

## ENHANCEMENT AND SHIFTS IN THE EXCITED-STATE RESONANCE RAMAN SPECTRUM OF $\text{Ru}(\text{bpy})_3^{2+}$ IN ANIONIC MICELLES

Joy T. KUNJAPPU<sup>1</sup>, P. SOMASUNDARAN

*Langmuir Center for Colloids and Interfaces, and Henry Krumb School of Mines, School of Engineering and Applied Science, Columbia University, New York, NY 10027, USA*

and

N.J. TURRO

*Department of Chemistry, Columbia University, New York, NY 10027, USA*

Received 31 May 1989; in final form 6 July 1989

Excited-state resonance Raman and luminescence spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  showed changes in frequencies and intensities in anionic micelles only. The data are interpreted in terms of the localization of the optical electron in a bipyridine ring that is some distance from the negative micellar surface.

### 1. Introduction

Recently, while looking for sensitive probes to explore the microstructure of hemimicelles (surfactant aggregates on solids), we identified tris(2,2'-bipyridyl)ruthenium(II),  $\text{Ru}(\text{bpy})_3^{2+}$ , as a potential candidate for excited state resonance Raman (ERR) spectroscopic studies [1]. This was a sequel to the observed enhancement in intensities and shifts in the frequencies of ERR lines of  $\text{Ru}(\text{bpy})_3^{2+}$  in micellar solutions of sodium dodecyl sulfate (SDS), and hemimicelles of  $\text{Al}_2\text{O}_3/\text{SDS}$ . Although the qualitative changes in the spectra led to important conclusions about the structural and evolutionary aspects of hemimicelles, the reasons for the above changes could not be ascertained or generalized even for micellar solutions.

The luminescence emission of ruthenium bipyridyl complexes has also been the focus of much discussion [2].  $\text{Ru}(\text{bpy})_3^{2+}$  gained popularity as a luminophore of the donor/quencher pair suitable for determining the aggregation number of anionic mi-

celles [3]. The long lifetime of the excited state of this compound made it suitable for ERR spectroscopic studies [4].

In this communication, we report the results of ERR studies with  $\text{Ru}(\text{bpy})_3^{2+}$  in micellar solutions of different types of surfactants – anionic, cationic and non-ionic. The excited state involved in the Raman scattering and luminescence emission of  $\text{Ru}(\text{bpy})_3^{2+}$  being the same, viz. its charge-transfer state, luminescence emission studies with these systems were performed side by side to supplement the Raman data.

### 2. Experimental

The surfactants used in this study had a purity of >99%: SDS was obtained from Biorad, sodium dodecyl sulfate from BDH, dodecyl trimethyl ammonium bromide (DTAB) from Aldrich, and ethylene oxide based non-ionic surfactants from Nikko Chemicals, Japan.  $\text{Ru}(\text{bpy})_3^{2+}$  was purchased from Alfa Products and used after repeated crystallization from methanol.

The EPR spectra were recorded using apparatus

<sup>1</sup> On leave of absence from the Chemistry Division, BARC, India.

already described in the literature [5]. The third harmonic of a Nd/YAG laser (354.5 nm, 5 mJ/pulse, 6 ns duration) served as the pump and probe pulses in a single color experiment. The sample solutions were pumped continuously to fall in a uniform stream and intercepted by the exciting-scattering laser pulse. Each spectrum was the average of a few hundred scans and was recorded in the range from 900 to 1800  $\text{cm}^{-1}$  after subtracting the water spectrum. The fluorescence measurements were performed with a Spex Fluorolog spectrofluorometer at an excitation wavelength of 450 nm and the intensities were monitored at the emission maximum in each case. Surface tension was determined by the Wilhelmy plate method. All solutions were prepared in triply distilled water at a  $\text{Ru}(\text{bpy})_3^{2+}$  concentration of  $1.25 \times 10^{-4} \text{ mol dm}^{-3}$  in  $10^{-1} \text{ mol dm}^{-3}$  NaCl.

### 3. Results and discussion

Fig. 1 shows excited-state Raman spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  in water and in SDS solutions of different concentrations. Fig. 1a is the spectrum in water; 1b, 1c and 1d represent premicellar solutions of SDS with concentrations of  $1.0 \times 10^{-5}$ ,  $1.0 \times 10^{-4}$  and  $5.2 \times 10^{-4} \text{ mol dm}^{-3}$  and 1e is the spectrum in SDS micelles at  $9.5 \times 10^{-3} \text{ mol dm}^{-3}$  (the presence of  $10^{-1} \text{ mol dm}^{-3}$  of NaCl in these solutions did not have any effect on the Raman spectra). The ERR spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  in water and in premicellar SDS solutions were identical indicating the absence of any specific effect of surfactant ions on the  $\text{Ru}(\text{bpy})_3^{2+}$  spectrum. But, the Raman spectrum in the postmicellar region of SDS (fig. 1e) is marked by both frequency shifts and intensity changes. Note that the peak at  $1213 \text{ cm}^{-1}$  undergoes a low energy shift of as much as  $5 \text{ cm}^{-1}$ . Small shifts are visible in other ERR lines also. Generally, an enhancement in the intensities of most of the peaks is observed. It is interesting to see that a peak at  $1563 \text{ cm}^{-1}$  attributable to a ground state transition becomes resolvable in the micellar spectrum as a result of the general enhancement in the intensity factor.

In order to check whether the spectral changes observed for  $\text{Ru}(\text{bpy})_3^{2+}$  in the SDS micellar solution are due to a general micellar environment effect or

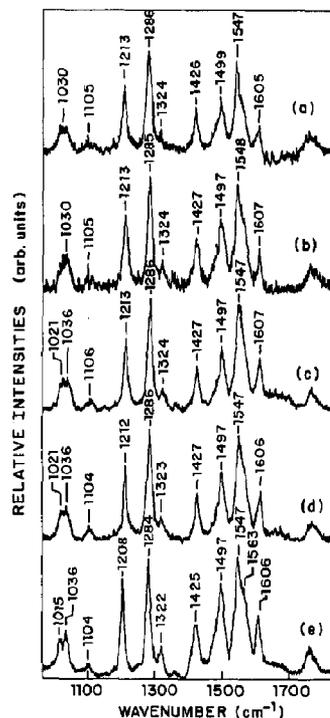


Fig. 1. Excited-state resonance Raman spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  in the anionic surfactant sodium dodecyl sulfate in pre- and post-micellar regions: (a) in water; (b), (c), (d) and (e) for  $[\text{SDS}] = 1.0 \times 10^{-5}$ ,  $1.0 \times 10^{-4}$ ,  $5.2 \times 10^{-4}$ , and  $9.5 \times 10^{-3} \text{ mol dm}^{-3}$ , respectively.  $[\text{Ru}(\text{bpy})_3^{2+}] = 1.25 \times 10^{-4} \text{ mol dm}^{-3}$  in  $10^{-1} \text{ mol dm}^{-3}$  NaCl.

a specific effect for SDS micelles alone, ERR spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  were recorded in pre- and post-micellar solutions of a number of amphiphilic molecules of different types:  $\text{C}_n\text{H}_{2n+1}(\text{EO})_m\text{OH}$  ( $n = 12$  and  $m = 5, 7, 8$ ;  $n = 14$ ,  $m = 8$ ;  $n = 16$ ,  $m = 8$ ; and  $n = 18$ ,  $m = 8$ ),  $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}^+\text{Br}^-$  and  $\text{C}_{10}\text{H}_{21}\text{SO}_4^- \text{Na}^+$ . Surprisingly, spectral changes were observed only in the case of sodium decyl sulfate (as in SDS), and non-ionic and cationic species did not cause any significant changes in the Raman spectra.

Table 1 shows some of the important frequency shifts and % enhancement of the intensities of Raman lines in SDS and sodium decyl sulfate. These changes were roughly the same for the two anionic surfactants.

Since the excited state properties appear to be important in understanding its scattering behavior, the luminescence emission from this probe was also investigated. The steady-state luminescence emission

Table 1

Shifts in frequencies and enhancement in intensities for some of the excited-state resonance Raman lines of  $\text{Ru}(\text{bpy})_3^{2+}$  in sodium dodecyl sulfate and sodium decyl sulfate micelles

Basic frequency ( $\text{cm}^{-1}$ )	Shift in frequency ( $\pm 1 \text{ cm}^{-1}$ )	% enhancement relative to $1286 \text{ cm}^{-1}$ line ( $\pm 3\%$ )
1213	5	27
1426	1	0
1499	2	55
1547	0	50
1605	-1	50

intensities were measured in micellar solutions of all three types of surfactants at the same probe and salt levels as used in the ERR studies. Here also, the anionic micellar environment only showed changes in the spectral features of luminescence emission. The  $\lambda_{\text{lu}}^{\text{max}}$  in the SDS micellar environment was shifted to 638 nm from a value of 626 nm in water. Fig. 2a, 2b and 2c depict the intensities of luminescence emission of  $\text{Ru}(\text{bpy})_3^{2+}$  in SDS,  $\text{C}_{12}\text{H}_{25}(\text{EO})_8\text{OH}$  and  $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}^+\text{Br}^-$  at the emission maximum of the micellar solutions as a function of the surfactant concentration. In addition, the surface tension of these samples is also shown to ensure that the measurements were performed well above the micellar concentration in each case.

While seeking the reasons for the changes in the spectral characteristics (enhancement in intensities and shifts in frequencies) one is confronted with the inevitable questions about the electromagnetic and molecular contributions to the signal modification [6]. This may arise either from the surface properties of the anionic micelles influencing the laser field in the ERR Raman experiments or from specific changes occurring in the optical properties of the  $\text{Ru}(\text{bpy})_3^{2+}$  molecule due to its binding to the anionic micelles. In any case, a meaningful analysis of this phenomenon requires a precise determination of the location of the probe in the micelles. Currently, attempts are being made in our laboratory to address this problem by considering both the electrostatic and hydrophobic properties of the probe.

The luminescence emission properties of  $\text{Ru}(\text{bpy})_3^{2+}$  and its alkyl derivatives in micellar solution have been analyzed earlier in connection with

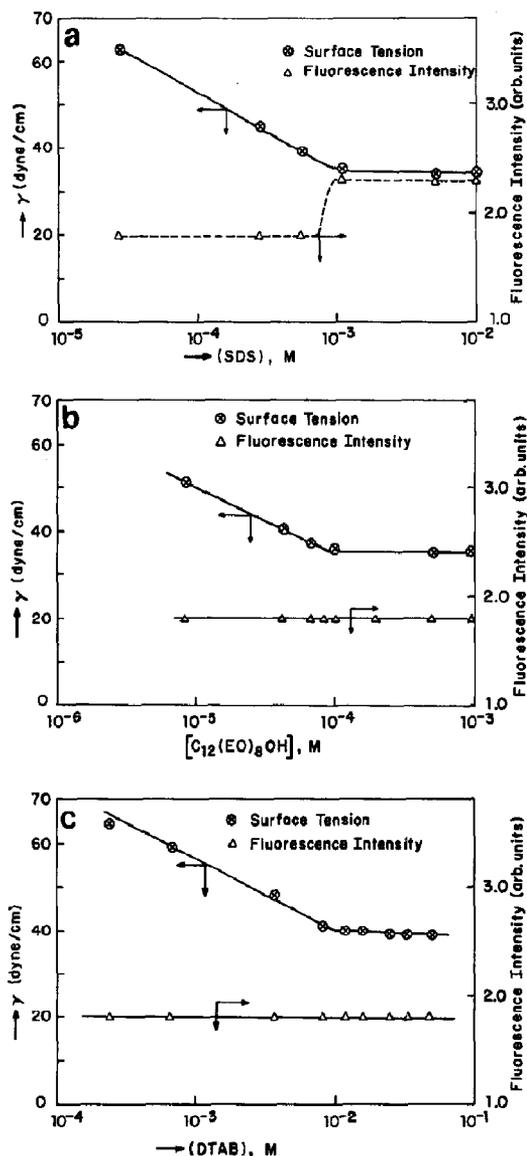
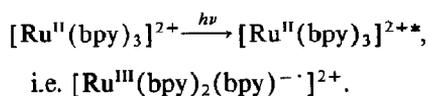


Fig. 2. Luminescence emission intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  in surfactant solutions of different types at the emission maxima, and their surface tension: (a) SDS, (b)  $\text{C}_{12}\text{H}_{25}(\text{EO})_8\text{OH}$ , and (c)  $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}^+\text{Br}^-$  (DTAB).  $[\text{Ru}(\text{bpy})_3^{2+}] = 1.25 \times 10^{-4} \text{ mol dm}^{-3}$  in  $10^{-1} \text{ mol dm}^{-3}$  NaCl.

the determination of the aggregation number of micelles [7]. Reasonably high charge densities are required to bind these probes with the micelles. From the luminescence data shown in fig. 2, it may be inferred that the optical properties of  $\text{Ru}(\text{bpy})_3^{2+}$  molecules are not modified by cationic and non-ionic

micelles. This may be understandable with cationic micelles where an unfavorable charge on the surfactant molecule reduces the chances of binding of  $\text{Ru}(\text{bpy})_3^{2+}$  on a positively charged micellar surface. But the lack of sensitivity observed in non-ionic micelles points to the importance of the negatively charged micellar surface in contributing to the observed spectral changes. Aside from the role of the micellar surface, the distance between the surface and molecules may also be important. In the case of anionic micelles, the favorable binding of the probe with the negative micellar surface may result in extended lifetimes of the luminescent state and increase the probability of the radiative process leading to enhancement in intensity at the emission maximum. A specific effect may also be considered in the case of  $\text{Ru}(\text{bpy})_3^{2+}$ : the charge-transfer luminescent state of  $\text{Ru}(\text{bpy})_3^{2+}$  in solution localized in one of the bipyridine rings immediately after excitation distributes itself in all the bipyridine rings with equal probability afterwards. The probability of localization of the optically excited electron in the charge-transfer state may be affected by the negatively charged atmosphere in anionic micelles since the optical electron may try to distance itself from the surface. This can result in its confinement in a bipyridine ring which resides in the interior of the micelle. It is quite likely that the octahedral structure of  $\text{Ru}(\text{bpy})_3^{2+}$  may be somewhat distorted in the bound state. The excitation process may be represented as follows:



Raman scattering from the excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  within the micelles may be sensitive to the polarity and viscosity of the environment. An unpublished study indicates that the ERR spectrum in different solvents was not influenced by the polarity of the medium [8]. The viscosity changes due to micellization may not be sufficient to perturb the spectra significantly as may be inferred from a report [9] which indicates complete broadening of the  $1500\text{ cm}^{-1}$  region of the ERR spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$  in a 1:1 water/glycol glass. It may be that the symmetry properties of the molecule and its environment are affected by the apparently perturbed excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  in anionic micelles leading

to differences in the Raman scattering characteristics.

A parallel may be drawn between the enhancement in the Raman spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  in an anionic micellar environment and under surface-enhanced (SERS) conditions at a metal-electrode/liquid interface. Tait et al. [10] has reported shifts and enhancement in the SERS of  $\text{Ru}(\text{bpy})_3^{2+}$  in non-aqueous solvents. This study was also done under resonance Raman conditions for different negative electrode potentials. The solvent environment in the quoted surface-enhanced resonance Raman studies and the micellar environment of  $\text{Ru}(\text{bpy})_3^{2+}$  in the present case are also comparable.

The influence of an anionic SDS micellar environment in stabilizing the cationic photochemical intermediate has been noted by Beck and Brus [11] who also interpret the observed enhancement in the transient resonance Raman spectrum of anthracene in terms of the coupling of the positively charged intermediate with the anionic micellar surface. However, they did not observe any change in the line positions.

Thus, the changes in the resonance Raman spectra of the excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  and the changes in its luminescence emission may be attributed to the favorable surface charge of the anionic micelles and the higher probability of radiative emission aside from the changes in the symmetry properties of the excited molecule and its environment. Conversely, caution must be exercised while adding surfactants into a matrix for solubilizing sparingly soluble organic compounds giving rise to apparent homogeneities in an ERR experiment.

### Acknowledgement

We acknowledge financial support from the National Science Foundation, IBM, Sohio and the Department of Energy. We thank Dr. C.V. Kumar for his help.

### References

- [1] P. Somasundaran, J.T. Kunjappu, C.V. Kumar, N.J. Turro and J.K. Barton, *Langmuir* 5 (1989) 215.
- [2] K. Kalyanasundaram, *Coord. Chem. Rev.* 46 (1982) 159.

- [3] N.J. Turro and A. Yekta, *J. Am. Chem. Soc.* 100 (1978) 5951.
- [4] R.F. Dallinger and W.H. Woodruff, *J. Am. Chem. Soc.* 101 (1979) 4391.
- [5] C.V. Kumar, J.K. Barton, I.R. Gould, N.J. Turro and J.V. Houten, *Inorg. Chem.* 27 (1988) 648.
- [6] H. Metiu, *Progr. in Surface Sci.* 17 (1984) 153.
- [7] G.G. Warr and F. Grieser, *Chem. Phys. Letters* 116 (1985) 505.
- [8] C.V. Kumar and N.J. Turro, unpublished results.
- [9] E. Krausz, *Chem. Phys. Letters* 116 (1985) 501.
- [10] C.D. Tait, T.M. Vess and D.W. Wertz, *Chem. Phys. Letters* 142 (1987) 225.
- [11] S.M. Beck and L.E. Brus, *J. Chem. Phys.* 75 (1981) 1031.