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PHOTOPHYSICAL ASPECTS OF POLARITY SENSITIVE FLUOROPHORE IN CATIONIC REVERSE MICELLES

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ABSTRACT

In recent years, the field of reverse micelles has witnessed a significant growth of interest, partly due to the finding that proteins, other biopolymers, and even bacterial cells can be solubilized in the reverse micellar systems. Among surfactants capable of forming water in oil microemulsion, the cationic surfactant cetyltrimethylammonium bromide (CTAB) has received particular attention because of its ability to solubilize relatively large amount of water in a variety of hydrophobic organic solvents. Due to versatile photochemical and photophysical properties of Ru(II) complexes, Ru(II)-phenanthroline and its derivatives were used in this present work to form CTAB cationic reverse micelles and studied to characterise their photophysical properties such as absorption, emission and excited state life time. The findings from the spectral data observed in the present study proves that the excited state properties of Ru(II)-phenanthroline complexes are dramatically altered in the presence of reverse micelle. Specifically reverse micelle encapsulation of $[Ru(dpphen)_3]^{2+}$ complex in restricted environment causes blue shift in the emission maximum as well as have longer radiative lifetime. The blue shift in the emission maximum in the case of $[Ru(dpphen)_3]^{2+}$ indicates that the probes are near the water in oil reverse micellar interface, tightly bound and are not displaced towards the water pool of the micelle even at the highest water loading W_0=50, which reveals the increased hydrophobicity. This highest fluorescence lifetime can serve as an excellent indicator to point out the location of the probe in a microheterogeneous system/environment.

Keywords: Ru(II)-phenanthroline complex, Reverse Micelles, CTAB, Excited State Life Time.

1. INTRODUCTION

The wide range of functions performed by biological membranes and membrane proteins have motivated the researchers to look for simple model system, which can mimic, at least in part, the physicochemical properties and functions of the membrane architecture. Typical examples of such membrane mimetic models are micelles and reverse micelles, which are organized assemblies of surfactants in aqueous and organic media respectively [1]. Among them, reverse micelles comprised of a polar solvent (water) sequestered by a surfactant (or surfactant-cosurfactant pair) in an oil (organic) phase. The resulting solution is optically clear and contains nanodroplets of water ranging in intramicellar diameter from approximately 0.3 to 20 nm, depending upon the molar waterto-surfactant ratio (W_0) [2].

Ruthenium complexes $[Ru(NN)_3]^{2+}$ holds unique and efficient contribution towards micelles and reverse micelles formation and its key application is of solar energy conversion [3-7]. Ru(II) complexes could form a strong binding with anionic, cationic, and neutral surfactants, due to a combination of hydrophobic and electrostatic interactions. Therefore, their luminescence intensity, quantum yield and lifetimes generally change in the presence of the structured microenvironment provided by the surfactants [8, 9].

In this work, the most hydrophobic phenanthroline complex $[Ru(phen)_3]^{2+}$ and its improved hydro phobic complexes by the introduction alkyl and aryl groups in the 4^{th} and 7^{th} positions of 1,10-phenanthroline were experimented. By far, the most common system used in reverse micelles studied is a ternary mixture of AOT/non-polar solvent/water system [AOT-sodium bis(2ethylhexyl)sulfosuccinate] [10-14]. Here the interaction of $[Ru(phen)_3]^{2+}$ complexes with cationic surfactant media namely CTAB, cetyltrimethyl-ammonium bromide have been discussed and depicted their photophysical properties.

2. EXPERIMENTAL

2.1. Synthesis of Tris(1,10-Phenanthroline) Ruthenium (II) Chloride ($[Ru(phen)_3]^{2+}$)

$RuCl_3.3H_2O$ (0.6 g, 3 mmol) was dissolved in 50 mL of ethanol containing one drop of 6 N HCl and a stiochiometric amount (1.6g, 9mmol) of phenanthroline was added slowly with stirring. The mixture was refluxed for 40 h. Then the mixture was filtered, and 10 mL of 6 N HCl was added drop wise with stirring to the hot filtered solution. If no solid had formed at this point, the volume of the solution was reduced by evaporation until crystals formed. The crude product was recrystallized from hot water. The absorption and emission maxima values are λ^{abs}_{max} = 446 nm and λ^{em}_{max} = 600 nm respectively.

2.2. Synthesis of Tris(4,7-Dimethyl-1,10-Phenanthroline)Ruthenium(II) Chloride ($[Ru(dmphen)_3]^{2+}$)

$RuCl_3.3H_2O$ (0.45 g, 1.5 mmol) and 4,7-dimethyl-phenanthroline (1.4 g, 4.5 mmol) were treated with 25 mL of ethyl alcohol and refluxed. After 5 minutes, two drops of 6 N HCl were added and continued to reflux until the greenish dark solution turned reddish. Then the solution was condensed and 2 mL of 6 N HCl was added. Further required little amount of HCl was added and the precipitate was filtered and dried. The absorption (λ^{abs}_{max}=446 nm) and emission (λ^{em}_{max}=608 nm), maxima were observed.

2.3. Synthesis of Tris(4,7-Diphenyl-1,10-Phenanthroline)Ruthenium(II) Chloride ($[Ru(dpphen)_3]^{2+}$)

The similar procedure was adopted as before using 4,7-diphenyl-1,10-phenanthroline in the place of 1,10-phenanthroline as ligand but the heating was continued for 72 h and the crude product was chromatographed using silica gel. The solution on evaporation yielded orange red crystals. The absorption maximum was found to be λ^{abs}_{max}=465 nm and emission maximum was λ^{em}_{max}=625 nm (in 2 percent ethanol solution).

2.4. Preparation of Cationic Reverse Micelles

Cationic reverse micelles were prepared by mixing the requisite volume (a few microlitre) of the stock solution of the complex in water (except $[Ru(dpphen)_3]Cl_2$ which was dissolved in 2% ethanol) with the calculated amount of double distilled water to yield a required W_0 and calculated quantity (0.5 mL) of 1 M CTAB solution. The final volume was adjusted with isooctane to yield a final concentration of 0.5 M CTAB surfactant in isooctane. Then the mixture was stirred at room temperature until water was solubilized to form optically transparent uniform solution. The concentration of CTAB in all samples was 0.5 M and spectroscopic grade n-hexanol was used as cosurfactant in CTAB/isooctane-n-hexanol/water microemulsions. The ratio of isooctane to n-hexanol was 9:1 and this ratio was maintained throughout the studies. The cationic reverse micellar solution was prepared in a 10 mL volumetric flask adding 0.183 g of CTAB (0.5 M) to the required volume of aqueous solution as the water pool to maintain the particular W_0, and filling the volumetric flask up to the mark with 9:1(v/v) mixture of isooctane/n-hexanol followed by vortexing for 10-15 s. The water content of the microemulsion is expressed as the molar concentration ratio W_0= $[H_2O]/[CTAB]$. Studies were performed at seven different W_0 values ranging from 6 to 50.

2.5. Absorption-Emission and Exited State Life Time measurements

All experiments were performed with freshly prepared solutions. UV-visible absorption spectra were obtained on a Hewlett Packard 8453A diode array spectrophotometer using 1 cm path length cuvette. The emission spectra were recorded with Jasco FP- 6300 spectrofluorometer using 1 cm path length quartz cuvette. Excitation and emission slits with a band-pass of 2.5 nm were used for all measurements. All the sample solutions used for emission measurements were deaerated for about 30 min by dry nitrogen gas purging by keeping solutions in cold water. Care had been taken to minimize solvent and/or water evaporation that could modify the water to surfactant molar ratio. The nitrogen gas is purified by passing through Fieser's solution to remove the oxygen present in the solution. The excited state lifetime of all the complexes at 298 K are measured using a laser flash photolysis set up with the third harmonic (λ = 355 nm) of a Nd:YAG laser (Quanta-Ray).

3. RESULTS AND DISCUSSION

3.1. Absorption spectra of Ru(II)-phenanthroline complexes in Cationic Reverse Micelles

Absorption spectra of the ruthenium(II)-phenanthroline complexes in water and in CTAB reverse micelle at various W_0 values are shown in Figs. 1-3. The ground state absorption maximum, λ^{abs}_{max}, of $[Ru(phen)_3]^{2+}$ is

red shifted approximately by 21 nm (from 445 nm to 466 nm) when we change the medium from aqueous to reverse micelle W_0 = 6. However the red shift in the absorption maximum is reversed when the value of W_0 is increased to10. Interestingly the λ^{abs}_{max} reaches a value of 447nm, close the value in aqueous medium, if W_0>10. The absorption spectral changes observed with $[Ru(dmphen)_3]^{2+}$ are different from that of $[Ru(phen)_3]^{2+}$. Here a blue shift is observed from 446 to 438 nm when the medium is changed from aqueous to W_0 = 6. There is an increase in W_0 value leads to decrease in molar absorption coefficient (ε_{max}) in all the cases. It shows the steady λ^{abs}_{max} value of 430 nm.

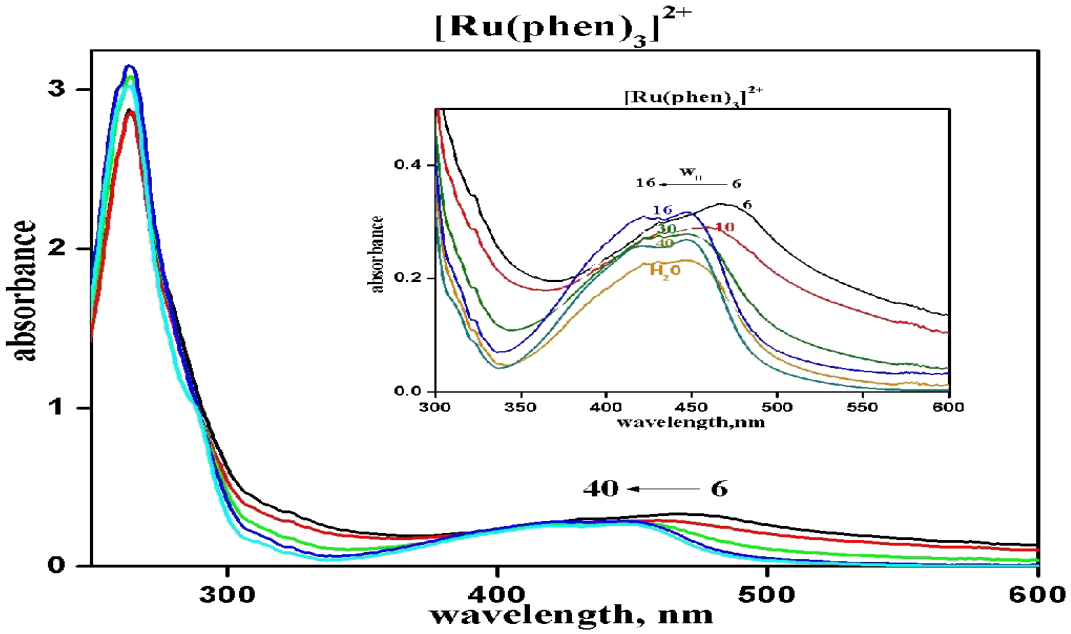


Fig. 1: Absorption spectra of $[Ru(phen)_3]^{2+}$ complex in water and in CTAB/n-hexanol-isooctane/water reverse micelle at various W_0. Inset shows the MLCT band between 300-600 nm

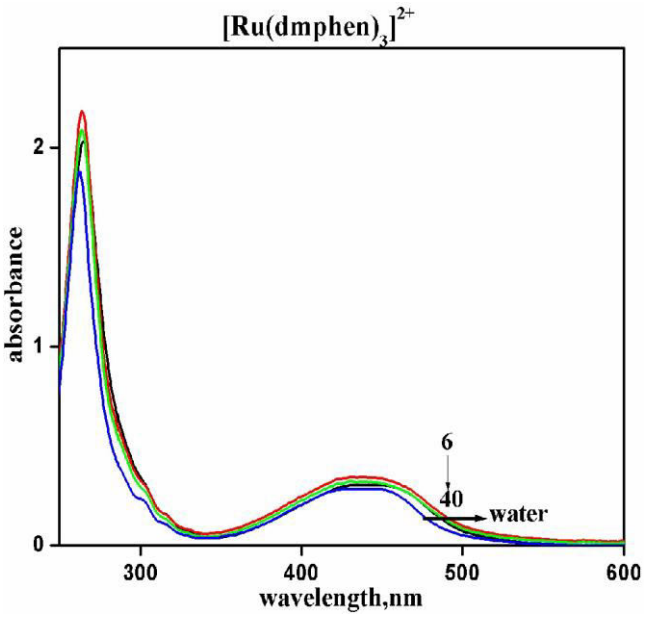


Fig. 2: Absorption spectra of$[Ru(dmphen)_3]^{2+}$ complex in water and in CTAB/n-hexanol isooctane/water reverse micelle at various W_0

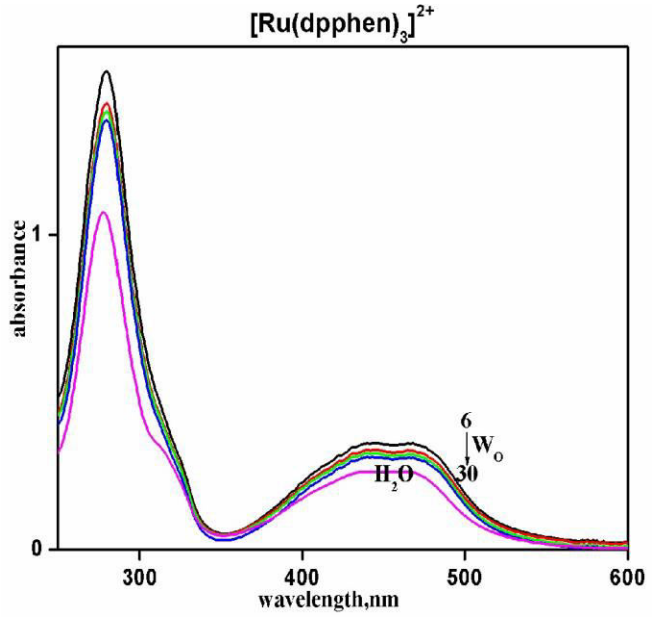


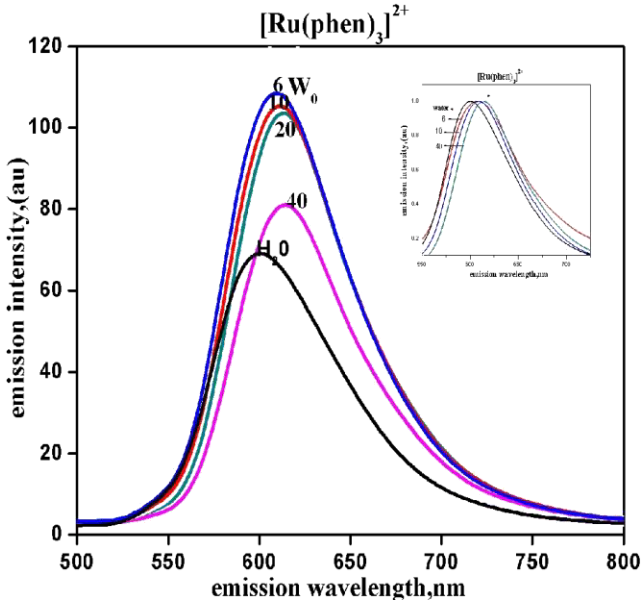
Fig. 3: Absorption spectra of $[Ru(dpphen)_3]^{2+}$ complex in water and in CTAB/n-hexanol-isooctane/water reverse micelle at various W_0

The absorption spectrum of $[Ru(dpphen)_3]^{2+}$ in water shows a broad band with two shoulders with the absorption maxima at 463nm and 441nm. In CTAB/n-hexanol-isooctane/water reverse micelle at W_0=6 it shows slight red shift in the absorption maximum, from 463 to 466 nm and increase in the intensity (ε_{max}). Further increase in W_0 value does not alter the spectral properties if W_0>10 in all the complexes. As the water concentration increases beyond W_0=10, there is practically no further shift in the λ_{max} value. The red shift in the absorption maximum in the case of $[Ru(phen)_3]^{2+}$, $[Ru(dmphen)_3]^{2+}$ and $[Ru(dpphen)_3]^{2+}$ indicates that the probes are tightly bound to the surfactant/n-hexanol-isooctane interface and they orient more toward the nonpolar organic phase because of their hydrophobic nature. The observed spectral results show that the probes are not displaced towards the water pool of the micelle even at highest water loading W_0=50. In CTAB/ n-hexanol-isooctane /water binding of cationic probe at the cationic surfactant/water interface is facilitated by the presence of cosurfactant with electronegative OH- groups at the interface. As the amount of water increases the size of the micelle increases and so the surfactant-probe interaction decreases as the probe can move easily towards the nonpolar region. But in the smaller micelle the probe's movement is restricted by the confined intramicellar environment.

3.2. Emission spectra of Ru(II)-phenanthroline complexes in Cationic Reverse Micelles

The emission maximum of $[Ru(phen)_3]^{2+}$ in CTAB reverse micelle is gradually red shifted approximately by 14 nm from 600 nm in water to 614nm in reverse micelle (W_0=16) with simultaneous increase in emission intensity and quantum yield. Emission spectra of $[Ru(phen)_3]^{2+}$ in bulk water and in CTAB/ n-hexanol-isooctane /water reverse micelle as a function of W_0 are shown in Fig.4.

Increase in W_0 has influence up to W_0=16, beyond which there is practically no change in emission maximum and only slight change in emission intensity. The emission maximum of $[Ru(dmphen)_3]^{2+}$ in CTAB reverse micelle is also red shifted approximately by 16 nm from 604nm in water to 620nm in reverse micelle (W_0=6) with an increase in emission intensity (Fig. 5). Further change in W_0 value has little influence on the emission maximum with slight decrease in emission intensity.



The inset shows the normalized emission spectra in water and CTAB reverse micelle at W_0 = 6, 10 and 20

Fig. 4: Emission spectra of $[Ru(phen)_3]^{2+}$ in CTAB / n-hexanolisooctane / water reverse micelle as a function of W_0 (λ_{exc}=445nm)

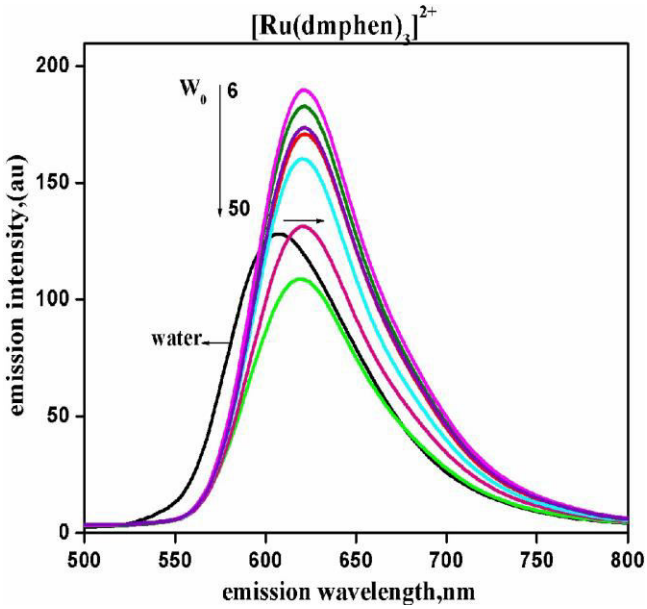
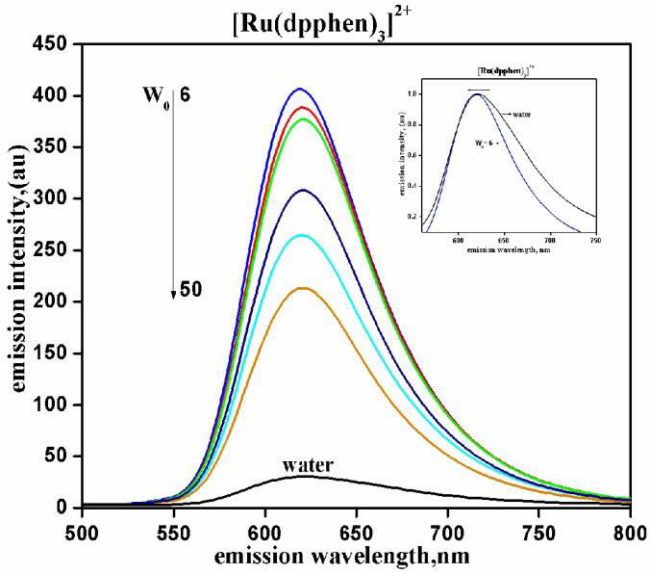


Fig. 5: Emission spectra of $[Ru(dmphen)_3]^{2+}$ in CTAB/ n -hexanolisooctane /water reverse micelle as a function of W_0 (λ_{exc}= 446nm)

Contrary to the red shifts observed with $[Ru(phen)_3]^{2+}$ and $[Ru(dmphen)_3]^{2+}$ there is an initial blue shift of 6nm in the emission maximum of $[Ru(dpphen)_3]^{2+}$ from 624nm to 618 nm with increase in the emission intensity when the medium is changed from water to

reverse micelle at W_0 = 6 (Fig.6). But no substantial shift in the emission maximum is observed with further increase in W_0 and there is an increase in emission intensity and it reaches a maximum at W_0=16 and then decreases gradually.



The inset shows normalized emission spectra at W_0 = 6 and in water

Fig. 6: Emission spectra of $[Ru(dpphen)_3]^{2+}$ in CTAB/ n-hexanol isooctane /water reverse micelle as a function of W_0 (λ_{exc}= 440nm).

An enormous increase in the emission intensity was observed in the low water content in the reverse micelle. The emission intensity decreases with increasing water content. The observation of this interesting phenomenon is caused by decreased rotational freedom of the entrapped probe molecule in interacting with the trimethyl ammonium at the interface and by dipole reorientation time scales [16]. The effect due to dipole reorientation can be explained as follows. Dipoles at the vicinity of the chromophore must reorient in response to the immediate change in electronic structure induced by light excitation. In liquids, this reorientation is rapid and chromophore emits light from a relaxed excited state. In the solid state or in viscous media, dipole reorientation times often become competitive with the excited state decay, resulting in hypsochromic shifts in the emission spectrum. As the W_0 increases the water pool radius increases and the probe is encapsulated near the water pool. This is evident from its emission spectrum and quantum yield. The blue shift in the emission maximum in the case of $[Ru(dpphen)_3]^{2+}$ indicates that the probes are near the surfactant interface, tightly bound and are not displaced towards the water pool of the micelle even at highest water loading W_0=50.

The red shift in the emission maximum of $[Ru(phen)_3]^{2+}$ and $[Ru(dmphen)_3]^{2+}$ is explained in terms of additional reorganization energy necessary to accommodate the reduced polypyridine ligand in the ^{3}MLCT excited state in the surfactant. Interactions between the probe and the surfactant may be responsible for this distortion, leading to an increase in reorganization energy. Further red shift in the emission maximum (λ^{em}_{max}) of $[Ru(phen)_3]^{2+}$ with increasing the W_0 value (water content) suggests that addition of water further affects the solvation sphere of the complexes. As the water content increases beyond W_0=10, there is practically no variation in the maximum position of the absorption band and there is a slight bathochromic shift and an increase in the intensity of the emission band in the case of $[Ru(phen)_3]^{2+}$. The emission maximum of $[Ru(dmphen)_3]^{2+}$ is not influenced by the change of W_0 i.e. size and polarity change in the micelles. The red shift in the emission maximum also indicates that the polarity of the microenvironment sensed by these probes increase in comparison to that in water and isooctane (all complexes are insoluble in isooctane) because of the gradual incorporation of the molecule into the CTAB reverse micellar interface. This red shift in emission maximum may be attributed to the stabilization of emitting ^{3}MLCT state compared to d-d state in reverse micelles compared to that in aqueous medium. Similar observations have been made in the presence of cationic micelles [17]. The effect is more pronounced in cationic micelle too inspite of similar charge on the probe and surfactant indicating that hydrophobic interactions between the ligands and cationic surfactant overcome the electrostatic repulsive forces between the similar charges of the cationic probe and positively charged surfactant interface to bring them closer, thereby stabilizing the emitting ^{3}MLCT state of the ruthenium(II)-complex [18, 19]. Moreover, similar emission spectral results are observed at different excitation wavelengths which indicate probe's homogeneity in the ground state of the molecule.

3.3. Emission lifetime of Ru(II)-phenanthroline complexes in CTAB / n-hexanol- isooctane /water reverse micelle

The absorption and excited state emission maxima and excited state lifetime of the three Ru(II)-phenanthroline complexes recorded in water and different W_0 values are shown in Tables 1-3. Representative luminescence decay of $[Ru(dpphen)_3]^{2+}$ at various W_0 is given in Fig.7.

Table 1: Absorption and emission maxima and excited state lifetime of $[Ru(phen)_3]^{2+}$ in 0.05 M CTAB/ n-hexanol-isooctane / water reverse micelle at room temperature

Complex	$[Ru(phen)_3]^{2+}$		
$W_0=[H_2O]/[CTAB]$	λ_{abs}, nm	λ_{em}, nm	τ, ns
Water	445	600	905
6, 5[a]	466	604	1404
10	460	608	1339
16, 15[a]	447	614	1270
20	447	612	1245
30	447	612	923
40	447	612	900
50	447	612	898

[a] *-collected from the Rack et al studies [15].*

Table 2: Absorption and emission maxima and excited state lifetime of $[Ru(dmphen)_3]^{2+}$ in 0.05 M CTAB/ n-hexanol-isooctane / water reverse micelle at room temperature

Complex	$[Ru(dmphen)_3]^{2+}$		
$W_0=[H_2O]/[CTAB]$	λ_{abs}, nm	λ_{em}, nm	τ, ns
Water	446	604	1680
6, 5[a]	438	620	2561
10	438	620	2478
16, 15[a]	438	620	2387
20	430	620	2074
30	430	620	1978
40	430	620	1050
50	430	620	936

Table 3: Absorption and emission maxima and excited state lifetime of $[Ru(dpphen)_3]^{2+}$ in 0.05 M CTAB/ n-hexanol-isooctane / water reverse micelle at room temperature

Complex	$[Ru(dmphen)_3]^{2+}$		
$W_0=[H_2O]/[CTAB]$	λ_{abs}, nm	λ_{em}, nm	τ, ns
Water	463, 441	624	3620
6, 5[a]	465, 440	618	4977
10	459, 440	620	4577
16, 15[a]	440	620	4469
20	440	620	3618
30	440	620	2018
40	440	620	1926
50	440	620	1133

Considerably large increase in the lifetime of the excited state Ru(II)-phenanthroline complexes is observed in CTAB microemulsion (Tables 1-3). The increase in the excited state lifetime is due to the more confined intramolecular environment in the reverse micelle. All modes of relaxations are restricted under confined environment like reverse micelle and so lifetime is enhanced under restricted environment. Long lifetime of these complexes was reported earlier in anionic and cationic micelles too [17, 20].

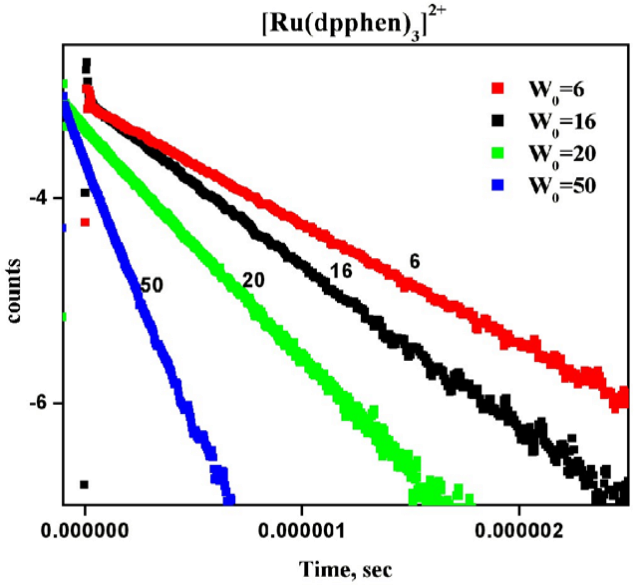


Fig. 7: Luminescence decay curves of $[Ru(dpphen)_3]^{2+}$ in CTAB / nhexanol-isooctane/ water reverse micelle at various W_0 values

Increase is appreciable up to $W_0 = 20$, beyond which lifetime decreases and reaches a saturation value which is comparable with that in water. In smaller micelle i.e. at $W_0 = 6$ probes may be at the interface and at the interface the complex will be tightly bound to the Stern layer and it will sense a more rigid intramolecular environment, where all modes of relaxations are restricted. Even the cationic probes bind well and encapsulated at the cationic interface because the hydrophobic interaction overcomes the coulombic repulsion between the like charges of the surfactant and probe. This is evident from the emission maximum, and enhanced lifetime at $W_0 = 6$. Further increase in the W_0 will enlarge the size of the micelle and enhance the polarity. That is why there is a decrease in emission lifetime as the W_0 increases. Earlier report shows that there is an appreciable increase in the lifetime values at high [CTAC] than that observed at high [SDS] pointing the importance of hydrophobic interactions offsetting the coulombic repulsion thereby bringing the positive probe close to the cationic micelle [17]. These results highlight the importance of hydrophobic effects over electrostatic forces [17, 20]. The long excited state

lifetime of the complexes in reverse micelle also indicates that the intramolecular water is a less effective quencher of the excited state energy than bulk water. One of the reasons for lifetime enhancement on micellization is reduced water exposure of the excited state in reverse micelle. Water is a known quencher of MLCT excited states, and reduction of water exposure by micellization reduces the $\acute{\omega}_H$ mode as a means of excited state deactivation [15].

The fluorescence lifetime serves as an excellent indicator to point out the location of the probe in a microheterogeneous system like the one used in the present study. The probe is soluble in water and in micellar phase but not in isooctane. The lifetime of the probes is much shorter in water than in reverse micelle. This indicates that the complexes are predominantly solubilized in the micellar phase and they are located in distinct region of the micelle depending on the size and charge of the micelle and probe. The blue shift in the absorption and emission maximum in the case of $[Ru(dpphen)_3]^{2+}$ with enhanced lifetime indicates that the probes are localized at the Stern layer of the micelle which is more inclined toward the nonpolar continuous medium and they are not sensing polar environment of the interface much. Though the size of the micelle is increased the probes do not move appreciably toward the water pool yet they sense more polarity as the water loading increases. The blue shift also indicates a decreasing surfactant interaction with $[Ru(dpphen)_3]^{2+}$.

4. CONCLUSION

The present investigation reported the study of interaction of polarity sensitive fluorescent probes in cationic reverse micellar microenvironment. $[Ru(phen)_3]^{2+}$ complex and its derivative complexes show more sensitive emission spectrum with the change of W_0 value that is to the change of polarity compared to the absorption spectra. The results depict that cationic Ru(II)- complexes bind too tightly to CTAB as the hydrophobic effect overcomes the electrostatic repulsion. The strength of binding can be attributed to a combination of electrostatic attractions or repulsions and hydrophobic effects. Electrostatic attraction of oppositely charged species always yields tight binding. However, it was found that complexes which are sufficiently hydrophobic (i.e.4, 7-diphenyl-1, 10-phenanthroline) can overcome electrostatic repulsions and bind to like-charged micelles. As a result, the use of $[Ru(dpphen)_3]^{2+}$ as a polarity sensitive hydrophobic fluorescent probe will throw more light on the study of biopolymers to understand the environment in detail.

5. ACKNOWLEDGEMENT

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Conflict of interest

None declared

6. REFERENCES

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