Chapter 6

Quinones in Imidazolium based Room Temperature Ionic Liquids: An Electrochemical Investigation

Prelude

This chapter presents voltammetric investigations on quinone-hydroquinone redox couple in \( {\text{1--butyl--3--methylimidazolium tetrafluoroborate (}}{\text{[BMIM][BF}}_4{\text{]}} \) and \( {\text{1--butyl--3--methylimidazolium hexafluorophosphate ([BMIM][PF}}_6{\text{]}} \) room temperature ionic liquids (RTILs). It is proposed that while in dry RTILs, electron transfer reaction is of simple EE type, in presence of proton donor/acceptor the electron transfer is followed by proton transfer (ECEC). A significant finding is that the thermodynamic and kinetic aspects of electron transfer depend on the nature of both cation and anion of the RTIL. The differences are ascribed to the viscosity and stabilization of electrogenerated species by the constituent ions of RTILs. The electroanalytical utility of quinone/hydroquinone electrochemistry for estimation of base concentration in RTILs is presented. The chapter also includes a brief discussion about voltammetric investigations, aimed to probe the potential use of \( {\text{Pd}}^{2+} \) plus benzoquinone in \([\text{BMIM}][\text{BF}_4]\) as green alternative to Wacker type catalytic systems.
6.1 (A) Mechanistic, Kinetic and Electroanalytical Aspects of Quinone – Hydroquinone Redox System in N–alkylimidazolium Based Room Temperature Ionic Liquids

6.1.1 Introduction

Room temperature ionic liquids (RTILs) continue to be an attractive choice as green and recyclable solvents for electroanalysis, electrosynthesis and other electrochemical investigations [1–4]. Structural organization prevailing in RTIL bulk and that confined to interfaces [5, 6] makes them a suitable solvent system with potential to mimic circumambiency of electron transfer sites in biological systems. Though features like tunable physicochemical characteristics, high thermal stability, ability to dissolve wide range of organic and inorganic substrates, stereoselective interactions of constituent ions with electrogendated species and above all the eco-green characteristics of RTILs, have attracted considerable attention [3, 4, 7–9], their use for understanding mechanism of electron transfers in living systems remains underexplored. Electrochemistry of quinones, which are well represented in biological systems: playing key roles in the photosynthetic reaction center, mitochondrial ATP synthesis, as essential part of vitamins [10–12] etc. seems to be a good choice, to be investigated in this regard. Quinones in many of their biological roles act as electron gates in structured hygroscopic environments, thus exploration of their electrochemical behavior in low water-content, structured solvents like RTILs will be very informative for comprehending certain aspects of bio-electron transfers. Complete understanding about redox behavior of quinones demands comprehensive exploration of environmental impact and RTILs present a unique situation to test the role of charge, size, intermolecular interactions and polarizability of ions on their redox characteristics without the complication of solvent effects. Moreover, the industrial [13, 14], synthetic [15] and pharmaceutical [16] uses of quinones, besides their role as model redox systems for broad understanding of organic redox chemistry and environmental impact on heterogeneous electron transfer [17–19], motivated us to explore their redox behavior in RTILs.

Cyclic voltammetry (CV), chronoamperometry (CA), chronocoulometry (CC) and differential pulse voltammetry (DPV) were used to probe mechanistic, kinetic and electroanalytical aspects of quinone/hydroquinone redox system in the 1-butyl-3-methylimidazoilum...
terafuoroborate ([BMIM][BF$_4$]) and 1-butyl-3-methylimidazoilum hexafluorophosphate ([BMIM][PF$_6$]).

6.1.2 Experimental section

Chemicals

Chemicals used were of analytical (AR) grade. Hydroquinone (H$_2$Q), acetonitrile (ACN), ethyl acetate (EA), HPLC grade dichloromethane (DCM), sodium bicarbonate (NaHCO$_3$) and sodium sulfate (Na$_2$SO$_4$) were purchased from Merck, India. 1-methylimidazole, 1-chlorobutane, tetrafluoroboric acid (42% aqueous solution of HBF$_4$) and hexafluorophosphoric acid (62% aqueous solution of HPF$_6$) were procured from Spectrochem India. 1,4-benzoquinone (BQ) was synthesized in the laboratory as per the published procedure [20]. Briefly, 3.3 g (33 mmol) of H$_2$Q was dissolved in 15 mL of 60% acetic acid, the mixture was cooled to about 0-5 °C in an ice bath. 4.2 g (42 mmol) CrO$_3$ was separately dissolved in 7 mL of water and 3 mL of glacial acetic acid. The resulting solution was added to the chilled hydroquinone solution slowly with constant stirring to prevent temperature rise above 5 °C. Reaction mass was stirred further for 70 minutes at the same temperature. The product was filtered, washed with 2-3 mL ice cold water several times. Bright yellow crystals of BQ were obtained (yield 60%) and tested for purity by the melting point measurement. The crystals being light sensitive were stored in dark colored sample vials. Fresh samples of RTILs were synthesized, purified and dried for electrochemical investigations, the details of the procedures are reported elsewhere [9].

Electrochemical measurements

All electrochemical measurements were performed in a specially designed water-jacketed three electrode setup glass cell with a 2 mL electroanalyte solution requirement and having accessories for vacuum drying and maintenance of inert atmosphere by purging high quality Ar gas. Temperature of the cell was controlled with an accuracy of ± 0.1 °C through circulation of water from water bath. Electrochemical measurements were performed with Metrohm PGSTAT100 Potentiostat/Galvanostat using 2 mm diameter glassy carbon (GC) as working, Pt mesh as counter and Ag wire as quasireference (QRE) electrode respectively. Cleaning of the electrodes and standardization of geometric area for
working electrode was performed as reported earlier [9]. All care was taken in cleaning and maintenance of inert thermostated conditions within the electrochemical setup. In-built positive feedback circuitry in the electrochemical work station was used to evaluate and compensate the solution resistance. Measurements were performed at relatively high electroanalyte concentrations (≥ 20 mM) in view of high viscosity of RTILs. All cyclic voltammetric data were background corrected prior to the analysis. Numerical calculations and data fitting was performed through codes written in, Origin 6.0 (Microcal Software Inc.).

6.1.3 Results and Discussion

Mechanistic aspects of BQ/H₂Q redox couple

Figure 6.1: Cyclic voltammogram recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF₄] at 298 K. The scan rate was 100 mVs⁻¹.

Figure 6.1 represents a typical CV recorded at GC electrode for 20 mM BQ in [BMIM][BF₄], dried under extreme conditions. The CV shows two cathodic peaks (C1, C2) and two anodic peaks (A1, A2). From peak clipping experiments it was established that, while peak A1 is correlated to peak C1, the peak A2 arises on account of species generated at C2. This behavior is typical for quinones in dry, neutral and aprotic media [18]. To establish the nature of intermediates formed during the electron transfer process, voltammetric behavior of quinone-hydroquinone redox couple was explored. As per literature reports [21, 22, 25], the electron transfer reactions of quinone and hydroquinone,
depending upon the prevailing conditions can occur through one of the pathways represented in $3 \times 3$, nine species array, as in scheme 1.

**Scheme 1.** $3 \times 3$ square scheme depicting possible electron pathways for quinone/ hydroquinone redox couple.

In the RTIL C2-H proton is considered most acidic but it has a very high $pK_a$ value of 23.0 [23, 24], that rules out any proton transfer by RTIL to the electrogenerated species from p-benzoquinone. The reported $pK_a$ values for $QH^+$ ($-7$) and $QH^{2+}$ ($\leq -7$) [26], rule out the possibility of protonated forms of BQ as intermediates, even if traces of water are left in RTIL. Hence, there remain only four possible pathways to account for the two electron reduction voltammogram depicted in Figure 6.1. To identify the followed

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**Figure 6.2:** Cyclic voltammograms recorded on GC electrode for (A) $H_2Q$ (B) $H_2Q$ in presence of ammonia (C) BQ (D) BQ in presence of propanoic acid, in [BMIM][BF$_4$]. The CVs were recorded at 298 K and the scan rate was 100 mVs$^{-1}$.
H$_2$Q in presence and absence of a proton acceptor (ammonia), were recorded and the same are depicted in Figure 6.2. As clear from Figure 6.2, the peaks in CV of BQ (in absence of propanoic acid-trace C) and H$_2$Q (in absence of ammonia-trace A) do not match each other, implying that different intermediates are produced in their redox cycle. However, comparison of CV for BQ in absence (trace C) and in presence of propanoic acid (trace-D) shows that in presence of a proton donor, a single pair of peaks instead of two pairs is observed. Comparison of traces C and D in Figure 6.2 also reveals that, though cathodic peak shifts positively in presence of propanoic acid, the peak to peak separation is much greater than in absence of propanoic acid. From thermodynamic and kinetic perspectives of electron transfer, these comparative features in CVs imply that, though the electron transfer in presence of propanoic acid is thermodynamically easier, overall kinetics of electron transfer is quite sluggish. Such sluggish nature of the electron transfer in light of the Laviron’s analysis [25, 26], implies that in presence of propanoic acid, electron transfer in BQ is associated with proton transfer from acid to the electron transfer products. The proton transfer shifts the equilibrium potential for the overall reaction positively and the equilibrium requirement as such demands current flow at potentials prior to E°, for which facile kinetics of electron transfer will be a prerequisite. Since electron transfer process for quinones is inherently slow, current does not flow until the potential is significantly negative to E°. The resulting significant over potential due to rapid protonation equilibria, will hence lead to sluggish kinetics of electron transfer in presence of propanoic acid. As expected, addition of electrons to quinone structure will increase the electron density on oxygen atoms, thereby increasing the basicity of the overall molecule. Thus pK$_a$’s of p-benzoquinone will be higher than that for semiquinone. Hence it may be argued that while in RTIL the overall electron transfer follows EE mechanism (top horizontal row of scheme-1), in presence of propanoic acid the electron transfer is followed by proton transfer (ECEC). Thus in presence of proton donor, after single electron reduction of Q to Q$^*$, the later is protonated to form QH$^*$. QH$^*$ being easily reducible, is reduced at the potential of the first wave to produce QH$^-$, which gets protonated to form QH$_2$. Thus the overall two electron-two proton transfer in presence of proton donor, proceeds through the scheme:
Ease of reduction of \( \text{QH}^\bullet \) is responsible for a single reductive peak (trace D) rather than a pair (trace C) as observed in absence of proton donor. This justification is also attested by our observations about the redox behavior of \( \text{H}_2\text{Q} \). In presence of ammonia (a proton acceptor - concentration less than twice the concentration of \( \text{H}_2\text{Q} \)), the CV of \( \text{H}_2\text{Q} \) shows two sets of peaks (trace B) instead of the single set that is observed in its absence (trace C). Interestingly, the position of the new set of peaks generated for \( \text{H}_2\text{Q} \) in presence of ammonia matches well the peak set for BQ in presence of proton donor. We also observed that in presence of excess ammonia (concentration equal to or more than twice the concentration of \( \text{H}_2\text{Q} \)), only one set of peaks that matches the CV peaks for BQ in presence of proton acceptor is observed. Thus, it may be argued that in presence of proton acceptor for \( \text{H}_2\text{Q} \) and proton donor for BQ, same intermediates are involved in the redox cycle and in their absence a different set of intermediates is involved. To sum up, the thermodynamic behavior predicts that the redox behavior of BQ in absence of proton donor is quite different than redox behavior of \( \text{H}_2\text{Q} \) in absence of proton acceptor (a weak base). However, in presence of proton donor for BQ and proton acceptor for \( \text{H}_2\text{Q} \), the redox behavior of the two match i.e. BQ and \( \text{H}_2\text{Q} \) are coupled under these conditions. The kinetic features associated with the CVs recorded under these conditions viz. shifting of the oxidative wave positively for quinone (thermodynamically easier), but with an increase of peak to peak separation (kinetically sluggish) indicate that electron transfer is followed by proton transfer [25, 26]. These features in the CV make us to propose that in presence of proton donor in case of BQ and proton acceptor in case of \( \text{H}_2\text{Q} \), it is not the CE mechanism as proposed earlier [27], but EC mechanism that operates. The presence of proton acceptor for \( \text{H}_2\text{Q} \) and proton donor for BQ leads to their conversion to BQ and \( \text{H}_2\text{Q} \) respectively, through ECEC mechanism during redox cycling. On the basis of above mentioned observations, we propose, in pure and dry RTILs, the BQ and \( \text{H}_2\text{Q} \) follow purely electron transfer pathways i.e., top and bottom pathway of scheme 1.

\[
\begin{align*}
Q + e^- & \longleftrightarrow Q^{\bullet -} \quad (6.1) \\
Q^{\bullet -} + H^+ & \longleftrightarrow QH^\bullet \quad (6.2) \\
QH^\bullet + e^- & \longleftrightarrow QH^- \quad (6.3) \\
QH^- + H^+ & \longleftrightarrow QH_2 \quad (6.4)
\end{align*}
\]
but in presence and absence of proton donor and acceptor, electron transfer is associated with proton transfer as depicted in scheme 2. Similar behavior has been earlier reported for BQ/H₂Q couple in buffered as well as unbuffered aqueous media, wherein the proton donor/acceptor concentration is greater than [BQ] and [H₂Q] [28].

**Scheme 2.** Mechanistic pathways for; Hydroquinone and quinone redox couple in [BMIM][BF₄] and [BMIM][PF₆].

After establishing the mechanism of electron transfer, our next aim was to unravel the kinetic and thermodynamic aspects of the oxidative and reductive electron transfers for hydroquinone and quinone in the RTILs.

**Hydroquinone in [BMIM][PF₆] and [BMIM][BF₄]**

Figure 6.3 shows CV recorded for 25 mM Hydroquinone in [BMIM][PF₆] at the GC electrode. A gap of 530 mV on potential scale between the anodic peak A1 and its associated cathodic peak C1 and other CV characteristics are an indication of an irreversible electron transfer [29, 30]. Similar behavior has been reported for H₂Q in acetonitrile [31, 32] and propylene carbonate [33]. In the segment a-b, the rate constant of electron transfer is very small and consequently the capacitive current is observed. In the segment b-A1, the rate constant varies exponentially with the potential and so does the current, while in region A1-c current falls due to increase in diffusion layer thickness. In the region c-d, the oxidative current falls slowly on account of progressive exhaustion of H₂Q concentration, while in the region d-e the fall in rate constant due to potential decrease leads to decrease in the current. In the CV, the regions b-A1-c and e-C1-f represent the
potential/diffusion dependent electron transfer for processes;

\[ H_2Q - 2e \rightarrow H_2Q^{2+} \]  \hspace{1cm} (6.5)

\[ H_2Q^{2+} + 2e \rightarrow H_2Q \]  \hspace{1cm} (6.6)

respectively. CVs were recorded at changing scan rates from 50-1000 mVs\(^{-1}\), which are depicted in Figure 6.4. Linear dependence of peak current in the CVs on the square root of scan rate for both peaks in the entire scan rate range investigated (inset Figure 6.4), imply a diffusion controlled process. Similar features were seen in the CVs recorded for
H$_2$Q in [BMIM][BF$_4$], however the peak positions were shifted more positive to those observed in [BMIM][PF$_6$]. Double potential step chronocoulograms were recorded to estimate the diffusion coefficients and to look into adsorption if any of H$_2$Q and its oxidized form H$_2$Q$^{2+}$. The Anson plot corresponding to charge-time transients recorded during chronocoulometric investigations is shown in Figure 6.5. As clear from the intercepts there seems to be no adsorption of H$_2$Q or H$_2$Q$^{2+}$ during the redox process. The Cottrell plot for the forward and reverse steps led to diffusion coefficient values of $6.72 \times 10^{-7}$ and $2.6 \times 10^{-7}$ cm$^2$s$^{-1}$ for H$_2$Q and H$_2$Q$^{2+}$ respectively. The diffusion coefficient is about two orders of magnitude less than that reported for H$_2$Q in ACN [34], which can be attributed to high viscosity of the RTIL that leads to slower mass transport. The diffusion coefficient of H$_2$Q$^{2+}$ is almost three times less than that of the H$_2$Q perhaps due to electrostatic interactions of former with the RTIL anions. Using Cottrell equation, the chronocoulometric data recorded for H$_2$Q in [BMIM][BF$_4$], gives a value of $1.51 \times 10^{-06}$ cm$^2$s$^{-1}$ for diffusion coefficient of H$_2$Q. This value is an order of magnitude higher than the value estimated in [BMIM][PF$_6$], which can be attributed to higher viscosity of the later. Anodic peak potential vs. log (scan rate) was plotted for the estimation of product of electron transfer coefficient and number of electrons involved in the rate determining step ($\alpha \times n$). From slope of the said plot, $\alpha \times n$ was found to be equal to.
1.08, a value well expected in view of the shape of experimentally recorded voltammogram [30]. For the present case this magnitude of $\alpha \times n$ can be treated as an evidence for the second electron transfer being the rate determining step. For estimation of standard heterogeneous electron transfer rate constant ($k^o$), the LSVs recorded at changing scan rates were convoluted using the algorithm suggested by Lawson and Maloy [35]. The limiting current in convoluted LSVs as shown in Figure 6.6 (inset), was found to be independent of the scan rate, confirming the absence of chemical reactions preceding and succeeding the electron transfer. Using the standard equations valid for the current and the convoluted current of LSVs in irreversible electron transfer [29], the $k^o$ value was found to be $1.06 \times 10^{-6}$ cms$^{-1}$.

**Benzoquinone in [BMIM][PF$_6$] and [BMIM][BF$_4$]**

Figure 6.7 shows CVs recorded for 20 mM BQ in [BMIM][BF$_4$] and [BMIM][PF$_6$] at the GC electrode, exhibiting similar features. Based on the discussion in preceding sections, we assume that the CVs presented in Figure 6.7 correspond to a two-step two-electron pathway for reduction of Q to $Q^{*+}$ at peak C1 which is subsequently reduced to $Q^{2-}$ at peak C2, while $Q^{2-}$ is oxidized back to $Q^{*+}$ at peak A2 which is further oxidized to Q at peak A1. From the CVs in Figure 6.7, it appears (more negative peak potential, greater peak to peak separation, and broader peaks in case of [BMIM][PF$_6$]) that both kinetically and thermodynamically the reduction steps of BQ especially the second one is easier in
Figure 6.7: Cyclic voltammogram recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF$_4$] (red) and [BMIM][PF$_6$] (black) at 298 K. The scan rate was 100 mVs$^{-1}$.

[BMIM][BF$_4$] than in [BMIM][PF$_6$]. As has been reported earlier, both thermodynamics and kinetics of electron transfer in quinones is strongly dependent on the solvent polarity [36], nature and concentration of the supporting electrolyte [37] and presence of acidic additives [38]. Considering the established relationship between electron affinities and $E_{1/2}$ [39] values for quinones, viz.,

$$E_{1/2} = -E_{m+1} + C$$  \hspace{1cm} (6.7)

where $E_{m+1}$ is the energy of lowest unoccupied molecular orbital of quinone and $C$ a measure of difference in solvation energy between the oxidized and reduced forms. In present case where the polarity of the two RTILs does not differ much [40], we ascribe the variations in $E_{1/2}$ to solvent specific solvation energies on account of ion pairing. This is further supported by greater differences in the extent of stabilization of electro-generated species from peak C2 than that from peak C1 in the two RTILs. The observed trend suggests that the imidazolium cations are more effective in stabilizing the negatively charged intermediates of the redox process, in presence of [BF$_4$]$^-$ than [PF$_6$]$^-$ and the dianion is stabilized to greater extent than the monoanion. Similar trend in ion pair stabilization of quinone radical anion and dianion by imidazolium RTILs has been reported by Islam et al. [41].

As evident, the peak height corresponding to second electron transfer (C2) in both RTILs is lesser in comparison to that corresponding to first electron transfer (peak C1). This has
also been reported earlier by many groups for quinones in aprotic media [38, 41]. Dismutation of radical anion to regenerate BQ [42], smaller diffusion coefficient of the electron accepting species for peak C2 [43, 44] and complexation of dianion with BQ [38] have been proposed to be responsible for the said feature in CV. Qualitative analysis of CVs using the peak width measurements \((E_p - E_{p/2})\), for C1-A1 peaks - 60 mV (close to 58 mV as required for a reversible electron transfer) and for C2-A2 - greater than 80 mV (as expected for a quasireversible electron transfer reaction) establishes their reversible and quasireversible redox characteristics respectively. Semiderivative convolution of voltammograms depicted in Figure 6.7, consist of two mirror image peaks corresponding to C1-A1 couple, while two peaks with slight offset in peak potentials, for C2-A2 couple. These voltammetric features establish that the voltammograms in Figure 6.7 correspond to two successive electron transfer reactions in which the first electron transfer is thermodynamically as well as kinetically more facile than that of the second electron transfer. Similar findings have been reported earlier for benzoquinone in nonaqueous aprotic media [38]. Figure 6.8 shows a comparison between the experimentally recorded CV and

![Figure 6.8: Comparison of experimentally recorded cyclic voltammogram recorded on GC electrode for 20 mM BQ in [BMIM][BF_4] (black), at the scan rate of 100 mVs^{-1} to the one theoretically generated (red) with the approximation of \(E_rE_q\) mechanism for two electron transfer.](image)

the one generated theoretically on \(E_rE_q\) mechanism approximation. Good match between the two voltammograms supports our approximation of \(E_rE_q\) type electron transfer reaction. Though there is a good match between the experimental and theoretical CVs, some nonidealities, though minor, are visibly prominent in the experimental CV. The experimental CV shows an extra current at the foot of the first cathodic wave, besides an extra
current between the two successive cathodic peaks. A variety of reasons such as weak adsorption of reactants, edge diffusion, unequal diffusion coefficients of quinone radical anion and dianion and reduction of weakly adsorbed radical anion to strongly adsorbed dianion [45–47] have been put forth to be responsible for such nonidealties.

To have a clear understanding of the overall voltammetric behavior, CVs at changing scan rates from 100 to 1000 mVs$^{-1}$ were recorded and are presented in Figure 6.9. At all scan rates it was found that for peak C1, the peak potential remains almost unchanged and $E_p-E_{p/2}$ value remains in the range as expected for the reversible electron transfer in the entire scan rate range investigated. However, for the peak C2, the peak position significantly moves cathodically with increasing scan rate and the value of $E_p-E_{p/2}$ is in the range of a quasireversible electron transfer process. Quantification of peak characteristic parameters in light of the established theories of heterogeneous electron transfer, was undertaken to unravel the associated kinetic and thermodynamic aspects. Thus it was found that for peaks C1 and A1 in Figure 6.9, the peak current exhibits a linear dependence on the square root of scan rate as shown in inset of Figure 6.9. This implies a diffusional control on the shape of C1-A1 peak pair. However, for the peak C1, the current function $i_p/\nu^{1/2}$ was found to be scan rate dependent as depicted in Figure 6.10, showing a decrease with increase of scan rate. Similar analysis for peak C2 reveals an initial decrease followed by almost constancy of current function with increase of scan rate. Though peak

Figure 6.9: Cyclic voltammograms at changing scan rates recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF$_4$] at 298 K. The scan rate range is from 50 to 1000 mVs$^{-1}$. The inset shows $I_p$ vs square root of scan rate for the peaks C1 and A1 of the recorded CVs.
Figure 6.10: Current function ($\frac{i_p}{v^{1/2}}$) vs. scan rate for peaks C1 and C2 of the CVs recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF$_4$] at 298 K. The scan rate range is from 50 to 1000 mVs$^{-1}$.

Potential for C1 remains almost constant, for peak C2, it shows an initial cathodic shift and then a constant value with increase of scan rate. When we calculated the peak current ratio $I_p$C2/$I_p$C1, it shows an initial decrease followed by a constant value with increase of scan rate, a trend similar to the one observed for variation of peak potential of peak C2. At all scan rates investigated, the ratio $I_p$C1/$I_p$A1 was found to be very close to unity, negating the possibility of EC mechanism for peak C1. However, hydrogen bonding of electrogenerated radical anion and dianion with RTIL constituents can be taken as chemical step following the electron transfer. Similar observation were reported by Hui et al. [48] for vitamin K (napthaquinone derivative) in dry aprotic solvents. In light of these reports, we assume that the above mentioned variations in current functions can be an outcome of complexation reaction of dianion with the starting material [38] and the counter cation [37] in the RTILs as per the reactions:

$$Q^{2-} + Q \rightleftharpoons (Q)_{2}^{2-} \quad (6.8)$$

$$\quad (Q)_{2}^{2-} \rightleftharpoons Q^{*-} + Q^{*-} \quad (6.9)$$

and

$$Q^{2-} + 2[BMIM]^+ \rightarrow Q^{2-}([BMIM]^+)_{2} \quad (6.10)$$

Double potential step chronocoulograms were recorded to estimate the diffusion coefficients and to look into adsorption, if any, of BQ and its radical anion during potential...
scan. The resulting data using Cottrell equation gives diffusion coefficient for benzoquinone as $5.34 \times 10^{-7}$ and $1.70 \times 10^{-6}$ cm$^2$s$^{-1}$ in [BMIM][PF$_6$] and [BMIM][BF$_4$] respectively. The Anson plots for the coulometric data gave similar intercepts for forward and reverse potential steps of C1-A1 couple establishing the absence of BQ or its radical anion adsorption. The formal redox potentials of the two electron transfers were calculated from the average of peak potentials corresponding to peaks C1-A1 and C2-A2 in the semiderivative convoluted voltammograms. The $E_1^o$ and $E_2^o$ were respectively found to be -0.325 and -0.666 V vs. Ag respectively in [BMIM][BF$_4$], a separation of formal redox potentials by about 331 mV. With this much separation, the electrode processes for two electron transfer are always more complicated than the appearance of the voltammogram. In such cases, both heterogeneous electron transfer and homogeneous electron transfer occur and hence disproportionation or conproportionation reactions make the simple EE mechanism more complicated. The thermodynamic probability of disproportionation reaction \( \text{viz.} \)

\[
Q^* + Q^* \rightarrow Q^{2-} + Q
\]

calculated through equation,

\[
K_{dis} = \exp \left( \frac{nF (E_2^o - E_1^o)}{RT} \right)
\]

comes out to be $1.70 \times 10^{-6}$ and $5.28 \times 10^{-7}$ in [BMIM][BF$_4$] and [BMIM][PF$_6$] respectively. The larger magnitude in former may be on account of its lesser viscosity and greater ability to stabilize the dianion than the later. In both cases the magnitude of disproportionation constant is greater than the one reported in acetonitrile and dimethyl-sulfoxide [41], implying a greater stabilization of dianion by RTILs especially by the [BMIM][BF$_4$]. All these observations make us presume that the anomalies in CV current and potential characteristics are on account of dismutation of electrogenerated product from peak C1 and weak binding of radical anion whose reduction gives strongly bound dianion [45]. Using Nicholson’s method [49], from the values of peak separations on potential axis in respective couples, the $k^o$ values for the reduction of quinone to its radical anion and the reduction of radical anion to dianion in [BMIM][BF$_4$] were calculated to be $6.47 \times 10^{-3}$ and $3.59 \times 10^{-4}$ cms$^{-1}$ respectively. These values for the $k^o$ are two orders of magnitude lesser than those reported in ACN and seem low in light of the reversibility characteristics of CV especially for C1-A1 couple. Similar features about heterogeneous
electron transfer in RTILs have been reported earlier [50, 51]. As discussed in chapter 4 of thesis, we propose that slow solvent relaxation dynamics and high viscosity of RTILs is responsible for observed reversibility characteristics of CV with low magnitude of rate constants.

**Electroanalytic utility of H$_2$Q/BQ redox**

We observed an interesting change in CVs recorded for H$_2$Q during experiments aimed to probe the impact of base concentration on redox behaviour of H$_2$Q in [BMIM][BF$_4$]. Development of a new oxidative peak in the CV prior to original peak, as shown in Figure 6.11, was observed in the CVs with the addition of a base (propylamine). With continued addition of base, the height of this new peak increases at the expense of height of original peak and varies linearly with concentration of the base added. For better sensitivity differential pulse voltammograms(DPVs) at changing concentration of added amine were recorded with modulation time of 0.02 s, modulation amplitude 0.06 V and a step potential of 10 mV. The peak height in DPVs (Figure 6.11) was found to be a linear function of the added amine concentration. This feature wherein the H$_2$Q redox behavior seems to be a good indicator of base concentration in the electrolyte solution, seems valuable from analytic point of view. From our observations we recommend the analytic determination of base using hydroquinone redox through the use of DPV rather

![Figure 6.11: Cyclic voltammetric responses of 25 mM H$_2$Q to increasing concentration of propylamine in [BMIM][BF$_4$] at GC electrode. Insert graph: A plot of the anodic peak current (pre-peak) at +0.25 V against the concentration of propylamine](image)
CV method because of greater sensitivity of the former. Though any dry aprotic solvent is expected to be useful for such analysis [33], RTILs seem to provide better choice due to their low volatility and recyclability in such procedures [27].

6.1.4 Conclusion

The redox behavior of quinone-hydroquinone in [BMIM][BF$_4$] and [BMIM][PF$_6$] RTILs was investigated. It was observed that while in absence of proton donor/acceptor species the quinone and hydroquinone undergo a two electron EE transfer reaction, in presence of such species electron transfer is followed by proton transfer and not the reverse as reported earlier. It was also observed that the investigated RTILs stabilize the electrogenerated species to different extents highlighting the solvent specific effects of imidazolium based RTILs. The quinone-hydroquinone redox couple was found to have potential for design of an electroanalytical method for estimation of weak bases.

6.2 (B) Electrochemical Investigations on Pd$^{2+}$ plus Benzoquinone in Imidazolium Based Room Temperature Ionic Liquids: A Step Towards Wacker Catalysis

6.2.1 Introduction

Wacker type catalytic systems serve as efficient and selective means of homogeneous catalysis in many synthetic pathways of organic chemistry [52–54]. In a Wacker system, organic substrates are oxidized by Pd$^{2+}$, which gets reduced to Pd$^0$ in the process. The Pd$^0$ produced during the oxidation process of an organic substrate, is reoxidized to Pd$^{2+}$ by an appropriate oxidant to continue the catalytic cycle. Cu$^{2+}$ is the preferred terminal oxidant in these systems, which is regenerated through use of atmospheric oxygen [55]. Requirement of high chloride ion concentration for the Cu$^{2+}$ regeneration in these systems leads to complications like corrosion of reaction vessel and formation of chlorinated byproducts. These practical complications have stimulated many workers to design some easy to use, chloride free oxidant for Pd$^{2+}$ regeneration in these systems. Use of Keggin type molybdovanadophosphate + Pd$^{2+}$ catalyst systems, which can work in the absence of or at low concentration of chloride has been reported in this regard [56–60]. In these reports, molybdovanadophosphate has been used to oxidize hydroquinone (H$_2$Q) to para-benzoquinone (BQ), which reoxidizes Pd$^0$ to Pd$^{2+}$. In light of our observations regarding
redox behavior of quinones in imidazolium based RTILs, it seems that oxidation of BQ$^{2-}$ in an electrochemical setup can be used for regeneration of BQ to continue the Pd$^{2+}$ catalyzed oxidation of organic substrates by Pd$^{2+}$ plus BQ reagent combination. The use of nonvolatile and easy to recycle RTILs, which ensures the ease of product recovery and solvent recycle in such electrochemical setups, seems to have many advantages over the conventional Wacker systems. In light of above mentioned facts, we investigated the redox behavior of Pd$^{2+}$ and Pd$^{2+}$ plus BQ in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]). The aim of these investigations was to explore the use of Pd$^{2+}$ plus BQ in RTIL based electrochemical setup as an eco-green alternative to conventional Wacker type catalytic systems.

6.2.2 Experimental section

Chemicals

Palladium acetate and palladium chloride were procured from Sigma-Aldrich. Fresh samples of [BMIM][BF$_4$] and BQ were synthesized and purified as mentioned previously.

Electrochemical measurements

All electrochemical measurements were performed using a computer controlled Metrohm PGSTAT100 Potentiostat/Galvanostat in a three electrodes setup. A thermostatted ($\pm$ 0.1 °C) and airtight jacket glass cell having an arrangement to place the electrodes at a distance of 5 mm from one another was designed. Prior to the experiment, the cell was immersed in 2 M HNO$_3$ for 24 hours, rinsed thoroughly with copious amount of Millipore water and dried at 60 °C in an oven. All the measurements were carried out in an inert atmosphere. For that, Ar gas was passed continuously through the solution for ca. 15 minutes. Moreover, the measurements were performed under the Ar blanket. Ag wire (99.9%) and a platinum (99.9%) mesh were used as a quasireference and counter electrode, respectively. Prior to use, these were washed with dilute HNO$_3$ and then rinsed with copious amount of Millipore water. A 2 mm diameter platinum disk electrode (Pt) was used as working electrode (WE). Before its use for electrochemical
measurements, it was cleaned mechanically, chemically and electrochemically. The electrode surface was gently polished over Alumina powder (0.25 µ size) and rinsed with a jet of Millipore water. This mechanical cleaning was followed by ultrasonic washing in 1:1 by volume, ethanol plus water solution and then electrochemical cleaning by scanning potential (scan rate = 0.5 Vs⁻¹), between the anodic and cathodic limits in 0.5 M H₂SO₄ solution. Special care was taken for estimation and compensation of uncompensated resistance through positive feedback circuitry, during electrochemical measurements.

6.2.3 Results and discussion

Figure 6.12: Cyclic voltammograms recorded at Pt electrode (2 mm diameter) in (A) Vacuum dried and Ar gas saturated [BMIM][BF₄] (B) 20 mM palladium chloride in vacuum dried and Ar gas saturated [BMIM][BF₄]. The scan rate was 0.1 Vs⁻¹ and temperature maintained as 298 K.

Figure 6.12(A) depicts three successive CVs recorded at Pt electrode in vacuum dried [BMIM][BF₄] with a scan rate was 0.1 Vs⁻¹. As seen in the CVs, the RTIL shows no electrochemical activity in the investigated potential range. Figure 6.12(B) depicts CV recorded at Pt electrode for 20 mM palladium chloride in [BMIM][BF₄], the scan rate was 0.1 Vs⁻¹. The CV shows two cathodic peaks C1 and C2 besides an anodic peak A1. We used peak clipping approach in CV measurements to establish the interdependency of the peaks in recorded CVs. A set of CVs recorded during these peak clipping studies, is presented in Figure 6.13. As seen from this figure 6.13, the peak A1 arises due to oxidation of species generated in the potential range under peaks C1 and C2. Another feature that needs consideration about these CVs is that, as the cathodic limit of potential scan moves more towards peak C2, the broadness of peak A1 increases. It is also apparent
that when potential scan is restricted to the potential range of peak C1 only, the anodic peak A1 is sharp in appearance (inset Figure 6.13).

Based on these observations we propose that the peak C1 corresponds to two electron reduction of Pd$^{2+}$ to Pd$^{0}$ on the surface of Pt electrode, while peak C2 is due to reduction of Pd$^{2+}$ to Pd$^{0}$ at Pd surface generated at the WE in the potential range under peak C1. Peak A1 is attributed to desorptive oxidation of Pd$^{0}$ to Pd$^{2+}$. Thus it seems, the reduction of Pd$^{2+}$ to Pd$^{0}$ is thermodynamically more facile at Pt surface than at Pd. From the variations in the peak shape and position of A1 with the variations in cathodic limit of potential scans, it seems that thermodynamically as well as kinetically the desorptive oxidation of Pd$^{0}$ to Pd$^{2+}$ is more facile for Pd$^{0}$ adsorbed on Pt surface than at Pd surface.

Figure 6.14 shows CVs recorded at Pt electrode before (trace A) and after addition of 20 mM BQ (trace B) to 20 mM solution of Pd$^{2+}$ in [BMIM][BF$_4$]. Addition of BQ to Pd$^{2+}$ in [BMIM][BF$_4$] results in two additional cathodic peaks C3 and C4 and two additional anodic peaks A/ and A// in addition to the peaks C1, C2 and A1 in the CV recorded when no BQ was added. Besides, while C1 and C2 move slightly towards less negative position, the peak A1 of the original solution is pushed considerably towards more positive potential. Also while there is slight increase in the height of peaks C1 and C2, the peak height of A1 is increased to a large extent. Based on our observations as presented in previous sections, we attribute the peak C3 to reduction of BQ to its radical.
anion (BQ$^{\cdot-}$), and peak C4 to reduction of BQ$^{\cdot-}$ to dianion of BQ (BQ$^{2-}$). The peak A$^\prime$ is attributed to oxidation of BQ$^{2-}$ to BQ$^{\cdot-}$, while peak A$^\prime\prime$ is attributed to oxidation of BQ$^{\cdot-}$ to BQ. From the observed increase in peak height of A1, it seems that the presence of BQ in solution of Pd$^{2+}$ enhances the oxidation reaction of Pd$^0$ to Pd$^{2+}$. Similar observations were made for the solution in which instead of palladium chloride, palladium acetate was used as source of Pd$^{2+}$. We also investigated the variations in peak height of A1 with addition of BQ. We observed that beyond ratio 1:3 (Pd$^{2+}$: BQ), addition of BQ leads to a decrease in peak height of A1, similar observations have been made earlier in aqueous systems [60, 61]. These observations about the investigated system indicate its potential use as substitute to conventional Wacker type catalytic systems in organic synthesis. However, for practical applications detailed studies are needed.

6.2.4 Conclusion

Cyclic voltammetric investigations for Pd$^{2+}$/Pd$^0$ redox couple in [BMIM][BF$_4$] show that addition of benzoquinone increases the oxidative current corresponding to desorption of electrodeposited Pd$^0$ on Pt electrode. These observations show that addition of benzoquinone can enhance the catalytic activity of Pd$^{2+}$ for homogeneous oxidation of organic substrates in [BMIM][BF$_4$].
References


