CHAPTER 4
Hydrogen Bonding Effects and the Association Process between 1,4-benzoquinone and the series of Ru(II) Complexes in aprotic solvent

4.1 Introduction

The hydrogen bond plays an important role in controlling both the intra- and intermolecular structure in biological functions as an active site of quinoenzymes. The neutral quinones are good electron acceptors in the cascade of electron transfer reactions initiated when photosynthetic reaction centers are excited, and the reduced forms of quinones are very active with donor protons to generate mainly hydroquinone (or) hydrogen bonded complexes. Quinones and their intermediates play important roles as mediators in the electron transfers occurring in photosynthesis, phosphorylation. Studies on hydrogen bonds of semiquinone (Q\textsuperscript{+/-}) and quinone dianion (Q\textsuperscript{2--}) with hydrogen bond donors are particularly important to understand the electron and proton transfers in energy transducing membranes for respiration and photosynthesis. It was found that hydrogen-bonding between quinones and proteins in biological systems are responsible for adjusting the redox potentials of the quinones. The redox chemistry of naturally occurring para benzoquinone is an essential aspect of biological processes such as cellular respiration, photosynthesis and blood coagulation. Other quinones such as ubiquinones are well-known important functional moiety in various biological systems acting as an electron-proton carrier in respiratory assemblies and in photosynthetic electron flow systems. These \( p \)-quinones are reduced to semiquinones by mitochondrial NADH dehydrogenase. Hydrogen bonding and protonation are fundamental factors controlling potentials and mechanism in the reduction of quinones. In these solutions, the first step is generally reversible and the second is at least quasi-reversible. The potential of these reductions...
depend on the polarity of the solvent, the nature of the supporting electrolyte and the presence of acidic additives, ion-pairing and protonation equilibria. Luminescent $d^6$ transition metal complexes, particularly ruthenium(II) complexes are useful as photosensitizers for energy and electron transfer processes. Realising the importance of Ruthenium(II) polypyridyl complexes as model photosensitizers as electron donors in natural photosynthesis, we have investigated the redox properties of para quinones with Ruthenium(II) complexes carrying electron donating groups and electron withdrawing groups in the 4,4'-position of $2,2'$-bipyridine and 4,7-position of 1,10-phenanthroline, using Cyclic Voltammetry. In the previous studies, the electrochemical reduction of benzoquinone in presence of different solvents has been reported.

Keeping in view, the above applications of quinones and the Ruthenium(II) polypyridyl complexes, they were subjected to electrochemical studies for qualitative and quantitative information. The change in the shape of resulting voltammograms is used to discuss the qualitative behavior. On the other hand single global association model is used to quantify the hydrogen bonding interaction. Recently Ignacio Gonzalez and co-workers presented a new model for the characterization of hydrogen bonding in quinones. The model is based upon the concept that the association between donor protons and quinones takes place through successive equilibriums. In the present work the association between quinones with Ruthenium(II) polypyridyl complexes was treated in terms of single global association equilibrium constants ($K_{eq}^{(1)}$ and $K_{eq}^{(2)}$) and the number of ruthenium polypyridyl molecules (n and m) bonded with anion and dianion of quinones respectively.
4.2 Results and Discussion

The structures of the ligands, quinons, and the complexes used in the present study are given in scheme 4.1 and 4.2. The spectroscopic data including emission lifetimes ($\tau$) and redox potentials of Ru(NN)$_3^{2+}$ in acetonitrile are summarized in Table 4.1.

Scheme 4.1 Molecular structure of the ligands and the quinone used in the present study.
Scheme 4.2 Molecular structure of the complexes used in the present study.
Table 4.1 The Photophysical and Electrochemical data of Ruthenium (II) complexes in acetonitrile medium at room temperature.

<table>
<thead>
<tr>
<th>Complexes$^a$</th>
<th>Absorption Maxima,(nm)</th>
<th>Emission Maxima,(nm)</th>
<th>lifetime$^b$ $\tau_0$(ns)</th>
<th>$^d$Redox potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(bpy)}_3]^{2+}$</td>
<td>287, 456</td>
<td>598</td>
<td>850</td>
<td>$E_{pa}^{1/2}$ (V)</td>
</tr>
<tr>
<td>$[\text{Ru(dmbpy)}_3]^{2+}$</td>
<td>286, 458</td>
<td>620</td>
<td>740</td>
<td>$E_{pa}^{1/2}$ (V)</td>
</tr>
<tr>
<td>$\text{Ru(dcbpy)}_3^{2+}$</td>
<td>311, 468</td>
<td>626</td>
<td>1080</td>
<td>$E_{pc}^{1/2}$ (V)</td>
</tr>
<tr>
<td>$[\text{Ru(phen)}_3]^{2+}$</td>
<td>262, 443</td>
<td>604</td>
<td>460</td>
<td>$^c$</td>
</tr>
<tr>
<td>$[\text{Ru(dmphen)}_3]^{2+}$</td>
<td>263, 448</td>
<td>600</td>
<td>1740</td>
<td>$^c$</td>
</tr>
<tr>
<td>$[\text{Ru(dcbphen)}_3]^{2+}$</td>
<td>272, 459</td>
<td>610</td>
<td>1770</td>
<td>$^c$</td>
</tr>
<tr>
<td>$[\text{Ru(dpphen)}_3]^{2+}$</td>
<td>277, 463</td>
<td>595</td>
<td>4680</td>
<td>$^c$</td>
</tr>
</tbody>
</table>

$^a$ As PF$_6^-$ salts  
$^b$ Data collected from literature  
$^c$ Not observed  
$^d$ Volts vs (Ag wire) in acetonitrile solution with 0.1M tetra-n-butylammonium hexafluorophosphate, [(n-C$_4$H$_9$)$_4$N]PF$_6$, as supporting electrolyte
Figure 4.1 Absorption spectra of (1) [Ru(bpy)$_3$]$^{2+}$, (2) [Ru(dmbpy)$_3$]$^{2+}$, (3) [Ru(dcbpy)$_3$]$^{2+}$ in acetonitrile medium.
Figure 4.2 Absorption spectra of (1) [Ru(phen)$_3$]$^{2+}$, (2) [Ru(dmphen)$_3$]$^{2+}$, (3) [Ru(dphen)$_3$]$^{2+}$, (4) [Ru(dpphen)$_3$]$^{2+}$ in acetonitrile medium.
Figure 4.3 Emission spectra of (1) [Ru(bpy)$_3$]$^{2+}$, (2) [Ru(dmbpy)$_3$]$^{2+}$, (3) [Ru(dc bpy)$_3$]$^{2+}$ in acetonitrile medium.
Figure 4.4 Emission spectra of (1) [Ru(phen)$_3$$]^{2+}$ (2) [Ru(dmphen)$_3$$]^{2+}$ (3) [Ru(dcphen)$_3$$]^{2+}$ (4) [Ru(dpphen)$_3$$]^{2+}$ in acetonitrile medium.
4.3 Electronic Spectral Features

The UV/Visible absorption spectra of these complexes Ru(NN)$_3^{2+}$ showed intense MLCT (metal-to-ligand charge-transfer) and LC (ligand-centered) transitions around 450-500 nm ($\varepsilon = (1-2) \times 10^4$ M$^{-1}$ cm$^{-1}$) corresponds to the d $\pi$- $\pi^*$ transition and 250-300 nm ($\varepsilon = (5-10) \times 10^4$ M$^{-1}$ cm$^{-1}$) corresponds to the $\pi$- $\pi^*$ transition, respectively. The assignment of the LC transition was also confirmed by comparing the absorption spectra of free ligands. The MLCT transition involves electronic excitation from the metal orbital [d$\pi$ (Ru)] to the ligand centered acceptor $\pi^*$ orbitals (ligand). The absorption maximum of MLCT transition is red shifted by 2 nm and 12 nm when bpy is replaced by dmbpy and dcbpy respectively. The small red shift compared with the unsubstituted bipyridines is due to the slight electron donating effect of the methyl groups attached to the ruthenium bipyridine. However, the difference in energy is so small that no separate MLCT bands can be detected. The absorption maximum of MLCT transition is red shifted by 12nm when bpy is replaced by dcbpy. The introduction of –COOH group in bpy lowers $\pi^*$ level of the ligand and thus shifts the LC and MLCT transition to the red. A representative spectra of Ru(NN)$_3^{2+}$ complexes in acetonitrile at room temperature are shown in Figure 4.1 and 4.2. The emission maxima of these complexes are observed in the range of 600-625 nm and are attributed to the decay of the $^3$MLCT state of the ruthenium complexes. All the complexes have exactly the same emission properties, due to the slight electron donating properties of the methyl groups where the lowest excited state involves the unsubstituted bipyridines. The position of the emission is red shifted by 22 nm and 24 nm with respect to bipyridine when methyl group and acid group are introduced in the 4,4'-position of bpy which lowers the $\pi^*$ level of the ligand.
emission spectra of these complexes are shown in the Figure 4.3 and 4.4 and the values are given in the Table 4.1.

4.3.1 Interaction between 1,4-benzoquinone and ruthenium(II) polypyridyl complexes

All the spectroscopic titrations were carried out in acetonitrile solution at room temperature unless otherwise specified. Absorption titration can monitor the interaction of metal complexes with biologically important substance. Binding of the macromolecule leads to changes in the electronic spectrum of the metal complex. Base binding is expected to perturb the ligand field transition of the metal complex. Intercalative mode of binding usually results in hypochromism and bathochromism due to the strong stacking interaction between an aromatic chromophore and the base pairs of BQ. The extent of hypochromism parallels the intercalative binding strength.

On the otherhand, BQ, which bind non-intercalatively or electrostatically with [Ru(NN)₃]²⁺ may result in hyperchromism or hypochromism. The absorption spectra of BQ in the absence and the presence of [Ru(NN)₃]²⁺ is given in Figure 4.5, 4.6, 4.7, 4.9 and 4.10 respectively and the data are tabulated in table 4.2. Only very weak hypochromism and spectral shifts were found after BQ was mixed with [Ru(NN)₃]²⁺. The titrations in acetonitrile were done using a fixed BQ concentration to which increments of the [Ru(NN)₃]²⁺ stock solution were added. BQ solutions employed were 1x10⁻⁶ M in concentration and ruthenium(II) complex was added to a ratio 0-10. Ruthenium-BQ solutions were allowed to incubate for 10 min before the absorption spectra were recorded. With increasing the concentration of Ru(NN)₃²⁺, the hyperchromism increased and was accompanied by a red shift from 241-246 for BQ. In general, hypochromism and red-shift are associated with the binding of the
complex to the helix by an intercalative mode involving strong stacking interaction of
the aromatic chromophore of the complexes between the BQ base pairs\textsuperscript{43} are studied.

\textbf{Figure 4.5} Absorption spectra of 1,4-benzoquinone in acetonitrile medium.
Figure 4.6 Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(bpy)$_3^{2+}$ (1) 0.0 (2) $2.8 \times 10^{-6}$ (3) $5.6 \times 10^{-6}$ (4) $1.12 \times 10^{-5}$ (5) $1.68 \times 10^{-5}$ (6) $2.24 \times 10^{-5}$ (7) $2.8 \times 10^{-5}$ (8) $4.48 \times 10^{-5}$ (9) $5 \times 10^{-5}$ (10) $5.6 \times 10^{-5}$ M in acetonitrile medium.
Figure 4.7 Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(dmbpy)$_3^{2+}$ (1) 0.0 (2) $5 \times 10^{-6}$ (3) $1 \times 10^{-5}$ (4) $1.5 \times 10^{-5}$ (5) $2 \times 10^{-5}$ (6) $2.5 \times 10^{-5}$ (7) $3 \times 10^{-5}$ (8) $3.5 \times 10^{-5}$ (9) $4 \times 10^{-5}$ (10) $4.5 \times 10^{-5}$ M in acetonitrile medium.
Figure 4.8 Plot of $\frac{[\text{Ru(NN)}_3^{2+}]}{[\epsilon_a - \epsilon_d]}$ vs $[\text{Ru(NN)}_3^{2+}]$ for BQ with a) $[\text{Ru(bpy)}_3^{2+}]$ and b) $[\text{Ru(dmbpy)}_3^{2+}]$. 
Figure 4.9 Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(phen)$_3^{2+}$ (1) 0.0 (2) $1 \times 10^{-5}$ (3) $2 \times 10^{-5}$ (4) $3 \times 10^{-5}$ (5) $4 \times 10^{-5}$ (6) $4.5 \times 10^{-5}$ (7) $5 \times 10^{-5}$ (8) $5.5 \times 10^{-5}$ (9) $6 \times 10^{-5}$ M in acetonitrile medium.
Figure 4.10 Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(dmphen)$_3^{2+}$: (1) 0.0 (2) $2 \times 10^{-6}$ (3) $5 \times 10^{-6}$ (4) $1 \times 10^{-5}$ (5) $1.5 \times 10^{-5}$ (6) $2 \times 10^{-5}$ (7) $2.5 \times 10^{-5}$ (8) $3 \times 10^{-5}$ (9) $4 \times 10^{-5}$ (10) $4.5 \times 10^{-5}$ (11) $5 \times 10^{-5}$ M in acetonitrile.
Figure 4.11 Plot of $[\text{Ru(phen)}_3^{2+}] / [\varepsilon_a - \varepsilon_f]$ vs $[\text{Ru(phen)}_3^{2+}]$ for BQ with a) $[\text{Ru(phen)}_3^{2+}]$, b) $[\text{Ru(dmphen)}_3^{2+}]$
**TABLE 4.2 Spectroscopic properties on binding to [BQ]**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption$^a$</th>
<th>λ$_{max}$ (nm)</th>
<th>Δλ</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bpy)$_3^{2+}$</td>
<td>246</td>
<td>5</td>
<td>4.9x$10^{3}$</td>
<td></td>
</tr>
<tr>
<td>Ru(dmbpy)$_3^{2+}$</td>
<td>245</td>
<td>4</td>
<td>5.79x$10^{3}$</td>
<td></td>
</tr>
<tr>
<td>Ru(phen)$_3^{2+}$</td>
<td>224</td>
<td>17</td>
<td>4.19x$10^{3}$</td>
<td></td>
</tr>
<tr>
<td>Ru(dmphen)$_3^{2+}$</td>
<td>226</td>
<td>15</td>
<td>8.7x$10^{3}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$[BQ] = 1 x $10^{-6}$ M; all solutions in acetonitrile.
For phenanthroline series, by increasing the concentration of Ru(II) complexes with BQ, hyperchromism and blue shifts from 241nm-220 nm are observed and binding constant estimated using equation 4.1 is the order of $10^3$.

In order to compare quantitatively the binding strength of the BQ, the intrinsic binding constants $K_b$ of BQ with Ru(NN)$_3^{2+}$ were obtained by monitoring the changes in absorbance at 241 nm for BQ, with increasing concentration of Ru(NN)$_3^{2+}$. The intrinsic binding constant of the BQ with Ruthenium(II) complex was determined by using modified Benesi- Hildebrand equation$^{44}$. This equation can be written as follows:

$$\frac{[\text{Ru(NN)}_3^{2+}]}{[\varepsilon_a - \varepsilon_f]} = \frac{[\text{Ru(NN)}_3^{2+}]}{[\varepsilon_b - \varepsilon_f]} + \frac{1}{K_b [\varepsilon_b - \varepsilon_f]}$$ (4.1)

where $[\text{Ru(NN)}_3^{2+}]$ is the concentration of $[\text{Ru(NN)}_3^{2+}]$ in the base pairs. The apparent absorption coefficients $\varepsilon_a$, $\varepsilon_f$ and $\varepsilon_b$ correspond to $A_{obsd} / [\text{BQ}]$, the extinction coefficient for the free BQ and the extinction coefficient for the BQ in the fully bound form respectively. The slope and Y-intercept of the linear fit of $[\text{Ru(NN)}_3^{2+}] / [\varepsilon_a - \varepsilon_f]$ versus $[\text{Ru(NN)}_3^{2+}]$ give $1/[\varepsilon_b - \varepsilon_f]$ and $1/ K_b [\varepsilon_b - \varepsilon_f]$ respectively. The intrinsic binding constant $K_b$ can be obtained from the ratio of the slope to the Y-intercept.$^{45}$ The data obtained throughout this calculation were given in Table 4.2. In the plot of $[\text{Ru(NN)}_3^{2+}] / [\varepsilon_a - \varepsilon_f]$ vs $[\text{Ru(NN)}_3^{2+}]$, (Figure 4.9 and 4.11), the binding constant $K_b$ for bpy was $4.9 \times 10^3$ while the corresponding value for the phen was $4.19 \times 10^3$.

### 4.4 Redox Potentials

Cyclic Voltammetry has proved to be a very sensitive analytical technique to determine changes in redox behavior of metallic species in the presence of biologically important molecules$^{46,47}$. The redox behavior 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. All the measured ruthenium complexes were in oxidation state II. At positive potentials, cyclic voltammograms revealed electrochemically reversible metal-based Ru$^{II}$–Ru$^{III}$ oxidations. As can be seen in Table 4.1, the expected and well known dependence of the metal-based oxidation potential on the electron acceptor or donor nature of the attached ligand is clearly observed. 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.

In this section, the redox behavior of the complexes in acetonitrile was examined using cyclic voltammetry with a glassy carbon as a working electrode. The potentials are reported with reference to the silver wire, at the scan rate of 100 mV/s, unless otherwise mentioned.

The [Ru(bpy)$_3$]$^{2+}$ exhibits a reversible metal to ligand charge transfer oxidation at 1.28V. The difference between the cathodic and anodic currents to the Ru(II)/Ru(III) couple indicates the redox ability of the species. For the Ru(II)/Ru(III) couple, $\Delta E_p = 0.0591$ V was expected. However, the unexpected experimental values illustrate that the chemical reversibility ($I_{pc}/I_{pa} = 1$) is not synonymous with electrochemical reversibility ($\Delta E_p = 0.0591$ V), the Ru(bpy)$_3$$^{2+}$ oxidation is actually quasi-reversible.

In the absence of 1,4-benzoquinone, the Cyclic Voltammogram of the Ru(II) complexes (shown in Figures 4.12 (a), (b) and (c)) in acetonitrile solution exhibited only one redox couples at the formal potential $E_{1/2}$ of 1.24 V, $E_{1/2}$ of 1.03 V and $E_{1/2}$ of 1.20 V taken as the average of cathodic peak potential $E_{pc}$ and anodic peak potential $E_{pa}$ for Ru(bpy)$_3$$^{2+}$, Ru(dmbpy)$_3$$^{2+}$ and Ru(dcbpy)$_3$$^{2+}$ respectively. The redox
peaks were attributed to Ru(II)/Ru(III) couple reaction as shown in Figure 4.12 a, b and c. The separation of anodic and cathodic peaks, \( \Delta E_p = E_{pc} - E_{pa} \) \( \Delta E_p \) of 80 mV, \( \Delta E_p =74 \text{ mV} \) and \( \Delta E_p = 110 \text{ mV} \) which is more than the expected value (58 mV) for one-electron Nernstian process\(^{48}\), indicated a quasi-reversible one-electron redox process which is assigned to the Ru(II)/Ru(III) couple.

In the case of bipyridine series, the cathodic and anodic peak potentials were found to be at \( E^{1/2} = 1.38 \text{ V} \), \( E^{1/2} = 1.056 \text{ V} \) and \( E^{1/2} = 1.1 \text{ V} \) in the presence of 1,4-benzoquinone, as shown in the Figure 4.13 a,b and c. The peak to peak separation became narrow with \( \Delta E_p =59 \text{ mV} \) , for \( \text{Ru(dmbpy)}_3^{2+} \), indicating that in the presence of BQ, the electron-transfer process seemed to be improved, became reversible and the \( E^{1/2} \) value was shifted towards more negative region by about 10 mV. In the case of phenanthroline series, in the absence of BQ (shown in the Figure 4.14 (a), (b), (c) and (d), the peak potentials of Ru(II) complexes were found at \( E^{1/2} =1.20 \text{ V} \), \( E^{1/2} =1.26 \text{ V} \) and \( E^{1/2} =1.39 \text{ V} \) and the peak – peak separation is \( \Delta E_p =70 \text{ mV} \), \( \Delta E_p =78 \text{ mV} \), \( \Delta E_p =64 \text{ mV} \) which was considered to be also a quasi-reversible one for \( \text{Ru(phen)}_3^{2+} \), \( \text{Ru(dmphen)}_3^{2+} \) and \( \text{Ru(dpphen)}_3^{2+} \) respectively. As shown in the Figure 4.15, in the presence of BQ, at the same concentration of complex, the peak potentials were shifted to more negative potential (\( E^{1/2} = 1.19 \text{ V} \) and \( E^{1/2} = 1.049 \text{ V} \), \( E^{1/2} =1.33 \text{ V} \) and \( E^{1/2} = 1.32 \text{ V} \)) and the redox couple with \( \Delta E_p =55 \text{ mV} \) and \( \Delta E_p =59 \text{ mV} \) indicating a similar reversibility in the electron transfer process in the presence of BQ.
Figure 4.12 Cyclic voltammograms of (a) Ru(bpy)$_3^{2+}$, (b) Ru(dmbpy)$_3^{2+}$, (c) Ru(dcbpy)$_3^{2+}$ in acetonitrile. (scan rate 100 mVs$^{-1}$).
Figure 4.13 Cyclic Voltammograms of (a) [Ru (bpy)$_3$]$^{2+}$ (b) [Ru (dmbpy)$_3$]$^{2+}$ (c) [Ru(dcbpy)$_3$]$^{2+}$ with increasing concentrations of BQ in acetonitrile (scan rate 100 mVs$^{-1}$).
Figure 4.14 Cyclic voltammograms of (a) Ru(phen)$_3^{2+}$, (b) Ru(dmphen)$_3^{2+}$, (c) Ru(dphen)$_3^{2+}$ in acetonitrile (scan rate 100 mVs$^{-1}$).
Figure 4.15 Cyclic Voltammograms of (a) [Ru (phen)$_3$]$^{2+}$ (b) [Ru (dmphen)$_3$]$^{2+}$ (c) [Ru (dcphen)$_3$]$^{2+}$ with increasing concentrations of BQ in acetonitrile.
For the two series of complexes examined, both of the redox couples were found to be reversible in the presence of BQ, which clearly indicated that these complexes on interaction with BQ facilitated electron transfer process in a better way.

In the case of Ru(dcbpy)$_3^{2+}$ and Ru(dcphen)$_3^{2+}$, carboxylic acid groups readily remove electron density from the ruthenium centre via the bipyridine ring, rendering the RuII–RuIII oxidation more difficult. Complexes 4.12 (c) and 4.14 (c) did not show any sign of metal centred oxidation in acetonitrile at the expected potential range (see Table 4.1). This is related to the poor solubility of those complexes in acetonitrile because RuII–RuIII peak systems are seen in DMSO for the better solubility. Furthermore, ethanol was used as solvent in the literature. The electrochemical reactions that took place were mainly ligand-based reductions. In general, these reactions were irreversible. It is clearly seen that the electron withdrawing dcbpy ligands result in redox potentials at more positive values.

4.5 Redox Switching between Ru(II) and BQ

In nonaqueous media, the reduction of quinones takes place by two successive one-electron reduction steps in which the first step is completely reversible, while the second step quasi-reversible at customary scan rates. In the first step, the quinone becomes semiquinone and in the second step the semiquinone becomes quinone dianion. The two reduction steps are greatly influenced by nature of the solvents, intramolecular hydrogen bonding, protonation-deprotonation equilibrium, addition of acidic or basic additives or even addition of water, ion-pair formation, nature of supporting electrolyte, polarity of solvents and so forth.
4.5.1 Electrochemical reduction of 1,4-benzoquinone (BQ) in the presence of Ruthenium(II) polypyridyl complexes

In this section, the electrochemical reduction of 1,4-benzoquinone was studied in acetonitrile in the presence of Ruthenium(II) complexes at different concentrations. The hydrogen bond formation between the reduced species of quinones (\(Q^-\) and \(Q^{2-}\)) and the ruthenium complexes were studied. For comparison, some ruthenium complexes containing hydrogen bond donors have been used in this study. 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 Figures [4.16-4.18, 4.21-4.23]. In the absence of Ruthenium(II) complexes, BQ reduction produces two voltammetric signals, I and II, related to reactions (4.2) and (4.3) corresponding to two mono electronic, reversible reduction processes to produce the semiquinone \(Q^-\) and quinone dianion \(Q^{2-}\) respectively, (eqs. 4.2 and 4.3).\(^{57-59}\)

\[
\begin{align*}
Q + e^- & \rightleftharpoons Q^- & \text{4.2} \\
Q^- + e^- & \rightleftharpoons Q^{2-} & \text{4.3}
\end{align*}
\]

The molecular structure of the ruthenium(II) complexes and 1,4-benzoquinone used in the present study is given in Scheme 1. In dry and neutral aprotic solvent, the 1,4 benzoquinone studies showed two cathodic and anodic waves. The first reduction wave corresponds to the transformation of Quinone into semiquinone (\(Q^-\)) at \(E^{0}_{1/2} = -0.45\) V (Ag wire) and the second to the transformation of \(Q^-\) into quinone dianion (\(Q^{2-}\)) at \(E^{0}_{1/2} = -0.98\) V (Ag wire). From the peak potentials,
the half-wave reduction potentials were calculated. The results are in agreement with the reported values. The parameters $\Delta E_{p}^{c}/i_{p}^{c}/i_{p}^{a}$ and $[E_{p}^{c} - E_{1/2}]$ which are used to characterize reversibility, the peak width is comparatively more reliable and precise parameter and hence it has been used to explain reversibility.

We present the results obtained from the voltammetric behavior of 1, 4-benzoquinone in presence of ruthenium(II) complexes of bipyridine, phenanthroline series, in aprotic solvent, acetonitrile. The cyclic voltammograms of quinones were recorded at $1 \times 10^{-6}$ M concentration with 0.1M tetra butyl ammonium hexa fluro phosphate, supporting electrolyte. Cyclic voltammograms obtained for 1,4-benzoquinone show reversible behavior for first step and quasi-reversible in the second step. As increasing the concentration of the ruthenium bipyridine, $[\text{Ru(bpy)}_{3}]^{2+}$, the reduction signal I and II moved towards less negative potential. Figure 4.12 shows the voltammetric behaviour of 1,4-benzoquinone as a function of the concentration of $[\text{Ru(NN)}_{3}]^{2+}$, where NN = 2,2'bipyridine, 4,4'dimethylbipyridine, 4,4' dicarboxylic-2,2'bipyridine. In this Figure, it is observed that the half-wave potential of signal I is not modified significantly by the ruthenium bipyridine concentration, which indicates that the association of Q$^{\cdot}$ with this complex is not important. Contrasting with this result, the half-wave potential of signal II related to the oxido-reduction of Q$^{2\cdot}$ is shifted toward less negative values when the ruthenium bipyridine concentration is increased. The shift observed in first reduction peak is negligible but quite significant in second reduction peak. The positive shift increases from -0.86 V to -0.80V and -0.75V and -0.74V (Figure 4.16) smoothly with increase in concentration of complex without disturbing symmetry of the voltammograms, which indicates the absence of protonation of the semiquinone and the quinone dianion. In the case of $[\text{Ru(dmbpy)}_{3}]^{2+}$, the reduction signal I and II move towards
more negative potential (Figure 4.17) due to the greater basicity, from -0.89 V to -0.97 V, -1.0 V, -1.02 V, -1.05 V smoothly with increase in concentration of complex. In [Ru(dcbpy)$_3$]$^{2+}$, the signals move towards more negative potential from -0.83 V to -0.88 V, -0.99 V, -1.03 V (Figure 4.18) with increasing the concentration of complex. The Ruthenium(II) complexes used (Scheme 4.1) have the following increasing basicity strength on the basis of the substituents attached with ruthenium complex,

\[[\text{Ru(dmbpy)}_3]^{2+} > [\text{Ru(bpy)}_3]^{2+} > [\text{Ru(dcbpy)}_3]^{2+} \text{ and } [\text{Ru(dmphen)}_3]^{2+} > [\text{Ru(phen)}_3]^{2+} > [\text{Ru(dcphen)}_3]^{2+}\]

A systematic decrease in positive shift is followed by BQ with bipyridyl and pheanthroline complexes according to decreasing trend of their basicity. In the case of phenanthroline series, the reduction peaks of BQ (shown in the Figures 4.20-4.23) 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, 4,7dicarboxylic 1,10 phenanthroline, 4,7dimethyl 1,10phenanthroline.

For the given complexes, the shift is much larger for the second reduction step as compared to first step. The magnitude of this shift ranges from 80 mV to 110 mV. The effects of less basic ruthenium complexes are different only in magnitude of positive shift but similar qualitatively. This will be enlightened in quantitative data of hydrogen bonding. 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 [Ru(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 hydrogen bonding and the strength of hydrogen bonding 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. This specific interaction is nothing but hydrogen-bonding.

4.5.2 Quantitative Treatment of Intermolecular Hydrogen Bonding Interaction:

For quantitative treatment of intermolecular hydrogen bonding interaction the following reaction scheme is adopted as given by previous workers\(^{60-61}\).

\[
\text{Q} + e^- \longleftrightarrow Q^- \\
Q^- + n [\text{Ru}(\text{NN})_3]^{2+} \longleftrightarrow Q^- ([\text{Ru}(\text{NN})_3]^{2+})_n \\
Q^- (\text{Ru}(\text{NN})_3)^{2+})_n + e^- \longleftrightarrow Q^- (\text{Ru}(\text{NN})_3)^{2+})_n \\
Q^- (\text{Ru}(\text{NN})_3)^{2+})_n + (m-n)[\text{Ru}(\text{NN})_3]^{2+} \longleftrightarrow Q^- (\text{Ru}(\text{NN})_3)^{2+})_m
\]

Peover and Davis interpreted these reactions in terms of cation-anion association equilibrium. By analogy with their treatment and as proposed by Gupta and Linschitz,\(^{60}\) for first reduction step, we have

\[
E_{1/2} = E^0_{1/2} + (RT/F) \ln (1 + K_{eq}^{(1)} [\text{Ru}^{2+}]^n \quad (4.4)
\]

where \(E^0_{1/2}\) is the half-wave potential of BQ in the absence of metal complex and \(K_{eq}^{(1)}\) is the equilibrium constant for first reduction step in presence of metal complex. The equation (4.4) can be written as

\[
\Delta E_{1/2} = n (RT/F) \ln [\text{Ru}^{2+}] + (RT/F) \ln K_{eq}^{(1)} \quad (4.5)
\]

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ΔE_{1/2} is the difference between the electrochemical potentials for BQ reduction at a
given [Ru(NN)_{3}]^{2+} concentration above 0.0 mM and the potential at [Ru(NN)_{3}]^{2+} = 0
mM. The factor ‘n’ represents the number of [Ru(bpy)_{3}]^{2+} molecules per BQ^{-}
monoanion. If Keq^{(1)}[Ru(NN)_{3}]^{2+} ≥ 1 then a plot of ΔE_{1/2} vs. log [Ru(NN)_{3}]^{2+}
should give a straight line with slope 2.303nRT/F, from which the value of n can be
estimated. The equilibrium constant for the first reduction step can be estimated from
intercept or rearranging equation 4.4 to obtain,

\[ \exp(f \Delta E_{1/2} ) = 1+ Keq^{(1)} [Ru^{2+}]^{n} \]  \hspace{1cm} (4.6)

Where \( f = F/RT \), \( \Delta E_{1/2} = E_{1/2} - E_{0}^{1/2} \).

Using the same analogy, for hydrogen bonding equilibrium of second reduction step,
we have

\[ \exp(f \Delta E_{1/2} ) = (1+Keq^{(1)} [Ru^{2+}]^{m}) / (1+Keq(1) [Ru^{2+}]^{n}) \]  \hspace{1cm} (4.7)

Where m and Keq^{(2)} are the number of molecules of [Ru(NN)_{3}]^{2+}
hydrogen bonded to Q^{2-} and corresponding equilibrium constant respectively. For
strong hydrogen bonding neglecting “1” in numerator and denominator, we can write
the eqn (4.7)

\[ \Delta E_{1/2} = 1/ f \ln (K_{eq}^{(2)}/K_{eq}^{(1)}) + (m - n) \ln [Ru^{2+}] \]  \hspace{1cm} (4.8)

Substituting ‘n’ from the earlier calculation in equation (4.8) values and by plotting
\( \Delta E_{1/2} \) vs. log [Ru(bpy)_{3}]^{2+} ‘m’ may be calculated. Keq^{(2)} can be determined from
the intercept of the plot or it may be calculated directly from equation (4.8).
Figure 4.16 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of Ru (bpy)$_3^{2+}$ (a) 0.0 (b) 4 X 10$^{-5}$ (c) 8 X 10$^{-5}$ (d) 1 X 10$^{-4}$ (e) 1.6 X 10$^{-3}$M in acetonitrile.
Figure 4.17 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of Ru (dmbpy)$_3^{2+}$ (a) 0.0 (b) 1 $\times 10^{-5}$ (c) 4 $\times 10^{-5}$ (d) 6 $\times 10^{-5}$ (e) 1 $\times 10^{-4}$ (f) 4 $\times 10^{-4}$ M in acetonitrile.
Figure 4.18 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of Ru (dcbpy)$_{2+}$ (a) 0.0 (b) 2 X 10$^{-5}$ (c) 4 X 10$^{-5}$ (d) 6 X 10$^{-5}$ (e) 8 X 10$^{-5}$ M in acetonitrile.
Figure 4.19 Plots of $\Delta E_{1/2}^{(2)}$ vs a) log $[\text{Ru(bpy)}_3]^{2+}$ b) log $[\text{Ru(dcbpy)}_3]^{2+}$ for BQ in AN
Figure 4.20 Plot of $\Delta E_{1/2}^{(2)}$ of BQ vs log $[\text{Ru(dmbpy)}_3]^{2+}$ in AN.
Table 4.3 Electrochemical parameters for hydrogen-bonding of 1,4 benzoquinones in presence of [Ru (NN)$_3$]$^{2+}$ Complexes in acetonitrile medium. Values obtained from linear fit to experimental data of $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$ as a function of ln [Ru (NN)$_3$]$^{2+}$, according to Equation 4.5.

<table>
<thead>
<tr>
<th>BQ+complex</th>
<th>n</th>
<th>$K_{eq}^{(1)}$, M$^n$</th>
<th>m</th>
<th>$K_{eq}^{(2)}$, M$^m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>0.8</td>
<td>5.7 $\times$10$^3$ M$^{-0.8}$</td>
<td>3</td>
<td>6.5$\times$10$^{10}$ M$^{-3}$</td>
</tr>
<tr>
<td>[Ru(dmbpy)$_3$]$^{2+}$</td>
<td>1.3</td>
<td>8.2$\times$10$^6$ M$^{-1.3}$</td>
<td>3.2</td>
<td>9.4$\times$10$^{12}$ M$^{-3.2}$</td>
</tr>
<tr>
<td>[Ru(dcbpy)$_3$]$^{2+}$</td>
<td>1.0</td>
<td>1.1$\times$10$^5$ M$^{-1.0}$</td>
<td>3.5</td>
<td>3.56$\times$10$^{18}$ M$^{-3.5}$</td>
</tr>
<tr>
<td>[Ru(phen)$_3$]$^{2+}$</td>
<td>1.07</td>
<td>5.25$\times$10$^5$ M$^{-1.07}$</td>
<td>1.7</td>
<td>1.9$\times$10$^{9}$ M$^{-1.7}$</td>
</tr>
<tr>
<td>[Ru(dmphen)$_3$]$^{2+}$</td>
<td>1.2</td>
<td>1.9$\times$10$^6$ M$^{-1.2}$</td>
<td>2.4</td>
<td>6.15$\times$10$^{11}$ M$^{-2.4}$</td>
</tr>
<tr>
<td>[Ru(dcphe)$_3$]$^{2+}$</td>
<td>1.03</td>
<td>6.9 $\times$10$^6$ M$^{-1.0}$</td>
<td>3.3</td>
<td>1.1$\times$10$^{22}$ M$^{-3.3}$</td>
</tr>
</tbody>
</table>

Units of $K_{eq}^{(1)}$ = M$^n$ and $K_{eq}^{(2)}$ = M$^m$
Figure 4.21 Cyclic Voltammograms of 1,4-benzoquinone with increasing concentrations of Ru (phen)$_3^{2+}$ (a) 0.0 (b) 2 X 10$^{-5}$ (c) 4.5X 10$^{-5}$ (d) 6 X 10$^{-5}$ (e) 8 X 10$^{-5}$ M in acetonitrile.
Figure 4.22 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of Ru (dmphen)$_{3}^{2+}$ (a) 0.0 (b) 2 X $10^{-5}$ (c) 4 X $10^{-5}$ (d) 8 X $10^{-5}$ (e) 1.2 X $10^{-4}$ (f) 1.4 X $10^{-4}$ M in acetonitrile.
Figure 4.23 Cyclic Voltammograms of 1, 4-benzoquinone with increasing concentrations of Ru (dephen)$_3^{2+}$ in the range[0- 2 X 10^{-4} M] in acetonitrile.
Figure 4.24 Plots of $\Delta E_{1/2}^{(2)}$ vs a) log $[\text{Ru (phen)}_3^{2+}]$ b) log $[\text{Ru(dmphen)}_3^{2+}]$ c) log $[\text{Ru (dcphen)}_3^{2+}]$ for BQ in acetonitrile using the data obtained.
$K_{eq}^{(2)}$ varies with the substituents present in the ruthenium complex. From the table 4.3, it can be seen that $K_{eq}^{(2)}$ is higher for electron withdrawing groups due to hydrogen bond formation than electron donating groups. In the $[\text{Ru(bpy)}_3]^{2+}$ concentration interval from 0 to $1 \times 10^{-4}$M, the maximum number of associated species of $Q^{-}$ is 0.8 (Table 4.3). However, since the values of the $K_{eq}^{(1)}$ association constants are less than 300, the association processes between $Q^{-}$ and $[\text{Ru(bpy)}_3]^{2+}$ are not really quantitative. Considering the association of $Q^{2-}$ with $[\text{Ru(bpy)}_3]^{2+}$ within the same concentration interval, the number of $[\text{Ru(bpy)}_3]^{2+}$ molecules that can be associated is between 1 and 6. Since the values of $K_{eq}^{(2)}$ 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 $Q^{-}/Q^{2-}$ couple. Data from Figure (plot 4.19) were analyzed to determine the number of molecules associated with $Q^{-}$ and $Q^{2-}$. At concentrations above 0.01M, a linear regression analysis, based on Equation 4.3, demonstrated that the approximate number of molecules associated with $Q^{-}$ is 0.8 and $Q^{2-}$ is 3 that the association constant, $K_{eq}^{(1)}$ is approximately $5.7 \times 10^3$ M$^{0.8}$ and $K_{eq}^{(2)}$ is $6.5 \times 10^{10}$ M$^{-3}$ respectively. $K_{eq} (BQ^{2-})$ represents a cumulative association constant for the binding of 3 $[\text{Ru(NN)}_3]^{2+}$ molecules per benzoquinone monoanion. When calculating a mean association constant per individual $[\text{Ru(bpy)}_3]^{2+}$ molecule, one obtains ($6.5 \times 10^{10}$ M$^{-1/3})^{1/3} = 4.02 \times 10^3$ M$^{-1}$. Thus, we may conclude that reduction of $BQ^{-}$ to $BQ^{2-}$ increases the number of $[\text{Ru(bpy)}_3]^{2+}$ molecules that are hydrogen-bonded to a given benzoquinone moiety from 1 to 3, and at the same time the (mean) binding constant per $[\text{Ru(NN)}_3]^{2+}$ molecule increases from $\sim$1 to $4.02 \times 10^3$ M$^{-1}$. In other words, not only are there more $[\text{Ru(NN)}_3]^{2+}$ molecules that bind to $BQ^{2-}$ than to charge-neutral BQ, but also the individual $[\text{Ru(NN)}_3]^{2+}$ molecules bind significantly more tightly. It
is evident from the tabulated data (Table 4.3) 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 hydrogen bonding is manifested well from large values of $K_{eq}^{(2)}$. The only difference is that the values of $m$ and $K_{eq}^{(2)}$ are quite large as compared to $n$ and $K_{eq}^{(1)}$ respectively. The large values of $K_{eq}^{(2)}$ confirm the strong interaction of $Q^2-$ and $[Ru(NN)_3]^{2+}$ 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 $[Ru(NN)_3]^{2+}$ as given in Figures(4.19, 4.20 and 4.24). In this work, it is proposed that the hydrogen bonding association between the $Q^-\$ and $Q^{2-}$ species with a hydrogen bond donor (DH) occurs over successive steps which occurs in a wide range of the DH concentration. According to this model we established a method to determine the thermodynamic parameters characterizing those association processes. The method proposed here allows evaluation of the number of hydrogen bond donor molecules associated to the acceptor species over a broad range of donor concentration. Considering that the association processes are successive, this method also permits evaluation of the association constant values, $K_{eq}^{(2)}$, for each step. By analyzing the half-wave potential variations according to DH concentration, we determined the association constants for the $Q^-\$ and $Q^{2-}\$ species with the different ruthenium(II) complexes studied here. The more $K_{eq}^{(2)}$ value of carboxylic bipyridine and phenanthroline of ruthenium(II) complexes were attributed to the formation of intermolecular hydrogen bonding, not protonation takes place as there is no loss in reversibility by the addition of RuII complex. Since the potential shift moves towards less positive potential, there is an intermolecular weak hydrogen bond formation takes place.
4.6 Steric Effect

In this section, we explain the synthesis of Ruthenium(II) complexes with sterically hindering methyl substituted 2,2’-bipyridine and methyl substituted 1,10-phenanthroline ligands and the steric effect of these substituents on redox reaction of the complexes. The data of absorption, emission and association constant for substituted complexes have been shown in the table 4.1 along with unsubstituted complexes for the purposes of comparison. The $K_{eq}$ value observed for Ru(dcbpy)$_3^{2+}$ and Ru(dcphen)$_3^{2+}$ is higher than the other [Ru(NN)$_3$]$_{2+}$ complexes. This is because the presence of carboxyl groups in the ligand make the Ru(II) complex bulky compared to the parent complex [Ru(bpy)$_3$]$_{2+}$, and Ru(phen)$_3^{2+}$ respectively. As expected the product yields were lowest for the most sterically hindering dimethyl-substituted ligands with the rigid ring system of phenanthroline giving lower yields than bipyridine (Table 4.3). The most probable explanation for this observation is that the complex containing –COOH group in the bipyridine ligand is able to form hydrogen bonding with the acceptors (quinones). The anion radical formed due to the electron transfer from Ru(dcbpy)$_3^{2+}$ to quinone is stabilized by the intermolecular hydrogen bonding. This type of stabilization of radical intermediate through hydrogen bonding has been well established in recent years.62

4.7 Conclusion

In this chapter, a comprehensive study was carried out to investigate the hydrogen bonding in potential of 1,4-benzoquinone. BQ studied in acetonitrile showed well separated two reduction and two oxidation peaks. In general the first reduction step is reversible in BQ while second reduction step is reversible or at least quasi-reversible. In the electrochemistry of quinones in neutral aprotic solvents,
hydroxylic additives cause such large effects at such low concentrations that specific interactions between additives and quinone species must occur. Continuous shifts in potential with no change in wave height, reversibility, or appearance of new waves indicate hydrogen-bonding of reduction products. Reduced species of 1,4-benzoquinone (BQ) interact with the Ru(II) complexes by means of hydrogen bonding and/or protonation processes. Addition of Ru(II) complexes (additives) with such low concentrations, cause a systematic positive shift in the redox waves of the quinones. This shift is attributed to specific interaction, hydrogen-bonding, between anions and dianions of quinones with the added complexes. The resulting anodic shift is very small in the first wave but sufficiently 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. Hydrogen-bonding interaction was found to be increased with the increasing basicity of quinones within a series. The Ru(dcbpy)$_3^{2+}$ interacts weakly with semiquinone ($Q^·$) and strongly with the dianion ($Q^{2-}$). This interaction takes place by hydrogen bonding between the COOH group of dcbpy and the negatively charged oxygen atoms of the reduced species of BQ.

Quantitative analysis was made in terms of electrochemical hydrogen-bonding parameters, $n$, $m$ and $K_{eq}$. It was found that the values are in good agreement with the positive shifting observed in Cyclic Voltammograms in a given quinone-complex couple. The more $K_{eq}^{(2)}$ value of carboxylic acid of bipyridine and phenanthroline of Ruthenium(II) complexes were attributed to the formation of intermolecular hydrogen bonding, not protonation takes place as there is no loss in reversibility by the addition of Ru(II) complex. Since the potential shift moves towards less positive potential, there is an intermolecular weak hydrogen bond formation takes place. The
experimental evidence suggests that in the specific case of our benzoquinone electron/proton acceptors the overall process takes place in consecutive electron transfer, hydrogen-bonding re-equilibration steps. This is similar to the redox chemistry of the quinone at the end of the electron transfer cascade in photosynthetic reaction centers of bacteria, where the first reduction step is a pure electron transfer reaction that is conformationally gated, and only subsequently is there fast proton transfer re-equilibration coupled to reduction by a second equivalent\textsuperscript{63}. 
4.8 References

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