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Catalytic Behavior of Iron(III)-8-quinolinol Complex in the Chemiluminescence Reaction of Luminol with Hydrogen Peroxide in Reverse Micelles

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Upon mixing of tris(8-quinolinolato)iron(III), an enhancement in the chemiluminescence emission resulting from the luminol-hydrogen peroxide reaction in reversed micellar solution was observed. Uptake of the complex by reverse micelles and its subsequent decomposition in the micelles appear to occur easily in the process.

There has been an increased interest in the numerous potential applications of organized media like colloids, microemulsions, micelles, etc. and their analytical uses have been reviewed recently.[1] Although many applications are possible using reverse micelles as reaction media, an interesting example cited is the use of reversed micellar system in chemiluminescence (CL) analysis. In a previous paper,[2] we have reported our first observations of the CL generation from the reaction of iodine with luminol in a reversed micellar solution of hexadecyltrimethylammonium chloride (CTAC): An aqueous solution of luminol in a basic buffer is dispersed in a chloroform-cyclohexane mixture containing CTAC. As a result, the water pools formed by water molecules are included in the core of reverse micelles, which function as microreactors for the CL reaction. Iodine uptake by reverse micelles also plays an important role in the CL process. Recently, such a reversed micellar solution has been used to amplify the CL of luminol-hydrogen peroxide system at mild pH (7.8-9.1).[3] In this work, an enhancement of the CL emission was observed upon mixing iron(III) complex of 8-quinolinol (oxine), $Fe(oxine)_3$, with reversed micellar solution. In spite of the fact that the oxine complex is only slightly soluble in aqueous medium of the basic buffer, uptake of the complex by reverse micelles into aqueous pools occurs easily, followed by the catalyzed luminol reaction.

The oxine complex used was prepared under the conventional method of mixing sodium acetate solution of iron(III) nitrate (Kanto Chemical) with a solution of oxine (Wako Pure Chemical) in ethanol. The complex was recrystallized from acetone with water, and then dried at 110 °C. A sample solution of 1.8×10^{-7} M $Fe(oxine)_3$ (1 M = 1 mol dm^{-3}) dissolved in chloroform (Wako Pure Chemical HPLC grade), was used to perform optimization studies of experimental conditions for CL analysis. Luminol (Aldrich) was dissolved in the buffer solution of 0.2 M Na_2CO_3 (pH 11.5). The reversed micellar solutions of luminol and of H_2O_2

(Mitsubishi Gas Chemical) were prepared daily according to the literature[2,3] and were mixed just before use. The luminol and H_2O_2 optimum concentrations of 4.0×10^{-4} M and 2.0×10^{-2} M, respectively, calculated on the basis of final volume total solution, were chosen. A 6:5 (v/v) chloroform-cyclohexane (both Wako Pure Chemical HPLC grade) mixture, containing 0.1 M CTAC (Tokyo Kasei Kogyo), with a molar concentration ratio, R (= $[H_2O]/[CTAC]$) = 23.8 was used as a reversed micellar bulk solvent. All aqueous solutions were prepared with water from an Advantec Toyo (Tokyo, Japan) Model GSU-901 water purification system. Intensity-time profiles for the CL emission were recorded on a Hitachi (Tokyo, Japan) Model F-2000 fluorescence spectrophotometer at room temperature using a 1-cm cell in the batch procedure as reported before.[1] A flow injection system was also applied to obtain the CL intensities using a Hitachi Model K-1000 flow injection analyzer equipped with a 16-port rotary injection valve, as in our previous work.[1] Two carrier streams of chloroform were driven by pumps of the device, both at a flow rate of 2 cm^3 min^{-1}; with sample and reagent injection loops of 100 mm^3, were employed. A Niti-on (Funahashi, Japan) Model LF-800 photometer with a 70-mm^3 spiral flow cell was used to detect the CL signals. PTFE tubings (0.5-mm i.d.) were used between all components in the flow system. Visible absorption spectra of the oxine complex were measured on a Hitachi Model 228 A spectrophotometer in a 5-cm cell thermostated at 25 °C.

Figure 1 presents typical intensity-time profiles of CL emissions resultig from the luminol-H_2O_2 reaction in the reversed micellar solution in the absence and presence of $Fe(oxine)_3$, (a) and (b), respectively. The presence of oxine complex caused a pronounced enhancement in the CL emission. Visible absorption measurements showed that absorbances at 470 nm and 583 nm for the complex in the reversed micellar solutions of the carbonate buffer are lower than those in the chloroform-cyclohexane mixture alone (Fig. 2), suggesting that partial decomposition of the complex occurs immediately upon mixing with the

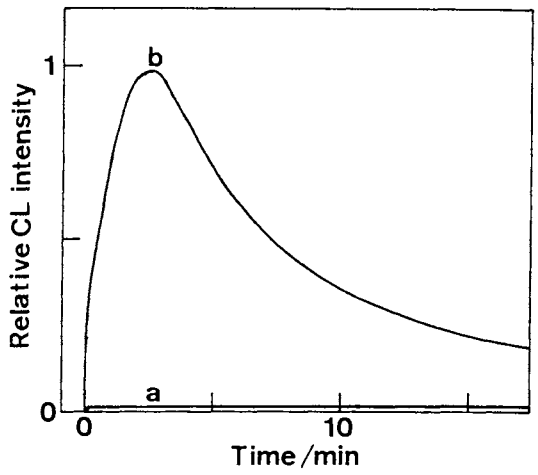

Fig. 1. Peak shape for CL signals observed from the luminol-H_2O_2 reaction in CTAC reversed micellar solution in the absence (a) and presence (b, 1.8×10^{-6} M) of $Fe(oxine)_3$.

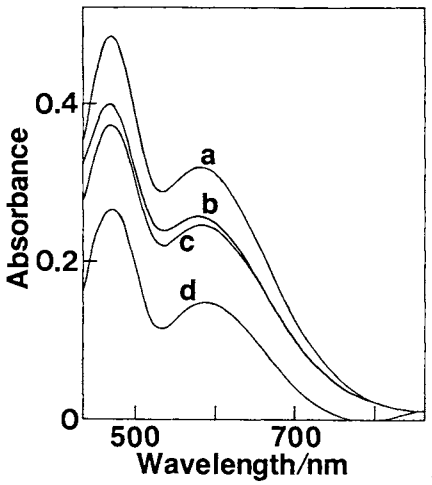

Fig. 2. Absorption spectra of $Fe(oxine)_3$; in 6:5 (v/v) chloroform-cyclohexane mixture (a), in reversed micellar solution with R (= $[H_2O]/[CTAC]$) = 8.97 (b), 12.7 (c), and 23.8 (d); $[H_2O]$ = 0.56 M; $[Fe(oxine)_3] = 1.8 \times 10^{-5}$ M.

reversed micellar solution. Moreover, an increase in the absorbance for the reversed micellar solution was observed when the aqueous basic buffer containing free oxine ligands was used as the dispersed phase in the reversed micellar system. For example, an excess amount, almost equal to 1/3 of the oxine ligand present in the complex, was required to get the original absorbance.

It has been concluded already[4] that the size of the reverse micelles depends primarily on the molar ratio, R. With an increase in R which causes an increase in the size, a decrease in equilibrium constant for complex formation between nickel(II) and murexide within a water pool has been reported.[5] Figure 2 shows that the absorbance for the complex decreased as the CTAC concentration was lowered at a constant amount of water in the reversed micellar system, resulting in an increased R value. The observed change in the absorbance reflects a decrease in the equilibrium constant for Fe(III)-oxine complexation with increasing R. On the other hand, the CL emission intensity in the presence of oxine complex was enhanced with increasing R even though there was a slight change in the CL signal in the absence of the complex (Fig. 3).

This unique behavior could be explained with the following proposed processes:

(a) Uptake of the complex by reverse micelles,

$Fe(oxine)_3$ (in organic bulk phase) $\rightleftharpoons$ $Fe(oxine)_3$ (in a water pool),

(b) decomposition of the complex in the water pool,

$Fe(oxine)_3 \rightleftharpoons Fe(oxine)_{3-n}^{n+} + n\ oxine^-$.

By using normal aqueous solution of the basic buffer alone, the oxine complex in the chloroform-cyclohexane mixture could not be extracted from the organic phase into the aqueous phase. However, this limitation was overcome easily by using dispersed aqueous phase in the reverse micelles. This effect of reverse micelles might be attributed to a decrease in the interfacial tension of an oil-water interface in the presence of the

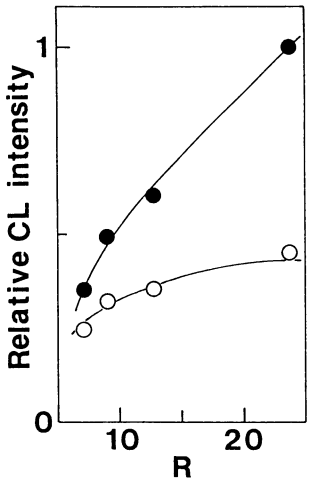

Fig. 3. Dependence of CL intensity for the luminol reaction on R (= $[H_2O]/[CTAC]$) in reversed micellar solution in the absence (○) and presence (● , 1.8 x 10^{-7} M) of $Fe(oxine)_3$. $[H_2O]$ = 1.11 M.

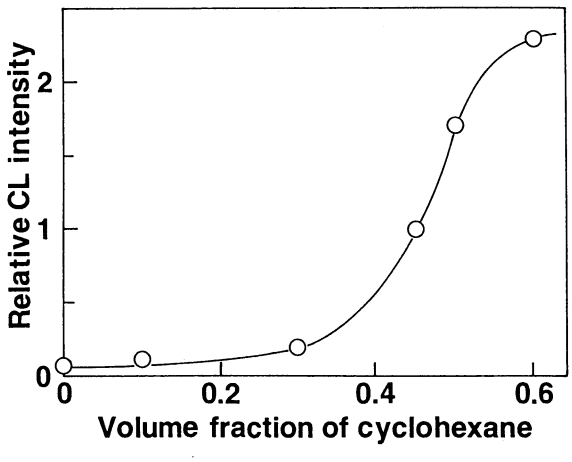

Fig. 4. Dependence of CL intensity for the $Fe(oxine)_3$-catalyzed luminol reaction on volume fraction of cyclohexane in reversed micellar system of CTAC/water/chloroform-cyclohexane.

surfactant. Furthermore, there was a decrease in the absorbance for the complex in the reversed micellar solution with rising cyclohexane content in the organic bulk phase. Since the oxine complex is readily dissolved in chloroform but is sparingly soluble in cyclohexane, it is reasonable that addition of cyclohexane will favor the complex uptake process (a), followed by its decomposition process (b). On the other hand, Figure 4 shows that the enhanced CL intensity was increased as the volume fraction of cyclohexane was increased in the reversed micellar system.

Generally, the luminol CL reaction is catalyzed by free transition metal ions but strong chelating reagents, such as EDTA, make the metal ions unavailable for the catalysis.[6] With the free oxine ligand present in excess as mentioned above, it was found that the CL intensity in the presence of oxine complex was suppressed to some extent, although oxine causes only a slight increase in light output over the blank. This suggests that $Fe(oxine)_3$ might not be an effective catalytic agent and in the decomposition process (b) of the complex, a catalytically active species, most probably Fe^{3+}, might be produced in the water pool. On the other hand, for the cobalt(II)-catalyzed CL reaction of luminol in aqueous solution, it has been reported that the CL intensity was increased with the addition of oxine ligand and reached its maximum when both the species were approximately equimolar in the sample but with further addition of oxine to the cobalt solution the luminescence was quenched.[7] This implys that the mono-oxine complex appears to have a catalytic activity. We intend to clarify this point in a later communication hopefully.

For iron analysis, the oxine complex of Fe(III) in chloroform was used as an analyte solution. The analytical signal is taken as the difference in the CL peak heights for the analyte and blank. A calibration graph obtained with the aforementioned optimum conditions was linear from a detection limit of 0.4 ng cm^{-3} up to 400 ng cm^{-3} Fe(III). CL methods have the advantages of high sensitivity, wide dynamic range, and simplicity of instrumentation, but in most cases suffer from problems of interference due to the presence of other species, especially, in the inorganic trace analysis. Thus, various techniques of separation, including chromatography and solvent extraction, have been applied to overcome these problems.[6] The present CL generation in reversed micellar solutions allows us to develop a new hybrid method of CL analysis by coupling solvent extraction and CL detection as proposed previously.[2] Further work on this possibility is currently under way.

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