

Effects of Pulsed Ultrasound on the Adsorption of *n*-Alkyl Anionic Surfactants at the Gas/Solution Interface of Cavitation Bubbles

Limei Yang,[†] Joe Z. Sostaric,[‡] James F. Rathman,[§] Periannan Kuppusamy,[‡] and Linda K. Weavers^{*,†}

Department of Civil and Environmental Engineering and Geodetic Science, Center for Biomedical EPR Imaging, Davis Heart and Lung Research Institute, and Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, Ohio 43210

Received: July 6, 2006; In Final Form: December 7, 2006

Sonolysis of argon-saturated aqueous solutions of the nonvolatile surfactants sodium dodecyl sulfate (SDS) and sodium 1-pentanesulfonate (SPSo) was investigated at three ultrasonic frequencies under both continuous wave (CW) and pulsed ultrasound. Secondary carbon-centered radicals were detected by spin trapping using 3,5-dibromo-4-nitrosobenzenesulfonic acid (DBNBS) and electron paramagnetic resonance (EPR) spectroscopy. Following sonolysis, $\cdot\text{CH}_2\cdot$ radicals were observed for both surfactants under both sonication modes. Under CW at 354 kHz, the maximum plateau $\cdot\text{CH}_2\cdot$ radical yield was higher for SPSo than for SDS, indicating that SDS, which is more surface active under equilibrium conditions, accumulates at the gas/solution interface of cavitation bubbles to a lesser degree, compared with the less surface active surfactant, SPSo. However, after sonolysis (354 kHz) under pulsed ultrasound with a pulse length of 100 ms and an interval of 500 ms, the $\cdot\text{CH}_2\cdot$ radical yield at the plateau concentrations was higher for SDS than for SPSo due to increased amounts of SDS accumulation on the bubble surfaces. In contrast to the findings following sonolysis at 354 kHz, sonolysis of aqueous surfactant solutions at 620 kHz and 803 kHz showed a higher $\cdot\text{CH}_2\cdot$ radical yield for SDS compared with SPSo under CW but lower $\cdot\text{CH}_2\cdot$ radical yield with increasing pulsing interval, indicating a frequency dependence on accumulation. Results indicate that pulsing the ultrasonic wave has a significant effect on the relative adsorption ability of *n*-alkyl surfactants at the gas/solution surface of cavitation bubbles.

Introduction

Sonochemical reactions are initiated by the ultrasound induced formation, growth, and fast, almost adiabatic collapse of cavitation bubbles in a liquid. The extremely high temperatures and pressures formed in collapsing cavitation bubbles in aqueous solutions lead to the thermal dissociation of water vapor into reactive hydroxyl radicals and hydrogen atoms.¹ In the absence of any solutes, these primary radicals of sonolysis mostly recombine to form water, hydrogen gas, and hydrogen peroxide. However, when aqueous sonolysis is conducted in the presence of organic solutes, a number of chemical processes can occur, depending on the physical and chemical nature of the solute.

Volatile organic solutes can evaporate into cavitation bubbles where they may react with the primary radicals of sonolysis or thermally decompose. Nonvolatile organic solutes at millimolar concentrations and above can react with $\cdot\text{OH}$ radicals, which escape into the bulk solution, and generally do not undergo pyrolysis, unless the bulk solute concentration is relatively high or if the nonvolatile solute has surfactant properties.^{2,3} It has been shown that the main pathway of decomposition of nonvolatile surfactants is by reaction with hydrogen atoms and

$\cdot\text{OH}$ radicals and/or pyrolysis, both of which occur at the cavitation bubble interface at relatively low bulk solute concentrations.⁴

A number of studies have investigated nonvolatile surfactants in sonochemistry^{5–10} and sonoluminescence (SL)^{11–13} as a means of understanding the effects of surfactants on the chemical and physical nature of acoustic cavitation. The results indicate that the rate of reaction or SL intensity depends on the ability of the surfactants to accumulate at the gas/solution interface of cavitation bubbles. It has been shown that the adsorption of simple alcohols to the gas/solution interface is governed by the equilibrium Gibbs surface excess.¹⁴ However, recent studies suggest that equilibrium adsorption does not always occur, especially for relatively long *n*-alkyl chain possessing surfactants.^{6,7} Furthermore, it has been shown that the accumulation of surfactants at the cavitation bubble interface depends on the ultrasonic frequency, intensity, operation mode, and surfactant properties.^{6,7,9,10}

The EPR spin-trapping technique has been used for identifying short-lived, organic free-radicals formed by sonolysis of various volatile and nonvolatile solutes in aqueous solutions.^{15–17} Furthermore, EPR and spin-trapping studies have shown that the physicochemical properties of nonvolatile surfactants, namely, chemical structure and dynamic and equilibrium surface activity, play an important role in the accumulation of surfactants at the bubble surfaces.⁶ When aqueous solutions of ionic sulfate or sulfonate surfactants possessing a single *n*-alkyl chain are exposed to ultrasound at concentrations below the critical micelle

* To whom correspondence should be addressed. Phone: (614)292-4061. Fax: (614)292-3780. E-mail: weavers.1@osu.edu.

[†] Department of Civil and Environmental Engineering and Geodetic Science.

[‡] Center for Biomedical EPR Imaging, Davis Heart and Lung Research Institute.

[§] Department of Chemical and Biomolecular Engineering.

concentration, the $\cdot\text{CH}$ radical yield increases until a maximum plateau yield is observed; i.e., the further addition of surfactant to the bulk solution no longer affects the carbon-centered radical yield.

It was found that, at the plateau concentrations, the radical scavenging efficiency of a homologous series of *n*-alkyl anionic surfactants exposed to ultrasound (47 kHz) in water increased with decreasing *n*-alkyl chain length.⁶ These results indicated that, not only the equilibrium properties of surfactants, but also their dynamic ability to diffuse in and out of the gas/solution interface of cavitation bubbles governed their maximum attainable interfacial concentration.⁶ It was later shown that, by increasing the frequency of sonolysis from 47 kHz to 1 MHz (thereby decreasing the rate of change of surface area of the cavitation bubble), the surfactant with the longer *n*-alkyl chain (SDS) eventually reached a similar radical scavenging efficiency as the surfactant possessing the shorter *n*-alkyl chain (SPSo).⁷ Interestingly, the maximum attainable $\cdot\text{CH}$ radical yield following sonolysis of SDS solutions compared with that of SPSo solutions (referred to as the $\text{CH}_{\text{SDS}}:\text{CH}_{\text{SPSo}}$ ratio) had a strong dependence on the ultrasound frequency, but was independent of any changes in the ultrasound intensity, at constant frequency. This was an important observation because any changes in ultrasound frequency during a sonochemical reaction also result in an unknown variation in "the amount of energy being converted by acoustic cavitation bubbles in producing a sonochemical effect."⁷ Thus, by considering the effect of ultrasound frequency on the $\text{CH}_{\text{SDS}}:\text{CH}_{\text{SPSo}}$ ratio, the energy supplied to the system was no longer a dependent parameter. Using this comparative method, conclusions were made about the effect of frequency on the relative ability of surfactants to accumulate at the gas/solution interface of cavitation bubbles without any underlying effects due to changes in energy input to the system that inherently occur with frequency or, as in the current work, pulsing.

With aims to improve the efficiency of ultrasonic degradation of surface active pollutants, we have focused our recent work¹⁰ on the effect of pulsing ultrasound. One of the advantages of pulsed ultrasound is the generation of cavitation bubbles with a longer lifetime than CW. The longer lifetime may allow more time for relatively large, surface active solutes to accumulate at the gas/solution interface of cavitation bubbles, where higher temperatures and radical concentrations exist. This previous work showed that the degradation of surfactants was enhanced under pulsed ultrasound, and we proposed that it was due to increased adsorption of surfactants on bubble surfaces. The enhancements were dependent on pulse length, pulse ratio, surfactant concentration, and equilibrium surface activity.¹⁰ We inferred from our results that surfactants that are more surface active under equilibrium conditions than similarly structured non-surfactants require more time to accumulate on bubble surfaces. That work supports the results of Sostaric and Riesz.⁷ However, to date, there is no direct evidence that pulsing the ultrasonic wave enhances the ability of surfactants to accumulate at the gas/solution surface of cavitation bubbles.

In order to gain a better understanding of the effect of pulsing on the ability of surfactants to accumulate at cavitation bubble interfaces, we used the methods of EPR and spin-trapping, following the work of Sostaric and Riesz.^{6,7} Similar to when the frequency is changed,⁷ when the sonication mode is switched from continuous to pulsed, the energy supplied to the system and that converted by the cavitation bubbles in producing a sonochemical effect may change. However, by using the comparative method, we assume that the number of bubbles,

the intensity of their collapse, and the absolute radical yield do not affect $\text{CH}_{\text{SDS}}:\text{CH}_{\text{SPSo}}$; therefore, the $\text{CH}_{\text{SDS}}:\text{CH}_{\text{SPSo}}$ ratio gives direct information on how adsorption of one surfactant relative to another surfactant is affected by pulsing the ultrasonic wave, compared with continuous irradiation. Thus, in the current study, the sonolysis of SDS and SPSo in aqueous solutions was studied to explore their relative accumulation in the interfacial region of cavitation bubbles. A water-soluble, nonvolatile, aromatic nitroso spin trap, 3,5-dibromo-4-nitrosobenzenesulfonic acid (DBNBS)¹⁸ was used in the current study because it has been shown to be a particularly effective spin trap for carbon-centered radicals formed during sonolysis.^{4,6,7} Pulse intervals and frequencies of the ultrasonic wave were varied to explore the effects of these parameters on the relative accumulation of SDS to SPSo at cavitation bubble surfaces.

Experimental Methods

Materials. Sodium dodecyl sulfate (SDS, $\geq 99.0\%$) and sodium 1-pentanesulfonate (SPSo, $\geq 99.0\%$) were purchased from Fluka. 3,5-Dibromo-4-nitrosobenzenesulfonic acid (DBNBS) was synthesized according to the method of Hamilton et al. (purification procedure followed "Synthesis type C"; see Table 1 in ref 19). Milli-Q filtered water was used for all sample preparation.

Sonochemical Experiments. All sonochemical experiments were carried out in a glass exposure vessel suspended in a bath containing 300 mL of water, which was used to couple a USW 51–52 ultrasonic transducer (ELAC Nautik, Inc., Kiel, Germany) operating at 354, 620, or 803 kHz. Pulse signals were produced by a SM-1020 Function/Pulse generator (Signametrics Corporation, Seattle, WA) and amplified by an AG 1021 linear amplifier (T & C Power Conversion, Inc., Rochester, NY). The amplifier was capable of generating ultrasonic waves in either continuous or pulse modes. A 100 MHz 54501A digitizing oscilloscope (Hewlett-Packard) was used to detect the pulse signals received by the transducer. The power input into solution for both CW and pulsed ultrasonic modes was 48 W, as measured by calorimetry.

Aqueous sample solutions (1 mL) containing DBNBS (8.2 mM) and select concentrations of surfactants were placed in a custom-made glass tube (i.e., the exposure vessel) with external dimensions of 13 mm \times 140 mm and a flat and thin bottom with a thickness of 0.7 mm. Before sonicating the sample solution, the coupling water (300 mL) in the main ultrasonic bath was sonicated for 10 min to reach a steady-state temperature of 20 ± 1 °C controlled by a 1006S Isotemp cooling system (Fisher Scientific, Pittsburgh, PA). During this presonation time, the exposure vessel was sealed using a rubber septum ("suba seal", Aldrich) and bubbled with argon for 5 min. The ultrasound system was then momentarily switched off during which time the exposure vessel was promptly positioned in the center of the ultrasonic bath at a depth so that the sample solution inside the vessel was at the same level as the water in the reactor bath. In this way, the exposure vessel could be positioned accurately and reproducibly. A sonolysis control experiment of 8.2 mM DBNBS solution was conducted, and no significant sonolytic decomposition products were observed.

EPR Measurements. DBNBS was used for spin-trapping carbon-centered radicals generated by sonolysis of aqueous surfactant solutions. The DBNBS-CH radical adducts are stable and do not decay significantly over the course of the experiment. Immediately after sonication, the sample solution was transferred to a 50 μL calibrated pipet (VWR International, West Chester, PA) for EPR analysis. EPR measurements were conducted on

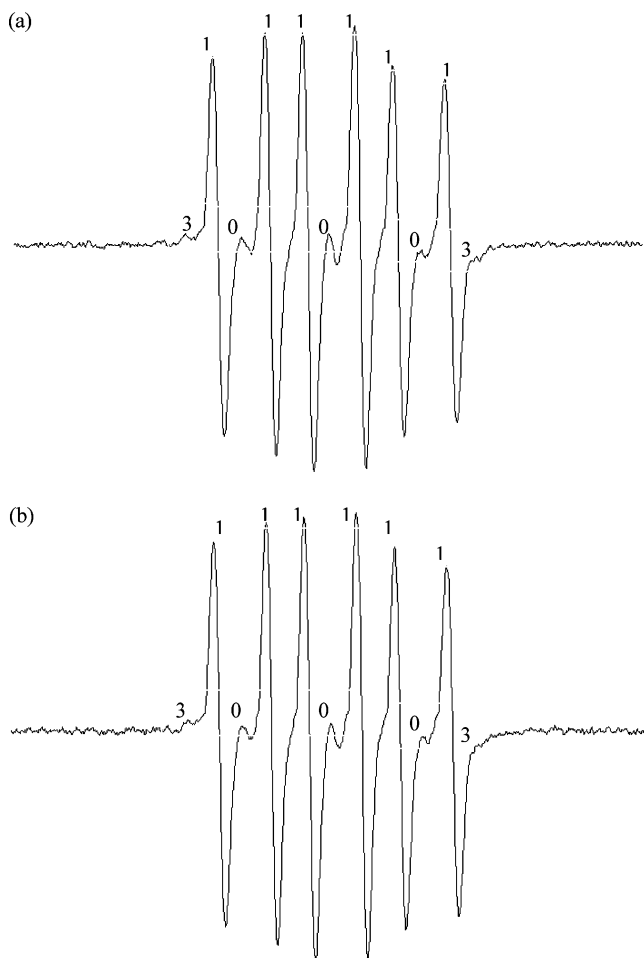


Figure 1. EPR spectra following sonolysis of 1 mM SDS in the presence of 8.2 mM DBNBS at 354 kHz under (a) CW (b) pulsed ultrasound with a pulse length of 100 ms and an interval of 500 ms. Lines labeled 1, 3, 0 represent secondary ($-\dot{\text{C}}\text{H}-$), methyl ($\dot{\text{C}}\text{H}_3$), and tertiary ($\dot{\text{C}}\text{R}_3$) radical spin adducts, respectively.

an X-band EMX spectrometer (Bruker BioSpin GmbH, Germany) operating at room temperature with a microwave frequency of 9.88 GHz and power of 15.8 mW. Other instrument settings were as follows: center field 3516 G, sweep width 100 G, modulation frequency 100 kHz, modulation amplitude 1 G, signal channel conversion 40.960 ms, time constant 81.920 ms, and sweep time 41.943 s.

Results

Identification of Spin-Trapped Radicals. EPR spectra of the spin adducts of DBNBS exhibit a triplet due to the interaction of the ^{14}N nucleus of the nitroxide group of the spin trap together with the secondary splitting that arises from the magnetic nuclei of the trapped radical.¹⁵ In general, the main splitting patterns depend on the number of hydrogen nuclei that are attached to the α -carbon atom of the spin adducts. From the splitting pattern and hyperfine coupling constants, the radicals generated following sonolysis were determined. The spectra of DBNBS radical adducts obtained by sonolysis of SDS (1 mM) in the presence of DBNBS (8.2 mM) under CW and pulsed ultrasound are shown in Figure 1. The spectra of the radical adducts formed following sonolysis of SPSO were similar to that of SDS for all experiments and were due almost entirely to carbon-centered secondary ($-\dot{\text{C}}\text{H}-$) radical adducts of DBNBS, as evidenced by the presence of a triplet of doublets labeled as 1 (Figure 1). A very minor contribution to the

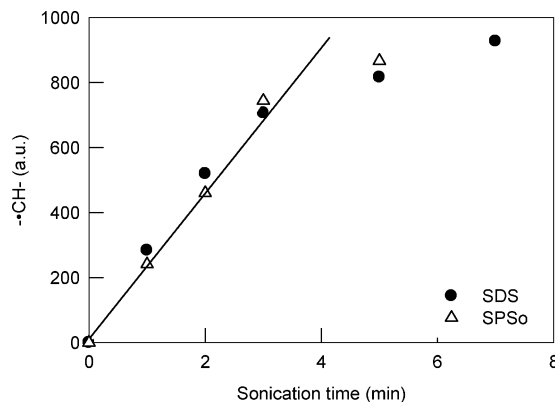


Figure 2. $-\dot{\text{C}}\text{H}-$ radical yields as a function of sonication time of 1 mM SDS and 5 mM SPSO surfactant solutions individually under continuous ultrasound at 354 kHz.

spectrum, which is labeled 3 is due to a typical $\dot{\text{C}}\text{H}_3$ radical splitting pattern is also shown.⁶ The three lines in the spectra that are labeled as 0 are attributed to small amounts of DBNBS decomposition during sonolysis.⁶ No $-\dot{\text{C}}\text{H}_2$ radicals were detected in any experiments.

These results indicate that the far majority of spin-trapped radicals are formed due to hydrogen-abstraction reactions between the primary radicals of sonolysis (i.e., H atom and OH radicals) and the *n*-alkyl hydrocarbon chain of the surfactants. As described in detail elsewhere,⁶ the $-\dot{\text{C}}\text{H}-$ radical yield is a measure of the amount of surfactant accumulated at the gas/solution interface of cavitation bubbles. Because the purpose of this study was not to determine absolute radical yields but rather to compare the carbon-centered radical yield of two different anionic surfactants after exposure to ultrasound under various conditions, throughout the study, the $-\dot{\text{C}}\text{H}-$ radical yield is shown in arbitrary units (a.u.).

Effects of Sonication Time on Radical Yield. In order to conduct a quantitative comparison of radical yields following sonolysis of SDS and SPSO, it was necessary to conduct experiments under conditions where the radical yield was directly proportional to the sonication time. Figure 2 shows the yield of $-\dot{\text{C}}\text{H}-$ radicals as a function of sonication time of aqueous SDS (1 mM) and SPSO (5 mM) solutions under CW ultrasound. The yield of $-\dot{\text{C}}\text{H}-$ radicals was directly proportional to sonication time up to 3 min. Therefore, a sonication time of 3 min was chosen for all of the experiments conducted under CW. Similarly, the yield of $-\dot{\text{C}}\text{H}-$ radicals as a function of sonication time of aqueous SDS (1 mM) and SPSO (5 mM) solutions under pulsed ultrasound was directly proportional to the sonication time up to 2 min for all the pulse conditions studied (data not shown). Thus, we chose a sonication time of 2 min for all experiments conducted under pulsed ultrasound.

Comparison of the $-\dot{\text{C}}\text{H}-$ Radical Yield Following Sonolysis of Aqueous SDS and SPSO Solutions. Figure 3 shows the yield of $-\dot{\text{C}}\text{H}-$ radicals as a function of the bulk solution concentration of surfactant during sonolysis of aqueous SDS and SPSO solutions under CW ultrasound. For SDS, the $-\dot{\text{C}}\text{H}-$ radical yield increased with increasing concentration up to 0.5 mM at which point the maximum, plateau yield for $-\dot{\text{C}}\text{H}-$ radicals was attained. Similarly, the $-\dot{\text{C}}\text{H}-$ radical yield for SPSO increased with concentration up to a bulk surfactant concentration of 5 mM at which point a maximum plateau $-\dot{\text{C}}\text{H}-$ radical yield was attained. At low concentrations (≤ 1 mM), the $-\dot{\text{C}}\text{H}-$ radical yield was greater for SDS than SPSO. In contrast, the $-\dot{\text{C}}\text{H}-$ radical yield at plateau concentrations was higher for SPSO than SDS.

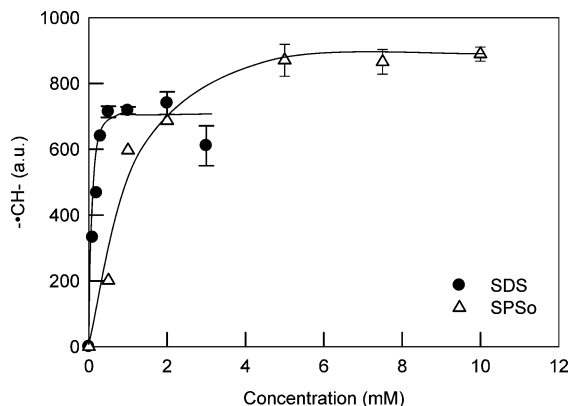


Figure 3. $\text{--}\dot{\text{C}}\text{H--}$ radical yields as a function of surfactant concentration following sonolysis of aqueous solutions of SDS and SPSO individually under CW at 354 kHz.

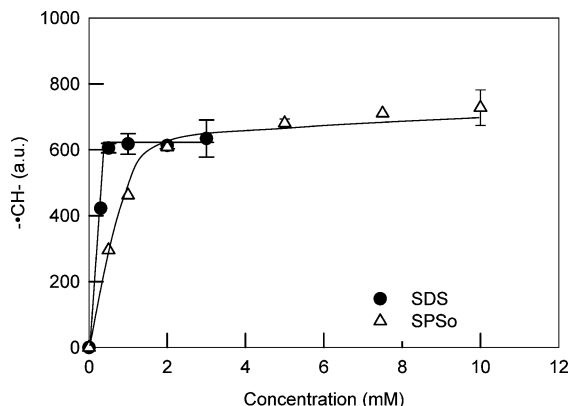


Figure 4. $\text{--}\dot{\text{C}}\text{H--}$ radical yields as a function of surfactant concentration following sonolysis of aqueous solutions of SDS and SPSO individually under pulsed ultrasound with a pulse length of 100 ms and a pulse interval of 100 ms at 354 kHz.

Effects of Pulsed Ultrasound. For pulsed ultrasound with a specified frequency, there is a minimum pulse length (T) that must be exceeded so that cavitation reactions can occur.²⁰ In the case of shorter pulse lengths, bubbles do not have sufficient time to grow to a size capable of collapse. However, pulse lengths that are too long were found to be less efficient due to continued growth of bubbles beyond their resonant size, because the bubbles are maximally effective at their resonant size.²¹ On the basis of our previous work, which showed that a pulse length of 100 ms at 354 kHz gave the maximum pulse enhancement for surfactant degradation,¹⁰ a pulse length of 100 ms was used in the current study.

$T = 100$ ms and $T_0 = 100$ ms at 354 kHz. The $\text{--}\dot{\text{C}}\text{H--}$ radical yield following sonolysis of aqueous solutions of SDS and SPSO under pulsed ultrasound at 354 kHz with a pulse length of 100 ms and an interval of 100 ms is shown in Figure 4. For SDS, the $\text{--}\dot{\text{C}}\text{H--}$ radical yield increased up to a concentration of 0.5 mM at which point a maximum plateau was reached. For SPSO, the $\text{--}\dot{\text{C}}\text{H--}$ radical yield also increased with increasing concentration. However, the plateau in the $\text{--}\dot{\text{C}}\text{H--}$ radical yield was observed at a SPSO concentration of 2 mM. At lower concentrations (≤ 1 mM), the $\text{--}\dot{\text{C}}\text{H--}$ radical yield was in the order of $\text{SDS} > \text{SPSO}$. At plateau concentrations, the $\text{--}\dot{\text{C}}\text{H--}$ radical yields for SDS and SPSO were essentially the same.

$T = 100$ ms and $T_0 = 500$ ms at 354 kHz. Figure 5 shows the yield of $\text{--}\dot{\text{C}}\text{H--}$ radicals as a function of concentration of SDS and SPSO under pulsed ultrasound with a pulse length of 100 ms and a pulse interval of 500 ms. For SDS, the $\text{--}\dot{\text{C}}\text{H--}$ radical yield increased as a function of concentration up to a maximum

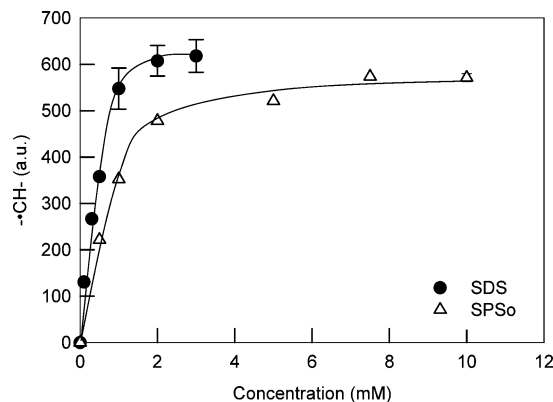


Figure 5. $\text{--}\dot{\text{C}}\text{H--}$ radical yields as a function of surfactant concentration following sonolysis of aqueous solutions of SDS and SPSO individually under pulsed ultrasound with a pulse length of 100 ms and a pulse interval of 500 ms at 354 kHz.

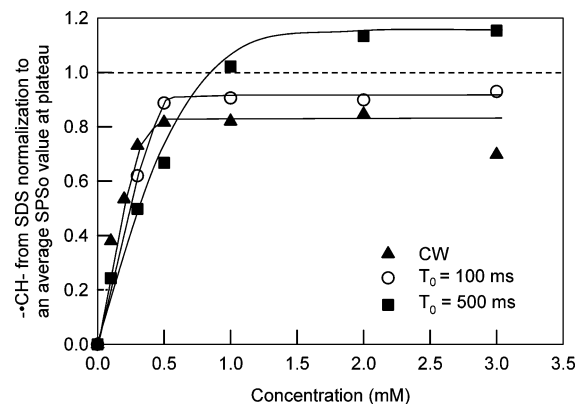


Figure 6. Relative $\text{--}\dot{\text{C}}\text{H--}$ radical yields as a function of surfactant concentration at 354 kHz following sonolysis of aqueous SDS solutions (the data points) compared with SPSO (the dashed line) under CW and pulsed ultrasound with a pulse length of 100 ms and pulse intervals of 100 and 500 ms, respectively. The dashed line represents an average SPSO plateau value normalized to 1.0 at all ultrasound conditions (SPSO data points not shown).

plateau radical yield, which occurred at 2 mM. For SPSO, the $\text{--}\dot{\text{C}}\text{H--}$ radical yield increased with increasing concentration up to 2 mM at which point the plateau concentration was attained. Interestingly, unlike the other sonication conditions, at all the concentrations studied, the $\text{--}\dot{\text{C}}\text{H--}$ radical yield was higher for SDS than for SPSO.

For clarity, a comparison of the radical yields for SDS and SPSO following sonolysis under all three ultrasound exposure conditions (i.e., from Figures 3 to 5) is shown in Figure 6. This figure was generated by normalizing the $\text{--}\dot{\text{C}}\text{H--}$ radical yield for SDS to an average SPSO plateau value. This was calculated from each of the figures (3–5) by taking an average of the $\text{--}\dot{\text{C}}\text{H--}$ radical yield data points that were determined to lie on the plateau following sonolysis of SPSO at each sonication condition. Therefore, within experimental error, the normalized SPSO plateau value was approximately equal to 1 at all sonication conditions (represented by the dashed line in Figure 6), to which the relative $\text{--}\dot{\text{C}}\text{H--}$ radical yield of SDS was compared. From Figure 6, it can be seen that as the ultrasound pulse off time increases (i.e., from CW to 100 to 500 ms) SDS becomes relatively more efficient at accumulating at the gas/solution surface of cavitation bubbles formed at 354 kHz, compared with SPSO.

Effects of Frequency. Figures 7 and 8 show the relative $\text{--}\dot{\text{C}}\text{H--}$ radical yields as a function of the bulk solution concentration of surfactant following sonolysis of SDS compared

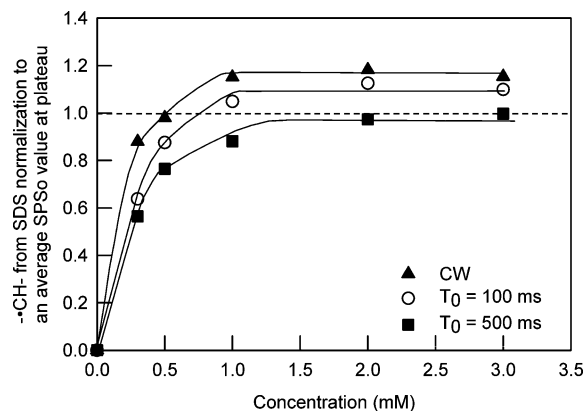


Figure 7. Relative $-\dot{\text{C}}\text{H}-$ radical yields as a function of surfactant concentration of sonolysis of SDS (the data points) compared with SPSO (the dashed line) under CW and pulsed ultrasound at 620 kHz with a pulse length of 100 ms and pulse intervals of 100 and 500 ms, respectively. The dashed line represents an average SPSO plateau value normalized to 1.0 at all ultrasound conditions (SPSO data points not shown).

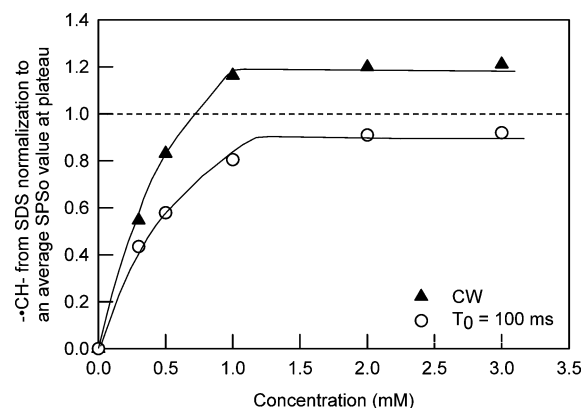


Figure 8. Relative $-\dot{\text{C}}\text{H}-$ radical yields as a function of surfactant concentration of sonolysis of SDS (the data points) compared with SPSO (the dashed line) under CW and pulsed ultrasound at 803 kHz with a pulse length of 100 ms and a pulse interval of 100 ms. The dashed line represents an average SPSO plateau value normalized to 1.0 at all ultrasound conditions (SPSO data points not shown).

with SPSO under CW and pulsed ultrasound with a pulse length of 100 ms and pulse intervals of 100 and 500 ms at 620 and 803 kHz, respectively. At 620 kHz, the maximum plateau yields were greater for SDS compared with SPSO under CW and a T_0 of 100 ms but was about the same for SDS as compared with SPSO under a T_0 of 500 ms. At 803 kHz, the maximum plateau yields were greater for SDS than for SPSO under CW but were lower for SDS than for SPSO at $T_0 = 100$ ms. These results are contrary to the results observed in Figure 6, which showed that pulsed ultrasound enhanced the accumulation of SDS to the bubble surface relative to SPSO.

Discussion

When an anionic surfactant adsorbs at the gas/solution interface, surface tension (γ) gradually decreases with increasing bulk concentration. The equilibrium surface excess (Γ_{eq}), a measure of the relative amount of surfactant at the gas/solution interface for an anionic surfactant with a single counterion, is described as²²

$$\Gamma_{\text{eq}} = -\frac{1}{2RT} \frac{d\gamma}{d(\ln C_i)} \quad (11)$$

where C_i is the bulk concentration of an ionic surfactant, R is the universal gas constant, and T is the temperature. At the critical micelle concentration (CMC), the maximum attainable interfacial concentration of surfactant under equilibrium conditions is reached. The CMC of SDS and SPSO are approximately 8 and 990 mM, respectively.²³ Although the presence of DBNBS in solution may affect the absolute CMC value, the CMC gives a good comparison of the equilibrium surface activity of these surfactants.

The equilibrium surface excess of SDS and SPSO solutions alone cannot explain the results of the current study. Figure 3 and the work of Sostaric et al.⁶ indicate that, at the plateau concentrations, the surfactant with a greater equilibrium surface activity accumulated at the gas/solution surface of cavitation bubbles with a lower efficiency than the less surface active surfactant. Thus, Γ_{eq} does not describe the adsorption of surfactants on cavitation bubble surfaces for certain anionic surfactants with a relatively long *n*-alkyl chain (e.g., SDS). The results indicate that dynamic accumulation properties of surfactants determine the limiting amount of surfactant that can accumulate at bubble interfaces formed under CW at 354, 620, and 803 kHz (Figures 3, 7, and 8) rather than thermodynamic adsorption properties of the surfactants.

When a new bubble surface is created in aqueous surfactant solutions, a certain time is required for equilibrium to be established between the surface concentration (Γ) and the bulk concentration (C_i). Therefore, Γ_{eq} is not instantaneously reached. Following sonolysis at 354 kHz, an increase in the $-\dot{\text{C}}\text{H}-$ radical yield was observed as the amount of SDS or SPSO was increased in solution at relatively low concentrations (Figure 3). This increase in $-\dot{\text{C}}\text{H}-$ radical yield is simply due to a gradual increase in the amount of solute available to accumulate at the gas/solution surface of cavitation bubbles. Because SDS (CMC = 8.1 mM) has a much greater thermodynamic tendency to accumulate at the gas/solution interface compared with SPSO (CMC = 990 mM), it is not surprising that the $-\dot{\text{C}}\text{H}-$ radical yield at relatively low bulk concentrations is greater following sonolysis of aqueous SDS solutions than for aqueous SPSO solutions (Figures 3–5).

However, when high enough concentrations of surfactant are reached so that enough surfactant is available to adsorb (i.e., > 1 mM), the relative adsorption ability of SDS compared with SPSO is determined by the dynamic adsorption properties of the surfactant. The maximum plateau yield of $-\dot{\text{C}}\text{H}-$ radical under CW was greater following sonolysis of aqueous SPSO solutions than for aqueous SDS solutions (Figures 3, 7, and 8). This observation supports previous work⁷ indicating that the limiting amount of surfactant able to adsorb to the gas/solution interface of acoustic cavitation bubbles in these systems is controlled by the dynamic adsorption properties of a surfactant rather than its thermodynamic properties. SPSO reaching a limiting absorption concentration at a bulk solution concentration of approximately 5 mM, well below the CMC of SPSO (990 mM), is further support of this adsorption mechanism.

As described elsewhere,^{6,7} surfactant molecules have to overcome a number of barriers for adsorption. These “barriers” may be diffusion, kinetic, or mixed kinetic-diffusion controlled.^{24,25} Ferri and Stebe²⁶ studied the equilibrium adsorption of a homologous series of *n*-alkyl chain possessing surfactants to the gas/solution interface and found that surfactants with a greater Γ_{eq} at a particular bulk concentration below the CMC reduce the surface tension to a larger degree at equilibrium. However, these surfactants require longer times to reach equilibrium. For surfactants possessing a relatively long *n*-alkyl

chain, this time is longer due to the relatively slow reorientation of surfactant molecules in the surface layer.²⁷

Cavitation bubble interfaces are in a constant state of motion, and the bubbles themselves have a certain lifetime. The time required for equilibrium adsorption of surfactants at the cavitation bubble surface is longer than the rate of change of the surface area of the bubble and may even be longer than the lifetime of a bubble.⁷ For this reason, under conditions of CW ultrasound, surfactants may not approach thermodynamic equilibrium with the bubble interface, and therefore, the value of surface excess, Γ , reached at the moment when the bubbles collapse is considerably smaller than Γ_{eq} .

If the above hypothesis is true, it would be expected that, when pulsed ultrasound is applied to the system, an increased amount of surfactant on cavitation bubble surfaces may be observed due to the longer lifetime of the bubble interface (which is no longer oscillating) and possibly due to increased bubble lifetimes, assuming bubbles survive during pulse intervals under appropriate pulse conditions. Given this, it would be expected that pulsed ultrasound should have a greater effect on SDS adsorption, because SDS has a greater thermodynamic surface activity, but slower adsorption onto the bubble surface from the bulk solution, compared with SPSO.

Indeed, in agreement with our above hypothesis, when the 354 kHz ultrasound wave was pulsed with an on time of $T = 100$ ms, the adsorption of SDS to the gas/solution surface of cavitation bubbles improved relative to SPSO adsorption in the order $CW < T_0 = 100$ ms $< T_0 = 500$ ms (Figure 6). This observation suggests that pulsing the ultrasonic wave allows the thermodynamic adsorption properties of the surfactants to play a much larger role in the overall adsorption process compared with their dynamic adsorption properties.

The increased radical yield of SDS compared with that of SPSO at the higher frequencies of 620 kHz (Figure 7) and 803 kHz (Figure 8) than the lower frequency of 354 kHz (Figure 6) under CW is due to the increased adsorption of SDS at the gas/solution interface of cavitation bubbles. These results are consistent with those of Sostaric and Riesz, concluding that the effects are due to the slower rate of change of surface area of stably oscillating bubbles at higher frequencies, that eventually undergo inertial collapse.⁷ This effect facilitates the adsorption of SDS at bubble surfaces compared with SPSO as the ultrasound frequency is increased under CW.

Although pulsing enhanced the accumulation of SDS compared with SPSO at the gas/solution interface of cavitation bubbles at 354 kHz (Figure 6), pulsing decreased the relative adsorption ability of SDS compared with SPSO during sonolysis at 620 kHz (Figure 7) and 803 kHz (Figure 8). This observation was not consistent with our hypothesis that the thermodynamic adsorption properties of surfactants would dominate surfactant adsorption at the gas/solution interface of cavitation bubbles during pulsing, compared with the dynamic adsorption properties of surfactants.

Recall that for our objectives the absolute radical yield may be neglected; $CH_{SPSO}:CH_{SDS}$ does not depend on the number of radicals formed. On the basis of $CH_{SPSO}:CH_{SDS}$, apparently, SPSO had become more efficient at adsorbing at the gas/solution surface of bubbles during pulsing at higher frequencies, compared with SDS (Figures 7 and 8). With this in mind, we propose that the frequency dependent resonant bubble size of a cavitation bubble plays a key role in the observations presented in Figures 7 and 8, compared with those of Figure 6.

The resonant size of a bubble depends on frequency and is smaller at 620 kHz (5.8 μ m) and 803 kHz (4.5 μ m) compared

with 354 kHz (10.1 μ m).²¹ During pulse intervals, bubbles lose gas and reduce in size due to the Laplace pressure (i.e., $2\gamma/r$, where γ = surface tension and r = radius) acting on the bubble.²² Because the Laplace pressure is higher in bubbles formed at higher frequencies, it is possible that, during the pulse interval, the rate of bubble dissolution is so fast that dynamic adsorption effects continue to predominate when ultrasound is pulsed at higher frequencies; i.e., the bubble shrinks before SDS can adsorb to its interface.

Note that, at concentrations of 1 to 3 mM of SDS, the bulk surface tension reduces from approximately 65 to 56 mNm⁻¹.²⁸ However, this bulk surface tension will not affect the Laplace pressure in cavitation bubbles; rather, the instantaneous surface concentration must be considered. SPSO reaches a plateau $-^{\bullet}CH-$ radical yield at just 5 to 10 mM (data not shown), and the $-^{\bullet}CH-$ radical yield is similar in magnitude to that in aqueous SDS solutions (Figures 7 and 8). It follows that the instantaneous surface concentration of SDS at the plateau concentrations must be well below that expected at equilibrium. Therefore, the surface tension at cavitation bubble interfaces in aqueous SDS solutions must be similar to that of bubbles suspended in aqueous SPSO solutions at the plateau concentrations (Figures 7 and 8). Thus, surface tension has a relatively small effect on the Laplace pressure under the conditions of the current experiment, but the smaller resonant size of bubbles as frequency increases results in dynamic adsorption controlling the adsorption.

Finally, pulsing at the higher frequencies resulted in an SDS $-^{\bullet}CH-$ radical plateau yield that is similar to the SPSO plateau yield (i.e., Figure 7; $T_0 = 500$ ms and Figure 8; $T_0 = 100$ ms). It is possible that pulsing has simply depleted the number of primary H and OH radicals available to participate in hydrogen abstraction reactions, and therefore, both SPSO and SDS have reached a high enough concentration at the gas/solution interface of cavitation bubbles to scavenge all of the primary radicals formed. Further experiments would be required to confirm this hypothesis.

Conclusions

The accumulation of surfactants at the gas/solution interface of cavitation bubbles depends on both their equilibrium and dynamic adsorption properties and can be controlled by varying the frequency and mode of ultrasound exposure. At 354 kHz, pulsed ultrasound with a longer pulse interval increases $-^{\bullet}CH-$ radical yield to a larger degree for the surfactant with a greater equilibrium surface activity (i.e., longer alkyl chain length). However, at frequencies of 620 and 803 kHz, pulsed ultrasound did not enhance accumulation of SDS at bubble surfaces compared with SPSO. Our results could not explain this observation; however, the results showed that pulsed ultrasound strongly affects the relative adsorption ability of surfactants to the interface of cavitation bubbles and that this effect is frequency dependent.

Acknowledgment. Financial support provided by the Office of Naval Research (ONR) is gratefully acknowledged.

References and Notes

- (1) Suslick, K. S. *Sci. Am.* **1989**, 260 (2), 80–86.
- (2) Henglein, A. *Ultrasonics* **1987**, 25 (1), 6–16.
- (3) Suslick, K. S., Ed. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH: New York, 1988.
- (4) Alegria, A. E.; Lion, Y.; Kondo, T.; Riesz, P. *J. Phys. Chem.* **1989**, 83, 4908–4913.

- (5) Vinodgopal, K.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2001**, *105* (16), 3338–3342.
- (6) Sostaric, J. Z.; Riesz, P. *J. Am. Chem. Soc.* **2001**, *123* (44), 11010–11019.
- (7) Sostaric, J. Z.; Riesz, P. *J. Phys. Chem. B* **2002**, *106*, 12537–12548.
- (8) Ashokkumar, M.; Niblett, T.; Tantiongco, L.; Grieser, F. *Aust. J. Chem.* **2003**, *56* (10), 1045–1049.
- (9) Pee, G.-Y.; Rathman, J. F.; Weavers, L. K. *Ind. Eng. Chem. Res.* **2004**, *43* (17), 5049–5056.
- (10) Yang, L.; Rathman, J. F.; Weavers, L. K. *J. Phys. Chem. B* **2005**, *109*, 16203–16209. Yang, L.; Rathman, J. F.; Weavers, L. K. *J. Phys. Chem. B* **2006**, *110*, 18385–18391.
- (11) Ashokkumar, M.; Hall, R.; Mulvaney, P.; Grieser, F. *J. Phys. Chem. B* **1997**, *101* (50), 10845–10850.
- (12) Tronson, R.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2003**, *107* (30), 7307–7311.
- (13) Sostaric, J. Z. Ph.D. Thesis, The University of Melbourne, Australia, 1999.
- (14) Sostaric, J. Z.; Mulvaney, P.; Grieser, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2843–2846.
- (15) Krishna, C. M.; Kondo, T.; Riesz, P. *J. Phys. Chem.* **1989**, *93* (13), 5166–5172.
- (16) Riesz P.; Kondo T.; Krishna C. M. *Ultrasonics* **1990**, *28* (5), 295–303.
- (17) Kondo, T.; Riesz, P. *Int. J. Radiat. Biol.* **1996**, *69* (1), 113–21.
- (18) Kaur, H.; Leung, K. H. W.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, *3*, 142–143.
- (19) Hamilton, L.; Nielsen, B. R.; Davies, C. A.; Symons, M. C. R.; Winyard, P. G. *Free Radical Res.* **2003**, *37* (1), 41–49.
- (20) Henglein, A.; Ulrich, R.; Lilie, J. *J. Am. Chem. Soc.* **1989**, *111*, 1974–1979.
- (21) Leighton, T. G. *The Acoustic Bubble*; Academic Press: London, 1994.
- (22) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*; Marcel Dekker: New York, 1997.
- (23) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; U.S. National Bureau of Standards: Washington, DC, 1971.
- (24) Eastoe, J.; Rankin, A.; Wat, R.; Bain, C. D. *Int. Rev. Phys. Chem.* **2001**, *20* (3), 357–386.
- (25) Eastoe, J.; Dalton, J. S. *Adv. Colloid Interface Sci.* **2000**, *85*, 103–144.
- (26) Ferri, J. K.; Stebe, K. J. *Adv. Colloid Interface Sci.* **2000**, *85*, 61–97.
- (27) Noskov, B. A. *Adv. Colloid Interface Sci.* **1996**, *69*, 63–129.
- (28) Mysels, K. J. *Langmuir* **1986**, *2*, 423–428.