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Acoustic Emission Spectra from 515 kHz Cavitation in Aqueous Solutions Containing Surface-Active Solutes

Muthupandian Ashokkumar,† Mark Hodnett,‡ Bajram Zeqiri,‡ Franz Grieser,†
and Gareth J. Price*,§

Contribution from the Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Victoria 3010, Australia, Quality of Life Division, National Physical Laboratory, Teddington, Middlesex TW11 0LW, U.K., and Department of Chemistry, University of Bath, Bath BA2 7AY, U.K.

Received November 7, 2006; E-mail: chsgjp@bath.ac.uk

Abstract: The effect of adding surface-active solutes to water being insonated at 515 kHz has been investigated by monitoring the acoustic emission from the solutions. At low concentrations (<3 mM), sodium dodecyl sulfate causes marked changes to the acoustic emission spectrum which can be interpreted in terms of preventing bubble coalescence and declustering of bubbles within a cavitating bubble cloud. By conducting experiments in the presence of background electrolytes and also using non-ionic surfactants, the importance of electrostatic effects has been revealed. The results provide further mechanistic evidence for the interpretation of the effect of surface-active solutes on acoustic cavitation and hence on the mechanism of sonochemistry. The work will be valuable to many researchers in allowing them to optimize reaction and process conditions in sonochemical systems.

Introduction

The passage of high-intensity ultrasound through liquids and the resulting acoustic cavitation has been used to stimulate a number of chemical reactions, such as metal ion reduction, oxidation of organic compounds, pyrolysis of volatile solutes, etc.[1,2] One of the challenges that faces scientists working in this research area is to precisely control the cavitation events, which requires an understanding of how various experimental parameters affect cavitation.

It is well recognized that acoustic cavitation in liquids, especially water, generates reactive intermediates such as radicals through breakdown of the solvent as well as producing light emission, known as sonoluminescence (SL).[3−7] For example, the concentration of hydroxyl radicals or the amount of hydrogen peroxide produced can be used for monitoring the extent of cavitation activity in aqueous solutions.[8] Over the past several years, our research groups have been studying the effect of surface-active solutes on cavitation.[9−12] Both sonochemistry[13] and sonoluminescence[14] have been used as tools for monitoring the effects of different experimental parameters, such as frequency and acoustic power, on cavitation activity.

The presence of surface-active solutes has been shown to decrease the amount of primary radicals that are available in solution for reaction. Henglein[15] reported that the presence of hydrophobic solutes led to a decrease in the amount of hydrogen peroxide detected in solution and argued that surface-active solutes adsorbed at the bubble interface trap some of the primary radicals that otherwise would have produced hydrogen peroxide. Grieser and co-workers[16] have shown that the reaction of the primary radicals with adsorbed solutes leads to the formation of secondary reducing radicals that can beneficially be used for metal ion reduction. They have also shown a strong correlation between the surface activity of the solutes and the concentration of metal ions reduced. It has been suggested that the extent of metal ion reduction is independent of the chain length of the solutes and is controlled by the number of surface-active molecules present at the bubble/solution interface. The importance of adsorption of surfactants to the bubble interface and their role in controlling the reactivity of sonochemically

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† University of Melbourne.
‡ National Physical Laboratory.
§ University of Bath.

(1) Ashokkumar, M.; Grieser, F. *Chem. Eng. Rev.* **1999**, *15*, 41.
(2) Suslick, K. S.; Price, G. J. *Annu. Rev. Mater. Sci.* **1999**, *29*, 295
(3) Leighton, T. *The Acoustic Bubble*; Academic Press: London, 1994.
(4) Young, F. R. *Cavitation*; Imperial College Press: London, 1999.
(5) Crum, L. A., Mason, T. J., Reisse, J. L., Suslick, K. S., Eds. *Sonochemistry and Sonoluminescence*; NATO ASI Series C, Vol. 524; Kluwer Publishers: London, 1999.
(6) Yasui, K. *J. Chem. Phys.* **2002**, *116*, 2945.
(7) Price, G. J., Ed. *Current Trends in Sonochemistry*; Royal Society of Chemistry: London, 1992.
(8) Price, G. J.; Garland, L.; Comina, J.; Davis, M.; Snell, D. J.; West, P. J. *Res. Chem. Intermed.* **2004**, *30*, 807.
(9) Ashokkumar, M.; Hall, R.; Mulvaney, P.; Grieser, F. *J. Phys. Chem. B* **1997**, *101*, 10845.
(10) Price, G. J.; Ashokkumar, M.; Grieser, F. *J. Am. Chem. Soc.* **2004**, *126*, 2755.
(11) Sunartio, D.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2005**, *109*, 20044.
(12) Price, G. J.; Ashokkumar, M.; Cowan, T. D.; Grieser, F. *Chem. Commun.* **2002**, 1740.
(13) Tronson, R.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2003**, *107*, 7307.
(14) Henglein, A. *Ultrason. Sonochem.* **1995**, *2*, S115.
(15) Henglein, A. *Adv. Sonochem.* **1993**, *3*, 17.
(16) Ashokkumar, M.; Grieser, F. *In Encyclopaedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker: New York, 2002; pp 4760−4774.

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generated radicals has also been demonstrated by Sostaric and Riesz using electron paramagnetic resonance.[17,18]

It has also been demonstrated that the extent of SL quenching caused by solutes when using 515 kHz ultrasound can be correlated with their surface excess concentration,[9] and it has been shown that solutes must be volatile and capable of evaporating into the bubble for SL quenching to occur.[11] Under some circumstances, involatile solutes may decompose to form volatile products which may enter bubbles and quench SL. Another parameter affecting the extent of SL quenching by surface-active solutes is the frequency of the ultrasound used. On the basis of SL quenching and reaction product analysis, it has been suggested that cavitation is predominantly of the "stable" type (i.e., bubbles undergoing many hundreds or thousands of oscillations) at high frequencies but mainly "transient" (i.e., bubbles undergoing only a few oscillations before inertial collapse) under the conditions pertaining to a 20 kHz horn sonicator.[10] It has also been shown that nonvolatile, ionic surfactants such as sodium dodecyl sulfate do not quench but rather enhance the SL at high frequencies.[12] This SL enhancement has been linked to effects from electrostatic interactions between bubbles as a consequence of the charged surfactant molecules adsorbed at the bubble/solution interface.

Thus, both sonochemical reactions and SL measurements can provide detailed information on how different experimental parameters can affect acoustic cavitation. Segebarth et al.[19] demonstrated that the acoustic emission generated by the cavitation bubbles can also be used to study the effect of solutes on cavitation. They reported that both sonoluminescence and sonochemistry can be correlated with the full width at half-maximum of the second harmonic of acoustic emission observed at 515 kHz ultrasound frequency. Price et al.[20] have extended this technique to compare the types of cavitation generated at 20 and 515 kHz in water. It has been shown, under the experimental conditions used in this study, that the acoustic emission characteristics of cavitation bubbles generated at 20 kHz are significantly different from those at 515 kHz. Lauterborn et al.[21] and Frohly et al.[22] have suggested explanations for the range of features displayed in the acoustic emission spectra of cavitating systems.

For this report, we have extended our investigation to study the effect of a number of surface-active solutes on acoustic emission characteristics at 515 kHz. The acoustic emission data are also compared with those from previously reported SL studies under similar experimental conditions.

Experimental Details

Sodium dodecyl sulfate (SDS, 99.0%) and alcohol solutes (>99%) were purchased from Ajax Chemicals and BDH, respectively. Dodecyl trimethylammonium chloride (DTAC) was purchased from Kodak Chemicals, and *n*-decyl-*N*,*N*-dimenthyl-3-ammonio-1-propanesulfonate (zwittergent, 99%) was purchased from Calbiochem. Zwittergent is a zwitterionic surfactant with a quaternary ammonium alkanesulfonic acid inner salt which retains its dual charge over a very wide pH range in aqueous solutions. The solutions were made using Milli-Q water with a resistance >10 MΩ at 20 °C.

The ultrasound generator/transducer system (Undatim UL03/1 reactor) used for the measurements was similar to the one used in our SL studies.[10] Acoustic emission was measured using a cavitation sensor developed at the National Physical Laboratory,[23,24] consisting of a 110 μm thick polyvinylene difluoride membrane sandwiched in polyurethane rubber which is acoustically matched to water. The sensor has a flat, usable response up to 10 MHz. Emission signals were measured from 130 cm^3 of aqueous solutions containing different concentrations of the solutes mentioned above on Agilent 4395A and HP3589 spectrum analyzers. The ultrasound intensities used were measured calorimetrically[7] and are given below as appropriate. Sonication was carried out for short times (~30 s) to minimize temperature changes; all results were recorded at 23−26 °C.

Results

The acoustic emission spectra observed during the sonication of water at 515 kHz as a function of different acoustic (input) intensities are shown in Figure 1. At low intensities, a signal at the fundamental frequency, $f_o = 515$ kHz, can be seen, and as the intensity increases, peaks at several harmonic frequencies ($2f_o = 1.1$ MHz, $3f_o = 1.6$ MHz, etc.) appear in the spectra. At intensities above 0.54 W cm^{-2}, the appearance of the spectrum changes markedly. Our previous report[20] showed that this was the level above which significant sonochemistry and SL emission occurred. At the higher powers, the acoustic emission spectra show a larger number of harmonic peaks across the whole frequency range. A number of ultraharmonic peaks ($1.5f_o = 765$ kHz, $2.5f_o = 1.3$ MHz, etc.) begin to grow in, and the amplitude of the harmonics is higher. A subharmonic peak ($0.5f_o = \sim 258$ kHz) is also evident. The increasing featureless, broadband emission onto which the harmonics are superimposed is significant in terms of detecting the type of cavitation occurring. Frohly et al.[22] observed similar development of features in the emission spectrum from water sonicated at a frequency of 1.075 MHz, as did Lauterborn and Cramer[25] using a cylindrical transducer at low frequencies.

In an ultrasound field, each bubble acts as a secondary emitter, and the measured spectrum from the cylindrical sensor is the average over a large number of emissions from individual bubbles. At low acoustic driving amplitudes, bubbles oscillate linearly, so only the fundamental frequency is seen in the emission spectrum. As the intensity increases, a degree of nonlinear motion is introduced due to forced oscillations, and so harmonics can be observed. Higher driving amplitudes lead to higher levels of nonlinearity, deviations from spherical motion, and a range of other bubble motions and nonlinear oscillations leading to emission at sub- and ultraharmonic frequencies. The broadband signal, termed "white-noise" by Neppiras,[26] arises from several sources, including chaotic, highly nonspherical oscillation of bubbles and shock waves generated on bubble collapse.[21,22,27,28] The presence of the broadband signal

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(17) Sostaric, J. Z.; Riesz, P. *J. Am. Chem. Soc.* **2001**, *123*, 11010.
(18) Sostaric, J. Z.; Riesz, P. J. *J. Phys. Chem. B* **2002**, *106*, 12537.
(19) Segebarth, N.; Eulaerts, O.; Reisse, J.; Crum, L. A.; Matula, T. J. *ChemPhysChem* **2001**, *8/9*, 536.
(20) Price, G. J.; Ashokkumar, M.; Hodnett, M.; Zequiri, B.; Grieser, F. *J. Phys. Chem. B* **2005**, *109*, 17799.
(21) Lauterborn, W.; Kurz, T.; Mettin, R.; Ohl, C. D. *Adv. Chem. Phys.* **1999**, *110*, 295.
(22) Frohly, J.; Labouret, S.; Bruneel, C.; Looten-Baquet, I.; Torguet, R. *J. Acoust. Soc. Am.* **2000**, *108*, 2012.
(23) Zeqiri, B.; Gélat, P. N.; Hodnett, M.; Lee, N. D. *IEEE Trans. Ultrason. Ferroelect. Freq. Control* **2003**, *50*, 1342.
(24) Zeqiri, B.; Lee, N. D.; Hodnett, M.; Gélat, P. N. *IEEE Trans. Ultrason. Ferroelect. Freq. Control* **2003**, *50*, 1351.
(25) Lauterborn, W.; Cramer, E. *Phys. Rev. Lett.* **1981**, *47*, 1445.
(26) Neppiras, E. A. *Phys. Rep.* **1980**, *61*, 159
(27) Ohl, C. D.; Kurz, T.; Geisler, R.; Lindau, O.; Lauterborn, W. *Philos. Trans. R. Soc. London A* **1999**, *357*, 269.
(28) Reference 3, pp 413−426.

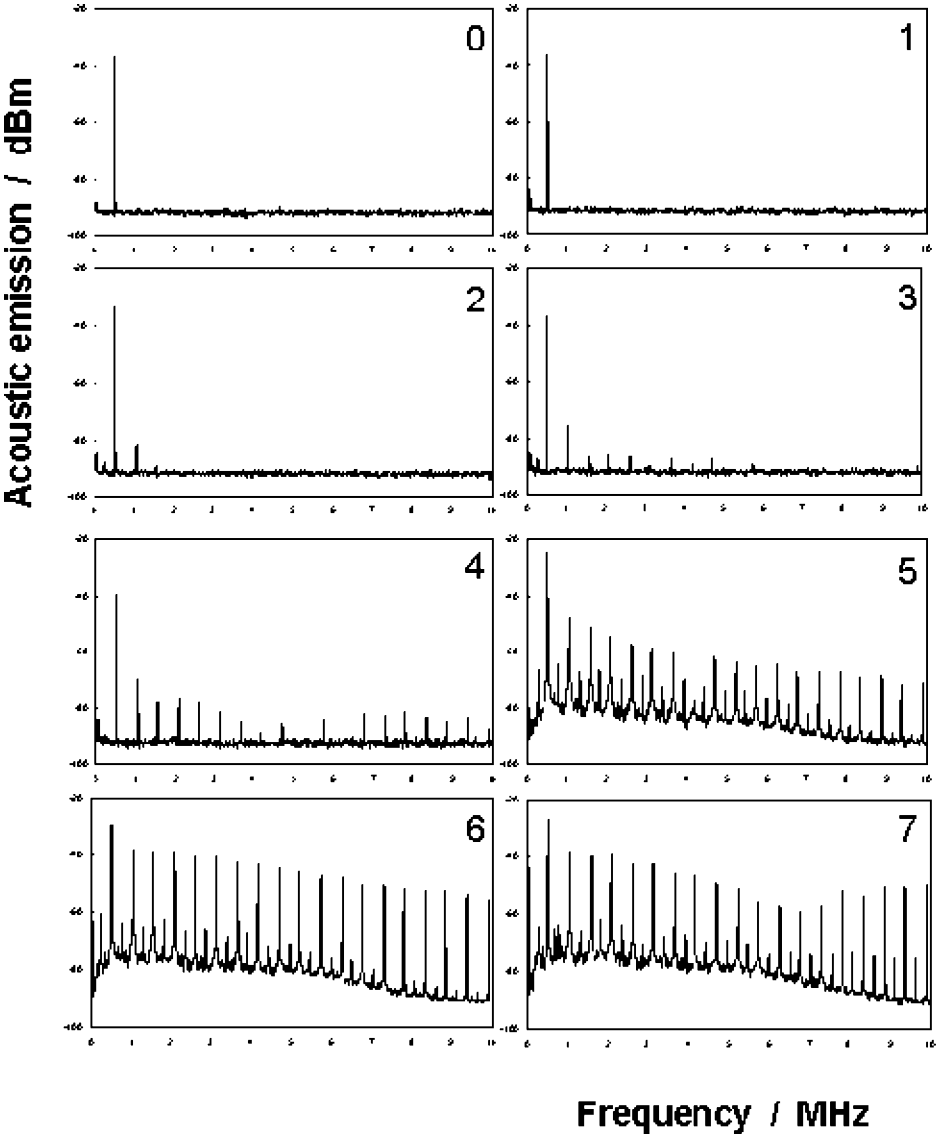

Figure 1. Acoustic emission spectra observed from water at different applied acoustic intensities: 0, 0 W cm^{-2}; 1, <0.05 W cm^{-2}; 2, 0.05 W cm^{-2}; 3, 0.08 W cm^{-2}; 4, 0.54 W cm^{-2}; 5, 0.7 W cm^{-2}; 6, 2.2 W cm^{-2}; 7, 6.8 W cm^{-2}.

is generally taken to be indicative of transient or "inertial" [3] cavitation and bubble collapse.[22] The sub- and ultraharmonic peaks are characteristic of a stable cavitation regime, although subharmonic oscillations can occur at relatively low acoustic intensities. The occurrence of subharmonic peaks has been interpreted as an indication of transient cavitation, although several workers[28,29,30] have suggested that this is not the case and that it arises from chaotic motions of bubbles larger than their resonant size. We suggest that[20] the observation of sharp overtone peaks up to the 20th harmonic shows that, under the conditions and frequency used here, both inertial and non-inertial cavitation occur, but it is predominantly of the stable or "non-intertial" [3] type. This is consistent with evidence from SL and sonochemical measurements previously reported, as discussed below.

Figure 2 shows the effect on the acoustic emission spectra as SDS is added to water sonicated with an intensity of 2.2 W cm^{-2}. Comparing the acoustic emission observed in water with that from a 0.5 mM solution of SDS shows the almost complete elimination of the broadband "white" noise from the spectrum as well as marked changes to the sub- and ultraharmonic structure. However, the intensity of the harmonic peaks remains approximately at the same height. The reduction in the broadband signal remains on further addition of SDS until a concentration of ∼3 mM is reached, at which point the spectrum returns to a structure similar to that observed with pure water. Further addition of SDS causes no significant change in the spectra.

The effects are perhaps more clearly visible in Figure 3, which shows the spectra around the second harmonic peak at ∼1.03−1.04 MHz. This is representative of the observations for the other harmonic peaks across the whole spectrum. The change in emission in terms of the reduction of broadband "noise" for low concentrations of SDS is readily apparent, as is the return of the emission intensity to water-like levels as the concentration of SDS is increased. The maximum intensity of the peak is relatively insensitive to SDS concentration. Similar changes in

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(29) Walton, A. J.; Reynolds, G. T. *Adv. Phys.* **1984**, *33*, 595.
(30) Vaughn, P. W.; Leeman, S. *Acustica* **1986**, *59*, 279.

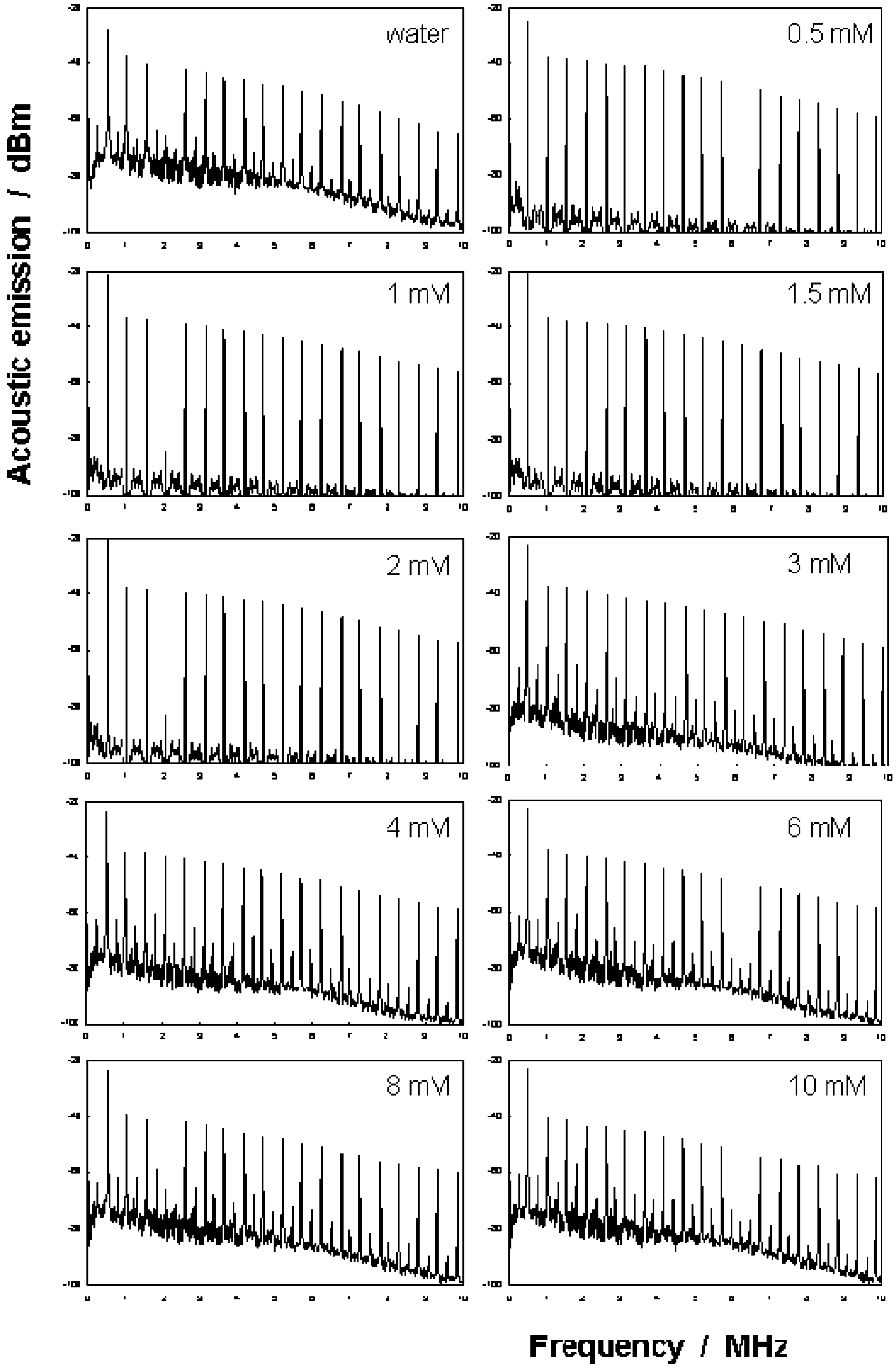

Figure 2. Acoustic emission spectra observed from aqueous solutions containing different concentrations of SDS at 515 kHz. (Acoustic intensity at 2.2 W cm^{-2}.)

acoustic emission were observed by Segebarth et al.,[19] who interpreted their spectra as a narrowing of the second harmonic peak as well as a reduction in the signal at the harmonic frequency. In this work, the harmonic peaks are much narrower (∼200−300 Hz, compared with 7−14 kHz from the data of Segebarth et al.), reflecting perhaps the different types of hydrophone used for the measurements. Our observations are better interpreted by assuming that there is a significant reduction in the broadband emission or “white noise” component of the spectrum.

The effect of SDS on cavitation has previously been interpreted[12] in terms of an electrostatic shielding effect and a retardation in coalescence between bubbles, resulting in a larger number of emitting bubbles, leading to an increase in SL intensity. In order to explore this hypothesis, a series of spectra was also recorded with increasing concentrations of SDS in a solution of 0.1 M $NaClO_4$, the expectation being that the background electrolyte would mask any electrostatic effects. The results are shown in Figure 4; differences from Figure 3 are readily apparent. Here, there is negligible difference between

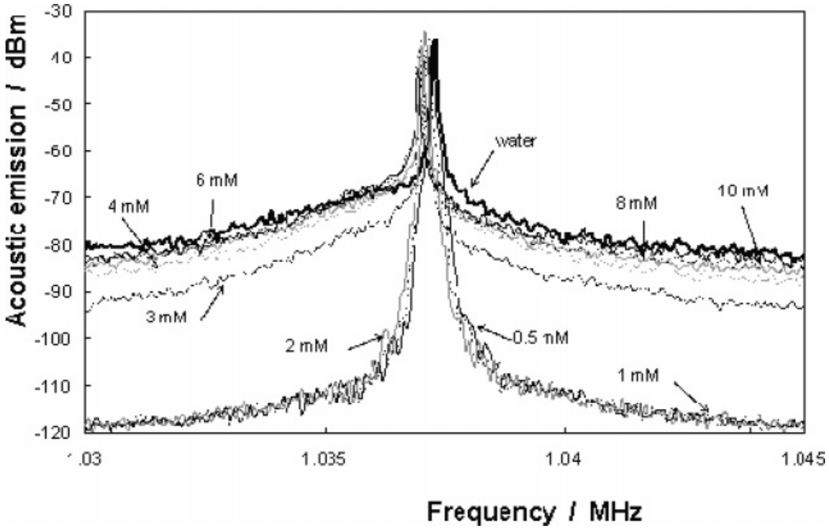

Figure 3. Second harmonic region of the acoustic emission spectra from sonication at 515 kHz of aqueous solutions of SDS with the indicated concentrations. (Acoustic intensity at 2.2 W cm^{-2}.)

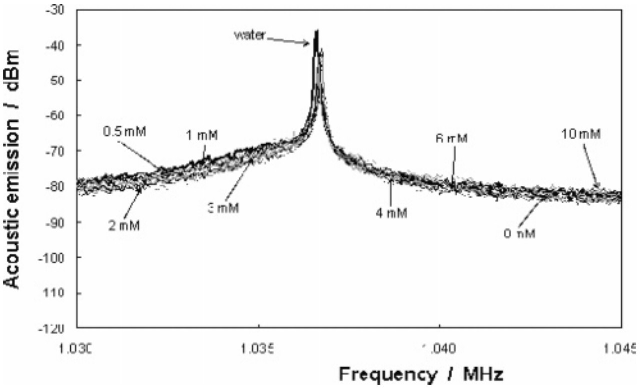

Figure 4. Second harmonic region of the acoustic emission spectra observed from aqueous solutions of SDS in the presence of 0.1 M $NaClO_4$ at 515 kHz. (Acoustic intensity at 2.2 W cm^{-2}.)

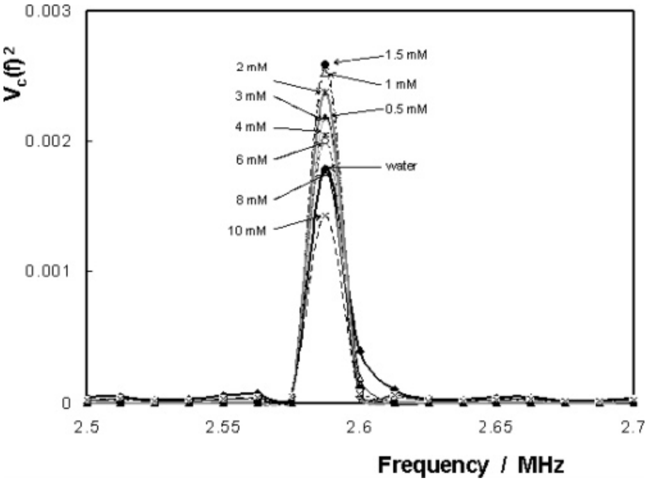

Figure 5. Change in total output signal from sonication at 515 kHz of aqueous solutions of SDS with the indicated concentrations. (Acoustic intensity at 2.2 W cm^{-2}.)

any of the spectra across the concentration range investigated. The addition of SDS therefore has little influence on the acoustic emission when a background electrolyte is present.

Discussion

In order to quantify the effects observed in Figures 2−4, the integrated energy output in the acoustic emission spectra has been calculated, as reported in our previous communication.[20] The emitted energy in the spectrum between two frequencies, f_1 and f_2, can be evaluated by integrating the squared acoustic response,[31]

$$\text{energy} = \int_{f_1}^{f_2} V_c(f)^2 \, df \qquad (1)$$

where $V_c(f)$ is the magnitude of the sensor response at frequency f. In this work, the spectrum has been integrated between 2.2 and 4.0 MHz; it was found that using different integration limits did not change the form of the results.

Looking at the data in Figure 3 suggests little variation in the signal intensities. The logarithmic nature of the signal hides the fact that there is a significant change in output as SDS is added, which is apparent if the data are replotted, as shown in Figure 5, in the form suggested by eq 1.

Effect of SDS on Cavitation. The variation of the total energy emitted between 2.2 and 4.0 MHz with changing SDS concentration in the presence and in the absence of 0.1 M $NaClO_4$ is shown in Figure 6. The total energy output increases up to a concentration of ∼2 mM, suggesting enhanced cavitation activity. Above 3 mM, the values return to levels similar to those observed in pure water. The presence of a background electrolyte, expected to mask any significant electrostatic effects, prevents the increase in the total emitted energy and in fact reduces it somewhat (although the observed effects are at the limit of experimental uncertainty and may not be significant).

The emitted (total) acoustic energy comprises the broadband emission and that from the harmonic peaks. In order to isolate these two contributions, the emission arising solely from the broadband is presented in Figure 7. In contrast to the total emission in Figure 6, the broadband component falls almost to zero in solutions of 0.5−2 mM in SDS, paralleling the qualitative observations of the effect of adding SDS reported

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(31) Hodnett, M.; Chow, R.; Zeqiri, B. *Ultrason. Sonochem.* **2004**, *11*, 441.

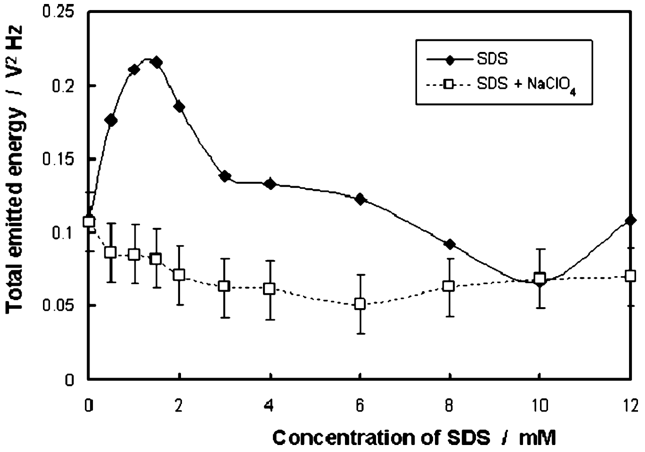

Figure 6. Change in total emitted energy in the acoustic spectra of aqueous solutions of SDS in the absence and in the presence of 0.1 M $NaClO_4$.

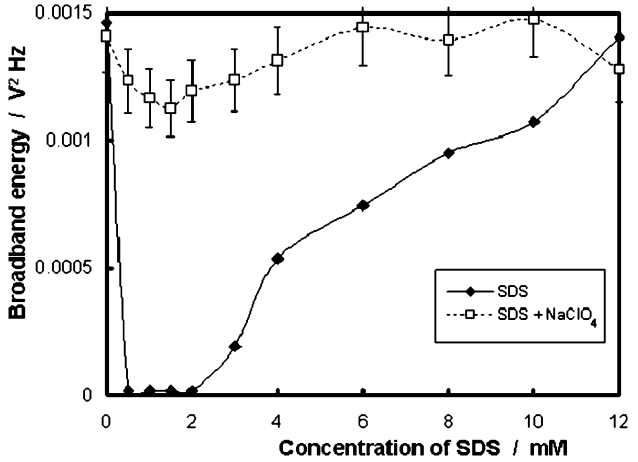

Figure 7. Change in broadband component of the energy in the acoustic emission spectra of aqueous solutions of SDS in the absence and in the presence of 0.1 M $NaClO_4$.

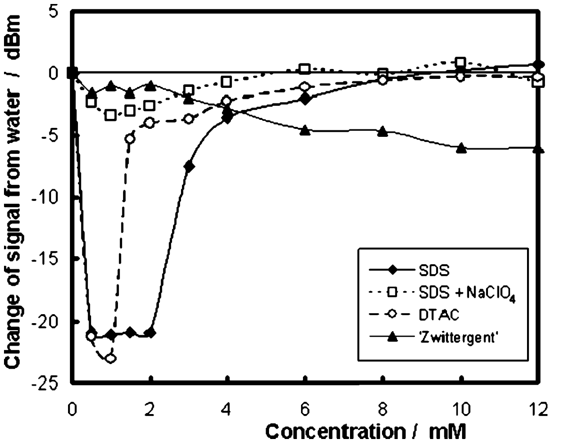

Figure 8. Broadband intensity averaged between 1.1 and 1.125 MHz in the presence of various surfactants.

above. Again, the levels return to those from water as the concentration increases. When the experiment is repeated in the presence of 0.1 M $NaClO_4$, there is a small reduction in broadband energy but much less than that observed in its absence. These results imply that the observed effects at low concentrations of SDS are primarily, though not exclusively, electrostatic in nature.

The data in Figures 5−7 show that, while the addition of low concentrations of SDS decreases the energy output through the broadband component, that in the harmonic peaks increases. The nature of the ultraharmonic peaks also changes (see Figure 2). It could be argued that the increase in acoustic emission seen in Figure 5 might be due to an increase in the total number of cavitation bubbles. However, if there was a significant increase in the number of active bubbles, then the broadband emission should also increase significantly, as suggested in our previous report[20] for sonication at 20 kHz. The fact that the broadband does not increase suggests that the increase in energy emission is not simply related to a significant increase in the number of bubbles but that other effects play a part.

An alternative way of exploring the change in the types of emission that occur in the acoustic spectra is to quantify the broadband intensities in a region of the spectrum away from the harmonic peaks. Figure 8 shows the change in spectral signal from that of water averaged between 1.1 and 1.125 MHz, which is well away from any harmonic or ultraharmonic frequency. Choice of other frequency ranges which show this criterion gave similar results. The results for SDS are similar to those seen in Figure 6, confirming the validity of the data treatment. A significant decrease in the magnitude of the broadband signal is seen for concentrations up to 2 mM; higher concentrations return the signal close to that seen for water. The lack of influence of SDS in the presence of background salt is again clearly demonstrated.

At this stage, it is appropriate to consider the potential effects of charged surfactants such as SDS on cavitation bubbles. In an acoustic field such as that in a sonochemical reactor, bubbles form clusters within a bubble cloud. Individual bubbles will undergo motion within these clusters due to streaming effects and Bjerknes forces. The latter will cause bubbles that are smaller than their resonant size to be attracted to each other. Therefore, bubbles undergoing motion in a cavitation field in water will come into contact with each other and may coalesce to form larger bubbles which are lost from the bubble cloud through buoyancy or forced to pressure nodes by acoustic field gradients and remain inactive. Segebarth et al.[19] observed similar effects and, while interpreting them differently, also concluded that SDS modified the coalescence behavior.

SDS is surface active and will therefore adsorb to the bubble−solution interface, giving it an overall negative charge, estimated to result in an electrostatic potential of about −100 mV.[32] Bubbles approaching each other will experience repulsion arising both from steric effects due to the adsorbed layer and from the electrostatic charges. Low concentrations of SDS will cause repulsion between bubbles, suppressing their coalescence and, as we have suggested previously,[33] leading to a degree of “declustering” of the bubbles in the bubble cloud. This means that there will be less interaction between bubbles and, on average, a relatively larger distance between them compared with those bubbles with no net surface charge. As its concentration rises, SDS will also act as an electrolyte in the bulk solution

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(32) Grieser, F.; Ashokkumar, M. *Adv. Colloid Interface Sci.* **2001**, *423*, 89−90.

(33) Lee, J.; Kentish, S.; Ashokkumar, M. *J. Phys. Chem. B* **2005**, *109*, 5095.

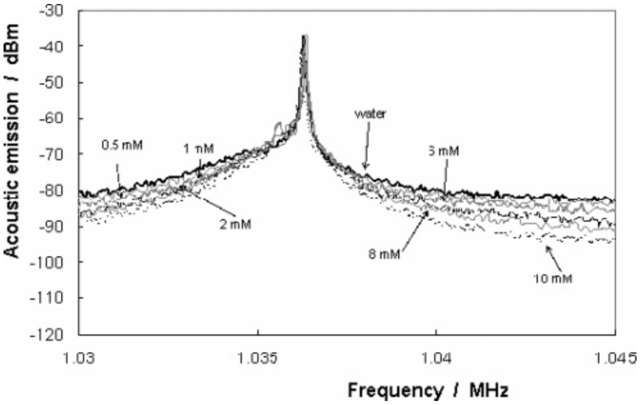

Figure 9. Second harmonic region of the acoustic emission spectra observed from aqueous solutions of zwittergent sonicated at 515 kHz. (Acoustic intensity at 2.2 W cm^{-2}.)

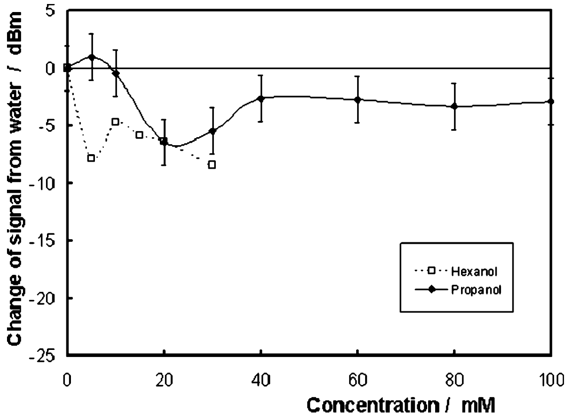

Figure 10. Broadband intensity averaged between 1.025 and 1.03 MHz from aqueous solutions in the presence of propanol and hexanol, sonicated at 515 kHz.

(the critical micelle concentration, cmc, is ~8 mM) and so mitigate any inter-bubble electrostatic effects. The observed variation is thus a balance of these two effects. It is estimated that the concentration at which the bulk electrolyte effects outweigh the electrostatic repulsion between bubbles for SDS is ~2 mM, as seen in Figures 6 and 7. As the concentration of bulk electrolyte increases, the signal returns to that seen with water, indicating that the "declustering" is no longer significant.

Effect of Adding Other Surfactants on Cavitation. In order to explore further the effects of interfacially adsorbed surfactants, two other surfactants were investigated. The data in Figure 8 shows that DTAC, a cationic surfactant which creates a positively charged bubble interface, gave results similar to to those obtained with SDS. However, DTAC is less surface active (its cmc is ~25 mM, compared with ~8 mM for SDS), so smaller amounts would be expected to adsorb to the bubble−water interface compared with SDS for a given bulk concentration. This would mean that the bulk electrolyte behavior of DTAC would become dominant at a lower concentration than SDS. The maximum effect of DTAC appearing at 1 mM is therefore consistent with the lower surface activity of DTAC compared with that of SDS.

Also shown in Figure 8 is the effect of "zwittergent", a zwitterionic surfactant. Here, the surface activity is comparable with that observed with SDS, but adsorption to the interface will lead to no net charge on the bubble, so the behavior would be expected to parallel that of SDS in the presence of a background salt. The second harmonic region of the spectrum is shown in Figure 9. Comparison with Figures 3 and 4 indicates that the behavior is different from that observed for SDS alone and much more similar to that seen when SDS is added in the presence of $NaClO_4$, although there is more variation in the signal. The data at low concentrations shown in Figure 8 support the argument of zwittergent behaving in a comparable manner to SDS in the presence of a background salt. At higher concentrations, there is a decrease in the broadband emission which is larger than for the other surfactants. The reason for this is unclear, but similar effects are observed for neutral solutes, as described below.

While the results discussed so far suggest strongly that the behavior of cavitation bubbles in the presence of low concentrations of ionic surfactants is influenced to a large extent by electrostatic effects, other effects, such as steric retardation of coalescence caused by the adsorbed layer, cannot be completely ruled out. Lee et al.[33] showed that the addition of small amounts of SDS retarded coalescence between cavitation bubbles and the presence of a background electrolyte reduced the effect, although the amount of coalescence did not return to that observed in water at higher SDS concentrations.

Effect of Non-ionic Solutes. To further investigate the importance of electrostatic effects, experiments were carried out using several other non-ionic solutes. Price et al.[10] and Sunartio et al.[34] have shown that bubble coalescence can be inhibited under various conditions by neutral solutes such as propanol or hexanol. Longer alcohols such as hexanol reduce coalescence very effectively (>80% reduction for 10 mM), whereas smaller alcohols such as propanol are less effective (~100 mM is required to reduce coalescence by 80%). This has been explained in terms of the interfacial concentrations of the alcohols, which depend on both the alcohol's concentration and its degree of hydrophobicity. Acoustic emission spectra from aqueous solutions containing propanol and hexanol were measured, and the results in terms of the change in broadband energy are shown in Figure 10. In the absence of electrostatic effects, the acoustic emission characteristics of alcohol and SDS solutions would be expected to be similar. Figure 8 shows that there is some effect at low concentrations, but this is close to the experimental uncertainty in the results and of a much lower magnitude than that observed with SDS (compare Figure 8, remembering that the *y*-axis is on a logarithmic scale). As the interfacial concentration of hexanol will be higher than that of propanol for the same bulk concentration, any effect on coalescence will be enhanced over that noticed at lower hexanol concentration, as is observed.

We also studied the effect of a polymer, poly(vinyl pyrollidinone), which is not surface active but can provide stabilization against bubble coalescence. A 1 wt % solution (corresponding to ~8 mM in monomer units) reduced the signal by around 4 dB from water, approximately equating to the behavior of hexanol in Figure 8. Thus, the observed changes for uncharged solutes are much less than for charged surfactants such as SDS or DTAC, confirming our hypothesis that electrostatic effects are of primary importance.

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(34) Sunartio, D.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2005**, *109*, 20044.

Effect of Solutes on Cavitation and Bubble Clouds. Returning to the effect of SDS (and DTAC) on the cavitation bubbles within the bubble cloud, our observations are clearly explained by assuming that the most important factor that is responsible for the observed changes at low concentrations of ionic surfactants is electrostatic repulsion between bubbles due to the adsorption of the charged surfactants at the bubble–solution interface. How the electrostatic effect leads to an increase in the harmonic intensity (and hence the total acoustic emission intensity, as shown in Figure 3) is discussed below.

In our previous report,[20] it was shown that most of the acoustic energy released at 20 kHz is in the form of broadband emission. This arises from the highly asymmetric collapse as well as shock wave generation characteristic of transient cavitation. At 515 kHz, acoustic emission is largely harmonic, arising mainly (>90%) from stable cavitation. The increase in the broadband and ultraharmonic emissions shown in Figure 1 as the acoustic intensity increases suggests that bubbles undergo symmetric oscillations at low driving pressures but that bubble oscillation becomes increasingly asymmetric as the pressure increases. Symmetric oscillation would be expected to lead to an increase in the symmetry of the bubble collapse. On addition of SDS at low concentrations (up to 2 mM), the broadband emission is eliminated and the energy in the harmonic emission goes up. This suggests that the number of bubbles that undergo asymmetric collapse decreases, with a concurrent increase in the number of bubbles that undergo symmetric collapse.

The adsorption of surface-active molecules prevents coalescence and leads to declustering of bubbles within bubble clouds, enhancing the sphericity of collapse due to a reduced influence on the sound field of neighboring bubbles, meaning that each bubble experienced a more uniform sound field, leading to a more even distribution of bubble sizes and an enhancement in the symmetry of the collapse. Symmetric collapse would lead to higher maximum temperatures and pressures and increased emission of acoustic energy. The effect that SDS has on the bubble field is further supported by the recent observations by Tervo et al., who showed[35] that subharmonic emission is also influenced by the behavior of bubble clusters as well as individual bubbles.

These explanations are consistent with reported results on the effect of charged surfactants on sonoluminescence intensity. Low amounts of charged surfactants such as SDS enhanced the SL intensity in aqueous solutions by up to 3-fold, but the intensity returned to the level observed in water upon addition of either higher concentrations of the charged surfactants or an electrolyte, such as $NaClO_4$. The trends observed for the SL intensity are thus the same as those seen here for the total acoustic energy output as well as the changes in the broadband spectral intensities. The increase in SL intensity may be caused by an increased number of active bubbles that undergo enhanced symmetrical collapse, leading to higher cavitation temperatures.

The correlation between these different measurements can be seen in Figure 11, which shows the relative changes in acoustic emission, the extent of bubble coalescence,[33] and the SL emission intensity[9] for SDS solutions in the presence and in the absence of salt in experiments using comparable ultrasound intensities. The extent of coalescence does not revert back to the water level either in the presence of higher SDS concentration or in the presence of an electrolyte, supporting our argument that coalescence alone is not responsible for the changes in the acoustic emission characteristics. A similar trend is seen for both SL and acoustic emission, suggesting that these changes have the same origin. The electrostatic effect causes a degree of declustering resulting in an increase in the collapse intensity of the bubbles, which in turn leads to the observed increase in both acoustic emission and SL intensity at low concentrations of charged surfactants.

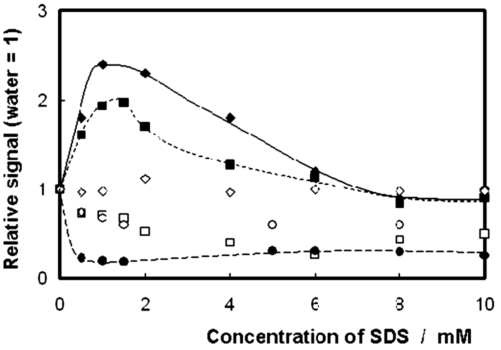

Figure 11. Comparison of acoustic energy emission (■, □), SL emission[9] (◆, ◇), and bubble coalescence[30] (●, ○) from solutions of SDS (filled points) and SDS + 0.1 M $NaClO_4$ (open points), sonicated at 515 kHz.

While accounting for their observations in terms of inhibiting bubble coalescence, Segebarth et al.[19] objected to the contention that electrostatics play a fundamental role in bubble interactions, since the Debye length for a 1 mM SDS solution is ~10 nm. Their calculations suggested that, for electrostatic repulsion to be important, bubble volume fractions should be ~45%, which is unreasonably high. We offer the following alternative approach using values similar to those used in their calculations.

In a bubble field, it is estimated that bubbles move with velocities in the region of 0.2 m s^{-1}. A 1 μm radius bubble moving at this velocity would therefore traverse a volume of 6.3×10^{-7} cm^3. Our reactor contained 130 cm^3 of solution so that, on average, for the total volume to be explored, an average of $\sim 2 \times 10^8$ bubbles would be needed, giving a bubble density of $\sim 1.6 \times 10^6$ bubbles cm^{-3}. This corresponds to a volume occupied per cubic centimeter of $\sim 6.7 \times 10^{-6}$, which is comparable with other reported values.[36] This represents the bubble fraction at which, on average, every bubble would undergo just one collision per second with another bubble. Within a cluster of bubbles at an antinode, a much higher bubble density would be expected and hence a greater rate of collision. Therefore, even though electrostatic effects will play a part only at very small interbubble separations, we are confident that such conditions will apply to our results.

Conclusions

The results reported here demonstrate that acoustic emission is a very useful technique for providing information on cavitation bubbles and their interactions. Low concentrations of charged surface-active agents such as SDS and DTAC have a significant effect on cavitation behavior at 515 kHz in enhancing bubble–bubble repulsions and inhibiting coalescence. It has been demonstrated that electrostatic interaction between bubbles is

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(35) Tervo, J. T.; Mettin, R.; Lauterborn, W. *Acta Acust.* **2006**, *92*, 178.

(36) Burdin, F.; Tsochatzidis, N. A.; Guiraud, P.; Wilhelm, A. M.; Delmas, H. *Ultrason. Sonochem.* **1999**, *6*, 43.

the major parameter that is responsible for the observed changes in the acoustic emission characteristics of cavitation bubbles at 515 kHz. Bubble collapse becomes more symmetric, leading to greater emission of acoustic energy. This is consistent with previous reports on sonochemistry and sonoluminescence emission from surfactant solutions.

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