



# Voltammetric studies in “wet” 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide ionic liquid using electrodes with adhered microparticles

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## ABSTRACT

The voltammetry of adhered microparticles provides a convenient method to access “water free” reversible potentials for water sensitive reduction of benzophenone and 1,4-benzoquinone in “wet” 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Bmpyrd][NTf<sub>2</sub>]) (water content ~0.13 M) ionic liquid. The outcome that reflects reversible potentials relevant to “dry” conditions is rationalized in terms of generation of high localized concentrations that significantly exceed the water concentration near the electrode surface.

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## 1. Introduction

Recently, room-temperature ionic liquids (RTILs) have attracted considerable interest [1–7]. However, despite many attractive properties, RTILs also suffer drawbacks such as high cost and difficulty of purification [8], which make large scale industrial applications impractical. Water is the most problematic impurity in RTILs since it is difficult to remove and can be easily introduced back into RTILs after purification. Moreover, it has been recognized that variable adventitious water content often accounts for the large variations in voltammetric behavior and physical properties of RTILs [5,6,9,10]. Water being a proton source also presents a chemical problem because it can directly participate in electrochemical reactions involving bases thereby altering the reaction pathway and even influencing the formal reversible potential ( $E^{0'}$ ) [11,12]. Thus, it is crucial to ensure that the water effect is negligible or accounted for when reporting  $E^{0'}$  values in RTILs.

The water effect can be minimized by at least three methods: (a) RTILs can be dried (water content ~10 ppm) at elevated temperature

and under vacuum conditions [13]. However, hydrophobic RTILs can reabsorb significant amount of water in a short time [14,15]; (b) reactions between H<sub>2</sub>O and electrogenerated bases are bimolecular, so the water effect can be minimized by using higher electroactive concentrations than normal; (c) very fast scan rates can be used in voltammetric measurements so that the contribution from a water based homogeneous reaction following electron transfer may be reduced.

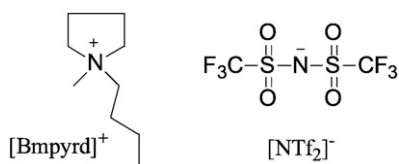
Voltammetry of microparticles adhered to an electrode surface provides a tool for investigation of the redox properties of poorly soluble or slowly dissolving species [16,17]. In RTILs, it has been found that  $E^{0'}$  values of inorganic and organometallic compounds [18–22] and the kinetics of first-order homogeneous reactions coupled to electron transfer can be obtained voltammetrically using adhered microparticles [23]. In this paper, voltammetric reduction of adhered benzophenone and 1,4-benzoquinone microparticles is reported in “wet” 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Bmpyrd][NTf<sub>2</sub>]) conditions encountered under bench top conditions. Benzophenone and 1,4-benzoquinone were chosen for this study due to the high sensitivity of their voltammetric reduction to proton availability from water [24,25] and their electrochemical significance in green chemistry and biochemistry [26,27]. The use of [Bmpyrd][NTf<sub>2</sub>], which does not contain any relatively available protons (Structure 1), ensures that the ionic liquid itself is not a proton source. To provide a basis for comparison, voltammetric studies of dissolved benzophenone and 1,4-benzoquinone were also undertaken in “wet” and extensively dried [Bmpyrd][NTf<sub>2</sub>].

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**Structure I.** Ionic components of [Bmpyrd][NTf<sub>2</sub>]; [Bmpyrd]<sup>+</sup> cation and [NTf<sub>2</sub>]<sup>-</sup> anion.

## 2. Experimental

### 2.1. Chemicals

Benzophenone (ReagentPlus<sup>®</sup>, 99%), 1,4-benzoquinone (98%) and ferrocene ( $\geq 98.0\%$ ) were purchased from Sigma Aldrich and used as received. [Bmpyrd][NTf<sub>2</sub>] (>99%) was purchased from IOLITEC (Germany). To obtain “dry” [Bmpyrd][NTf<sub>2</sub>], the commercial product was reacted with basic alumina for at least 24 h, then placed under vacuum at 80 °C for 24 h to give a water content of  $15 \pm 5$  ppm (about 1 mM) determined by Karl Fischer titration (Metrohm 831 Karl Fischer coulometer). To obtain “wet” [Bmpyrd][NTf<sub>2</sub>], 5 ml of the ionic liquid was left in a beaker under open bench top conditions. Continuous stirring for 24 h, allowed atmospheric water to equilibrate with [Bmpyrd][NTf<sub>2</sub>] to give a water content of  $2250 \pm 10$  ppm (about 0.13 M) under our laboratory conditions.

### 2.2. Instrumentation

Cyclic voltammetric measurements were undertaken with a CHI760 electrochemical analyzer (CH Instruments, Texas, USA) using a standard three-electrode electrochemical cell. For transient cyclic voltammetric experiments, a glassy carbon macrodisc electrode (GC, 1.0 mm diameter) or a 33  $\mu\text{m}$  diameter carbon fiber microelectrode was used as the working electrode, while platinum (Pt) wires were used as both the quasi-reference and counter electrodes. This Pt quasi scale was then converted to the Fc/Fc<sup>+</sup> (Fc = ferrocene) reference potential scale [18,19,28].

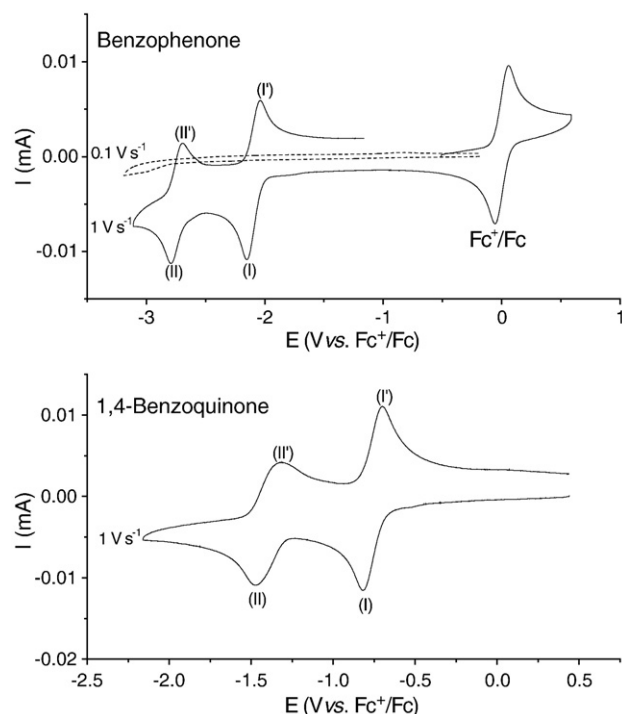
The procedure for mechanical attachment of microcrystalline microparticles onto electrodes surfaces has been reported in detail elsewhere [18–20,22]. In brief, a few milligrams of solid were placed onto weighing paper. The polished electrode was then pressed onto and rubbed over the compounds to transfer solid to the electrode surface.

All voltammetric experiments were undertaken at  $20 \pm 2$  °C. Experiments with “dry” [Bmpyrd][NTf<sub>2</sub>] were undertaken under a nitrogen atmosphere in a dry box to minimize the impact of atmospheric water and oxygen. Experiments with “wet” [Bmpyrd][NTf<sub>2</sub>] were carried out under bench top conditions using conventional nitrogen degassing methods to minimise the oxygen concentration.

## 3. Results and discussion

### 3.1. Voltammetry of dissolved benzophenone and 1,4-benzoquinone in [Bmpyrd][NTf<sub>2</sub>]

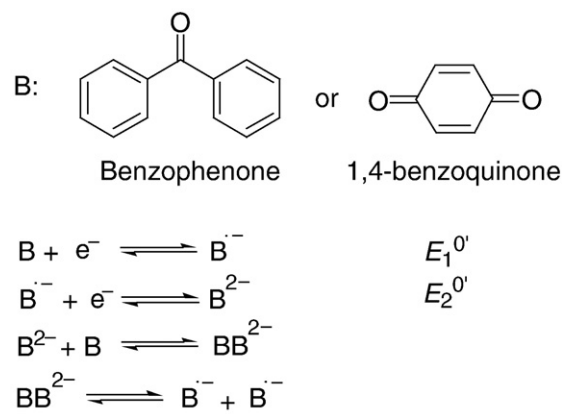
Cyclic voltammograms obtained for reduction of 10 mM benzophenone and 1,4-benzoquinone in “dry” [Bmpyrd][NTf<sub>2</sub>] at a 1 mm diameter GC working electrode at a scan rate of  $1 \text{ V s}^{-1}$  are shown in Fig. 1. Since 10 mM of analyte was used, the effect of residual water ( $\sim 1$  mM) should be negligible. Two well-defined reversible reduction processes (designated as I/I' and II/II' in Fig. 1) were observed for both compounds. The  $E^0$  values, calculated from the average of the reduction and oxidation peak potentials,  $(E_{\text{red}}^p + E_{\text{ox}}^p)/2$  with equal diffusion coefficients of both reduced and oxidized forms being assumed [29], are  $-2.095$  and  $-2.745$  V vs Fc<sup>+</sup>/Fc for processes I/I' and II/II', respectively, for benzophenone; and  $-0.760$  and  $-1.395$  V vs Fc<sup>+</sup>/Fc, respectively, for 1,4-benzoquinone. However, it should be noted that the diffusion coefficients associated with the



**Fig. 1.** Cyclic voltammograms for reduction of 10 mM benzophenone and 10 mM 1,4-benzoquinone in “dry” [Bmpyrd][NTf<sub>2</sub>] recorded with a 1.0 mm diameter GC electrode at a scan rate of  $1 \text{ V s}^{-1}$  in a dry box under a N<sub>2</sub> atmosphere. The cyclic voltammogram obtained in the absence of benzophenone (---) is included for comparison.

redox couple may differ substantially in ionic liquid media [28,30]. The separations between the reduction and oxidation peak potentials of 115 mV for process I/I' for both benzophenone and 1,4-benzoquinone, are the same as the value of 115 mV associated with the reversible Fc<sup>+</sup>/Fc couple. This observation implies that processes I/I' are reversible on the time scale of the measurements. The deviation of the peak-to-peak separations from the theoretical value of 56 mV, expected for a reversible one-electron transfer process at 20 °C [29] is attributed to a similar level of uncompensated resistance effect encountered.

A diminished second reduction peak current (Fig. 1), as found in voltammetric studies on related compounds, is attributed to the formation of an electroinactive complex between the electrogenerated dianion and the neutral species present in bulk solution [11,31] (see Scheme 1 where  $E_1^{0'}$  and  $E_2^{0'}$  represent the reversible potentials for the first (I/I') and modified second (II/II') reduction processes, respectively).



**Scheme 1.** Mechanisms proposed for reduction of benzophenone and 1,4-benzoquinone dissolved in dry [Bmpyrd][NTf<sub>2</sub>].

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