

## Visible light-induced reduction of Cr(VI) in cationic micelle solution

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**ABSTRACT:** Cr(VI) reduction was successfully achieved in the presence of cationic micelles (CMs) under visible light illumination. Micelle formation of cationic surfactants seems to be critical in Cr(VI) reduction. Cr(VI) was reduced very fast above the critical micelle concentration (cmc) of CTAB solutions, but was not reduced at all either below or around the cmc of CTAB. The reduction rate of Cr(VI) was enhanced in the absence of dissolved oxygen, supporting that the removal of Cr(VI) should be achieved via a reductive pathway. When CTAB was substituted by Brij 35 or SDS, the reduction of Cr(VI) was negligible. This indicates that the electrostatic interaction between Cr(VI) and headgroups of surfactants is important in the visible light-induced Cr(VI) reduction in micellar solutions.

Growing concerns about the contamination of the environment by heavy metal ions mainly come from their potential toxicity, and hexavalent chromium (Cr(VI)) is one of the most notorious heavy metal ions. Chromium has different physiochemical characteristics according to the oxidation states.<sup>1,2</sup> It has two stable oxidation states: Cr(VI) and Cr(III). Cr(VI) is toxic, highly acute, very dangerous carcinogenic, and mobile in nature. On the other hand, Cr(III) is 500 to 1000 times less toxic and precipitates at neutral or alkaline pH. Therefore, the reduction of Cr(VI) to Cr(III) is desirable. Cr(VI) is usually removed by chemical precipitation using reducing agents such as FeSO<sub>4</sub>, SO<sub>2</sub> or NaHSO<sub>3</sub> in industry. Although the treatment is effective and is suitable for automatic control, the sludge produced is considered as hazardous wastes and the quantities are too much to be disposed of.<sup>3</sup>

Light-induced energy and electron transfer in organized molecular assemblies, micelles, has received much scientific attention because of the higher possibility for the application.<sup>4-11</sup> Micelle is known as an ordered spherical structure formed with surfactant molecules in the solution<sup>12</sup>. Micelle structure resembles biological membranes, so it may be used as a model of electron conduction and interfacial charge transfer in membrane microenvironments. Also, micelles could be useful as a unit for utilizing solar energy by prolonging the lifetime of charge transfer states and accelerating charge separations.<sup>6,7</sup>

Here, we report visible light induced Cr(VI) reduction by cationic micelles in aqueous solution. To the best of our knowledge, this is the first study to apply cationic micelle systems to remove heavy metal ions under visible light illumination. This study is thought to be significant because Cr(VI) is reduced very rapidly in cationic micelle systems despite no absorption of visible light by cationic micelles.

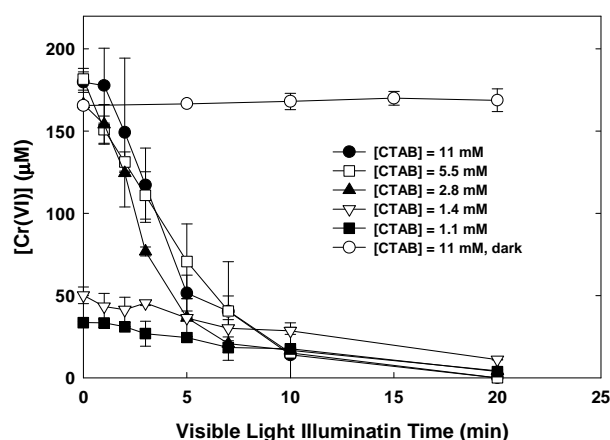
Cationic surfactants tested in this study include CTAB, CTAC, TTAB, DTAB, and OTAB. Nonionic surfactant tested includes Brij 35 and anionic surfactant tested includes sodium dodecylsulfate (SDS). The

characteristics of surfactants are listed in Table 1. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Aldrich) was used as a Cr(VI) precursor. Surfactant solutions were prepared in water to get desired concentrations. CTAB solutions were heated in the oven (65 °C) for about 5 min due to the difficulty of dissolution. Reagent of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was added to the surfactant solutions to get desired initial concentrations, mostly 100 μM (as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, [Cr(VI)] = [HCrO<sub>4</sub><sup>-</sup>] + 2[Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>]). The pH of solutions was adjusted to 3.0 with HCl standard solution. Total volume of the solution was 30 mL and the volume of a reactor was 33 mL. Solutions were equilibrated for 30 min prior to illumination. For deaerated experiments, a 60 mL-reactor was used and was purged with N<sub>2</sub> gas for 15 min. Solutions were magnetically stirred throughout the experiment. 300-W Xe Arc lamp (Oriel) was used as a light source. The light passed through a 10 cm IR water filter and a 420 nm cut-off filter and was focused on a reactor. Light intensity was 142 mW/cm<sup>2</sup> (420 < λ < 550 nm). Sample aliquots were taken intermittently to be analyzed. If needed, sample aliquots were filtered with a 0.45 μm PETE filter (Milipore) before analyzing.

**Table 1. Characteristics of Surfactants**

Surfactants	Type	Chemical formula	cmc (mM)	N <sub>agg</sub>
CTAB	Cationic	C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	0.8-0.9 <sup>a,b</sup>	92 <sup>a</sup>
TTAB	Cationic	C <sub>14</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	3.5 <sup>a</sup>	67 <sup>a</sup>
DTAB	Cationic	C <sub>12</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	15.0 <sup>a</sup>	50 <sup>a</sup>
OTAB	Cationic	C <sub>8</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	236 <sup>c</sup>	20 <sup>d</sup>
Brij 35	Nonionic	C <sub>12</sub> H <sub>25</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>23</sub> OH	15.9 <sup>b</sup>	40 <sup>b</sup>
SDS	Anionic	C <sub>11</sub> H <sub>23</sub> CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	8.06 <sup>b</sup>	62 <sup>b</sup>

a ref. 7. b ref. 8. c ref. 9. d ref. 13



**Figure 1.** Reduction of Cr(VI) (C<sub>0</sub> = 100 μM as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) in different CTAB concentrations under visible light illumination. ([Cr(VI)] = 2[Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>] + [HCrO<sub>4</sub><sup>-</sup>]). The experimental conditions were air-equilibrated; pH<sub>i</sub> = 3.0.

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Figure 1 compares Cr(VI) reduction in different CTAB concentrations. The critical micelle concentration (cmc) of CTAB is known to be around 1.0 mM.<sup>14</sup> Below or around the cmc of CTAB, Cr(VI) was aggregated during 30 min of equilibration time and the aggregates were visible. The low concentrations of Cr(VI) below or around cmc before illumination are due to the aggregates which were filtered out and the reduction of Cr(VI) was negligible. On the other hand, Cr(VI) was not aggregated above the cmc of CTAB and the solutions were transparent. In these cases, Cr(VI) was reduced very rapidly under visible light illumination. The reduction rates were similar once the micelles were formed and did not show any sign of saturation until 11 mM of CTAB concentration. The fact that the reduction of Cr(VI) alone was negligible under visible light illumination but Cr(VI) was reduced very rapidly in CTAB micelles indicates electron transfer and charge separation occur effectively in micelles. That is, micelles may play an important role in photo-induced electron transfer and charge separation. Most of Cr(VI) ions would be placed in the headgroup region of micelles because Cr(VI) is more soluble in water than in hexadecane. Since Cr(VI) acts as an electron acceptor, there must be an electron donor to happen electron transfer and charge separation. The headgroup region of micelle where Cr(VI) is placed usually contains water and counterions as well as headgroups. O<sub>2</sub> gas was not produced during photo-induced Cr(VI) reduction (data not shown), and the reduction rate of Cr(VI) was not changed when CTAC was used instead of CTAB (data not shown). Therefore, neither water molecule nor counter-anion is an electron donor, and it is not clear what molecule acts as an electron donor in our system. However, there is a non-excludable possibility that the alkyltrimethylammonium itself might be the electron donor.

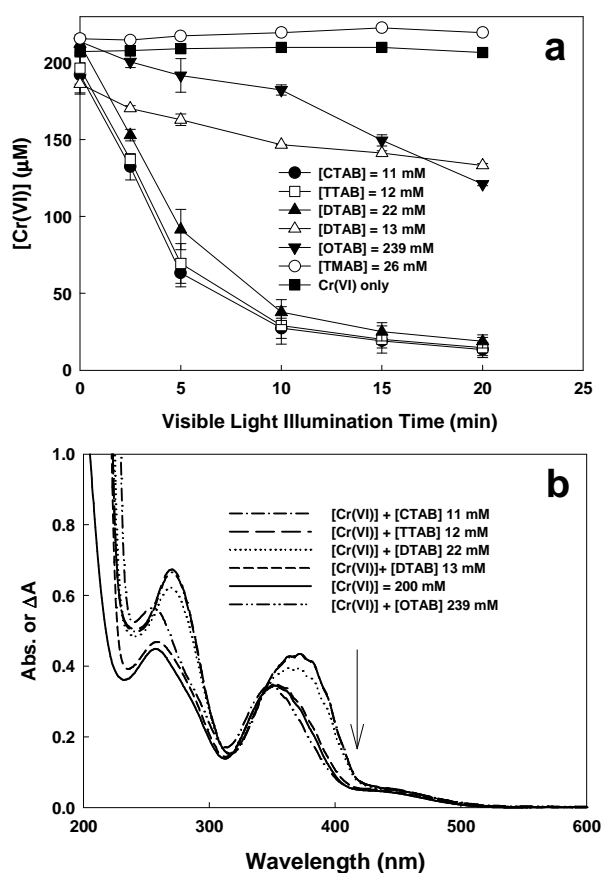


Figure 2. (a) Reduction of Cr(VI) ( $C_0 = 100 \mu\text{M}$  as  $\text{Cr}_2\text{O}_7^{2-}$ ) in different cationic micelle systems under visible light illumination.

( $[\text{Cr(VI)}] = 2[\text{Cr}_2\text{O}_7^{2-}] + [\text{HCrO}_4^-]$ ). The concentrations of surfactants were controlled to maintain similar micelle concentrations. The experimental conditions were air-equilibrated; pH = 3.0. (b) UV-Visible absorption spectra of Cr(VI) ( $C_0 = 100 \mu\text{M}$  as  $\text{Cr}_2\text{O}_7^{2-}$ ) and the mixture of Cr(VI) and cationic micelles.

The reduction of Cr(VI) in different surfactant solutions is shown in Figure 2a. Since the formation of micelles may play a significant role in Cr(VI) reduction, concentrations of surfactants were controlled to maintain similar micelle concentrations,  $\sim 100 \mu\text{M}$ . Micelle concentrations were calculated using eq 1.<sup>15</sup>

$$[\text{M}] = ([\text{S}] - \text{cmc}) / N_{\text{agg}} \quad (1)$$

Cr(VI) distribution in micelle solutions was estimated from Poisson distribution.<sup>16</sup> It supposes that 13% of micelles have no Cr(VI) molecule, 27% have one, 27% have two, 18% have three and 4% have four. The reduction rates of Cr(VI) in CTAB, TTAB and DTAB (22mM) micelle solutions were similar. However, Cr(VI) was reduced slowly in DTAB solution below the cmc (13mM) and in OTAB micelle solution. Cr(VI) was not reduced at all in TMAB solution. This implies the micelle formation and the chain lengths of surfactants influence on the electron transfer and charge separation, but the detailed mechanisms are unknown. Figure 2b compares the UV-Vis spectra of the mixtures of Cr(VI) and surfactant solutions. The spectral changes of TTAB and CTAB mixed solutions from Cr(VI) only spectrum are almost same. Two different spectra of DTAB mixed solutions show the importance of the micelle formation. Spectrum of the DTAB mixture above the cmc (22 mM) is closer to the spectra of the TTAB and CTAB mixtures than that below the cmc (13mM). The absorbance of OTAB mixed solutions was even slightly decreased around 350 nm. This little change and the difference in the absorption spectra of DTAB (13 mM) and OTAB mixed solutions compared with those of CTAB, TTAB and DTAB might be related with slow Cr(VI) reduction as shown in Figure 2a.

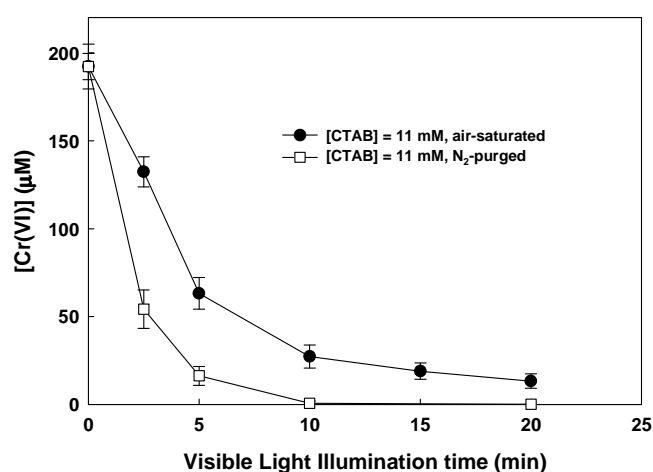
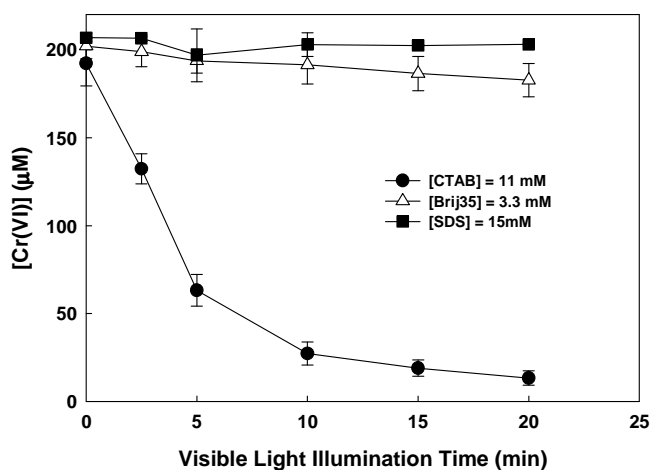


Figure 3. Effect of dissolved O<sub>2</sub> (air-equilibrated vs. N<sub>2</sub>-purged) on the reduction of Cr(VI) ( $C_0 = 100 \mu\text{M}$  as  $\text{Cr}_2\text{O}_7^{2-}$ ). ( $[\text{Cr(VI)}] = 2[\text{Cr}_2\text{O}_7^{2-}] + [\text{HCrO}_4^-]$ ). The experimental conditions were pH<sub>i</sub> = 3.0.

Figure 3 shows the effect of dissolved oxygen on the reduction of Cr(VI). The reduction rate was increased in the absence of O<sub>2</sub>, because both Cr(VI) and O<sub>2</sub> are accepting electrons competitively. This result supports the idea that Cr(VI) is removed via reductive pathways. The inhibiting effect of O<sub>2</sub> on the Cr(VI) reduction has

been investigated.<sup>2,17</sup> More Cr(VI) was photo-reduced if nitrogen gas was passed through the suspension in TiO<sub>2</sub>/Cr(VI)/UV system.

The headgroup charge of micelles also affects the reduction of Cr(VI) as shown in Figure 4. The headgroups are nonionic, anionic, and cationic for Brij35, SDS, and CTAB, respectively. All three surfactant concentrations were controlled to maintain similar micelle concentrations, ~100 μM, based on eq 1. Cr(VI) exists as a form of HCrO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> at pH 3,<sup>18</sup> and the reduction of Cr(VI) was negligible both in Brij 35 and SDS micelles, unlike the fast reduction in CTAB micelles. Therefore, the electrostatic interaction between Cr(VI) and the headgroups of micelles seem to be important to the Cr(VI) reduction.



**Figure 4.** Effect of the headgroup charges of micelles on the reduction of Cr(VI) ( $C_0 = 100 \mu\text{M}$  as  $\text{Cr}_2\text{O}_7^{2-}$ ). ( $[\text{Cr(VI)}] = 2[\text{Cr}_2\text{O}_7^{2-}] + [\text{HCrO}_4^-]$ ). The experimental conditions were air-equilibrated;  $\text{pH}_i = 3.0$ .

**KEYWORDS:** Cr(VI) reduction, Micellar photochemistry, Cationic micelle, Visible-light induced charge transfer

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#### REFERENCES AND NOTES

- Costa, M. *Toxicol. Appl. Pharmacol.* **2003**, 188, 1.
- Lin, W. Y.; Wei, C.; Rajeshwar, K. *J. Electrochem. Soc.* **1993**, 140, 2477.
- Ku, Y.; Jung, I.-L. *Wat. Res.* **2001**, 35, 135.
- Mandal, U.; Ghosh, S.; Dey, S.; Adhikari, A.; Bhattacharyya, K. *J. Chem. Phys.* **2008**, 128, 164505.
- Ding, H.; Yu, H.; Dong, Y.; Tian, R.; Huang, G.; Boothman, D. A.; Sumer, B. D.; Gao, J. *J. Control. Release* **2011**, 156, 276.
- Kopeć, M.; Niemiec, W.; Laschewsky, A.; Nowakowska, M.; Zapotoczny, S. *J. Phys. Chem. C* **2014**, 118, 2215.
- Tavernier, H. L.; Laine, F.; Fayer, M. D. *J. Phys. Chem. A* **2001**, 105, 8944.
- Alkaiis, S. A.; Beck, G.; Graetzel, M. *J. Am. Chem. Soc.* **1975**, 97, 5723.
- Hackett, J. W.; Turro, C. *J. Phys. Chem. A* **1998**, 102, 5728.
- Cho, Y.; Kyung, H.; Choi, W. *Appl. Catal. B: Environ.* **2004**, 52, 23.
- Cho, Y.; Park, H.; Choi, W. *J. Photochem. Photobiol. A: Chem.* **2004**, 165, 43.
- Long, J. A.; Rankin, B. M.; Ben-Amotz, D. *J. Am. Chem. Soc.* **2015**, 137, 10809.
- Shi, Z.; Sigman, M. E.; Ghosh, M. M.; Dabestani, R. *Environ. Sci. Technol.* **1997**, 31, 3581.
- Buwalda, R. T.; Jonker, J. M.; Engberts, J. B. F. N. *Langmuir* **1999**, 15, 1083.
- Cang, H.; Brace, D. D.; Fayer, M. D. *J. Phys. Chem. B* **2001**, 105, 10007.
- Turro, N. J.; Grätzel, M.; Braun, A. M. *Angew. Chem. Int. Ed.* **1980**, 19, 675.
- Muñoz, J.; Domènech, X. *J Appl Electrochem* **1990**, 20, 518.
- Giménez, J.; Aguado, M. A.; Cervera-March, S. *J. Mol. Catal. A: Chem.* **1996**, 105, 67.