Sonoluminescence quenching by organic acids in aqueous solution: pH and frequency effects

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The quenching of sonoluminescence from aqueous solutions by acrylic and methacrylic acids is dependent on whether the acid is ionised in solution, as controlled by the pH, but also by the frequency of ultrasound used.

The use of high intensity ultrasound in synthetic and materials chemistry is becoming commonplace.[1,2] There is also considerable interest in the sonochemistry of aqueous solutions from the point of view of environmental remediation.[3,4] However, despite these applications, there remain doubts as to the precise mechanisms of many of these reactions.

It is generally accepted that sonochemical processes mainly occur as a result of cavitation[5]—the growth and violent collapse of microscopic bubbles as the alternate compressions and rarefactions of the sound wave propagate through the liquid. One consequence of cavitational collapse is the emission of a brief flash of light—sonoluminescence, SL—from vibronically excited states of molecules produced during the high temperatures and pressures that are generated within the bubble.[6,7] The primary species formed during sonication of water are H· and OH· radicals.[8] These may recombine or react inside the bubble or they may diffuse into solution to react with dissolved species. A parallel reaction pathway exists for volatile solutes which may evaporate into the bubble and be pyrolysed by the high temperatures.

It has recently been shown that the SL emission caused by 515 kHz ultrasound can be enhanced by the addition of small amounts of surfactants, attributed to electrostatic shielding of the bubbles hindering clustering.[9] Conversely, small amounts of alcohols, amines and carboxylic acids in solution cause quenching of the SL by evaporation into the bubbles and reaction with excited state intermediates and/or by lowering the effective temperature at the bubble core.[10,11] Ashokkumar *et al.* recently showed that quenching of SL by carboxylic acids depended on the pH and occurred only at pH values where unionised acid was present in solution.[11,12]

A number of workers have applied ultrasound to the radical polymerisation of vinyl monomers, both water soluble and in emulsion reactions.[13–15] Thus in order to provide information on the mechanism of the polymerisation, it was of interest to determine whether unsaturated vinyl compounds are subject to the same reaction pathways. Additionally, most polymerisation work has been conducted at a sound frequency of 20 kHz. This communication therefore presents SL quenching results for two vinyl monomers, acrylic acid (AA) and methacrylic acid (MAA) at a frequency of 515 kHz (for comparison with previously reported results) and at 20 kHz. The work at 20 kHz yielded previously unreported effects on the frequency dependence of SL quenching.

Fig. 1 shows the SL emission (relative to that of pure water) for aqueous solutions of MAA sonicated at 515 kHz.‡ It is clear that the SL is quenched at low pH when the acid is in its molecular form in solution but that at high pH, where the acid is ionised, there is no significant quenching. At low pH, over
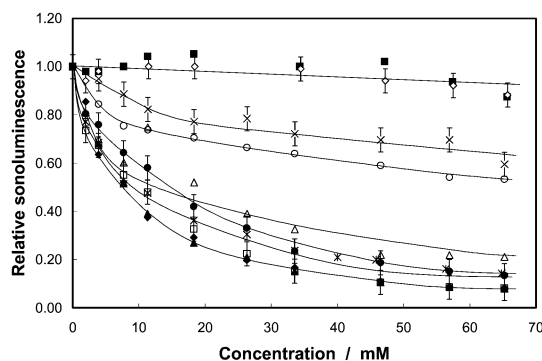
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Fig. 1 SL emission from aqueous solutions of MAA at the indicated pH. The indicated error bars are indicative for all curves. pH values: ■ 9.7; ◇ 8.8; × 7.8; ○ 6.9; △ 6.0; ●.6; * 5.1; □ 4.4; ◆ 3.2; ▲ 2.2.

90% of the emission is quenched at concentrations around 50 mM. Conversely, at high pH, the SL is within ±10% of that in water across the whole concentration range studied. The pH dependence is clearly demonstrated in Fig. 2 which shows the relative emission of solutions with MAA concentrations of 25 mM. The pK_a of MAA is 4.65[16] and the percentage of unionised acid remaining in solution calculated from this value is shown in Fig. 2 as the dashed line. These results are similar to those obtained in previously reported studies on aqueous solutions of saturated aliphatic carboxylic acids.[11,12] On increasing the pH, it is clear that the SL is quenched until a value, above the pK_a, is reached where the concentration of free acid is close to zero.

It is apparent that the SL is quenched if unionised acid is present in solution. Unionised MAA has appreciable volatility (saturated vapour pressure = 0.99 Torr at 25 °C[16]) and can therefore evaporate into the bubble. However, the ionic form is non-volatile and thus cannot enter the bubble to quench the SL.

Also shown in Fig. 2 are the SL quenching results obtained using an ultrasound frequency of 20 kHz. There is rather higher uncertainty in these results due to the nature of the sound field. However, it is apparent that there is no significant quenching of
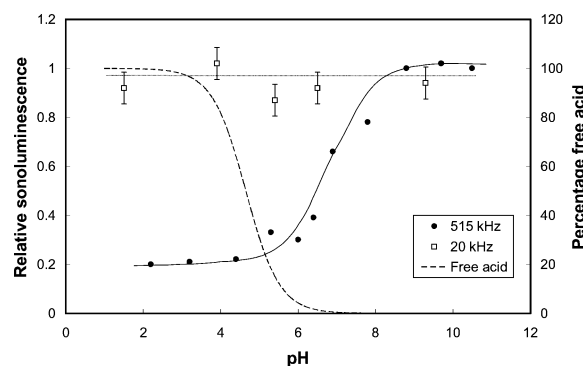

Fig. 2 pH variation of SL intensity of 25 mM solutions of MAA.

the SL across the complete pH range. As shown in Fig. 3, similar effects were noted for AA. With this monomer, there was a small amount (~ 20%) of quenching even at high pH. This may be due to a small amount of a volatile impurity in the AA.[17] However, as with MAA there was no significant difference in quenching between pH 2 and 10 using sound of 20 kHz even though quenching of 60–80% occurred at this concentration at low pH under sonication at 515 kHz.
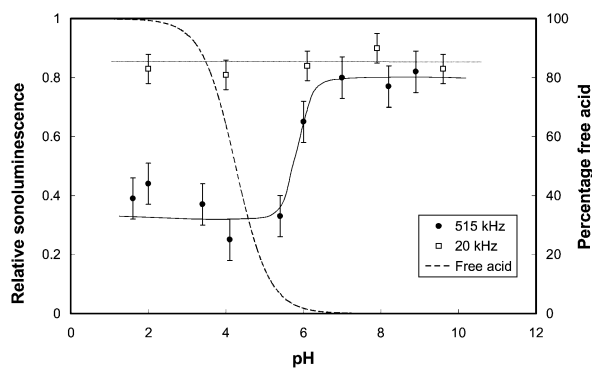

Fig. 3 pH variation of SL intensity of 25 mM solutions of AA.

The lack of quenching at 20 kHz has recently been noted with various aliphatic alcohol solutes.[18] One explanation for these observations is the differing nature of cavitation at the two frequencies. At 515 kHz, the predominant effect will be 'stable' cavitation where a bubble undergoes many oscillations during its lifetime.[5] This leads to significant amounts of dissolved material adsorbing to the bubble–solution interface and evaporating into the bubble.[11,12] The products of sonolysis reactions can accumulate in the bubble and quench the SL. These factors are significantly reduced in the case of 'transient' cavitation bubbles which predominate at lower frequencies such as 20 kHz. Here bubbles undergo only a few ocillations during their lifetime. However, they grow to a larger size and collapse more violently leading to the production of larger numbers of free radicals per collapse and giving larger mechanical effects such as the motion of solvent around the bubbles.[5,20] The overall frequency dependence of the rate of a sonochemical effect is thus a balance between the number of events per collapse and the number of collapses per unit time. However, the differences in cavitation type at the two frequencies may also lead to a different balance between the competing reaction mechanisms.

Further evidence for this interpretation comes from analysis of the reaction products of sonication of the unsaturated acids. Sealed vials of 30 mM solutions of MAA or AA were sonicated under the same conditions as used above and the headspace over the solutions sampled.[19] At pH 1.9, significant amounts of methane, acetylene and ethene were detected after 15–30 min sonication at 515 kHz. These have been shown to be major products of the pyrolysis due to sonolysis of this type of compound.[7] Sonication under the same conditions at pH 9.0 produced amounts of these products less than 1% of those at low pH after 120 min indicating that little material was subjected to pyrolysis. At 20 kHz, sonication at either pH for 6 hr produced no detectable methane, acetylene or ethene.

This frequency dependence of SL quenching has not previously been reported other than with alcohol solutes.[18] However, it does help to interpret some sonochemical effects that have been reported. For example, Henglein[21] reported that for a range of solutes in water, solvolysis (i.e. pyrolysis) was the main pathway at 1 MHz but that radical production and mechanical effects predominate at 20 kHz. Theron and coworkers[22] reported a similar difference in mechanism for the degradation of phenyltrifluoromethylketone in water at 30 kHz and 500 kHz. Several other reports of an apparently different mechanism as a function of frequency have appeared.[23,24]

In conclusion, we have shown that the unsaturated organic acids behave under sonication in the same manner as the saturated versions. Moreover, we have noted a frequency dependence of sonoluminescence and sonochemistry which points to a difference in the type of cavitation which operates at 20 and 515 kHz. Further work is underway to clarify this and to determine whether it is general effect or confined to this type of compound. If it is a widespread effect, the information should be of use in determining the optimum frequency to use for particular sonochemical applications.

Notes and references

† On sabbatical leave at the University of Melbourne.

‡ SL measurements were performed in air using a cylindrical Pyrex cell placed over the transducer. For the 20 kHz measurements, the emission from sonication of 100 cm^3 of solution with a Branson B-30 used in a 'cup horn' configuration was monitored by a Hamamatsu end-on photomultiplier responsive between 300–650 nm. At 515 kHz, 25 cm^3 of solution was used with an Undatim UL03/1 reactor. For both frequencies, calorimetric intensities in the range 0.1–0.2 W cm^{-2} were used with pulse widths of 5 ms and 15 ms between pulses. The temperatures were within the range 20–25 °C. The emission intensities, averaged over at least 500 pulses, were determined on an oscilloscope. To prevent any effects due to varying ionic strength, a constant background concentration of 0.1 M NaClO$_4$ was maintained for all measurements.

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