

Studies of Interactions between Ruthenium (II) Polypyridyl Complexes and 1,4 Benzoquinone

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Abstract

All the experiments explained in this paper involving the interaction of quinone with the complexes were carried out in acetonitrile. The interactions between Ruthenium polypyridyl coordination compounds $Ru(NN)_3^{2+}$ ($NN=1,10$ -phenanthroline(phen), and bipyridine(bpy)), 1,4-benzoquinone(BQ) have been investigated using electrochemical (cyclic voltammetry) and electronic absorption spectroscopy measurements. The Ru(II) complex shows characteristic broad and intense metal-to ligand charge transfer (MLCT) bands absorption. From the binding constant values, there is strong intermolecular electrostatic interaction between the Ruthenium polypyridyl (1,10-phenanthroline, and bipyridine) complexes and BQ, of which the binding of $Ru(bpy)_3^{2+}$ complex to BQ seems stronger than $Ru(phen)$ complex. as indicated by the UV spectra and electrochemical analysis.

Keywords: Cyclic Voltammetry, Ruthenium polypyridyl complexes, UV/Vis Spectroscopy, 1,4-benzoquinone, binding constant.

Introduction

Quinones have wide-spread importance in biology and chemistry. Quinones serve as an active site of quinoenzymes in biological systems. They also act as electron and proton transfer in energy transducing membranes for respiration and photosynthesis¹⁻⁴. In aprotic solvents quinones are reduced in two successive one electron step to form anion radical ($Q^{\cdot -}$) and quinone dianion (Q^{2-})⁵⁻⁷. The redox chemistry of naturally occurring para benzoquinone is an essential aspect of biological processes such as cellular respiration, photosynthesis and blood coagulation⁸. The photophysical properties of polypyridyl ruthenium(II) complexes have also received much scrutiny because of their potential as photosensitizers for electron-transfer processes⁹⁻¹². Because of the redox properties of $[Ru(NN)_3]^{2+}$ the complex plays an important role in a number of applications, for example it can function as a photocatalyst for the decomposition of water into hydrogen and oxygen. The interactions of BQ with different solvents have been studied in so many previous studies. These systems can be used as electronic devices¹³⁻¹⁵ electron-transfer mediators¹⁶⁻¹⁸ or electroanalytical sensors¹⁹. We present here a comprehensive study of interaction of quinone and Ru(II) complexes in aprotic solvent by using electrochemical and UV/Vis spectroscopic parameters.

Experimental Methods

Materials

The ruthenium polypyridyl complexes $[Ru(NN)_3]^{2+}$, where $NN=1,10$ -phenanthroline(phen), and bipyridine(bpy) were prepared by reacting $RuCl_3 \cdot 3H_2O$ with the corresponding ligands in 1:3 equivalence

by the known procedures²⁰⁻²⁴. 1,4-benzoquinone was purchased from Sigma Chemical Company. BQ was further purified by sublimation under vacuum method. Acetonitrile (CH₃CN) HPLC grade was used as the solvent. Tetrabutylammonium hexafluorophosphate (TBAPF₆) were obtained from Sigma Chemicals.

Electrochemical and Spectroscopic measurements

A glassy carbon electrode was used as a working electrode. The surface of the working electrode was polished with 0.05 μ alumina before each run. Prior to the electrochemical experiments, the solutions of BQ and Ru(II) complexes in dry acetonitrile containing 100mM tetrabutylammonium hexafluorophosphate, as the supporting electrolyte were purged with N₂ and inert atmosphere was kept during the course of the experiments. A platinum wire was used as a counter electrode. All potentials were reported vs. Ag wire reference electrode. The potential sweep rate was 100 mVs⁻¹. Potentials are reported in volts versus Ag wire. The absorption spectral measurements were carried out using Perkin Elmer, Lambda25, UV/VIS spectrophotometer. The acetonitrile used for electrochemical and spectrochemical experiments was of HPLC grade and purchased from Aldrich. The solution of the metal complexes and the quinone were freshly prepared using acetonitrile.

Results and Discussion

Interaction between BQ and Ruthenium polypyridyl complex

a) Absorption spectroscopic studies

All the spectroscopic titrations were carried out in acetonitrile at room temperature. A solution of BQ in CH₃CN gave an UV absorbance at 241. The UV/Visible absorption spectra of these complexes Ru(NN)₃²⁺ showed intense MLCT (metal-to-ligand charge-transfer) and LC (ligand-centered) transitions around 450-500 nm corresponds to the dπ- π* transition and 250-300 nm corresponds to the π- π* transition respectively. The spectral and electrochemical data for the complexes were given in Table 1. The absorption spectra of BQ in the absence and presence of Ru(II) complexes were illustrated in Fig. 1 and 2. With increasing Ru(II) complex concentration along with BQ, the hyperchromism increased and was accompanied by a shift for both of the two complexes (as shown in Figs 1 and 2). In order to compare quantitatively the binding strength of the two polypyridyl complexes, the intrinsic binding constants K_b of them with BQ were obtained by monitoring the changes in absorbance at 241 nm with increasing concentration of [Ru(NN)₃]²⁺. The following equation known as Benesi-Hildebrand procedure²⁵ was applied to calculate the binding constant:

$$[\text{Ru}(\text{NN})_3]^{2+} / [\epsilon_a - \epsilon_f] = [\text{Ru}(\text{NN})_3]^{2+} / [\epsilon_b - \epsilon_f] + 1 / K_b [\epsilon_b - \epsilon_f] \dots \dots \dots (1)$$

Where [Ru(NN)₃]²⁺ was the concentration of [Ru(NN)₃]²⁺, the apparent absorption coefficient ε_f, ε_a and ε_b corresponding to the extinction coefficient of the free BQ, the extinction coefficient for each addition of Ru(II) complexes to the BQ and the extinction coefficient for the BQ in the fully bound form, respectively. The slope and Y-intercept of the linear fit of [Ru(NN)₃]²⁺ / [ε_a-ε_f] versus [Ru(NN)₃]²⁺ give 1/[ε_b-ε_f] and 1/ K_b[ε_b-ε_f] respectively. The intrinsic binding constant K_b can be obtained from the ratio of the slope to the intercept²⁶. From the plot of [Ru(NN)₃]²⁺ / (ε_a - ε_f) vs. [Ru(NN)₃]²⁺, the binding constant K_b for phen complex was 4.19x10³ M⁻¹, while the corresponding value for the bpy complex was 4.9x10³ M⁻¹. From the binding constant values, there is an appreciable electrostatic interaction between BQ and Ru(bpy)₃²⁺ when compared with phenanthroline complex.

Complexes ^a	^b Redox potential, V		λ_{\max} , nm		lifetime ^c τ_0 (ns)
	$E_{pa}^{1/2}$	$E_{pc}^{1/2}$	absorption	Emission	
Ru(bpy) ₃ ²⁺	1.28	1.20	287, 456	598	850
Ru(phen) ₃ ²⁺	1.23	1.16	262, 443	604	460

^a As PF₆⁻ salts ; ^b Volts vs (Ag wire) ; ^c Data collected from literature

Table 1: Spectral and Electrochemical data in Acetonitrile

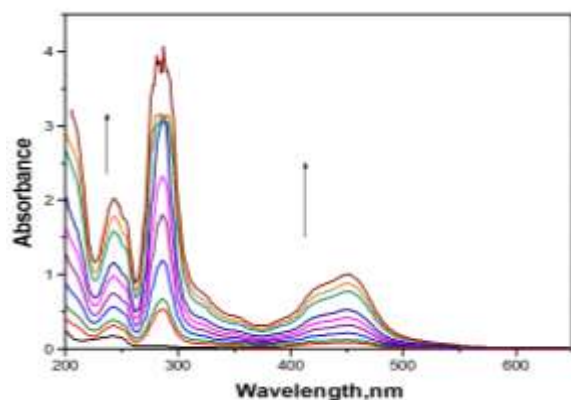


Figure 1 Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(bpy)₃²⁺ in acetonitrile medium

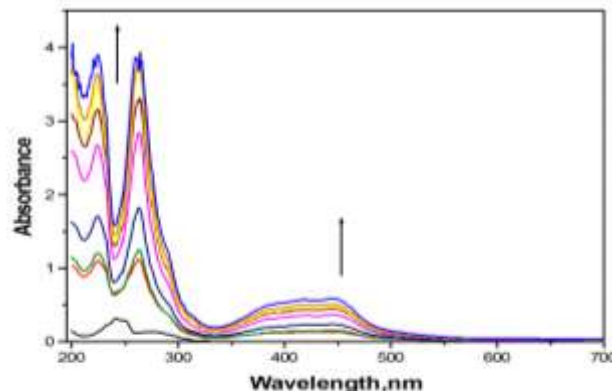


Figure 2 Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(phen)₃²⁺ in acetonitrile medium.

b) Electrochemical titration

The redox behaviour of metallic species is very sensitive to the coordination surrounding the metal centre (solvent, ligand, charge), therefore metal-based interaction can be detected using this technique. Cyclic voltammetry was used to study the reduction of 1,4-benzoquinone in acetonitrile onto a glassy carbon electrode in the presence of different concentrations of ruthenium(II) complexes. The cyclic voltammograms of 1,4-benzoquinone (Q) as a function of the concentration of ruthenium(II) complexes [Ru(NN)₃]²⁺ are shown in Figs 3 and 4. In the absence of [Ru(NN)₃]²⁺, the CV of BQ in acetonitrile solution exhibited two cathodic and anodic waves. The first reduction wave corresponds to the transformation of quinone into semiquinone (Q^{•-}) at $E_{1/2}^0 = -0.469$ V (Vs Ag wire) and the second to the transformation of Q^{•-} into quinone dianion (Q²⁻) at $E_{1/2}^0 = -0.868$ V (Ag wire). From the peak potentials, the half-wave reduction potentials were calculated. The results are in agreement with the reported values. As increasing the concentration of the ruthenium bipyridine, [Ru(bpy)₃]²⁺ with BQ, the reduction peak I and II of BQ moved towards less negative potential, shown in Fig.3. The shift observed in first reduction peak is negligible but quite significant in second reduction peak. The second peak Q²⁻ is shifted towards less negative potential without disturbing symmetry of the voltammograms, when the ruthenium bipyridine concentration is increased. In the absence of [Ru(bpy)₃]²⁺, the cathodic and anodic peak potentials of BQ were found to be at $E_{pc} = 848$ mV and $E_{pa} = 558$ mV. The separation of anodic and cathodic peaks, $\Delta E_p = 290$ mV, indicated a quasi-reversible, successive one-electron redox process [$i_{pc}/i_{pa} \approx 1$], in the presence of [Ru(bpy)₃]²⁺, as shown in the Fig.3, the cathodic and anodic peak potentials were found to be at $E_{pc} = 739$ mV and $E_{pa} = 608$ mV. The peak to peak separation became narrow with

$\Delta E_p = 131$ mV, indicating that in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ the electron-transfer process seemed to be improved, became reversible and the $E^{1/2}$ value was shifted towards less negative region by about 167 mV.

In the case of $[\text{Ru}(\text{phen})_3]^{2+}$, the shift goes towards more negative potentials without disturbing symmetry of the voltammograms, which indicates the absence of protonation of the semiquinone and the quinone dianion. In the case of $[\text{Ru}(\text{phen})_3]^{2+}$, in the absence of $[\text{Ru}(\text{phen})_3]^{2+}$ the peak potentials were found at $E_{pc}=848$ mV, $E_{pa}=692$ mV and $\Delta E_p=156$ mV, which was considered to be also a quasi-reversible one. In the presence of $[\text{Ru}(\text{phen})_3]^{2+}$, at the same concentration of BQ, the peak potentials ($E_{pc}=915$ mV and $E_{pa}=803$ mV) were shifted to more negative potential and the redox couple with $\Delta E_p=112$ mV. Thus, the apparent $E^{1/2}$ shifted to more negative potentials by 44 mV in the presence of $[\text{Ru}(\text{phen})_3]^{2+}$. For the two complexes examined, both of the redox couples were found to be reversible in the presence of $[\text{Ru}(\text{NN})_3]^{2+}$, which clearly indicated that BQ on interaction with $[\text{Ru}(\text{NN})_3]^{2+}$ facilitated electron transfer process in a better way. So there is strong interaction between the BQ and $[\text{Ru}(\text{bpy})_3]^{2+}$ than $[\text{Ru}(\text{phen})_3]^{2+}$, as revealed in the former absorption spectroscopic studies.

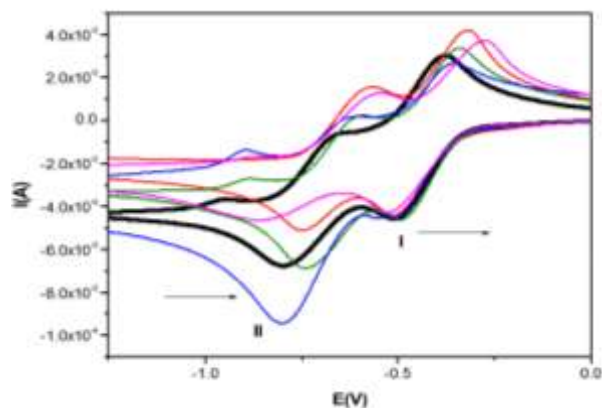


Figure 3 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile.

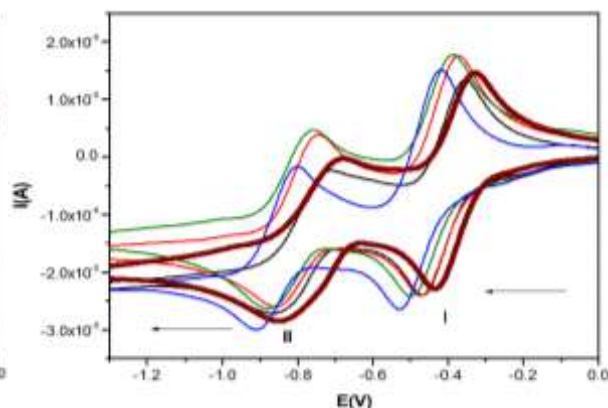


Figure 4 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of $\text{Ru}(\text{phen})_3^{2+}$ in acetonitrile.

Conclusions

The BQ binding with Ruthenium(II) complex containing bpy and phen ligands has been studied by absorption spectroscopy and electrochemical methods. The experimental results show that the interaction of BQ with $\text{Ru}(\text{NN})_3^{2+}$ complex is electrostatic. The binding constant value K_b for $\text{Ru}(\text{phen})_3^{2+}$ complex was $4.19 \times 10^3 \text{ M}^{-1}$, while the corresponding value for the $\text{Ru}(\text{bpy})_3^{2+}$ complex was $4.9 \times 10^3 \text{ M}^{-1}$. From the values, there is an appreciable intermolecular electrostatic interaction between BQ and $\text{Ru}(\text{bpy})_3^{2+}$ when compared with phenanthroline complex as indicated by the UV spectral and electrochemical analysis

Acknowledgement

I express my sincere gratitude to Dr. S. Abraham John, Gandhigram Rural University, Dindugul for his guidance to work in Cyclic Voltammetry and help with the analysis of CV images.

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