Imaging of the influence of surfactants on bubble structures

R. Mettin[1,*], T. Nowak[1], M. Ashokkumar[2], G. Price[3], D. King[3], W. Lauterborn[1], F. Grieser[2]

[1] *Drittes Physikalisches Institut, Universität Göttingen, Germany*

[2] *School of Chemistry, University of Melbourne, Australia*

[3] *Department of Chemistry, University of Bath, UK*

* *Email: R.Mettin@physik3.gwdg.de*

Introduction

The influence of surfactants on ultrasonic cavitation effects has recently been investigated in greater detail [1, 2]. Variations in sonochemical activity, sonoluminescence, and acoustic spectra have been reported for various concentrations and for different types of surface active solutes [3]. In particular, it was observed that charged surfactants, like sodium dodecyl sulfate (SDS) or dodecyl trimethyl ammonium chloride (DTAC), can significantly increase multibubble sonoluminescence emission [1, 4] and the chemical yield of H_2O_2 [2]. At the same time, in the acoustic emission spectrum the line width of the first harmonic is narrowed [2] and the broadband acoustic emission is quenched [3]. Additional parameters for this effect to be observed are surfactant concentrations of 1 - 2 mM and an acoustic frequency around $500\,kHz$ [5]. Addition of much more surfactant as well as a background electrolyte (NaCl or $NaClO_4$) reduces and finally removes the effects. It is also striking that the indicated influence of charged surfactants on acoustic cavitation seems not to be observable or significant for a horn transducer driven at an acoustic frequency of $20\,kHz$: The spectral characteristics (only few harmonics plus decaying braodband noise [6]) do not change much with addition of SDS [7].

Taken all facts together, a plausible explanation for the observations is an inhibition of bubble coalescence and/or clustering: the surfactant molecules adsorb to the bubble surface and lead to an electrostatic repulsive force between them. In turn, the short range interaction is altered in a way to prevent bubble agglomeration or merging [1, 2]. As the total acoustic cavitation process is a very dynamic one with permanent bubble nucleation, translation, coalescence, and splitting [8], the microscopic electrostatic forces can influence the whole bubble population and their spatial structures, and thus the macroscopic or net effects may as well be changed. If the merging of small bubbles is hindered, they need more time to grow to sizes where they either get surface unstable (and disintegrate or split again) or are driven to pressure nodes by the primary Bjerknes force (and become inactive "degassing" bubbles). Thus their average lifetime expands, leading to redistribution of acoustic energy from the broadband to the harmonics [3]. If without surfactant the bubble growth is dominated by merging and not by rectified diffusion, the whole bubble population shifts to smaller sizes; this has indeed been found for the indicated parameters from void volume measurements [9] and from sonoluminescence in pulsed sound fields [10]. In the extreme case,

no larger degassing bubbles are observed at all, which has also been reported [2] and is visible in Fig. 1.

The addition of surfactants also lowers the surface tension at the gas-liquid interface. An indication that the observed effects are nevertheless due to electrostatics and not to surface tension is the disappearance for added electrolytes: They might even decrease further the surface tension [2], but "short-circuit" or shield the electrostatic repulsion of neighbored bubbles.

Abbildung 1: Cavitation at $515\,kHz$ (frame width $\approx 1\,cm$, exposure time 0.8 ms). SDS: 1 mM, Salt: $0.1\,M\ NaClO_4$.
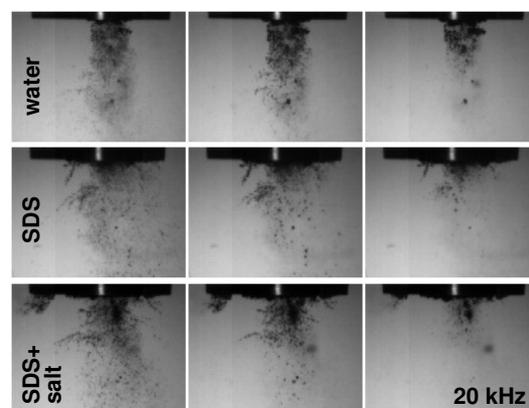

Abbildung 2: Cavitation below a sonotrode tip of diameter 1 cm at $20\,kHz$ (interframe time $11\,\mu s$, exposure time $2\,\mu s$).

The fact that the indicated effects of surfactants are not observed at $20\,kHz$ sonotrodes might be explained by a "frequency" argument or by a "transducer" argument:
The first would state that there is a fundamental difference of cavitation at $20\,kHz$ (compared to $500\,kHz$) that hinders the surfactant influence. This could be due to stability aspects (more "transient" cavitation) or magnitude of secondary Bjerknes forces [11] in relation to electrostatic repulsion.
The second idea would claim that the specific nature of the ultrasonic transducer is responsible for the difference. A sonotrode field and the respective bubble structures [8] are very different compared to the field in the $515\,kHz$ re-

actor [5]. In particular, the sonotrode field typically has a strong traveling wave component decaying far from the sonotrode tip, while the reactor yields more a standing wave field. If so, it would rather be coincidence to observe (or not observe) the surfactant effects at the one or the other frequency, just depending on the transducer type.

While a closer examination of the first argument might involve detailed calculations of inter-bubble forces including electrostatics, we suggest investigation of the second idea by inspection of (a) sonotrode fields at high frequency and (b) standing wave fields at low frequency. Here, we report on first results of (a).

Cavitation images

First, we show typical cavitation images at 515 kHz in the Undatim reactor, see Fig. 1. In pure water (left), the larger "degassing" bubbles are visible. In water and 1 mM SDS, they do not appear (middle). Adding 0.1 M $NaClO_4$ lets return the large bubbles. They now have frequently a rather aspherical shape, which is indication of the reduced surface tension.

As a comparison, Fig. 2 shows typical frames of cavitation below a 20 kHz sonotrode. Three successive frames from high-speed recordings are shown in each row. Differences between pure water (top), water and 1 mM SDS (middle) and additional 0.1 M $NaClO_4$ are rather subtle and are not always observable. However, the "active" region on the sonotrode tip, i.e. the zone where bubbles attach directly, is growing clearly for SDS and SDS + salt. This is probably a surface tension effect. Also, the cavitating region appears more extended, which however might be a consequence of the larger active zone. The bubble sizes might be slighly smaller for SDS than for the other two cases, but this impression might result from wishful thinking and is not yet really evaluated.

In Fig. 3 and Fig. 4 we show exposures of a 1 mm diameter sonotrode, driven at about 200 kHz at two different voltages. Again, three consecutive frames are given for water, water + SDS, and water, SDS + $NaClO_4$ (same concentrations as before). In all cases, cavitation is clearly visible and appears similar. Again, there might be subtle differences in cavitation zone extension or active area at the tip, but the rough picture is the same. The only obvious and reproducible difference was that with water + SDS the cavitation zone was almost all the time going upward, like in Fig. 3, second row. This might be an impedance effect, induced by surface tension, leading to a preferred different oscillation mode of the tip.

Conclusion

We have tried to image surfactant effects in acoustic cavitation for different frequencies and transducer set-ups. While the picture is strikingly different for the 515 kHz Undatim reactor, images of sonotrode tips driven at 20 kHz and at 200 kHz look rather similar for pure water, SDS, and SDS + salt solutions. This suggests that the observed phenomena may be partly related to the type of transducer arrangement. However, this statement is only preliminary, as more experiments might give a clearer
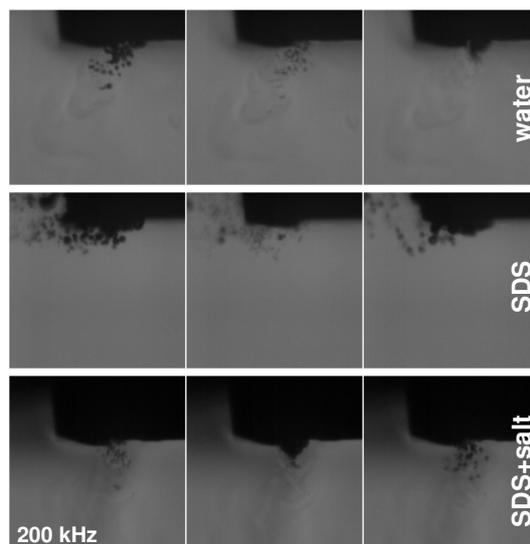

Abbildung 3: Cavitation at a 200 kHz sonotrode at 340 V (frame width 0.65 mm, interframe time 100 μs, exposure 2 μs).
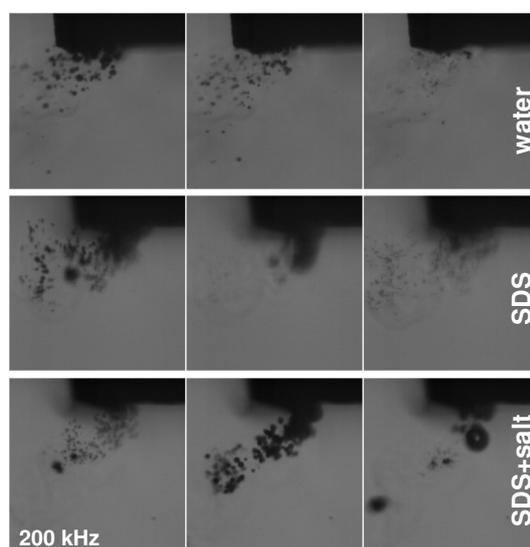

Abbildung 4: As Fig. 3 at about 480 V, same scale.

and maybe different answer in the future. In particular, it appears interesting to investigate 20 kHz standing wave fields, and sonotrodes of even higher frequency. Complementary, sonoluminescence, sonochemistry, and acoustic spectra should be examined for the different transducer set-ups as well.

Literatur

[1] M. Ashokkumar *et al.*, J. Phys. Chem. B **101**, 10845 (1997).
[2] N. Segebarth *et al.*, Chem. Phys. Chem. **2**, 536 (2001).
[3] M. Ashokkumar *et al.*, J. Am. Chem. Soc. **129**, 2250 (2007).
[4] K. Barbour *et al.*, J. Phys. Chem. B **103**, 9231 (1999).
[5] Observations in an Undatim UL03/1 reactor, up to 8 W/cm² at 515 kHz in 130 ml solution.
[6] G. J. Price *et al.*, J. Phys. Chem. B **109**, 17799 (2005).
[7] Price *et al.*, submitted.
[8] R. Mettin, in: A. A. Doinikov (ed.): *Bubble and Particle Dynamics in Acoustic Fields: Modern Trends and Applications*, Research Signpost, Kerala (India) 2005, 1.
[9] J. Lee *et al.*, J. Phys. Chem. B **109**, 5095 (2005).
[10] J. Lee *et al.*, J. A. Soc. Chem. **127**, 16810 (2005).
[11] R. Mettin *et al.*, Phys. Rev. E **56**, 2924 (1997).