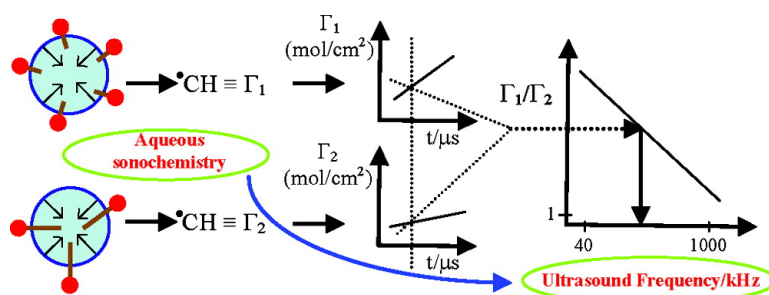


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A Chemical Sensor That Can Detect the Frequency of Ultrasound

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Sensors and sensory systems come in various forms. Classical examples are rhodamine dyes¹ and the Fricke and terephthalate² dosimeters. Temperature measurements with fluorescent dyes and proteins³ and detection of humidity, gases, and solution pH/ions as well as biosensing with polymeric materials⁴ have been described, while synthetic receptors⁵ and nanoparticles⁶ have potential applications in chemo- and biosensing. In this study a physicochemical-based sensory system that can detect ultrasound frequency is described.

Exposure of water to ultrasound forms cavitation bubbles⁷ that collapse almost adiabatically resulting in high temperatures⁸ at which water dissociates into $\cdot\text{H}$ and $\cdot\text{OH}$ radicals.⁹ Unlike photolysis and radiolysis, where radiation energy is converted into predictable chemical yields, sonochemical yields depend not only on the ultrasound energy but also on any parameter that affects acoustic cavitation, e.g., ultrasound frequency, geometry of the exposure system, viscosity, and ambient pressure.¹⁰ Consequently, no universally applicable relationship exists between the chemistry associated with multibubble cavitation and any physical characteristic of the ultrasonic wave. Herein is described a quantitative relationship between ultrasound frequency and chemical yields during sonolysis of aqueous surfactant solutions.

Compared to hydrophilic solutes, surfactants preferentially adsorb at the interface of cavitation bubbles,¹¹ and it has been shown that adsorption of *n*-alkyl sulfate or sulfonate surfactants is limited by their kinetic adsorption properties.¹² This effect can be observed by detecting $\cdot\text{CH}$ radical yields following sonolysis, which correlate to the amount of surfactant adsorbed at the gas/solution interface of cavitation bubbles.¹² As the bulk concentration of surfactant is increased, a maximum plateau in the $\cdot\text{CH}$ yield is attained that is greater in magnitude following sonolysis (354 kHz) of aqueous sodium pentane sulfonate (SPSo) solutions than that for sodium dodecyl sulfate (SDS) solutions.¹³ This result is consistent with dynamic surface tension studies which have shown that although a surfactant with a relatively small *n*-alkyl chain length possesses a lower thermodynamic tendency to adsorb at the gas/solution interface, its rate of adsorption is faster.¹⁴ Interestingly, when the ultrasound frequency was increased from 354 kHz to 1 MHz, both SPSo and SDS adsorbed to the bubble surface to similar limiting $\cdot\text{CH}$ radical yields (i.e., $\text{CH}_{\text{SPSo}}/\text{CH}_{\text{SDS}} = 1$), indicating frequency dependence.¹³ Comparing two similar sonochemical reactions in this way is useful in that the effect of a limited number of variables is investigated.^{13,15} In the example above, the relative ability of two surfactants to adsorb at the interface of cavitation bubbles.

Aqueous solutions (1 mL) of either SDS or sodium butane sulfonate (SBSO) were exposed to ultrasound, and the effect of ultrasound frequency in the range 40.1 kHz to 1057 kHz on the $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio was investigated. The total $\cdot\text{CH}$ yield (CH_{TOT}) was detected using spin trapping with 3,5-dibromo-4-nitrosobenzenesulfonic acid-*d*₂ (DBNBS-*d*₂; 2.7 mM) and electron

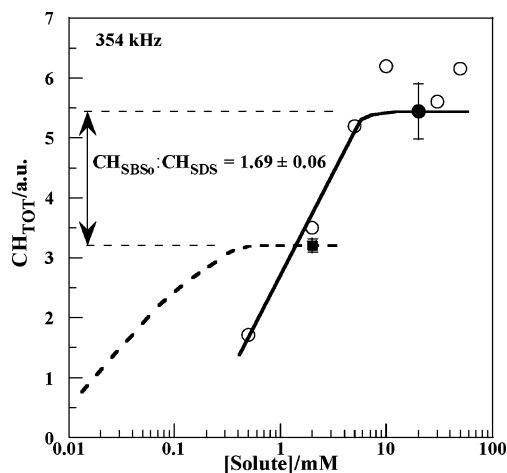


Figure 1. Determination of the $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio from CH_{TOT} observed at plateau surfactant concentrations.

spin resonance (EPR) spectroscopy (see Supporting Information). As described in detail elsewhere,¹³ 1 mL of aqueous SDS (Fluka, $\geq 99\%$) or SBSO (Fluka, $\geq 99\%$) solution was transferred into a glass exposure tube and reproducibly clamped into a 300 mL water bath (20 °C) in contact with flat plate transducers (ELAC-Nautik, GmbH) that were geometrically equivalent and operated at frequencies of 40.1, 354, 614, 821, and 1057 kHz. Power input to the transducers was 60 W. Sonolysis times were 3 min at all frequencies except 1057 kHz (5 min) and were chosen in a region where CH_{TOT} had a linear dependence on sonolysis time. Prior to sonolysis, the 1 mL samples were bubbled with argon (5 min) to avoid the formation of organic peroxy radicals that cannot be spin trapped by DBNBS-*d*₂.

The maximum plateau yield of CH_{TOT} for aqueous SBSO solutions occurred between 5 and 10 mM (Figure 1, open circles). An accurate value for CH_{TOT} at the plateau was obtained by sonolysis of aqueous SBSO solutions at 20 mM (a plateau concentration) a total of 8 times (Figure 1, filled circle; mean \pm SD).

Previous studies showed that the CH_{TOT} plateau arises at bulk SDS concentrations of 0.5 to 1 mM at ultrasound frequencies in the 42 to 1057 kHz range.^{12,13,16} At 354 kHz, this is represented by the dashed line in Figure 1. Similarly to the SBSO experiment described above, CH_{TOT} at the plateau concentrations was also determined following sonolysis (354 kHz) of 8 separate SDS (2 mM) solutions (Figure 1, filled square; mean \pm SD). CH_{TOT} for SBSO was divided by that of SDS to give the $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio for 354 kHz sonolysis (see Figure 1).

Solutions of SBSO (20 mM) or SDS (2 mM) were sonicated, and the $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio was determined in this way as a function of ultrasound frequency, as shown in Figure 2. To understand the linear relationship between the $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio and ultrasound frequency, sonochemically active bubbles need to be described and the surfactant adsorption process considered. Sonochemically active

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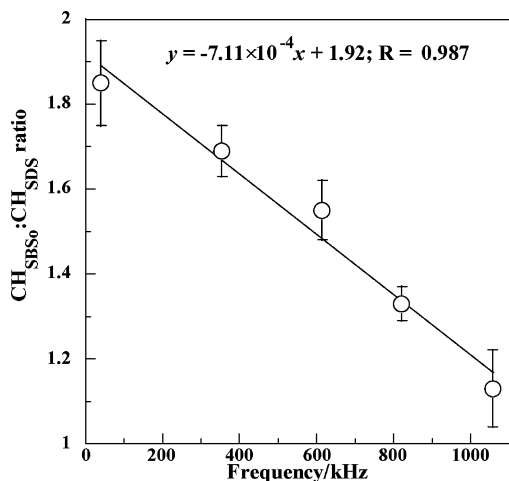


Figure 2. A calibration curve for the $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio as a function of ultrasound frequency.

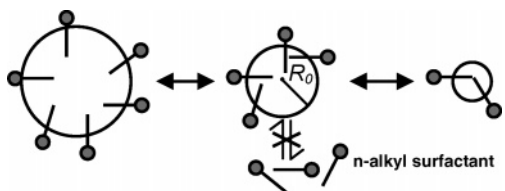


Figure 3. Adsorption of *n*-alkyl surfactants at the gas/solution interface of rapidly oscillating, HES cavitation bubbles is a nonequilibrium process.

bubbles are either stable or transient in nature. Leighton defined sonochemically active, stable bubbles as high-energy stable (HES) bubbles.¹⁷

HES bubbles oscillate about an equilibrium radius (R_0 ; Figure 3) and eventually grow in size over hundreds of acoustic cycles to a radius (R_T) where they can oscillate in resonance with the applied ultrasonic field. This is followed by rapid growth during a rarefaction half-cycle to a maximum size (R_{max}) at which the bubble collapses to form a hot spot. Since transient bubbles exist for only a few acoustic cycles (i.e., 3 to 60 μs at 42 to 1057 kHz), there is little time for surfactants to adsorb at the gas/solution interface of these bubbles during the growth and collapse phases.¹³ A similar situation arises for HES bubbles during rapid growth from R_T to R_{max} and the collapse phase. However, surfactants can adsorb to the interface of HES bubbles during the cyclic growth phase (Figure 3). Surfactant adsorption at HES bubble interfaces needs to be considered in describing Figure 2.

The oscillation rate of HES bubbles increases with increasing ultrasound frequency. However, R_T and oscillation amplitude decrease. It has been shown that this results in a reduced rate of change of interfacial area of HES bubbles at higher ultrasound frequencies.¹³ Therefore, the ability of SDS to accumulate at the gas/solution interface of HES bubbles compared to SBSO increases at higher frequencies, due to the greater thermodynamic tendency for SDS to adsorb to the gas/solution interface.¹³ Although this discussion is consistent with the decreasing trend in $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ ratio observed with increasing frequency, it does not explain the observed linear dependence (Figure 2).

The rate of adsorption of SDS to a newly formed gas/solution interface is not diffusion controlled at short interfacial lifetimes but is limited by the presence of an adsorption barrier.¹⁸ The origins of this adsorption barrier probably lie in electrostatic interactions of ions at the interface and changes in entropy associated with the exchange of water at the interface with surfactant from the bulk.¹⁸

In this region of short interfacial lifetimes and relatively slow adsorption rates, there is a linear decrease in surface tension as a function of surface lifetime.^{18,19}

Although an increasing ultrasound frequency (as discussed above) causes the rate of change of surface area of HES bubbles to decrease, it can be concluded from Figure 2 and from dynamic surface tension studies^{18,19} that it does so in a region where there is a linear dependence between the amount of SPSO (or SDS) adsorbed to the interface of HES bubbles (Γ) and the interfacial lifetime. Therefore, taking a ratio of the amount of surfactant adsorbed to the bubble interface at a given interfacial lifetime (i.e., $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}} \equiv \Gamma_{\text{SBSO}}/\Gamma_{\text{SDS}}$) will always result in a linear change in the ratio as a function of frequency. On the basis of this discussion, the amount of surfactant adsorbed to the interface of HES bubbles under continuous ultrasound exposure must be far from that expected under equilibrium adsorption conditions.

It has been shown that $\text{CH}_{\text{SBSO}}/\text{CH}_{\text{SDS}}$ is independent of ultrasound intensity (therefore the number of bubbles)¹³ and geometry²⁰ of various exposure systems in the frequency range of 40.1 to 1057 kHz (see Supporting Information for currently known constraints). The possibility that the calibration curve in Figure 2 is universally applicable to any ultrasound apparatus requires further investigation, and like any calibration curve, variations due to solution purity (therefore the rate of adsorption of surfactants on the surface of HES bubbles) need also be considered.

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Supporting Information Available: EPR spectra on sonolysis of aqueous SBSO and SDS solutions. Currently known constraints for Figure 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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