Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(*S*)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids

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The electrochemical properties of the room temperature ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$), 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM^+PF_6^-$) and 1-methyl-3-[2,6-(*S*)-dimethylocten-2-yl]imidazolium tetrafluoroborate ($MDIM^+BF_4^-$) as solvents have been studied using micro-samples, with a volume of 10 μL, of the ionic liquids under vacuum conditions and under conditions with controlled gas and moisture supplies. The impact of water—absorbed into the ionic liquid in a controlled manner from the gas phase—on the voltammetry of dissolved redox systems and on the accessible potential window of the ionic liquids was investigated. The diffusion coefficients for three representative redox systems, the oxidation of neutral *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), the reduction of cationic methyl viologen (MV^{2+}) and reduction of anionic hexacyanoferrate(III), $Fe(CN)_6{}^{3-}$, have been determined as a function of the water content of the ionic liquids. Water is shown to have a much more dramatic acceleration effect on the diffusion of the ionic compounds compared to its effect on neutral species in ionic liquids. A model based on nanoscale structural features of wet ionic liquid materials is proposed. The novel methodology, which employs redox-active compounds dissolved or partitioned in microdroplets of ionic liquid, uses conditions suitable for the study of ionic liquids for applications in electrochemical gas phase reactors and gas sensor systems.

Introduction

In the light of their promising physical and chemical properties, room temperature ionic liquid systems based upon *N*,*N*′-dialkyl-substituted imidazolium cations are attracting increasing attention for applications in liquid–liquid extraction[1,2] or gas chromatography[3] and as versatile electrolytes for diverse technologies, *e.g.* in batteries, photoelectrical cells and other electrochemical devices.[4–6] This growing interest can be attributed to a number of desirable properties. Amongst them, the wide range of the liquid state of about 300 °C,[7] negligible volatility, high ionic conductivity and a wide potential window[8,9] are most important. Fine tuning of the ionic liquid properties by changing the length and nature of the alkyl substituents at the imidazolium cation or by substituting the anion is possible. In particular, the hexafluorophosphate and tetrafluoroborate salts have been reported to be air and moisture resistant,[4,8] making them preferable for potential applications in electrochemical devices.

Although some ionic liquids, such as 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM^+PF_6^-$), are essentially insoluble in water, they can absorb a considerable amount of water[10] resulting in changes in the physical and chemical properties. There are only few literature reports on the influence of moisture on the electrochemical behaviour of room temperature ionic liquids.[11,12] In a recent study,[13] ion partitioning processes between aqueous solutions and ionic liquid film and droplet deposits have been studied. Surprisingly, some ions, in particular those interacting with the imidazolium cation, such as $Fe(CN)_6{}^{3-}$, undergo selective accumulation in the ionic liquid phase.

Under biphasic ionic liquid–aqueous conditions, water is present in the ionic liquid phase and this causes some considerable changes in the physical and chemical properties compared to those of the 'dry' ionic liquid. In the present study, work focuses on the impact of moisture on the electrochemical properties of three imidazolium-type ionic liquids with hexafluorophosphate and tetrafluoroborate anions. A novel electrochemical cell has been developed, which enables voltammetric studies in a μL volume under vacuum conditions and under conditions with controlled gas flow and moisture supply.

The impact of moisture on the steady state and transient voltammetry of redox active compounds dissolved in the ionic liquids undergoing chemically reversible reduction or oxidation at the electrode is investigated. Changes in the electrochemical characteristics and in the transport properties of ionic liquid solutions of neutral *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), cationic methylviologen (MV^{2+}) and of anionic hexacyanoferrate(III) $\{Fe(CN)_6{}^{3-}\}$ upon addition of water are compared. A considerable difference in the behaviour of neutral compared to ionic materials dissolved in the ionic liquids is detected and interpreted in terms of structural effects in the 'wet' ionic liquid.

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Experimental

Reagents

$K_3[Fe(CN)_6]$, NBu_4PF_6, methylviologen dichloride hydrate (1,1′-dimethyl 4,4′-bipyridinium chloride hydrate) and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) were used as purchased from Aldrich. Demineralised and filtered water was taken from an Elgastat water purification system (Elga, Bucks, UK) with a resistivity of not less than 18 MΩ cm. Argon (Pureshield, BOC) was used to provide an inert atmosphere. The synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ($BMIM^+BF_4^-$ and $BMIM^+PF_6^-$) has been described in detail elsewhere.[14] 1-Methyl-3-[2,6-(*S*)-dimethylocten-2-yl]imidazolium tetrafluoroborate ($MDIM^+BF_4^-$) was prepared and characterised following a procedure reported recently.[13]

The preparation of solutions of methyl viologen and TMPD in the ionic liquids was carried out using the following solvent evaporation-based procedure. First, 0.1 M stock solutions of MV^{2+} or TMPD in dichloromethane were prepared. An adequate quantity of the stock solution was added to 100 mg of the dry ionic liquid to yield a concentration of 10 mM after evaporation of the dichloromethane *in vacuo*. Ferricyanide in the form of its potassium salt is insoluble in ionic liquids and, therefore, partitioning of $Fe(CN)_6^{3-}$ from an aqueous phase into the $MDIM^+BF_4^-$ ionic liquid phase was used.[13] A 100 μL volume of a 20 mM solution of $K_3Fe(CN)_6$ in water was added to 100 μL of $MDIM^+BF_4^-$ to give a biphasic mixture. Fast equilibration was achieved by sonication in an ultrasonic bath for five minutes. After separation of the two phases (30 min) the aqueous phase was removed with a micropipette. The ionic liquid solution was then placed into the electrochemical cell and dried *in vacuo*.

Instrumentation

Electrochemical experiments were performed with a μ-Autolab system (Eco-Chemie Utrecht, Netherlands). Platinum disc microelectrodes (Micro Glass Instruments, Greensborough, Victoria 3088, Australia) with nominal diameters of 2, 5 and 50 μm were used as working electrodes. For vacuum experiments, a Metrovac rotary pump GDR1 (0.05 Torr) connected to a vacuum system *via* a liquid nitrogen trap was utilized. All experiments were carried out at a temperature of 22 ± 2 °C.

Fig. 1 shows a cross section of the electrochemical cell developed for studying the electrochemistry of ionic liquids under vacuum conditions and for the exposure of the ionic liquid sample to a gas flow. The glass electrochemical cell contained a three-electrode arrangement with two Pt wires (0.1 mm diameter), one being used as a counter electrode and the other serving as a pseudo-reference electrode. For the measurement, a drop of the ionic liquid (10 μL) was placed on the surface of the working electrode, which was then fitted into the vacuum cell as shown in Fig. 1. The electrochemical cell was contained in a Faraday cage. All gas flow experiments were carried out with a flow rate of 200 cm^3 min^{-1}.

Quantitative determination of the water uptake from the gas phase

In order to quantify the degree of water uptake of the ionic liquids from a water-saturated gas phase, the following procedure was chosen. The ionic liquid samples (10 μL) were placed on a glass plate and the weight monitored as a function of time of exposure to a stream of water-saturated argon. The liquids were dried *in vacuo* (0.05 Torr) until the weight of the liquid became constant (after *ca.* 12 h). Then a stream of argon, pre-saturated with water by bubbling through a wash bottle (vapour pressure of argon *ca.* 100 kPa and of water *ca.* 2.5 kPa), was passed over the surface of the liquid and the weight was monitored as a function of time. The water absorption from the gas phase in wt.% was then calculated as the difference of the weight between the wet and the dry ionic liquid. The possibility that significant argon absorption into the ionic liquid occurs cannot be entirely ruled out. However, no effect due to argon was observed in electrochemical experiments and, therefore, argon is assumed to be 'inert' and not affecting the results.

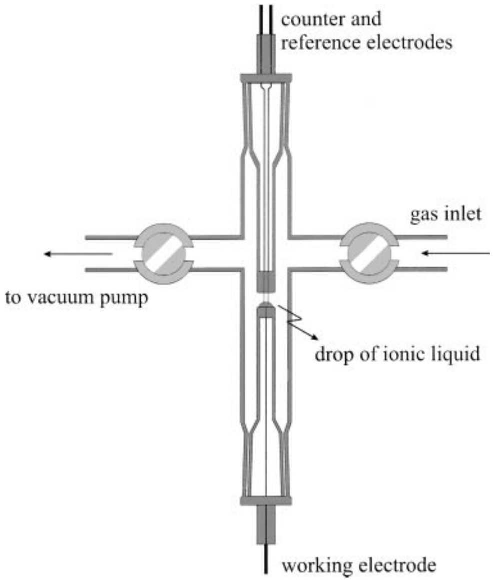


Fig. 1 Cross section of the electrochemical cell employed for voltammetric measurements in 10 μL ionic liquid samples under vacuum or controlled gas atmosphere conditions.

Determination of diffusion coefficients

Diffusion processes in ionic liquids were found to be slow compared to those observed in conventional solvents, in agreement with the higher viscosity of the ionic liquid medium.[9,10,14] Planar microdisc electrodes of 5 and 2 μm diameters were used to study voltammetric responses under steady-state and transient conditions. A 2 μm diameter Pt microelectrode was found to give the most reliable results with well defined steady-state limiting currents and high signal to noise ratio. Prior to electrochemical measurements, the diameter (d) of the electrodes was calibrated based on the steady-state voltammetric limiting current for the oxidation of a 1 mM solution of ferrocene in acetonitrile (0.1 M NBu_4PF_6). The diffusion coefficients (D) of compounds dissolved in ionic liquids were then determined from the steady state current (I_{ss}) of the cyclic voltammograms, using eqn. 1 (for a one electron transfer process).[15]

$$D = \frac{I_{ss}}{2Fdc} \tag{1}$$

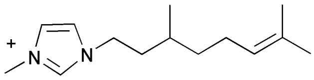
In this equation, F denotes the Faraday constant, d is the electrode diameter and c is the concentration of redox active compound. Additionally, and in particular for $Fe(CN)_6^{3-}$ partitioned into the ionic liquid, a chronoamperometric method was used to simultaneously determine both the concentration of the redox reagent in the ionic liquid and the diffusion coefficient.[5,16]

Results and discussion

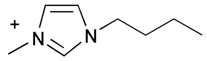
Effect of water on the electrochemical characteristics of the ionic liquids

Three types of ionic liquids, 1-methyl-3-[2,6-(*S*)-dimethylocten-2-yl]imidazolium tetrafluoroborate ($MDIM^+BF_4^-$), 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$)

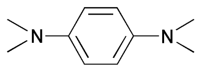
and hexafluorophosphate ($BMIM^+PF_6^-$), were studied in respect of their ability to sustain electrochemical processes in vacuum and in water-saturated or ambient atmosphere. The water miscibility of ionic liquids is determined by the hydrophobicity of the alkyl substituents of the imidazolium cation and the type of anion. $BMIM^+BF_4^-$ is fully miscible with water at temperatures above 5 °C,[14] whereas $BMIM^+PF_6^-$ and $MDIM^+BF_4^-$ are only partially miscible at room temperature. However, the physical and electrochemical properties of all three ionic liquid materials are considerably affected by the presence of water, even in the low concentration absorbed from the gas phase. In order to obtain information about the solubility of water in the ionic liquids, the uptake of moisture from a flow of water-saturated argon into a 10 µL ionic liquid sample was determined by monitoring the weight change during the course of equilibration (*vide supra*). The maximum water uptake for the three ionic liquid materials in the presence of water-saturated argon after complete equilibration (60 h) are summarised in Table 1. A trend of increasing water uptake by the more water-soluble materials can be observed, in the order $BMIM^+BF_4^- > MDIM^+BF_4^- > BMIM^+PF_6^-$.



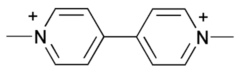
$MDIM^+$



$BMIM^+$



TMPD



MV^{2+}

The presence of water in the gas phase has a considerable impact on the electrochemical properties of the ionic liquids. Fig. 2 shows cyclic voltammograms recorded in neat $BMIM^+BF_4^-$ under dry conditions (Fig. 2A) and after exposure to water-saturated argon (Fig. 2B) for 120 min. Clearly, a dramatic narrowing in the potential window available for voltammetric studies in the ionic liquid is detected. In order to correlate the gradual water uptake and the narrowing of the potential window, a comparison of the time dependence of both processes for $BMIM^+PF_6^-$ exposed to water-saturated argon is shown in Fig. 2C and D. The plot in Fig. 2C suggests that the saturation limit is reached only after about 50 h. In contrast to this, the reduction of the potential window is a very fast process with a dramatic decrease over the first 30 min (corresponding to a water uptake of less than 1 wt.%), apparently reaching equilibrium after only two hours, which corresponds to a content of approximately 3 wt.% water in the ionic liquid. Similar characteristics were found for the ionic liquids $MDIM^+BF_4^-$ and $BMIM^+BF_4^-$. Table 2 gives a summary of the potential window data. It can be seen that the narrowing of the potential window occurs for both the cathodic and anodic limit. The processes responsible for the narrowing of the potential window are likely to be associated with water electrolysis.

Table 1 Water content of ionic liquids, determined gravimetrically after complete equilibration (60 h) in a stream of water-saturated argon (flow rate 0.2 L min^{-1})

	Water content/wt.%
$BMIM^+PF_6^-$	12.1
$BMIM^+BF_4^-$	25.2
$MDIM^+BF_4^-$	15.8

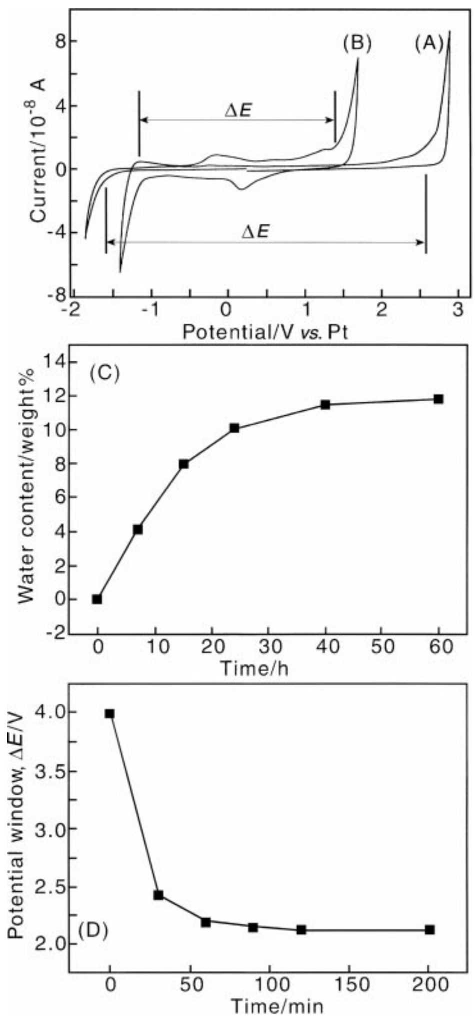


Fig. 2 Cyclic voltammograms recorded in neat $BMIM^+BF_4^-$ at a 50 µm Pt disc electrode, (A) under 'dry' conditions and (B) with a water content of approximately 3% in the ionic liquid (scan rate 100 mV s^{-1}). (C) Plot of the dependence of the water content of $BMIM^+PF_6^-$ on the time of exposure to water-saturated argon. (D) Plot of the dependence of the potential window ΔE measured in $BMIM^+PF_6^-$ at a 50 µm diameter Pt disc electrode on the time of exposure to water-saturated argon.

The oxidation of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD)

Next, the effect of water vapour on the electrochemical behaviour of model redox systems is investigated. *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) is soluble in both ionic liquid and aqueous media. Fig. 3 shows cyclic voltammograms for the oxidation of 10 mM TMPD dissolved in dry $MDIM^+BF_4^-$ (A) and $BMIM^+PF_6^-$ (B) at a 2 µm diameter platinum disc electrode. For $MDIM^+BF_4^-$ two well-defined oxidation responses are detected. The two oxidation processes associated with the steady-state voltammetric responses I and

Table 2 Potential window ΔE of ionic liquids in 'dry' state (0.05 Torr vacuum, 2 h) and a 'wet' state after exposure to water-saturated argon (water content >3 wt.%) determined voltammetrically (scan rate 100 mV s^{-1}, 50 µm diameter Pt disc electrode)

	Anodic limit/V		Cathodic limit/V		ΔE/V	
	Dry	Wet	Dry	Wet	Dry	Wet
$BMIM^+BF_4^-$	2.50	1.02	−1.60	−0.93	4.10	1.95
$BMIM^+PF_6^-$	2.55	1.00	−1.60	−1.12	4.15	2.1
$MDIM^+BF_4^-$	1.40	0.95	−2.4	−1.05	3.80	2.0

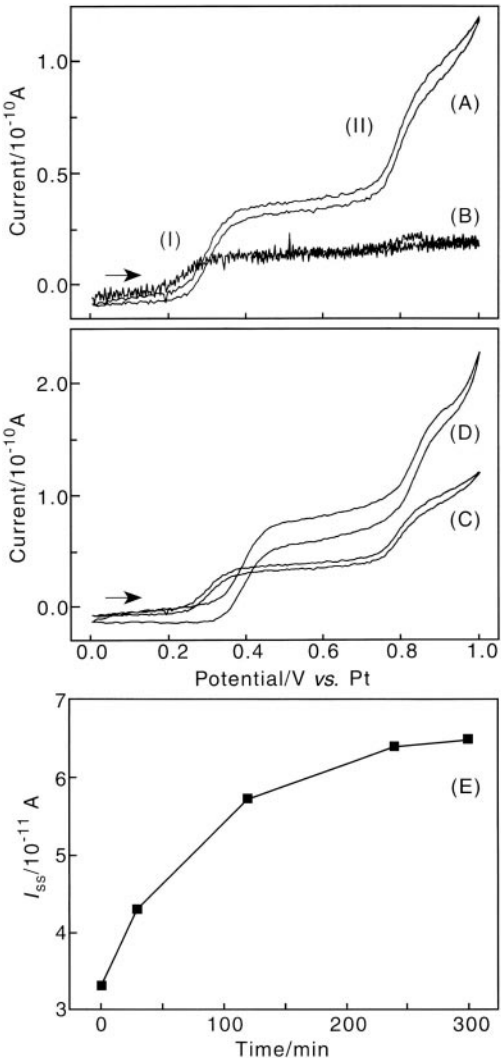


Fig. 3 Steady-state voltammograms for the oxidation of 10 mM TMPD in (A) $MDIM^+BF_4^-$ and (B) in $BMIM^+PF_6^-$ under 'dry' conditions recorded at a 2 μm diameter Pt disc electrode (scan rate 10 mV s^{-1}). (C) Steady-state voltammograms for the oxidation of 10 mM TMPD in $MDIM^+BF_4^-$ in the presence of 3 wt.% water in an argon atmosphere and (D) in the presence of a dioxygen atmosphere. (E) Plot of the dependence of the limiting current for the first oxidation of TMPD (process I) on the time of exposure of $MDIM^+BF_4^-$ to water-saturated argon.

II can be identified as the first and second one electron oxidation of TMPD (eqn. 2 and 3).

$$\text{Process I:} \qquad \text{TMPD} \longrightarrow \text{TMPD}^+ + e^- \qquad (2)$$

$$\text{Process II:} \qquad \text{TMPD}^+ \longrightarrow \text{TMPD}^{2+} + e^- \qquad (3)$$

The voltammetric responses for the oxidation of 10 mM TMPD in dry $MDIM^+BF_4^-$ (Fig. 3A) is fully reversible for both oxidation steps based on comparison with the Tomeš criterion,[17] $E_{3/4}$–$E_{1/4}$ = 54 mV for process I and $E_{3/4}$–$E_{1/4}$ = 50 mV for process II. Interestingly, the $TMPD^{2+/+}$ oxidation process in $BMIM^+PF_6^-$ (Fig. 3B) is inhibited and observed only as a very weak signal. This inhibition effect cannot be explained in terms of a blocking of the electrode surface, because no decrease in current and no 'stripping' process on the reverse scan are detected. Voltammetric responses of this type are commonly observed[18] for processes in which a solid precipitate, here $TMPD^{2+}(PF_6^-)_2$, participates in a dynamic redox conproportionation equilibrium with the neutral solution species, TMPD (eqn. 4).

$$\text{TMPD}^{2+}(\text{PF}_6^-)_2 + \text{TMPD} \longrightarrow 2\,\text{TMPD}^+ + 2\,\text{PF}_6^- \qquad (4)$$

In Fig. 3C and D, it can be seen that the presence of water in the $MDIM^+BF_4^-$ ionic liquid causes the limiting current for both TMPD redox process, oxidation I and II, to increase considerably. However, the relative height of the limiting currents for the two processes as well as the potential gap, $\Delta E = E_{1/2,\mathrm{I}} - E_{1/2,\mathrm{II}}$, remain constant. When the voltammetric response is monitored as a function of time exposed to water-saturated argon, the increase in the limiting current is initially rapid (3 h) up to a water uptake, up to 5 wt.%. At this level of water uptake, the current reaches its maximum value and further uptake of water has only an insignificant effect on the magnitude of the limiting current. Fig. 3E shows the time dependence of the limiting current for process I during the course of water uptake from a water-saturated argon atmosphere.

The shift in half wave potential for the two redox processes I and II may be partially attributed to a drift in the reference potential of the Pt wire pseudo-reference. However, no significant shift in the half wave potential, $E_{1/2}$, for the two oxidation processes relative to each other has been observed. In Table 3, the diffusion coefficients of TMPD in $MDIM^+BF_4^-$ and $BMIM^+PF_6^-$, calculated from the steady-state limiting currents for the first oxidation of TMPD (eqn. 2) are summarised. The uptake of water causes the diffusion coefficients to increase by a factor of 2. This increase in the rate of diffusion can be attributed to a decrease in the viscosity.

The reduction of methylviologen (MV^{2+})

Next, methylviologen, which is initially present in the form of the dication, was studied as a cationic model redox system. Two chemically reversible reduction processes (processes III and IV in Fig. 4), yielding the mono cation MV^+ and the neutral MV^0, are observed (eqn. 5 and 6).[19]

$$\text{Process III:} \qquad \text{MV}^{2+} + e^- \longrightarrow \text{MV}^+ \qquad (5)$$

$$\text{Process IV:} \qquad \text{MV}^+ + e^- \longrightarrow \text{MV}^0 \qquad (6)$$

In the dicationic form, MV^{2+} is highly soluble in both aqueous and ionic liquid media. Fig. 4A shows the cyclic voltammogram for the reduction of 20 mM methylviologen dissolved in dry $BMIM^+PF_6^-$ at a 50 μm diameter platinum disc electrode with a scan rate of 100 mV s^{-1}. The voltammetric responses detected under vacuum conditions or after extended exposure to a stream of dry argon are identical and, therefore, argon appears to have no effect on the electrochemical process under these conditions. Both reduction steps are chemically and electrochemically reversible with a peak to peak separation ΔE_p = 63 mV for process III and ΔE_p = 66 mV for process IV. The peak currents detected for the reduction processes follow a square root dependence of the scan rate, consistent with diffusion control.

Table 3 Diffusion coefficient data for TMPD (concentration 10 mM) as a function of the water content of the ionic liquid determined from the limiting current for the oxidation process I at a 2 μm diameter Pt disc electrode

	D^a_{dry}/cm^2 s^{-1}	D^b_{wet}/cm^2 s^{-1}
$BMIM^+PF_6^-$	2.6×10^{-8}	5.2×10^{-8}
$MDIM^+BF_4^-$	8.5×10^{-8}	1.7×10^{-7}

[a] Measured after 2 h 0.05 Torr vacuum. [b] Value corresponds to the limiting value measured at a water content equal to or higher than approximately 5 wt.%.

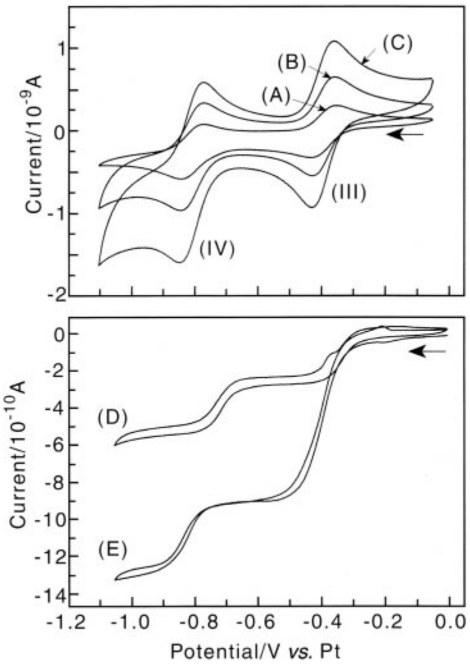


Fig. 4 Cyclic voltammograms obtained for the reduction of 20 mM methylviologen dissolved in $BMIM^+BF_4^-$ at a 50 μm diameter Pt disc electrode (A) under dry conditions, (B) after 45 min, and (C) after 90 min exposure to water-saturated argon (scan rate 100 mV s^{-1}). Steady-state voltammograms obtained for the reduction of 20 mM methylviologen dissolved in $BMIM^+BF_4^-$ at a 5 μm diameter Pt disc electrode under 'wet' conditions with a water content of *ca.* 6 wt.% (D) under argon and (E) after 10 min exposure to air (scan rate 10 mV s^{-1}).

The presence of water in the ionic liquid again has a dramatic effect on the voltammetric behaviour. Analogous to the effects observed for the oxidation of TMPD, the uptake of water into the ionic liquid causes an increase in the voltammetric signals, which is indicative of a considerable change in the rate of diffusion. From the increase in peak current (Fig. 4B and C), it can be concluded that the effect of water on the MV^{2+} diffusion is considerably more pronounced compared to the effect observed for the oxidation of TMPD.

A steady-state voltammetric response for the reduction of a solution of 10 mM MV^{2+} in $BMIM^+BF_4^-$ with a water content of about 6 wt.% obtained at a 5 μm diameter platinum disc electrode is shown in Fig. 4D. Well-defined electrochemically reversible responses (close to the Tomeš criterion with $E_{3/4}$–$E_{1/4}$ = 64 mV for process III and with $E_{3/4}$–$E_{1/4}$ = 61 mV for process IV) are detected. In a series of experiments, the change in the diffusion coefficient upon changing the amount of water in the ionic liquids $BMIM^+BF_4^-$, $BMIM^+PF_6^-$ and $MDIM^+BF_4^-$ has been determined. In contrast to the effect of water on the diffusion coefficient of TMPD (Fig. 5A) the diffusion coefficient for MV^{2+} continues to increase proportionally with water content (Fig. 5B). As shown in Table 4, the values for the MV^{2+} diffusion coefficients increase by more than one order of magnitude as the water content changes from 0 to 6 wt.%. In $BMIM^+PF_6^-$, the voltammetric reduction response for MV^{2+} becomes irreproducible at a water content higher than 6 wt.%. Additional peak responses are observed (not shown) and attributed to the formation of deposits at the electrode surface. Similar effects have been reported in purely aqueous media.[20]

It is interesting to compare the diffusion coefficient data for methylviologen and TMPD in ionic liquid and in aqueous media. Depending on the aqueous electrolyte composition, typical diffusion coefficients of 8.1×10^{-6} cm^2 s^{-1} for MV^{2+} and 8.4×10^{-6} cm^2 s^{-1} for TMPD (both in aqueous KCl at 25 °C) have been reported in the literature.[21–24] These values are two orders of magnitude above the diffusion coefficients determined in this study in the dry ionic liquids. In contrast to data for TMPD, for MV^{2+}, the increase in the diffusion coefficients with water content was found to be approximately proportional to the molar fraction of water in the ionic liquid and converging roughly towards the value anticipated for an aqueous environment (see Fig. 5).

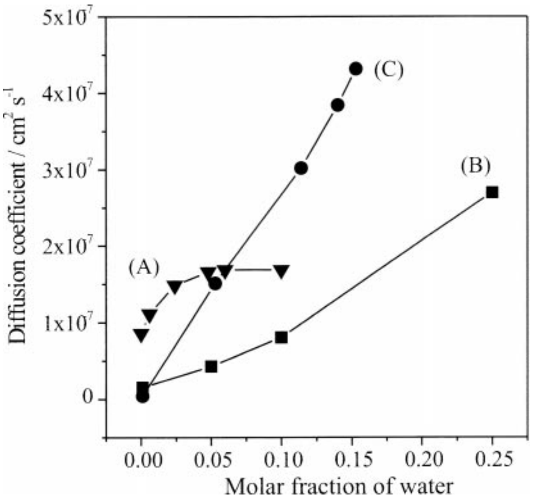


Fig. 5 Plot of the dependence of the diffusion coefficients for neutral and ionic redox reagents on the molar fraction of water absorbed from the gas phase into ionic liquids. Data is based on the analysis of the steady-state limiting current for (A) the oxidation of 10 mM TMPD in $MDIM^+BF_4^-$, (B) the reduction of 10 mM methylviologen in $BMIM^+BF_4^-$, and (C) the reduction of 5 mM $Fe(CN)_6^{3-}$ in $MDIM^+BF_4^-$.

Methyl viologen in the mono-reduced state, MV^+, is known to be reactive towards dioxygen in aqueous solutions.[25] In Fig. 4E preliminary results for this process are shown and it can be seen that the oxidation of MV^+ back to MV^{2+} by dioxygen also occurs in wet $BMIM^+BF_4^-$ ionic liquid media. This process, which is of considerable interest in gas sensor applications,[26] is affected by both the water content of the ionic liquid and the partial pressure of dioxygen in the electrochemical cell. However, the rate of the dioxygen mass transport as a case of neutral species diffusion in a wet ionic liquid may be relatively constant over a given range of water content and the number of effectively transferred electrons, n_{eff}, obtained as the ratio of the limiting currents for process III in the presence and absence of dioxygen may be of future use for this kind of application.

The reduction of $Fe(CN)_6^{3-}$

Recently, the selective partitioning of $Fe(CN)_6^{3-}$ ions from aqueous solution into droplets of $MDIM^+BF_4^-$ ionic liquid has been reported.[13] It was proposed that this process is driven by $Fe(CN)_6^{3-}$–imidazolium interaction and associated with an exchange of tetrafluoroborate ions from the ionic liquid (il) phase (eqn. 7).

Table 4 Diffusion coefficient data for methylviologen, MV^{2+} (concentration 20 mM), under dry conditions, as well as after exposure to water-saturated argon, determined from the limiting current for the reduction process III at a 2 μm diameter Pt disc electrode

	D_{dry}/cm^2 s^{-1}	D_{wet}/cm^2 s^{-1}
$BMIM^+BF_4^-$	1.5×10^{-8}	2.7×10^{-7}[a]
$BMIM^+PF_6^-$	1.1×10^{-8}	1×10^{-7}[b]
$MDIM^+BF_4^-$	1.3×10^{-8}	1.6×10^{-7}[c]

[a] 25 wt.% water content. [b] 6 wt.% water content. [c] 16 wt.% water content.

$$3\,BF_4^-(il) + Fe(CN)_6^{3-}(aq) \longrightarrow 3\,BF_4^-(aq) + Fe(CN)_6^{3-}(il) \quad (7)$$

Although the potassium salt of ferricyanide is highly insoluble in the ionic liquids studied here, this facile ion exchange process (eqn. 7) allows solutions of $Fe(CN)_6^{3-}$ in ionic liquids to be prepared by placing an equal volume of an aqueous solution of ferricyanide and ionic liquid in contact with each other. Ferrocyanide, $Fe(CN)_6^{4-}$, and many other ionic compounds cannot be exchanged into the ionic liquid under similar conditions due to less favourable equilibria.[13]

Fig. 6 shows the cyclic voltammograms obtained for the reduction of 5 mM $Fe(CN)_6^{3-}$ in $MDIM^+BF_4^-$ ionic liquid. Voltammogram (A) represents the electrochemical behaviour of the ferricyanide anion in the 'dry' ionic liquid at a 50 μm diameter Pt disc electrode, whereas voltammogram (B) and (C) were obtained after exposing the ionic liquid to a stream of humid argon for 45 and 120 min. Well-defined voltammetric responses were detected with a peak to peak separation of *ca.* 64 mV, indicating diffusion control. A tremendous increase in the rate of diffusion of the ferricyanide ion with the increase in water content can be inferred from the huge change in peak current and from the change of the shape of the voltammetric response.

Steady-state voltammograms obtained at a 5 μm diameter Pt disc electrode for the reduction of 5 mM $Fe(CN)_6^{3-}$ in $MDIM^+BF_4^-$ are shown in Fig. 5D–I. The Tomeš criterion of reversibility for the 5 μm electrode was found to be approximately obeyed with $E_{3/4}–E_{1/4} = 60 \pm 4$ mV for a water content ranging from approximately 0.5 to 5%, consistent with a well-defined diffusion-controlled process. From the voltammogram obtained under vacuum conditions (Fig. 6D) it can be seen the diffusion coefficient for the ferricyanide ion in 'dry' $MDIM^+BF_4^-$ is extremely small (estimated to be lower than 3×10^{-9} cm^2 s^{-1}), whereas it increases dramatically in the presence of water. Similarly to the observations made for the reduction of methylviologen, the rate of diffusion grows approximately proportionally with the molar fraction of water in the ionic liquid (Fig. 5C). Extrapolation of the plot in Fig. 5C to purely aqueous conditions is approximately consistent with the value for the diffusion coefficient of ferricyanide in water 7.6×10^{-6} cm^2 s^{-1}.[27]

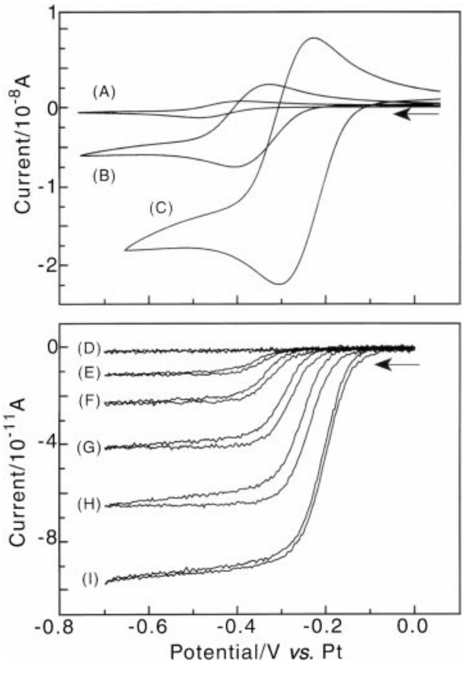


Fig. 6 Cyclic voltammograms obtained for the reduction of 5 mM $Fe(CN)_6^{3-}$ in $MDIM^+BF_4^-$ at a 50 μm diameter Pt disc electrode (A) under dry conditions, (B) after 45 min, and (C) after 120 min exposure to water-saturated argon (scan rate 10 mV s^{-1}). Steady-state voltammograms for the reduction of 5 mM $Fe(CN)_6^{3-}$ at a 5 μm diameter Pt disc electrode (D) under 'dry' conditions, and with a water content of (E) 1, (F) 5, (G) 11, (H) 14, and (I) 15.3 wt.%.

From the results obtained for the diffusion of ferricyanide ions in 'wet' and 'dry' ionic liquids, it can be inferred that, in the absence of water, the diffusion of $Fe(CN)_6^{3-}$ is strongly inhibited, possibly due to the highly charged anion being virtually 'frozen' into the ionic liquid structure *via* a strong interaction with the imidazolium cation. The dramatic increase in the rate of diffusion in the presence of water shows similar characteristics to those observed for MV^{2+}. Clearly, very different effects of water on the rate of diffusion of ionic and neutral species in the ionic liquid are observed and the conventional correlation of rate of diffusion and viscosity (Stokes–Einstein) fails. A plausible explanation for this behaviour is the presence of a 'nanostructure' in the 'wet' ionic liquid, which allows neutral molecules to reside in less polar regions and ionic species to undergo faster diffusion in the more polar or 'wet' regions. This type of nano-inhomogeneity, which is also encountered in some liquid crystalline or concentrated surfactant media,[28] has very interesting implications for electrochemical processes involving both neutral and ionic materials, and may be of considerable benefit in electrochemical processes coupled to gas phase reactions.

Conclusions

It has been shown that traces of water can have a dramatic effect on the electrochemical characteristics and the rate of diffusion observed voltammetrically in ionic liquid media. In particular, the contrast in the effect of water on the diffusion coefficient for neutral and for ionic species suggests that 'wet' ionic liquids may not be regarded as homogeneous solvents, but have to be considered as 'nano-structured' with polar and non-polar regions.

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