CHEMISTRY LETTERS, pp. 1139-1142, 1982.

DYNAMIC STUDY ON THE QUENCHING OF THE EMISSION OF TRIS(BIPYRIDINE) RUTHENIUM(II) BY N,N'-DIMETHYL-4,4'-BIPYRIDINIUM (DMBP) WITH SODIUM DODECYLSULFATE IN THE PREMICELLAR REGION: ENHANCED ELECTRON TRANSFER IN DMBP-INDUCED PREMICELLES

Hiroyasu SATO,* Masahiro KAWASAKI, Kazuo KASATANI, and Taketora BAN
Chemistry Department of Resources, Faculty of Engineering,
Mi'e University, Tsu 514

A dynamic study was made on the quenching of the emission of tris(bipyridine)ruthenium(II) by N,N'-dimethyl-4,4'-bipyridinium (DMBP) in the presence of sodium dodecylsulfate, most enhanced in the premicellar region. It revealed that the enhancement is due to the DMBP-induced formation of premicelles in which a very effective electron transfer occurs.

Bimolecular excited-state processes in organized assemblies such as micelles have received increased attention.1) At the same time, the electron transfer reaction of the cationic metal complex tris(bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$ (hereafter abbreviated as R) in the charge-transfer excited state2) to a suitable electron acceptor like N,N'-dimethyl-4,4'-bipyridinium (methylviologen) dication (DMBP) has been the subject of intense study, in relation to its possible promise for solar energy conversion processes.3) Meisel et al.4) studied the effects of micellar solutions of sodium dodecylsulfate (SDS) on the kinetics of the electron-transfer reaction between R^* and e_{aq}^-, Cu^{2+}, etc. above the critical micelle concentration (cmc). Rodgers and Becker5) studied the electron transfer rate of the reaction $R^* \rightarrow$ DMBP as a function of [SDS] by the decay of the emission at 630 nm. They found the enhancement of the electron transfer in the premicellar region, i.e., [SDS] below the cmc, and attributed this to the formation of "submicellar aggregates". In the present paper, the mechanism of the enhancement of electron transfer in the premicellar region is studied in terms of the effect of DMBP on the nature of the R-SDS aggregates, from the shift of the emission bands and the variation of the emission decay characteristics caused by the addition of DMBP.

The ruthenium complex used is a generous gift of Dr. Haga, Faculty of Education, Mi'e University. DMBP (dichloride, Wako G. R.) and SDS (Nakarai, protein research grade) were used without further purification. The cmc of SDS was determined conductometrically to be 7.4 ± 0.1 mM† (at 25.0 ± 0.1°C). Water was distilled twice. Absorption and emission spectra were recorded on a Shimadzu UV 200 and a Hitachi 650-10S recording spectrophotometer, respectively. Emission lifetimes were measured by using a TEA nitrogen laser (pulse width 1.5 ns) and a Hamamatsu 1P28A photomultiplier with a fast response circuitry.6) Oscillograms on a Tektronix 7904 oscilloscope were photographed and analysed. A Toshiba L-39 filter was used to cut off the

---

† $1\ M = 1\ mol\ dm^{-3}$ and $1\ mM = 1 \times 10^{-3}\ mol\ dm^{-3}$ in this paper.

scattered light of the laser. Toshiba O-54 and R-62 filters were used to select the emission bands. All experiments were made at room temperature for aerated solutions.

Some of the emission spectra of R-SDS and R-DMBP-SDS systems are given in Fig.1. The quenching of the emission of R by DMBP is little both in aqueous solution and in SDS solutions above the cmc. The extensive quenching occurred at [SDS] = 1 - 10 mM, and especially at [SDS] = 2 - 5 mM, i.e., in the premicellar region. This finding is essentially in accordance with that of Rodgers and Becker.5) The emission peak (λ^{E}_{max}) at 610 nm for [SDS] = 0, that at 630 nm for [SDS] $\geqq$ 5 mM, and the absorption peak (λ^{A}_{max}) at 455 nm for [SDS] = 0 and [SDS] $\geqq$ 5 mM did not shift on the addition of DMBP. At [SDS] = 1 mM, λ^{E}_{max} at 585 nm and λ^{A}_{max} at 470 nm of R-SDS did not shift on DMBP addition. Small particles, characteristic of 1 : 2 complex (vide infra) found for R-SDS did not disappear on DMBP addition. At [SDS] = 2 mM, λ^{E}_{max} at 585 nm of R-SDS shifted to 630 nm on DMBP addition. The shift of λ^{A}_{max} from 470 nm to 455 nm and the disappearance of small perticles were also found.

Meisel et al.4) observed three emission bands of R*, depending on the concentration of SDS ([SDS]); 605 nm (in aqueous solution), 625 nm (in micellar solutions), and 578 nm (for [SDS] << cmc). Precipitation due to $(R\cdot 2DS)_n$-type aggregate was observed in the region where the 578 nm emission was found. (DS is a dodecylsulfate ion.) They attributed the 625 nm emission to R residing in micelles. The bathochromic shift on changing the medium from water to micelles was attributed to the interaction of R with the hydrocarbon chains in micelles. Although Meisel et al.4) reported the 625 nm emission only above the cmc, our study revealed the presence of the emission (630 nm in our case) not only above the cmc but also for some [SDS] region below the cmc ([SDS] $\gtrsim$ 5 mM). This shows that R is present in an environment like that in micelles in this region.

The formation of dye-detergent aggregates in the premicellar region has been reported for many dye-detergent systems when the dye and detergent have the opposite charges.7-13) The position of emission band in [SDS] region just below the cmc remains the same as that for [SDS] $\gtrsim$ cmc. This has been attributed to the incorporation of dyes in dye-rich induced micelles (premicelles) below the cmc.9,12) The enhancement of the energy transfer efficiency between two cationic dyes in the dye-SDS systems observed in the premicellar region was attributed to the incorporation of dyes in premicelles.10-12) A similar enhancement of energy transfer efficiency between R and a cationic dye14) and an enhanced quenching of R* by

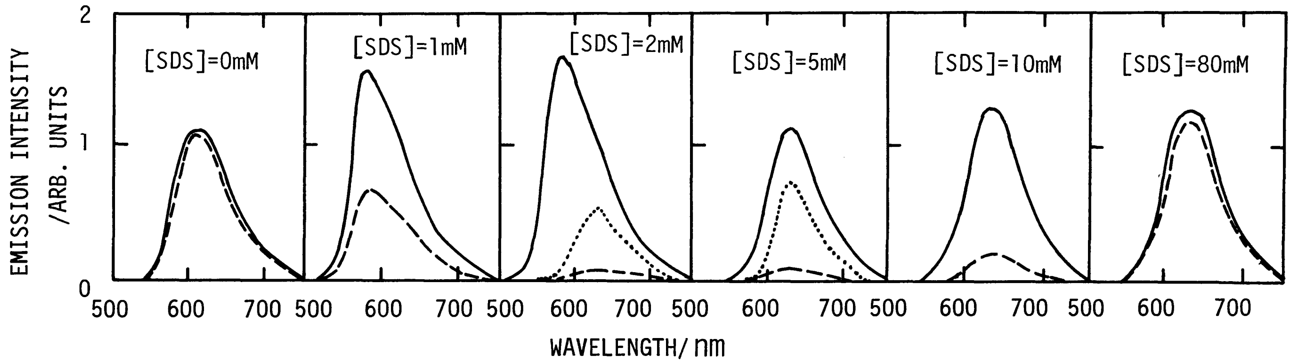

Fig. 1. Emission Spectra. ——: $[Ru(bpy)_3]^{2+}$ 8×10^{-5}M, ----: $[Ru(bpy)_3]^{2+}$ 8×10^{-5}M and DMBP 7×10^{-4}M, ····:---- multiplied by 10.

9-methylanthracene[15) were found in the presence of SDS below the cmc. These are attributed to the formation of premicelles. All of these facts support the presence of premicelles in the R-SDS system and the assignment of the 630 nm emission below the cmc to R in premicelles.[16)

Mukerjee and Mysels[8) have shown two types of the aggregate for pinacyanol (P, a cationic dye)-SDS system, i.e., the $(P\cdot DS)_n$-type 1:1 complex at [SDS] << cmc and "dye-rich induced micelles" in the [SDS] region just below the cmc. Small particles in the solution observed at [SDS] << cmc was attributed to $(P\cdot DS)_n$ complex. These disappeared with the increase in [SDS], because the 1:1 complex is reorganized into dye-rich induced micelles. These two types of aggregate are formed for many cationic dyes with SDS.[9,10,13) The 585 nm emission (578 nm by Meisel et al.[4)) in the present system, accompanied by the presence of small particles, is undoubtedly due to $(R\cdot 2DS)_n$-type complexes (1:2 complexes).

Taking these into account, the results mentioned above reveals the following. The maximum enhancement of the electron transfer efficiency occurred at the boundary [SDS] region where $(R\cdot 2DS)_n$-type complexes (λ^{E}_{max} = 585 nm) are reorganized into premicelles (λ^{E}_{max} = 630 nm) with the increase in [SDS] in the R-SDS system. Then, does the most effective electron transfer occur in premicelles or in 1:2 complexes ? The results of dynamic emission decay studies (Table 1) give the answer. Each decay was exponential as found by Rodgers and Becker.[18) As can be seen, the decay of the 630 nm emission became much faster on addition of DMBP, while the decay of the 585 nm emission remained essentially unchanged. This shows that the electron transfer occurs in premicelles.

On the lower edge of the boundary [SDS] region, i.e., at [SDS] = 2 mM, the shift in λ^{A}_{max} and disappearance of small particles on DMBP addition indicate the following mechanism. The $(R\cdot 2DS)_n$-type complexes are reorganized into premicelles by the action of DMBP, and an enhanced electron transfer occurs in the premicelles thus formed. (DMBP must be strongly bound to premicelles, since it is known to be bound strongly to anionic micelles.[17)) In decay studies, the addition of DMBP changed the decay into a double-exponential one. By using filters to distinguish the 585 nm and 630 nm emissions, it turned out that the lifetime of the former (much weakened but still observed) did not change appreciably. That of the latter, appeared on DMBP

Table 1. Lifetimes of $[Ru(bpy)_3]^{2+}$ emission (ns)

[R] = 8×10^{-5} M, [DMBP] = 0 M

	Emission bands		
[SDS]/mM	585nm	610nm	630nm
0		370±40	
1	370±40		
2	350±40		
5			440±50
10			470±50
20			460±50
40			500±50
80			470±50

[R] = 8×10^{-5} M, [DMBP] = 7×10^{-4} M

	Emission bands		
[SDS]/mM	585nm	610nm	630nm
0		330±30	
1	360±40		
2	310±30		16±2*
5			16±2
10			50±5
20			210±20
40			390±40
80			380±40

* not observed without DMBP.

addition, was very short. These facts provide a strong evidence for the mechanism mentioned above.

In these experiments, [DMBP] was much larger than [R]. For more detailed study of the action of DMBP on the aggregation state of R in R-SDS solutions, the experiments were made in which [DMBP] was varied for constant [R]'s (in the range [R] = $5 \times 10^{-6} - 5 \times 10^{-5}$ M) at [SDS] = 2 mM. The emission peak at 585 nm for [DMBP] $\lesssim$ [R] shifted to 630 nm for [DMBP] > [R]. A very short lifetime was obtained for the latter. These findings show that the action of DMBP to induce the change $(R \cdot 2DS)_n \rightarrow$ (R in premicelles) takes effect for [DMBP]/[R] > 1.

It is known that the electron transfer occurs between the electron donor and acceptor very closely located. The enhanced electron transfer in premicelles is due to the high local concentrations and hence the small mutual distances of R and DMBP in these premicelles.

The authors are grateful to Dr. Masaaki Haga, Faculty of Education, Mie University, who kindly donated the ruthenium complex used. The present study is partly supported by the Grant-in-Aid of the Ministry of Education, Science and Culture.

References

1) For reviews see: J. K. Thomas, Acc. Chem. Res., 10, 133 (1977).
2) G. D. Hager and G. A. Crosby, J. Am. Chem. Soc., 97, 7031 (1975).
3) N. Sutin, J. Photochem., 10, 19 (1979).
4) D. Meisel, M. S. Matheson and J. Rabani, J. Am. Chem. Soc., 100, 117 (1978).
5) M. A. J. Rodgers and J. C. Becker, J. Phys. Chem., 84, 2762 (1980).
6) G. Beck, Rev. Sci. Instrum., 47, 537 (1976).
7) N. Mataga and M. Koizumi, Nippon Kagaku Zasshi, 75, 237 (1954), Bull. Chem. Soc. Jpn., 27, 197 (1954).
8) P. Mukerjee and K. J. Mysels, J. Am. Chem. Soc., 77, 2937 (1955).
9) H. Sato, M. Kawasaki, K. Kasatani, Y. Kusumoto, N. Nakashima, and K. Yoshihara, Chem. Lett., 1980, 1529.
10) Y. Kusumoto and H. Sato, Chem. Phys. Lett., 68, 13 (1979).
11) H. Sato, Y. Kusumoto, N. Nakashima, and K. Yoshihara, Chem. Phys. Lett., 71, 326 (1980).
12) H. Sato, M. Kawasaki and K. Kasatani, J. Photochem., 17, 243 (1981).
13) M. Katsumata, K. Kasatani, M. Kawasaki, and H. Sato, Bull. Chem. Soc. Jpn., 55, 717 (1982).
14) K. Mandal and J. N. Demas, Chem. Phys. Lett., 84, 410 (1981).
15) J. H. Baxendale and M. A. J. Rodgers, Chem. Phys. Lett., 72, 424 (1980).
16) One may argue on "the formation of premicelles below the cmc". The cmc is usually determined by a break in some *macroscopic* physicochemical quantity such as electric conductivity. The presence of premicelles caused only a very small shift (such as 0.5 - 0.6 mM) to the lower [SDS] on the cmc of R-SDS and dye-SDS systems (Refs. 4,8,10).
17) T. K. Foreman, W. M. Sobol, and D. G. Whitten, J. Am. Chem. Soc., 103, 5333 (1981).
18) Ref. 5. However, these authors did not report on the 585 nm band. They did not refer to [SDS] = 1 - 2 mM.

(Received April 1, 1982)