

Note

Catalytic behavior of tris(2,2'-bipyridine)iron(II) complex in chemiluminescence reaction of luminol in reversed micellar medium of cetyltrimethylammonium chloride

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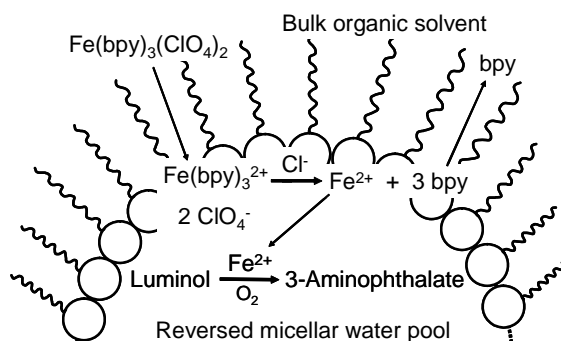
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Abstract

Tris(2,2'-bipyridine) complex of iron(II) was found to cause an increase in the chemiluminescence (CL) emission of luminol dispersed in the reversed micellar medium of cetyltrimethylammonium chloride (CTAC) in 1:1 (v/v) dichloromethane–cyclohexane/water, when the iron(II) complex in dichloromethane was mixed directly with the reversed micellar solution containing luminol. Visible absorption measurements showed that, when dispersed in the CTAC reversed micellar medium, the iron(II) complex dissociates easily. In the reverse micelle, subsequently the free iron(II) ion produced may catalyze the CL oxidation of luminol even in the absence of hydrogen peroxide. The CL emission produced under the optimized experimental conditions was detectable at a minimum iron(II) concentration of 1.0×10^{-9} M using a flow injection system.

Graphical abstract

A unique ability of the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex to enhance the luminol chemiluminescence following the dissociation of the complex into the iron(II) ion in the CTAC reverse micelle is demonstrated.



Keywords: Luminol chemiluminescence; Reversed micellar medium; Cetyltrimethylammonium chloride; Tris(2,2'-bipyridine)iron(II) complex; Dissociation

1. Introduction

Surfactant molecules encompass tiny water droplets and are converted into homogeneously distributed assemblies of reversed micelles after reaching a critical micellar concentration in an organic bulk solvent. Both the size and composition of reversed micellar assemblies are directly related to the amount of water present in the center of the reversed micellar core or so-called water pool [1]. The physico-chemical characteristics of the water pool are quite different from the bulk water. When reversed micellar media of cetyltrimethylammonium chloride (CTAC) are used as micro-reactors in a luminol chemiluminescence (CL), it has been pointed out that the surfactant-water pool interface may play an important role in the CL process [2–5].

Certain transition metals such as iron(II) and copper(II) can catalyze the CL reaction of luminol in usual aqueous media [6, 7]. Generally, chelating reagents make the metal ions unavailable for CL catalyses due to formation of stable metal complexes [8]. In this work, we observed an enhancement of CL emission when the tris(2,2'-bipyridine)iron(II) ion, $[\text{Fe}(\text{bpy})_3]^{2+}$, was mixed with the CTAC reversed micellar solution containing luminol in 1:1 (v/v) dichloromethane–cyclohexane/water, although this complex is well known to be stable in aqueous medium [9]. In the resultant solution, it was also observed that in the visible spectrum of the complex, the maximal absorption band at 522 nm disappeared. This revealed the reversed micellar mediated dissociation of the iron(II) complex, implying uptake of the dissociation product, iron(II) ion, by the reverse micelle into its water pool, where the free iron(II) ion may catalyze the CL oxidation of luminol. Using the bromide salt of cetyltrimethylammonium as a surfactant in 1:1 (v/v) chloroform-hexane/water, such dissociation of $[\text{Fe}(\text{bpy})_3]^{2+}$ has been also reported [10]. For the uncharged iron(III) complex of 8-quinolinol, we also observed its dissociation in the CTAC reversed micellar medium in chloroform-cyclohexane/water [11],

followed by similar CL behavior in the luminol reaction with H₂O₂. In the present investigation, we found that the iron complexes of 2,2'-bipyridine and 8-quinolinol were quite different from each other in the dissociation behavior: When the water-to-surfactant molar ratio R ($= [H_2O]/[CTAC]$) in the reversed micellar medium was decreased, the dissociation of the 8-quinolinol complex was suppressed as reported previously [11], while an enhancement of the dissociation reaction was observed for the 2,2'-bipyridine complex in this work. This finding implies that higher concentration of the counter chloride ions of the CTAC surfactants in the reverse micelle may be significant for the dissociation of the positively charged complex of 2,2'-bipyridine. These behaviors in the iron uptake by reverse micelles are interesting because of a similarity to that observed for the iron-store protein, ferritin micelle [12]. Furthermore, it is first noted in this work that strong CL emission may generate from the luminol-iron(II) system without hydrogen peroxide in the reversed micellar medium as well as in usual aqueous media. The chemical parameters related to the participation of $[Fe(bpy)_3]^{2+}$ in the reversed micellar mediated CL (RMM-CL) reaction of luminol are investigated here.

2. Experimental

All chemicals were of reagent grade and used as received. The perchlorate and sulphate salts of the $[Fe(bpy)_3]^{2+}$ complex were prepared and recrystallized from water according to the conventional procedure as described previously [13,14]. De-ionized water, freshly collected from a water purification apparatus (Advantec Toyo, GSU-901), was used in the preparation of all aqueous solutions.

Spectral measurements were made on a spectrophotometer (Hitachi, 228-A) using a 5-cm cell thermostated at 25.0 °C. For flow injection (FI)-CL measurements, the multi-component instrument, composed of a FI analyzer (Hitachi, K-1000) equipped with a programmed automatic

rotary injection valve, a pump unit (Tosoh, CCPM), and a photometer (Niti-on, LF-800) with a spiral flow cell (70 μl), was used as before [15,16]. PTFE tubing of 0.5 mm i.d. was used throughout the flow system. Working solutions of $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ in dichloromethane were made by serial dilution of a 1.0×10^{-4} M stock solution of $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ with dichloromethane. The reversed micellar solution of the luminescent reagent was prepared as reported earlier [17] by dispersing a certain volume of carbonate (0.3 M Na_2CO_3)-buffered stock solution (pH = 11.9) of luminol (Wako Pure Chemical) in a reversed micellar bulk solvent of dichloromethane-cyclohexane (1:1 v/v) containing 0.084 M CTAC (Tokyo Kasei), with a water-to-surfactant molar ratio R ($= [\text{H}_2\text{O}]/[\text{CTAC}]$) of 13. The luminol concentration was 5.0×10^{-5} M, calculated on a final total volume basis. Using the rotary injection valve, the reversed micellar solution (100 μl) of luminol and the $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ solution (100 μl) were sucked and inserted simultaneously in separate channels of carrier streams of dichloromethane; the carrier flow rates of sample and reagent lines were 2 ml min^{-1} . The sample and reagent channels were mixed in the flow cell, and the resultant CL signal was recorded.

3. Results and discussion

The visible spectrum of the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex was measured with its concentration of 1.0×10^{-5} M in the final total volume of the reversed micellar solution; the dispersed sulfate salt, $[\text{Fe}(\text{bpy})_3]\text{SO}_4$, is insoluble in the organic bulk and thus likely to locate entirely in the water pool of the reverse micelle. Figure 1 shows that the absorbance of the complex in the CTAC reversed micellar solution decreases down to zero, indicating a gradual dissociation of the complex with the passage of time, although the absorbance maximum of the iron(II) complex is almost the same as reported earlier in water (522 nm) [18]. The first order rate constants for the dissociation reaction were obtained by analyzing the decline in the absorption band of $[\text{Fe}(\text{bpy})_3]^{2+}$.

As shown in Fig. 2, the rate constant for the dissociation reaction increased with decreasing R , where the R value was decreased along with an increase in the CTAC content at a constant water concentration ($[\text{H}_2\text{O}] = 1.1 \text{ M}$) in the reversed micellar solution. The R dependence of the iron(II) complex dissociation is quite different from that observed for the iron(III) complex of 8-quinolinol, of which the dissociation was suppressed with a decrease in the R value [11]. It has been noted that a decrease in R causes a decrease in the size of the reverse micelle or of the reversed micellar water pool [1], in which the counter chloride ions of the CTAC surfactants are accumulated, thus leading to an increase in the effective Cl^- concentration in the water pool. These observations imply that likely at the CTAC reversed micellar interface, nucleophilic attack of the Cl^- ion to the central metal of the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex may occur due to its high donicity as indicated in an earlier paper [19]. Since Cl^- ions are highly hydrated, an increase in hydration number of the Cl^- ion with increasing R is also expected. This may lead to suppressing its nucleophilic attack to the complex at the reversed micellar interface as noted previously [20].

After the dissociation, the hydrophobic bipyridine ligands may go out into the organic bulk while the hydrophilic iron(II) ion should localize in the water pool, where then the iron(II) ion may participate in a luminol CL reaction. In a conventional or usual aqueous basic solution of luminol, in fact, no increase in the CL intensity was provoked by the addition of a slight amount of the $[\text{Fe}(\text{bpy})_3]^{2+}$ chelate. When luminol in the reversed micellar solution was mixed directly with the $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ solution at a trace level in dichloromethane, however, a pronounced enhancement in the CL emission was produced even in the absence of an oxidizing agent like hydrogen peroxide. In a previous study on the luminol CL in the absence of hydrogen peroxide in conventional aqueous solutions, it was proved that particularly for iron(II) there is a dramatic drop in CL intensity when oxygen is removed from the solution [7]. In this work, a comparative inquiry into CL behavior was carried out using deaerated solutions of basic buffer for preparation of the luminol solution, dispersed in the water pool of the reversed micellar solution: The

deaerated solutions of basic buffer were made by ultrasonication, while the organic solvents used were not deaerated. It appears quite likely that oxygen diffuses back by small portions into the water pool during the course of the preparation and CL measurements. For the reversed micellar luminol solution, mixed with the $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ solution (1.0×10^{-7} M), it was nevertheless observed that the CL out-put was about 5 times lower than that for solutions run without deaeration of the basic buffer solutions. This indicated that the presence of dissolved oxygen might affect the CL reaction of luminol in the reversed micellar water pool as noted earlier [15].

The RMM-CL activity as well as the dissociation of $[\text{Fe}(\text{bpy})_3]^{2+}$ is expected to be directly or indirectly related to R of the reversed micellar medium. In this work, the effect of R on CL emissions was thus investigated where the value of R was changed either by changing the amount of water at a constant surfactant concentration ($[\text{CTAC}] = 0.084$ M) or by changing the concentration of surfactant at a fixed amount of water ($[\text{H}_2\text{O}] = 1.1$ M). In both cases as shown in Fig. 3, the CL intensities initially increased with an increase in R , reached a maximum around R of 13, and then decreased. With lower R , lower CL intensity has been usually observed for the RMM-CL emission [2,3,5,11]. It can therefore be presumed that the occurrence of bulk-like water in the reversed micellar aqueous core at higher R facilitates the RMM-CL reaction of luminol. At the higher R values, however, there should be more hydrated Cl^- ions [20] which may be unavailable for the dissociation of the iron(II) complex as mentioned above, resulting in release of less iron(II) species in the water pool.

In a brief study on the effect of the buffer concentration, it was observed that with an increase in the Na_2CO_3 concentration in the water pool, both the dissociation and the RMM-CL emission were enhanced drastically and the CL signal reached a maximum at 0.4 M Na_2CO_3 . Around this concentration, however, formation of turbid or milky solutions occurred gradually. The Na_2CO_3 concentration of 0.3 M is thus recommended for CL work. In our previous studies, a similar

enhancing effect of carbonate on the RMM-CL reactions of luminol with oxovanadium(IV) [4] and iodine [21] was observed.

The nature of the reversed micellar bulk organic solvent also has an impact on the RMM-CL out-put as pointed out previously [4,11,17]. Dichloromethane alone was not suitable for making the reversed micellar solutions of CTAC. With an increase in the volume of cyclohexane in suitable mixtures, the CL intensity decreased and then CTAC became less soluble. A similar suppressing effect of cyclohexane in the CTAC reversed micellar solutions was obtained on dissociation of the (5,10,15,20-tetraphenylporphyrinato)zinc(II) complex where nucleophilic attack of the Cl^- ion to the central zinc of the complex may play a significant role [22].

By the FI-CL measurements using $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ as a sample in dichloromethane under the optimized experimental conditions, it was obtained that a minimum detectable concentration of $[\text{Fe}(\text{bpy})_3]^{2+}$ was 1.0×10^{-9} M. This concentration is close to the published practical iron(II) detection limit of about 10^{-9} M obtained with usual aqueous solutions [23]. This implies that the dissociation and uptake of the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex by the CTAC reverse micelle may occur completely and then in the water pool all the released iron(II) species could catalyze the oxidation of luminol just as an iron(II) ion.

4. Conclusions

The present work demonstrates a unique and specific ability of the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex to enhance the luminol CL emission in the CTAC reversed micellar medium even in the absence of hydrogen peroxide, following the dissociation of the iron(II) complex upon mixing it with the reversed micellar solution. This novel behavior suggests that the surfactant-water pool interface may provide a unique reaction field, where the stable $[\text{Fe}(\text{bpy})_3]^{2+}$ complex dissociates easily, the hydrophilic iron(II) ion produced should localize in the water pool, and probably before its

hydrolysis, immediately catalyze the CL oxidation of luminol, while the hydrophobic bipyridine ligands released may go out into the organic bulk. Also, such iron uptake by reverse micelles is interesting because of a similarity to that reported for the iron-store protein, like ferritin micelle.

Acknowledgments

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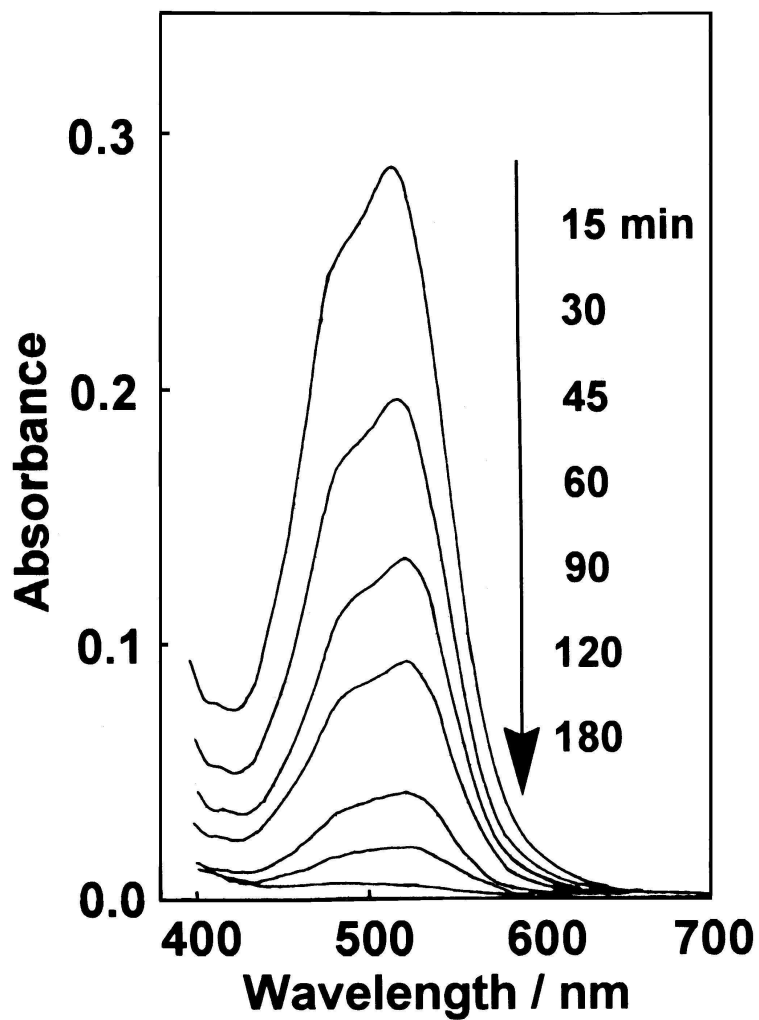


Fig. 1. Typical change in the absorption spectrum of $[\text{Fe}(\text{bpy})_3]^{2+}$ dispersed in a CTAC reversed micellar solution in dichloromethane-cyclohexane (1 : 1 v/v)/water (pH = 5.3) at 25.0°C.

R = 13, [CTAC] = 0.084 M.

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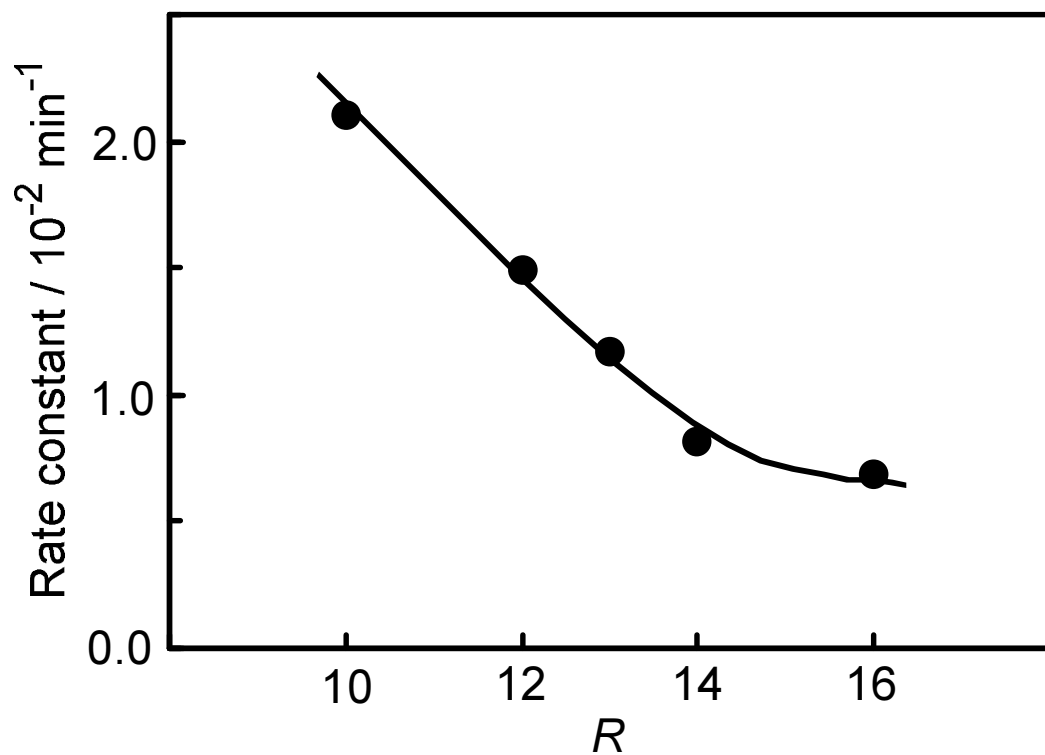


Fig. 2. Variation of the rate constant for the dissociation of $[\text{Fe}(\text{bpy})_3]^{2+}$ with the R value in the reversed micellar solution in dichloromethane-cyclohexane (1 : 1 v/v)/water (pH = 5.3) at 25.0°C. $[\text{H}_2\text{O}] = 1.1 \text{ M}$.

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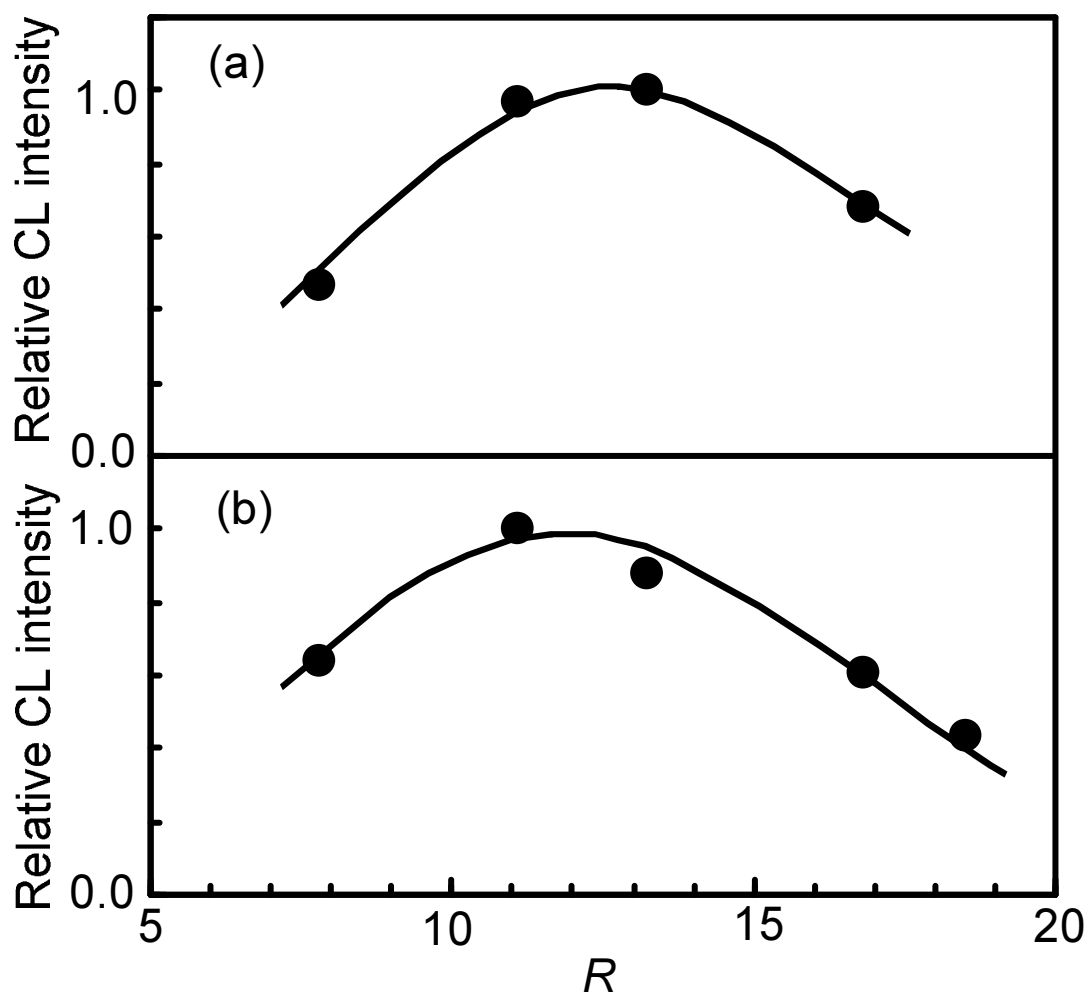


Fig. 3. Variation of the CL intensity with the R value in the reversed micellar solution in dichloromethane-cyclohexane (1 : 1 v/v)/water (0.3 M Na₂CO₃, pH = 11.9). (a) [CTAC] = 0.084 M; (b) [H₂O] = 1.1 M.

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