

Novel complexation between ferric ions and nonionic surfactants (Brij) and its visible light activity for CCl₄ degradation in aqueous micellar solutions

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Abstract

Wide attentions are recently focused on the use of surfactants for the remediation of contaminated soil and groundwater. UV photolysis has been often studied for the post-treatment of the contaminated surfactant solutions. In this study, we report a novel photolysis system where a recalcitrant perchloro compound can be degraded in a surfactant solution under visible light ($\lambda > 420$ nm) illumination: CCl₄ could be successfully dechlorinated in a nonionic surfactant (Brij) solution under visible light. The addition of Fe³⁺ in this surfactant solution enables the visible light induced dechlorination of CCl₄ because Fe³⁺ ions form complexes with the surfactant molecules (carrying the polyoxyethylene group) to act as a visible light sensitizer. A broad UV-Vis absorption band, which is centered around 370 nm and extended into the visible region, appears as a result of this complexation. The generation of this visible light absorption band is observed only in the Brij + Fe³⁺ solution and absent in other surfactant + Fe³⁺ solutions. Accordingly, the visible light induced dechlorination of CCl₄ is significant only in the Brij + Fe³⁺ solution. It is proposed that the Fe(III)–Brij complexing centers are excited by absorbing visible light and subsequently transfer electrons to adjacent CCl₄ molecules confined within the same micelle. Direct evidences for the visible light activation of the Fe³⁺-complexed Brij micelles were obtained from the photocurrent measurement. Effects of various experimental parameters and proposed mechanism for this visible light photochemical process are discussed.

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1. Introduction

Soil and groundwater contamination by hazardous organic pollutants has been a hot issue of environmental concern since it is persistent, widespread, and not easily remediable. One of the most widely used remedies for the contaminated soil and groundwater is the pump-and-treat technology. However, this conventional *ex situ* remediation method is often slow, costly, inefficient, and socially unpopular. Recently, soil flushing or washing that uses surfactant solutions to assist the solubilization of hydrophobic contaminants is gaining wide attentions because this method is faster, economic, and more efficient [1–5]. The surfactant can rapidly desorb the hydrophobic organic pollutants sorbed on soil, and then transfer them into the mobile aqueous micelles, which can be easily recovered by pumping. However, the

post-treatment processes are required to remove organic pollutants remaining in the surfactant solution.

Advanced oxidation processes (AOPs) such as radiolysis [6,7] and UV photolysis [8–13] have been investigated for the post-treatment process of the recovered surfactant solution. In particular, UV photolytic treatment has several advantages over other technologies in (i) no need of chemical additives; (ii) potential use of solar light; (iii) relatively fast degradation; (iv) possible reuse of surfactants. Many advanced remedial processes that are being intensely investigated are based on photochemical reactions, which include heterogeneous or homogeneous photocatalysis [14–19] and photo-Fenton reaction [20]. Organic pollutants whose photolytic reactions in UV-illuminated surfactant solutions have been reported include polychlorinated biphenyls (PCBs) [12,21,22], polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) [23], 2-chlorophenol [10], DDT [13], nitroaromatic compounds [24], polychlorobenzene [9], and CCl₄ [25]. Upon absorbing UV light, an excited aromatic compound undergoes successive electron transfer,

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C–Cl bond cleavage, and H-atom abstraction reactions with surrounding surfactant molecules to yield dechlorinated products. In this case, the surfactants not only concentrate chlorinated compounds within the hydrophobic core of micelles but also serve as electron and H-atom donors in the photochemical conversion process. However, the use of visible light in the photolytic treatment of surfactant solutions has not been reported, whereas it is essential for utilizing solar light in photochemical remediation processes [26–28].

Here we report a novel case of visible light utilization in CCl_4 degradation in aqueous surfactant solutions containing ferric ions, which is the first example, to the best of our knowledge, of truly visible light photolysis of chlorinated compounds in surfactant micelles. The nonionic surfactant (Brij) that contains alkyl and polyoxyethylene chains was mainly used in this study. Although neither CCl_4 nor the surfactant is directly photoexcited under visible light, an unusual complexation between ferric ions and nonionic surfactants serve as a visible light sensitizer to dechlorinate CCl_4 . Effects of various experimental parameters and suggested mechanism for this visible light induced CCl_4 degradation in an aqueous micellar solution are described. This novel photochemical process could be useful as a basis of new solar remediation technology using surfactants especially when the reductive conversion of pollutants is involved.

2. Experimental

2.1. Chemicals and reagents

Surfactants used in this study include: Brij series, Triton X series, cetyl trimethylammonium bromide (CTAB) (from Aldrich) and sodium dodecyl sulfate (SDS) (from Kanto). Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was obtained from Kanto Chemical. CCl_4 (J.T. Baker) was purified by distillation. The water used was ultrapure ($18 \text{ M}\Omega \text{ cm}$) and prepared by a Barnstead Purification System. All other chemicals used were of reagent grade and used without further treatments.

2.2. Optical measurements

Fe^{3+} stock solution (2 mM) was prepared by dissolving ferric nitrate in deionized water, and immediately acidified with HClO_4 to pH 2.5. The optical absorption spectra of the aqueous solution of ferric ions and/or surfactants were recorded with a UV-Vis spectrophotometer (Shimadzu UV-2401PC). Fe^{3+} solution and surfactant + Fe^{3+} solution were filtered through a $0.45\text{-}\mu\text{m}$ PTFE filter (Millipore) before measuring the absorption spectra to remove any possible undissolved aggregates. The pH of both Fe^{3+} and surfactant + Fe^{3+} solutions was adjusted to 2.8.

2.3. Photolysis and analysis

For a typical photolysis experiment, an air-equilibrated aqueous solution with a desired surfactant (usually 4.0 g/l)

and Fe^{3+} concentration (usually 1 mM) was prepared in a 30-ml quartz reactor. A calculated amount of CCl_4 was added directly into the reactor to give a desired concentration (typically 1 mM). The solution was stirred for 30 min before the photolysis to assure the complete dissolution of CCl_4 in the surfactant solution. The initial pH of this solution was around 3. Photolyses were performed using a 300 or 450-W Xe-arc lamps (Oriel) as a light source. Light passed through a 10-cm IR water filter and a long pass filter ($\lambda > 420 \text{ nm}$), and then the filtered light was focused onto the reactor. Light intensity was measured by chemical actinometry using (*E*)- α -(2,5-dimethyl-3-furylethylidene) (isopropylidene)succinic anhydride (Aberchrome 540) [29]. The actinometry monitored the photobleaching kinetics of the colored Aberchrome 540 solution in toluene spectrophotometrically. A typical incident light intensity (I_{inc}) was estimated to be about 4×10^{-3} Einstein/l min in the wavelength range 420–550 nm. Sample aliquots of 1 ml were withdrawn intermittently from the illuminated reactor with a 1-ml syringe, filtered through a $0.45\text{-}\mu\text{m}$ PTFE filter (Millipore). More than duplicate experiments were done for each photolysis. The filtered solution was analyzed by an ion chromatograph (IC) to determine the chloride concentration. The IC system was a Dionex DX-120 with a conductivity detector and a Dionex IonPac AS-14 wide bore column ($4 \text{ mm} \times 250 \text{ mm}$). The eluent contained 1 mM NaHCO_3 and 3.5 mM Na_2CO_3 . CCl_4 and intermediates were extracted from the aqueous solution with pentane in a sealed 1.8-ml glass vial. Extracted CCl_4 and intermediates were analyzed by using a Hewlett-Packard (HP6890A) gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) and a HP-5 column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$). Nitrogen was used as a carrier gas. Duplicate injections were made for each sample analysis.

2.4. Photoelectrochemical measurement

The visible light sensitizing activity of the surfactant solution was tested by measuring visible light induced photocurrents collected on an inert Pt electrode immersed in the surfactant solution. The short-circuit photocurrent generated in a surfactant micellar solution in the presence or absence of Fe^{3+} was measured with a potentiostat (EG&G, Model 263A) at an applied electrode potential where the dark current in a specific surfactant solution was zero. The photocurrent generation was monitored under the visible light ($\lambda > 420 \text{ nm}$) illumination (300-W Xe lamp). The photoelectrochemical reactor had a Pt-gauze working electrode, a graphite counter electrode, and a reference saturated calomel electrode (SCE).

3. Results and discussion

3.1. Visible light induced dechlorination of CCl_4

Fig. 1 shows that visible light ($\lambda > 420 \text{ nm}$) irradiation of the solution of nonionic surfactant [Brij-35:

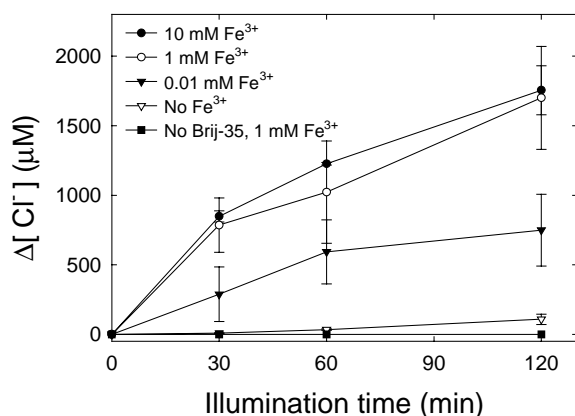
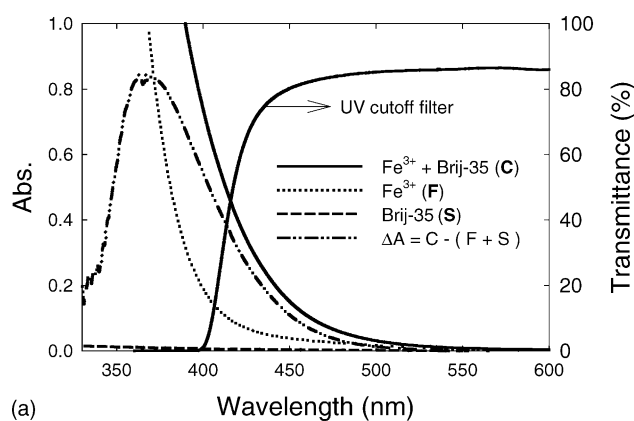


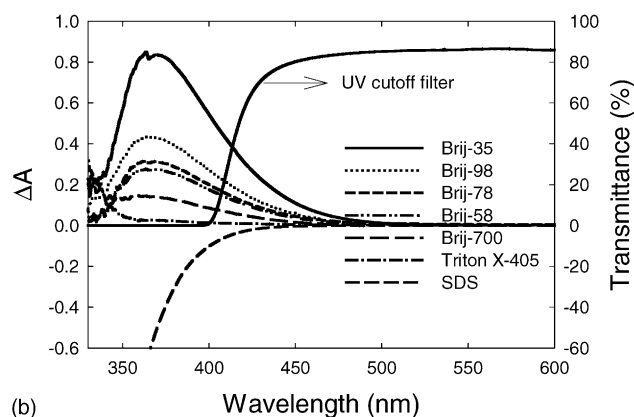
Fig. 1. Time-dependent chloride production from the visible light ($\lambda > 420$ nm) induced degradation of CCl_4 in aqueous micellar solution in the presence or absence of Fe^{3+} ions. Experimental conditions were: $[\text{Brij-35}] = 4.0$ g/l; $[\text{CCl}_4] = 1$ mM; air-equilibrated.

$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$] and ferric ions leads to the dechlorination of CCl_4 . The dechlorination with the surfactant alone was insignificant. The addition of ferric ions into this surfactant solution drastically increases the CCl_4 dechlorination rates whereas the photolysis of $\text{CCl}_4 + \text{Fe}^{3+}$ solution in the absence of the surfactant produces no chloride. Therefore, the role of ferric ions associated with the surfactant micelles seems to be responsible for this visible light activity. The initial dechlorination rate obtained with Brij-35 and Fe^{3+} (1 mM) corresponds to an apparent photonic efficiency [$\Psi = (d[\text{Cl}^-]/dt)_i / I_{\text{inc}}$] of 0.007.

The visible light reactivity for CCl_4 dechlorination indicates that visible light should be absorbed by the surfactant solution and the effect of Fe^{3+} implies that some kind of complexation between the surfactant and ferric ions should be responsible for the visible light absorption. A yellowish color of the Brij + Fe^{3+} solution was immediately noticed upon mixing. Fig. 2a compares the UV-Vis absorption spectra of Brij-35, Fe^{3+} , and $\text{Fe}^{3+} + \text{Brij-35}$ solutions. The absorbance difference (ΔA) between the $\text{Fe}^{3+} + \text{Brij-35}$ solution and the sum of each component (absorbance of Fe^{3+} only solution + absorbance of Brij-35 only solution) is shown together. It clearly shows that Fe^{3+} ions form complex with Brij-35 surfactants with red-shifting the absorption onset into the visible region. The ΔA spectrum represents the absorption from the Fe^{3+} -Brij-35 complex that should act as a visible light sensitizer. The complex absorption band is maximal around 370 nm and is well extended into the visible region. Fig. 3 shows the initial dechlorination rates of CCl_4 as a function of illuminating wavelengths. The wavelength-dependent profile of the dechlorination rate is very similar to that of ΔA (Fig. 2a), which assures that the complex formation is responsible for the visible light reactivity. The ΔA spectra of other surfactant solutions containing Fe^{3+} are compared in Fig. 2b and will be discussed in the later section.



(a)



(b)

Fig. 2. UV-Vis absorption spectra of aqueous surfactant solutions. (a) Absorption spectra of Brij-35 (S), Fe^{3+} (F), Brij-35 + Fe^{3+} (C) solutions, and the absorbance difference (ΔA) between $\text{Fe}^{3+} + \text{Brij-35}$ solution (C) and the sum of each component (absorbance of Fe^{3+} only solution + absorbance of Brij-35 only solution) is shown together. (b) Comparison of ΔA and surfactant solutions for various surfactants. The optical cell pathlength was 5 cm. The light transmittance profile through the UV cutoff filter ($\lambda > 420$ nm) that was used in the photodegradation experiment is compared along with the spectra. Experimental conditions were: $[\text{Fe}^{3+}] = 1$ mM; [surfactant] = 4.0 g/l; pH 2.8.

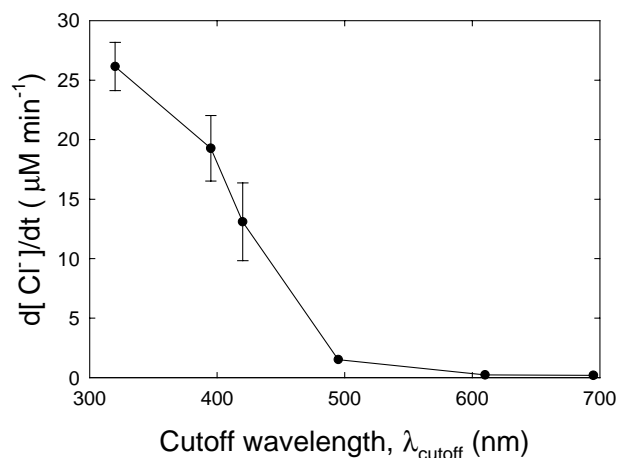


Fig. 3. Initial dechlorination rates of CCl_4 as a function of the illuminating wavelength range. The wavelength of the abscissa represents the 50% cutoff wavelength of the long-pass filter used in illumination (i.e., illumination wavelengths $> \lambda_{\text{cutoff}}$). Experimental conditions were: $[\text{Fe}^{3+}] = 1$ mM; $[\text{CCl}_4] = 1$ mM; $[\text{Brij-35}] = 4.0$ g/l; air-equilibrated.

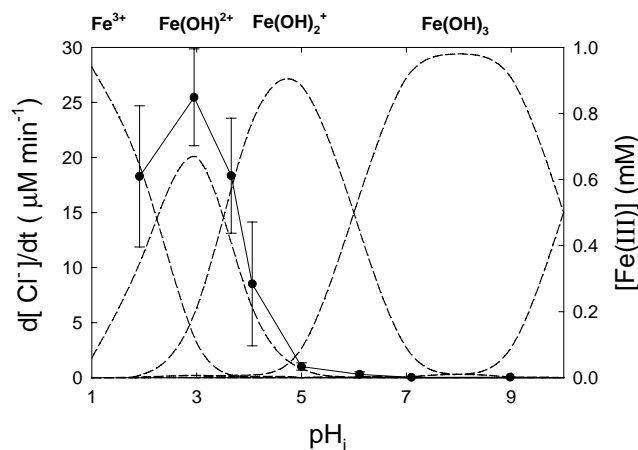


Fig. 4. Initial dechlorination rates of CCl_4 in the visible light illuminated Fe^{3+} + Brij-35 solution as a function of the initial pH. The calculated pH-dependent speciation of Fe(III) is shown in dashed lines along with the dechlorination data. Experimental conditions were: $[\text{Fe}^{3+}] = 1 \text{ mM}$; $[\text{CCl}_4] = 1 \text{ mM}$; $[\text{Brij-35}] = 4.0 \text{ g/l}$; air-equilibrated.

3.2. Effect of pH and surfactant structure on the visible light activity

The surfactant–Fe(III) complex formation can be dependent on the pH of the solution since the distribution of ferric species is pH-dependent. Fig. 4 shows the visible light induced dechlorination rates as a function of pH along with the pH-dependent Fe(III) speciation. The Fe(III) speciation was calculated using the following equilibrium constants ($-\log K$) for successive reactions of Fe(III) hydrolysis [30]: 2.2 for $\text{Fe}^{3+}/\text{Fe}(\text{OH})^{2+}$, 3.5 for $\text{Fe}(\text{OH})^{2+}/\text{Fe}(\text{OH})_2^+$, 6 for $\text{Fe}(\text{OH})_2^+/\text{Fe}(\text{OH})_3$, 10 for $\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_4^-$. The CCl_4 degradation rate is maximized around pH 3 and reduced at lower pH where free Fe^{3+} species are dominant or at higher pH where the condensation or precipitation of hydroxyferric species is favored. It should be noted that the dechlorination rates closely correlate with the concentration profile of $\text{Fe}(\text{OH})_2^+$ species, which implies that this monohydroxyl ferric species could be responsible for the complex formation with oxygen atoms of the polyoxyethylene groups (or terminal OH groups) in Brij surfactants (S). This is similarly

compared with the case of visible light induced degradation of Acid Orange 7 complexed with ferric ions [28], in which the visible light activity of the complex was the highest with $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_2^+$ species.

On the other hand, since the surfactant–Fe(III) complex formation should be critically dependent on the surfactant structure as well, the visible light activity of CCl_4 dechlorination in other surfactant solutions was tested. In agreement with this expectation, the CCl_4 dechlorination rates in micellar solutions strongly depend on the kind of surfactant as presented in Table 1. While Brij series surfactants show high activities in the dechlorination of CCl_4 , a cationic surfactant (CTAB), and an anionic surfactant (SDS) were inactive. The ΔA spectra shown in Fig. 2b, an indicator of the complex formation, are consistent with the visible light activity data in Table 1 although the correlation is not quantitative. Only Brij surfactants that exhibit significant visible light activity induce the complexation band whereas Triton and SDS do not. In particular, SDS exhibits a large negative ΔA band on the contrary. This indicates that the complexation between the ferric ions and the sulfate groups in SDS bleaches the characteristic yellowish color of the hydroxy ferric species. Since the addition of sulfates to Fe^{3+} solution induces the formation of FeSO_4^+ complex as a dominant species [28], the Fe^{3+} –SDS complex formation should be favored over hydroxy ferric species in the presence of excess SDS ($\sim 14 \text{ mM}$). The ΔA spectra of CTAB is not shown in Fig. 2b because the addition of Fe^{3+} in CTAB solution induced the formation of turbid precipitates. Judging from the above observations, the presence of polyoxyethylene groups in the surfactant structure is critical in forming the visible light-absorbing complexes with the hydroxy ferric species and in enabling the visible light induced electron transfer from the complexing center to CCl_4 .

However, it should be noted that Triton X-114 and Triton X-405, which also have polyoxyethylene groups in their molecular structure, show negligible visible light activity. The main difference between the Brij and Triton X series surfactants is that the latter has a benzene ring at the connection between the alkyl group and the polyoxyethylene group. A similar difference is also noted when comparing Brij-78 and Brij-98. Although they are identical except that

Table 1

Initial rates ($\mu\text{M}/\text{min}$) of CCl_4 dechlorination in various surfactant solutions illuminated with visible light ($\lambda > 420 \text{ nm}$) in the presence of ferric ions^a

Surfactant	Type	Chemical formula	$d[\text{Cl}^-]/dt$
Brij-35	Nonionic	$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$	27.0 ± 3.0
Brij-58	Nonionic	$\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$	24.5 ± 4.3
Brij-78	Nonionic	$\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$	37.9 ± 10.0
Brij-98	Nonionic	$\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$	3.3 ± 0.5
Brij-700	Nonionic	$\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{100}\text{OH}$	8.6 ± 5.9
Triton X-114	Nonionic	$4-(\text{C}_8\text{H}_{17})\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_8\text{OH}$	0.2 ± 0.1
Triton X-405	Nonionic	$4-(\text{C}_8\text{H}_{17})\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{40}\text{OH}$	0.5 ± 0.3
CTAB	Cationic	$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	0.4
SDS	Anionic	$\text{C}_{11}\text{H}_{23}\text{CH}_2\text{OSO}_3^-\text{Na}^+$	<0.1

^a Experimental conditions were: $[\text{Fe}^{3+}] = 1 \text{ mM}$, $[\text{surfactant}] = 4.0 \text{ g/l}$, $[\text{CCl}_4] = 1 \text{ mM}$.

Brij-98 has a double bond in the middle of the alkyl group, the photoreactivity of Brij-98 is drastically reduced. We may speculate that the presence of a benzene ring or double bond makes the surfactant molecule somewhat rigid (less flexible) and could inhibit the complex formation with Fe^{3+} . Alternatively, the presence of π electrons in a surfactant molecule might inhibit the photoinduced electron transfer process in the CCl_4 –surfactant– Fe^{3+} system. A noncovalent intermolecular force through the cation– π interaction in aqueous media is now widely recognized [31]. Therefore, the presence of π electrons in the surfactant chain could make the $\text{Fe(III)}-\pi$ interaction favorable and inhibit the Fe(III) –polyoxyethylene complexation.

3.3. Effect of dissolved gas and surfactant concentration

The effect of dissolved gas in the surfactant solution was investigated, and shown in Fig. 5. The chloride generation from CCl_4 degradation in N_2 - or air-saturated solution shows little difference. However, chloride production was significantly suppressed in the O_2 -saturated solution because dissolved O_2 should compete with CCl_4 for the electron from the photoexcited Fe^{3+} –surfactant complex. The quenching effect of O_2 in the visible light induced CCl_4 dechlorination has been also observed in a dye-sensitized TiO_2 system [19] where both O_2 and CCl_4 compete for conduction band electrons. The inhibiting effect of dissolved O_2 supports that the visible light induced degradation of CCl_4 in the Brij + Fe^{3+} system should proceed through a reductive path.

Fig. 6 shows that the chloride production rates are linearly proportional to the surfactant concentration up to $[\text{Brij-35}] = 4.0 \text{ g/l}$, which is far beyond the critical micellar concentration (CMC) of Brij-35, 0.19 g/l [10]. Increasing the surfactant concentration increases the number of micelles, which in turn increases both the number of Fe^{3+} -complexing sites and the total volume of hydrophobic cores that hold CCl_4 .

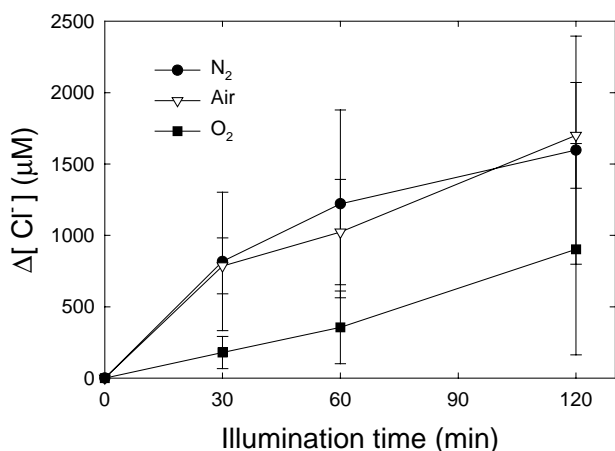


Fig. 5. Effect of dissolved gas on the visible light induced dechlorination of CCl_4 in the Brij-35 + Fe^{3+} solution. The solutions were sparged with O_2 , N_2 , or air before adding the surfactant and CCl_4 . Experimental conditions were: $[\text{Brij-35}] = 4.0 \text{ g/l}$; $[\text{Fe}^{3+}] = 1 \text{ mM}$; $[\text{CCl}_4] = 1 \text{ mM}$.

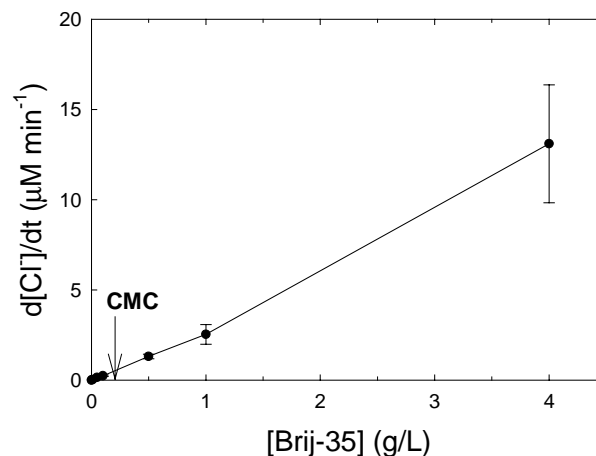


Fig. 6. Initial dechlorination rates of CCl_4 as a function of the surfactant (Brij-35) concentration. Experimental conditions were: $[\text{Fe}^{3+}] = 1 \text{ mM}$; $[\text{CCl}_4] = 1 \text{ mM}$; air-equilibrated.

The fact that the visible light reactivity does not show any sign of saturation with respect to the surfactant concentration implies that the supply of complexing sites in Brij micelles is limited compared with the number of ferric ions available under the present experimental condition. The molar ratio of surfactant molecules to ferric ions is about 3:1 with $[\text{Brij-35}] = 4 \text{ g/l}$ and $[\text{Fe}^{3+}] = 1 \text{ mM}$ and the average number of Brij-35 surfactant molecules per micelle has been estimated to be about 40 [10]. Since the dechlorination rates show little difference between the Fe^{3+} concentrations of 1 and 10 mM (Fig. 1), the visible light activity seems to be saturated at the condition of about thirteen Fe^{3+} ions incorporated within a micelle. This number should be taken as an upper limit because only a fraction of ferric ions are incorporated within the micelles.

3.4. Photoelectrochemical evidence of visible light sensitization

The visible light induced dechlorination of CCl_4 indicates that electrons should be transferred to CCl_4 from the visible light-absorbing centers in micelles. Therefore, the visible light induced electron transfers in micellar solution could be converted to photocurrent when an inert collector electrode is immersed in the illuminated micellar solution as illustrated in Fig. 7a. With this setup, direct evidences for the visible light activation of surfactant micelles can be obtained from the photocurrent measurement. A Pt electrode was immersed in a surfactant solution and then illuminated by visible light. The generation of anodic photocurrents in Brij-35 solution under various conditions is compared in Fig. 7b and those in other surfactant solutions containing Fe^{3+} are shown in Fig. 7c. Significant photocurrent generation was observed only in Brij-35 solution, while negligible photocurrents were detected in SDS, Triton X-114, Triton X-405, and CTAB solutions. This is consistent with the photoreactivity data in

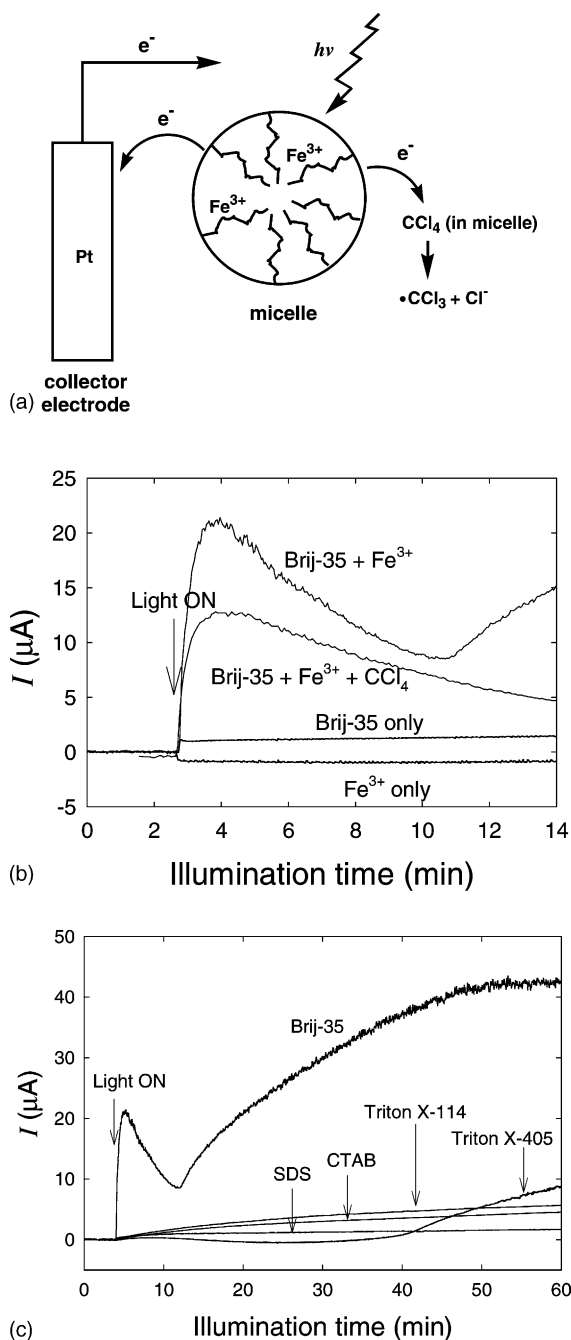


Fig. 7. (a) Schematic illustration of the visible light induced photocurrent collection on a Pt electrode in the surfactant + Fe^{3+} solution. The current collection and CCl_4 dechlorination are competing processes. (b) Anodic photocurrent generation in the visible light illuminated Brij-35 solution with or without Fe^{3+} and CCl_4 . (c) Anodic photocurrent generation in various surfactant solutions containing Fe^{3+} . Experimental conditions were: [surfactant] = 4.0 g/l; [Fe^{3+}] = 1 mM; [CCl_4] = 1 mM; air-equilibrated; the Pt electrode held at 0.6 V (vs. SCE).

Table 1. Surfactants that generate photocurrents under visible light should show high activities in the visible light induced dechlorination of CCl_4 . The photocurrent generation in the surfactant solutions with Fe^{3+} is likely to involve the same mechanism as that of CCl_4 dechlorination: visible

light induced electron transfers from the Fe^{3+} -complexing centers in micelles. As for Brij-35, the magnitude of photocurrent is significant only in the presence of ferric ions and is markedly reduced in the presence of CCl_4 (Fig. 7b). The visible light excited Fe^{3+} -surfactant complex can transfer electrons either to a Pt electrode or to CCl_4 as proposed in Fig. 7a. As a result, the photocurrent is reduced in the presence of competing CCl_4 molecules. The current generation profile shown in Fig. 7c may imply that there are different kinds of complexing centers in Brij-35 micelles. The anodic current peak around 4 min is followed by a slowly rising current profile, which indicates that electrons collected on the Pt electrode are extracted from easily oxidizable complexing centers first, and then from less oxidizable centers.

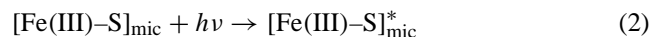
3.5. Proposed visible light activation mechanism

A possible mechanism for this visible light induced CCl_4 dechlorination process is proposed as follows. The oxygen atoms of the polyoxyethylene group (or the terminal OH group) in Brij surfactants coordinate a Fe^{3+} ion to form a visible light-absorbing complex as illustrated in Scheme 1 (reaction 1).

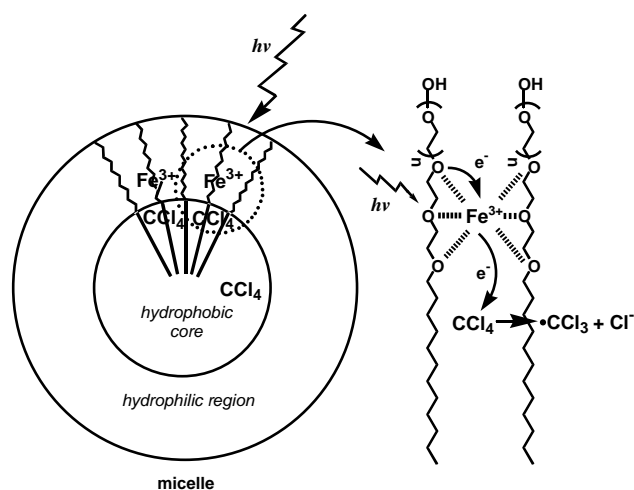
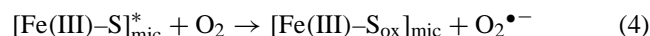
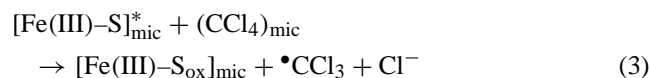
Complexation:



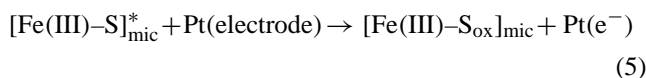
Visible light absorption:



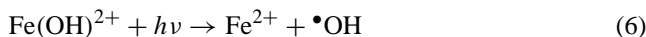
Electron transfers:



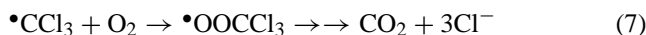
Scheme 1. An illustrated mechanism of the surfactant- Fe(III) complex sensitized dechlorination of CCl_4 in micelles under visible light illumination.



The complex formation seems to be the most efficient with $\text{Fe}(\text{OH})^{2+}$ species. Incidentally, it is interesting to note that $\text{Fe}(\text{OH})^{2+}$ is the most active $\text{Fe}(\text{III})$ aquacomplex in generating OH radicals through the following photolysis [32]:

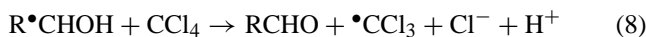


The photoinduced degradation of alkylphenol ethoxylate, a nonionic surfactant similar to Brij, has been demonstrated using reaction 6 [33]. However, the quantum yield of reaction 6 is negligibly small in the visible region ($\lambda > 420 \text{ nm}$) [28]. In addition, the OH radicals are not reactive with CCl_4 at all. Therefore, any possible contribution from reaction 6 in this visible light induced reaction should be excluded. The visible light excitation induces an electron transfer from the oxygen atom of the surfactant to Fe^{3+} center (reaction 2), through a ligand-to-metal charge transfer, which is subsequently followed by an electron transfer to adjacent CCl_4 molecules confined within the same micelle (reaction 3). The resulting $\bullet\text{CCl}_3$ radicals may abstract H-atoms from the surfactant molecules and produce CHCl_3 . However, no significant amount of CHCl_3 was detected as a byproduct of CCl_4 dechlorination in this study, which indicates that the trichloromethyl radicals immediately react with dissolved O_2 to yield CO_2 as a final product.



The electron transfer to dissolved O_2 (reaction 4) or a collector electrode (reaction 5) could be also possible.

As a result of the electron transfer reactions in micelles, the surfactant molecules should be oxidized although the analytical characterization of the oxidized surfactant products was not carried out in this study. Therefore, the surfactant molecule serves as both a Fe^{3+} -complexing ligand and an electron donor in this visible light induced redox reaction. The oxidized surfactant (S_{ox}) might react further with CCl_4 in case S_{ox} has sufficient reducing potentials. For example, hydroxyalkyl radicals might be generated from the oxidation of Brij surfactant, which are strongly reducing. Their reaction with CCl_4 could induce the dechlorination (reaction 8) [34].



In order to assess the possible involvement of reducing radicals generated from the surfactant oxidation in the CCl_4 dechlorination, the effect of H_2O_2 addition on the visible light induced dechlorination was investigated. The visible light excited Fe^{3+} -surfactant complexes may reduce H_2O_2 directly to generate OH radicals (reaction 9), which subsequently oxidize surfactant molecules to generate more hydroxyalkyl radicals (reaction 10).

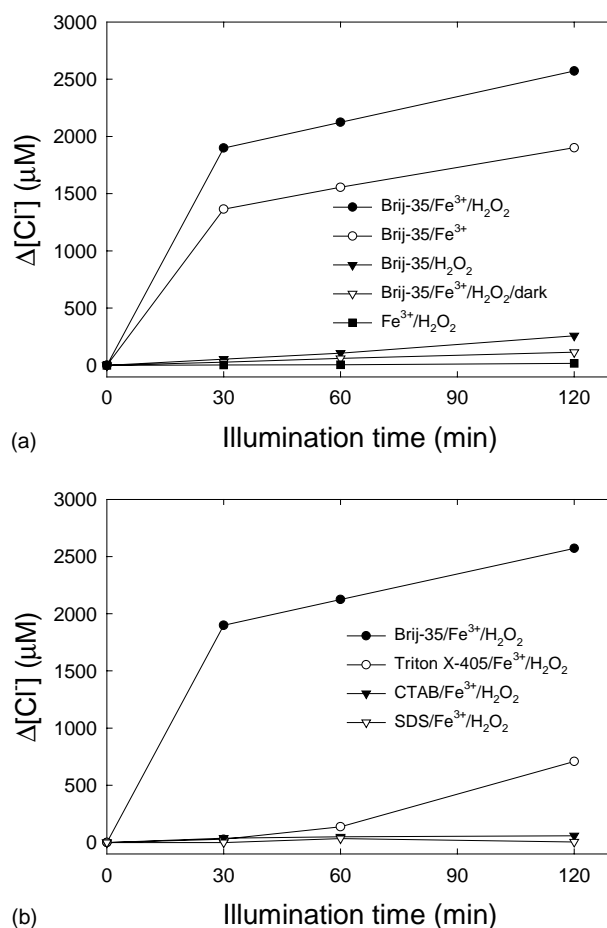
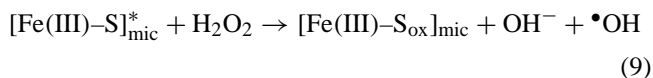


Fig. 8. Effect of H_2O_2 addition on the visible light induced dechlorination of CCl_4 : (a) in Brij-35 solutions with different reagents and (b) in different surfactant solutions containing Fe^{3+} . Experimental conditions were: [surfactant] = 4.0 g/l; $[\text{Fe}^{3+}] = 1 \text{ mM}$; $[\text{CCl}_4] = 1 \text{ mM}$; $[\text{H}_2\text{O}_2] = 1 \text{ mM}$; air-equilibrated.



Fig. 8a shows that there is some H_2O_2 -enhanced effect in the Brij-35 + Fe^{3+} solution. Since neither H_2O_2 nor OH radical directly reacts with CCl_4 , the dechlorination should be initiated through a reductive path and only the reaction of hydroxyalkyl radicals (reaction 8) can account for the observed H_2O_2 -enhanced effect. Therefore, it is likely that surfactant radicals might be involved in the CCl_4 dechlorination reaction to some extent. Although both $\text{Fe}(\text{III})$ -surfactant exciplexes (reaction 3) and oxidized surfactant radicals (reaction 8) may induce the CCl_4 dechlorination reaction, their relative contribution cannot be clearly determined. Considering that the H_2O_2 -induced enhancement in CCl_4 dechlorination was much lower than the dechlorination in the absence of H_2O_2 and was observed only in the initial reaction period (<30 min) during which most H_2O_2 should be depleted, the contribution from the surfactant radicals (reaction 8) seems to be minor in the absence of H_2O_2 . In addition, Fig. 8b shows that Triton surfactant, which could

generate hydroxyalkyl radicals in a similar way as Brij surfactant, does not exhibit significantly enhanced dechlorination in the presence of H_2O_2 . This also supports that the role of reducing surfactant radicals in CCl_4 dechlorination is minor. The dominant dechlorination path seems to be the direct reduction of CCl_4 by excited Fe^{3+} -Brij complexes.

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