Binding Studies of Ruthenium(II) Polypyridyl Complexes with Quinones in Triton X-100

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Abstract: The binding of Ru(II) polypyridyl complexes $[Ru(bpy)_3]^{2+}$, $[Ru(dmbpy)_3]^{2+}$ with 1,4-benzoquinone (BQ) and 2,6-dimethyl -1,4-benzoquinone (DMBQ) have been studied in triton x-100 using absorption spectral technique. The binding constant (K_b) for these reactions are determined from the Benesi-Hildebrand equation by means of absorption intensity data. Values of the binding constant reveal that they depend on the nature of the ligand, medium and also on the structure of the quinones. The ground state interaction between the luminophore and the quencher are hydrophobic in nature. Hydrophobic and structural effects play a vital role on the binding of the quinones with Ru(II) complexes.

Keywords: Binding, Quenching, Quinones, Ligands, Quenchers

Introduction

Quinones have considerate application in the field of biology and pharmacy. They are ET mediators between PSI and PSII and act as anticancer drugs in medicine[1-7]. They play an important role in the biochemistry of living cells. These quinones have a broad variety of pharmacological properties like antimicrobial, antiparasitic, antiviral and anticancer activities[8]. Therefore the search for new chemotherapeutics focuses in metal complexes with different mode of action. The development of transition metal complexes is an emerging field in order to target and material with proteins, antioxidants**,** metal complexes of phenanthroline, bipyridine activity. Ruthenium complexes of various ligands have attracted great interest as alternative drugs to cisplatin in cancer therapy. The significant structural differences between ruthenium and most platinum have antitumour drugs give a promising alternative to cisplatin and carboplatin[9]. Among the transition metal complexes, ruthenium(II) polypyridyl complexes $[Ru(NN)_3]^{2+}$ have particularly drawn significant interest to develop new therapeutic agents. They undergo binding with DNA, proteins, RNA. Based on the literature survey, the present study concentrates on the binding studies of quinones with Ru(II) complexes in Triton x-100.

The Ru(II) complexes have been used as probes in micellar medium and the properties vary with the nature of surfactant and the concentration. Ru(II) polypyridyl complexes have been designed with hydrophobic ligands and thus they provides an opportunity to bind to the initial interfacial region in micro heterogeneous systems. These aqueous micelle-bound catalytic systems are attractive alternatives to highly toxic, expensive organic solvents and precursors to future designs of surfactant assemblies that may include redox reactions in biological membranes. These organized micellar media can promote ET from electron donor to acceptor by concentrating them.

Experimental

$RuCl_3.3H_2O$, ligands (2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-ditertiary butyl -2,2'-bipyridine (dtbpy)) and the quinones (1,4-benzoquinone (BQ), 2,6-dimethyl-1,4-benzoquinone (DMBQ)) were procured from Sigma -Aldrich. The double distilled deionized water was used for the binding studies. The three $[Ru(NN)_3]^{2+}$ complexes {where NN=2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-ditertiary butyl-, 2'-bipyridine (dtbpy)] were synthesized by reacting $RuCl_3.H_2O$ with the corresponding ligands by the known procedures[10-11].

Absorption spectral measurements were carried out using SYSTRONICS double beam spectrophotometer 2203. Quartz cuvettes with a path length of 1 cm were used throughout. The emission intensity measurements were recorded using JASCO/FP-8600 spectrofluorometer with a 1cm path length quartz cell, equipped with a 150W Xenon source, a red sensitive photomultiplier tube. The binding of $[Ru(NN)_3]^{2+}$ complexes with various concentration $(4\times10^{-6}$ M - 2.8×10^{-7} M) of BQ, MBQ, DMBQ have been studied by absorption spectral technique. All the sample solutions were freshly prepared. The binding constant (k_b) of the Ru(II) complexes with quinones were determined from the Benesi-Hildebrand equation using the absorption intensity data.

$$\frac{1}{\Delta A} = \frac{1}{k_b} \Delta \in \varepsilon [H] + \frac{1}{\Delta \varepsilon}[Q] \tag{1}$$

Where ΔA is the change in absorption of the complex with different concentrations ([Q]) of the quinones. The plots of $1/\Delta A$ *verses* $1/[Q]$ gives a straight line. The binding constant k_b is got from the ratio of *Y-* intercept to the slope of the straight line.

Results and Discussion

The structure of the ligands and the quinones used in the presence study are shown in Figure 1. The photophysical properties like absorption and emission spectral data and excited state lifetimes of $[Ru(NN)_3]^{2+}$ complexes in aqueous and triton x-100 are given in Table 1. The photophysical properties of the $[Ru(NN)_3]^{2+}$ complexes change from homogeneous to micro heterogeneous medium.


bpy   dmbpy   dtbpy
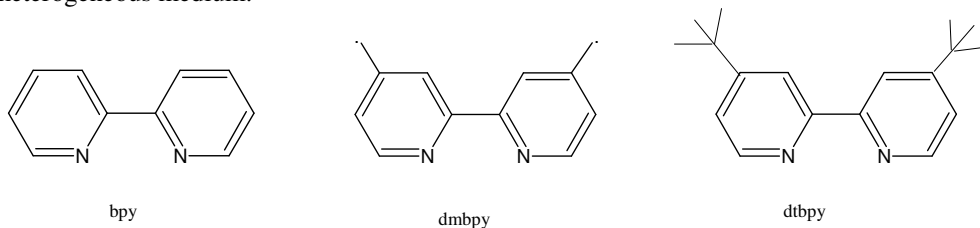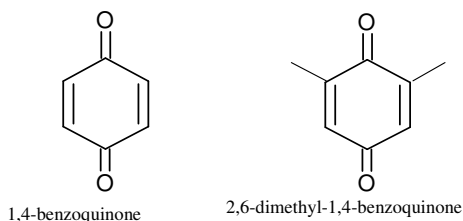
1,4-benzoquinone   2,6-dimethyl-1,4-benzoquinone
Figure. 1 Structure of ligands and quenchers

Table 1. Absorption, emission spectral data and excited state lifetime of $[Ru(NN)_3]^{2+}$ complexes in aqueous and triton x-100[12]

| Complex	Absorption maximum, nm		Emission maximum, nm		Excited state lifetime (ns)	
	aqueous	Triton x-100	aqueous	Triton x-100	aqueous	Triton x-100
$[Ru(bpy)_3]^{2+}$	448	451	595	595	614	600
$[Ru(dmbpy)_3]^{2+}$	458	458	604	615	380	360
$[Ru(dtbpy)_3]^{2+}$	457	465	610	617	510	654

The absorption spectral studies of the $[Ru(NN)_3]^{2+}$ complexes show a slight increase in the MLCT absorption maximum with incremental addition of the quinones. This mediate the formation of ground state complex (Figure 2). The binding constant (k_b) of $[Ru(NN)_3]^{2+}$ complexes with the quinones calculated from the Benesi-Hildebrand plot (Figure 3) for the absorption spectral date and emission spectral data in triton x-100 medium is given in Table 2. The k_b values obtained for the quinones with $[Ru(NN)_3]^{2+}$ are in the complexes order of 10^3 to 10^4.
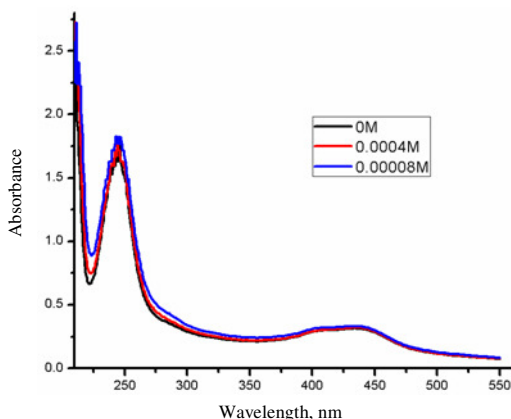
Figure 2. Absorption spectrum of $[Ru(bpy)_3]^{2+}$ with incremental concentration of 1,4-benzoquinone in triton x-100.

Table 2. Binding constant, k_b $[M^{-1}]$ from absorption and emission data for the quinones with $[Ru(NN)_3]^{2+}$ in Triton x-100

Complex	Absorption data		Emission date	
	BQ	DMBQ	BQ	DMBQ
$[Ru(bpy)_3]^{2+}$	5.59×10^4	9.13×10^4	3.42×10^4	3.47×10^4
$[Ru(dmbpy)_3]^{2+}$	6.35×10^4	7.11×10^4	1.8×10^4	1.96×10^4
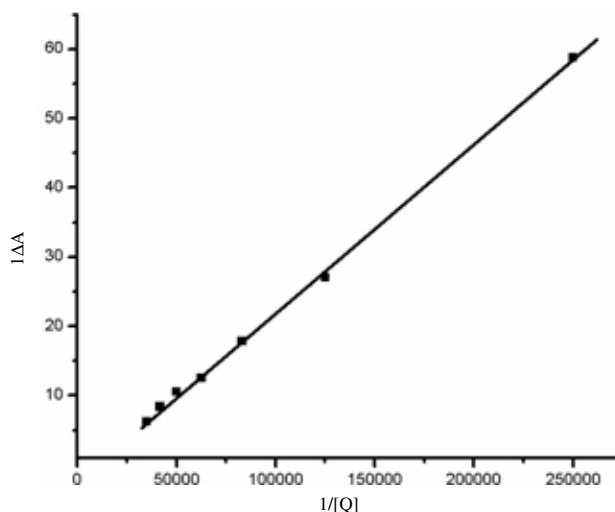
Figure 3. Benesi-Hildebrand plot on MLCT absorption of $[Ru(bpy)_3]^{2+}$ complex with incremental addition of BMBQ in triton x-100 medium

The addition of the neutral surfactant triton x-100 resulted in the red shift to the tune of 3-8 nm for the absorption maximum. The ground state interaction between uinines and the bipyridyl rings of the luminophore are hydrophobic or π-stacking in nature. Binding becomes stronger due to π-π stacking interaction. The hydrophobicity increases from $[Ru(bpy)_3]^{2+}$ to $\{Ru(dtbpy)_3\}^{2+}$. It is due to the presence of bulky alkyl to substituted ligands. K_b value increases with the increase in hydrophobicity. This result shows that k_b values are sensitive to the hydrophobic nature of the ligands.

It is seen that K_b values increases when the substituent in the 1,4-benzoquinone is changed. On moving from BQ to DMBQ, the size increases. The k_b value also shows an increase. This result shows that k_b is value is also sensitive to the structure of the uinines. Thus we find the k_b values are sensitive to the nature of the ligand, medium and structure of the quenches 1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone.

Conclusion

The binding of 1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone with $[Ru(NN)_3]^{2+}$ complexes in triton x-100 has been studied by absorption spectral techniques. The k_b values of the $[Ru(NN)_3]^{2+}$ complexes with 1,4-benzoquinone and 2,6-dimethyl-1, 4-benzoquinone are determined from the Benesi-Hildebrand plot. The k_b values depend on the nature of the ligand medium as well as the structure of uinines. 2,6-dimethyl-1,4-benzoquinone shows high binding constant compared to 1,4-benzoquinone. This may be attributed due to the structural change. The study confirms the structural effects, hydrophobicity as well as the effect of medium on the binding of uinines with $[Ru(NN)_3]^{2+}$.

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