Sonochemical degradation of surfactants with different charge types: Effect of the critical micelle concentration in the interfacial region of the cavity

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ABSTRACT

Ionic surfactants tend to accumulate in the interfacial region of ultrasonic cavitation bubbles (cavities) because of their surface active properties and because they are difficult to evaporate in cavitation bubbles owing to their extremely low volatilities. Hence, sonolysis of ionic surfactants is expected to occur in the interfacial region of the cavity. In this study, we performed sonochemical degradation of surfactants with different charge types: anionic, cationic, zwitterionic, and nonionic. We then estimated the degradation rates of the surfactants to clarify the surfactant behavior in the interfacial region of cavitation bubbles. For all of the surfactants investigated, the degradation rate increased with increasing initial bulk concentration and reached a maximum value. The initial bulk concentration to obtain the maximum degradation rate had a positive correlation with the critical micelle concentration (cmc). The initial bulk concentrations of the anionic surfactants were lower than their cmc, while those of the cationic surfactants were higher than their cmcs. These results can be explained by the negatively charged cavity surface and the effect of the coexisting counterions of the surfactants.

1. Introduction

Ultrasonic irradiation of a liquid induces formation, growth, and collapse of gas microbubbles, cavities. During cavity collapse, local reaction zones with extremely high temperature (several thousand of degrees) and pressure (several hundred atmosphere pressure) are produced [1,2]. In aqueous solution, reactive OH radicals and hydrogen atoms are formed by sonolysis of water [3,4]. Therefore, it is considered that sonochemical degradation of organic compounds proceeds by the direct pyrolysis reaction inside cavities and by OH radicals in the interfacial region of cavities. Previous reports have shown that organic compounds with high hydrophobicity and high volatility are readily decomposed by sonochemical reactions [5] because hydrophobic compounds accumulate in the interfacial region of cavities during the bubble growth process [6]. Volatile compounds vaporize in cavity and are then thermally decomposed [7]. The interfacial region of the cavity has attracted attention since the early stages of sonochemistry [8]. Therefore, many studies have investigated this target by sonolysis of surfactants [9–24].

We previously investigated the physicochemical properties of the interfacial region of cavities by sonochemical degradation of anionic surfactants [25,26]. We found that the initial degradation rates of linear alkylbenzene sulfonates (LASs) were strongly dependent on their concentrations. However, the degradation rates of LASs with different carbon chain lengths had different maximum values at different initial bulk concentrations. In addition, there was a clear relationship between the maximum degradation rate and the critical micelle concentration (cmc) for each LAS. Furthermore, the concentrations of the LASs when the degradation rates reached their maximum values were smaller than their cmcs. We suggested that the micelles formed in the interfacial region of the cavitation bubbles could reduce the cavitation efficiency, although the detailed mechanism was unclear.

In the present study, we performed sonochemical degradation of surfactants with different charge types, such as the cationic surfactant benzylalkyldimethyl ammonium chloride (BAC) with different alkyl chain lengths. Based on the degradation rates, the effect of micelle formation on the cavitation efficiency is discussed. Furthermore, we investigated the surface potential of the cavity on the basis of the degradation behavior of surfactants with different charge types. The microbubbles generated by the aerator in the water reservoir are considered to be negatively charged because of excess adsorption of OH− compared with H+ at the air–water interface owing to the...
difference in the hydration energies [27]. However, the details of the surface potential of ultrasonic cavitation bubbles remain unclear. Based on the degradation rates of various surfactants with different charge types, the effect of the cavitation surface charge on the surfactant counterion, and subsequent micelle formation of the surfactant in the interfacial region of the cavity was suggested.

2. Experimental section

2.1. Materials

Benzylldimethyldodecyl ammonium chloride (BAC C\textsubscript{12} > 98.0%), benzyldimethyloctadecyl ammonium chloride (BAC C\textsubscript{14} > 98.0%), benzylldimethylhexadecyl ammonium chloride (BAC C\textsubscript{16} > 97.0%), benzylldimethyltridecyl ammonium chloride (BAC C\textsubscript{18} > 97.0%), octylphenolethoxylate (PE C\textsubscript{8} n = approx.10), dodecyldimethyl (3-sulfopropyl)ammonium hydroxide inner salt (SAA C\textsubscript{12} > 98.0%), and octadecyldimethyl (3-sulfopropyl) ammonium hydroxide inner salt (SAA C\textsubscript{16} > 99.0%) were supplied by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Sodium p-octylbenzene sulfonate (LAS C\textsubscript{8}) and sodium p-decylbenzene sulfonate (LAS C\textsubscript{10}) were supplied by Nacalai Tesque Inc. (Kyoto, Japan). Dodecyldimethyl glycine (Gly C\textsubscript{12} > 95.0%) was supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All of the surfactant solutions were prepared with Milli-Q water.

2.2. Methods

Ultrasonic irradiation was performed with a 65 mm diameter oscillator (Kaijo 4611type, MFG. No. S644, frequency 200 kHz), which was operated at 200 W. The diameter of the reaction vessel was 55 mm, the base of the vessel was 1 mm thick, and the distance from the oscillator was fixed at 4 mm. The details of the irradiation setup and the characteristics of the reaction vessel are described elsewhere [28]. An Ar-saturated aqueous solution of each surfactant (60 mL) was sonicated in a water bath maintained at 20\degree C by a compact handy cooler with a temperature controller (AS ONE 102TCN).

2.3. Analysis

The concentration of each surfactant in the aqueous solution was monitored by high-performance liquid chromatography (HPLC, Shimadzu LC-20AD, SPD-20AV) with ultraviolet (UV) detection using a C18 column with a mobile phase of acetonitrile/50 mM NaClO\textsubscript{4} aqueous solution (80:20 v/v) flowing at 1.0 mL min\textsuperscript{-1}. The initial degradation rate was determined by plotting the concentration of the BAC during sonication as a function of the cavitation time and then fitting the time profile to a logarithmic equation. The obtained logarithmic equation was differentiated with respect to the sonication time, and time $t = 0$ was substituted into the differential equation to obtain the initial degradation rate [29]. The rate was determined as the average value from several experimental runs. The critical micelle concentration (cmc) values were determined by the electrical conductivity method. The electrical conductivity measurements of the surfactant solutions were performed at room temperature (25\degree C). Surfactant solutions containing 3 mmol L\textsuperscript{-1} tert-butanol as a OH radical scavenger were also sonicated to estimate the contribution of the direct pyrolysis reaction [30]. The yields of methane, ethane, ethylene, and acetylene gases were determined by gas chromatography (Shimadzu GC-2025) with a flame ionization detector and an Alumina BOND/Na\textsubscript{2}SO\textsubscript{4} column (RESTEK). Gas samples were taken from the headspace of the vessel for analysis after 60 min sonication.

3. Results and discussion

3.1. Effect of carbon chain length on degradation rate

The surfactant concentration change with time during sonication with an initial bulk concentration of 6 mmol L\textsuperscript{-1} is shown in Fig. 1. We confirmed that these results have good reproducibility. The degradation rate increased with decreasing carbon chain length in the order BAC C\textsubscript{16} < BAC C\textsubscript{14} < BAC C\textsubscript{12}. These results agree well with the order of the degradation rates of the LASs in our previous report [26]. A surfactant with shorter carbon-chain-length has lower activation energy for adsorption [31]. Consequently, the degradation rate of surfactant increased because the adsorption step on gas–liquid interface became faster. The degradation rate of each BAC as a function of the initial bulk concentration is shown in Fig. 2. For all of the BACs, the degradation rate gradually increased to a maximum value with increasing initial bulk concentration, and then decreased at different concentrations. The maximum degradation rates of the BACs depended on their carbon chain lengths. These trends are also similar to the degradation results of the LASs. The degradation rates of BAC C\textsubscript{12}, C\textsubscript{14}, and C\textsubscript{16} reached the maximum values when their initial bulk concentrations were about 12, 10, and 6 mmol L\textsuperscript{-1}, respectively.

3.2. Effect of micelle formation on maximum degradation rate

Considering the cause of the local maximum value of the degradation rate, we expected involvement of micelle formation of the surfactant. It has previously been reported that micelle formation can reduce the cavitation efficiency [20,21]. In addition, based on the clear relationship between the maximum degradation rate and cmc for LASs, we suggested that micelles formed in the interfacial region of the cavity by accumulation of the anionic surfactant even when the concentration was less than the cmc and reduced the cavitation efficiency [25]. We then investigated the relation between the maximum degradation rate and the cmc for surfactants with different charge types. The data of electrical conductivity to estimate cmc values for anionic and cationic surfactants are shown in Fig. S1. The other cmc values for zwitterionic and nonionic surfactants were taken from a data book [32] because the electrical conductivity was too small to measure. The relation between the initial

![Fig. 1. Sonochemical degradation of BAC C\textsubscript{12} (○), BAC C\textsubscript{14} (□), and BAC C\textsubscript{16} (×) in aqueous solution under an Ar atmosphere. The initial bulk concentrations of the BACs were 6 mM.](image-url)
represents the 1:1 relation. Charge type of the surfactant: degradation rate reaches the maximum value and the cmc. The gray dashed line Fig. 3.

relationship between the initial BAC C\textsubscript{12} concentration and the BAC degradation rate for BAC C\textsubscript{12} (○), BAC C\textsubscript{14} (□), BAC C\textsubscript{16} (○), and BAC C\textsubscript{18} (×). The error bar indicates standard deviation based on 3 times experiments.

bulk concentration for the maximum degradation rate and the cmc for each surfactant is shown in Fig. 3. For comparison, the data for LAS C\textsubscript{0} and C\textsubscript{12} are also plotted [25]. If micelle formation of the surfactant reduced the cavitation efficiency, the degradation rate should reach the maximum value when the initial bulk concentration is the cmc (dashed line in Fig. 3). For the zwitterionic and nonionic surfactants, the degradation rates had maximum values at around the cmcs. However, the degradation rates of the anionic surfactants reached their maximum values at lower bulk concentrations than their cmcs. In contrast, the degradation rates of the cationic surfactants increased even above their cmcs. Destallats et al. [20] and Vinodgopal et al. [11] also indicated that the degradation rates decreased above cmc for non-ion surfactants, alkylphenol ethoxylate and Teric GN9, respectively. Yang et al. [22] reported that under pulse sonication the degradation rate of anion surfactants, dodecyl benzenesulfonate and octyl benzenesulfonate, decreased at the surfactant concentration over 20% of cmc. Sostaric et al. [18] showed that the radical yields from the sonication of anion surfactant peaked out at the surfactant concentration much below cmc while that for non-ion surfactant reached maximum values at around cmc. These results were well accorded with our results, indicating the effect of the electric charge of the surfactant on the relation between the maximum degradation rate and the cmc. However, adsorption or repulsion of the surfactant owing to its electrical charge cannot explain these results.

3.3. Contribution of pyrolysis

Based on the assumption that the cavity has a negatively charged surface [27], the cationic surfactant could electrostatically adsorb on the cavity surface. Surfactant adsorption on the cavity surface can be confirmed by the contribution ratios of pyrolysis in sonolysis for the BACs (Fig. S2). The pyrolysis contribution was estimated from the results of sonolysis with 3 mmol L\textsuperscript{-1} tert-butanol as a OH radical scavenger. The scavenging ability of tert-butanol for the OH radical has been previously reported [6,7,33,34]. The adsorbed surfactant in the interfacial region of the cavity thermally decomposed. The contribution ratios of pyrolysis in sonolysis for the BACs were constant at almost 100% irrespective of the initial bulk concentration and carbon chain length. Corresponding results of surfactant adsorption on the cavity surface have been reported in previous studies [9,12,17,18]. Nevertheless, the contribution ratio of pyrolysis was constant even above the cmc (Fig. S2). Based on these results, the further increases of the degradation rates of the BACs above their cmcs can be explained by adsorption of the cationic surfactant even in the micellar state. This is unreasonable from the viewpoint of the surface activity of the surfactant.

3.4. Ionic strength in the interfacial region of cavity

On the basis of the above results, we focused on the effect of the counterion of the surfactant. From the viewpoint of ion size, the surfactant counterions, such as the sodium and chloride ions, diffuse faster from the bulk solution to the cavity surface than the surfactant ions. For the cationic surfactants, the Cl\textsuperscript{-} counterion is electrostatically repulsed by the negatively charged cavity surface, as shown in Fig. 4(a). Consequently, the ion strength in the interfacial region increases and the surfactant activity decreases on the basis of Debye–Hückel theory. In general, the attracting force between ions involved in the dissociation equilibrium is shielded efficiently by dissolved solutes. Then, the actual concentration (activity) of ion decreased and the equilibrium was shifted [35]. In the interfacial region of cavity of the present study, high concentration of Cl\textsuperscript{-} counterion shifted the equilibrium of surfactant to dissociated state. Therefore, the decrease of the surfactant activity makes micelle formation difficult, and the cmc of the cationic surfactant increases. Conversely, the counterion of the anionic surfactants (Na\textsuperscript{+}) is electrostatically attracted to the negatively charged cavity surface, as shown in Fig. 4(b). The increase of the surfactant activity owing to the decreased ion strength in the interfacial region results in a decrease in the cmc. These hypotheses were different from the results of previous study about the effect counterions on micelle formation in the surfactant solution with adding salt [36]. To verify the above hypotheses, we measured the cmcs of surfactant solutions containing 10 mmol L\textsuperscript{-1} HCl (Cl\textsuperscript{-}) under the assumption of electrostatic repulsion by the negatively charged cavity surface in the interfacial region. The electrical conductivity of each surfactant aqueous solution with addition of HCl is shown in Fig. S3. We chose the HCl concentration considering the effect of the solution pH on dissociation of the surfactants. The relation between the initial bulk concentration for the maximum degradation rate and the cmc in the surfactant solution with HCl is shown in Fig. 5. The cmc of the anionic surfactant decreased, whereas that of the cationic surfactant

![Fig. 2. Relationship between the initial BAC C\textsubscript{12} concentration and the BAC degradation rate for BAC C\textsubscript{12} (○), BAC C\textsubscript{14} (□), BAC C\textsubscript{16} (○), and BAC C\textsubscript{18} (×). The error bar indicates standard deviation based on 3 times experiments.](image1)

![Fig. 3. Relationship between the initial surfactant concentration when the degradation rate reaches the maximum value and the cmc. The gray dashed line represents the 1:1 relation. Charge type of the surfactant: □ anionic, ○ cationic, ⋄ zwitterionic, and △ nonionic.](image2)
increased. These results with adding acid were different from the widely known relations between cmc and electrolyte concentration in the presence and absence of added salts. For the nonionic and zwitterionic surfactants, the cmcs remained almost the same with addition of Cl\textsuperscript{-}.

Accordingly, these plots fit on the 1:1 line, as shown in Fig. 5. While some of the cationic surfactants had values below the 1:1 line, these plots fitted the 1:1 line when the cmc was estimated for the surfactant solution with higher Cl\textsuperscript{-} concentration (20 mmol L\textsuperscript{-1} HCl).

3.5. Critical micelle concentration in the interfacial region of cavity

From the above results, it was considered that it was clarified that formation of micelles in the interfacial region of the cavity surface inhibited surfactant degradation. This inhibition mechanism can be explained as follows. The temperature of the hotspot and/or the number of cavities might decrease because the micelles decrease the acoustic pressure of ultrasound against the cavities by the shelter effect. Alternatively, the micelles might prevent surfactant molecules from diffusing from the bulk solution to the cavities. To investigate the mechanism, we measured the yields of C\textsubscript{2} hydrocarbons (ethane, ethylene, and acetylene) as the degradation products of surfactant sonolysis. In addition, based on the hydrocarbon yields, we estimated the average temperatures of the cavities by the methyl radical recombination method [1,37–39]. The total yields of C\textsubscript{2} hydrocarbons (ethane, ethylene, and acetylene) and average cavity temperatures estimated from sonolysis of BAC C\textsubscript{12} for different initial bulk concentrations are shown in Fig. 6. Based on comparison with the degradation results in Fig. 2, the hydrocarbon yields increased even when the initial bulk concentration was above that for the maximum degradation rate (around 12 mmol L\textsuperscript{-1}). Furthermore, the average cavity temperature was almost the same (about 2500 K) regardless of the initial bulk concentration. From these results, the inhibition of degradation rate by micelle formation was difficult to be explained by quenching of cavitation bubbles. Inherently,
On the basis of the findings of this study, sonolysis of surfactants has the tants were electrostatically affected by the negatively charged surface. These results can be explained by the negative charge of the cavitation bubble surface and the effect of the coexisting counterions of. These results can be explained by the negative charge of the cmcs in the cavity interfacial region and bulk solution. In contrast, the anionic and cationic surfactants showed different behavior during cavitation by the analysis of a heterogeneous reaction kinetics. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors are grateful to Mr. Kosaku Matsuo for assistance. This work was funded by a research grant from the Amano Institute of Technology. We thank Tim Cooper, PhD, from Edanz Group (www.edanzediting.com/ac) for editing a draft of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultrasonch.2020.105354.
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