

Preliminary experiments were conducted with ultrasound pulses of 20 kHz and 515 kHz in order to examine the evolution, with the number of pulses, of the SL signal generated in water at the two different frequencies. In Figure 1 are shown the initial pulse trains at the two frequencies. At 20 kHz, a significant SL intensity is present at the very first pulse with some variation in intensity with subsequent pulses. (This behavior is quite similar to that reported for the chemiluminescence generated in pulsed 20-kHz luminol solutions.<sup>19</sup>) As the ultrasound power was increased, the SL intensity correspondingly increased, but the pattern of the SL pulses was much the same as that shown in Figure 1a. The fluctuations in intensity of the individual pulses has been reported previously<sup>20</sup> and has been attributed to temporal changes in the intensity of the sound field due to



**Figure 2.** Individual sonoluminescence pulse shapes in water averaged over about 100 pulses for various pulse widths, as shown, for (a) 20 kHz and (b) 515 kHz. The maximum pulse intensities have been normalized relative to the 3.5-ms pulse for each of the two frequencies.

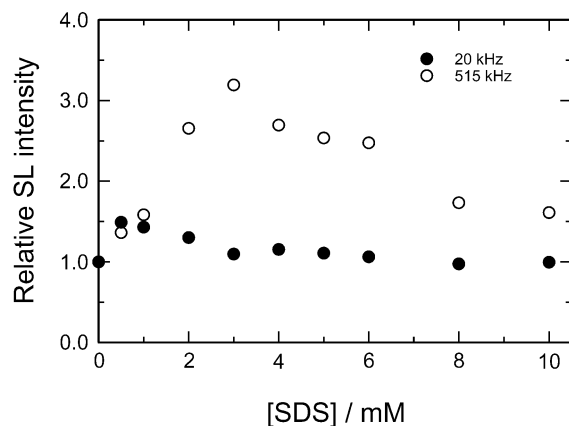


**Figure 3.** Averaged relative sonoluminescence intensity as a function of alcohol concentration and type for 20-kHz (solid symbols) and 515 kHz (open symbols), 3.5-ms pulses. The intensities have been normalized to the average SL intensity in water.

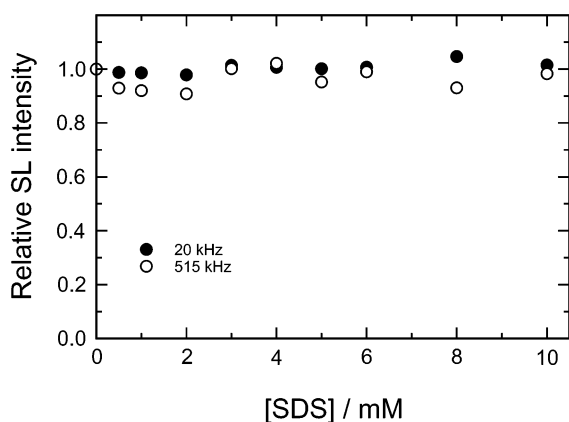
changes in the spatial distribution of bubbles in the liquid. In contrast to these results, the SL generated by 515-kHz pulses increased in intensity over the first 10–15 pulses before a maximum intensity was reached. The pulse behavior described above was observed at both frequencies over the whole range of powers used.

An examination of the mean SL pulse shapes was also undertaken for 3.5-ms and longer pulse times. These traces are shown in Figure 2. These mean pulse shapes represent the average emission pulse when the system has been exposed to several hundred individual ultrasound pulses. At 20 kHz, the SL continues to grow over the lifetime of the pulse. However, for the SL pulses at 515 kHz, the emission intensity quickly reaches a maximum near the beginning of the pulse and then shows a slight decline toward the end of the pulse. Again, this latter behavior has been previously reported and is believed to be associated with the formation of bubble clusters during the pulse time.<sup>14,20</sup>

The effect of low concentrations of aliphatic alcohols on the averaged SL intensity at 20 and at 515 kHz is shown in Figure 3. It can be seen that at 515 kHz significant quenching of the SL signal occurs, with the effect being more pronounced the longer the alkyl chain length of the alcohol. These results are consistent with those previously reported.<sup>14</sup> However, at 20 kHz, regardless of the alcohol chain length, essentially no SL quenching is observed with increasing alcohol concentration.



**Figure 4.** Averaged relative sonoluminescence intensity as a function of SDS concentration for 3.5-ms pulses of 20- and 515-kHz ultrasound. The intensities have been normalized to the average SL intensity in water.

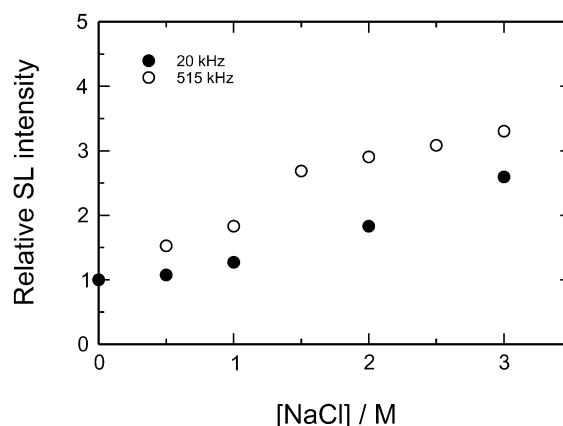


**Figure 5.** Averaged relative sonoluminescence intensity as a function of SDS concentration in the presence of 0.1 M NaCl for 3.5-ms pulses. The intensities have been normalized to the average SL intensity in 0.1 M NaCl.

Because there are only 70 acoustic cycles in a 3.5-ms 20-kHz pulse, compared with 1800 cycles in a 3.5-ms 51-kHz pulse, the possibility that the difference in the number of cycles between the two pulses was in some way responsible for the lack of SL quenching at 20 kHz needed to be considered. It was found, however, that when 300-ms pulses (6000 cycles) and 1-s pulses (20 000 cycles) of 20 kHz were used, still no SL quenching was observed in the presence of the alcohols.

The effect of two types of nonvolatile solutes, namely, a surfactant and a simple electrolyte, on the SL intensity was also examined. In Figure 4 is shown the SL intensity generated at 20 and 515 kHz in the presence of SDS. It can be seen that at 515 kHz the SL intensity increases with SDS concentration, reaching a maximum around 2 to 3 mM. The SL intensity then decreases and at higher SDS concentrations approaches the level measured in pure water. For 20-kHz pulses, a similar response in the SL signal is observed, although a much smaller variation over the same SDS concentration range is evident. Notably, with the additional presence of 0.1 M NaCl, the SL signal remains the same at all SDS concentrations for both 20- and 515-kHz pulses (see Figure 5).

Finally, the effect of NaCl concentration on the SL signals produced by 20- and 515-kHz pulses was measured, and the results are shown in Figure 6. It can be seen that at 515 kHz the SL signal increases substantially with increasing concentra-



**Figure 6.** Averaged relative sonoluminescence intensity as a function of NaCl concentration for 3.5-ms pulses of 20- and 515-kHz ultrasound. The intensities have been normalized to the average SL intensity in water.

tion of NaCl whereas for the 20-kHz pulses an increase is also observed, although not to the same extent as for the higher frequency.

It should be noted that for both surfactant systems and NaCl solutions at 20 kHz, the same behavior was noted for 1-s pulses as was observed for the 3.5-ms pulses. This suggests that the observations are not dependent on the number of acoustic cycles the bubbles experience at 20 kHz.

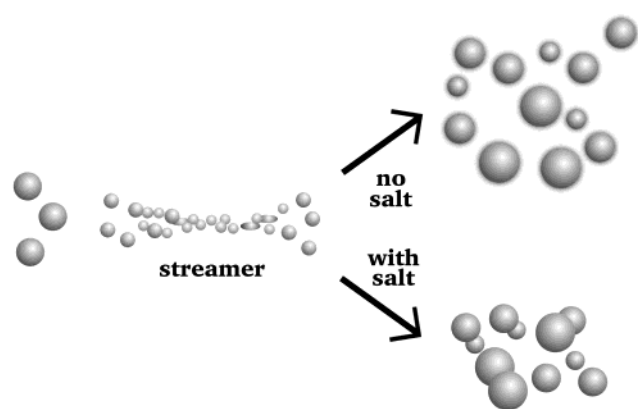
## Discussion

On comparing the effects of the various water-soluble additives on the SL generated in aqueous solutions using 20- and 515-kHz ultrasound, it is evident that the solutes used have a relatively much weaker influence on the SL signal when 20-kHz pulses are applied. To interpret the results presented, it is relevant to review briefly our understanding of the effects of the additives at 515 kHz from our previous studies, albeit at slightly different conditions from those used in the present study.

For the case of alcohols, the SL quenching has been linked with the accumulation of volatile hydrophobic decomposition products in the bubble core.<sup>16</sup> The build up of gaseous products within an "active" bubble has been suggested as being responsible for a lowering of the bubble core temperature, and this in turn, to diminish the SL intensity produced. The reason for the lower core temperature, as noted by a number of researchers,<sup>21–23</sup> can be attributed to a lowering of the polytropic ratio ( $C_p/C_v$ ) by the polyatomic gas present in the core and the energy consumed in the decomposition of these molecules.

It has been shown that other volatile organic solutes,<sup>24</sup> such as short-chain aliphatic amines and carboxylic acids, as well as low molecular weight aromatic compounds also quench the SL signal in aqueous solution.<sup>16,17</sup> It has also been found that the effect is directly related to the concentration of these solutes at the surface of the cavitating bubbles. Hence, the more surface active the solute (e.g., the longer the alkyl chain length of a particular alcohol, amine, etc.), the greater is its quenching effect for a given concentration. This has been found to be the case for both multibubble<sup>14,16</sup> and single-bubble systems.<sup>25</sup>

The effect of SDS, a nonvolatile solute, on the SL signal can be seen to be concentration-dependent. The increase in the SL intensity with an increase in SDS at low concentrations (<3 mM) has previously been explained as being due to an electrostatic effect between interacting bubbles.<sup>14</sup> This interpretation was based on the observation that the effect could be eliminated by the addition of electrolyte (cf. Figures 4 and 5)



**Figure 7.** Formation of bubble clouds through streamers. Bubble interactions within the streamers lead to different spatial structures of the bubble clouds produced. See the text for a full description.

and that it did not occur when a net neutral charged surfactant, *n*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate, was used instead of SDS. It has been proposed that the structure of the bubble clusters produced in solution is more open when electrostatic interactions between bubbles exist. The consequence of these more open “bubble clouds” is that the acoustic field is able to produce more bubbles that implode to yield SL. With more dense bubble clusters, the bubbles on the outside of the cluster effectively shield the inner bubbles from the acoustic field, thereby limiting the number of bubbles that are of the size that gives rise to SL. Support for the description above is given by the recent work of Segebarth et al.<sup>26</sup>

The basis of the electrostatic effect is the adsorption of negatively charged SDS molecules at the bubble–solution interface. We have estimated<sup>15</sup> that an electrostatic surface potential on the order of  $-100$  mV exists on the bubbles at the SDS concentrations used in the present study. However, it is unlikely that the electrostatic field surrounding the bubbles is the primary cause for the postulated lower bubble cloud density in the presence of SDS. This conclusion is based on the knowledge that the electric field surrounding the bubbles has a Debye length on the order of  $10$  nm under the solution conditions used whereas the spacing between low volume fraction bubbles can be expected to be tens of micrometers.<sup>27</sup> At present, we can only speculate on how the interfacial charge on the bubbles influences the spatial distribution of bubbles within a bubble cloud. It is possible that when bubbles are produced and convectionally driven to the antinodes in solution a close approach of bubbles occurs. In such a dynamic process, electrostatic bubble–bubble interactions may take place and so determine the spatial arrangement of the bubbles in a cluster. Diagrammatically, this is depicted in Figure 7. The top part of the Figure shows the formation of an “open” bubble cloud, as a consequence of bubble–bubble interactions during its formation. In the bottom part of the Figure, the formation of a more compact bubble cluster is shown, which we suggest is favored when the electrostatic interactions between bubbles during cluster formation is negligible. This would be the situation if salt were added to a low-concentration SDS solution or at high SDS concentrations ( $>3$  mM). The latter would be the case as SDS is a strong electrolyte; therefore, as its concentration was increased, so too would be the solution ionic strength, hence reducing the electrostatic interaction between charged bubbles.

The rise in the SL intensity on increasing the concentration of NaCl, as seen in Figure 6, for both 515- and 20-kHz pulses, has been explained as being due to a decrease in the gas content (air) in solution with increasing salt concentration.<sup>18</sup> The lower

the gas levels in solution, the lower the amount of gas that can accumulate inside an oscillating bubble. The lower the amount of air within a collapsing bubble, the higher the core temperature of the bubble during compression and hence the greater the SL intensity.

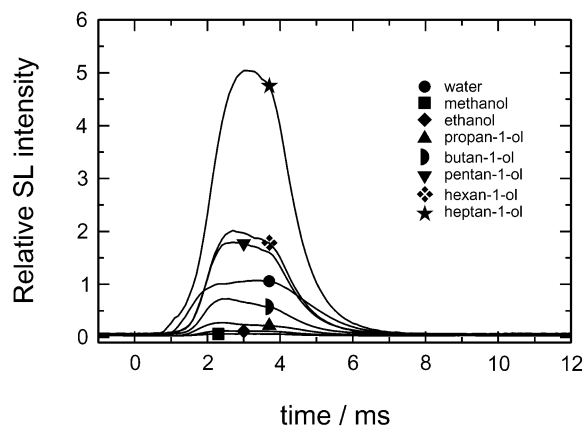
Although there are some similarities between the trends obtained on the addition of the solutes to the SL produced by 515- and 20-kHz ultrasound, in all cases the results obtained using 20-kHz ultrasound differ substantially from the solute effects seen at 515 kHz. At 20 kHz, there is essentially no quenching induced by the alcohols regardless of the alkyl chain length of the alcohol. Similarly, the addition of SDS has only a small effect on the SL intensity relative to the changes observed at the higher frequency used. Also, the addition of NaCl has a smaller effect on the SL intensity relative to the change observed using 515 kHz.

At this point, it is necessary to consider the type of bubbles that are produced in an acoustically cavitating system. Leighton<sup>2</sup> has described in some detail the possible types of cavitation that can occur in a fluid exposed to an acoustic field. Of the different possibilities, only those forms of cavitation that involve violent collapse (i.e., inertial collapse) will produce SL. There are two types of bubbles that fit these requirements, transient bubbles and repetitive transient bubbles (sometimes referred to as stable bubbles), although strictly the term “stable bubbles” also includes those bubbles that oscillate without emitting SL.<sup>2</sup> Stable bubbles are considered to undergo a large number of oscillations during their existence, whereas transient bubbles may exist only for a few oscillation cycles. In explaining the effect that solutes have on 515-kHz SL, it has been assumed in our previous work that the bubbles are primarily of the stable type. That is, they undergo a large number of oscillations<sup>28</sup> and in doing so exist for a sufficient time for surface-active solutes to adsorb to the bubble/solution interface, accumulate gaseous decomposition products, and allow a significant amount of the gases solubilized in solution to enter the bubble. In contrast, for transient bubbles, these events can be expected to be significantly reduced. This of course implies that transient bubbles produced in solutions containing solutes, to a first approximation, should behave the same as bubbles generated in pure water. Qualitatively, this is what the results from 20-kHz ultrasound pulses appear to show; that is, there is no SL quenching observed with the addition of alcohols and relatively minor effects when NaCl and SDS are present in solution.

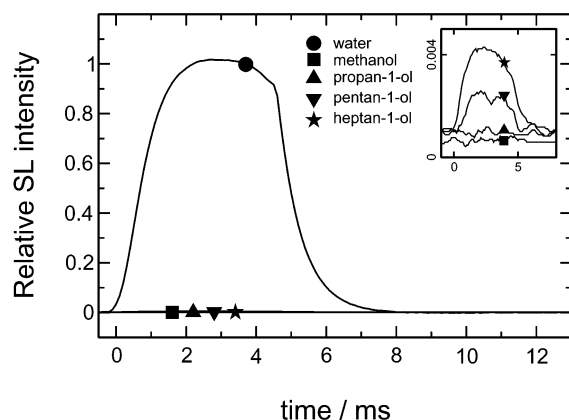
The conclusion that the SL from 20 kHz ultrasound is primarily produced from transient bubbles and that the SL from 515 kHz ultrasound stems predominantly from a type of stable cavitation is supported by the results of Figures 8 and 9. It can be seen in Figure 8 that the intensity of the SL signal produced by 20-kHz pulses increases as the alkyl chain length of the neat alcohol increases. This trend is in keeping with a decrease in the vapor pressure of the alcohol with an increase in its molecular weight. The significance of this is that if it is accepted that transient bubbles are responsible for the observed SL then only the vapor from the alcohols will be present within transient cavitating bubble during one or few oscillations of its existence. In such a situation, the temperatures produced within the bubble core, and hence the SL intensity, will be strongly affected by the amount of alcohol vapor in the core during bubble collapse. Therefore, it can be expected that the more volatile the given alcohol the lower the bubble core temperature and so too the associated SL intensity.

In contrast to the results at 20 kHz, the SL signal obtained in neat alcohol exposed to 515-kHz ultrasound pulses is extremely





**Figure 8.** Averaged relative sonoluminescence intensity for a 3.5-ms pulse at 20 kHz in various neat alcohols and water. The intensities have been normalized to the average SL intensity obtained in water.



**Figure 9.** Averaged relative sonoluminescence intensity for a 3.5-ms pulse at 515 kHz in various neat alcohols and water. The intensities have been normalized to the average SL intensity in water. The inset shows the SL signals on an expanded scale.

weak, as can be seen in Figure 9, relative to the signal from water. This is consistent with the results in Figure 3 and the explanation that the SL quenching in stable bubbles arises from the accumulation of volatile, water-insoluble decomposition products. The build up of the products over many oscillation cycles contributes to the lowering of the bubble core temperature and hence the decrease in the SL intensity. (It is interesting that from a close inspection of the weak SL signal in the various alcohols (see insert to Figure 9) the order of the intensity of the signals is similar to that found at 20 kHz. (This observation suggests, on the basis of the arguments above, that the weak residual SL is from a small fraction of transient bubbles generated at 515 kHz.)

## Conclusions

Collectively, the results obtained at 20- and 515-kHz ultrasound frequencies suggest that the cavitating bubbles obtained at 20 kHz are of a transient type (i.e., undergoing one or only a few oscillations during their existence), whereas at 515 kHz, the majority of the bubbles undergo multiple oscillations and can be considered to be of a repetitive transient type. These conclusions have important implications for sonochemical studies, particularly for those conducted in water. The stable bubbles at 515 kHz can be seen as microreactors producing pyrolysis products from volatile solutes. However, transient bubbles will be less efficient with respect to pyrolysis reactions for the type of solutes examined here, and it may be anticipated that radical-initiated reactions will be more dominant under these

conditions. Certainly, these predictions need to be tested, but we know from our own experiments that the sonication of aqueous alcohol solutions at 20 kHz is far less efficient at producing hydrocarbon products (e.g., methane, ethane, acetylene, etc.) than when the same solutions are sonicated at 515 kHz. On the basis of the above conclusions, it can be predicted that it should be possible to choose the type of sonochemical reactions that take place in solution by a careful choice of the insonation frequency employed.

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