



Electroreduction of 1,4 - benzoquinone in Presence of Ruthenium II Complexes Using Cyclic Voltammetry

KEYWORDS

Ruthenium polypyridyl complexes, 1,4-benzoquinone, steric effect, Cyclic voltammetry.

S. SORNALATHA

Research Scholar Department of Chemistry,
Manonmaniam Sundaranar University, Tirunelveli – 627
012.

K. Swarnalatha

Assistant Professor, Department of Chemistry,
Manonmaniam Sundaranar University, Tirunelveli – 627
012.

ABSTRACT The interactions between Ruthenium polypyridyl coordination compounds $[Ru(NN)_3]^{2+}$ (N= 1,10 phenanthroline (phen), 4,7-dimethyl 1,10-phenanthroline(dmphen) and 4,7 diphenyl 1,10-phenanthroline(dpphen) and 1,4-benzoquinone(BQ) in aprotic solvent have been investigated using electrochemical method. Results indicate that there is an obvious interaction equilibrium between $[Ru(NN)_3]^{2+}$ and BQ. In this work, it is considered that charged molecules such as the semiquinone ($Q^{\cdot-}$) and the benzoquinone dianion (Q^{2-}) interact with Ruthenium II complexes through consecutive association steps. The quantitative data was obtained by calculating the thermodynamic association constants and the number of Ru(II) complex associated with both semianion and dianion of the quinone.

INTRODUCTION

Quinones and their intermediates play important roles as mediators in the electron transfers occurring in photosynthesis, phosphorylation¹⁻³. The redox chemistry of naturally occurring para benzoquinone is an essential aspect of biological processes such as cellular respiration, photosynthesis and blood coagulation⁴. Luminescent d^6 transition metal complexes, particularly Ruthenium (II) complexes are useful as photosensitizers for energy and electron transfer processes⁵⁻¹⁵. Realising the importance of Ruthenium (II) polypyridyl complexes as model photosensitizers as electron donors, in order to understand the electron accepting properties of quinones in natural photosynthesis, we have investigated the redox properties of benzoquinone with Ruthenium (II) complexes carrying electron donating groups in the 4,7-position of 1,10-phenanthroline, using Cyclic Voltammetry. On the other hand single global association model is used to quantify the bonding interaction. In the present work the association between the quinone with Ruthenium II polypyridyl complexes was treated in terms of single global association equilibrium constants ($Keq^{(1)}$ and $Keq^{(2)}$) and the number of Ruthenium polypyridyl molecules (n and m) bonded with anion and dianion of quinone respectively.

EXPERIMENTAL SECTION

The three complexes of ruthenium polypyridyl complexes $[Ru(NN)_3]^{2+}$ were prepared by reacting $RuCl_3 \cdot 3H_2O$ with the corresponding ligands in 1:3 equivalence by the known procedures¹⁶⁻²⁰. BQ (1,4-benzoquinone) was purchased from Sigma Aldrich and further purified by sublimation method. Cyclic voltammetric experiments were done using a conventional three-electrode cell, with glassy carbon as working electrode, Platinum wire as counter electrode and silver wire as reference electrode. The working electrode was carefully polished with alumina powder (0.05 μ) to clean the surface of the glassy carbon electrode, and ultrasonically rinsed with distilled water before each run. Measurements were recorded with [H] CH Instruments, electrochemical analyser. The supporting electrolyte was tetrabutyl ammonium hexafluorophosphate (TBAPF₆, 0.1 M) in acetonitrile and the scan rate was 100 mVs⁻¹ throughout the experiments. All electrochemical experiments were performed at 25°C under nitrogen atmosphere. Solutions

were purged with N₂ gas to provide oxygen free atmosphere and was passed over the solutions during the measurements.

RESULTS AND DISCUSSION

We present the results obtained from the voltammetric behavior of 1, 4-benzoquinone in presence of ruthenium(II) complexes having phenanthroline ligand series, in acetonitrile. The Cyclic voltammograms of quinone were recorded at $1 \times 10^{-6} M$ concentration with 0.1M tetra butyl ammonium hexa fluoro phosphate, supporting electrolyte. Cyclic voltammograms obtained for 1,4-benzoquinone show quasi-reversible. The first reduction wave corresponds to the transformation of Q into semiquinone ($Q^{\cdot-}$) at $E_{1/2}^0 = -0.45 V$ and the second to the transformation of $Q^{\cdot-}$ into quinone dianion (Q^{2-}) at $E_{1/2}^0 = -0.98 V$. As increasing the concentration of the ruthenium phenanthroline, $[Ru(phen)_3]^{2+}$, the reduction signal I and II moved towards more negative potential. Fig.(1) shows the voltammetric behaviour of 1,4-benzoquinone as a function of the concentration of $[Ru(NN)_3]^{2+}$ where NN= 1,10 phenanthroline, 4,7dimethyl-1,10-phenanthroline, 4,7diphenyl 1,10phenanthroline. In this figure1, it is observed that the half-wave potential of peak I is not modified significantly compared with peak II by the ruthenium phenanthroline concentration, which indicates that the association of $Q^{\cdot-}$ with this complex is not so strong. By analyzing the half-wave potential variations according to complex concentration, we determined the association constants Keq for the $Q^{\cdot-}$ and Q^{2-} species with the different Ruthenium II complexes studied here. The Ruthenium II complexes used have the following increasing basicity strength on the basis of the substituents attached with ruthenium complex, $[Ru(bathophen)_3]^{2+} > [Ru(dmphen)_3]^{2+} > [Ru(phen)_3]^{2+}$. A systematic decrease in positive shift is followed by BQ with phenanthroline complexes according to decreasing trend of their basicity. In the phenanthroline series, the reduction peaks of BQ (figure 1a and 1b) shift towards more negative potential by increasing the concentration of $[Ru(NN)_3]^{2+}$ complex gradually, (where NN= 1,10 phenanthroline, 4,7dimethyl-1,10-phenanthroline). But the shift goes towards less negative potential in the case of Ruthenium bathophenanthroline (Figure 1c).

For the given complexes, the shift is much larger for the second reduction step as compared to first step. Three possible modes of host-guest interaction (reduced quinone being host and the added ruthenium complexes being guest) are (a) a coupled chemical reaction (b) pi-pi stacking and (c) hydrogen bonding. The possibility of coupled chemical reaction before or after the reduction may be excluded because no additional peak appeared or distortion in the shape of the cyclic voltammograms has been observed. Since anodic waves remained intact even after the addition of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes, protonation is also excluded. Therefore the most likely interaction between the reduced form of quinone and the $[\text{Ru}(\text{NN})_3]^{2+}$ is pi-pi stacking and the strength of interaction increases with decreasing trend of basicity of $[\text{Ru}(\text{NN})_3]^{2+}$. This shift is not because of solvent polarity but ascribed to specific metal complex - quinone interaction. Since the values of $K_{\text{eq}}^{(2)}$ are greater than 300, the association equilibria are quantitative. This is as expected since the most significant variations in half-wave potential were observed for the reduction wave of the $\text{Q}^{\cdot-}/\text{Q}^{2-}$ couple. Data from Figure 2 were analyzed to determine the number of additive molecules associated with $\text{Q}^{\cdot-}$ and Q^{2-} . It is evident from the tabulated data (Table 1) that the association constant value increases with decrease of basicity. This may be attributed to the inductive effect and steric effect of the substituents attached. The strong anodic shift in second wave because of intermolecular interaction is manifested well from large values of $K_{\text{eq}}^{(2)}$. The only difference is that the values of m and $K_{\text{eq}}^{(2)}$ are quite large as compared to n and $K_{\text{eq}}^{(1)}$

respectively. The large values of $K_{\text{eq}}^{(2)}$ confirm the strong interaction of Q^{2-} and $[\text{Ru}(\text{NN})_3]^{2+}$ couple and are in good agreement with the shift in cyclic voltammograms as confirmed above. The above discussion is further supported by the plots of $\Delta E_{1/2}$ vs $\log [\text{Ru}(\text{NN})_3]^{2+}$ as given in Figure 2. The more $K_{\text{eq}}^{(2)}$ value of Ruthenium II complexes were attributed to strong intermolecular interaction, not protonation takes place as there is no loss in reversibility by the addition of RuII complex.

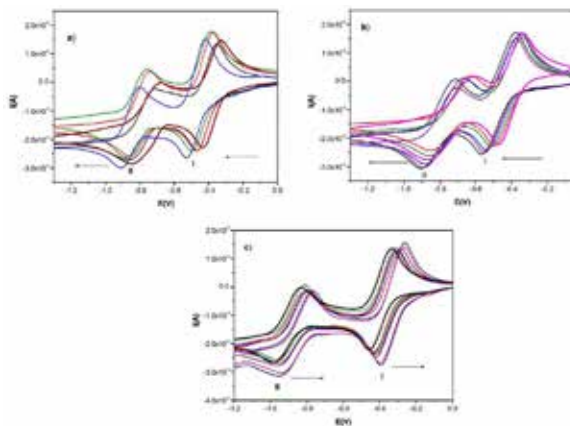


Figure 1: CV of BQ with increasing concentration of a) $[\text{Ru}(\text{phen})_3]^{2+}$ b) $[\text{Ru}(\text{dmphen})_3]^{2+}$ c) $[\text{Ru}(\text{bathophen})_3]^{2+}$ at the scan rate 100 mV^{-1}

Table 1: Electrochemical parameters of 1,4 benzoquinone in presence of $[\text{Ru}(\text{NN})_3]^{2+}$ Complexes.

Complex	$E_{\text{pa}}^{1/2}$	$E_{\text{pc}}^{1/2}$	n	$K_{\text{eq}}^{(1)}, \text{M}^{-n}$	m	$K_{\text{eq}}^{(2)}, \text{M}^{-m}$
$[\text{Ru}(\text{phen})_3]^{2+}$	1.23	1.16	1.07	$5.25 \times 10^5 \text{ M}^{-1.07}$	1.7	$1.9 \times 10^9 \text{ M}^{-1.7}$
$[\text{Ru}(\text{dmphen})_3]^{2+}$	1.08	1.007	1.2	$1.9 \times 10^6 \text{ M}^{-1.2}$	2.4	$6.15 \times 10^{11} \text{ M}^{-2.4}$
$[\text{Ru}(\text{bathophen})_3]^{2+}$	1.42	1.35	0.5	$5 \times 10^2 \text{ M}^{-0.5}$	1.25	$3.02 \times 10^6 \text{ M}^{-1.25}$

Units of $K_{\text{eq}}^{(1)} = \text{M}^{-n}$ and $K_{\text{eq}}^{(2)} = \text{M}^{-m}$

STERIC EFFECT

In this section, we explain the synthesis of Ruthenium II complexes with sterically hindering methyl and phenyl substituted 1,10-phenanthroline ligands and the steric effect of these substituents on redox reaction of the complexes. The data of association constant for substituted complexes have been shown in the table 1 along with unsubstituted complex for the purpose of comparison. The K_{eq} value observed for $\text{Ru}(\text{dmphen})_3^{2+}$ is higher than the parent complex $[\text{Ru}(\text{phen})_3]^{2+}$. This is because the presence of the electron donating methyl group in the ligand make the Ru(II) complex bulky compared to the parent complex $\text{Ru}(\text{phen})_3^{2+}$. As expected the product yields were lowest for the most sterically hindering diphenyl-substituted ligands with the rigid ring system of phenanthroline giving lower yields than phenanthroline (table 1). The lowest binding constant (K_{eq}) value for $\text{Ru}(\text{dpphen})_3^{2+}$ is due to the steric effect of the bulky phenyl group present in the phenanthroline complex than $\text{Ru}(\text{phen})_3^{2+}$.

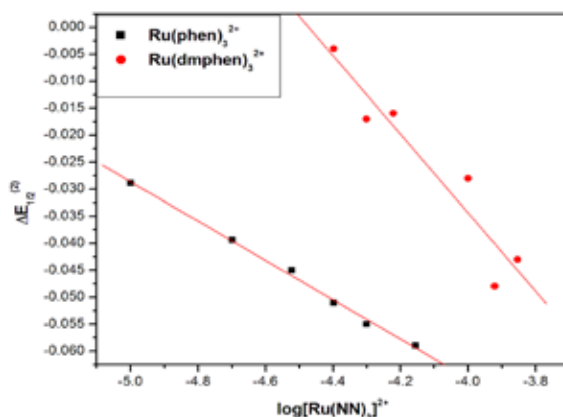


Figure 2: Plots of $\Delta E_{1/2}$ vs a) $\log [\text{Ru}(\text{phen})_3]^{2+}$ b) $\log [\text{Ru}(\text{dmphen})_3]^{2+}$

CONCLUSION

In the present study, we have synthesised a series of Ruthenium(II) polypyridyl complexes containing phenanthroline ligands and characterized them by electrochemical method. Electrochemical studies of Ruthenium polypyridyl complexes showed a reversible Ru(II)/Ru(III) oxidation process at 1.28V, 1.01V and 1.42 respectively. The

1,4-benzoquinone(BQ) studied showed quasireversible behaviour in acetonitrile. Addition of different complexes caused a systematic more positive /negative shift in the redox waves of the quinone. This shift is attributed to specific interaction between anions and dianions of quinone with the added complexes. The resulting anodic shift was very small in the first wave but significantly large in the second wave. This depicts the weak interaction of semiquinone-complex interaction in comparison to strong dianion-complex interaction for the same concentration of complex. Quantitative analysis was made in terms of electrochemical parameters, n , m and K_{eq} . It was found that these values are in good agreement with the shifting observed in cyclic voltammograms in a given quinone-complex couple.

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