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Using pulsed wave ultrasound to evaluate the suitability of hydroxyl radical scavengers in sonochemical systems

Ruiyang Xiao^a, David Diaz-Rivera^b, Ziqi He^c, Linda K. Weavers^{a,*}

^a Department of Civil, Environmental and Geodetic Engineering, The Ohio State University, Columbus, OH 43210, USA

^b Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, USA

^c HSA Engineers & Scientists, Fort Myers, FL 33919, USA

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ABSTRACT

Hydroxyl radical (·OH) scavengers are commonly used in sonochemistry to probe the site and nature of reaction in aqueous cavitation systems. Using pulsed wave (PW) ultrasound with comparative sonochemistry we evaluated the performance of ·OH scavengers (*i.e.*, formic acid, carbonic acid, terephthalic acid/terephthalate, iodide, methanesulfonate, benzenesulfonate, and acetic acid/acetate) in a sonochemical system to determine which ·OH scavengers react only in bulk solution and which ·OH scavengers interact with cavitation bubbles. The ability of each scavenger to interact with cavitation bubbles was assessed by comparing the pulse enhancement (PE) of 10 μM of a probe compound, carbamazepine (CBZ), in the presence and absence of a scavenger. Based on PE results, acetic acid/acetate appears to scavenge ·OH in bulk solution, and not interact with cavitation bubbles. Methanesulfonate acts as reaction promoter, increasing rather than inhibiting the degradation of CBZ. For formic acid, carbonic acid, terephthalic acid/terephthalate, benzenesulfonate, and iodide, the PE was significantly decreased compared to in the absence of the scavenger. These scavengers not only quench ·OH in bulk solution but also affect the cavity interface. The robustness of acetic acid/acetate as a bulk ·OH scavenger was validated for pH values between 3.5 and 8.9 and acetic acid/acetate concentrations from 0.5 to 0.1 M.

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1. Introduction

The transformation of organic pollutants in aqueous solution using ultrasound has been studied for decades [1–3]. In general, ultrasonic waves produce cavitation bubbles in water and the collapse of cavitation bubbles generates localized hot spots [4]. The hot spots initiate thermolytic and redox reactions with pollutants [4]. Hydroxyl radical (·OH) is the primary species attributed to redox reactions. ·OH forms in the gaseous bubble core and diffuses to bulk solution to oxidize contaminants [5]. This process is considered an important degradation pathway for hydrophilic and polar pollutants [6,7].

It is generally accepted that [·OH] is highest at the bubble–water interface and the amount of ·OH escaping from the hot spot and diffusing to bulk solution is small [8]. However, the question regarding how much ·OH escapes to bulk solution and contributes to the overall degradation of a pollutant remains unclear, since there is no direct measurement of free ·OH in bulk solution.

Two methods are commonly used to detect ·OH in cavitation systems. Electron spin resonance (ESR) spectroscopy measures ·OH by detecting the spin signal of the ·OH-trap adduct [9]. The

terephthalate dosimeter measures ·OH by detecting the fluorescence signal of the ·OH-trap adduct [10]. However, these methods do not sufficiently differentiate the locations of ·OH reaction, because the ·OH-trap adduct forms proportionally based on the concentrations of ·OH and the ·OH trap in the cavitation bubble, at bubble–water interface and in bulk solution.

The question of location of reaction is important. It not only helps one to estimate the contribution of bulk solution ·OH to contaminant degradation as a whole, but also to understand the spatial distribution of reaction sites. Therefore, researchers have used ·OH scavenger studies in attempts to answer this question [11–20]. Frequently used scavengers include terephthalic acid/terephthalate [11,12], iodide [13,14], and *t*-butanol [11,15]. Less commonly used scavengers include bicarbonate [16], acetic acid/acetate [17], and benzoic acid/benzoate [18]. These studies implicitly assume that the scavenger only quenches ·OH.

In reality, the ·OH scavengers may interact with the bubble–water interface and enter cavitation bubbles. Volatile scavengers not only quench ·OH in gas, interfacial, and bulk regions of cavitation bubbles, but also decrease the energy available for thermolysis of H₂O, reducing ·OH formation [19–21]. For example, Rae et al., demonstrated that even trace amounts of alcohols (such as *n*-butanol or *t*-butanol) evaporated into the bubble during the expansion phase of bubbles, decreasing the measured bubble

* Corresponding author. Tel.: +1 614 292 4061; fax: +1 614 292 3780.

E-mail address: weavers.1@osu.edu (L.K. Weavers).

temperature [21]. Therefore, because alcohol scavengers, such as *t*-butanol, methanol, and *n*-hexanol, are already known to interact with cavitation bubbles [21], they were not investigated in our study. ·OH scavenging compounds with surface activity may interact with cavitation bubbles, affecting bubble collapse dynamics. As these surface active compounds preferentially partition to bubble surfaces, they affect assessments of bulk ·OH reactivity as well. As a consequence, without assurance that scavengers do not interact with cavitation bubbles, attempts to infer mechanisms or sites of reaction, such as bulk ·OH reaction, to overall contaminant degradation using these scavengers is speculative.

In this study, pulsed wave (PW) ultrasound was used to systematically study whether and how ·OH scavengers affect cavitation bubbles. Previous studies [22–25] found that PW ultrasound, under certain optimal conditions, enhances the degradation of a compound, because it allows time for the compound to diffuse to bubble–water interfaces, the sources of reactivity. On the contrary, an ideal bulk ·OH scavenger stays in bulk solution and does not accumulate in the interfacial and gas region of cavitation bubbles between two successive pulses. We used a surface active probe compound, CBZ, as a reference compound that undergoes faster degradation under PW conditions compared to CW due to CBZ accumulation at bubble–water interfaces. Thus, in the presence of a bulk ·OH scavenger, faster degradation under PW over CW is expected. The PW enhancement is due to accumulation at the bubble–water interfaces. Using this comparative sonochemistry technique, any change in the enhancement is an indication of interaction of the scavengers with CBZ or the cavitation bubbles.

2. Experimental

CBZ (Sigma–Aldrich, 99%), KI (Acros, 99%), sodium formate (Fluka, 99%), sodium acetate (Fisher–Scientific, 99%), sodium bicarbonate (Fisher, 99%), sodium phosphate (monobasic and dibasic) (Fisher–Scientific, 99%), terephthalic acid (TA) (Sigma–Aldrich, 98%), benzenesulfonate (BS) (Sigma–Aldrich, 98%), methanesulfonate (MS) (Sigma–Aldrich, 98%), and phosphoric acid (Fisher–Scientific, 85%) were used as received. Stock solutions of these chemicals were prepared using Millipore purified water (Millipore) with the resistivity $R = 18.2 \text{ M}\Omega \text{ cm}$.

A $10 \mu\text{M}$ initial concentration of CBZ was used for all experiments. The ·OH scavenger concentration was 1 mM , a 100-fold excess relative to CBZ, unless specified. A 1 mM phosphate buffer was used because of its low ·OH reactivity (10^4 – $10^5 \text{ M}^{-1} \text{ s}^{-1}$) [26]. The pH of solution was adjusted by adding phosphoric acid or NaOH (reagent ACS, pellets 97%, Fisher Scientific).

Ultrasound at 205 kHz was emitted from a USW 51-52 ultrasonic flat plate transducer ($A = 23.4 \text{ cm}^2$) (ELAC Nautik, Inc., Kiel, Germany) into a glass vessel with a volume of 300 mL . The reactor was equipped with a cooling water jacket to maintain solutions at 20°C . A SM-1020 Function/Pulse generator (Signametrics Corp., Seattle, WA) generated sound waves continuously or by pulsing with an operation mode of 100 ms on and 100 ms off. The total experimental time for PW ultrasound was doubled as compared to CW ultrasound in order to have a comparable ultrasonic irradiation time for both CW and PW ultrasound. A linear amplifier (T & C Power Conversion, Inc., Rochester, NY) magnified the generated electrical signal. The acoustic energy density to the reactor, determined by calorimetry, was measured to be 45 W/L . Calorimetry was monitored periodically during experiments to confirm system functionality. During sonication, 0.5 mL samples were taken from the reactor at designated times using a 1 mL glass syringe (Gastight 1001, Hamilton Corp.) for chemical analysis. The sample volume taken during the course of sonication did not exceed 1% of the total volume in order to maintain the distribution of the acoustic field in

the reactor. The experiments were carried out, at least, in duplicate. Statistical *t*-test analysis was conducted using SPSS 13.0 (LEAD Technologies Inc).

A Hewlett–Packard 1100 high performance liquid chromatograph (HPLC) equipped with a diode array detector (DAD) was used to analyze the concentration following sonolysis of CBZ. A $5 \mu\text{M}$, $150 \times 2.1 \text{ mm}$ SB-C18 column (883700-922, Agilent Technologies) was employed. An isocratic flow of acetonitrile/water (40/60, v/v) was the mobile phase for the quantification of CBZ. The injection volume was $50 \mu\text{L}$ and the UV wavelength was set at 220 nm .

Gibbs surface tension (γ) was measured by a McVan Analite Surface Tension meter (2141, McVan Instruments) with a glass Wilhelmy plate. All measurements were carried out in triplicate at room temperature. Gibbs surface excess (Γ) was obtained from the change of surface tension (γ),

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln[C]} \quad (1)$$

where R is gas constant, T is temperature, and C is concentration of solute. Surface tension was smoothed using a Fast Fourier Transform (FFT) tool to eliminate instrument noise (Origin 8.1, OriginLab Inc).

3. Results and discussion

3.1. Degradation of CBZ

The sonochemical degradation rate of the probe compound, CBZ, in the absence and presence of ·OH scavengers at pH 3.5 is shown in Fig. 1. In the absence of ·OH scavengers, CBZ degraded 5.8% ($p < 0.01$) faster by PW ultrasound compared to CW ultrasound. Similar to previous work [22–25], the higher degradation rate under PW ultrasound indicates that a higher fraction of CBZ is degraded in the interfacial region of cavitation bubbles.

During the time interval between two successive pulses, CBZ molecules accumulate on the surface of the bubble. In the subsequent pulse more CBZ molecules react compared to CW ultrasound. Faster degradation by PW ultrasound is consistent with Naddeo et al. [27]. They attributed the majority of decomposition of CBZ to reaction in the vicinity of the cavitation bubbles.

Fig. 1 also shows the initial degradation rates of CBZ in the presence of 1 mM concentration of each individual ·OH scavenging agent. With the exception of MS, the presence of the ·OH scavenger reduced the initial degradation rate of CBZ in both CW and PW

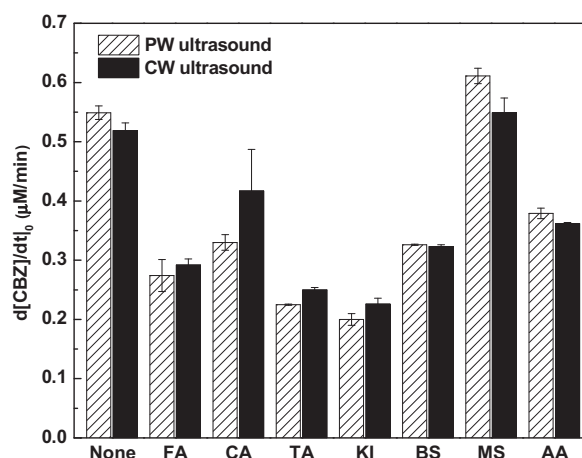


Fig. 1. Initial degradation rates of $10 \mu\text{M}$ CBZ in the absence and presence of 1 mM ·OH scavenger candidates under PW and CW ultrasound at pH 3.5.

conditions. Using Eq. (2), the inhibitory effect of each individual scavenger on the sonolysis of CBZ was calculated.

$$\text{Inhibition (\%)} = \frac{\left(\frac{d[C]}{dt}\right)_{\text{without scavenger}} - \left(\frac{d[C]}{dt}\right)_{\text{with scavenger}}}{\left(\frac{d[C]}{dt}\right)_{\text{without scavenger}}} \times 100\% \quad (2)$$

where $\left(\frac{d[C]}{dt}\right)_{\text{with scavenger}}$ and $\left(\frac{d[C]}{dt}\right)_{\text{without scavenger}}$ are the initial degradation rates of CBZ with or without an $\cdot\text{OH}$ scavenger, respectively. Fig. 2 indicates that these seven scavengers have different effects on the sonolysis of CBZ.

The changing level of inhibition of all the scavenger candidates, as shown in Fig. 2, implies that they exert different influences on the sonochemical system. In addition, the benefit of pulsing in the presence of the scavenger is only observed with MS and AA.

3.2. PE of CBZ in the presence of the $\cdot\text{OH}$ scavengers

In order to investigate the effects of scavengers on cavitation bubbles, a pulse enhancement (PE) was calculated. By comparing the degradation of CBZ between CW and PW ultrasound, the effect of pulsing was determined:

$$\text{PE(\%)} = \frac{\left(\frac{d[C]}{dt}\right)_{\text{PW}} - \left(\frac{d[C]}{dt}\right)_{\text{CW}}}{\left(\frac{d[C]}{dt}\right)_{\text{CW}}} \times 100\% \quad (3)$$

where $\left(\frac{d[C]}{dt}\right)_{\text{CW}}$ and $\left(\frac{d[C]}{dt}\right)_{\text{PW}}$ are the degradation rates of CBZ under CW or PW ultrasound, respectively. In the presence of a bulk $\cdot\text{OH}$ scavenger, the PE of CBZ is expected to be equal to that in the absence of the scavenger. Other than scavenging bulk $\cdot\text{OH}$, the presence of a true bulk scavenger does not have any pronounced effects on the degradation of CBZ, such as competing for adsorption sites at the interface and diffusing to the gas region.

Comparative sonochemistry has been applied previously [24,25,28–30] to understand the relative roles of an effect rather than the absolute role of an effect. This study is employing comparative sonochemistry to determine the relative effect of a scavenger on PE compared without the scavenger present. An important assumption in our use of this method is that the amount of bulk $\cdot\text{OH}$ does not change significantly between CW and PW ultrasound. For a bulk $\cdot\text{OH}$ scavenger, a similar inhibition level in the presence and absence of pulsing indicates that the amount of bulk $\cdot\text{OH}$ does not change significantly between CW and PW conditions. However, a similar inhibition level does not necessarily indicate that an $\cdot\text{OH}$

scavenger is a bulk $\cdot\text{OH}$ scavenger because an $\cdot\text{OH}$ scavenger that is not a true bulk $\cdot\text{OH}$ scavenger may interact with cavitation bubbles under both CW and PW conditions.

In the absence of $\cdot\text{OH}$ scavengers, the PE of CBZ is 5.8%. The PE of CBZ in the presence of various scavengers is shown in Fig. 3. In the presence of FA, CA, TA, and KI, the PE of CBZ is negative ranging from -20% to -5% . Again, a similar PE value with and without the scavenger indicates its influence on cavitation bubbles is negligible. The results suggest that FA, CA, TA, and KI not only scavenge $\cdot\text{OH}$ in the system but also significantly affect cavitation bubbles. In the presence of MS, BS, and AA, the PE ranges from 0.9% to 11.3% , suggesting little influence on cavitation bubbles. To understand the effects of these scavengers on cavitation bubbles, we will discuss each scavenger separately below.

3.2.1. Formic acid

FA has been characterized as an ideal $\cdot\text{OH}$ scavenger in radiolysis [31]. It has a fast reaction rate constant and known reaction pathways with $\cdot\text{OH}$. However, when it comes to its application in sonochemistry, FA shows a negative pulse enhancement (PE = -6.2%).

Partitioning of FA and its ultrasound-induced reaction products to the gaseous bubble and bubble interface has been reported in the literature. Hart and Henglein observed CO production during sonication of FA [32]. Substantial formation of CO in sonicated aqueous FA solution is attributed to thermal decomposition of FA (Eq. (4)), indicating that FA enters the high temperature gas region of cavitation bubbles.



In addition, Jolly et al., investigated products formed from $\cdot\text{OH}$ reacting with FA during laser-irradiated photolysis [33]. They proposed that the oxidation of FA by $\cdot\text{OH}$ releases CO_2 according to Eqs. (5) and (6):



Gaseous CO_2 formed enters cavitation bubbles and decreases the polytropic index, κ , ($\kappa_{\text{air}} = 1.405$ and $\kappa_{\text{CO}_2} = 1.312$) of the gas phase, resulting in a decreased bubble collapse temperature as shown in Eq. (7):

$$T_{\text{max}} = T_0 \left[\frac{P_m(\kappa - 1)}{P} \right] \quad (7)$$

where T_{max} is the maximum bubble collapse temperature; T_0 is the ambient temperature of the liquid; P_m is the liquid pressure at the moment of transient collapse; and P is the pressure in the bubble at

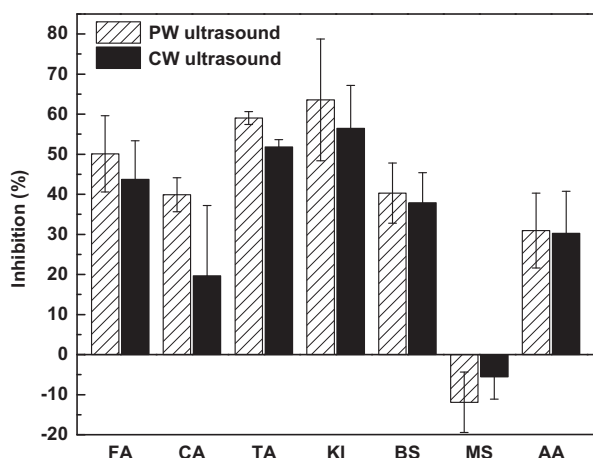


Fig. 2. Inhibitory effects of each bulk $\cdot\text{OH}$ scavenger candidate on the sonolysis of $10 \mu\text{M}$ CBZ under CW and PW ultrasound at pH 3.5.

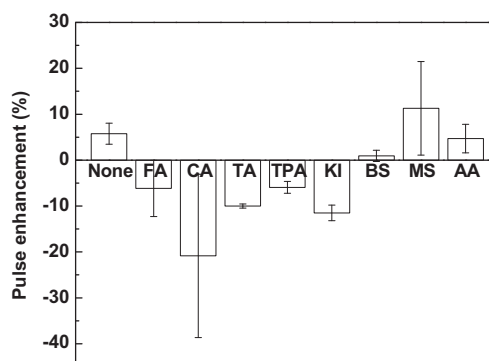


Fig. 3. PE of $10 \mu\text{M}$ CBZ in the absence and presence of the various bulk $\cdot\text{OH}$ scavenger candidates at pH 3.5 (TPA was tested at pH 7.4).

its maximum size. The lower collapse temperature of the bubble produces comparatively less $\cdot\text{OH}$. Therefore, we do not recommend the use of FA as bulk $\cdot\text{OH}$ scavenger in cavitation systems.

3.2.2. Carbonic acid

CA has not been reported as a $\cdot\text{OH}$ scavenger. Our interest in CA was primarily to explore the effect of CO_2 on the cavitation bubbles, rather than as an $\cdot\text{OH}$ scavenger. Based on FA results, we suspected that H_2CO_3 would significantly affect cavitation bubbles mostly due to its equilibrium with gaseous CO_2 in aqueous solution at pH 3.5.



The negative PE for CA in Fig. 3 shows that CA significantly affects cavitation bubbles, resulting in the lowest pulse enhancement –20.9% among the scavengers tested. Gaseous CO_2 is expected to enter stable microbubbles during the interval between the pulses, reducing the bubble collapse temperature, resulting in less reaction of CBZ under PW ultrasound. In addition, Henglein observed that the main product of the sonolysis of CO_2 is CO [34], which is also capable of reducing the maximum bubble collapse temperature, T_{max} , (Eq. (7)) due to a decrease in the polytropic index κ ($\kappa_{\text{Air}} = 1.405$ and $\kappa_{\text{CO}} = 1.380$). Further, CO formation is attributed to thermal decomposition of CO_2 [34].



Thus, CO_2 reduces the temperature of collapsing cavitation bubbles, resulting in a negative impact on $\cdot\text{OH}$ formation and contaminant degradation.

3.2.3. Terephthalic acid/terephthalate

TA has been widely used as an $\cdot\text{OH}$ scavenger in sonochemistry, radiochemistry, and photochemistry due to its high sensitivity to trap $\cdot\text{OH}$ to form the fluorescent product, hydroxyterephthalate [35–38]. In addition, in neutral and basic solution, the anionic form of TA, terephthalate (TPA), dominates ($\text{pK}_{\text{a},1} = 3.52$ and $\text{pK}_{\text{a},2} = 4.46$). Thus, the polar anionic TPA is assumed to reside in bulk solution and not partition to the interface or vapor region of cavitation bubbles [10,11]. At pH 3.5, the PE of 1 mM TA was –10.0%, suggesting that TA interacts with the bubble–water interface. As TA is not in its anionic form at pH 3.5, we retested at pH 7.4. However, the PE remained negative (–5.9%). Unlike FA and CA which enter into microbubbles, we suspect that TA/TPA competes for adsorption sites during the silent cycle, and accumulates at the interface of oscillating and collapsing gas bubbles, causing reduced degradation of CBZ in PW as compared to CW. As a result, a negative PE was observed.

This result is in agreement with our previous work investigating the sonolysis of ibuprofen and ciprofloxacin in the presence of TPA [39]. To understand these results we calculated the hydrophobic enrichment factor, $C_{\text{interface}}/C_{\text{aq}}$, following the method from Tauber et al. [13]. Tauber et al. used this concept to study the enrichment of 4-nitrophenol at the interfacial region and concluded that 4-nitrophenol, with $C_{\text{interface}}/C_{\text{aq}} \approx 80$, primarily degraded in the gas–liquid boundary layer. $C_{\text{interface}}/C_{\text{aq}}$ for TA was calculated to be 7.7 at pH 3.5, indicating that TA partitions to the bubble–water interface. Thus, we do not recommend the use of TA or TPA as a bulk $\cdot\text{OH}$ scavenger in cavitation systems.

3.2.4. Potassium iodide

KI is one of the most popular $\cdot\text{OH}$ scavengers [13,14,20]. Fig. 3 shows a PE of –11.5% for CBZ when KI is present. The reduced PE of CBZ with KI compared to in the absence of KI suggests that KI interacts with the bubble–water interface, resulting in a reduced degradation rate of CBZ in PW mode compared to CW mode.

Although iodide is a non-volatile solute, the sonication of a solution of KI liberates considerable iodine [40], and, in fact, is the reported pathway for quantifying the reaction of KI with $\cdot\text{OH}$:



Kotronarou [40] observed that the rate of I_3^- formation in an aqueous solution decreased by 1/3 when the ports of the sonication reactor were left open compared to closed conditions, suggesting substantial iodine degassing. Although no studies directly report iodine entering into the gas phase of cavitation bubbles, I_2 is volatile with a reported Henry's law constant of $0.0245 \text{ atm m}^3/\text{mol}$ [41]. For comparison purposes, Drijvers et al., [18] investigated the sonolysis of chlorobenzene with a Henry's law constant of $0.00311 \text{ atm m}^3/\text{mol}$ in aqueous solution. They concluded that chlorobenzene penetrated the gas/liquid boundary layer, lowering the specific heat ratio of the gas inside the cavitation bubbles, reducing the bubble collapse temperature, and ultimately reducing degradation of chlorobenzene by ultrasound. The Henry's law constant of iodine is nearly one order of magnitude greater than that of chlorobenzene, suggesting that the ultrasound-induced byproduct, iodine, partitions to the gas phase of cavitation bubbles. Our suggestion is consistent with Gutierrez et al. [42]. The authors sonicated I_2 with the spin trap, 5,5-dimethylpyrroline N-oxide, in aqueous solution and speculated that I_2 evaporates into the gas phase [42]. In addition, Liu et al., [43] revealed that the hydrogen bonding network at the air/water interface is disturbed by the addition of iodide due to its large size and high polarizability, suggesting iodide itself perturbs the bubble–water interface. Therefore, I^- itself and its reaction product I_2 interact with cavitation bubbles; we do not recommend the use of KI as bulk $\cdot\text{OH}$ scavenger in cavitation systems.

3.2.5. Benzenesulfonate

Although not a commonly reported $\cdot\text{OH}$ scavenger, BS was considered in our study since it is hydrophilic (apparent $\log K_{\text{ow}} = -2.93$ at pH 3.5) [44] due to its sulfonate functional group, and sensitively traps $\cdot\text{OH}$ ($4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [26]. Thus, we expected BS to effectively scavenge $\cdot\text{OH}$ in bulk solution. In Fig. 3, the PE in the presence of 1 mM BS (0.93%) is statistically less than in its absence (5.8%) ($p < 0.01$). This reduction in PE with BS suggests that BS affects cavitation bubble collapse. Measurements of the Gibbs surface tension of BS showed that the surface excess remained unaltered until the concentration of BS reached 0.1 M (Fig. 4). The Gibbs surface excess

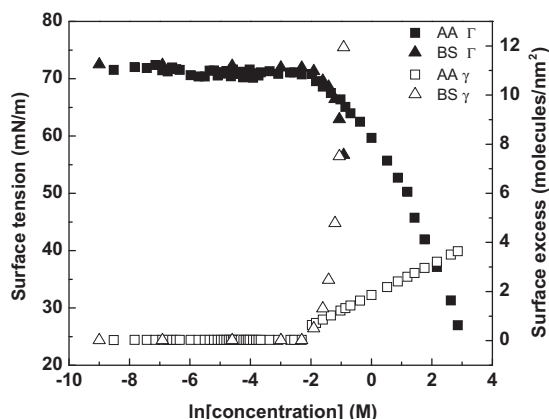


Fig. 4. Gibbs surface tension (Γ) and surface excess (γ) for acetic acid (AA) and benzenesulfonate (BS) as a function of concentration at room temperature.

of a substance, which has been directly correlated to the intensity of sonoluminescence, is a measure of enrichment of the substance at the bubble–water interface [45,46]. Although Gibbs surface excess changes were not detected at low concentration (<0.1 M), the hydrophobic enrichment factor, $C_{\text{interface}}/C_{\text{aq}}$, was calculated to be 40.7 for BS. Because of the lower PE of CBZ in the presence of BS and the high calculated enrichment factor, we do not recommend the use of BS as a bulk $\cdot\text{OH}$ scavenger in cavitation systems.

3.2.6. Methanesulfonate

MS shows a greater pulse enhancement (PE = 11.3%), as compared to that in the absence of MS (5.8%) ($p < 0.01$). In addition, the presence of MS promoted, rather than inhibited the degradation of CBZ. Enhanced degradation of CBZ with MS may be attributed to the production of reactive secondary species [47]. Therefore, because of the enhanced degradation of CBZ with MS, it is not appropriate for use as an $\cdot\text{OH}$ scavenger.

3.2.7. Acetic acid

The PE of CBZ in the presence of AA was 4.6%, as compared to 5.8% in the absence of the scavenger (Fig. 3). Unlike the other scavengers tested, the lack of statistical difference in PE values ($p < 0.01$) suggest that AA and its by-products neither perturb the adsorption sites of CBZ at the bubble–water interface, nor partition into gas microbubbles during the silent cycles in PW mode, but rather reside in bulk solution.

To confirm that AA does not partition to the bubble–water interface of cavitation bubbles, surface tension measurements and corresponding Gibbs surface excess calculations were performed for the AA–water binary system at room temperature. Results indicate that AA does not accumulate on gas–water interfaces until the AA concentration reaches 140 mM (Fig. 4). This observation is similar to experiments with multi-bubble sonoluminescence of acetate solution [48]. The reported sonoluminescence intensity of acetate remained relatively constant until the concentration reached 100 mM, indicating that acetate does not accumulate on the bubble surface at concentrations lower than 100 mM; thus, no sonoluminescence quenching was observed. The similar point at which acetic acid (140 mM) and acetate (100 mM) appear to accumulate on interfaces suggests that AA and acetate behave similarly in the ultrasonic field.

In addition to surface accumulation, AA has the potential to enter the gas phase of cavitation bubbles. Henry's law predicts the distribution of AA between aqueous solution and the gas at equilibrium. Nanzai et al., investigated the sonolysis of twelve organic compounds with Henry's law constant (K_H) ranging from 7.34×10^{-9} to 1.05×10^{-2} atm m³/mol. Their results showed that the effect of the Henry's law constants on the degradation rates became pronounced at K_H above 2.40×10^{-5} atm m³/mol and the correlation between degradation and K_H was observed only at high K_H values [49]. Chiha et al., examined sonochemical degradation of phenol ($K_H = 3.33 \times 10^{-7}$ atm m³/mol), 4-isopropylphenol ($K_H = 1.09 \times 10^{-6}$ atm m³/mol), and Rhodamine B ($K_H = 2.20 \times 10^{-21}$ atm m³/mol) in aqueous solutions [50]. They claimed that these compounds are not degraded inside the cavitation bubbles because of their low Henry's law constants. Based on these studies of the effects of Henry's law constants on sonolysis of contaminants, AA, with a Henry's law constant 1.00×10^{-7} atm m³/mol [41], does not appear likely to diffuse to the gas phase of cavitation bubbles to a large degree.

Calculations were also conducted to validate our conclusion that AA will not migrate to bubble interfaces or interiors. Based on the method from Tauber et al., [13] the hydrophobic enrichment factors, $C_{\text{interface}}/C_{\text{aq}}$ and C_{aq}/C_g , for acetic acid were calculated to be 0.8 and 8.13×10^4 , respectively. Both factors indicate that AA preferentially stays in bulk solution.

While our macroscopic observations and calculations do not provide molecular level information regarding AA on the bubble–water interface, Johnson et al., studied the AA [51] and acetate [52] molecular orientation and speciation at the air interface by vibrational sum frequency spectroscopy. They found that the structure of the interface is disrupted in the presence of 0.3 mol% (0.165 M) AA with AA covering 7% of the interface [51], whereas acetate was not observed to disrupt the interface [52]. Although they did not investigate lower AA concentrations, their work is consistent with our surface tension measurements; thus, we expect the observed perturbation of the interface they observed will disappear at concentration below 0.1 M.

The kinetics and mechanism of the sonolysis of acetate solution was studied by Gutierrez et al. [8]. A large concentration (~ 0.1 M for acetate and ~ 0.01 M for acetic acid) was required to suppress the overall formation of 50% H_2O_2 . However, based on product formation yields, half of $\cdot\text{OH}$ in bulk solution was scavenged at an acetate concentration of 1.2 μM , four to five orders of magnitude less than the bulk acetate concentration. Based on the low CO to H_2 product formation ratio at $[\text{acetate}]_0 = 0.1$ M, they stated that the sonolysis of acetate (≤ 0.1 M) occurs via decomposition of water, attack of acetate by $\cdot\text{OH}$, and the reaction of the secondary radicals with the oxygen. The trace amount of CO formed at 0.1 M acetate may be due to sputtering of acetate in bulk solution into the gas bubbles during sonolysis [20,53]. They concluded that the amount of $\cdot\text{OH}$ in bulk solution is small, and acetate is inert toward the interfacial and gas region.

Fig. 2 depicts the effectiveness of AA scavenging for $\cdot\text{OH}$ on sonochemical degradation of CBZ. In the absence of AA, the degradation rates of CBZ were 0.519 and 0.549 $\mu\text{M min}^{-1}$ under CW and PW, respectively. In the presence of 1 mM AA the observed rate was 0.362 and 0.379 $\mu\text{M min}^{-1}$ under CW and PW, respectively, representing a $\sim 30\%$ inhibition in the presence of a bulk $\cdot\text{OH}$ scavenger in both modes of ultrasound. The result indicates that $\cdot\text{OH}$ in bulk solution is responsible for $\sim 30\%$ of CBZ degradation, confirming our assumption that the interfacial region of the cavitation bubbles are the dominant location responsible for CBZ degradation.

AA/acetate has been investigated in sonochemical system previously as a pollutant and a co-existing pollutant. [8,17,54,55]. Findik and Gunduz investigated the degradation of AA in the presence of NaCl to examine the salting-out effect on sonolysis [55]. The presence of NaCl exhibited a positive enhancement on AA degradation until its concentrations reached 0.75 M, suggesting that AA favors bulk solution, thus, a high NaCl concentration is needed to push AA from bulk solution to the bubble interface. For comparison purposes, Seymour and Gupta examined the salting-out effect on the sonolysis of chlorobenzene, a surface active pollutant with major degradation occurring in the gas and interfacial region of cavitation bubbles [56]. In their study, the degradation efficiency is enhanced by 10% with 0.17 M NaCl as compared to in its absence. Tiehm and Neis [17] examined sonochemical degradation of chlorophenol in the presence of acetate and observed that the degradation rate was reduced slightly less than it was in the presence of glucose. They concluded that hydrophilic acetate or glucose did not interfere with chlorophenol, which was mainly degraded in the bubble–water interface. These studies confirm that AA preferentially stays in bulk solution.

3.3. Robustness of AA/acetate as bulk solution $\cdot\text{OH}$ scavenger

In order to determine the range of conditions in which AA/acetate acts as a bulk $\cdot\text{OH}$ scavenger, its effect on CBZ degradation was tested under different conditions. Our goals were to explore the concentration and pH conditions at which AA/acetate adequately scavenges bulk $\cdot\text{OH}$ but does not affect cavitation bubbles. First,

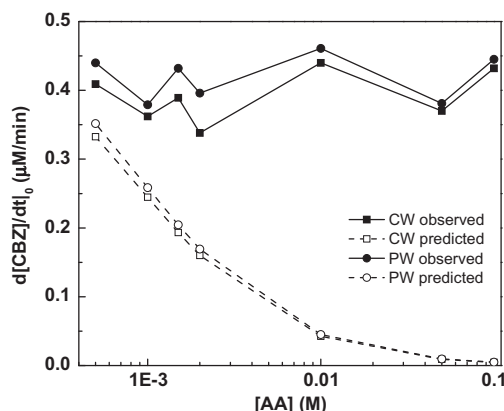


Fig. 5. Observed and predicted initial degradation rates of 10 μM CBZ at pH 3.5 under CW and PW ultrasound as a function of acetic acid concentration, ranging from 0.5 to 100 mM.

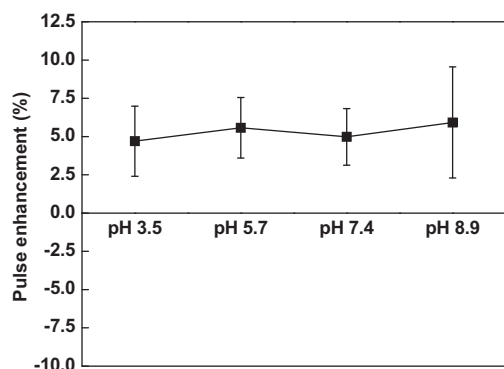


Fig. 6. PE of 10 μM CBZ in the presence of 1 mM bulk phase $\cdot\text{OH}$ scavenger, AA/acetate, as a function of pH.

the sonolysis of the probe compound, CBZ, was conducted at pH 3.5 with an AA concentration ranging from 0.5 to 100 mM.

Fig. 5 illustrates that with different concentrations of AA, the reported initial degradation rates of CBZ remain relatively constant in both CW and PW ultrasound. At high concentrations of AA/acetate, AA/acetate has been shown to interact with cavitation bubbles, while at very low concentrations AA/acetate may not adequately scavenge $\cdot\text{OH}$ in bulk solution. The degradation rate of CBZ in the presence of AA was predicted by multiplying the degradation rate of the target compound in the absence of AA by the quenching ratio, Q , the ratio of reaction occurring by $\cdot\text{OH}$ between competing solutes. Q of AA of the degradation of CBZ was predicted from Eq. (13):

$$Q = \frac{k_{\text{CBZ}}C_{\text{CBZ}}}{k_{\text{AA}}C_{\text{AA}} + k_{\text{CBZ}}C_{\text{CBZ}}} \times 100\% \quad (13)$$

where k_{CBZ} and k_{AA} are the second order rate constants of $\cdot\text{OH}$ reacting with CBZ and AA, respectively, and C_{CBZ} and C_{AA} are the concentrations of CBZ and AA, respectively.

The predicted initial degradation rates monotonously decrease from 0.35 to 0.0048 $\mu\text{M min}^{-1}$ under either CW or PW ultrasound. The significantly higher and relatively stable observed initial rates of CBZ degradation compared to predicted initial rates suggests that CBZ diffuses to the interfacial region of cavitation bubbles, regions of high temperature and $\cdot\text{OH}$ concentration. The lack of effect of AA within a wide concentration range indicates that AA does not affect the interfacial and gas region of cavitation bubbles. Further, because adding more of the $\cdot\text{OH}$ scavenger does not alter the initial

degradation rate of CBZ, the lowest concentration of AA appears to adequately scavenge the bulk $\cdot\text{OH}$. Only a small amount of $\cdot\text{OH}$ diffuses to bulk solution during sonication; thus, the presence of small amount of AA sufficiently outcompetes CBZ, scavenging the $\cdot\text{OH}$ in bulk solution. An increase in the AA concentration has little impact on the observed initial degradation rates of CBZ for the concentration of CBZ used. Generalizing to other systems, the lowest concentration of AA may or may not be appropriate for all conditions. If a high compound concentration will be used and AA is used as a bulk $\cdot\text{OH}$ scavenger, adequate scavenging by AA should be confirmed, especially at the lowest AA concentration we used.

Next, we tested the robustness of AA/acetate within a range of pH values. Sonolysis of 10 μM CBZ was conducted in the presence of 1 mM AA/acetate from pH 3.5 to 8.9. Fig. 6 shows that the PE of CBZ remains constant through the entire pH range tested. Henglein and Kormann [20], suggested that both AA and acetate have similar scavenging behaviors based on the concentration needed to inhibit formation of 50% H_2O_2 . Our results are consistent with their work, suggesting that acetate behaves similarly to AA.

4. Conclusions

The effects of the $\cdot\text{OH}$ scavengers, FA, CA, TA/TPA, KI, MS, BS, and AA/acetate, on cavitation bubbles have been examined with the sonolysis of the probe compound, CBZ, under CW and PW ultrasound. PW ultrasound provides a technique to determine whether scavengers affect the interfacial and gas region of cavitation bubbles. All the scavengers, except for MS, exhibited inhibitory effects on CBZ sonolysis. Based on the reduction in PE of CBZ, all the scavengers except AA/acetate affect cavitation bubbles and are not recommended to use as bulk $\cdot\text{OH}$ scavengers in cavitation systems.

We recommend acetic acid/acetate as a bulk $\cdot\text{OH}$ scavenger. It efficiently quenches $\cdot\text{OH}$ in bulk solution, resulting in a reduced degradation rate of CBZ. The range of utility of AA/acetate as a bulk $\cdot\text{OH}$ scavenger was tested under different concentrations and pH values. The observed degradation rates of CBZ within the range of concentrations and pH values tested were unaltered. Evidence suggests that at AA/acetate concentrations below 0.1 M and all pH values tested, AA/acetate is an ideal bulk $\cdot\text{OH}$ scavenger in sonochemical systems.

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References

- [1] L.K. Weavers, N. Malmstadt, M.R. Hoffmann, Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation, and sonolytic ozonation, *Environ. Sci. Technol.* 34 (2000) 1280–1285.
- [2] M.R. Hoffmann, I. Hua, R. Hochemer, Application of ultrasonic irradiation for the degradation of chemical contaminants in water, *Ultrason. Sonochem.* 3 (1996) S163–S172.
- [3] E.J. Hart, C.H. Fischer, A. Henglein, Sonolysis of hydrocarbons in aqueous solution, *Radiat. Phys. Chem.* 36 (1990) 511–516.
- [4] K.S. Suslick, D.A. Hammerton, R.E. Cline, The sonochemical hot spot, *J. Am. Chem. Soc.* 108 (1986) 5641–5642.
- [5] Y.G. Adewuyi, Sonochemistry in environmental remediation. 1. Combinative and hybrid sonophotochemical oxidation processes for the treatment of pollutants in water, *Environ. Sci. Technol.* 39 (2005) 3409–3420.
- [6] F. Mendez-Arriaga, R.A. Torres-Palma, C. Petrier, S. Esplugas, J. Gimenez, C. Pulgarin, Ultrasonic treatment of water contaminated with ibuprofen, *Water Res.* 42 (2008) 4243–4248.
- [7] R.J. Emery, M. Papadaki, L.M.F. dos Santos, D. Mantzavinos, Extent of sonochemical degradation and change of toxicity of a pharmaceutical precursor (triphenylphosphine oxide) in water as a function of treatment conditions, *Environ. Int.* 31 (2005) 207–211.

- [8] M. Gutierrez, A. Henglein, C.H. Fischer, Hot spot kinetics of the sonolysis of aqueous acetate solutions, *Int. J. Radiat. Biol.* 50 (1986) 313–321.
- [9] T. Kondo, C.M. Krishna, P. Riesz, Free-radical generation by ultrasound in aqueous-solutions of nucleic-acid bases and nucleosides – an electron-spin-resonance and spin-trapping study, *Int. J. Radiat. Biol.* 53 (1988) 331–342.
- [10] T.J. Mason, J.P. Lorimer, D.M. Bates, Y. Zhao, Dosimetry in sonochemistry – the use of aqueous terephthalate ion as a fluorescence monitor, *Ultrason. Sonochem.* 1 (1994) S91–S95.
- [11] W.H. Song, T. Teshiba, K. Rein, K.E. O'Shea, Ultrasonically induced degradation and detoxification of microcystin-LR (cyanobacterial toxin), *Environ. Sci. Technol.* 39 (2005) 6300–6305.
- [12] D.F. Rivas, A. Prosperetti, A.G. Zijlstra, D. Lohse, H.J.G.E. Gardeniers, Efficient sonochemistry through microbubbles generated with micromachined surfaces, *Angew. Chem. Int. Ed.* 49 (2010) 9699–9701.
- [13] A. Tauber, H.P. Schuchmann, C. von Sonntag, Sonolysis of aqueous 4-nitrophenol at low and high pH, *Ultrason. Sonochem.* 7 (2000) 45–52.
- [14] D.G. Wayment, D.J. Casadonte, Frequency effect on the sonochemical remediation of alachlor, *Ultrason. Sonochem.* 9 (2002) 251–257.
- [15] R. Czechowska-Biskup, B. Rokita, S. Lotfy, P. Ulanski, J.M. Rosiak, Degradation of chitosan and starch by 360 kHz ultrasound, *Carbohydr. Polym.* 60 (2005) 175–184.
- [16] M.A. Beckett, I. Hua, Impact of ultrasonic frequency on aqueous sonoluminescence and sonochemistry, *J. Phys. Chem. A* 105 (2001) 3796–3802.
- [17] A. Tiehm, U. Neis, Ultrasonic dehalogenation and toxicity reduction of trichlorophenol, *Ultrason. Sonochem.* 12 (2005) 121–125.
- [18] D. Drijvers, H. Van Langenhove, K. Vervaeke, Sonolysis of chlorobenzene in aqueous solution: organic intermediates, *Ultrason. Sonochem.* 5 (1998) 13–19.
- [19] S.N. Nam, S.K. Han, J.W. Kang, H.C. Choi, Kinetics and mechanisms of the sonolytic destruction of non-volatile organic compounds: investigation of the sonochemical reaction zone using several OH center dot monitoring techniques, *Ultrason. Sonochem.* 10 (2003) 139–147.
- [20] A. Henglein, C. Kormann, Scavenging of OH radicals produced in the sonolysis of water, *Int. J. Radiat. Biol.* 48 (1985) 251–258.
- [21] J. Rae, M. Ashokkumar, O. Eulaerts, C. von Sonntag, J. Reisse, F. Grieser, Estimation of ultrasound induced cavitation bubble temperatures in aqueous solutions, *Ultrason. Sonochem.* 12 (2005) 325–329.
- [22] L. Yang, J.F. Rathman, L.K. Weavers, Degradation of alkylbenzene sulfonate surfactants by pulsed ultrasound, *J. Phys. Chem. B* 109 (2005) 16203–16209.
- [23] L. Yang, J.F. Rathman, L.K. Weavers, Sonochemical degradation of alkylbenzene sulfonate surfactants in aqueous mixtures, *J. Phys. Chem. B* 110 (2006) 18385–18391.
- [24] L. Yang, J.Z. Sostaric, J.F. Rathman, L.K. Weavers, Effect of ultrasound frequency on pulsed sonolytic degradation of octylbenzene sulfonic acid, *J. Phys. Chem. B* 112 (2008) 852–858.
- [25] D.M. Deojay, J.Z. Sostaric, L.K. Weavers, Exploring the effects of pulsed ultrasound at 205 and 616 kHz on the sonochemical degradation of octylbenzene sulfonate, *Ultrason. Sonochem.* 18 (2011) 801–809.
- [26] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($\cdot\text{OH}/\text{O}^-$) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [27] V. Naddeo, S. Meric, D. Kassinos, V. Belgiorno, M. Guida, Fate of pharmaceuticals in contaminated urban wastewater effluent under ultrasonic irradiation, *Water Res.* 43 (2009) 4019–4027.
- [28] C. Petrier, A. Jeunet, J.L. Luche, G. Reverdy, Unexpected frequency-effects on the rate of oxidative processes induced by ultrasound, *J. Am. Chem. Soc.* 114 (1992) 3148–3150.
- [29] J.Z. Sostaric, P. Riesz, Adsorption of surfactants at the gas/solution interface of cavitation bubbles: an ultrasound intensity-independent frequency effect in sonochemistry, *J. Phys. Chem. B* 106 (2002) 12537–12548.
- [30] D.J. Casadonte, M. Flores, C. Petrier, Enhancing sonochemical activity in aqueous media using power-modulated pulsed ultrasound: an initial study, *Ultrason. Sonochem.* 12 (2005) 147–152.
- [31] J.A. LaVerne, OH radicals and oxidizing products in the gamma radiolysis of water, *Radiat. Res.* 153 (2000) 196–200.
- [32] E.J. Hart, A. Henglein, Sonolysis of formic-acid water mixtures, *Radiat. Phys. Chem.* 32 (1988) 11–13.
- [33] G.S. Jolly, D.J. Mckenney, D.L. Singleton, G. Paraskevopoulos, A.R. Bossard, Rates of OH radical reactions.14. Rate-constant and mechanism for the reaction of hydroxyl radical with formic-acid, *J. Phys. Chem.* 90 (1986) 6557–6562.
- [34] A. Henglein, Sonolysis of carbon-dioxide, nitrous-oxide and methane in aqueous-solution, *Z. Naturforsch.*, B: Chem. Sci. 40 (1985) 100–107.
- [35] G.J. Price, E.J. Lenz, The use of dosimeters to measure radical production in aqueous sonochemical systems, *Ultrasonics* 31 (1993) 451–456.
- [36] X.W. Fang, G. Mark, C. vonSonntag, OH radical formation by ultrasound in aqueous solutions.1. The chemistry underlying the terephthalate dosimeter, *Ultrason. Sonochem.* 3 (1996) 57–63.
- [37] S.E. Page, W.A. Arnold, K. McNeill, Terephthalate as a probe for photochemically generated hydroxyl radical, *J. Environ. Monit.* 12 (2010) 1658–1665.
- [38] R.W. Matthews, The radiation-chemistry of the terephthalate dosimeter, *Radiat. Res.* 83 (1980) 27–41.
- [39] R. Xiao, Z. He, D. Diaz-Rivera, G. Pee, L.K. Weavers, Sonochemical degradation of ciprofloxacin and ibuprofen in the presence of matrix organic compounds, *Environ. Sci. Technol.*, in preparation.
- [40] A. Kotronarou, Ph.D thesis, Ultrasonic irradiation of chemical compounds, in: California Institute of Technology, Pasadena, California, 1992.
- [41] EPI-Suite, Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.10, in: United States Environmental Protection Agency, Washington, DC, USA, 2008.
- [42] M. Gutierrez, A. Henglein, J.K. Dohrmann, H atom reactions in the sonolysis of aqueous-solutions, *J. Phys. Chem.* 91 (1987) 6687–6690.
- [43] D.F. Liu, G. Ma, L.M. Levering, H.C. Allen, Vibrational spectroscopy of aqueous sodium halide solutions and air-liquid interfaces: observation of increased interfacial depth, *J. Phys. Chem. B* 108 (2004) 2252–2260.
- [44] ACD/Labs6.00, in: Advanced Chemistry Development Inc., Toronto, Canada, 2002.
- [45] M. Ashokkumar, R. Hall, P. Mulvaney, F. Grieser, Sonoluminescence from aqueous alcohol and surfactant solutions, *J. Phys. Chem. B* 101 (1997) 10845–10850.
- [46] M. Ashokkumar, K. Vinodgopal, F. Grieser, Sonoluminescence quenching in aqueous solutions containing weak organic acids and bases and its relevance to sonochemistry, *J. Phys. Chem. B* 104 (2000) 6447–6451.
- [47] L. Zhu, J.M. Nicovich, P.H. Wine, Temperature-dependent kinetics studies of aqueous phase reactions of hydroxyl radicals with dimethylsulfoxide, dimethylsulfone, and methanesulfonate, *Aquat. Sci.* 65 (2003) 425–435.
- [48] M. Wall, M. Ashokkumar, R. Tronson, F. Grieser, Multibubble sonoluminescence in aqueous salt solutions, *Ultrason. Sonochem.* 6 (1999) 7–14.
- [49] B. Nanzai, K. Okitsu, N. Takenaka, H. Bandow, Y. Maeda, Sonochemical degradation of various monocyclic aromatic compounds: relation between hydrophobicities of organic compounds and the decomposition rates, *Ultrason. Sonochem.* 15 (2008) 478–483.
- [50] M. Chiha, S. Merouani, O. Hamdaoui, S. Baup, N. Gondrexon, C. Petrier, Modeling of ultrasonic degradation of non-volatile organic compounds by Langmuir-type kinetics, *Ultrason. Sonochem.* 17 (2010) 773–782.
- [51] C.M. Johnson, E. Tyrode, S. Baldelli, M.W. Rutland, C. Leygraf, A vibrational sum frequency spectroscopy study of the liquid-gas interface of acetic acid-water mixtures: 1. Surface speciation, *J. Phys. Chem. B* 109 (2005) 321–328.
- [52] C.M. Johnson, E. Tyrode, C. Leygraf, Atmospheric corrosion of zinc by organic constituents I. The role of the zinc/water and water/air interfaces studied by infrared reflection/absorption spectroscopy and vibrational sum frequency spectroscopy, *J. Electrochem. Soc.* 153 (2006) B113–B120.
- [53] P. Gunther, W. Zeil, U. Grisar, E. Heim, Versuche Über Die Sonolumineszenz Wassriger Lösungen, *Z. Elektrochem.* 61 (1957) 188–201.
- [54] H.H. Sun, S.P. Sun, J.Y. Sun, R.X. Sun, L.P. Qiao, H.Q. Guo, M.H. Fan, Degradation of azo dye black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, *Ultrason. Sonochem.* 14 (2007) 761–766.
- [55] S. Findik, G. Gunduz, Sonolytic degradation of acetic acid in aqueous solutions, *Ultrason. Sonochem.* 14 (2007) 157–162.
- [56] J.D. Seymour, R.B. Gupta, Oxidation of aqueous pollutants using ultrasound: salt-induced enhancement, *Ind. Eng. Chem. Res.* 36 (1997) 3453–3457.