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Mechanistic, kinetic and electroanalytical aspects of quinone–hydroquinone redox system in N-alkylimidazolium based room temperature ionic liquids

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1. Introduction

Room temperature ionic liquids (RTILs) continue to receive considerable attention from the scientific and industrial communities in general and electrochemists in particular [1-4]. A recent attraction to the RTILs is the structural organization prevailing in their bulk and RTILs confined to interfaces [5,6], that makes them suitable solvent systems 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, stereo-selective interactions of constituent ions with electrogenerated species, and above all the eco-green characteristics of RTILs, have attracted considerable attention [3,4,7-10], their use for understanding mechanism of electron transfers in living systems remains under explored. Electrochemistry of quinones, which are well represented in biological systems: playing key roles in the photosynthetic reaction center, mitochondrial ATP synthesis and as essential part of vitamins [11-13] 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 is expected to be very useful for comprehending many unexplored aspects related to bio-electron transfers. Complete understanding of the

ABSTRACT

Voltammetric investigations of quinone-hydroquinone redox couple in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) room temperature ionic liquids (RTILs) are reported. In dry RTILs, the mechanism is found to be electron transfer followed by electron transfer (EE) type, while in presence of proton donor/acceptor the electron transfer is followed by proton transfer (ECEC). Dependence of the thermodynamic and kinetic aspects of electron transfer on the nature of RTIL is explained in light of the viscosity and stabilization of electrogenerated species. The electronalytical utility of quinone/hydroquinone electrochemistry for estimation of base concentration in RTILs is also presented.

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redox behavior of guinones demands a comprehensive exploration of environmental impact and RTILs present unique media to test the role of charge, size, intermolecular interactions and polariziblity of ions on their redox characteristics without the complication of solvent effects. In this regard few reports with a limited emphasis on kinetic and mechanistic aspects of electron transfer related to the electrochemistry of quinones in RTILs have been published recently [14,15]. Pertinent to mention these reported studies have been carried over metal electrodes (Pt, Au) and it has been well established that both BQ and H₂Q show significant adsorption over these metal surfaces [16-18] that largely affects the electrode kinetics and mechanism. Hence a clear understanding about impact of RTIL specific effects on the redox behavior of BQ/H₂Q system demand comprehensive voltammetric investigations of the said system over electrode surfaces wherein minimal adsorption effects are expected. In view of the reported electrochemical characteristics of glassy carbon electrode (GC) [19], GC seems to be an excellent choice for such studies. In addition to the above cited reasons, the industrial [20,21], synthetic [22] and pharmaceutical [23] uses of quinones, besides their role as model redox systems for broad understanding of organic redox chemistry and environmental impact on heterogeneous electron transfer [24,25,17], motivated us to explore their redox behavior over GC electrode 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-3methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]).

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2. Experimental

2.1. Chemicals

Chemicals used were of analytical (AR) grade. Hydroquinone (H₂Q), acetonitrile (ACN) and ethyl acetate (EA), HPLC grade dichlomethane (DCM), Sodium bicarbonate (NaHCO₃) and sodium sulfate (Na₂SO₄) were purchased from Merck, India. 1-methylimidazole, 1-chlorobutane, tetrafluoroboric acid (42% aqueous solution of HBF_4) and hexafluorophosphoric acid (62% aqueous solution of HPF₆) were procured from Spectrochem India. 1,4-benzoquinone (BQ) was synthesized in the laboratory as per the published procedure [26]. Briefly, 3.3 g (33 mmol) of H₂Q 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) CrO₃ 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 min 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 [9,10].

2.2. Electrochemical measurements

All electrochemical measurements were performed in specially designed jacket glass cell (2 mL capacity) and having a provision for vacuum drying and maintenance of inert atmosphere by purging high purity 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 guasireference (QRE) electrode. For the sake of reliable and reproducible measurements, all care was taken in cleaning and maintenance of inert thermostatted conditions within the electrochemical setup. Inbuilt positive feed back circuitry in the electrochemical work station was used to evaluate and compensate the solution resistance. Measurements were performed at relatively high electroanalyte concentrations (\geq 20 mM) in view of high viscosity of RTILs. Though both BQ and H₂Q have appreciable solubility in the used RTILs, their dissolution kinetics was observed to be very slow. An indirect procedure was followed for the preparation of desired concentrated solutions of BQ and H₂Q in the RTILs. Initially an accurately weighed amount of BQ and H₂Q was dissolved in DCM this was followed by addition of a specific volume from this solution to known volume of RTIL and the removal of DCM under vacuum. All cyclic voltammetric data were background corrected prior to the analysis. Details related to the electrochemical measurements are discussed elsewhere [9,10]. Numerical calculations, convolution analysis and data fitting was performed through codes written in, Origin 6.0 (Microcal Software Inc.) and MATLAB 7.0.4. Digital simulations were carried out with GPES software version 4.9 from Eco Chemie B. V. Ultrecht, Netherland.

3. Results and discussion

3.1. Mechanistic aspects of BQ/H₂Q redox couple

Fig. 1 represents a typical CV recorded at GC electrode for 20 mM BQ in pre-dried [BMIM][BF₄]. The CV shows two cathodic peaks



Fig. 1. Cyclic voltammogram recorded on GC electrode (2 mm diameter) for 20 mM BQ in $[BMIM][BF_4]$ at 298 K. The scan rate was 100 mV s⁻¹.



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

at -0.76 V and -1.11 V (marked as C1, C2) and two anodic peaks at -0.69 V and -1.01 V (marked as A1, A2). From Peak clipping experiments (Fig. S1 in Supporting information) 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 [25]. To establish the nature of intermediates formed in the electron transfer process, quinone–hydroquinone redox couple was explored. The electron transfer reactions of quinone and hydroquinone, depending upon the prevailing conditions, can occur through one of the pathways represented in a 3 \times 3, nine species array [27–29] as in Scheme 1.

The reported pK_a values for QH⁺ (-7) and QH₂²⁺ (\leq -7) [30], do not support the formation of protonated forms of BQ as intermediates even in presence of trace amounts of water in RTIL. Hence, there remain only four possible pathways to account for the two electron reduction voltammogram in Fig. 1. To identify the path followed, CVs for BQ in presence of varying amounts of proton donor (propanoic acid) and for H₂Q in presence varying amounts of proton acceptor (ammonia), were recorded and the same are presented in Fig. S2 in the Supporting information. Representative CVs from these voltammogramms to depict the voltammetric response for BQ in absence/presence of proton donor and for H₂Q in presence/absence of proton acceptor are presented in Fig. 2. As clear from Fig. 2, the peaks of BQ (in absence of propanoic acid-trace C) and H_2Q (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) reveals 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 Fig. 2 also reveals that, though



Fig. 2. Cyclic voltammograms recorded on GC electrode for (A) $H_2Q(B) H_2Q$ in presence of ammonia (30 mM) (C) BQ (D) BQ in presence of propanoic acid (100 mM), in [BMIM][BF₄]. The CVs were recorded at 298 K and the scan rate was 100 mV s⁻¹.

cathodic peak shifts negatively in presence of propanoic acid, the peak separation between the two is much greater than in absence of propanoic acid. Thus, even though $E_{1/2}$ value is still more positive to peak potential, the peak separation is very large. From thermodynamic and kinetic perspectives, these comparative features in CV imply that, though the electron transfer in presence of propanoic acid is thermodynamically easier, the kinetics of the overall process is quite sluggish. Such sluggish nature of the electron transfer in the light of Laviron's analysis [29,30] implies that in presence of propanoic acid, electron transfer in BQ is associated with proton transfer from the 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^0 , for which facile kinetics of electron transfer is a prerequisite. Since the electron transfer process for quinones is inherently slow, current does not flow until the potential is significantly negative to E⁰. 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 is observed in the recorded CVs. As expected, addition of electrons to quinone structure will increase the electron density on the oxygen atoms thereby increasing the basicity of the overall molecule. Thus pK_a values of p-benzoquinone will be higher than that for semiquinone. In the RTIL C2-H proton is considered most acidic but it has a very high pK_a value of 23.0 [31,32], that rules out any proton transfer by RTIL to the electrogenerated species from p-benzoquinone. 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 transfers are 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[•], which is reduced at the potential of the first wave to produce QH^- and which in turn is protonated to form QH_2 . Thus the overall two electron-two proton transfer in presence of proton donor, proceeds through the scheme:

$$\mathbf{Q} + \mathbf{e}^{-} \rightleftharpoons \mathbf{Q}^{\bullet^{-}} \tag{1}$$

$$Q^{\bullet^-} + H^+ \rightleftharpoons QH^{\bullet} \tag{2}$$

 $QH^{\bullet} + e^{-} \rightleftharpoons QH^{-}$

$$QH^- + H^+ \rightleftharpoons QH_2 \tag{4}$$

Ease of reduction of QH• is responsible for a single reductive peak (trace D) rather than a pair (trace C) as in absence of proton donor. This justification was further confirmed by observations in the redox behavior of H_2Q . In presence of ammonia(at concentration less than twice the concentration of H_2Q) the CV of H_2Q shows two



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

sets of peaks (trace B) instead of the one set that is observed in its absence (trace A). Interestingly the position of this new set of peaks (generated for H_2Q in presence of ammonia) matches well the peak set for BQ in presence of proton donor and not with that of BQ alone. In presence of excess ammonia (concentration equal to or more than twice the concentration of H_2Q) only one set of peaks that matches the CV peaks for BQ in presence of proton acceptor were observed. Thus, it may be argued that in presence of proton acceptor for H_2Q and proton donor for BQ same intermediates are involved in the redox cycle, while in their absence a different set of intermediates is involved. To sum up, while the redox behavior of BQ in presence of proton donor matches that of H_2Q in presence of proton acceptor, they follow a different redox path in absence of proton donor and proton acceptor respectively.

The kinetic features associated with the CVs, i.e., shifting of the oxidative peak positively for quinone (thermodynamically easier), but with an increase of peak to peak separation (kinetically sluggish) is a signature of electron transfer followed by the proton transfer [29,30]. 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 H₂Q it is not the CE mechanism as proposed earlier [33], but EC mechanism that operates. The presence of proton acceptor for H₂Q and proton donor for BQ leads to their conversion to BQ and H₂Q respectively during redox cycling through ECEC mechanism. Thus we propose that, in pure and dry RTILs, BQ and H₂Q follow purely electron transfer pathways, i.e., top and bottom pathway of Scheme 1, and electron transfer associated with proton transfer in presence and absence of proton donor and acceptor respectively as depicted in Scheme 2. Similar behavior has been earlier reported for BO/H₂O couple in buffered as well as unbuffered aqueous media wherein the proton donor/acceptor concentration is greater than [BQ] and [H₂Q] [34]. After establishing the mechanism of the 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.

3.2. Hydroquinone in [BMIM][PF₆] and [BMIM][BF₄]

(3)

Fig. 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 electrochemically irreversible electron transfer [35,36]. Similar behavior has been reported for H₂Qin acetonitrile [37,38] and propylene carbonate [39]. In the segment a–b, the rate constant of electron transfer is very small and consequently a capacitive current is observed. In



Fig. 3. Cyclic voltammogram recorded on GC electrode (2 mm diameter) for 25 mM H_2Q in [BMIM][PF₆] at 298 K. The scan rate was 100 mV s⁻¹.



Fig. 4. Cyclic voltammograms at changing scan rates recorded on GC electrode (2 mm diameter) for 25 mM H₂Q in [BMIM][PF₆] at 298 K. The scan rate range is from 50 to 1000 mV s⁻¹. The inset shows I_p vs. square root of scan rate for the anodic and cathodic peaks of the recorded CVs.

the segment b–A1, the rate constant varies exponentially with the potential and so does the current which in the region A1-c falls due to increase in diffusion layer thickness. In the region c–d the oxidative current falls slowly on account of progressive exhaustion of H_2Q 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 the potential/diffusion dependent electron transfer for processes;

$$H_2Q - 2e \rightarrow H_2Q^{2+} \tag{5}$$

$$H_2 Q^{2+} + 2e \to H_2 Q \tag{6}$$

respectively. CVs were recorded at changing scan rates from $50-1000 \text{ mVs}^{-1}$, and the same are presented in Fig. 4. Linear dependence of peak current in the CVs on the square root of scan rate for both peaks over the entire scan rate range investigated (inset Fig. 4), implies a diffusion controlled process. Similar features were seen in the CVs recorded for H₂Q in [BMIM][BF₄], however the peak positions were shifted more positive to those observed in [BMIM][PF₆].

Double potential step chronocoulograms were recorded to estimate the diffusion coefficients and to look into adsorption if any of H₂Q and its oxidized form H₂Q²⁺ and the Anson plot for recorded data is shown in Fig. 5. As clear from the intercepts there seems to be no adsorption of H₂Q or H₂Q²⁺ during the redox process. The Cotrell plot for the forward and reverse steps led to diffusion coefficient values of 6.72×10^{-07} and 2.6×10^{-07} cm² s⁻¹ for H₂Q and H₂Q²⁺ respectively. The diffusion coefficient is about two orders of magnitude less than that reported for H₂Q in ACN [40] which



Fig. 5. Anson plot for double potential step chronocoulometric data recorded on GC electrode (2 mm diameter) for 25 mM H_2Q in [BMIM][PF₆] at 298 K.



Fig. 6. Linear sweep voltammogram (LSV) and its convoluted form recorded on GC electrode (2 mm diameter) for 25 mM H₂Q in [BMIM][PF₆] at 298 K, the scan rate was 100 mV s⁻¹. Inset of the figure shows convoluted LSVs recorded at changing scan rates.

can be attributed to high viscosity of the RTIL ($\eta_{[BMIM][PF_G]} = 207 \text{ cP}$ [41]) that leads to slower mass transport. The diffusion coefficient of H_2Q^{2+} is almost three times less than that of the H_2Q , perhaps due to its electrostatic interactions with the RTIL anions. The chronocoulometric data recorded for H₂Q in [BMIM][BF₄] using Cottrell equation gives a value of 1.51×10^{-06} cm² s⁻¹ for diffusion coefficient of H₂Q, an order of magnitude higher than that estimated in [BMIM][PF₆] which can be attributed to higher viscosity of the latter ($\eta_{[BMIM][BF_4]} = 34 \text{ cP} [42]$). From the slope of the anodic peak potential vs. log of scan rate plot the magnitude of the product of electron transfer coefficient and number of electrons involved in the rate determining step ($\alpha \times 3n$) was found to be 1.08, a value well expected [36] from the shape of the voltammogram (Fig. 3). 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 heterogeneous electron transfer rate constant (k_0) the LSVs recorded at changing scan rates were convoluted using the algorithm suggested by Lawson and Maloy [43]. In the convoluted current (I(t)) vs. potential plots (Convoluted LSVs) that are presented in Fig. 6, the limiting current was found to be independent of the scan rate. This confirms the absence of preceding and succeeding chemical reactions associated with the electron transfer. Using the standard equations valid for the current and the convoluted current of LSVs in irreversible electron transfer [35], the k_0 value was found to be 1.06×10^{-06} cm s⁻¹ almost similar to the value reported by Wang et al. [15] in 1-ethy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.



Fig. 7. Cyclic voltammogram recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF₄] (red) and [BMIM][PF₆] (black) at 298 K. The scan rate was 100 mV s^{-1} . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.3. Benzoquinone in [BMIM][PF₆] and [BMIM][BF₄]

Fig. 7 shows CVs recorded for 20 mM BQ in [BMIM][BF₄] and [BMIM][PF₆] at the GC electrode, exhibiting similar features. The CVs show two cathodic peaks C1 and C2 and two anodic peaks A1 and A2 with $E_p - E_{p/2}$ in the range $\approx 60 \,\text{mV}$. The observed differences in peak heights can be attributed to the higher viscosity of [BMIM][PF₆] in comparison to that of [BMIM][BF₄]. In view of the previously published reports [14], the values observed for $E_p - E_{p/2}$ and the discussion in Section 3.1, it can be safely argued that the CVs presented in Fig. 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 $Q^{\bullet-}$ at peak A2 which is further oxidized to Q at peak A1. From the CVs in Fig. 7, it appears (more negative peak potential, greater peak to peak separation, and broader peaks in case of [BMIM][PF₆]) that both kinetically and thermodynamically the reduction steps in BQ especially the second one is easier in [BMIM][BF₄] than [BMIM][PF₆]. As has been reported earlier that both thermodynamics and kinetics of electron transfer in quinones is strongly dependent on the solvent polarity [44], nature and concentration of the supporting electrolyte [45] and presence of acidic additives [46]. Considering the established relationship between electron affinities and $E_{1/2}$ [47] values for quinones, viz.,

$$E_{1/2} = -E_{m+1} + C \tag{7}$$

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 the present case where the polarity of the two RTILs does not differ much ($\epsilon_{[BMIM][BF_4]} = 11.7$ and $\epsilon_{[BMIM][PF_6]} = 11.4$) [48], we ascribe the variations in $E_{1/2}$ to solvent specific solvation energies on account of ion pairing. This is further supported by the extent of stabilization of electrogenerated charged species in the two RTILs, which differs more for peak C2 than C1. The observed trend suggests that the imidazolium cations are more effective in stabilizing the 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 is evident from the results published by Islam and Ohsaka [49]. This RTIL specific stabilization of electrogenerated species has been attributed to the RTIL specific multilayer structural organization prevailing across electrode/RTIL interface [50].

As evident from Fig. 7, the peak height corresponding to second electron transfer (C2) in both RTILs is lesser in comparison to the first electron transfer, a fact also reported earlier by many



Fig. 8. Comparison of experimentally recorded cyclic voltammogram recorded on GC electrode for 20 mM BQ in [BMIM][BF₄] (black), at the scan rate of 100 mV s⁻¹ to the one theoretically generated (red) with the approximation of E_rE_q mechanism for two electron transfer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

groups for quinones in aprotic media [46,49]. Dismutation of radical anion to regenerate BQ [51], smaller diffusion coefficient of the electron accepting specie for peak C2 which is generated in the peak span of C1 [52,53] and complexation of dianion with BQ have been proposed to be responsible for the said feature [46]. 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 the reversible and quasireversible redox characteristics respectively of successive electron transfers. Semiderivative convolution of voltammograms depicted in Fig. 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 respectively. Both these features imply that the voltammograms in Fig. 7 correspond to two successive electron transfer reactions in which the first electron transfer is thermodynamically as well as kinetically more facile than second one. Similar findings have been reported earlier for benzoquinone in nonaqueous aprotic media [46]. Fig. 8 shows a comparison between the experimentally recorded CV and the one generated theoretically on E_rE_q mechanism approximation. Though there is a good match between the experimental and theoretical CVs, some minor nonidealities are visible in the experimental one. The experimental CV shows an extra current at the foot of the first cathodic peak besides extra current between the two successive cathodic peaks. A variety of reasons, viz., weak adsorption of reactants, edge diffusion, unequal diffusion coefficients of quinone radical anion and dianion, reduction of weakly adsorbed radical anion to strongly adsorbed dianion [54-56] have been put forth to be responsible for such nonideality.

To have a clear understanding of the overall voltammetric behavior, CVs at changing scan rates from 100 to 1000 mV s⁻¹ were recorded and the same are presented in Fig. 9. At all scan rates it was found that for peak C1, the peak potential remains almost unchanged, while $E_p - E_{p/2}$ value remains in the range as expected for reversible electron transfer for the entire scan rate range investigated. However, for the peak C2, the peak position significantly moves cathodically with increasing scan rate with $E_p - E_{p/2}$ value in the range of quasireversible electron transfer process. Quantification of peak characteristic parameters in the light of 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 Fig. 9 the peak current exhibits a linear dependence (inset Fig. 9) on the square root of scan rate. This implies diffusion control on the shape of C1-A1 peak pair. However, interestingly for the peak C1, the current function



Fig. 9. Cyclic voltammograms at changing scan rates recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF₄] at 298 K. The scan rate range is from 50 to 1000 mV s⁻¹. The inset shows I_p vs. square root of scan rate for the peaks C1 and A1 of the recorded CVs.



Fig. 10. Current function $(I_p/\nu^{1/2})$ vs. scan rate for peaks C1 and C2 of the CVs recorded on GC electrode (2 mm diameter) for 20 mM BQ in [BMIM][BF₄] at 298 K. The scan rate range is from 50 to 1000 mV s⁻¹.

 $(I_p/v^{1/2})$ was found to be scan rate dependent as depicted in Fig. 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 the peak potential for C1 remains almost constant, for peak C2, it shows an initial cathodic shift followed by constancy with increase of scan rate. When we calculated the peak current ratio $I_p C2/I_p C1$, the ratio shows an initial decrease followed by constancy with scan rate, the trend being similar to the variation of peak potential for peak C2. At all scan rates investigated the ratio of C1/A1 peak currents was found to be very close to unity, negating the possibility of EC mechanism for peak C1. Similar observations have been reported for napthoquinone derivatives [57] and for vitamin K [58] in dry aprotic solvents. Such variations in current functions, we assume, can be an outcome of complexation reaction of dianion with the starting material [46] and the countercation [45] in the RTILs as per the reactions:

$$Q^{2-} + Q \rightleftharpoons (Q)_2^{2-} \tag{8}$$

$$(Q)_{2}^{2-} \rightleftharpoons Q^{\bullet-} + Q^{\bullet-} \tag{9}$$

$$Q^{2-} + 2[BMIM]^+ \longrightarrow Q^{2-}([BMIM]^+)_2$$
(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 gave diffusion coefficients as $5.34 \times$

 10^{-07} and 1.37×10^{-06} cm²s⁻¹ for benzoguinone in [BMIM][PF₆] and [BMIM][BF₄] 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 of the semiderivative convoluted voltammograms. The E_1^0 and E_2^0 were respectively found to be -0.325 and -0.666 V respectively in [BMIM][BF4], a separation of about 341 mV between the two. 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 and homogeneous electron transfer occurs and hence disproportionation or comproportionation reactions make the simple EE mechanism more complicated. The equilibrium constant for disproportionation reaction, viz.,

$$\mathbf{Q}^{\bullet-} + \mathbf{Q}^{\bullet-} \to \mathbf{Q}^{2-} + \mathbf{Q} \tag{11}$$

calculated through equation,

$$K_{\rm dis} = \exp\left(\frac{nF(E_2^0 - E_1^0)}{RT}\right) \tag{12}$$

comes out to be 1.70×10^{-06} and 5.28×10^{-07} in [BMIM][BF_4] and [BMIM][PF₆] 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 dimethylsulfoxide [49] indicating greater stabilization of dianion by RTILs especially by the [BMIM][BF₄]. All these observations make us to presume that the anamolies 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 [54]. Using Nicholson's method [59], from the values of peak separations on potential axis for respective couples the k_0 values for the reduction of quinone to its radical anion and the reduction of radical anion to dianion in [BMIM][BF₄], were calculated to be 6.47 \times 10⁻⁰³ and 3.59 \times 10^{-04} cm s⁻¹ respectively. The values for the heterogeneous rate constants are two orders of magnitude lesser than that reported in ACN and seems 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 [60.61] and it is proposed that slow solvent relaxation dynamics of RTILs and their high viscosity is responsible for reversibility characteristics of CV with low magnitudes of rate constants through solvent dynamic control on the charge transfer.

3.4. Electroanalytic utility of H₂Q/BQ redox

An interesting feature, viz presence of an additional oxidative peak (A2) in the CV prior to original peak (A1), as shown in Fig. 2(trace B) and Fig. S2(B) (Supporting information), was observed in the CVs recorded to explore the impact of base concentration on the H₂Q redox behavior in the investigated RTILs. The height of this new peak was observed to increase while that of the original peak decrease with increasing concentration of the base added (Fig. S2(B)). It was found that the height of this new peak increases linearly with the increase in concentration of the base added. In light of the discussion in section 3.1, it is proposed that while peak A1 in the CVs (Fig. 2 (trace B), Fig. S2(B) - Supporting information) arises due to oxidation of H_2Q to H_2Q^{2+} , the new peak (A2) (observed in CVs recorded in presence of base) arises on account of oxidation of H₂Q to BQ in presence of the added base that acts as proton acceptor. In view of the considerable nonfaradaic currents in the recorded CVs, the impact of added base



Fig. 11. Plot for anodic peak current (peak A2, Fig. S3(B)) vs. concentration in the DPVs recorded for H_2Q in presence of propylamine in [BMIM][BF₄] at GC electrode.

concentration on the voltammetric response of H₂O redox behavior was investigated through differential pulse voltammetry (DPV). 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. While DPV in absence of base shows a single peak (Fig. S3(A) Supporting information), an additional peak (A2) was observed in presence of base in the H₂Q plus RTIL solution (Fig. S3(B) Supporting information) where in some base had been added. The peak height of this new peak (A2) in DPVs was found to be a linear function of the added amine concentration as depicted in Fig. 11. This feature seems valuable from analytic point of view where in the H₂Q redox behavior seems to be a good indicator of base concentration in the electrolyte solution. Since in presence of considerable magnitude of non-faradaic currents in CVs, it is usually difficult to measure the height of peak A2 (Fig. S2(B) – Supporting information) especially at low base concentration, the analytic determination of base through the use of DPV rather CV method is recommended. Though any dry aprotic solvent is expected to be useful for such analysis [39], RTILs seem to provide better choice [33] due to their low volatility and recyclability in such procedures.

4. Conclusions

The redox behavior of quinone–hydroquinone in [BMIM][BF₄] and [BMIM][PF₆] 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 (ECEC-pathway) and not the reverse (CECE-pathway) 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 that can be utilized for electroanlytical quantification of proton acceptors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta. 2012.07.059.

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