LIFETIMES OF THE LOWEST EXCITED STATE OF TRIS(2,2′-BIPYRIDINE)RUTHENIUM(II) AND ITS AMPHIPATHIC DERIVATIVE IN MICELLAR SYSTEMS

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Summary

The luminescence decay lifetimes of tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) and its amphipathic derivative (*N*,*N*′-di(dodecyl)-2,2′-bipyridine-4,4′-dicarboxyamide)bis(2,2′-bipyridine)ruthenium(II) ($[RuC_{12}B]^{2+}$) measured in H_2O, D_2O, CH_3OH, CD_3OH and CH_3OD solutions as well as in micellar solutions of sodium dodecylsulphate in H_2O and D_2O reveal the role of the protic solvent molecules in the deactivation of the excited ruthenium(II) complexes. The lifetimes of the complexes reduce with increasing size of the water pool in the inverted micellar solution. $[Ru(bpy)_3]^{2+}$ is present in the water pool, whereas $[RuC_{12}B]^{2+}$ is buried inside the anionic interface with its aliphatic side-chains penetrating deep into the hydrophobic domain. In aqueous micellar solution $[Ru(bpy)_3]^{2+}$ is on the micellar surface only of the anionic detergent, whereas $[RuC_{12}B]^{2+}$ is partially buried inside the micelles regardless of whether they are anionic, cationic or non-ionic. In fact *N*,*N*′-dimethylaniline, which dissolves only in the hydrocarbon region of the micelles, is a good quencher for $[RuC_{12}B]^{2+}$ in aqueous micellar solution but does not quench $[Ru(bpy)_3]^{2+}$.

1. Introduction

Extensive studies of photochemistry and photodynamics in organized media have recently been performed [1]. However, very little is known about the microscopic environment of solvent molecules around micelle-bound photosensitizers.

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The excited state lifetime of tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) in solution varies with the solvent [2]. The rate of luminescence decay has been ascribed to the sum of the rates for radiative and non-radiative decay of the lowest metal-to-ligand charge-transfer excited state and the rate for internal conversion via thermal activation to the low-lying (d, d*) excited state [2 - 6]. It has been noted that the excited state lifetimes of $[Ru(bpy)_3]^{2+}$ and its analogues as well as those of many other transition metal complexes increase in D_2O [4, 7 - 12].

In aqueous micellar solutions the cation complex tends to associate with water whereas the hydrophobic ligands associate with the hydrocarbon region of the micelles. The deactivation of excited ruthenium(II) complexes is attributable to coupling of the ligand with associated solvent molecules in the second coordination sphere. If the complex is buried in the hydrophobic domain, only a small fraction of the water molecules are accompanied. Thus the difference between the lifetimes in H_2O and D_2O varies depending on whether the complexes are in surfactant-free media or are bound in micelles. Since the solvent deuteration effect has been observed even with neutral or anionic ruthenium(II) complexes in aqueous anionic micellar solutions, a rather strong hydrophobic interaction between the ligands and the hydrocarbon core of the micelles has been proposed [12]. The hydrophobic interaction is the only interaction of importance in non-ionic Triton X-100 micellar solution [13].

In the present work the excited state lifetimes of $[Ru(bpy)_3]^{2+}$ and its amphipathic derivative (*N*,*N*′-di(dodecyl)-2,2′-bipyridine-4,4′-dicarboxyamide)bis(2,2′-bipyridine)ruthenium(II) ($[RuC_{12}B]^{2+}$) were measured in deuterated solvents, aqueous micellar systems and an inverted micellar solution. The reductive luminescence quenching of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in aqueous micellar systems by *N*,*N*′-dimethylaniline (DMA), which dissolves only in the hydrocarbon region of the micelles, was also studied. Since the quenching is effective for $[RuC_{12}B]^{2+}$ but not for $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$ is not necessarily in the hydrocarbon core even in anionic micellar solutions whereas the complex head of $[RuC_{12}B]^{2+}$ is buried inside the micelles regardless of the type of detergent.

2. Experimental details

2.1. Materials

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was prepared from $K_2[RuClH_2O]$ using the literature method [14] and was recrystallized first from water and then several times from an acetone–water mixture.

$[RuC_{12}B](ClO_4)_2 \cdot 6H_2O$ was prepared and purified using the method described in ref. 15.

Cetyltrimethylammonium chloride (CTAC) was repeatedly recrystallized from acetone [16]. Sodium dodecylsulphate (SDS) was purified by Soxhlet extraction of dodecanol with hexane for 30 h and was then re-

crystallized from a 95:5 acetone–water mixture [16]. Triton X-100 was commercially available and was used without further purification. Sodium bis(2-ethylhexyl)sulphosuccinate (Aerosol OT (AOT)) was dissolved in methanol and the solution was filtered and then evaporated under vacuum [17]. After repeated recrystallization, a white precipitate was collected and was dried in a vacuum desiccator over P_2O_5.

DMA was repeatedly distilled under reduced pressure. Heptane was distilled after reflux on sodium metal. Acetonitrile was distilled after being dried over calcium hydride. Methanol (Dojin Luminasol) was used without further purification. D_2O, CD_3OH and CH_3OD were obtained from Merck.

2.2. Preparation of the micellar solutions

An aliquot of a methanol solution of the ruthenium complex of known concentration was evaporated to dryness. The residue was dissolved in a known amount of aqueous detergent solution which had been prepared previously and was then sonicated using a Sharp UT-51N sonicator for 5 - 10 min. Concentrations of the surfactant greater than the critical micelle concentration were used as summarized in Table 1. The concentration of the ruthenium complex used for measurements of the absorption and emission spectra and the luminescence decay lifetimes was typically 10^{-5} M.

The micellar solutions for luminescence measurements were saturated with dry nitrogen gas by means of the freeze–pump–thaw technique. The inverted micellar solutions of AOT in heptane were bubbled with dry nitrogen gas which was saturated with heptane.

TABLE 1

The concentrations of surfactant used for lifetime measurements

Surfactant	*Concentration used for the measurements*	*Micellar aggregation number* $\bar{n}$	*Critical micelle concentration* [18]
CTAC	1×10^{-2} M	61	9.2×10^{-4} M
SDS	1×10^{-2} M	54	9.8×10^{-3} M
Triton X-100	1 vol.%	10	0.54 vol.%

2.3. Measurements

The absorption spectra were obtained on a Shimadzu recording spectrophotometer (model MPS 50). The luminescence and excitation spectra were recorded on a Hitachi fluorescence spectrophotometer (model MPF-2A) using a Hamamatsu Photonics R928 photomultiplier. Transient measurements were achieved using pulses of 4 ns duration generated by a National Research Group dye laser (model NRG-DL-003) excited by 5 ns pulses from a nitrogen laser (model NRG-0.5-5-150/B). The excitation wavelength was set at 433 nm using an aqueous solution of coumarin 120 (Eastman Kodak). The luminescence emission from the sample solution was detected through

Toshiba 0-54 glass filters by a Hamamatsu Photonics R446 photomultiplier placed in a direction perpendicular to the propagation of the excitation pulses. The photomultiplier output, which was detected for a termination of 50 Ω through a connection with larger decoupling capacitors [19] and amplified by means of an Avantek module amplifier (model SAG3060B), was digitized and accumulated for 512 or 1024 excitation pulses on a Kawasaki Electronica M-50E transient memory with 50 ns time resolution equipped with an averager (model TMC-400). The decay lifetime was evaluated from the decay curve by using the weighted least-squares method on a Commodore CBM 3032 microcomputer interfaced to the transient memory digitizer. The data were displayed on a Hewlett-Packard 9872A graphic plotter which was interfaced with the microcomputer. Decays with lifetimes less than 200 ns were displayed on a Tektronix 475A oscilloscope and photographed using Polaroid 410 films. The photographed decay curves were digitized on a Hewlett-Packard 9872A graphic plotter and analysed on its interfaced personal computer (model 9825A).

The temperature of the solutions was kept at 25 °C by circulating water from a Haake FK thermostat in the cell compartment.

3. Results and discussion

3.1. Spectroscopy and luminescence decay lifetime measurements

The absorption spectra of $[Ru(bpy)_3]^{2+}$ in a variety of aqueous micellar solutions conform with that in aqueous solution as shown in Fig. 1. A slight blue shift and broadening of the band at 22×10^3 cm^{-1} are observed in aqueous SDS micellar solution. It should be noted that $[Ru(bpy)_3]^{2+}$ in the aqueous cores of AOT inverted micelles formed in heptane exhibits a spectrum which is similar to that of the aqueous solution. $[RuC_{12}B]^{2+}$ is soluble in methanol and aqueous micellar solutions, whereas it is only sparingly soluble in water. The absorption spectra of $[RuC_{12}B]^{2+}$ in aqueous micellar solutions exhibit a split band at 22×10^3 cm^{-1} and are different from that in methanol. However, the spectrum of $[RuC_{12}B]^{2+}$ in the inverted micellar solution, which exhibits no splitting of the charge-transfer band, shows much better agreement with that of $[Ru(bpy)_3]^{2+}$ in aqueous solution than does the spectrum of $[RuC_{12}B]^{2+}$ in methanol.

The complex (2,2′-bipyridine-4,4′-dicarboxylic acid)bis(2,2′-bipyridine)-ruthenium(II) ($[Ru^{II}(bpy)_2bpy(COOH)_2]$) exhibits a split band at 22×10^3 cm^{-1} when the carboxyl groups are protonated whereas no splitting is observed when these groups are deprotonated [20]. Band splitting is also observed for the surfactant complex $[Ru^{II}(bpy)_2bpy(COOC_{18}H_{37})_2]^{2+}$ but not for $[Ru^{II}(bpy)_2bpy(C_{19}H_{39})_2]^{2+}$ [21, 22]. Since the carboxyamide groups of $[RuC_{12}B]^{2+}$ are on the micelle surface, it can be hydrogen bonded in aqueous micellar solutions. This yields an increase in the electron affinity of the bipyridine moiety with $—CO—NH—C_{12}H_{25}$ groups which breaks down the equivalence of the three bipyridine ligands and thus causes splitting of the

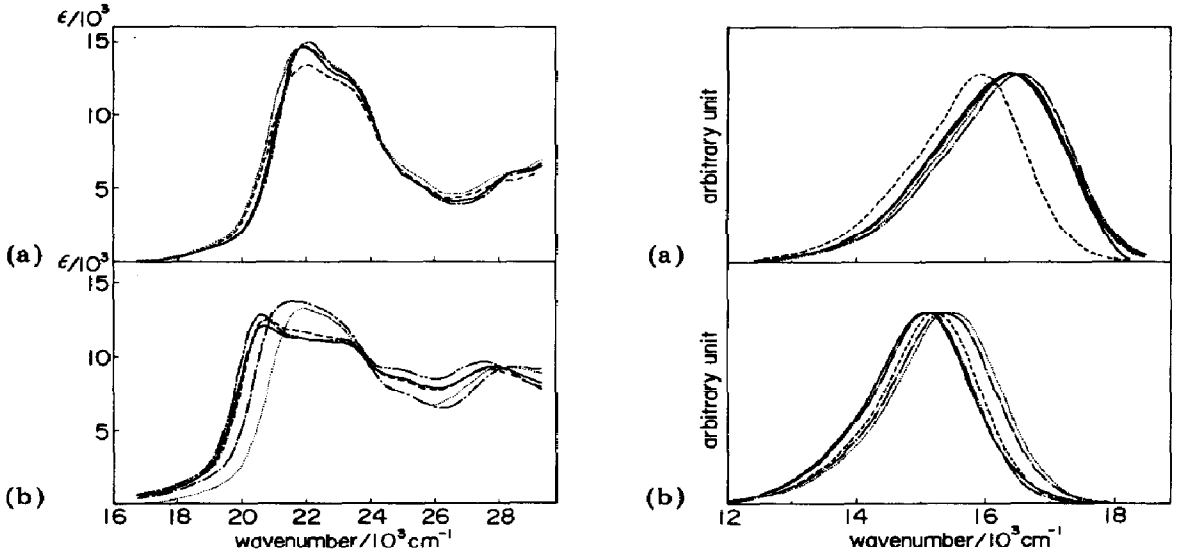


Fig. 1. Absorption spectra of (a) $[Ru(bpy)_3]^{2+}$ and (b) $[RuC_{12}B]^{2+}$ in CH_3OH (— · —), aqueous solutions of Triton X-100 (———), CTAC (— ·· —) and SDS (— — —), and a heptane solution of AOT containing 1% H_2O (·····). The spectra of $[Ru(bpy)_3]^{2+}$ in aqueous micellar solutions of Triton X-100 and CTAC coincide with that of the aqueous solution.

Fig. 2. Emission spectra of (a) $[Ru(bpy)_3]^{2+}$ and (b) $[RuC_{12}B]^{2+}$ in CH_3OH (— · —), CH_3CN (·····) and aqueous micellar solutions of Triton X-100 (———), CTAC (— ·· —) and SDS (— — —). The spectrum of $[Ru(bpy)_3]^{2+}$ in an aqueous micellar solution of CTAC coincides with that in the aqueous solution.

band at 22×10^3 cm^{-1}. The spectrum of $[RuC_{12}B]^{2+}$ in the inverted micellar solution, however, indicates that the carboxyamide groups are almost free from hydrogen-bonding perturbations of water molecules in the water pool.

Figure 2 shows the emission spectra of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in a variety of media.

Table 2 shows the luminescence decay lifetimes of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ measured in H_2O, D_2O, CH_3OH, CD_3OH and CH_3OD solutions as well as in micellar solutions of SDS in H_2O and D_2O. All the luminescence decays were single exponential. The lifetimes of $[Ru(bpy)_3]^{2+}$ in CH_3OH and CD_3OH were the same but those in CH_3OH and CH_3OD were different,

TABLE 2

The effect of solvent deuteration on the luminescence decay lifetime τ at 25 °C

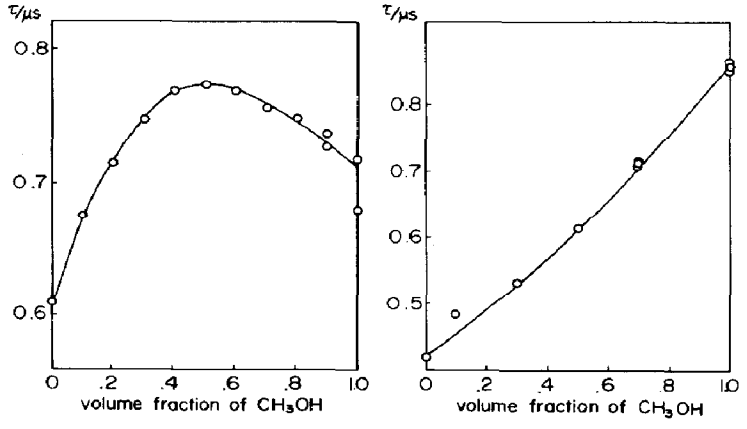
	τ (μs)						
	H_2O	*D_2O*	*SDS–H_2O*	*SDS–D_2O*	*CH_3OH*	*CD_3OH*	*CH_3OD*
$[Ru(bpy)_3]^{2+}$	0.61	1.00	0.82	1.03	0.72	0.72	0.76
$[RuC_{12}B]^{2+}$	(0.42)[a]	(0.61)[a]	0.73	0.96	0.85	0.84	0.98

[a] The complex may form an aggregate in water.

and this difference was enhanced for $[RuC_{12}B]^{2+}$. In the case of $[Ru(bpy)_3]^{2+}$ the deuteration of the medium does not result in a marked change in the rate of radiative and non-radiative decays of the lowest metal-to-ligand charge-transfer excited states, but a decrease in the rate of internal conversion involving thermal activation to the low-lying (d, d*) excited state is observed [4]. This effect has been attributed to a difference in the efficiency of energy transfer to the OH- or OD-accepting modes in protic solvents [12]. In the lowest metal-to-ligand charge-transfer excited state a promoted electron hops between three ligands, thus conserving the symmetry of the electron wavefunction in the ligand orbital and the hole wavefunction in the metal orbital. During the excited state lifetime, however, the hopping electron is temporarily trapped at the site of one of the ligands by a significant attack of protic solvent molecules, which results in configuration admixing of a sizeable number of excited states and a breakdown of the symmetry of electron–hole interaction. Therefore efficient recombination of the electron in the ligand and the hole in the metal occurs.

The luminescence decay lifetime of $[Ru(bpy)_3]^{2+}$ depends on the CH_3OH content in H_2O–CH_3OH mixed media as shown in Fig. 3. The maximum lifetime is obtained in the 1:1 mixture. The maximum volume contraction and the maximum viscosity of the H_2O–CH_3OH mixture are obtained when the CH_3OH contents are 60 vol.% and 40 vol.% respectively. This indicates that the attack of protic solvent molecules is rather retarded when highly ordered hydrogen bonds are formed between the protic solvent molecules. In the case of D_2O–CH_3OD media, however, the lifetime decreases monotonically from the value in pure D_2O (1.0 μs) to that in pure CH_3OD (0.76 μs) and no maximum is observed.

The decay lifetime of $[RuC_{12}B]^{2+}$ in H_2O–CH_3OH mixed media increases almost linearly from the value in pure H_2O (0.42 μs) to that in pure CH_3OH (0.86 μs) with increasing CH_3OH content. Since $[RuC_{12}B]^{2+}$ is only sparingly soluble in water, a self-aggregation may arise in solutions as dilute



(a) (b)

Fig. 3. Decay lifetimes of (a) $[Ru(bpy)_3]^{2+}$ and (b) $[RuC_{12}B]^{2+}$ in H_2O–CH_3OH mixed media.

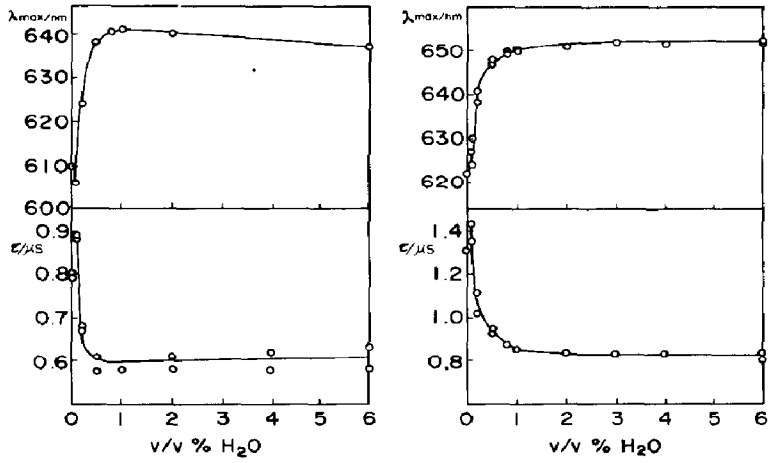
as 10^{-7} M even when they are sonicated. In an aggregate of the detergent complex quenching is attributable to energy and/or electron transfer between the chromophores over a short distance. However, the observed decay of $[RuC_{12}B]^{2+}$ in aqueous solution was single exponential.

The decay lifetimes of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in aqueous SDS micellar solutions are longer than those in aqueous solutions. Since the cation complex must be bound to the surface of the anionic detergent micelle, the excited complex will be shielded to some extent from attack by the solvent water molecules.

3.2. Complexes in the inverted micelle

The emission spectra and decay lifetimes of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in AOT inverted micelles were measured for water pools of various sizes. Figure 4 shows the emission maximum and decay lifetime as a function of the water content in the medium.

In a 3% solution of AOT in heptane, the AOT molecules are aggregated in uniformly sized assemblies of rounded cylindrical shape, each consisting of 23 AOT molecules [23]. Upon addition of water, a spherical water pool surrounded by a monolayer of AOT molecules is formed. Micellar compositions in solutions of 3 wt.% (0.067 M) AOT in heptane are known to be a function of the water content (in volume per cent) [17]. The excited state lifetime in the inverted micellar solution is reduced on increasing the water content to 1 vol.% and then converges to a constant value on increasing the water content further. When the water content is 1 vol.% 2600 water molecules are enclosed in the water core of a micelle which has a radius of 23.2 Å [17]. The lifetime of $[RuC_{12}B]^{2+}$ in the inverted micelle is longer than those observed in aqueous micellar solutions and that of $[Ru(bpy)_3]^{2+}$ in the inverted micelle. When the water content is greater than 1 vol.% the excited



(a) (b)

Fig. 4. The emission maxima and decay lifetimes of (a) $[Ru(bpy)_3]^{2+}$ and (b) $[RuC_{12}B]^{2+}$ in solutions of AOT in heptane as a function of the water content.

$[Ru(bpy)_3]^{2+}$ in the inverted micelle decays in the same way as in aqueous solutions. The emission maximum is red shifted with increasing water content up to 1 vol.%. The $[Ru(bpy)_3]^{2+}$ maximum is then shifted in the reverse direction with further increase in water content, but the blue shift is too small to recover the maximum in aqueous solution whereas that of $[RuC_{12}B]^{2+}$ converges to a wavelength shorter than those observed for aqueous micellar solutions. The red shifts of the emission maximum and the reduction of the excited state lifetime observed with the increase in water content up to 1 vol.% indicate enhanced interactions of the anionic interfacial region and the water molecules with the excited species. In fact the absorption spectra of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in the inverted micellar solution containing 1 vol.% H_2O are similar to that of $[Ru(bpy)_3]^{2+}$ in aqueous solution.

The $[Ru(bpy)_3]^{2+}$ in the spherical water pool is in contact with the anionic interfacial region of the AOT micelle, whereas the complex head of $[RuC_{12}B]^{2+}$ is present inside the anionic interface and its aliphatic side-chains penetrate deep into the hydrophobic domain of the micelle. In this situation water molecules in the water pool interact with excited $[Ru(bpy)_3]^{2+}$ and to a lesser extent with excited $[RuC_{12}B]^{2+}$. As the water content increases, the excited state lifetime of $[Ru(bpy)_3]^{2+}$ is reduced but that of $[RuC_{12}B]^{2+}$ is not. Since a single band rather than a split band is observed at 22×10^3 cm^{-1}, water molecules in the water pool do not undergo hydrogen-bond interactions with the $-CO-NH-C_{12}H_{25}$ group of $[RuC_{12}B]^{2+}$ in the inverted micellar solution, in contrast with their behaviour in aqueous micellar solutions.

3.3. Complexes in aqueous micellar systems

The decay lifetimes of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ measured in a variety of aqueous micellar solutions are summarized in Table 3 and the corresponding emission maxima are given in Table 4. The absorption and emission spectra as well as the lifetimes of $[Ru(bpy)_3]^{2+}$ in aqueous Triton X-100 and CTAC micellar solutions are the same as those in aqueous solutions. However, a red shift of the emission maximum and an increase in the

TABLE 3

The decay lifetimes τ at 25 °C of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in aqueous micellar solutions

Complex	τ (μs)				
	H_2O	CH_3CN	*Aqueous micellar solution*		
			CTAC	*Triton X-100*	*SDS*
$[Ru(bpy)_3]^{2+}$	0.61	0.87	0.61	0.63	0.82
$[RuC_{12}B]^{2+}$	(0.42)[a]	1.26	0.56	0.60	0.73

[a] The complex may aggregate in H_2O.

TABLE 4

Emission maxima at 25 °C of $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ in aqueous micellar solutions

Complex	*Emission maximum* (nm)				
	H_2O	CH_3CN	*Aqueous micellar solution*		
			CTAC	*Triton X-100*	*SDS*
$[Ru(bpy)_3]^{2+}$	609	609	609	611	628
$[RuC_{12}B]^{2+}$	(663)[a]	646	663	665	659

[a]The complex may aggregate in H_2O.

lifetime are observed in aqueous SDS micellar solution. $[Ru(bpy)_3]^{2+}$, which is situated on the surface of the anionic detergent micelle, is more shielded from attacks of water molecules, and this particular cation complex does not undergo a primary interaction with cationic or non-ionic detergent micelles. It should be noted that $[Ru(bpy)_3]^{2+}$ in aqueous SDS micellar solution displays a red shift of the emission band but no sizeable shift of the absorption band compared with $[Ru(bpy)_3]^{2+}$ in aqueous solution. Meisel *et al.* [24] also found that the emission band of $[Ru(bpy)_3]^{2+}$ underwent a red shift in aqueous SDS micellar solutions and ascribed the shift to a static interaction of $[Ru(bpy)_3]^{2+}$ with the hydrocarbon chains rather than with the polar head group. However, the red shift should be attributed to a dynamic effect; a dipole moment induced within the complex by the metal-to-ligand charge-transfer excitation displaces or reorients to the most stable orientation on the anionic surface of SDS micelles during the excited state lifetime.

In the case of $[RuC_{12}B]^{2+}$ the band at 22×10^3 cm^{-1} in the absorption spectrum is split. The splitting, which is induced by hydrogen bonding of protic solvent molecules to the $-CO-NH-C_{12}H_{25}$ group, is observed in aqueous micellar solutions regardless of whether the detergent is anionic, cationic or non-ionic. The cation head is on the ionic surface of the micelle and the alkyl chains penetrate into the hydrocarbon region of the micelle. The lifetime of $[RuC_{12}B]^{2+}$ in aqueous SDS micellar solutions is longer than those in aqueous CTAC and Triton X-100 micellar solutions. This implies that the cation head is partially buried in the anionic surface of the SDS micelle.

DMA quenches excited $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$. It is soluble only in the hydrocarbon region of aqueous micelles but not in pure water. Figure 5 shows the Stern–Volmer plots of τ_0/τ for $[Ru(bpy)_3]^{2+}$ and $[RuC_{12}B]^{2+}$ against the DMA concentration. The plots obtained from the lifetime measurements τ_0/τ coincide with those obtained from the quantum yield measurements ϕ_0/ϕ. Thus the quenching arises from dynamic encounters of the excited ruthenium(II) complex with DMA. DMA in the hydrophobic domain can donate an electron to the excited complex on encounter.

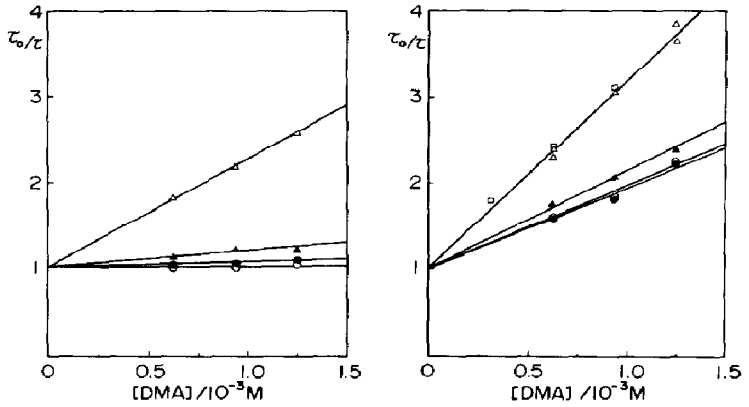


Fig. 5. Stern–Volmer plots of τ_0/τ for (a) $[Ru(bpy)_3]^{2+}$ and (b) $[RuC_{12}B]^{2+}$ against the concentrations of DMA in CH_3CN (▲) and aqueous micellar solutions of Triton X-100 (●), CTAC (○) and SDS (△). The Stern–Volmer plot for ϕ_0/ϕ is also given for $[RuC_{12}B]^{2+}$ in aqueous SDS micellar solution (□).

In the case of aqueous CTAC or Triton X-100 micelles, DMA is concentrated in the hydrophobic domain and cannot readily react with the excited $[Ru(bpy)_3]^{2+}$ which is dispersed in the bulk of the aqueous media. In aqueous SDS solution excited $[Ru(bpy)_3]^{2+}$ is present on the anionic surface. However, the quenching rates are much less than those observed in DMA-containing CH_3CN solutions. However, the rates for $[RuC_{12}B]^{2+}$ in DMA-containing aqueous SDS micellar solutions are greater than those found in DMA-containing CH_3CN solutions. Since the complex head is on the surface and in contact with the hydrocarbon region of the micelles regardless of the type of detergent, the electron transfer reaction is accelerated.

The degassed solution containing $[RuC_{12}B]^{2+}$ and DMA with appropriate amounts of surfactants yields the ion radical pair $[RuC_{12}B]^{+}$–DMA^{+} on irradiation at wavelengths longer than 340 nm [25]. The recombination of $[RuC_{12}B]^{+}$ and DMA^{+} in the media results in a decay of $[RuC_{12}B]^{+}$ which can be followed by absorbance measurements at 515 nm. The rate of electron transfer between the excited complex and DMA in SDS solution is as fast as a typical diffusion-controlled rate. However, the ion pair formed is not sufficiently separated to produce free DMA^{+} since DMA^{+} is attracted to the anionic micellar surface where the counterpart $[RuC_{12}B]^{+}$ is present. In fact the decay of $[RuC_{12}B]^{+}$ in the SDS system is too fast to be detected by measurements with millisecond time resolution [25]. The rate of electron transfer in micellar solutions of CTAC and Triton X-100 is not as fast as that in SDS solution, and the rate of recombination is strongly retarded in micellar solutions. In these cases a rather high yield of the ion radical pair can be detected [25]. DMA^{+} migrates in a hydrophilic region into the bulk of the aqueous media, whereas $[RuC_{12}B]^{+}$ is fixed on the micelle surface. In this situation Coulomb repulsion between DMA^{+} in the hydrophilic region

and the positive charges on the surface of the CTAC micelles or on the complex heads situated on the surface of CTAC and Triton X-100 micelles prohibits the recombination.

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