Tris(2,2′-bipyridine)ruthenium(II) in Sodium Dodecyl Sulfate-γ-Alumina Hemimicelles. Enhanced Electron Transfer and Exchange Hemimicellization with 1,1′-Dimethyl-4,4′-bipyridinium

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Synopsis. On addition of 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen, MV^{2+}) to tris(2,2′-bipyridine)-ruthenium(II) (R^{2+}) solubilized in sodium dodecyl sulfate (SDS)-γ-alumina hemimicelles (HM), an effective quenching due to electron transfer occurs in HM. Addition of a large amount of MV^{2+} expels R^{2+} out of HM into the aqueous phase, as a result of exchange hemimicellization.

Photochemistry in micelles continues to attract a great deal of current attention in connection with the fabrication of functionalized molecular assemblies.[1] The enhancement of energy- or electron-transfer in these systems has been intensively studied.[2,3] Such an enhancement occurs also in the detergent solutions in the premicellar region, i.e., below the critical micelle concentration (cmc).[3-5] It is related to many anomalous behaviors in absorption and emission spectra observed in this region.[3-10] When a cationic species like pinacyanol (hereafter abbreviated as PC^+, a cationic dye),[3,6] tris(2,2′-bipyridine)ruthenium(II) (R^{2+}),[7-9] or 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen, MV^{2+})[8,9] is dissolved in the solution of sodium dodecyl sulfate (SDS, an anionic detergent) below the cmc, many peculiar behaviors as described below are found. For PC^+- and R^{2+}-SDS, a suspension of minute insoluble particles is formed in the [SDS] region far below the cmc. This particle is a "complex" (salt) with the composition like $(PC^+\ DS^-)_n$ or $(R^{2+}\ 2DS^-)_n$, where DS^- denotes dodecyl sulfate ion.[6,7] In this region PC^+ is colored red (absorption maximum λ_{abs}=480 nm[3,6]), and the emission maximum wavelength (λ_{em}) of R^{2+} is 585 nm.[7-9] When one adds more SDS to this suspension, the insoluble particles are dissolved and a homogeneous solution is obtained above some boundary [SDS] (called $[SDS]_b$ in this paper) which is still below the cmc. The spectral feature, such as λ_{abs} and λ_{em}, changes drastically at $[SDS]_b$. PC^+ is now colored blue (λ_{abs}=610 nm).[3,6] For R^{2+}, λ_{em} changes into 630 nm.[7-9] These spectral features are the same as those above the cmc, indicating that these cationic species are present in the molecular environment as in micelles. However, such micelle-like species are different from ordinary micelles. The formation of these species is induced with the cationic substrate.[3,6,9,10a] Their concentration is very low and increases with the total concentration of the substrate.[11,12] They are called dye-rich induced micelles (DRIM)[3,4] or substrate-rich induced micelles (SRIM).[9,10a]

Some detergent, below the cmc, forms hemimicelles (HM) on the particle surface of some metal oxides like γ-alumina.[13-15] HM are the two-dimensional analogue of micelles in the bulk, and the detergent molecules in these HM are in the environment close to that in ordinary micelles. For example, Nunn et al.[13] reported that the red color of PC^+ in sodium *p*-(1-propylnonyl)-benzenesulfonate (an anionic detergent) solution below the cmc turned blue by the adsorption on γ-alumina. It is intriguing to study the photochemistry of cationic substrates in HM of an anionic detergent and to see whether the enhancement of electron transfer occurs in HM as in SRIM or ordinary micelles. In the present paper, R^{2+} was solubilized in SDS-γ-alumina HM. The electron transfer[16] to MV^{2+} was studied by the effect of added MV^{2+} on the emission of R^{2+}. In the course of the study, the exchange hemimicellization of R^{2+} with MV^{2+} was found.

Experimental

The ruthenium complex (R^{2+}, dichloride) was a generous gift of Dr. Masaaki Haga, Faculty of Education, Mi'e University. MV^{2+} (dichloride, Wako, G. R.) and SDS (Nakarai, protein research grade) and PC^+ (chloride, Eastman-Kodak) were used as received. γ-Alumina was kindly prepared by Dr. Katsuhisa Tanaka of this Department. The cmc of SDS was determined conductometrically to be 7.4±0.1 mM (1 M=1 mol dm^{-3} and 1 mM=1×10^{-3} mol dm^{-3} in this paper) at 25.0±0.1 °C. Water was distilled twice. An absorbent polymer Foxorb 15 (AVEBE, Holland)[17] was used in the measurements of absorption and emission spectra so cited. All experiments were made at room temperature for aerated solutions. In all samples used in this paper, [SDS]=2 mM and $[R^{2+}]$=2×10^{-5} M. All concentrations shown are those of the final solutions before the addition of γ-alumina.

Results and Discussion

Hemimicellization of R^{2+}. To verify that HM were formed in the system, γ-alumina (5 mg to 10 ml suspension) was added to the red suspension of PC^+ chloride (5×10^{-4} M) in the SDS solution. The sample changed into a colorless supernatant plus a blue-colored precipitate (γ-alumina), showing the formation of HM.[13] When R^{2+} dichloride was added to the SDS solution, a yellowish suspension with λ_{abs}=470 nm and λ_{em}=585 nm was obtained (Fig. 1 (i)). The insoluble "complex" was formed. γ-Alumina (5 mg to 10 ml suspension) was added to this suspension with stirring, and the sample was let stand for a couple of hours. γ-Alumina particles precipitated with a yellow color, leaving colorless supernatant. The absorption spectrum of the precipitate (measured with Foxorb) showed λ_{abs}=455 nm. Its emission spec-

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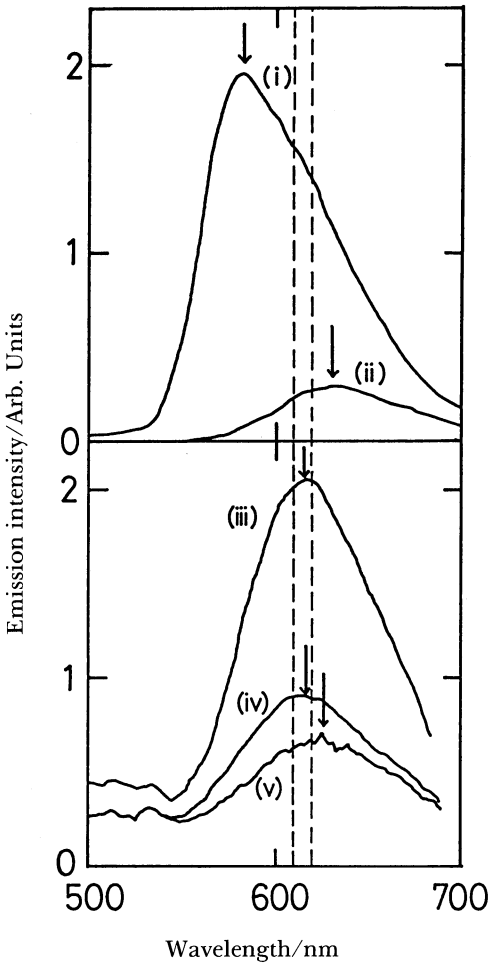

Fig. 1. Emission spectra. (i): a suspension with $[R^{2+}]=2\times10^{-5}$ M and [SDS]=2 mM, (ii): the precipitate (HM) obtained when γ-alumina (0.5 mg ml^{-1}) was added to (i), (iii): the supernatant obtained when MV^{2+} (3×10^{-3} M) was added to (ii), (iv) and (v): the solution (including SRIM) obtained when the aqueous solution of SDS (2 mM and 4 mM, respectively) was added to (iii) in the volume ratio of 1 : 1. Vertical broken lines (λ=610 and 620 nm) are drawn to clarify the shift of bands.

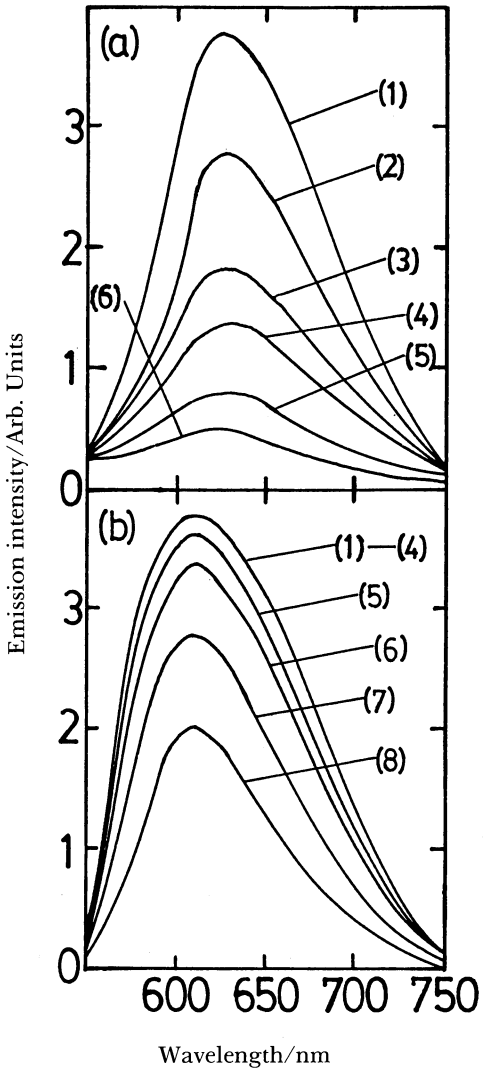

Fig. 2. (a) Emission spectra of R^{2+}-SDS-γ-alumina systems in the absence and presence of MV^{2+} (emission of the precipitate). $[R^{2+}]=2\times10^{-5}$ M, [SDS]= 2 mM, $[MV^{2+}]$=0(1), 5×10^{-6} M(2), 2×10^{-5} M(3), 5×10^{-5} M(4), 2×10^{-4} M(5), 5×10^{-4} M(6).
(b) Emission spectra of aqueous solutions of R^{2+} (2×10^{-5} M) in the absence and presence of MV^{2+}. $[MV^{2+}]$ is the same as above for (1)—(6), 2×10^{-3} M(7); 5×10^{-3} M(8).

trum showed λ_{em}=630 nm (Fig. 1 (ii)). These spectral features were very similar to those of R^{2+} in ordinary micelles (λ_{abs}=455 nm and λ_{em}=630 nm), indicating that R^{2+} was solubilized in HM.

Enhanced Electron Transfer and Exchange Hemimicellization with MV^{2+}. MV^{2+} chloride was added to the R^{2+}-SDS-γ-alumina system (solution with precipitate), and the stirring-standing procedure was followed. For $[MV^{2+}]=5\times10^{-6}$ M—5×10^{-5} M, the appearance of the sample mixture did not change (a yellow precipitate and a colorless supernatant). The intensity of the emission band of the precipitate at λ_{em}=630 nm decreased with $[MV^{2+}]$ as shown in Fig. 2 (a). For $[MV^{2+}]=2\times10^{-4}$ M to 5×10^{-4} M, the color of the supernatant turned into yellow, while the precipitate remained yellow. The precipitate showed λ_{em}=630 nm. The supernatant (the spectrum not shown) gave λ_{em}=618 nm.[18] For $[MV^{2+}]=2\times10^{-3}$ M—5×10^{-3} M, the precipitate was almost colorless (The addition of MV^{2+} deprived the precipitate of the yellow color of R^{2+}.), and the precipitate gave the emission of hemimicellized R^{2+} no more. The yellow color of R^{2+} was transferred into the supernatant which showed λ_{em}=615 nm (Fig. 1 (iii), $[MV^{2+}]=3\times10^{-3}$ M). This λ_{em} value is close to that of free R^{2+} in the aqueous solution (610 nm). Apparently, the addition of MV^{2+} to the R^{2+}-SDS-γ-alumina system expelled some portions of R^{2+} out of HM into the aqueous phase. This was further supported by the measurement of the absorbance of the supernatant at 455 nm (this wavelength corresponds to λ_{max} of R^{2+} in the aqueous solution). The apparent molar extinction coefficient (ε_{app}=absorbance/(light path length $\times$total concentration of initially added R^{2+})) increased with $[MV^{2+}]$, the concentration of total MV^{2+} added

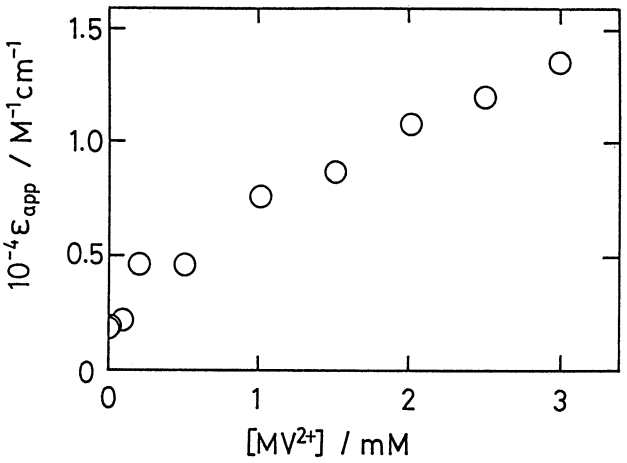

Fig. 3. Absorbance of the supernatant at 455 nm by the addition of MV^{2+} to the R^{2+}-SDS-γ-alumina system. [MV^{2+}] is the concentration of added MV^{2+}.

(not the MV^{2+} concentration of the supernatant in equilibrium with HM), as shown in Fig. 3. It approached the value of ε of R^{2+} in aqueous solution, 1.5×10^4 $M^{-1}cm^{-1}$. (The accomplishment of the relation $\varepsilon_{app}=\varepsilon$ means a complete desorption of R^{2+}.) This verified that MV^{2+} expelled some portions of R^{2+} out of HM into the aqueous phase. It should be noted that λ_{em} of R^{2+} in the aqueous phase (615 nm) is close to that of free R^{2+} in the aqueous solution (610 nm) rather than that of R^{2+} in SRIM (630 nm). This indicates that R^{2+} was expelled by itself, not with SDS, into the aqueous phase. In other words, SDS remained almost completely in the HM. (Otherwise, we should have λ_{em} close to that in SRIM.)

The experimental findings show the occurrence of an extensive quenching of emission of R^{2+} by MV^{2+} in HM. The decrease in the emission intensity of R^{2+} in HM (Fig. 2 (a)) is in part due to the desorption process mentioned above. However, the enhancement of quenching in HM compared to that in aqueous solutions (shown in Fig. 2 (b)) is apparent, since an extensive decrease in emission intensity (much larger than in aqueous solutions) occurs for MV^{2+} concentrations where the above-mentioned desorption effect is not important (i.e. [MV^{2+}] $\leqslant 5\times10^{-5}$ M). This shows that the electron transfer from R^{2+} to MV^{2+} is significantly enhanced in HM.

To the yellow supernatant (Fig. 1 (iii)) was added the aqueous solution of SDS (2 mM or 4 mM) in the volume ratio 1 : 1. The emission spectra obtained are shown in Fig. 1 (iv) and (v), respectively. The λ_{em} shifted to 618 and 625 nm, respectively. The latter wavelength is very close to that of R^{2+} in SRIM. These results indicate that the original supernatant contained little amount of SDS (that is, SDS was almost exclusively in HM) and that SRIM incorporating R^{2+} were formed by newly added SDS (which makes [SDS]≈1 mM and 2 mM, respectively).

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17) Foxorb is a carboxymethylated natural polysaccharide based on potato starch, and it does not dissolve in water but only swells. It holds HM well dispersed among its swelled polymer chain, giving an almost transparent appearance to the sample, thus making the spectral measurements easier.
18) The emission band is due to the superposition of that of R^{2+} in "complex" (λ_{em}=585 nm), and that in SRIM (λ_{em}=630 nm).